Characterization of anaerobic membrane digesters for stabilization of waste activated sludge

by
Martha Dagnew

A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Doctor of Philosophy
in
Civil Engineering

Waterloo, Ontario, Canada, 2010

Author's Declaration

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

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

Abstract

Anaerobic membrane bioreactors may provide a sustainable technological solution for digestion of waste activated sludge due to their capacity to achieve substantial volatile solids (VS) destruction and positive energy balances with reduced digester volumes. However, membrane integrated anaerobic systems may have limitations that are imposed by membrane fouling and a decrease in biomass activity due to possible exposure of biomass to high shear conditions. This study characterised bioprocess and membrane performance under varying conditions, identified foulant type and origin and mechanism of fouling, and developed fouling control strategies by using low cross flow velocity and pressure anaerobic membrane systems.

The study employed a pilot scale anaerobic digester integrated with negative and neutral tubular membranes; pilot and bench scale control digesters supported with bench scale filtration unit parametric studies. The membranes were polyvinylidene difluoride based with an average pore size of 0.02 micron and were operated at a constant cross flow velocity of 1 ms^{-1} and constant trans-membrane pressure of 30 kPa. Four operating conditions consisting of different combinations of HRT and SRT were evaluated.

By integrating membranes into the digesters it was possible to simultaneously enhance digestion and increase throughput of the digesters without affecting its performance. The anaerobic membrane digester showed 48-49% volatile solids destruction at 30 days SRT under conventional and higher loadings of 1.2±0.4 and 2.1±0.6 kg COD $m^{-3}day^{-1}$. This was a 100% increase in performance compared to a control digester subjected to higher loading. This result was supported by the associated specific methane generation. The control digesters operated at a relatively higher SRT showed comparable VS destruction and gas generation to the anaerobic membrane running at a similar SRT. However the extra gas generated didn't compensate heat required to maintain larger volume of the digester. In case of anaerobic membrane digesters due to the high rate feeding, increase biogas production and co-thickening, the energy balance increased by 144 and 200% under conventional and higher loading conditions respectively.

Characterization of membrane performance showed that the average sustainable flux was 23.2±0.4 and 14.8±0.4 LMH during HRT-SRTs of 15-30 and 7-15 days respectively. The critical fluxes were in the range of 30-40, 16-17 and 20-22 $LM^{-2}H^{-1}$ during HRT-SRTs of 15-30, 7-30 and 7-15 days respectively. The decline in membrane performance at a higher loading was associated with the formation of cake layers on the membrane surface that led to reversible fouling. The additional decline in performance at extended SRT was attributed to irreversible fouling.

The colloidal fraction of the sludge showed an overall higher fouling propensity during the long term pilot studies and short term filtration tests. The suspended solids fraction of the sludge showed a positive impact at concentration below 15 g/L but resulted in a decrease of membrane performance at higher concentrations. Further studies of foulant origin through a series of microscopic, membrane cleaning and sludge characterization studies showed that the colloidal proteins, soluble carbohydrates and inorganic materials such as iron, calcium and sulfur and their interaction to have a significant impact on membrane fouling. To control anaerobic membrane fouling by the digested sludge, integration of membrane relaxation techniques in the filtration cycle were found effective. By incorporating a unique relaxation technique to tubular membranes, it was possible to increase the sustainable flux to 29.2±1.8 and 34.5±2.5 $LM^{-2}H^{-1}$ for neutral and negative membranes during 15-30 HRT-SRT process condition. Addition of cationic polymers and sequential mechanical-citric acid membrane cleaning, that targeted both reversible and irreversible fouling was also found effective.

Acknowledgements

It is a pleasure to thank the many people who made this thesis possible.

I would like to extend my sincere thanks to my thesis supervisor Dr. Wayne Parker for his excellent guidance in the completion of this thesis in particular and my stay at Waterloo in general. His dedication to research and expertise in various aspects of Environmental engineering has been a source of inspiration and motivation throughout the course of this study. I greatly appreciate his way of critical thinking and questioning whilst allowing me the room to work in my own. I will always cherish my association with him.

I also acknowledge members of my PhD committee: Drs. Eberhard Morgenroth, William Anderson, Peter Huck and Christine Moresoli for taking their time to read the thesis and provide valuable feedback through the course of my research work.

I am thankful to Dr. Peter Seto for allowing use of the pilot facility at the wastewater technology centre, Environment Canada. Without his support it wouldn't have been possible to carry out my research. I would also like to thank Steven Lee and Sam Dith who thought me the nitty-gritty of piloting (that we don't learn at school) and helping me troubleshoot and successfully operate the pilot plant. Special thanks also go to Jane Challen Urbanic and Scott Dunlop for their technical support and Kyle Waldner for his assistance in reactor operation and sampling.

I would also like to thank the inorganic laboratory at WTC for providing analytical services. The assistance of Drs Steven Liss and Mahendran Basuvaraj at University of Guelph for conducting microscopic analysis on membrane specimens and interpreting the results is greatly appreciated.

My colleagues and coffee crew at WTC: Roxana, Syed, Youngseck, Domenico, Shawn, Mark, Mike and David made the long working hours pleasant. I thank you all for the interesting, motivating and all rounded discussions. I also thank my colleagues in Waterloo: Peiman, Daniela and Weiwei for their friendship and support.

I am deeply thankful to my husband Girma Bitsuamlak for his love, unparalleled support, encouragement and patience during my PhD program. I would also like to express my deep appreciation to my parents and brothers for being a source of love and support in all my pursuits. Lastly I would like to dedicate this thesis to my mother, Melshew Misalew who thought me to be unconventional and inspires me on my daily life. Her dedication to academic and bettering the life of others was no other.

Thank you.

Martha Dagnew
University of Waterloo

Table of Contents

List of Figures

List of Tables

Nomenclature

α	VFA to alkalinity ratio
α_c	Specific cake layer resistance ($m.kg^{-1}$)
α^*	Distance specific cake resistance (m^{-2})
α_1	Pore blockage parameter (m^2kg^{-1})
α_{pore}	Volume of foulant
ε	Cake layer porosity
η	Pump efficiency
μ	Permeate viscosity (Pa. s)
ρ	Density (kgm^{-3})
ρ_c	Density of the solid particles forming the cake layer ($kg.m^{-3}$)
ρ_L	Density of the feed solution (kg/m^3)
ρ_{sludge}	Density of sludge in kg m^{-3}
σ	Cake layer thickness (m)
σ_m	Membrane thickness (m)
AD	Anaerobic digestion
A_m	Membrane area available for filtration (m^2)
AnM	Anaerobic membrane
AnMBR	Anaerobic membrane bioreactor
ANOVA	Analysis of variance
A_o	Initial membrane area (m^2)
A_s	Specific surface of a cake layer particle (m^{-1})
BAP	Biomass associated product
C:P	Carbohydrate to protein
C_b	Bulk foulant concentration (gL^{-1})
$C_{i,b}$	Concentration of the clogging particles in the bulk liquid
cCOD	Colloidal COD (fCOD-pCOD)
CFV	Cross flow velocity
CLSM	Confocal laser scanning microscopy
C_m	Concentration of clogging particles on the membrane surface
COD	Chemical oxygen demand
COD_{fed}	Mass of COD fed (kg/day)
$COD_{effluent}$	Mass of wasted sludge and permeate COD (kg/day)
COD_r	COD removal in percent
CSTR	Completely stirred tank reactor
EDX	Energy dispersive x-ray

EPS	Extracellular polymeric substance
f'	Fraction of foulant convected to the membrane that actually adds to the growing deposit
fCOD	Filtered COD
FSS	Fixed suspended solids
FTIR	Fourier transform infrared
Hc	Calorific value
HF	Hollow fibre
HRT	Hydraulic retention time
ICP	Inductively coupled plasma
J	Membrane flux ($Lm^{-2}h^{-1}$)
K	Kozeny's constant
k_c	Detachment coefficient to account for the crossflow effect
k_i	Fouling strength of the internal foulant, specific resistance (mkg^{-1})
LMH	Liters per meter square per hour
MATH	Microbial adherence to hydrocarbons
MBR	Membrane bioreactor
m_c	Mass of cake layer accumulated on membrane surface ($kg.m^{-2}$)
MF	Microfiltration
m_i	Amount of internal pore foulant (kgm^{-2})
MLSS	Mixed liquor suspended solids
MWCO	Molecular weight cutoff, Daltons
$m\left(S_{fed}^{cumulative}\right)$	Slope of the cumulative sludge fed (g/day)
$m\left(S_{wasted}^{cumulative}\right)$	Slope of the cumulative sludge wasted (g/day)
NF	Nanofiltration
OLR	Organic loading rate
PAC	Powdered activated carbon
pCOD	COD of permeate
PE	Polyethylene
PES	Polyethylsulphone
PF	Plate and frame
PLC	Programmable logic controller
PP	Polypropylene
PS	Primary sludge
PSD	Particle size distribution
PVDF	Polyvinylidene difluoride
$P_{feed\text{-}heat}$	Heat to warm/ elevate feed sludge temperature, $kJ*day^{-1}$
P_{loss}	Heat energy lost through digester walls and roof, $kJ*day^{-1}$
$P_{methane}$	Energy recovered from methane produced during the anaerobic digestion

	process, $kJ*day^{-1}$
P_{pump}	Energy required for recycling and/ or permeation ($kJ*day^{-1}$)
Q_P	Permeate flow rate ($Lday^{-1}$)
Q_w	Volume of sludge wasted per day (L/day)
$Q_{recycle}$	Recycle rate (kg/s)
R_c	Cake layer resistance (m^{-1})
R_f	Fouling resistances
RH	Relative hydrophobicity
R_i	Internal pore fouling (m^{-1})
R_m	Intrinsic membrane resistance (m^{-1})
RO	Reverse osmosis
R_{sup}	Filtration resistances associated with the supernatant
R_{whole}	Filtration resistance of whole sludge
SC	Surface charge
sCOD	Soluble COD
SEM	Scanning electron microscopy
S_{fed}	Daily mass fed
S_i	Non-biodegradable soluble material
SMP	Soluble microbial products
SRT	Sludge retention time
SS	Suspended solids
SW	Spiral wound
T	Tubular
TCOD	Total COD
TKN	Total kjeldhal nitrogen
TMP	Transmembrane pressure
T-RFLP	Terminal restriction fragment length polymorphism
TS	Total solids
TSS	Total suspended solid
TWAS	Thickened waste activated sludge
UAP	Utilization associated product
UF	Ultrafiltration
V	Volume of digester
VFA	Volatile fatty acids
Vperm	Permeate volume
VS	Volatile solids
VS_r	Volatile solids removal (%)

VSS	Volatile suspended solids
$VSS_{destroyed}$	Destroyed volatile suspended solids
$VS_{effluent}$	Mass of sludge (VS) wasted
VS_{fed}	Mass of sludge (VS) fed
WAS	Waste activated sludge
WEF	Water Environment Federation
WTC	Wastewater Technology Center
WWTP	Wastewater treatment plant
X	Biomass concentration (gL^{-1})
X_a	Active biomass concentration
X_i	Non-biodegradable particulate
X_s	Biodegradable particulate

Chapter 1

1. INTRODUCTION

1.1 Statement of the problem

Large quantities of sludge are produced in the treatment of municipal and industrial wastewaters. The sludge removed from the raw wastewater (primary sludge) and from the biological wastewater treatment processes (waste activated sludge) is often putrescible and needs to be stabilized for safe disposal or other applications. A widely accepted stabilization practice is anaerobic digestion due to its distinctive attributes of volume reduction, energy yield in the form of biogas and production of an organic residue that can be used as a soil conditioner.

The anaerobic digestion process is a biological process in which the organic substrate (sludge) is transformed into biogas, mainly made up of methane (55-75%), carbon dioxide (30-45%) and final organic stabilized products. The anaerobic biodegradation happens in the absence of oxygen and is mediated by mainly anaerobic bacteria through three main steps referred as hydrolysis, acidogensis and methanogensis. Of these steps it has been documented that often the rate of hydrolysis and at times the rates of growth of methanogenic bacteria are the rate limiting steps. This requires a relatively large sludge retention time for effective volatile solids destruction and biogas production and limits the volumetric throughput of the digester. To address this issue, improvements on the conventional anaerobic digester design generally involve methods to selectively retain the solids in the digester (increase the sludge retention time) without increasing the size of the digester, thickening and/or pretreatment of raw feed sludge.

The efficiency and sustainability of anaerobic digesters stabilizing waste activated sludge (WAS) can be improved by integrating membranes with anaerobic digesters and converting them into anaerobic membrane (AnM) digesters. The application of AnM digesters for WAS treatment is expected to have benefits such as:

1. allowing particulate substrate to remain longer in the digesters thereby allowing more time for the slowly biodegradable material to breakdown and enhance bioavailability
2. retaining biomass to increase the population of slowly growing methanogenic bacteria for a given digester volume
3. retaining extracellular enzymes to create an active environment for biochemical reactions
4. allowing digesters to operate at higher feed rates to reduce digester volume and associated digester heating and operational costs
5. enabling concurrent thickening of sludge during the digestion process to decrease the volume of sludge to be handled in downstream processing
6. increasing net energy production per given sludge flow and digester volume

Also, the ease of integrating membranes into digesters without substantial changes to existing infrastructure makes this approach an attractive option for WWTPs that are near their maximum digester capacity, hence delaying the construction of additional digesters. However, the operation of membrane integrated anaerobic systems may have limitations that are imposed by membrane fouling and a decrease in biomass activity due to possible exposure of biomass to high fluid flow velocities through the membrane unit. Thus knowledge on the fundamental mechanisms of fouling and identification of the foulant type is required to run a successful fouling control strategy. In addition, the impact of the membrane process on the bioprocess needs to be characterized.

1.2 Objectives and scope

The objectives of this research were to:

- Examine the performance of a low pressure and low cross-flow velocity tubular anaerobic membrane (AnM) digester with respect to bioprocess stability, solids and COD removal, biogas production, digested sludge quality and overall energy balance.
- Assess the impacts of SRT and HRT on the AnM digester sludge stabilization efficiency in comparison with conventional (control) digesters.
- Evaluate the impact of membrane type, membrane flux, digested sludge fractions and pretreatment on membrane fouling using short term bench scale tests.

- Identify changes in anaerobic digested sludge characteristics and their effect on long term membrane performance at various combinations of HRT and SRT in a pilot scale AnM digester.
- Identify the type of foulants, mechanisms of fouling, characteristics of fouling layer and contribute towards a fundamental understanding on AnMBR fouling,
- Propose a strategy to minimize fouling.

This research was carried out using a pilot scale membrane coupled mesophilic anaerobic digester and bench scale conventional anaerobic digesters operating in parallel at the Wastewater Technology Centre (Science and Technology Branch of Environment Canada), Burlington, Canada.

The research presented in this thesis is unique with respect to the scale of the AnM digester, the feed type and the process parameters employed in the digesters. The use of a low pressure and low cross flow velocity tubular membrane with membrane relaxation has not previously been reported for anaerobic digestion of WAS. Beyond the contribution to scientific knowledge, findings from this research are expected to directly benefit existing and new wastewater treatment processes. On one hand the membrane systems may be easily added to existing anaerobic digestion processes leading to efficient sludge treatment. On the other hand the increased methane production from this system may be used as an energy source for the different process operations in the wastewater treatment facility, thereby making them more sustainable.

1.3 Thesis Structure

This thesis is organized into six chapters and seven appendices. Chapter 1 briefly introduces the current WAS stabilization practices and potential benefits of AnMBR processes. Chapter 2 presents background on waste activated sludge (WAS) digestion and the state of the art on anaerobic membrane bioreactor AnMBR processes for high solids applications. Chapter 3 presents the methodology employed and the results of a study of AnMBR bioprocess performance including solids removal, biogas production, digested sludge quality, process stability and an overall energy balance relative to conventional systems. Chapter 4 presents the methodology employed and the results of pilot and bench scale filtration studies characterizing

membrane performance, types of foulants, mechanisms of fouling and fouling control strategies in AnMBRs. Lastly conclusions and suggestions for future work are presented in Chapters 5 and 6.

Chapter 2

2. BACKGROUND AND LITERATURE REVIEW

2.1 Wastewater sludge

Wastewater sludge can be derived from primary clarification or from biological processes (e.g. activated sludge) and are referred to as primary sludge (PS) and waste activated sludge (WAS) respectively. The production of these sludges at wastewater treatment plants causes significant economical and environmental problems since sludge stabilization governs a large portion of plant operational costs and its disposal is also expensive and may cause environmental degradation. Sludge disposal by land filling and incineration is declining due to increasingly stringent environmental regulations. Thus treatment and reutilization is a preferred alternative for sludge management. Sludge stabilization and dewatering are the two most common sludge treatments (Metcalf and Eddy, 2003). The main objectives of wastewater sludge stabilization are to meet regulatory requirements with regard to pathogen, odor and volatile solids reduction and to facilitate handling and decrease costs by reducing sludge volume (Speece, 1996). Stabilization of PS and WAS can be done either separately or in combination. In this research stabilization and thickening of waste activated sludge using enhanced anaerobic digestion was considered.

2.2 Anaerobic digestion process

Sludge stabilization through anaerobic digestion is a commonly employed process. From an economic and environmental standpoint anaerobic digestion has always been a choice when considering different options for the stabilization of wastewater sludge (Bolzonella et al., 2002). The method provides several advantages, including low sludge production, low energy consumption, waste stabilization and biogas recovery (Speece, 1996). It is accomplished through conversion of organics into carbon dioxide and methane in an oxygen free environment (Parkin and Owen, 1986). Although the actual process is complex, often anaerobic digestion of organic materials is described as a three-stage process involving hydrolysis (solubilization of complex and organic compound using extracellular hydrolytic enzymes), acidogenesis and methanogenesis (methane formation) (Metcalf and Eddy, 2003). The first two steps don't provide stabilization, however are required for producing the

substrate for methanogenic bacteria. In the first step organic materials are solubilized and made ready for consumption by microorganisms. In acidogenesis, hydrolyzed organic compounds are fermented to propionic, butyric and valeric acid and further to acetic acid (Speece, 1996). The stabilization of waste occurs during the methanogenesis step by conversion of acetic acid to methane and carbon dioxide. Figure 2-1 shows a simplified version of the anaerobic process scheme as proposed by Gujer and Zehnder (1983).

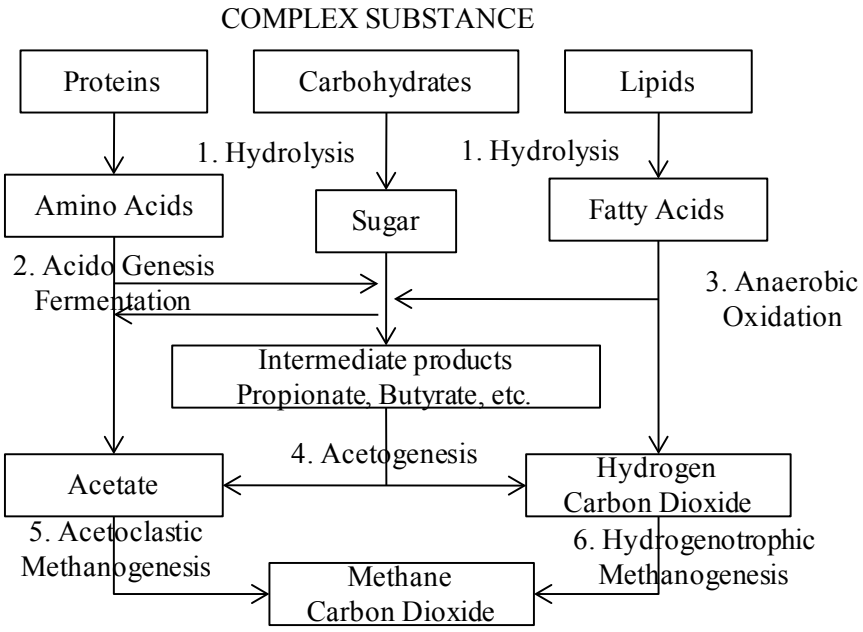


Figure 2-1 Anaerobic digestion process scheme (adapted from: Gujer and Zehnder, 1983)

Of all the processes, either hydrolysis or methanogenesis are typically assumed to be rate limiting. The whole process is expected to involve five groups of bacteria (Parkin and Owen, 1986). The bacteria responsible for the acidogenesis process may be facultative anaerobes, strict anaerobes or a combination of both. On the contrary the methane forming (methanogenic) bacteria are strict anaerobes. In general the methane bacteria have a slower growth rate and they are more sensitive to environmental stress than the acid forming bacteria (Rittmann and McCarty, 2001). Thus successful operation of an anaerobic digestion process requires a large and stable population of methane forming bacteria. To ensure this the bacteria must have enough time in the reactor (increased sludge retention time) to allow substrate

metabolism and prevent washout. Having a stable and large microbial population will also buffer any temperature fluctuations, inadequacy in mixing, and system failure from introduction of toxic substance encountered during digester operation (Parkin and Owen, 1986).

In addition to optimum retention time, successful digestion of organic material and methane generation can be affected by the mixing strategy and intensity. The anaerobic biomass is very sensitive to pH and each population has an optimal range of pH. Temperature has been shown to have an effect on both the microbial growth rates and diversity hence maintenance of constant temperature is important for successful anaerobic digestion process. The optimum conditions for efficient digestion are: pH of 6.5 to 7.6; temperature of 30-38^{o}C (mesophilic range) or 50-60^{o}C (thermophilic range) (Parkin and Owen, 1986). The feed characteristics and presence of toxic materials can also affect the digestion process. Fresh feed sludge has higher biomethanisation potential as compared to aged sludge. Therefore, any prior biodegradation of the feed material before its introduction to the digester will reduce methane production. The existence of toxic materials at an amount greater than their inhibitory amount could affect the performance of the system negatively. Macronutrients such as nitrogen and phosphorus and micro nutrients are also essential for proper operation of the digestion process.

If one or more of the above conditions are not satisfied and if the system has an imbalance in performance it will be manifested through increased levels of short chain fatty acids and hydrogen levels or decreased level of alkalinity (Speece, 1996). Often these parameters are monitored to indicate process stability. In a properly working digester the volatile fatty acid to alkalinity ratio is within the range of 0.02 to 0.2 (Metcalf and Eddy, 2003). Other parameters that often describe the performance of the digester include the amount of methane produced relative to the maximum methane production per unit of organic matter destroyed and the percent volatile solids destruction.

2.2.1 Characteristics of waste activated sludge (WAS)

Waste activated sludge (WAS) is derived from a biological treatment unit and consists mainly of microbial cell biomass, an extracellular floc matrix, particulates and soluble materials from

the wastewater. Due to the cell walls and the floc matrix that are very resistant to degradation, WAS is characterized as being a slowly biodegradable material (Baier and Schmidheiny 1997). In comparison to the untreated PS (5-9%), untreated WAS has relatively lower (0.4-1.2 %) solids concentrations (WEF, 2009, Metcalf and Eddy, 2003). Its quality is affected by the process parameters and feed characteristics of the upstream biological treatment unit such as the solids residence time (SRT), temperature, chemical addition and process configuration (Ekama et al., 2007). For example, sludge originating from an extended aeration process is less biodegradable than sludge from a high load process. Typical WAS characteristics as summarized in WEF (2009) are presented in Table 2-1.

Table 2-1 Typical WAS characteristics: adapted from WEF (2009)

Characteristics	Value
Total solids (TS)	0.4-1.2 %
Volatile solids	0.6-0.85 % of TS
Protein	0.32-0.41 % of TS
Nitrogen	0.024-0.07 % of TS
pH	6.5-8.0

2.2.2 Anaerobic digestion of WAS

Waste activated sludge (WAS) being a by-product from a biological process is mainly composed of bacteria and other slowly biodegradable particulates and it is relatively dilute in nature. Often its stabilization through anaerobic digestion requires large digester volumes and is not efficient and sustainable in comparison with that of primary sludge. Therefore prior to stabilization it is a common practice to condition and thicken the sludge to increase the digestion efficiency. For efficient digestion, typically sludge concentrations from 1% solids to 5% solids are required (Pierkiel and Lanting, 2005). Membrane coupled anaerobic digestion utilizes a concept of simultaneous sludge digestion and thickening.

In conventional anaerobic digestion (AD) of thickened waste activated sludge (TWAS) from the secondary treatment unit, volatile solids (VS) reductions between 30 and 45% can be

achieved and more than 50% of the organics in the sludge are either non-biodegradable or not readily available for biodegradation due to the slower rates of hydrolysis (Gossett and Belser, 1982). To accommodate the slow rate of hydrolysis either longer sludge retention time or techniques to accelerate sludge hydrolysis would be required. Previous study has shown that WAS digestion and specific methane production can be improved by increasing solids residence times up to 60 days (Jones et al., 2008). From a process point of view increasing the reactors SRT should result in an increase in the fraction of sludge hydrolysed and allow a larger anaerobic bacteria population for a given volume of digester hence improving the biodegradation of sludge (Zhang and Noike, 1994; Miron et al., 2000; De la Rubia et al., 2006; Ponsa et al., 2008). However, SRT has a direct influence on treatment costs, including capital investment (i.e. digester volume), as well as operation and maintenance costs (i.e. digester heating, mixing and pumping). Hence, there is an interest in developing technologies that could increase the SRT of the bioreactor without increasing its volume.

In comparison with primary sludge, WAS has relatively lower biogas yields. This yield becomes significantly lower for activated sludge processes that are running at increased sludge retention time (> 10 days) to meet stringent effluent standards for COD, nitrogen and phosphorus content. This is due to the partial sludge stabilization that occurs in activated sludge processes running at higher SRTs. As a result the energetic balance of the anaerobic digestion is often negative if sludges are not properly thickened (Bolzonella et al., 2002). Puchajda and Oleszkiewicz (2008) and Bolzonella et al. (2002) have shown that the sustainability of anaerobic digestion can be enhanced by increasing the loading rate and getting the maximum energy value of the sludge through thickening. WAS digestion using the membrane coupled anaerobic digestion process, would address this concern.

2.2.3 Summary of limitations of conventional WAS digestion process

Historically the application of anaerobic digestion was limited to primary sludge and its application to waste activated sludge is relatively recent. Hence there are still issues in process performance that could be improved upon.

1. Slow hydrolysis and the requirement for longer residence times: Anaerobic processes require long residence times to obtain good quality biosolids. A process that would

help reduce residence time requirements without incurring large capital cost is desirable,

2. Low biogas production per given digester volume: a process that decouples the HRT from SRT and allow high rate feeding is desirable
3. Inadequate temperature control in the digester: Anaerobic digesters are relatively large in size, thus it is difficult to maintain even temperature in a large digester. A process that would result into smaller sized reactors per given feed volume is desirable.
4. Requirement for mixing energy: thickened WAS requires less digester volume thus reducing the energy demand for mixing.

The membrane coupled anaerobic digestion process would be expected to alleviate most of these deficiencies.

2.3 Membrane technology

2.3.1 Process fundamentals

A membrane is a synthetic barrier, which prevents the transport of certain components based on various characteristics. Membranes are diverse in nature with one unifying theme which is the separation of components. They can be liquid or solid, homogenous or heterogeneous and can range in thickness. They can be manufactured to be electrically neutral, positive, negative or bipolar. Membranes are classified based on physical characteristics such as pore size, chemical properties such as material of construction and also the types of modules into which they are configured. These classifications are briefly reviewed below.

Pore size: Membrane pore size is often the most important factor in selecting a membrane for a particular application. The pore size influences the permeate flux, solute rejection capability of the membrane and the types of problems that may occur during membrane operation. Based on the pore size or molecular weight cut-off (MWCO) there are four main categories of membrane filtration: reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). MF and UF are the membranes that have been employed in municipal sludge thickening. Table 2-2 summarizes the filtration categories and the corresponding

particle size rejection or MWCO values and different types of modules in which membranes are configured in.

Table 2-2 Membrane classification (Judd, 2006)

Filtration Type	Particle size rejection (μm)	MWCO* (Daltons)	Modules**
Reverse Osmosis	≤ 0.001	≤100	HF, PF
Nanofiltration	0.001-0.01	100 -1000	HF,PF,SW,T
Ultrafiltration	0.01 to 0.1	1000-500,000	HF, SW, T
Microfiltration	≥ 0.1	≥ 500,000	HF, SW, T

* MWCO means that 90% of spherical uncharged solutes with that molecular weight will be retained on the feed side
** HF = hollow fibre, PF = plate and frame, SW = spiral wound and T = tubular

Material of construction: Membranes can be made from a wide variety of materials that can be generally classified as either synthetic (non-cellulosic) or naturally occurring (cellulosic). Non cellulosic materials include polymers (most common include polyvinylidene difluoride (PVDF), polyethylsulphone (PES), polyethylene (PE) and polypropylene (PP)), ceramics (aluminum and zirconium oxide), glass (borosilicate glass fiber), and metal (silver and stainless steel). Cellulosic materials include cellulose acetate and cellulose tri acetate. Ceramics and polymers are the most commonly used membrane construction materials for use in wastewater applications (Judd, 2006).

Membrane modules: Membranes are enclosed in modules for the provision of support and flow separation. Modules are available in four different forms: spiral wound (SW), hollow fibre (HF), plate and frame (PF) and tubular (T). Of these, spiral and hollow fibre membranes pack large amounts of membrane per unit volume making them less expensive per unit of area. Hollow fibre membranes are less tolerant to the presence of suspended solids in the feed stream, thus their application often requires pretreatment of the feed to prevent the membranes from clogging (Judd, 2006). Spiral wound membrane modules have moderate tolerance for suspended solids. Hence their application for treating high solids wastewater is limited. On the other hand tubular and plate and frame membranes handle feed solutions with high concentrations of solids. Tubular membranes are especially easy to operate, clean and also to maintain the turbulent flow conditions with limited pressure drop. On the contrary, plate and

frame modules are difficult to clean because of the mechanical arrangement and are more susceptible to fouling because of the potential formation of stagnant zones. In comparison to hollow fibre and spiral wound, these membranes are more expensive (Judd 2006).

Membrane operation: There are two approaches to membrane operation. The membrane may be operated under pressure or suction. In the first approach, pressure is employed to push liquid into the membrane unit and permeate through the membrane. In suction systems, a pump or gravity (in some cases) is used to pull permeate through the membrane. Both operational approaches may also be used in side stream or submerged membrane configuration (Figure 2-2). In the side stream configuration, the velocity of the liquid across the membrane surface serves as the principle mechanism to disrupt cake formation on the membrane. In the submerged configuration the membrane can be placed directly into reactor tank and cake formation can be disrupted by vigorously bubbling gas across the membrane surface.

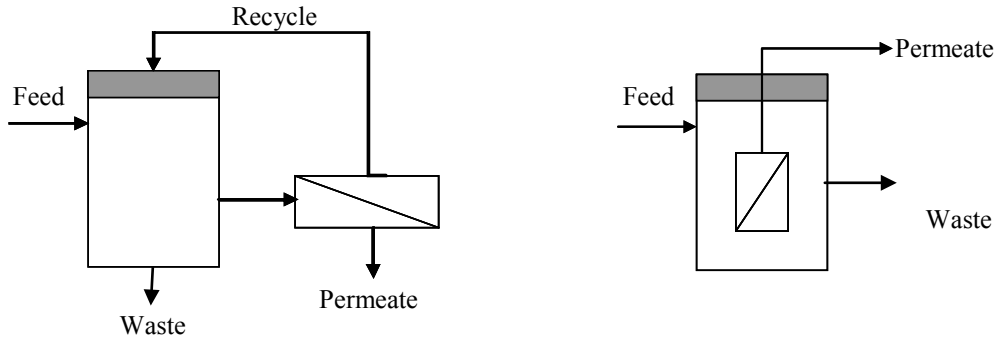


Figure 2-2 Configurations of a membrane bioreactor a) side stream b) submerged

2.3.2 Membrane performance indicator parameters

Flux, transmembrane pressure (TMP) and permeability: The performance of a membrane used for solid-liquid separation can be characterized by monitoring changes in flux (Equation 2-1) or trans-membrane pressure (Equation 2-2) depending on the mode of operation. During constant pressure mode of operation the permeate flow rate is monitored and the membrane flux is calculated as per Equation 2-1. The permeability term (Equation 2-3) is used to compare membrane performances irrespective of the mode of operation.

$$Flux\ (J) = \frac{Permeate\ flow\ rate}{membrane\ surface\ area}, \quad \text{Equation 2-1}$$

$$TMP = \left(\frac{Pressure_{feed} + Pressure_{concentrate}}{2}\right) - Pressure_{permeate}\ , \quad \text{Equation 2-2}$$

$$Permeability = \frac{Flux}{TMP}, \quad \text{Equation 2-3}$$

The most common units used for flux, TMP and permeability are LMH (Liters per meter square per hour), kPa (killo Pascal) and LMH/bar respectively.

Fouling index (rate): Often the interest is how the flux or the TMP value changed over a specific period of time. The term fouling index represents the change in membrane performance over a period of time (Equation 2-4)

$$FI = \frac{flux_{final\ time} - flux_{initial\ time}}{Final\ time - Initial\ time}, \quad \text{Equation 2-4}$$

Critical flux: Critical flux has become a widely accepted parameter for assessing the fouling behavior and comparing the impact of different operating conditions on membrane performance (Le-Clech et al., 2003). Critical flux is defined as the flux below which minimal fouling occurs. The concept is introduced by Field et al. (1995). Different techniques exist to determine the critical flux including the flux step method (Le-Clech et al., 2003). This method involved increasing the permeate flux in steps for a fixed duration and monitoring the TMP at each flux value. This is expected to result in a linear relationship between TMP and flux within the sub-critical flux region and an exponential increase in TMP indicating rapid accumulation of foulants at fluxes beyond the critical flux value. The flux steps used and the duration of the test at a given flux step varied between authors.

2.4 Membranes for solid-liquid separation of sludge

The application of membrane filtration processes in wastewater has been limited to aerobic treatment of wastewaters like municipal wastewater while application to anaerobic wastewaters and sludge treatment is still in its infancy. In these applications the membrane is integrated with the biological unit and its main purpose is for solid-liquid separation. Depending on the redox condition of the biological unit, the integrated membrane-biological

process can be classified either as a membrane bioreactor (MBR) or as an anaerobic membrane bioreactor (AnMBR). Typical examples include membrane integration with the activated sludge unit as in the case of membrane bioreactors (MBR) and with anaerobic - digestion unit for wastewater treatment as in the case of anaerobic membrane bioreactors (AnMBR).

In general, there are several advantages to integrating the membrane unit directly into the biological process. First the membrane provides complete biomass retention thereby decoupling the sludge retention time from the hydraulic retention time (Liao et al., 2006; Perkiel and Lanting, 2005). The retention of biomass within the bioreactor provides better control of the microbial population, facilitating the development of many slow growing microorganisms required for the degradation of more complex organics and may enhance hydrolysis of particulates (Cicek et al., 2001). Maintenance of a biological unit at much higher biomass concentrations reduces the total volume of the system and results in a small plant footprint and/ or allows it to operate at higher organic loading rate. In addition, the membrane can also retain many active extracellular enzymes creating an active environment for microbial biochemical reactions (Cicek et al., 2001). Extracellular enzymes produced by micro-organisms can play a critical role in the hydrolysis of certain substrates. Despite these advantages, the membrane filtration process in anaerobic environment has been limited by membrane fouling.

In comparison to AnMBRs, the application of MBRs is well established (Liao et al., 2006) and has been proven for aerobic municipal and industrial wastewater treatment (Judd, 2006). Liao et al. (2006) reviewed the AnMBR technology potential for application to synthetic wastewaters (Harada et al., 1994; Fuchs et al., 2003), food processing wastewaters (Bailey et al., 1994; He et al., 2005), industrial wastewater (Hogetsu et al., 1992), high strength particulate wastewater (Perkiel and Lanting 2005; Pillay et al., 1994) and low strength wastewater (Ho et al., 2005). Since then significant advances have been made in AnMBR research for low strength and high strength soluble wastewater treatment. Research on the application of AnMBRs for high strength particulate wastewater is still limited. It is expected that the behavior and performance of membranes operated under aerobic versus high strength particulate anaerobic conditions (the subject of this study) will differ, however the knowledge

gained from MBRs and AnMBRs treating low strength and high strength soluble wastewaters processes was used as a starting point and considered in devising methodologies and understanding the fouling phenomena in the present work.

2.4.1 Anaerobic membrane bioreactors for high strength particulate wastewater treatment

2.4.1.1 Anaerobic digester performance of AnMBR system

One of the main disadvantages of anaerobic digestion of high strength particulate wastewater is the requirement for large retention times to accommodate the slow solubilization of particulates and the slow growing methanogenic bacteria (Verstraete and Vandevivere, 1999). Hence solids retention and recycling may enhance digester performance. The anaerobic process performance for this type of waste stream is evaluated based on the solids removal, biogas production per solids fed and process stability.

The wastewater streams that contain a high proportion of particulates include wastewater treatment plant sludges, the organic fraction of municipal solid waste, animal processing plant effluents such as slaughter house effluents and manures (Liao et al. 2006). In conventional systems digestion is usually performed in completely mixed reactors at low organic loading rates (OLR) of < 1 kg COD $m^{-3}d^{-1}$ and a minimum of 15 days hydraulic retention time (HRT) (which is same as the sludge retention time (SRT)) (Verstraete and Vandevivere, 1999; Metcalf and Eddy, 2003) for wastewater sludges. The common OLR for animal processing and manure wastewater is 1-3 kg COD $m^{-3}d^{-1}$ (Liao et al., 2006). Thus the expectation is for the AnMBR system to result in increased OLR or decreased HRT while keeping the SRT at an optimum condition.

There has been a limited work on the evaluation of AnMBR systems for high strength particulate wastewater and the details of the previous studies are summarized in Table 2-3. Most of the trials for wastewater sludge (Table 2-3) showed an increase in volumetric throughput capacity and solids loading in the digester except for that of Ghyoot and Verstraete (1997). In this case the filtration unit was not connected to the digester. Sludge was withdrawn daily and filtration was conducted offline for a period of time long enough to produce 6 liters of permeate per day to maintain 20 days HRT. The concentrate returned to the digester. During

this process the feed sludge (primary digested sludge) was re-circulated through the filtration unit using a 1.5 HP centrifugal pump that resulted in a cross flow velocity of 2.3 to 6.5 m/s. During the 40 days operational period of the AnMBR, the HRT was kept constant, sludge was not wasted and an increase in TS from 22 to 35 g/L was observed. During this period the daily VS removal decreased from 58 to 28% as a result the loading rate was decreased.

Pillay et al. (1994) showed that coupling the anaerobic digester with a woven membrane increased the reactor solids concentration from 2.6% to 5.5% and reduced the HRT to 16 days while the SRT remained at 26 days (Table 2-3). However bioprocess performance data was not presented. Enhanced digestion using AnMBR was reported by Pierkiel and Lanting (2005) and Zitomer et al. (2005) for PS-WAS (for a mixture of primary and waste activated sludge) and dairy waste respectively (Table 2-3).

The results from Pierkiel and Lanting (2005) showed that it was possible to operate the digester at 1-12 day dynamic HRTs and 4-70 day dynamic SRTs while achieving 59% average volatile solids reduction (Table 2-3). However the HRTs were varied within 70 days of the experimental period and their long term impact on the digesters performance was not characterized. Similarly, sludge was not wasted from the reactors. That resulted in continuous increase of the sludge age during the 70 days operation. This limited the evaluation of SRT and HRT impacts on the bio-process performance under steady state condition. In the current study the AnMBR was operated long enough under specific SRT and HRT conditions and its performance was characterized at steady state.

Padmasiri et al. (2007) achieved successful digester performance (96 % VS removal) at VS loading rates of 1 kg VS $m^{-3}d^{-1}$ (Table 2-3). However the performance deteriorated (increased levels of VFA) with an increase of the loading rate to 2-3 kg VS $m^{-3}d^{-1}$.

Ghyoot and Verstraete (1997) and Padmasiri et al. (2007) attributed the poor performance in their studies to a decline in microbial activity resulting from displacement of the sludge through the pump. Similar reduced performance was observed in an AnMBR processes treating wastewater at a higher OLR of 3-5 kg COD $m^{-3}d^{-1}$ (Brockmann and Seyfried, 1997;

Hernandez et al., 2002). Brockmann and Seyfried (1997) observed a loss of 50% of the specific activity of anaerobic biomass treating potato starch wastewater, following recirculation of the entire contents of the digester 20 times. The authors hypothesized that the reduction in performance was due to physical interruption of the syntrophic association of acetogenic bacteria and their methanogenic partners.

Padmasiri et al. (2007) monitored the archeal population dynamics in the reactor with terminal restriction fragment length polymorphism (T-RFLP). The results of this study indicated that hydrogen utilizing methanogens increased in abundance during the period where the system deteriorated. This suggested that these hydrogen utilizing methanogens were active and their associations with the syntrophic bacteria were intact. Therefore the suggested alternate explanation for system deterioration was the increased rate of hydrolysis with the increase in shear conditions in the system leading to buildup of fermentation products.

The literature indicates that to minimize the shear effect, the digester contents should be circulated gently while operating the membranes. This concept was addressed in the present work.

Table 2-3 Comparison of anaerobic digester performance in AnMBR systems treating high solid waste

Types of wastewaters	**PS and WAS**	**PS**	**Thickened PS**	**SS from sewage**		**Potato solids WW**			**Swine waste**			**Dairy waste**	**Chicken slaughter**
Scale	Pilot	Pilot	Pilot	Pilot		Lab			Bench			Pilot	Lab
Type of Reactor	CSTR	Up-flow	CSTR	CSTR		CSTR			CSTR			CSTR	CSTR
Volume (L)	550	120	1800	500		25			6			340	7
Operation day	63	40	NA	-	-	90	59	45	52	44	166	105	-
Temp (^{o}C)	35	35	35	35	35	35			37			55	30
HRT (days)	1.7-11.8[b]	20	14	7.8	8.4	16	9	7	6			23	-
SRT (days)	No wasting	No wasting	26	335	197	Varied wasting[c]			No wasting			30	-
VSLR[a], kg VS $m^{-3}d^{-1}$	0.4-3 [b]	0.4-0.68	3.2	0.93	1.16	3.4[e]	6	7.3	1	2	3	1.9	4.3
Feed TS (gL^{-1})	6	44.4	56	0.16		39.2			6	12	18	44	2.4-4.7
Digester TS (gL^{-1})	18	22-35	55	40-50		40[d]			22[d]	40[d]	-	29	22
VS removal (%)	59	25-59	NA	79	78	99.5[f]	99.6	99.4	96	-	-	49	90d
Reference	Pierkiel and Lanting (2005)	Ghyoot and Verstraete (1997)	Pillay et al. (1994)	Murata et al. (1994)		Hulse et al. (2009)			Padmasiri et al. (2007)			Zitomer et al. (2005)	Fuchs et al. (2003)

[a] VSLR = volatile solids loading rate
[b] The HRT and VSLR changed from 11.8 to 1.7 during the 63 days operation and their long term impact not evaluated
[c] Volume of sludge wasted varied to keep MLSS in the range of 40 g/L
[d] MLSS
[e] OLR, kg COD $m^{-3}d^{-1}$
[f] COD removal (%)

2.4.1.2 Membrane performance of AnMBR systems treating high solid wastewater

Depending on the mode of operation, the membrane flux and/or trans-membrane pressure are the main parameters used to evaluate membrane performance. In general, the membrane for wastewater applications is not only operated to maximize the membrane throughput or flux (i.e., optimal TMP) but also to minimize the rate of fouling (accumulation of foulant material on the membrane surface). In wastewater systems the feed consists of high solids materials and operation at a higher permeate flux could increases the rate of mass transfer of material to towards the membrane surface. As a result the rate of fouling increases (Wen et al., 1999). Therefore, a balance between a high permeate flux, fouling rate and long filtration runs must be achieved for successful operation.

Factors affecting membrane performance: Generally the characteristics of membranes that affect the permeate flux include membrane properties (hydrophobicity/charge, ceramic versus polymeric membrane, pore size), operational condition (cross flow velocity (CFV), TMP or Flux, temperature) and sludge properties. The sludge properties affecting the permeate flux are often related to the characteristics of the raw feed being treated and the operating parameters of the biological process.

Relatively extensive studies of the application of AnMBR for municipal wastewater treatment have evaluated the effects of membrane properties (Shimizu et al., 1989; Pillay et al., 1994; Kang et al., 2002; Ho et al., 2005), sludge properties (Choo and Lee, 1996a) and operational and environmental conditions (Choo et al., 2000; Pillay, 1994) on permeate flux.

Shimizu et al. (1989) reported that a negatively charged membrane had a greater flux in cross-flow filtration of anaerobic digestion broth as compared to neutral or positively charged membranes. This was attributed to the stronger repulsion between the negatively charged colloids and the membrane surfaces. Kang et al. (2002) reported that an organic (polypropylene) membrane had a lower flux than an inorganic (Zirconia) membrane as the former had a rough and fibrous nature in comparison to the smooth nature of the inorganic membrane making it susceptible to biomass accumulation. However the absence of a cake

layer on inorganic membranes has been reported to result in a reduction in permeate flux over time (Kang et al., 2002).

Choo et al. (2000) evaluated the impact of CFV on flux and observed an insignificant decrease in resistance beyond a Reynolds number of 2000. A similar result was reported by Kang et al. (2002). Increasing the cross flow velocity beyond a Reynolds number of 2000 decreased the cake layer resistance however fouling became more severe due to thinning of the cake layer deposit on the membrane surface which served as a barrier to the passage of inorganic foulants. In addition, high shear forces can reduce the size of the biosolids and increase the release of soluble microbial products which in turn affects the permeate flux negatively (Berube et al., 2006). Similarly, increasing the TMP beyond a certain limit compressed the cake layer (increased resistance) thereby decreasing the flux rate (Pillay, 1994).

Berube et al. (2006) conducted a comprehensive review to identify the parameters governing permeate flux in an anaerobic membrane bioreactors treating low strength municipal wastewaters. Their survey indicated that the optimal membrane system for an AnMBR treating low strength wastewater consisted of an organic, hydrophilic, and negatively charged membrane with a pore size of approximately 0.1 μm.

Summary of AnMBR treating high strength particulate wastewater: Flux values and other operational parameters of the membrane unit in previous AnMBR systems treating high strength particulate wastewater are summarized in Table 2-4. However it has to be recognized that most of the tabulated work was preliminary in nature and limited evaluations to assess the effect of membrane type, pore size, membrane configuration and process parameters such as HRT and SRT on flux have been reported.

Most of the membrane configurations used for these applications were external, tubular ultra-filtration membranes. Pillay et al. (1994) used a non-woven fabric membrane formed in 28 mm tube. The membrane had a large pore size and very low intrinsic resistance as compared to commercial membranes and the filtration occurred in the fouling layer. The system treated screened primary sludge without cleaning for an extended period.

Table 2-4 Comparison of membrane performance in AnMBR systems treating high solid wastes

Types of wastewaters	**PS and WAS**		**PS**	**Thickened PS**	**Potato solid**			**Swine waste**		**Dairy manure**
Configuration/ module	External/ Tubular	External/vibrating plate and frame	External/ Tubular	External, tubular (28 mm tube)	Submerged/ plate and frame			External/ Tubular		External/
Membrane materials	Titanium dioxide/stainless steel support	Polymeric Teflon	Ceramic	Woven fibre	Polyethylene			Polyether sulfone		Sintered titanium
Operation day	7	56	40	-	90	59	45	52	82	105
Membrane operation	Continuous	Continuous	Short term	Short term	Continuous			Continuous		
Pore size, μm	0.1	0.05	0.1	NA	0.4			20,000 Da		0.2
Surface area, m^2	1.4	1.6	0.05	NA	0.33			0.0377		0.09
TMP, KPa	480-550	345	200	200	1.74	1	1	20-70		NA
Flux, L/m^2-hr	146	66.7 – 83	100	50	11.8	7.1	4.6	5-10[f]		40-80
CFV (m/s)	5	1.9 cm, 51 HZ[a]	4.5	2	Biogas sparging			1.5-1.9		3.3
MLSS, g/L	10	5-20	22-35 (TS)	1.8	42	36	42	27	49	29
HRT, days	Dynamic HRT (1.7-11.8)[b]		20	14	16	9	7	6		23
SRT, days	Dynamic SRT (4.2 to 70.5)[c]		Dynamic [c]	26	Dynamic SRT (20-150)[c]			Dynamic [c]		30
Temperature , ^oC	35	35	35	35	35	35	35	37		55
Relaxation, min	-	-	-	-	Every 9 minutes for 1 minute			-		-
Back flushing	-	-	Every 5 min for 3 sec	-	-			-		-
Cleaning	Daily[d]	Monthly[d]	Daily rinse	-	At the end of each experiment			-	-	Frequent[d]
Reference	Pierkiel and Lanting (2005)		Ghyoot & Verstraete (1997)	Pillay et al. (1994)	Hulse et al. (2009)			Padmasiri et al. (2007)		Zitomer et al. (2005)

[a] Torsion shear applied at the bottom of the stack at 1.9 cm vibration amplitude and frequency of 51 HZ.
[b] Stepwise HRT increase during the 70 days experimental period
[c] No sludge or minimal sludge wasting, the sludge wasting volume was changing daily
[d] Phosphoric acid and sodium hydroxide wash
[e] Frequent cleaning to meet design flux (alkali acid cleaning using 3.5% NaOH followed by 3% phosphoric acid cleaning)
[f] Initial flux was 100 LMH

In most of the cases the reactors were operated without wasting sludge except Pillay et al. (1994) and Zitomer et al. (2005). The reactors were also operated at a very high cross flow velocity and trans-membrane pressure. Due to this higher TMP, the studies for wastewater sludge demonstrated a flux of 50-150 LMH (Table 2-4). However the membranes in these studies were only operated for a short period of time (on a daily basis) or required daily cleaning to maintain the reported higher flux. Pierkiel and Lanting (2005) evaluated a tubular and vibrating plate and frame configured UF membranes, the results showed stable operation of the membrane at an average flux of 146 and 74 LMH, respectively (Table 2-4). The tubular membranes required daily cleaning to maintain the higher flux (Table 2-4).

Comparatively Padmasari et al. (2007) and Zhang et al. (2007) operated a tubular external AnMBR for swine manure treatment at a sustainable flux of 5-10 LMH , TMP of 20 to 70 kPa and at a relatively higher CFV (Table 2-4). Their study showed constant flux despite a suspended solids increase from 27 to 49 g/L. While the CFV helped to maintain the flux, Padmasari et al. (2007) reported a reduction in bioprocess performance with an accumulation of VFA.

Recently Hulse et al. (2009) evaluated the performance of a submerged flat sheet configured, MF membrane treating primary clarifier sludge blended with centrifuge cake solids from a potato processing plant (Table 2-4). During their study the MLSS in the digester was kept constant at 40 g/L and the OLR was varied from 3.4, to 6 and 7.3 kg $CODm^{-3}d^{-1}$. The suggested optimal fluxes were 12, 7 and 5 LMH respectively yielding a TMP of 1.74, 1 and 1 kPa respectively. Similar to previous observations in the swine manure treatment; the bioprocess became unstable at higher OLR. During the swine manure treatment reduction in the bio-process performance was related to the higher CFV. In the potato solid waste treatment study the sludge was not subjected to high shear condition. The main reason for the reported instability could be due to washout of anaerobic biomass. Despite the OLR increase, the process was maintained to run at a fixed MLSS. Maintaining a constant MLSS required increased wasting which decreased the SRT and increased the food to micro organism ratio. This may have resulted to accumulation of organic acid and led to process instability.

2.4.2 Membrane fouling: mechanisms and foulant types

One of the critical issues in the design and operation of any membrane bioreactor is membrane fouling. Membrane fouling is characterized as a reduction of permeate flux (increase in TMP) through the membrane, as a result of increased flow resistance due to pore blocking, concentration polarization, and cake formation (Lim and Bai, 2003). For microfiltration and coarse ultrafiltration membranes, the fouling by concentration polarization may be negligible due to the large size of the retained particles (Lim and Bai, 2003). Rather, flux decline in cross-flow filtration appears to be due to two mechanisms: pore plugging by particle adsorption on the membrane surface and pores and cake formation considered as irreversible and reversible in nature respectively.

There have been limited studies that have tried to identify the type of foulants and mechanisms of fouling in anaerobic digestion/ membrane processes treating high solid wastes. However, research results on AnMBR technology as used for low and high strength soluble wastewater are subsequently summarized below. Similar fouling phenomena were expected with high strength particulate wastewater processes but the complex nature of the feed, coupled with very high solids concentrations, may exacerbate fouling.

In anaerobic MBR systems both mechanisms of fouling can occur simultaneously (Liao et al., 2006). There are different theories, yet under investigation, as to what leads to these mechanisms. This depends mainly on the membrane operating strategy, bioprocess operating parameters, membrane type and feed characteristics (Cho and Fane, 2002; Choo and Lee, 1996a and b; Kang et al., 2002).

Fouling materials can generally be categorized based on size, chemical type and origin of source and surface charge/chemistry. Previous MBR studies have suggested that the size of the foulant has the greatest impact on fouling propensity (Judd 2006). Sludge can be characterized based on size as being either solid or supernatant (colloidal and soluble) fractions. Upon scrutiny of the different sludge components with respect to their fouling potential, Choo and Lee (1996b) found that fine colloidal components in the broth were more responsible for the cake layer resistance, even if they accounted for only 5% of the total solids (TS) concentration.

On the another hand Liao et al. (2006) stated that in comparison to conventional(MBR) operations, the high concentrations of MLSS in AnMBRs, when presented to the membrane, will increase cake deposition. According to Rosenberger et al. (2005), the relationship between MLSS and flux is complex. An increase in MLSS at low MLSS levels (< 6g/L) resulted in reduced fouling while an increase beyond a critical MLSS level (15 g/L) exacerbated fouling. A change in MLSS concentration between 8-12 g/L showed no effect on fouling. Sludge viscosity was observed to remain the same with an increase MLSS concentration in the range of 10-17 g/L, while beyond this critical concentration the viscosity increased exponentially with MLSS concentration (Itonaga et al. 2004). This effect was attributed to the complex relationship between feed MLSS concentration and viscosity. At increased MLSS concentration, the particle to particle interaction formed a network that resulted in an increase in viscosity (Ho and Sung, 2009). In general increase in viscosity of the feed results in reduced turbulence and increased cake deposition on the membrane.

Based on the origin of source, membrane fouling can be classified as (Lim and Bai, 2003; Liao et al., 2006):

- Organic fouling
    - biological origin (bio-fouling) and/ or
    - other particulate and dissolved organic matter origin
- Inorganic fouling: inorganic origin

Organic fouling: Organic fouling describes the flux decline as a result of interactions between membrane surfaces with biological components (biofouling) and other dissolved and particulate organic materials incoming with the feed. The biological foulants in AnMBR processes can include the biomass, floc associated and solution biopolymers commonly referred as extracellular products (EPS) and soluble microbial products (SMPs) respectively (Kang et al., 2002). Studies in AnMBR systems treating wastewater (Liao et al., 2006; Huang et al., 2009; Lin et al., 2009; and An et al., 2009) have linked membrane fouling to the presence of floc associated and solution biopolymers (i.e. proteins and carbohydrates). These materials are major components of microbial floc that form a complex matrix of microbial cells, cellular debris and inorganic materials. They contribute to the physico-chemical

characteristics of the sludge and play an important role in bioflocculation by binding cells and other particulate matter together and/or floc adhesion on to membrane surfaces (Tansel et al., 2006). The latter could result in membrane fouling either through direct deposition and adsorption on the membrane surface and/or cake layer formation through creation of a hydrated gel matrix (Cho and Fane, 2002; Liao et al., 2004). However the relative contribution of the different biopolymer fractions such as loose versus bound biopolymers and/or proteins versus carbohydrates to membrane fouling is not fully understood owing to the complex interactions in sludge matrices.

Few investigations have characterized membrane fouling in this type of process. Researchers have observed positive (Chang and Lee 1998 and Huang et al. 2009), negative (Lin et al. 2009; Cho and Fane, 2002) and no relationship (Yamato et al. 2006) between bound EPS and membrane fouling. A recent study by Wu et al. (2009) on filtration of aerobically digested WAS using flat sheet membranes showed no relationship between the critical flux and bound EPS. In earlier studies of sludge dewaterability and settling it has been identified that EPS and cations promote bioflocculation which assists in aggregation and improving the settlability and/or dewaterability of sludge flocs (Raszka et al. 2006). However excess EPS was reported to have a negative impact on these responses.

Huang et al. (2009), Lee et al. (2003), Meng et al. (2006) and Liang et al. (2007) have reported that soluble biopolymers had a considerable influence on membrane fouling. The studies showed a significant effect of soluble carbohydrates on flux however have shown no significant relationship between soluble protein and flux.

Recently the fouling of membranes had been associated with the carbohydrate to protein ratio however the results vary between different authors. Huang et al. (2009) observed an increase in the fouling propensity of sludges with increased soluble carbohydrate to protein (C:P) ratios. Conversely, Lin et al (2009) observed an increase in fouling propensity of sludges with a decrease in the bound carbohydrate to protein ratios respectively.

Biofouling can be identified by using non-destructive tests (through measuring EPS and SMP concentration in sludge) and correlating them with membrane performance terms or destructive tests (such as membrane autopsy).

Quantification of biofoulants mainly proteins and carbohydrates in EPS (bound biopolymer) and SMP (loose biopolymer) fraction include separation of SMP from the sludge by centrifuging, EPS extraction and analysis. There is no standard method for extracting EPS from sludge samples. Various physical and chemical extraction methods have been reported including formaldehyde, centrifugation, heating, cation exchange resin, sulphide and Ethylenediamine tetraacetic acid (EDTA). The literature showed that the EPS composition and concentration varied with the extraction method (Liu and Fang 2002). This made comparison of EPS values in literature difficult. The most commonly used method for analysis of the protein and carbohydrate concentrations in SMP and Extracted EPS samples are the phenol-sulfuric acid (Dubois et al. 1956) and Lowry method (Lowry et al., 1951). Other spectroscopic methods such as excitation-emission matrix (EEM) fluorescence spectroscopy have also been applied to obtain information on characteristics of SMP samples.

Inorganic fouling: Inorganic fouling refers to the flux decline as a result of interactions between membrane surfaces with the inorganic chemical components such as cations in the membrane feed (Choo and Lee, 1996; and An et al., 2009). Choo and Lee (1996) and Kang et al. (2002) showed that inorganic materials in solution can be responsible for irreversible membrane fouling by precipitating within the membrane pores as well as accumulating on the membrane surface. In addition, floc-associated and solution cations have been shown to play a role in consolidation of biomass cakes and further enhancement of the compactness of the fouling layer. This may be caused by charge neutralization of functional ionizable anionic groups such as carboxylic and phosphate groups, deposits of metal salts and/or bridging between deposited biopolymers on the membrane surface (Choo and Lee, 1996; Seidel and Elimelech, 2002; and An et al., 2009).

The types of foulants causing chemical fouling in AnMBRs have been reported to include struvite ($MgNH_4PO_4.6H_2O$), $K_2NH_4PO_4$ and $CaCO_3$ (Yoon et al., 1999; Choo and Lee, 1996a;

Liao et al., 2006). These studies suggested that struvite accumulation in pores is the main mechanism of chemical fouling for inorganic membranes. In the case of organic membranes the struvite forms a cake layer due to incorporation into the biological foulant due to its relatively rougher surface morphology (Kang et al., 2002; Choo and Lee, 1996a; Yoon et al., 1999). Zhang et al. (2007) calculated the saturation index to determine the potential for precipitation of inorganic salts during AnMBR treatment of swine manure. The results identified struvite, hydroxyapatite ($Ca_{10}(PO_4)_6)(OH)_2$), dolomite ($CaMg(CO_3)_2$) and Calcite ($CaCO_3$) as the major contributors of inorganic precipitates within a digester and on the membrane surface.

The impacts of biopolymers and cations on membranes treating sludge in an anaerobic environment have not yet been fully investigated for AnMBR digesting WAS. Various studies have shown that divalent and trivalent cations such as calcium, magnesium and iron neutralize the negative charge associated with biopolymers and can act as bridges to stabilize the floc structure. During anaerobic digestion processes the bond between the cations and biopolymers can break down to release cations into solution (Park et al., 2006; Park and Novak, 2007). This is expected to have a detrimental effet on fouling of the membrane.

The chemical fouling by inorganic species can be quantified from the spent solution after washing membrane with acidic and basic solutions (Kang et al., 2002) or by directly measuring the inorganic species using energy-dispersive x-rays (EDX) to examine the membrane surface (Wallberg et al., 2001).

2.4.3 Membrane fouling management methods

The immediate effect of fouling is to cause a reduction in permeate flux. The long term effect may lead to irreversible fouling from bio- and inorganic foulants and the reduction of membrane lifetime. To maintain the economic viability of a membrane process, membrane fouling has to be kept to a minimum. Methods that have been evaluated to minimize fouling in AnMBR include:

- Modifying membrane characteristics to increase back transport of the foulants away from the membrane surface into the bulk solution (Bailey et al., 1994; Choo et al., 2000),
- Pretreatment of the feed solution such as addition of powdered or granular activated carbon (Imasaka et al., 1989; Choo et al., 2000; Park et al., 1990, Aquino et al., 2006; Akram and Stuckey, 2008),
- Increasing cross flow velocity in tubular membranes (Brockmann and Seyfried, 1995; sparging rate and membrane relaxation in submerged membranes,
- Chemical cleaning (Wallberg et al., 2001; Lee et al., 2001; Zhang et al., 2007).
- Subcritical flux operation (Jeison and van Lier, 2006)

Membrane properties modification: Bailey et al. (1994) smoothed the membrane surface with a precoat layer of diatomaceous earth powder that reduced anaerobic bacteria accumulation. Choo et al. (2000) modified the hydrophobic membrane surface to become hydrophilic through graft polymerization and as a result managed to increase the flux.

Feed pretreatment: Imasaka et al. (1989) reported that injection of polymeric particles into the membrane module were effective for scouring the biomass cake away from the membrane. Choo et al. (2000) showed addition of powdered activated carbon (PAC) to the reactor contributed to the reduction of a polymeric membrane fouling caused by organic adsorption and fine colloid deposition by sorbing and/ or coagulating dissolved and colloidal matter present in the bioreactor. When Park et al. (1999) added PAC to a synthetic wastewater, the particle size distribution shifted to a relatively high range of sizes i.e. increasing from 7.5 to 22μm. The PAC can sorb and coagulate dissolved organics and fine colloids. In addition PAC has a higher scouring effect and lower specific cake resistance than biosolids. Akram and Stuckey (2008) showed the addition of PAC increased the flux of flat sheet submerged anaerobic membrane bioreactor treating synthetic wastewater (4 g COD/L) from 4 to 9 LMH.

Cross flow velocity: Most fouling control in tubular membranes has been achieved by increasing the CFV. However, increasing CFV in the case of AnM digester operation has been reported to cause shear effects on the anaerobic biomass and subsequent reduction of digester

performance (Brockmann and Seyfried, 1997; Ghyoot and Verstraete, 1997; Padmasiri et al., 2007).

Gas sparging and membrane relaxation: The concept of CFV is not applicable for suction, submerged membranes. However biogas sparging has been used to disrupt the formation of the cake layer (Hulse et al., 2009). In addition, for suction operation membrane relaxation (interruption of the permeation cycle to allow deposits to relax) has been used as a way of controlling fouling. Hulse et al. (2009) incorporated a 9 minutes permeation followed by 1 minute relaxation cycle during a flat sheet AnMBR filtration of potato solid wastewater.

Gas sparging and membrane relaxation are standard fouling controlling strategies in MBRs (Jude, 2006). At present the gas sparging and relaxation conditions used in AnMBRs are simply adopted from the MBR studies. There appear to be limited information in AnMBRs that clearly indicate the impacts of these parameters on flux recovery.

Membrane cleaning: Efficient chemical cleaning requires selection of cleaning chemicals that target the dominant foulants and have less adverse impact to the membrane. In addition allowing enough contact time between the chemical solution and membrane surface, creating high shear condition and optimum temperature are detrimental for breaking the bonds between the membrane surface and the fouling material. Wallberg et al. (2001) concluded that if the fouling is inorganic, it is possible to remove the fouling substances using acidic cleaning agents. If the fouling is organic, oxidizing cleaning agents, bases and surfactants can be used.

For AnMBR treating alcohol fermentation wastewater, Kang et al. (2002) showed that acidic cleaning doubled the flux. Lee et al. (2001) followed a sequential alkaline solution followed by acidic agents and obtained a flux recovery of up to 86% of the original membrane flux for AnMBR treating swine manure. Zhang et al. (2007) obtained better flux recovery at higher temperature for AnMBR treating swine manure. According to Zhang et al. (2007), just flushing the membrane resulted in a decrease of the fouling resistance from an average 65 to 26 x $10^{12}m^{-1}$ (59% flux recovery) however subsequent cleaning with EDTA and NaOH at 25^{o}C resulted in limited recovery. Additional sequential chemical cleaning at a higher (50^{o}C)

temperature resulted in a substantial reduction of the fouling resistance by 29% (5.4 x 10^{12} 1/m). In all cases the use of mechanical cleaning methods other than flushing has not been reported.

Operation below critical flux: Operation below the critical flux (flux that exists at startup below which a decline of flux with time does not occur; above it fouling is observed), is expected to have little or even no effect fouling (Field et al., 1995; Jeison and van Lier, 2006). While this could lower the rate of fouling, observations have shown that fouling takes place even at fluxes below the critical flux (Fan et al. 2006).

2.5 Modeling approaches

2.5.1 Classical models

The main objectives of membrane models have been to either predict the flux decline over time and/ or to assist in the identification of the mechanisms of fouling. Although there are numerous models developed for other disciplines, membrane fouling models for use in wastewater applications are limited. Irrespective of the complexity associated with the fouling phenomena, the most common approach for analyzing flux decline and identifying the mechanism of fouling has been to use simple classical models that include: complete pore blockage, standard pore blockage (pore constriction), intermediate pore blockage, and cake filtration (Figure 2-3, Table 2-5) (Ho and Zydney, 2006). Pore plugging (blockage) occurs only when the foulant in the feed is smaller than the pore size or the MWCO. Complete pore blockage occurs when particles become stuck in the pores of the membrane (Figure 2-3). In cake filtration, a cake is formed on the upper surface of the membrane (Figure 2-3). The model assumes proportionality between an increase in cake layer resistance and rate of particle convection to the membrane (Table 2-5).

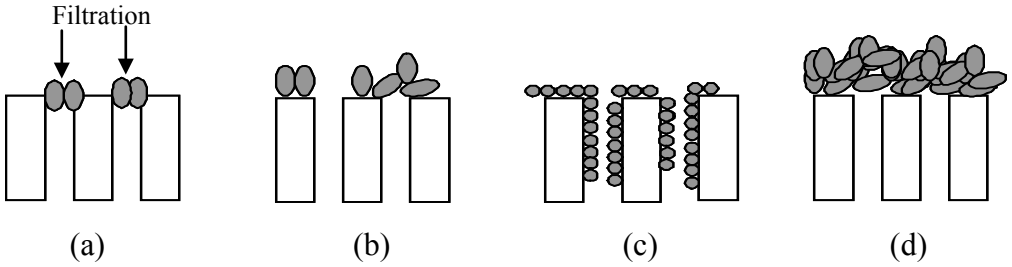


Figure 2-3 Classical fouling mechanisms (a) complete blocking (b) intermediate blocking (c) standard blocking (d) cake formation (adopted and modified from: Judd, 2006)

Table 2-5 Classical membrane fouling models (adopted and modified from: Ho and Zydney, 2006)

Model type	Assumption	Model
Pore blockage model (complete blocking)	$\frac{dA_m}{dt} = -\alpha_1 Q C_b$	$Q = Q_0 \exp\left(-\frac{\alpha_1 TMP C_b}{\mu R_m} t\right)$
Intermediate pore blockage model	$\frac{dA/A_0}{dt} = -\alpha_1 Q C_b$	$Q = Q_0 \exp\left(1+\frac{\alpha_1 TMP C_b}{\mu R_m} t\right)^{-1}$
Pore constriction model (standard blocking)	$\frac{d(N\pi r_p^{\,2}\delta_m)}{dt} = -\alpha_{pore} Q C_b$	$Q = Q_0\left(1+\frac{\alpha_{pore} Q_0 C_b}{\pi r_0^2 \delta_m} t\right)^{-2}$
Cake filtration model	$\frac{dR_c}{dt} = \alpha_c f' J C_b$	$Q = Q_0\left(1+\frac{2f'\alpha_c Q_0 C_b}{A_0 R_m} t\right)^{-2}$

Where A_m = membrane area (m^2); α_1 = pore blockage parameter (m^2kg^{-1}), membrane pore area blocked per unit mass of foulant); C_b = bulk foulant concentration (gL^{-1}); Q_0 = initial permeate flow rate through the membrane surface; TMP = transmembrane pressure (bar); N = total number of pores; σ_m = membrane thickness (m); α_{pore} = volume of foulant deposited in the pore interior per unit mass of foulant filtered through the membrane; f' = fraction of foulant convected to the membrane that actually adds to the growing deposit.

All the above classical models are derived based on a generalized form of Darcy's law (Equation 2-5):

$$J = \frac{dV_{perm}}{A_m dt} = \frac{TMP}{\mu(R_m + R_f)}, \quad \text{Equation 2-5}$$

Where J = permeate flux (ms^{-1}); V_{perm} = permeate volume per unit surface area (m^3); A_m = membrane area (m^2); TMP = transmembrane pressure, μ = permeate viscosity (Pa. s), R_m = intrinsic membrane resistance which is assumed to be constant (m^{-1}), R_f = other resistances (internal fouling (R_i) and cake layer (R_c)) due to fouling, which are a function of time. The mechanism of fouling is typically identified by fitting the linearized forms of the equations in Table 2-5 to the experimental data (Lim and Bai, 2003; Farizoglu and Keskinler, 2006). However the flux decline over time is estimated with further modification of the classical models as discussed below.

2.5.2 Flux decline prediction models

Models of long term flux decline are generally either empirical or semi-empirical in their approach. The models are specific to the nature and the mechanism of the foulant: cake layer versus pore fouling. The models in the literature vary widely in explaining the fouling phenomena with respect to the adopted mode of operation (cross flow versus dead end filtration) and their consideration of material attachment/ detachment phenomena (back transport versus forward transport of foulants) and the properties and composition of the feed solution (particle size distribution, total solids concentration, colloid concentration) and are subsequently discussed.

i. Cake layer fouling (R_c)

This form of membrane fouling is due to the growth of a cake layer on the membrane surface. Formation of the cake layer is a function of the concentration of feed material as well as the flux (Nagaoka et al., 1998; Ho and Zydney, 2006). Membranes are recommended to operate below the critical flux (the flux below which no deposition of foulant matter takes place). If operated at super-critical flux (flux higher than the critical flux) a cake layer is expected to form (Giraldo and LeChevallier, 2006). Even membrane operations under sub-critical flux (operation below the critical flux) condition have shown cake layer buildup after a period of operation. Liang et al. (2006), Giraldo and LeChevallier et al. (2006), Nagaoka et al. (1998) and Wintgens et al. (2003) have used a variation of the cake filtration model for estimating cake layer formation over time for MBR systems. According to the classical cake filtration model, the resistance from the cake layer (R_c, m^{-1}) can be expressed by Equation 2-6. In MBR

application, this expression was modified in the means by which mass of cake layer accumulated on membrane surface (m_c, kg.m^{-2}), specific cake layer resistance (α, m.kg^{-1}), and cake layer compressibility were described.

$$R_c = \alpha_c m_c, \qquad \text{Equation 2-6}$$

The parameters m_c and α are determined as follows:

a) Mass of cake layer accumulated on membrane surface (m_c): The mass of cake layer can be directly estimated from equation 2-7. The cake layer thickness (σ, m) can be directly measured using scanning electron microscope (Psoch and Schiewer, 2006).

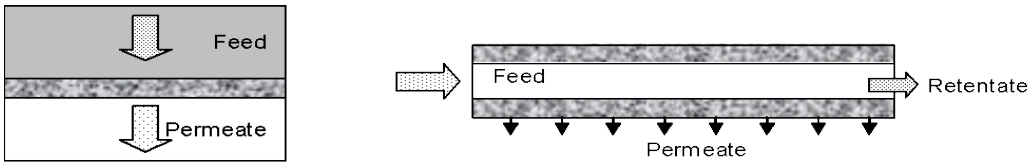
$$m_c = \sigma * \rho_c, \qquad \text{Equation 2-7}$$

where ρ_c = density of the solid particles forming the cake layer (kg.m^{-3})

However often the change in growth term is estimated from equation 2-8 or 2-9:

Dead-end filtration assumption (Psoch and Schiewer, 2006): In dead end operation there is no retentate flow (Figure 2-4a). The thickness of the cake formed on the membrane is proportional to the total volume of filtrate passed.

$$\frac{dm_c}{dt} = JC_b = \frac{V_{perm}}{A_m t} C_b, \qquad \text{Equation 2-8}$$



(a) (b)

Figure 2-4 Schematics of (a) Dead end and (b) Cross-flow filtration

Crossflow filtration assumption: In crossflow filtration, it is assumed that the mass of the foulant accumulates onto the membrane surface by the work of advection, while it is detached

by the shear stress caused by cross flow of the suspension. In almost all of the models for wastewater applications, the back transport phenomenon (addition of a term to account for removal of particles from the membrane) is considered (Equation 2-9) (Liang et al. 2006; Nagaoka et al. 1998; Giraldo and LeChevallier 2006). Thus the rate of cake growth in the cake filtration model becomes

$$\frac{dm_c}{dt} = JC_b - k_c m_c, \qquad \text{Equation 2-9}$$

where k_c = detachment coefficient to account for the cross flow effect

b) Specific cake layer resistance (α_c)

Another variation of the cake filtration model involves a modification of the approach used to determine the specific cake layer resistance (α_c) of equation 2. The specific cake resistance represents the hydrodynamic resistance to the flow due to the secondary membrane (Farizoglu and Keskinler, 2006). The value has been obtained either through direct measurement (equation 2-10) or estimated on the basis of the Carman Kozeny equation (equation 2-13).

Direct measurement (Farizoglu and Keskinler, 2006)**:** Direct measurement of α_c involves calculating the term from other measured variables.

$$\frac{t}{V_{perm}} = \frac{R_m \mu}{A_m TMP} + \frac{\alpha_c C_b \mu}{2A_m^2 TMP} V_{perm}, \qquad \text{Equation 2-10}$$

α_c was estimated by plotting t/V_{perm} versus V_{perm} to yield a straight line with a slope ($\alpha_c C_b \mu / 2A_m^2 TMP$). The slope was employed to evaluate α_c as all other variables were known for a given experiment.

Theoretical estimation: Psoch and Schiewer (2006) and Giraldo and LeChevallier (2006) estimated α based on the Carman-Kozeny equation. The Carman-Kozeny equation (equation 2-11) describes the head loss *h* for filtration through a porous medium:

$$h = \frac{\Delta P}{\rho L g} = \frac{R_c \mu J}{\rho L g} = \frac{\sigma \mu k A_s^2 (1-\varepsilon)^2 J}{\rho L g \varepsilon^3}, \quad \text{Equation 2-11}$$

hence:

$$\alpha^* = \frac{k A_s^2 (1-\varepsilon)^2}{\varepsilon^3}, \qquad \text{Equation 2-12}$$

$$\alpha_c = \frac{\alpha^*}{\rho c} = \frac{k A_s^2 (1-\varepsilon)^2}{\rho c\, \varepsilon^3}, \qquad \text{Equation 2-13}$$

Where σ is the cake layer thickness (m), k = Kozeny constant, A_s = specific surface of a cake layer particle (m^{-1}), ε = cake layer porosity, ρ_L = density of the feed solution (kg/m^3), ρ_c = density of the solid particle forming the cake layer (kg/m^3), α^* = distance specific cake resistance (m^{-2}) and g is the gravitational constant (m/s^2). Calculations of the cake resistance are commonly done for model solutions with clearly defined particle size distributions, shape factors, surface areas and so on. For real wastewater samples a spherical particle assumption is often used (Giraldo and LeChevallier, 2006)

c) Cake layer compression

If a cake layer is considered incompressible, the porosity and specific cake layer resistance are independent of the transmembrane pressure. The models described to this point have been based on this assumption. However recognizing that the cake layers can be composed of microbial cells and other materials which are highly compressible, Lee and Wang, 2003; Psoch and Schiewer, 2006; Farizoglu and Keskinler, 2006) have incorporated the effect of a decrease in cake porosity and an increase in specific resistance with increase in transmembrane pressure. Farizoglu and Keskinler (2006) used an empirical equation (equation 2-14) to account for this effect.

$$\alpha_{comp} = \alpha_c \left(1 + \frac{TMP_A}{TMP_T}\right)^n, \qquad \text{Equation 2-14}$$

For incompressible cakes, $n = 0$ and the higher the compressibility coefficient, the more compressible the cake. TMP_A is the applied trans membrane pressure, TMP_t is the threshold pressure below which no cake compression occurs, and the exponent n is the cake compressibility.

ii. Internal fouling (R_i)

Internal fouling is often modeled by using one of the classical models including pore blockage, pore constriction or intermediate pore blockage (Table 2-5). Internal fouling has been described to exist during the operation of the membrane at the sub-critical flux (Giraldo and LeChevallier, 2006) and is often caused by the deposition of soluble microbial products (SMPs) on the membrane surface (Liang et al., 2006). Different approaches have been employed to estimate the foulant concentration. Liang et al (2006) considered the foulant concentration on the membrane surface as equal to the bulk concentration (equation 2-16) whereas Giraldo and LeChevallier (2006) estimated the concentration of the clogging particle at the membrane surface using equation 2-17. In effect the latter considers the possibility of some particles being retained by the cake layer during the filtration process.

$$R_i = \alpha_i m_i, \quad \text{Equation 2-15}$$

$$\frac{dm_i}{dt} = JC_{i,b}, \quad \text{Equation 2-16}$$

$$\frac{dm_i}{dt} = JC_{i,m}, C_{i,m} = C_{i,b} * e^{\frac{k\sigma}{J}}, \quad \text{Equation 2-17}$$

Where R_i = internal pore fouling (m^{-1}); k_i = fouling strength of the internal foulant, specific resistance (mkg^{-1}); m_i = amount of internal pore foulant (kgm^{-2}); C_m = concentration of clogging particles on the membrane surface, $C_{i,b}$ = concentration of the clogging particles in the bulk liquid and k is the first order particle removal coefficient.

2.6 Summary

The literature review indicated limited research on an AnMBR treating high strength particulate wastewater. Most of the studies for wastewater sludge application were found to be preliminary in nature. The membrane configurations used for these applications were external tubular ultrafiltration membranes and were operated at a higher shear condition. However the increase in shear was associated with decline in the bioprocess performance.

In most of the cases sludge had not been wasted from the reactors which led to significantly higher SRT. However the impact of SRT on the bioprocess and membrane performance has not been investigated. The review indicated despite significant work done on MBR fouling, limited studies characterized membrane fouling under anaerobic condition treating wastewater and no previous data is available for wastewater sludge. The limited research on AnMBR fouling indicated that the nature of MBR versus AnMBR fouling varies. Under AnMBR fouling both organic and inorganic type of fouling existed. To date mechanisms of fouling and foulant type for AnMBR stabilizing sludge have not been identified. The impacts of process parameters, membrane type and/or feed characteristics on membrane fouling have not yet been investigated.

Chapter 3

3. DIGESTION PERFORMANCE OF ANMBR STABILIZING WASTE ACTIVATED SLUDGE UNDER VARYING HRT AND SRT CONDITIONS

3.1 Background

Waste activated sludge (WAS), being a by-product from a biological process is mainly composed of bacteria and other slowly biodegradable particulates and it is relatively dilute in nature. Often its stabilization through anaerobic digestion is not efficient and sustainable in comparison with that of primary sludge. In the anaerobic digestion of WAS hydrolysis is often regarded as the rate limiting stage of the overall process (Vavilin et al., 2008) as it affects the amount of particulates converted into soluble components for microbial consumption. Acidogenesis and methanogensis processes also play a key role in process stability. These processes are affected by operational parameters like SRT and organic loading rate, environmental factors like temperature, pH and reactor configuration.

A previous study has shown that WAS digestion and specific methane production can be improved by increasing solids residence times up to 60 days (Jones et al., 2008). From a process point of view increasing the reactors SRT should result in an increase in the fraction of sludge hydrolysed and allow a larger anaerobic bacteria population for a given volume of digester hence improving the biodegradation of sludge (Zhang and Noike, 1994; Miron et al., 2000; De la Rubia et al., 2006; Ponsa et al., 2008). However, SRT has a direct influence on treatment costs, including capital investment (i.e. digester volume), as well as operation and maintenance costs (i.e. digester heating, mixing and pumping). Hence, there is an interest in developing technologies that could increase the SRT of the bioreactor without increasing its volume.

Puchajda and Oleszkiewicz (2008) and Bolzonella et al. (2002) have shown that the sustainability of anaerobic digestion can be enhanced by increasing the loading rate and getting the maximum energy value of the sludge through thickening. This is an important aspect when it is considered that many WWTP have adopted increased SRT operation

(SRT>10 days) that results in partial stabilization in the aeration basin and resulting in decreased biogas production during digestion.

In theory, anaerobic membrane digesters (AnM digesters) could help to achieve both of these objectives. Membranes allow complete solid-liquid separation and their integration into digesters can lead to longer SRTs and retention of anaerobic bacteria and slowly biodegradable particulates with a potential to enhance solids stabilization. These configurations also allow high rate feeding and co-thickening. The co-thickening potential reduces the volume of produced biosolids and associated handling costs.

Despite the aforementioned potential, limited research has been done on the application of anaerobic membrane digesters for sludge stabilization. To date no data exist on the impact of SRT and HRT on anaerobic membrane digester performance treating sludge. Previous research on integrated membrane and anaerobic processes reported an overall enhanced performance at an organic loading of 1-2 kg COD/m^3/day (Pierkiel and Lanting, 2005; Ghyoot and Verstraete, 1997; and Padmasiri et al. 2007). However, deterioration of digester performance at higher loading rates has been reported by Brockmann and Seyfried, 1997; Hernandez et al., 2002; and Padmasiri et al., 2007). The poor performance at higher loading rates was attributed to a decline in microbial activity due to floc shear and physical interruption of the syntrophic association of acetogenic bacteria and their methanogenic partners (Brockmann and Seyfried, 1997; Hernandez et al., 2002). Most of these studies were conducted using bench scale digesters and had higher recirculation rates that led to floc shear. In other cases sludge flocs were exposed to excess shear that was required for scouring and controlling build up of the cake layer on the membrane surface. To minimize the shear effect the sludge should be circulated gently while operating the membranes.

Therefore the objectives of this study were to examine the performance of a low pressure and low cross-flow velocity tubular anaerobic membrane digester with respect to process stability, solids and COD removal, biogas production, digested sludge quality and overall energy balance. In addition, the impacts of SRT and HRT on the AnM digester sludge stabilization efficiency were examined and compared with conventional (control) digesters.

3.2 Methodology

3.2.1 Raw feed sludge

The waste activated sludge (WAS) used was obtained from the Skyway municipal wastewater treatment plant (WWTP) located in Burlington, Ontario, Canada. A relatively constant feed solids concentration of 2 ± 0.7% was maintained by mixing volumes of WAS with thickened waste activated sludge (TWAS) to make up the feed. The feed was delivered twice per week and stored at 5^{o}C until use. The inocula used to seed the pilot and bench digesters were obtained from the same plant's anaerobic digestion unit that digests a mixture of primary and thickened waste activated sludge.

3.2.2 Experimental setup

A series of long-term studies were carried out using one pilot-scale AnM digester, one pilot conventional (control) digester and two bench-scale conventional digesters that also acted as controls at varying SRT and HRT combinations. A detailed description of each system setup follows.

3.2.2.1 Pilot AnM digester (test digester)

The pilot plant was constructed and installed at the Wastewater Technology Center (WTC) in Burlington. It consisted of an anaerobic digester that was integrated with two parallel tubular membrane units. A schematic diagram of the membrane unit coupled to the reactor is shown in Figure 3-1. The AnM digester consisted of a 76.2 cm diameter, vertical cylinder that was 160 cm high resulting in a total working volume of 570 L. Details on tank dimensions and pictures are attached in Appendix-A.

Sludge was pumped to the digester from the feed tank via a Moyno pump and digested sludge was wasted at the bottom of the digester. The reactor was mixed using a centrifugal recycle pump, where sludge was withdrawn from the bottom and recycled back to the top of the reactor. The temperature of the digester was maintained at 35±1^{o}C by heating tape that was controlled by a temperature controller which was linked to a temperature sensor in the digester. Most of the pilot operation and data acquisition was controlled using a programmable logic controller (PLC). The program logic is attached in Appendix-A. To

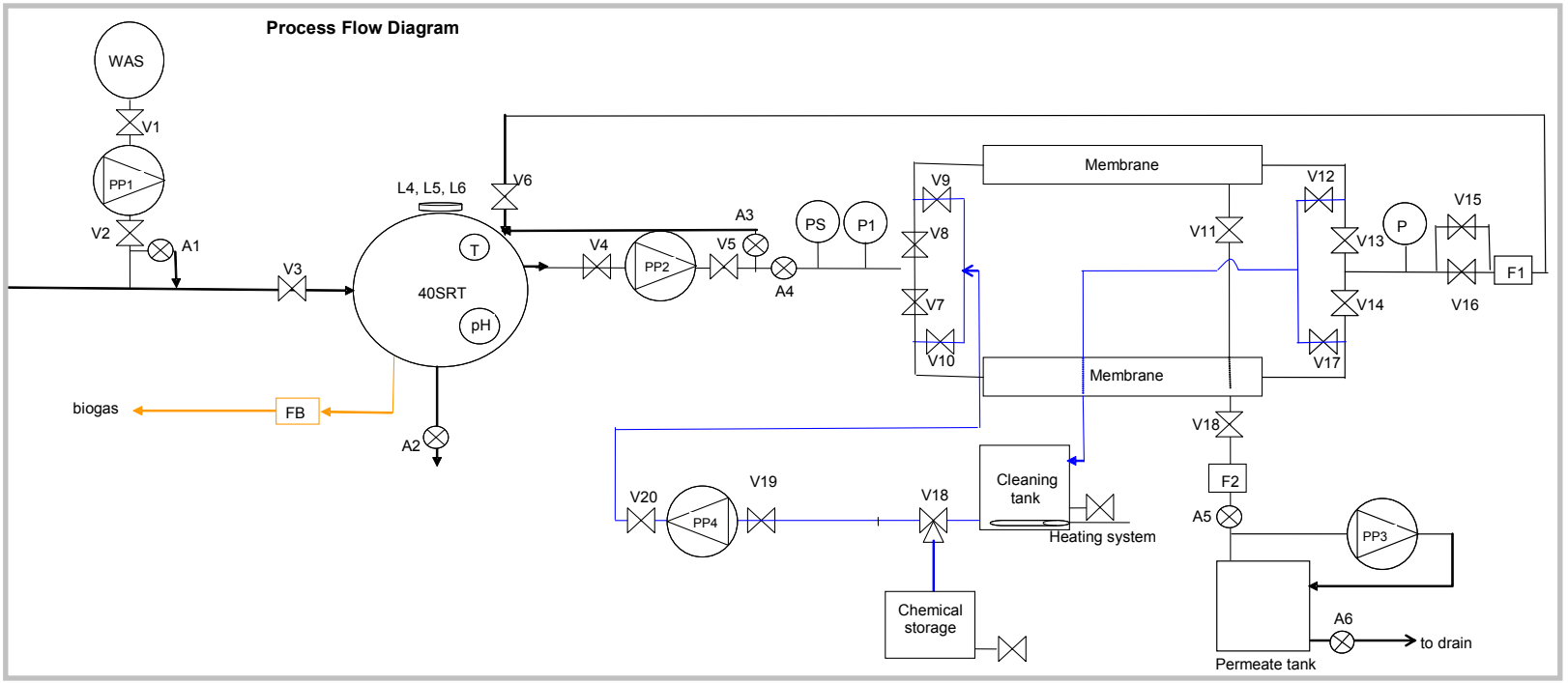
facilitate automatic pumping and wasting of sludge, the weight of the digester was monitored through load cells installed at the base of the digester. Digestion process parameters such as temperature and biogas production were monitored online and recorded every minute.

The HRT of the reactor was maintained by withdrawing a desired amount of liquid both through the membrane unit and from the digester contents and feeding an equal amount of raw sludge with a Moyno pump. The permeate flow rate was measured using a magnetic flow meter. The SRT of the reactor was established by controlling the amount of wasted sludge.

$$HRT = \frac{V}{Q_w + Q_p} \qquad \text{Equation 3-1}$$

$$SRT = \frac{V \quad X_{VSS}}{Q_w X_w + Q_p X_{VSS,P}} \qquad \text{Equation 3-2}$$

Where V = anaerobic digester volume (L); Q_W = effluent flow rate ($Lday^{-1}$); Q_P = permeate flow rate ($Lday^{-1}$); X_{VSS} = volatile solids concentration in the digester ($mgVSS.\ L^{-1}$); $X_{VSS,P}$ = permeate volatile suspended solids concentration ($mg\ VSS.\ L^{-1}$).



CODE	SPECIFICATIONS	CODE	SPECIFICATIONS
PP1	Moyno pump	PS	Pressure sensor
PP2	Small centrifugal pump	F1, F2	Flow meter
PP3	Suction pump	V1 to V15, V17	1" Manual ball valve
PP4	High centrifugal pump	V16	1" Diaphragm valve
A1 to A6	1" Automated ball valve	V11, V18	1/4" Manual ball valve
L1 to L6	Load cell	V19	1" 3-Way manual ball valve
T	Temperature probe	P1	Inlet pressure gauge
pH	pH Meter	P2	Outlet pressure gauge
FB	Biogas flow-meter		

Figure 3-1 Schematic of pilot membrane anaerobic digestion system

3.2.2.2 Conventional (control) digesters

The bench-scale digesters had a 20 L working volume and were equipped with mechanical mixers operating at 90 rpm (Figure 3-2). The digesters were operated semi continuously and fed manually once a day after wasting sludge from the bottom of the reactor. Subsequently an equal volume of feed was pumped to the feed port located on top of the reactor using a peristaltic pump. The biogas production was measured using custom-made laser bubble counters. The temperature of the digesters was maintained at 35±1^{o}C using heat tape connected to a temperature controller.

The pilot conventional digester had a working volume of 530 L and had similar dimensions and operating parameters to that of the digester integrated with the membrane. All conventional reactors had equal SRT and HRT values achieved by wasting and feeding an equal volume of digested and raw sludge respectively (Equation 3-3).

$$HRT = SRT = \frac{V_R}{Q_{inf}} \qquad \text{Equation 3-3}$$

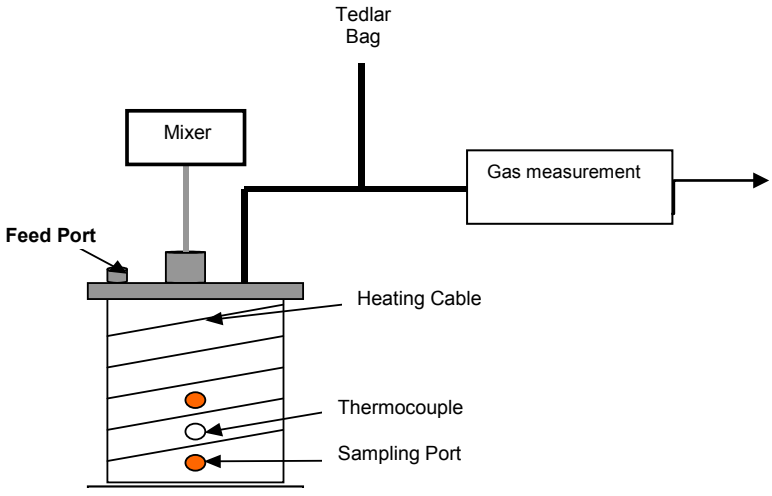


Figure 3-2 Schematic of bench scale anaerobic digester

3.2.3 Experimental plan

Table 3-1 shows the parameters that were varied in the AnM and conventional digesters in a series of experiments, which resulted in 6 different operating scenarios. The hydraulic retention time varied from 7 to 15 days. The SRT varied from 15 to 30 days. The organic loading rate (OLR) calculated based on 2% feed TS concentration and design HRT (1.7% VS and 22 g/L of COD) varied from 0.73 to 3.14 kg COD/m^3/day. The volatile solids loading rate varied from 0.57 to 2.42 kg VS/m^3/day.

Table 3-1 Experimental conditions for conventional and AnMBR digesters

Parameters	AnM digesters HRT - SRT			Conventional digesters (CD) HRT = SRT			
	15-30	7-30	7-15	30	15	7	15[a]
HRT	15	7	7	30	15	7	15
SRT	30	30	15	30	15	7	15
VSLR [b]	1.13	2.42	2.42	2.42	1.13	2.42	1.13
OLR [c]	1.47	3.14	3.14	0.73	1.47	3.14	1.47
Experiment	1	1	2	3	1	2	3

[a] Pilot control digester
[b] Volatile solids loading rate (kg VS/m^3.day), based on average feed VS concentration
[c] Organic loading rate (kg COD/m^3.day), based on average feed COD concentration

Testing of the AnM digester was conducted using a factorial experimental design to evaluate the impacts of the main effects, HRT and SRT, and their interaction on the performance of the membrane-coupled anaerobic digester with respect to VS destruction, biomass yield, biogas production, process stability and digested sludge quality (Table 3-2). The conventional digesters were designed to evaluate the impact of SRT on digester performance. Tables 3-2 and 3-3 show the experimental design for the pilot plant and control digesters.

Table 3-2 Factorial design setup for pilot digester

Factors	Levels	
	High (+)	Low(-)
HRT (days)	15	7
SRT (days)	30	15

Table 3-3 Experimental design for conventional (control) digesters

Factor	Levels		
SRT = HRT, days	7	15	30
Loading classification	High loading	Normal loading	Low loading

The selection of target SRTs and HRTs was based on existing anaerobic digestion practices. According to Metcalf and Eddy (2003), the minimum amount of time required for sludge digestion is around 15 days. Most existing facilities are designed based on a minimum 15 day SRT value. As existing facilities are conventional digesters and don't recycle sludge, the SRT and HRT values are equal.

Experiment 1 was performed at a similar HRT condition to existing facilities but had an extended sludge retention time. The methanogenic bacteria, bacteria responsible for conversion of the hydrolyzed sludge into methane, are slow growing and are mainly responsible for methane production in an anaerobic environment. Thus increasing the sludge age by retaining and recycling the biomass in the reactor using the membrane unit was expected to increase the VS destruction and associated methane production. The bench scale anaerobic digesters were operated in parallel to reflect the conventional operation respectively. For example, experiment 1 refers to a pilot scale operation with SRT and HRT values of 30 and 15 days, respectively. One bench scale reactor (30-30) was run at an SRT of 30 days and the second one (15-15) at 15 days. This facilitated further comparison of the AnM digester 15-30 with the two reference conditions CD-15 and CD-30. Experiments 2 and 3 were designed at shorter HRTs where the interest was to evaluate the increase in OLR and its impact on the AnMBR performance at normal and longer SRTs.

All the digesters were started by filling the digester with active digested sludge from the Skyway WWTP and feeding of digesters was initiated at 25% of the design HRT. This condition was kept for a week and then the feeding rate was increased to 50% of HRT. This was repeated till a 100% HRT feeding rate was achieved. Similarly while changing from one HRT and/or SRT to another value a similar procedure was followed to minimize sudden changes and process upsets.

The conventional bench scale digesters were fed once a day. The conventional pilot digesters operated at 15 days HRT were fed 4 times a day. The AnM digesters were fed 4 times a day during the 15 day HRT period and 6 times a day during the 7 day HRT period.

3.2.4 Sample collection and analysis

Table 3-4 shows the sampling frequency of each analytical parameter for each of the transient and steady state periods. The digesters were operated for at least 3 SRTs before steady state data collection began and, at steady state, digesters were operated long enough to collect sufficient data (60 days during experiment-1, 30 days during experiment-2 and 15 days during experiment-3). To minimize short circuiting and contamination with undigested sludge, samples were collected from the digesters by withdrawing sludge just before the daily feeding.

Duplicate raw sludge, digested sludge and permeate samples were collected on a biweekly basis for solids and COD analysis and on a weekly basis for individual volatile fatty acids, alkalinity and nitrogen fraction analysis (Table 3-4).

Solids and COD fractions: Total solids, volatile solids, total suspended solids and volatile suspended solids concentration were measured according to Standard Methods (method 2540, APHA et al., 1998). A pore size of 1.5 micron was used to filter TSS and VSS samples. The chemical oxygen demand of sludge samples, the filtered COD (fCOD), soluble COD (sCOD) and permeate COD (pCOD) was measured using Hach Analytical reagent vials. Samples were centrifuged at 4000 xg for 10 minutes and filtered through a 1.5 micron filter for fCOD analysis. Subsequently the filtered samples were further passed through 0.45 micron filter for sCOD analysis. Further details of the analytical procedures are described in Chapter 4.

Table 3-4 Digester sampling strategy

Characteristic	Sampling frequency
Solids fractions (TS, VS, TSS, VSS)	Twice per week
COD fractions (TCOD, fCOD, sCOD, pCOD)	Twice per week
Individual VFAs (acetic, priopionic, isonutyrate, butyrate, isovaleric and valeric acids)	Once per week
Nitrogen fraction (TKN, NH_4-N)	Once per week
Alkalinity	Once per week
Salmonella	Once per week during steady state
Fecal coliform	Once per week during steady state

Nitrogen fractions, individual volatile fatty acids (VFAs) and alkalinity: Samples were analyzed by the Environment Canada-Wastewater technology centre laboratory for nitrogen fraction, volatile fatty acids and alkalinity. The TKN samples were digested using a Technicon BD-40 Block Digester. The TKN content of the digested samples and NH_4-N content of the filtered samples were analyzed colourimetrically using a Technicon TRAACS 800 equipped with a 660 nm filter (Technicon TRAACS 800 Method Industrial Manual no. 780-86T, 1986). The individual VFAs (acetic, priopionic, isonutyrate, butyrate, isovaleric, valeric acids) were analyzed by ion chromatography according to Dionex Method 15.7 (Determination of Inorganic Anions and Low Molecular Weight Organic Acids using an IONPAC AS15-5um Column) The weakly retained anions were resolved using a 10 mM KOH solution, while the highly retained anions were eluted using a KOH gradient. The alkalinity was measured according to Standard Methods (method 2320 B, APHA), with pH 4.3 as the titration end point.

Fecal coliform and *Salmonella*: The potential effect of extended SRT operation on pathogen destruction was also evaluated through measurement of fecal coliforms and *Salmonella* following the neo-grid® membrane filtration system (NEO-GRID®/ISO-GRID® total coliform and Salmonella detection methods). The NEO-GRID system is based on the principle of hydrophobic grid membrane filtration. The pathogen indicators were enumerated through the use of a unique membrane filter containing 1600 squares. A sample is filtered through a hydrophobic membrane, and the membrane is placed on an agar plate (EF-18 Agar (6901A)

and MF-C medium were used for *Salmonella* and fecal coliform respectively). Then the plates were incubated at 44^{o}C for 24 hours. After incubation, the membrane was examined, and all squares were containing the target organism were counted and the total number of positive squares were converted to the corresponding most probable number.

Gas volume and composition: The quantity of gas production was measured on a daily basis using a thermal mass flow meter (FCI ST98L model) and custom made laser bubble counters for the pilot and bench scale units respectively. The composition of the digester gas was determined using a gas chromatograph (GC/TCD Agilent 3000A micro GC system) equipped with a thermal conductivity detector. A molecular sieve column was used to separate methane, nitrogen, oxygen and hydrogen. A second column, porous layer open tubular (PLOT-U) was used to separate hydrogen sulfide and carbon dioxide. Helium and argon were used as carrier gases for columns 1 and 2 respectively.

3.2.5 Energy Balance model

To evaluate and compare the sustainability of the AnM digester process to that of conventional digestion, an energy model was developed that took into account the major energy demand/loss and recovery processes (Figure 3-3, Equation 3-4). The energy demand in this context was defined as the energy required for process operation for heating feed sludge (P_{heat_sludge}, Equation 3-5), compensation of energy lost through the walls and roof of the digester (P_{loss}, Equation 3-6), and for operation of a recycling pump used for mixing and/or permeation ($P_{pumping}$, Equation 3-7). Recovered energy was energy associated with the methane content of biogas ($P_{methane}$, Equation 3-8 and 3-9). Equations 3-4 to 3-9 were used to calculate and compare the normalized net energy (energy/volumetric feed flow of digester feed) consumption of the AnM and conventional digesters at each SRT.

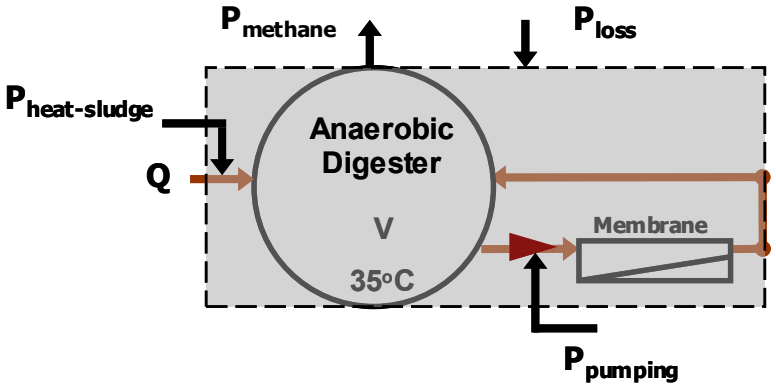


Figure 3-3 Energy balance framework

$$\Delta P_{net} = P_{methane} - \left(P_{feed-heat} + P_{loss} + P_{pump}\right) \quad \text{Equation 3-4}$$

where ΔP_{net} is the net energy and the other variables are defined below.

- $P_{feed-heat}$ is the heat to warm/ elevate feed sludge temperature, kJ*day^{-1}

$$P_{feed-heat} = Q_{feed} * \rho_{sludge} * C_p(T_{digester} - T_{feed}) \quad \text{Equation 3-5}$$

where Q_{feed} is volumetric flow of digester feed (m^3/day), ρ_{sludge} is the density of sludge(kg/m^3), C_p is the specific heat capacity of sludge and was assumed equal to that of water, $T_{digester}$ = 35 ^{o}C and T_{feed} = 5 ^{o}C.

- P_{loss}: heat energy lost through digester walls and roof, kJ*day^{-1}

$$P_{loss} = (A_{cone} + A_{cylinder})k * t(T_{digester} - T_{surrounding}) \quad \text{Equation 3-6}$$

where A is area (m^2), k is heat transfer coefficient for insulated concrete (kJ hr^{-1}m^{-2}^{o}C^{-1}) (Metcalf and Eddy, 2003), $T_{digester}$ = 35 ^{o}C and $T_{surrounding}$= 20 ^{o}C

- P_{pump}: energy required for recycling and/ or permeation (kJ*day^{-1}) (Lubken et al., 2007)

$$P_{pump} = Q_{recycle} * H * \rho_{sludge} * g * t * \frac{1}{\eta} \quad \text{Equation 3-7}$$

Where $Q_{recycle}$ was the recycle rate (kg/s) H is the head (m), ρ_{sludge} is density of sludge in kg m^{-3}, g acceleration due to gravity (m s^{-2}), t is time for pumping (h day^{-1}) and η is pump efficiency.

- $P_{methane}$ is the energy recovered from methane produced during the anaerobic digestion process, kJ*day^{-1}

$$P_{methane\ (electrical)} = Q_{CH_4} * H_c * \eta_{electrical} \qquad \text{Equation 3-8}$$

$$P_{methane\ (thermal)} = Q_{CH_4} * H_c * \eta_{thermal} \qquad \text{Equation 3-9}$$

$$P_{methane} = P_{methane\ (electrical)} + P_{methane\ (thermal)} \qquad \text{Equation 3-10}$$

Where Q_{CH4} methane production per day (m^3day^{-1}), H_c is the calorific value of methane, $\eta_{electrical}$ *(=0.35) and* $\eta_{thermal}$ *(= 0.5)* electrical and thermal degree of efficiency.

3.2.6 Statistical analysis

Statistical analyses were performed to compare the significance of the impact of the experimental factors (SRT and HRT) on the AnM digester performance as determined by its stable operation, COD and VS removal efficiencies, biogas generation, quality of the digested sludge and overall normalized net energy balance. The ANOVA of 2^2 factorial experiments were conducted using the summary data of each response variable (mean, standard deviation, number of samples). Analyses were also conducted to evaluate the significance of the impact of SRT on the aforementioned response variables during conventional digester operation. In this case single factor ANOVA analyses were conducting using the summary data of each response variable. Multiple mean comparisons a posteriori tests were conducted using a Tukey's honestly significant difference (HSD) test to determine which means were statistically significant. Factors were considered statistically significant at a 95% confidence interval ($p < 0.05$). Prior to calculating summary data, all raw data were checked for normal distribution and a p value greater than 0.05 indicated normal distribution.

3.3 RESULTS and DISCUSSION

3.3.1 Feed characteristics

Feed sludge characteristics at each SRT and HRT during the three experiments are summarized in Table 3-5. The average (standard deviation) feed total solids concentration was 17.1(4.4) g/L and average volatile solids concentration was 12.2 (3.3) g/L. The VS to TS ratio was 0.71(0.27). Significance difference were not observed in the feed solids (VS) concentrations and composition (VS/TS) during the various experimental periods (single factor ANOVA, p=0.35 and 0.95 respectively) (Table 3-5). The average feed total COD concentration was 19.4(5.5) g/L and significant differences were not observed between the various experiments (ANOVA, p=0.29). The sCOD concentration ranged between 380 and 860 mg/L during experiments 2 and 3, and these difference was significant (ANOVA, $p<0.0$). The feed sCOD concentration was not measured during Experiment-1. The fCOD concentrations ranged between 450 and 1200 mg/L. Higher fCOD concentrations were observed during experiments 1 and 3. This increase could be attributed to seasonal impacts.

The feed TKN and normalized TKN values ranged between 1.11 to 1.62 g/L and 7 to 9% of TS and no significant difference was observed between the various experiments (ANOVA, p=0.1 and 0.6 respectively). However the NH_4-N concentration varied significantly (ANOVA, p=0.003) with an average NH_4-N concentration of 120 mg/L for the feed collected over the summer time versus 30 mg/L for the feed collected during the winter season. The feed alkalinity concentration ranged between 869 to 1685 mg/L and showed significant variation between winter and summer feed samples (p=0.02). Raw feed sludge was also analyzed for individual volatile fatty acids (C2-C6). Acetic acid and priopionic acid concentrations are summarized in Table 3-5. Overall the acetic acid concentration ranged between 86 to 261 mg/L and propionic acid concentration between 34 to 134 mg/L.

The feed sludge composition- with respect to the ratios of VS to TS and TKN to TS were within the range reported in literature (Metcalf and Eddy 2003, WEF 2009). The raw feed data are tabulated in Appendix B.

Table 3-5 Summary of raw feed sludge characteristics

	Mean (standard deviation) (number of samples) (normality: P value*)		
Parameters	**Exp-1 (HRT,SRT)** AnM 15,30 CD 30,30 &15,15	**Exp-2 (HRT,SRT)** AnM 7,30 CD 7,7	**Exp-3(HRT,SRT)** AnM 7,15 CD 15,15**
Solids fractions (g/L)			
TS	16.2 (4.3) (19) (0.3)	15.9 (2.5) (13) (0.5)	18.3 (4.1) (8) (0.9)
VS	11.9 (3.3) (19) (0.3)	11.4 (2.0) (13) (0.4)	13.4 (3.0) (7) (0.4)
VS/TS	0.70 (0.29)	0.72 (0.17)	0.73 (0.23)
COD fractions (g/L)			
TCOD	19.8 (6.3) (20) (0.03)	17.4 (4.7) (13) (0.03)	21.3 (5.7) (8) (0.9)
sCOD	NA	0.38 (0.17) (10) (0.03)	0.86 (0.21) (7) (0.4)
fCOD	1.2 (0.5) (17) (0.3)	0.45 (0.16) (12) (0.03)	0.97 (0.20) (7) (0.9)
sCOD/TCOD		0.02 (0.01)	0.04 (0.01)
Nutrients (g/L)			
TKN	1.11 (0.31) (11) (0.3)	1.21 (0.28) (6) (0.2)	1.62 (0.01) (2) (0.2)
NH4-N	0.14 (0.06) (11) (0.7)	0.03 (0.00) (5) (0.8)	0.11 (0.00) (2) (0.2)
sTKN		0.07 (0.06) (4) (0.1)	0.2 (1)
NH4-N/TKN	0.12 (0.11)	0.03 (0.01)	0.07 (0)
TKN/TS	0.07 (0.03)	0.08 (0.00)	0.09 (0.02)
Acid/base (mg/L)			
Acetic acid	86 (78) (9) (0.3)	110 (43) (5) (0.6)	261 (81) (2) (0.2)
Propionic	34 (28) (9) (0.5)	58 (25) (5) (0.8)	134 (67) (2) (0.2)
Alkalinity	1136 (349) (10) (0.5)	891 (201) (6) (0.2)	1685 (50) (2) (0.2)
Timeline	01-Apr 2008 to 06-June-2008	06-Jan-2009 to 24-Feb-2009	13 April 2009 to 15 May 2009

*****Data evaluated for normal distribution prior to calculating the statistics, p value > 0.05 indicated the data is normally distributed at α=0.05

** Pilot control reactor

3.3.2 AnM and conventional digester operation

Table 3-6 summarizes the actual operating conditions for the digesters for each experimental condition. The actual HRTs and SRTs varied between 7.1 to 28.6 days and 7.1 to 30 days respectively. These values were close to the design HRT and SRT values. The average COD and VS loading rates for the digesters operated under normal loading conditions (HRT=15 days) were 1.3-1.4 kg COD/m^3·day and 0.8 kg VS/m^3·day respectively. The high rate

digesters (HRT=7 days) had loadings of 2.1-2.8 kg COD/m^3·day and 1.4-1.8 kg VS/m^3·day respectively. The raw data for HRT, SRT, OLR and VSLR throughout the experimental periods are shown in Appendix C.

Table 3-6 Summary of actual steady state operating conditions of AnM and conventional digesters

Parameters	AnMBR digesters			Conventional digesters			
	15,30	7,30	7,15	30	15	7	15[a]
Actual HRT	15.8	8.4	7.6	28.6	14.3	7.1	16.4
Actual SRT	29.6	30	15.9	28.6	14.3	7.1	15.9
VSLR	0.76 (0.11)	1.36 (0.23)	1.76 (0.28)	0.42 (0.21)	0.84 (0.33)	1.60 (0.47)	0.82 (0.10)
OLR	1.25 (0.40)	2.08 (0.65)	2.81 (0.85)	0.70 (0.22)	1.40 (0.44)	2.40 (0.66)	1.28 (1.0)
Run time, days	160	160	75	160	160	75	365
Experiment	1	2	3	1	1	2	3

[a] Volatile solids loading rate (kg VS/m^3.day), based on average feed VS concentration
[b] Organic loading rate (kg COD/m^3.day), based on average feed COD concentration

3.3.3 Digester stability

The concentration of intermediate products like volatile fatty acids (VFA) and the ratio of VFA to alkalinity are common indicators of process stability. An accumulation of VFA in the digester may result from problems in the syntrophic bacterial relationships between the H_2 producing and consuming bacteria and/or insufficient methanogenic population to utilize all VFA produced. The ratio of volatile fatty acids to alkalinity (α) has been used as a parameter to indicate process stability. For a digester to have a stable operation it's α value should be less than 0.2 (Poggi-Varaldo and Oleszkiewicz, 1992).

Average alkalinity and normalized alkalinity, acetic acid and acetic acid to alkalinity ratio (α) values for the AnM and conventional digesters at each SRT are summarized in Table 3-7. The alkalinity concentration in the conventional digesters ranged from 2200 to 3200 mg/L and the normalized alkalinity concentration ranged from 0.16 to 0.27 mg alkalinity/mg TS. The alkalinity and normalized alkalinity increased with SRT and the variations were significant (ANOVA: P<0.00). A multiple mean comparison test showed that the differences were only significant when the shorter SRT (7 days) was compared against the longer SRTs (15 and 30 days). No difference was observed between 15 and 30 day SRTs.

Higher values of alkalinity at longer SRTs were likely related to a greater amount of protein degradation. During anaerobic de-amination of proteins, ammonia is produced and its reaction with carbon dioxide and water results in the production of ammonium bicarbonate (Speece 1996). In the AnM digesters the normalized alkalinity was between 0.17 to 0.20 g alkalinity/g TS and significant difference was not observed. Overall the observed normalized alkalinity concentrations were generally lower at 7 day SRTs. However the AnM digester operated at 7-15 days and the control pilot digester operated at 15-15 HRT-SRT had alkalinity concentrations anomalously high, this perhaps was related to the changes in feed sludge. As shown in Table 3-5 the feed to these reactors had significantly higher alkalinity and TKN concentrations (Exp-3). The data for alkalinity and acetic acid are presented in Appendix F.

Table 3-7 Summary of alkalinity and acetic acid concentrations in the digested sludge

Parameters	**AnMBR digesters**[a]			**Conventional digesters**[a]		
	15,30	7,30	7,15	30	15	7
Alkalinity[b]	3.7 (4.8)	5.7 (1.1)	5.8 (0.8)	3.2 (0.3)	3.0 (0.4)	2.1 (1.0)
Acetic[b]	8.2 (8.0)	3.7 (2.5)	6.7 (1.6)	11.0 (8.3)	8.9 (3.4)	7.5 (2.6)
Propionic[b]	0.9 (1.1)	ND	ND	0.8 (1.18)	1.3 (1.1)	ND
Alpha	0.002	0.0006	0.001	0.003	0.003	0.003
n[c]	10	6	2	8	9	5
Alk:TS	0.19 (0.03)	0.17 (0.04)	0.20 (0.03)	0.27 (0.04)	0.24 (0.04)	0.16 (0.01)

[a] Average values during steady state and standard deviations are in parenthesis
[b] Units for alkalinity = g/L as $CaCO_3$ and for acetic and propionic acid =mg/L
[c] n=number of samples during steady state operation

Table 3-7 also summarizes the acetic and propionic acids measured in the digesters. The acetic acid concentration in the digesters ranged between 3.7 to 11 mg/L and the variations between the digesters were not significant (ANOVA: P>0.5). Other VFAs including propionic, valeric, butyric and isobutyric were not detected. The very low VFA concentrations were indicative of stable operation of the digesters.

The average COD and VS loading rates for the digesters operated under normal loading conditions (HRT=15 days) were 1.3-1.4 kg COD/m^3·day and 0.8 kg VS/m^3·day respectively. The high rate digesters (HRT=7 days) had loadings of 2.1-2.8 kg COD/m^3·day and 1.4-1.6 kg VS/m^3·day respectively. The potential for unstable operational at higher loadings were carefully monitored through alkalinity and VFA measurements. No reactor failures from sharp drops in pH as a result of imbalance between acidogens and methanogens were observed. The pH in all the digesters remained between 6.9 and 7.1 throughout the studies. All digester configurations, including conventional digesters fed at high rates demonstrated stable performance with α values of less than 0.003 (Table 3-7). This was attributed to the relatively slow hydrolysis rates for the TWAS solids as well as the substantial release of NH_3 that is associated with digestion of these types of solids.

3.3.4 Volatile solids and COD removal

The VS content was used as an indicator of the amount of organic matter contained in the sludge. Volatile solids and COD changes were used to represent the evolution of the organic matter during the anaerobic digestion processes.

3.3.4.1 Solids and COD concentration

The AnMBR and conventional digesters were operated for about 160, 160 and 75 days during experiments 1, 2 and 3 respectively. The average TS, VS, TSS and VSS and COD concentrations of the digesters are summarized in Table 3-8. Overall the concentrations of solids decreased with increasing HRTs for conventional digesters. For AnM digesters a concurrent digestion and thickening took place. Hence the solids and COD concentrations in these digesters were dependent not only on HRT but also on the SRT to HRT ratio where an overall decrease in solids concentrations were observed with an increase in HRT and decrease

in SRT to HRT ratio. The general trend of the TCOD concentration agreed with the trend in solids concentrations. The average COD to VS ratio in all the reactors was about 1.56±0.01 and was comparable to theoretical values (MetCalf and Eddy 2003). The raw data for solids and COD concentrations are presented in Appendices D and E, respectively.

Table 3-8 Summary of solids and TCOD concentrations of AnM and conventional digesters

Parameters	AnMBR digesters			Conventional digesters			
	15,30	7,30	7,15	30	15	7	15[a]
TS, g/L	19 (1.8)	30.9(3.9)	29.2(2.0)	11.6(0.9)	12.5(1.3)	13.5(1.3)	13.6(1.3)
VS, g/L	11.9(1.3)	19.3(2.6)	18.2(1.3)	7.1(0.5)	7.9(0.9)	8.7(0.9)	8.5(0.9)
TSS, g/L	17.2(2.3)	28.3(3.8)	25.8(1.9)	10.1(1.0)	11.1(1.4)	11.0(1.4)	10.5(1.2)
VSS, g/L	11.2(1.5)	18.4(2.4)	17.6(1.2)	6.6(0.8)	7.5(1.0)	8.5(1.0)	8.2(0.9)
TCOD, g/L	17.9(2.2)	28.9(3.7)	27.4(1.7)	11.0(1.2)	12.2(1.2)	14.0(1.2)	12.6(1.1)
n[b]	19	13	8	17	18	15	18
Experiment	1	2	3	1	1	2	3

[a] Pilot control digester
[b] number of samples during steady state operation

3.3.4.2 Calculations of COD and VS removal

The VS and COD removal efficiencies of the digesters were evaluated following a cumulative mass balance approach. This approach was utilized to facilitate data interpretation and account for the daily solids and COD variation within the digesters in response to variations in the feed TWAS/WAS concentrations. The method involved calculation of the mass of solids fed into the digester and the mass wasted from the digester during the steady state period as per equation 3-11 and 3-12. For the AnM digesters the mass of COD wasted was calculated by adding the sludge and permeate COD. Subsequently the cumulative mass of VS and COD fed and cumulative mass of VS and COD wasted were plotted versus time and the slopes were calculated using a simple linear regression model. The COD and VS removal efficiencies were then calculated from the slopes as per equation 3-13. The cumulative VS and COD fed and wasted versus time plot for the AnM digester operated at 15-30 HRT-SRT is shown in Figures 3-4a and b. Additional plots for the AnM and conventional digesters are presented in Appendix D.

$$S_{fed} = S_{in} * (Q_w + Q_p) \qquad \text{Equation 3-11}$$

$$X_{wasted} = X * Q_w \qquad \text{Equation 3-12}$$

$$\%\, removal = 100 * \left[\frac{m\left(S_{fed}^{cumulative}\right) - m\left(X_{wasted}^{cumulative}\right)}{m\left(S_{fed}^{cumulative}\right)}\right] \qquad \text{Equation 3-13}$$

where:

- S_{fed} is the daily mass fed to digester (g/day), S_{in} feed sludge concentration (g/L), Q_w is the volume of sludge wasted per day (L/day) and Q_p is the volume of permeate per day (L/day). The specific gravity of sludge assumed as 1. Experimental data of specific gravity of sludge over range of solids concentrations is presented in Appendix C.
- X_{wasted} is the mass of digested sludge wasted (g/day),
- $m\left(S_{fed}^{cumulative}\right)$ is the slope of the cumulative sludge fed (g/day) and $m\left(S_{wasted}^{cumulative}\right)$ is the slope of the cumulative sludge wasted during steady state period.

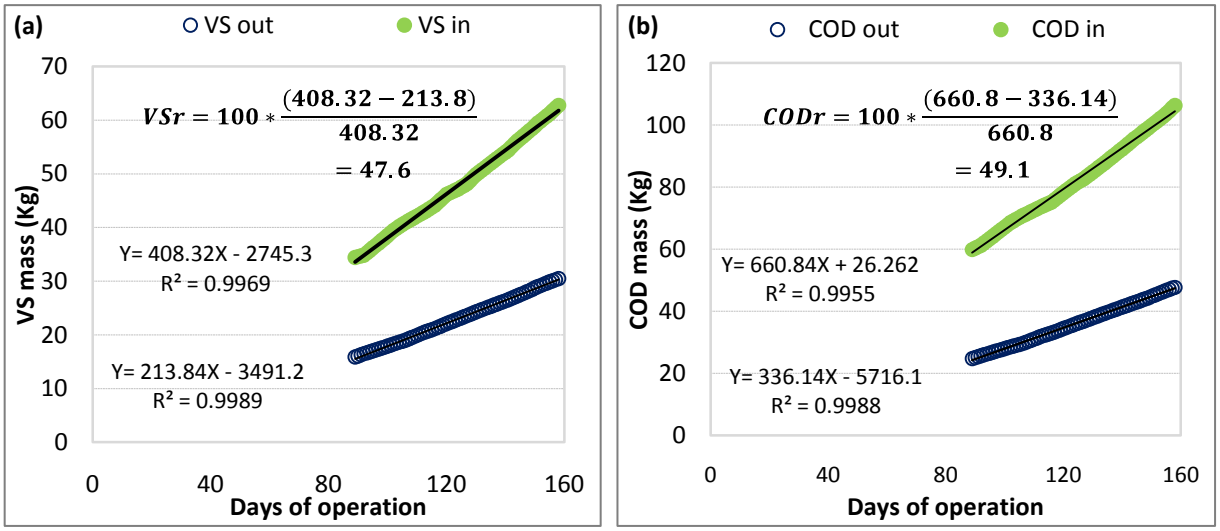


Figure 3-4 (a) VS and (b) COD removal calculation based on cumulative mass balance: AnM digester 15-30 HRT-SRT

3.3.4.3 SRT and HRT on COD and VS removal

Table 3-9 summarizes the average VS and COD removal efficiencies for both conventional and AnM digesters at each SRT. VS removals of 25 to 50% were observed when digesting sludge at SRTs of 7 to 30 days. The lowest removal of 25% VS destruction was observed during conventional digester operation at a higher loading. Under this condition the digester failed to meet regulatory requirements as under mesophillic conditions a volatile solids reduction of at least 37% is required for sewage sludge to be considered as stabilized sludge (WEF 2009).

Overall, for conventional digesters; where the SRT=HRT, a decrease in VS destruction was observed with decreasing solids/hydraulic residence time (Table 3-9). An increase in SRT from 7 days to 15 and 30 days led to 42% and 78% increases (relative to 7 days) in the VS destruction respectively. Analysis of variance showed the differences were statistically significant for all levels (P<0.0).

Table 3-9 Summary of VS and COD removal at steady state for AnM & conventional digesters

AnM digester					**Conventional digester**			
SRT	HRT	VS_r (%)	COD_r(%)	n[a]	SRT=HRT	VS_r (%)	COD_r(%)	n[a]
30	15	47.6(1.9)	49.1(2.0)	20	30	43.8(2.6)	44.0(2.1)	18
30	7	48.6(3.1)	50.8(3.8)	14	15	35.2(3.4)	38.0(2.5)	19
15	7	36.0(1.5)	40.6(1.8)	9	7	24.7(1.8)	24.9(3.5)	16
					15[b]	32.5(2.4)	37.3(1.7)	16

[a] n= number of samples
[b] Pilot conventional digester

For the AnMBR digesters 35 to 49% VS removals were observed. When the AnMBR digester was operated at an SRT of 30 days and operated at normal loading (15 day HRT) and high loading (7 day HRT), VS destructions of 48 and 49% were achieved (Table 3-9). These differences were not statistically significant. For the digester operated at a 7 day HRT but a 15 day SRT the VS removal was 36% and extending the SRT to 30 days resulted in an increase of VS destruction to 49% (increase by 35% relative to 7 days CD). Statistical analysis showed the

VS and COD percent removals were significantly affected by SRT ($P<0.0$) however the effects of HRT and the HRT by SRT interaction were not significant (Factorial analysis).

A comparison of the AnM and conventional digesters fed with a higher loading showed significant difference in the degree of VS stabilization. For example the VS removal of a conventional digester operated at 7 days SRT (HRT) was only 25% (as shown previously). Comparatively when integrating membrane and extending the SRT from 7 to 15 and 7 to 30 days an increase in VS removal by 46 and 100 % (relative to the conventional 7 days digester) was observed.

These results suggest that the integration of the membrane allowed a substantial increase in feeding rate without compromising the digester's performance. Previous studies have reported a decline in AnMBR performance associated with shearing of the anaerobic biomass in the filtration process (Brockmann and Seyfried, 1997; Ghyoot and Verstraete, 1997; Padmasiri et al., 2007). In this study a negative effect was not observed and this could be attributed to the low pressure and velocity of membrane operation that minimized floc shear.

3.3.4.4 Empirical and kinetic models for the estimation of VS reduction

Empirical models: Liptak et al. (1974) had developed a non linear regression model (equation 3-14) to estimate the VS destruction based on SRT and raw feed sludge VS destruction. To date the equation is commonly used to estimate the percent volatile destruction for preliminary design purposes. In this case the equation was used to estimate the VS destruction. However it overestimated the VS destruction over all ranges of SRT (Figure 3-5a) as the model was developed based on primary sludge. In this study as HRT was found not to have effect on the overall VS destruction, the VS removal data was pooled from all experiments and plotted against the SRT respectively, Figures 3-5. The best fit to the data was a logarithmic function as shown in equations 3-15 and 3-16 with R^2 values of 0.95 and 0.92 for VS and COD removal respectively.

$$VS_r = 13.7\ ln\ (SRT) + 18.9 \qquad \text{Equation 3-14}$$

$$VS_r = 15.4\ ln\ (SRT) - 3.8 \qquad \text{Equation 3-15}$$

where VS_r is the volatile solids removal (%) and SRT is the sludge retention time in days.

The application of these equations could be limited to the experimental data. To further compare the experimental data with information available in the literature and better understand the expected process parameter and performance relationships, a kinetics model was evaluated.

Kinetic model: A simple steady state model was introduced to characterize the theoretical relationship between process parameters and process performance of the AnMBR and conventional systems. The steady state model was based on the rate of hydrolysis, assuming it is the slowest kinetic rate that governs the overall behavior of WAS digestion and relating this process rate to the design and operating parameters.

For particulate material the hydrolysis rate can be expressed by assuming first order kinetics corrected by the non degradable fraction as follows:

$$r_h = k_h(X - \beta X_o) \qquad \text{Equation 3-16}$$

Where $r_h$the rate of solids degradation, k_h is the first-order kinetics constant, X is the concentration of solids, β is the non degradable fraction of the solids and X_o is the initial solids concentration. Based on equation 3-15 and assuming most of the biodegradable VS was degraded at 60 days SRT, the calculated biodegradable VS fraction was 60%.

Further, by employing a steady state mass balance equation on the particulate fraction (X) and assuming the accumulation of endogenous decay products is negligible, the fraction remaining after digestion (1-VS reduction) was determined as follows:

$$\frac{X}{X_o} = \left(\frac{SRT}{HRT}\right)\frac{(k_h \beta HRT+1)}{(k_h HRT+1)} \qquad \text{Equation 3-17}$$

This equation was used to estimate the VS reduction for conventional (CSTR) and AnMBR digesters over a range of SRTs. Figure 3-5(a) presents a comparison of the model predictions with the experimental VS reduction data. Overall, the model predictions were in the same order of magnitude as the experimental AnMBR and CSTR data. It can be seen that the model overestimated the VS reduction for shorter SRTs when a 0.25 d^{-1} hydrolysis rate constant was assumed (Vavilin et al., 1996) however were in agreement for longer SRTs. Subsequently, the hydrolysis rate constant was calibrated to the experimental data. The calibrated model based on K_h value of 0.11 d^{-1} fits the data better for all ranges of the SRT and the different reactor configurations. This indicates that the behavior of the AnMBR was similar to the CSTR and can be explained using a hydrolysis model. Secondary sludge hydrolysis rate constants reported in literature were 0.17-0.6 (Ghosh, 1981), 0.22 (Gosett and Belser, 1982), 0.25 (Siergrist etal., 1993). Comparatively the hydrolysis rate constant obtained for the current dataset was slightly lower. This could be due to partial stabilization of the highly degradable fractions on the upstream process where the aeration basin was operated at a relatively extended SRT. In this case major components of the activated sludge could be proteins and lipids that have a relatively lower hydrolysis rate.

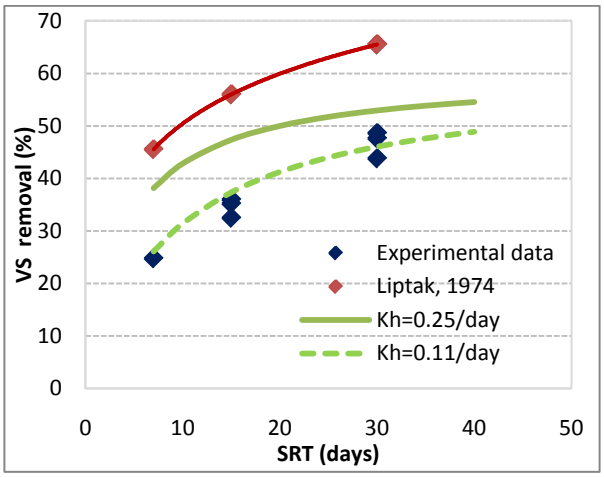


Figure 3-5 Percent VS removal

3.3.5 Gas production

The COD removed in the anaerobic digesters is converted into methane. To determine the amount of methane produced from the removed COD, the volume and composition of gas produced from the AnM digesters and conventional digesters were measured continuously. Comparisons were made based on the amount of gas produced per COD or VS fed (specific methane production), amount of gas produced per VS removed (methane yield) and based on the daily methane production rate (MPR).

3.3.5.1 Specific methane production and methane yield calculation

Similar to VS and COD concentrations, the gas produced in the digester varied in response to variations of the feed sludge concentration. Hence the cumulative approach discussed in section 3.3.4.2 was followed to calculate the specific methane production per unit of COD and VS fed. Figures 3-8a and b show plots of the cumulative VS and COD mass fed to the digester and cumulative volume of gas generated during a steady state operational period of the AnM digester when operated at a 15 day HRT and 30 day SRT. Subsequently the specific methane production per units of COD and VS fed were calculated as per equation 3-18:

$$SMP = 100 * \left[\frac{m\left(Q_{CH4}^{cumulative}\right)}{m\left(S_{fed}^{cumulative}\right)}\right] \qquad \text{Equation 3-18}$$

where *SMP* is the specific methane produced per unit of COD or VS of sludge fed (m^3 CH_4/kg sludge fed), $m\left(Q_{CH4}^{cumulative}\right)$ and $m\left(S_{fed}^{cumulative}\right)$ are the volume of cumulative methane generated and mass of sludge fed during steady state operation. In these analyses the volume of the solublized methane fraction that was exiting the system with the permeate was determined to be very small and were not included in the methane yield data. A similar approach was followed to calculate the methane yield. In this case the methane yield was calculated by (equation 3-19):

$$methane\ yield = \frac{m\left(Q_{CH4}^{cumulative}\right)}{m\left(S_{fed}^{cumulative}\right) - m\left(S_{wasted}^{cumulative}\right)} \qquad \text{Equation 3-19}$$

where the methane yield is in L CH4/g sludge (COD or VS) removed, $m\left(Q_{CH4}^{cumulative}\right)$ is in L/day, and $m\left(S_{fed}^{cumulative}\right)$ and $m\left(S_{wasted}^{cumulative}\right)$ are in g/day.

As an example, Figures 3-9a and b show plots of the cumulative methane generation, and COD and VS fed and wasted during a steady state operation of the AnM digester when operated at a 15 and 30 day HRT and SRT. The cumulative plots of AnM and conventional digesters and respective specific methane production and yield calculations at each HRT-SRT combination are presented in Appendices D and E.

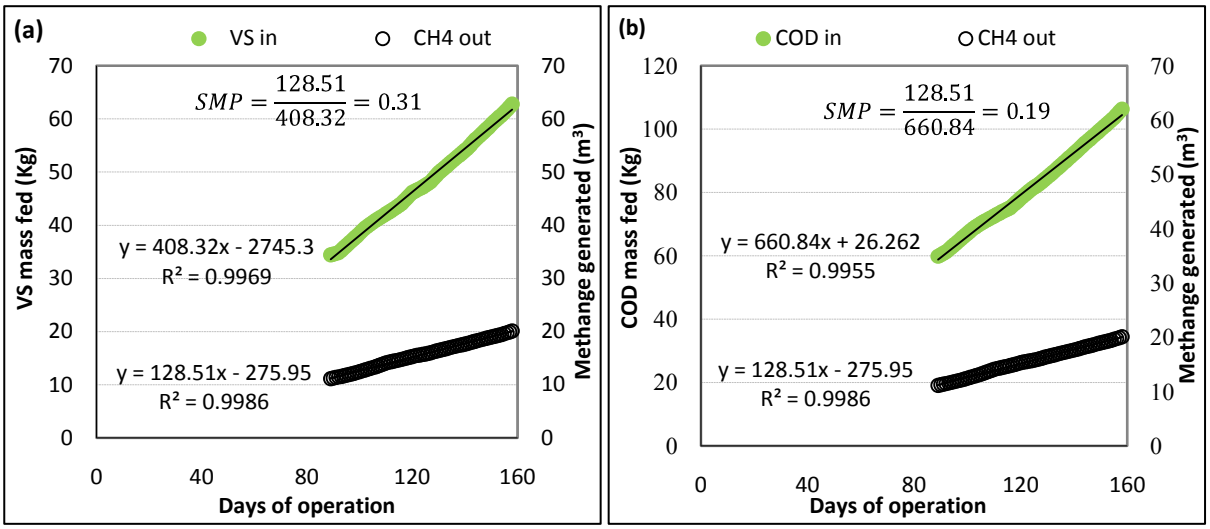


Figure 3-6 Specific CH_4 production (a) per VS fed (b) per COD fed calculation based on cumulative mass balance: AnM 15-30 HRT-SRT digester

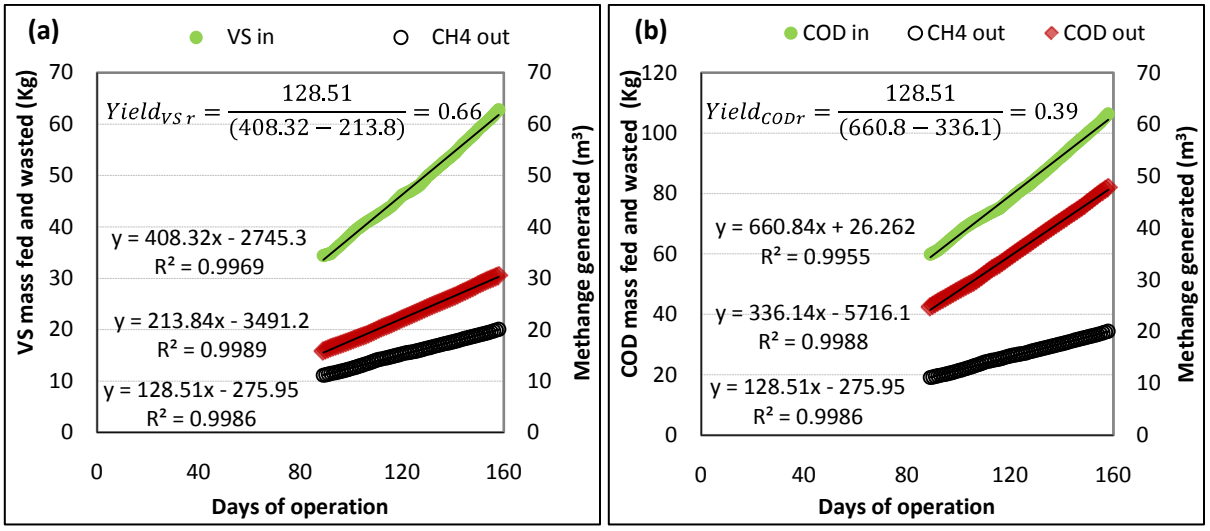


Figure 3-7 Methane yield per (a) VS removed and (b) COD removed calculation based on cumulative mass balance: AnM 15-30 HRT-SRT digester

3.3.5.2 Impact of SRT and HRT on specific methane production and methane yield

Table 3-10 summarizes the values of specific methane production, methane yield (methane produced per COD and VS removed) and methane concentration in the conventional and AnM digesters at each SRT.

The values of specific methane production for 15-30, 7-30 and 7-15 AnM digesters were 0.19, 0.19 and 0.14 m^3 CH_4/kg of COD fed and 0.31, 0.28 and 0.23 m^3 CH_4/kg of VS fed respectively. The results showed the AnMBR at a higher SRT enhanced the specific methane generation irrespective of the volume of feed added to the digesters. The specific methane production for 30, 15 and 7 days conventional digesters were 0.16, 0.13 and 0.09 m^3 CH_4/kg of COD fed and 0.27, 0.2 and 0.15 m^3 CH_4/kg of VS fed respectively. Overall, for conventional digesters; where the SRT=HRT, a decrease in specific methane production was observed with decreasing solids/hydraulic residence time (Table 3-10). A decrease in SRT from 30 days to 15 and 7 days led to 25% and 57% decreases (relative to 30 days) in the specific methane production. At a higher loading (7 days HRT) integrating the membrane and allowing the reactor to run at a relatively longer 30 days SRT increased the CH_4 production per g COD fed by 111 % (relative to the 7 days conventional reactor).

Table 3-10 Summary of SMP and methane yield for AnM and conventional digesters

Parameters	**AnMBR digesters (HRT,SRT)**			**Conventional digesters (HRT=SRT)**		
	15,30	7,30	7,15	30	15	7
SMP ($L\ CH_4/g\ COD_{fed}$)	0.19(0.01)	0.19(0.01)	0.14(0.01)	0.16(0.01)	0.13(0.01)	0.09(0.02)
SMP, ($L\ CH_4/g\ VS_{fed}$)	0.31(0.01)	0.28(0.01)	0.23(0.01)	0.27(0.02)	0.20(0.01)	0.15(0.03)
CH_4 yield, ($L\ CH_4/gCOD_r$)	0.40(0.06)	0.37(0.07)	0.35(0.09)	0.37(0.07)	0.33(0.06)	0.37(0.14)
CH_4 yield ($L\ CH_4/g\ VS_r$)	0.66(0.02)	0.58(0.02)	0.65(0.03)	0.61(0.04)	0.58(0.03)	0.60(0.15)
CH_4 concentration (%)	67.9(2.7)	71.8(5.1)	70.2(2.2)	67.9(2.5)	65.4(2.7)	58.6(6.3)

*Number of samples was similar to the ones reported in Table 3-9

The corresponding values of methane yield based upon VS destroyed were about 0.66, 0.58 and 0.65 m^3 CH_4/kg of VS for AnMBR operating at 15-30, 7-30 and 7-15 HRT-SRT respectively. For the conventional digesters the yield values were 0.61, 0.58 and 0.60 and were within the range of literature values. Metcalf and Eddy (2003) indicate the average methane yield per kg of VS destroyed to be 0.66 m^3. Similarly the methane yield expressed as m^3 CH_4/kg COD_r remained between 0.35 to 0.4 and 0.33 to 0.37 for the AnM and conventional digesters respectively. These values are in the range of the theoretical value of 0.40 m^3 CH_4/g COD_r (at T=35^{o}C and standard pressure). The gas production results also agree with the previously presented volatile solids destruction results. Based on mass balances, similar solids destruction efficiencies should result in similar gas production.

The percent methane in the biogas varied between 65-71%, and remained similar in all cases except for the conventional digester operated at 7 days HRT=SRT. The lowest value was observed at 7 days HRT conventional digester (~ 59%).

3.3.6 COD mass balances

COD mass balances were conducted for the steady state operation to assess the quality of the experimental COD, VS and biogas data. The equations used for the COD balance were:

$$COD_{fed} = COD_{effluent} + COD_{CH_4} \quad \text{Equation 3-20}$$

$$VS_{fed} = VS_{effluent} + \frac{1}{1.6} COD_{CH_4} \quad \text{Equation 3-21}$$

Where COD_{fed} and VS_{fed} are the mass of COD and VS fed during steady state period (kg/day), $COD_{effluent}$ is the mass of wasted sludge and permeate COD (kg/day). The COD equivalent of methane (COD_{CH4}) was quantified using the stoichiometric coefficient 0.4 m^3 CH_4/kg COD. $VS_{effluent}$ is the mass of sludge VS wasted (the permeate VS concentration was assumed negligible. A constant $\frac{1}{1.6}$ was used to convert COD to VS (1 kg of COD=1.6 kg of VS) (WEF 2009).

Table 3-11 shows a summary of the mass balance data. An overall good agreement was observed between the feed and waste sludge and biogas measurements with only small deviation in mass balance closure.

Table 3-11 Summary of mass balance data based on COD and VS

Parameters[1]	AnMBR digesters (HRT,SRT)			Conventional digesters (HRT=SRT)		
	15,30	7,30	7,15	30	15	7
COD_{fed}	660.8	1092.7	1503	13.9	26.9	53.7
$COD_{effluent}$	336.1	537.8	893	7.8	16.7	40.3
COD_{CH4}	321.2	518.5	530.7	5.7	8.5	12.2
Percent difference	**-0.5**	**-3.3**	**-5.3**	**-3.3**	**-6.5**	**-2.2**
VS_{fed}	408.3	729.6	912.6	8.5	16.7	32.6
$VS_{effluent}$	213.8	374.7	584.3	4.8	10.8	24.6
VS_{CH4}	200.8	324.0	331.7	3.5	5.3	7.6
Percent difference	**1.5**	**-4.2**	**0.4**	**-2.3**	**-3.5**	**-1.4**

[1] COD and VS values were in kg/day.

3.3.7 Generation of soluble sludge components

Changes in soluble products are often indicative of the extent of biodegradation of particulate material. The behavior of soluble anaerobic digestion products was examined to obtain more information on the impact of digester configuration and operating conditions on digestion performance. The most substantial changes in sludge solution during anaerobic digestion included the production of NH_4-N due to biological degradation of nitrogenous matter, the increase in soluble COD (sCOD) and the increase in solution polymeric substances (Novak et al. 2003). The NH_4-N and soluble COD concentrations in the digested sludge are summarized in Table 3-12.

The sCOD concentrations of the digesters at the 7 day HRT were 235 mg/L (SRT of 7 days), 354 mg/L (SRT of 15 days) and 373 mg/L (SRT of 30 days). Hence, a comparison between digesters operated at 7 days HRT but of varying SRT showed increases in sCOD concentration by 32% and 60% with increase in SRT to 15 and 30 days respectively (relative to 7 days SRT). Similarly a comparison sCOD concentration between digesters operated at 15 days SRT showed a 53% increase when the SRT was extended from 15 to 30 days (AnM 15-30 versus CD 15-15, Table 3-12).

The average (standard deviation) feed NH_4-N concentration were 95 (57) mg/L. Upon digestion the ammonia concentration increase by 4 to 8 fold depending on the process condition. The lowest increase in ammonia concentration was observed when the digester was operated at a 7 day HRT and SRT. Under this HRT condition, the AnM digester operated at 15 and 30 days SRT showed an increase in NH_4-N generation by 70 and 50 % (relative to the 7 days conventional digester). The AnM digester operated at 7-15 had NH_4-N concentrations that were anomalously high, that may have been related to the feed sludge. As shown in Table 3-5 the feed to these reactors had significantly higher alkalinity and TKN concentration (Experiment-3). A modest 5% increase in NH_3-N was observed when the digester with 15 days HRT was operated with a 30 days SRT (relative to the 15 days conventional digester).

The observed higher NH_4-N and sCOD concentrations at longer SRTs indicated a greater extent of protein and COD biodegradation respectively as compared to the shorter SRTs. These results confirmed the greater VS destruction and CH_4 production that were observed under these conditions.

Table 3-12 Summary of NH_4-N and sCOD concentrations in AnM and conventional digesters

Parameters*	**AnMBR digesters (HRT,SRT) mean (SD)**			**Conventional digesters (HRT=SRT) mean (SD)**		
	15,30	7,30	7,15	30	15	7
sCOD, mg/L	675(81)	373(82)	354(82)	500(103)	440	235(25)
NH_4-N, mg/L	743(66)	611(121)	746(49)	767(20)	715(47)	435(33)

*Standard deviations in parenthesis

3.3.8 Digested sludge and permeate quality

To assess the quality of the digested sludge; the TS, TKN and pathogen indicator data were compared for the AnM and conventional digesters at each SRT. *Salmonella* and fecal coliform concentrations in the digesters were measured as indicators of pathogens. The permeate quality among the AnM digesters were also compared based on the COD and NH_4-N concentrations. Table 3-13 shows a summary of TS, TKN, normalized TKN, *Salmonella* and fecal coliform concentrations for the digested sludge. Table 3-14 depicts a summary of the permeate COD and NH_4-N concentrations.

Overall the TS concentration in the digesters ranged between 11.6 to 32.8 g/L and the concentration were affected by both the digestion and co-thickening process as in the AnM digesters. For conventional digesters the TS concentration decreased with an increase in the HRT (i.e. 13.5 at 7 day HRT and 11.6 g/L at 30 day HRT). For the AnMBR digesters operated at a similar loading (7 days HRT) but operated at 30 days SRT, the solids concentration increased to 32.8 g/L. These digesters were operated with a similar feed concentration. The TS in these digesters were increased by a factor of SRT/HRT ratio multiplied by the ratios in the solids removal rate as per equation 3-22:

$$TS^{7,30} = \frac{SRT(=30\ days)}{HRT(=7\ days)} * TS^{7,7}\left[\frac{VS_r^{7,7}}{VS_r^{7,30}}\right] \qquad \text{Equation 3-22}$$

This resulted in about a 2.5 times concentrated sludge to that of the corresponding conventional digesters fed with an equal load, hence minimizing the volume of biosolids for downstream processing.

Table 3-13 Summary of TS, TKN and pathogen indicators of AnM and conventional digesters

Parameters	AnMBR digesters			Conventional digesters		
	15,30	7,30	7,15	30	15	7
TS, g/L	19 (1.8)	32.8(4.2)	29.2(2.0)	11.6(0.9)	12.5(1.3)	13.5(1.3)
Digester FSS, g/L	5.9(1.1)	9.8(1.9)	8.6(0.9)	3.5(1.3)	3.5(0.6)	2.7(0.5)
Feed FSS	3.5(1.0)	2.6(1.0)	4.4(2.1)	3.5(1.2)	3.5(1.2)	2.6(3.3)
TKN, g/L	1.44(0.03)	2.26(0.03)	1.97(0.03)	1.17(0.11)	1.23(0.14)	1.14(0.03)
TKN/TS	0.08(0.06)	0.07(0.06)	0.07(0.06)	0.10(0.08)	0.10(0.08)	0.09(0.06)
Salmonella[1]	$12.1 *10^3$	$12.1 *10^3$	NM	$7*10^3$	$9.84*10^3$	$7*10^3$
Fecal coliforms[2]	$2.8*10^4$	$2.9*10^4$	NM	$1.9*10^4$	$1.43*10^4$	$1.6*10^4$

[1]Feed *Salmonella* concentration was $5*10^5$ MPN/g VS
[2]Feed fecal coliform concentration was $1.53*10^6$ MPN/g VS

One possible drawback for the implementation of AnM digesters is the possibility of accumulation of inert solids in the digester and reduction in the active volume of the digester.

To assess this effect the fixed suspended solids (FSS) concentrations were calculated and compared among the AnM and with the conventional digesters relative to the feed sludge FSS's concentration. The results showed that in the conventional digesters the FSS concentration in the digesters remained similar to the feed sludge concentration (Table 3-13). In the case of AnM digesters the FSS concentrations in the digester were higher indicating an accumulation of inert materials in the digester. The FSS concentrations in the AnM digesters were accumulated at the ratio rate of SRT/HRT and final concentrations corresponded to the SRT/HRT multiplied by the feed FSS concentrations.

The increase in FSS concentration in the 15-30 and 7-30 (HRT-SRT) resulted in a loss of about 1 and 2 % volume of the digester (with SRT/HRT ratio of 2 and 4) and the impact was not that pronounced. However if the digestion process was operated at a very high SRT (for example 60 days) and a shorter HRT (like 4 days), the accumulation of inert materials could have cause about 7.5% loss in digester volume. The accumulation factor and loss of digester volume is not significant when the feed has a lower FSS concentration. However at higher FSS feed concentrations, using raw feed sludge screens may minimize the introduction and further accumulation of fixed suspended solids within the digester.

The concentration of TKN increased with increase in HRT and was slightly higher for AnMBRs mainly due to the co-thickening (Table 3-13), however the ratio of TKN to TS concentration remained constant and was within the range of 0.08 to 0.1 for all digesters. This was similar to the normalized feed TKN concentration. These results are expected as nutrient removal is not accomplished with the anaerobic treatment processes.

The impact of the digester configuration and operating condition (SRT, HRT) were also examined with respect to pathogen destruction. The results showed an overall 1 and 2 log reductions for *Salmonella* and fecal coliform concentrations respectively. However no difference was observed between the pathogen destruction potential with changes in SRT and among the digesters. This is in agreement with previous studies that suggested that further destruction of fecal coliform and/or *Salmonella* would require thermophilic operating conditions.

The permeate COD ranged between 174 to 209 mg/L (Table 3-14). The sCOD concentration for the 15-30, 7-30 and 7-15 digesters were 675, 373 and 354 mg/L. The NH_4-N concentrations of the permeate were higher than the feed and consistent with the sludge NH_4-N. With the higher NH4-N concentration, the permeate could either be returned back to the secondary process or followed by a nutrient recovery unit prior to disposal.

Table 3-14 Summary of permeate quality during steady state operation

Parameters	AnMBR digesters		
	15,30 (days)	7,30 (days)	7,15 (days)
Permeate COD, mg/L	209(80)[1]	179(28)[1]	174(18)[1]
Permeate NH_4-N, g/L	757(82)	683(94)	759(151)

[1]number of samples were 13, 9 and 7 respectively

3.3.9 Sustainability of AnMBR versus Conventional Digesters

Table 3-15 presents the results of energy balances that were conducted for the conventional and AnM digesters when operating in the various configurations. Overall it appeared that much of the energy was required to heat the feed sludge. In the case of the conventional digester operated at a 30 day SRT, an equal amount of energy was also required to maintain the temperature of the digester itself. In all cases the pumping energy required for recycling/permeation was very low.

For conventional digesters, the energy balances were negative (Table 3-15). The additional VS destruction and methane production achieved by extending the SRT to 30 days did not provide sufficient additional energy to compensate for the energy required to maintain the heat loss from the digester walls and roofs. By comparison the energy balance for AnM digester operation was higher. The AnMBR provided two advantages from an energy balance aspect: a longer SRT that resulted in additional VS destruction with the associated methane recovery, and also co-thickening, which decreased the volume of digester and decreased the heat requirement to maintain digester temperature. Overall the AnM digester operating at the higher

loading rate (7 days HRT) and longer SRT of 30 days appeared to be most beneficial from an energy recovery point of view.

These results were somewhat specific to the pilot operating conditions. For example in this study, the feed was chilled all the time and its temperature was 5^{o}C. In full scale applications the temperature could range as high as 30^{o}C and low as 5^{o}C and hence less energy would be required to heat the feed sludge. Further for full scale applications, due to the decrease in surface to volume ratio the energy lost from the surface of the digesters is negligible. The energy required for pumping remained similar to values reported in Table 3-15. In this case the conventional digesters have a positive net energy balance. Therefore under full scale condition an increase in the net energy balance is mainly associated with increase in the amount of methane production per volume of feed

Table 3-15 Energy balance comparison between conventional and AnMBR digesters

Energy per fed	AnMBR digesters			Conventional digesters		
GJ m^{-3}fed	15,30	7,30	7,15	30	15	7
$P_{feed\ heating}$	-126	-126	-126	-126	-126	-126
$P_{surface\ loss}$	-64	-30	-30	-30	-64	-127
P_{pump}	-2.4	-4.1	-2.8	-0.53	-1.0	-1.7
$P_{methane}$	+214	+214	+150	+107	+150	+188
Balance	**+22**	**+54**	**-8.8**	**-49.2**	**-40.8**	**-66.5**
Fed vol., $m^{-3}day^{-1}$	0.035	0.076	0.076	0.018	0.035	0.076

3.4 SUMMARY

This chapter compared AnMBR performance and sustainability with conventional digesters, discusses changes in biosolids composition and quality and addresses challenges of AnMBR when operating at conventional and high loading rates and extended solids residence times. It was confirmed experimentally that increasing SRT resulted in significant improvement of the percent COD and VS removal efficiency and associated increase in gas production and improvement in the energy balance of the process.

A pilot scale AnMBR operating at a 30 day SRT and 15 day HRT demonstrated 35% more solids destruction than a conventional digester operating at 15 days when fed with 1.34 kg COD/m^3day. The net energy balance for the AnMBR was positive (22 GJ/m^3) as compared to that of the conventional digester that was negative (-40.8 GJ/m^3). When the HRT of the AnMBR was decreased to 7 days (COD loading of 2.35 kg COD/m^3day) the VS destruction was maintained and hence an increase in the net energy balance by 60 % was observed. By comparison with a conventional digester operated at 7 days HRT, an increase in VS removal by 100% was observed by integrating the membrane with the digester and extending the SRT.

The increase in solids residence time appeared to increase degradation of protein containing materials as shown by an increase in the NH_4-N concentration from 421 to 740 mg/L. In all cases the biosolids remained as Class B type, with an average 2 log fecal coliform reductions. However AnM digesters produced thickened digested sludge, minimizing the volume of sludge per digester volume for downstream processing. With the AnM digesters also an accumulation of fixed suspended solids were observed, however it resulted only in 1 and 2% loss of digester volume. However inert accumulation could be an issue at shorter HRTs and longer SRTs than the one's considered in this study.

Chapter 4

4. MEMBRANE PERFORMANCE IN ANMBR DIGESTING WAS

4.1 Background

Anaerobic membrane bioreactors (AnMBRs) provide a sustainable technological solution for digestion of WAS due to their capacity to achieve substantial volatile solids destruction and positive energy balances with reduced digester volumes. A major concern in the application of AnM digesters for WAS stabilization is the possible decline of the permeation flux as a result of membrane fouling. Unlike MBRs treating wastewater, AnM digesters treating WAS are subjected to sludge with high fouling characteristics such as relatively higher concentrations of suspended solids, colloidal organic and soluble inorganic materials that are released upon digestion, and an increased fraction of smaller size particles. The development of innovative membrane materials and the identification of optimized process conditions that improve the filterability of biosolids are expected to address a number of these issues. Previous studies have examined the application of AnM digesters for high solids wastes including sludge (Perkiel and Lanting, 2005; Pillay et al., 1994; Ghyoot and Verstraete, 1997), swine manure (Padmasiri et al., 2007) and dairy waste (Zitomer et al., 2005).

Most prior research has focused on evaluating the general performance of AnM digester processes under one set of conditions. However, what is lacking is detailed examination of the membrane performance, as well as insights into the fouling mechanisms, foulant types and foulant layer characterization in relation to SRT and HRT dependent parameters. Also there is no guidance with respect to selecting membrane and digester process parameters and their effect on biosolids characteristics which in turn affect the performance of the AnM digesters treating high solid wastes. This research was conducted to address most of these issues.

4.1.1 Conceptual model to describe behavior of foulants in AnM digester

Fouling materials can generally be categorized based on size, surface charge/chemistry, chemical type and origin of source. Previous MBR studies have suggested that the size of the foulant has the greatest impact on fouling propensity (Judd 2006). Hence, in this study the

digested sludge was fractionated and characterized based on size as being either solid or supernatant (colloidal and soluble) components of sludge. The solid fractions consists primarily of the suspended solids and include anaerobic biomass and decay products, non biodegradable particulates coming with the feed, bound biopolymers and associated cations that are present mainly within the floc matrix. The supernatant fraction consists of cellular products that are excreted and/or released during cell lysis and decay, biodegradable and non biodegradable soluble and colloidal materials coming with the feed, and cations released into solution. Upon stabilization, the behavior of these components changes: some being generated, others consumed, accumulated or remaining constant.

Figure 4-1 shows the classification of sludge components that may affect membrane flux and result in membrane fouling. In this classification there exists no standard method to fractionate sludge components hence the categories such as suspended, colloidal and soluble are an operationally defined scheme depending on the measurement method used. Following the classification a conceptual model was laid out a priori to facilitate development of the research objectives and experimental plan, aid in identification of sampling protocols and carrying out of mass balances thus enabling an understanding of the behavior of potential foulants and their origin. Figure 4-2 shows a schematic diagram of an AnM digester system with mass balance components.

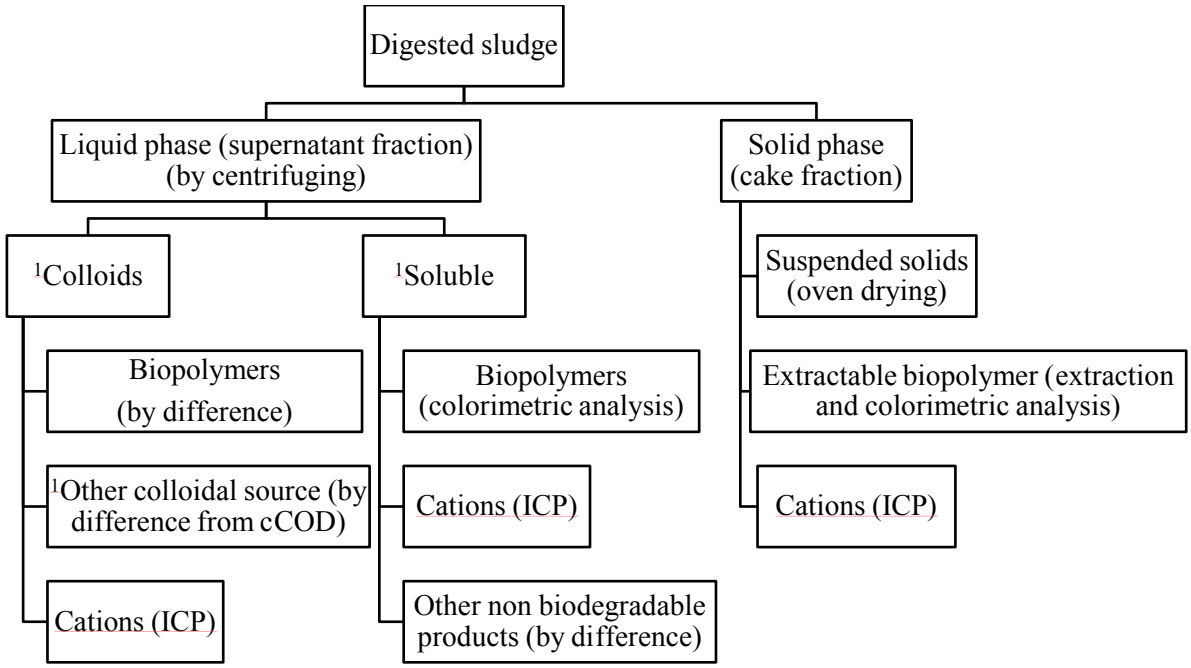


Figure 4-1 Sludge fraction components and their composition

[1]Soluble refers to a centrifuged sludge component that could pass through 0.45 µm standard filter. The colloidal component refers to sludge components present after filtration of a centrifuged sample using 1.5 µm filter (which are referred to as filtered components to denote that they are not necessarily soluble) minus permeate or the soluble fraction. Centrifuging of the sample prior to filtration was a critical step to minimize formation of secondary filter layer and colloidal matter retention on the filter.

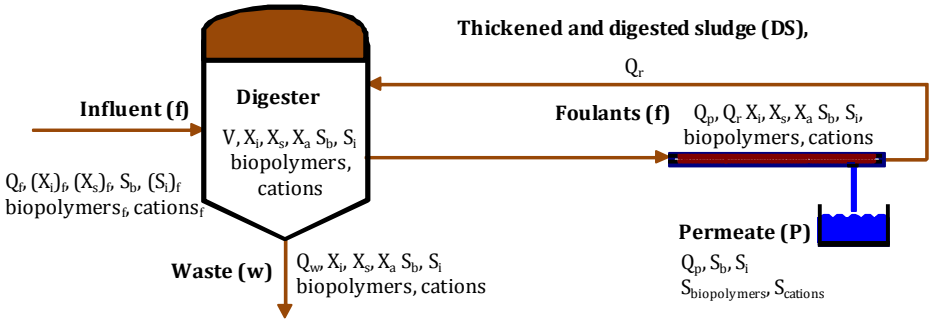


Figure 4-2 Schematic of AnM digester process with mass balance components

Where subscript *f, p, w* and *r* are influent, permeate, waste and return concentration and/or flow; Q = flow; V = volume of digester; X_a = active biomass concentration; X_i = non-biodegradable particulate; X_s = biodegradable particulate; S_b = biodegradable soluble, S_i = non-biodegradable soluble material; biopolymer could be extracted, filtered or soluble ($S_{biopolymer}$); similarly cations include the ones found within flocs ($X_{cations}$) or in solution ($S_{cations}$)

For AnM digesters stabilizing WAS, no previous sludge characterization data was available to indicate the changes in the sludge components and composition when operated at a range of SRT and HRTs. Similarly no data was available to describe membrane performance as a function of digester operational parameters. However previous studies with aerobic membrane bioreactor (MBR) systems treating wastewater have shown that the concentration and composition of various sludge components and hence their impact on fouling propensity were influenced and relatively controlled through the reactor design parameters such as HRT and SRT (Le-Clech et al., 2006). For example as the SRT of an MBR increases while keeping a short hydraulic retention times (HRT):

1. An increase in suspended solids concentration and a decrease in extractable biopolymer in the solids fraction were observed (Brookes et al., 2003)
2. In the liquid phase (supernatant) fraction:
    a. a decrease in colloidal biopolymer, a decrease in other biodegradable colloidal components was observed
    b. a decrease in soluble biopolymers and other organic fractions was observed (Brookes et al., 2003; Grelier et al., 2006 and Rosenberger et al., 2006)
3. Overall, previous MBR studies treating wastewater have shown that operating MBRs at increased SRTs results in a decrease of foulant concentrations thereby resulting in better membrane performance (Trussell et al., 2006 and Grelier et al., 2006).

In the case of sludge digestion research has shown that with increase in SRT, the fraction of hydrolyzed sludge increases. This results in release of colloidal and soluble organic and inorganic materials. Also sludge contains a relatively larger fraction of non- and very slowly biodegradable materials. Hence with a decrease in HRT and an increase in SRT to HRT ratio accumulation of the non- and slowly biodegradable particulates was expected.

Therefore in this study it was hypothesized that in an AnM digester stabilizing WAS, extended SRTs and short HRTs would increase the generation of sludge colloidal fractions and the concentration of sludge solid fractions and hence membrane performance would decline.

In this study selected SRT and HRT combinations were examined to determine whether their variation would impact the physical, chemical and biological characteristics of the digested

sludge and ultimately affect membrane performance. Hence, the mechanism of fouling, methods of fouling control and the ability to recover membranes through cleaning was also anticipated to differ. The interrelationships of process design parameters, sludge characteristics and membrane performance that were investigated are summarized in Figure 4-3.

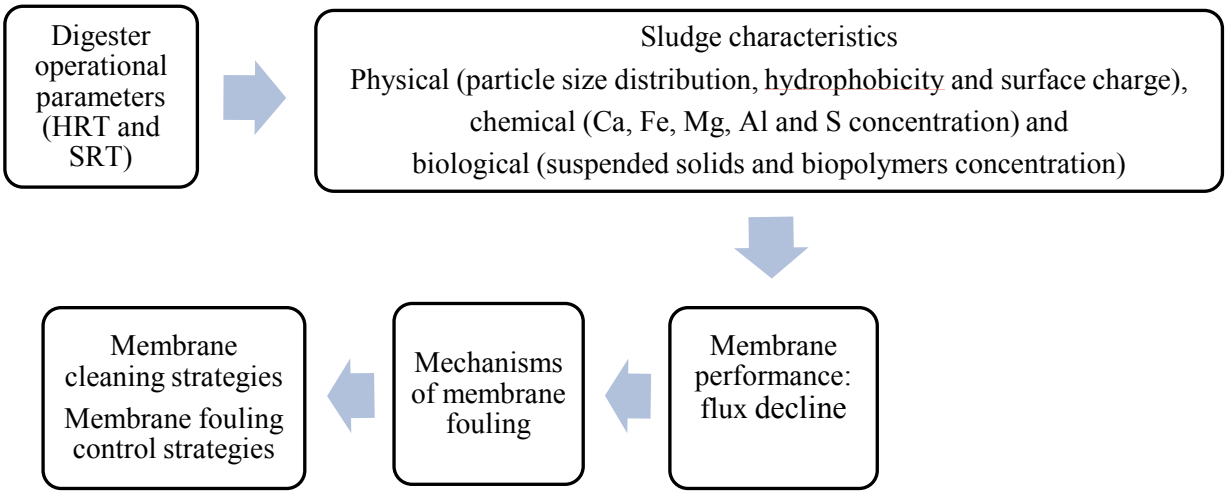


Figure 4-3 Interrelationships investigated

4.1.2 Summary of objectives

The primary objectives addressed through this study are summarized as follows:

1. Evaluate the impact of membrane type, membrane flux, digested sludge concentration, composition and pretreatment on membrane fouling using short term bench scale tests

2. Identify changes in anaerobic digested sludge characteristics and their effect on membrane performance at varying HRT and SRT at pilot scale

3. Identify the type of foulants, mechanisms of fouling, characteristics of fouling layer and fouling control strategies for a negative and neutral membranes operating under differing conditions.

4.2 Materials and methods

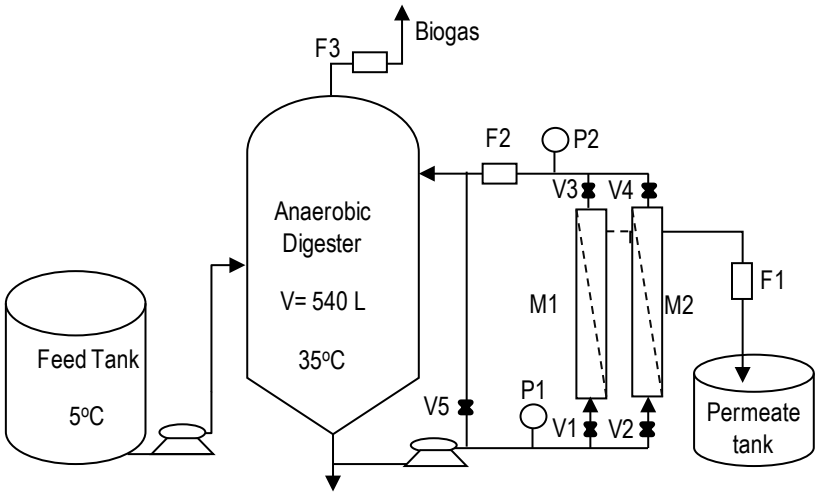
One of the critical issues in the application of any membrane bioreactor is membrane fouling which refers to the decline in membrane flux over time. Selection of design and operating conditions, cleaning approach and frequency, feed pretreatment requirements and overall cost considerations are all affected by membrane fouling. Hence, any application of AnMBR requires a detailed understanding of fouling behavior, mechanisms, foulant types and fouling control strategies. Although research on the fouling behavior of AnM digesters treating sludge is limited, quite a number of studies have been done on AnMBRs treating relatively dilute wastewaters. Accordingly, membrane fouling in these types of membrane bioreactor operations was attributed to 1) adsorption of soluble organics and biopolymers on and within the membrane pores 2) attachment/deposition of microbial flocs and fine colloids on the external surface of the membrane, and 3) deposition of inorganic precipitates at the membrane surface (Choo and Lee, 1996; Liao et al., 2006; Huang et al., 2009; Lin et al. 2009 and An et al., 2009).

The mechanism of fouling or the type of foulant could depend on several factors including wastewater strength, redox environment (aerobic versus anaerobic), membrane configuration (submerged versus external), composition of the feed, bioreactor operating conditions and surface properties of the membrane. In the application of AnM digesters to sludge, the complex nature of the feed sludge, coupled with very high solids concentrations, was expected to exacerbate the problems of membrane fouling as compared to previous studies in wastewater treatment. Hence, short and long term filtration tests were conducted through bench and pilot scale experimental setups respectively to study the membrane performance, fouling behavior, foulant type and fouling control strategies when employing AnM digester for concurrent thickening and digestion of WAS.

4.2.1 Pilot membrane setup and operation

The pilot anaerobic digester employed in this study had a working volume of 540 L and was integrated with a membrane module (KOCH, ABCOR®-FEG™ PLUS MODULE) that had two parallel membranes (Figure 4-4). The membranes represented as M1 and M2 in Figure 4-4 had neutral (ABCOR®-FEG™ PLUS MODULE: 10-HFM-276-PVI) and negatively

(ABCOR®-FEG™ PLUS MODULE: 10-HFP-276-PVI) charged surface respectively. The pilot was built to allow the use of one membrane at a time. For example during M1 operation, valves V1 and V3 were open and valves V2 and V4 were closed and vice versa. The membranes were integrated into the recycle line of a centrifugal recycle pump (G and L Goulds, NPO) that also provided continuous mixing of the digester. This allowed use of the mixing pump for generation of trans-membrane pressure (TMP) gradient to drive the membrane and created a CFV to scour and lessen cake formation on the membrane surface.



where F1, F2 and F3 represent permeate flow meter, membrane feed flow meter and gas flow meter respectively. P1 and P2 represent feed and concentrate pressure respectively. And V1, V2, V3 and V4 represent ball valves and V5 represent a bypass valve

Figure 4-4 Schematics of pilot AnM digester

Most of the membrane operation and data acquisition was controlled using a programmable logic controller (PLC) and Labview software respectively. The membrane inlet pressure, (feed pressure; P_f) and the pressure on the permeate side (permeate pressure; P_p) were monitored online using pressure sensors (Endress+Hauser PMC 131). The pressure on the membrane outlet (concentrate pressure; P_c) was monitored using a pressure gauge. Magnetic flow meters (Endress+Hauser Promag 53) were used to record and monitor the feed flow rate to the membrane (Q_f) and the permeate flow rate (Q_p). The permeate flow was periodically checked

using a graduated cylinder and stopwatch. The volume of the digester was continuously monitored using load cell sensors mounted at the bottom of the digester. Signals from the load cell were automatically fed back to the PLC to regulate the opening and closing of permeate, feed and wasting valves. In doing so, the daily volume of permeate, amount of digested sludge to be wasted and amount of raw sludge fed to the digester were automatically controlled. The HRT and SRT of the digester were regulated by controlling the daily mass fed and wasted sludge using load cells and as per equations 4-1 and 4-2,

$$HRT = \frac{V}{Q_f}, \qquad \text{Equation 4-1}$$

$$SRT = \frac{V}{Q_{ds}}, \qquad \text{Equation 4-2}$$

where V is volume of digester (L), Q_f is daily feed to the AnM digester ($Lday^{-1}$) and Q_{ds} is daily sludge wasted from the AnM digester ($Lday^{-1}$). In this case the specific gravity of both raw feed and digested sludge was assumed as 1. Experimental data on the density of raw and digested sludge are shown in Appendix C.

The AnM digester temperature was set at 35^{o}C and all the membranes, hoses and tubes connecting the membranes to the digester were insulated to minimize heat loss. The temperature of the digester was monitored online using a resistance temperature detection (RTD) probe. The temperatures along the pipelines and membrane unit were periodically verified using a mercury thermometer.

To perform periodic cleaning-in-place of the membrane the unit was equipped with a chemical cleaning tank that could be heated up to 60^{o}C and a pump that was dedicated to providing water at 53 $Lmin^{-1}$ from the tank to the membrane in the opposite direction of the feed flow. This same tank was also used as a clean water tank for clean water flux analysis. A detailed flow sheet of the AnM digester is presented in Appendix A.

The membranes were of equal size with surface and cross-sectional areas of 0.2 and 0.00049 m^2 respectively. Both membranes were made of polyvinylidene fluoride (PVDF) material and had similar operating ranges. In contrast to the membranes often used in MBRs for municipal

wastewater treatment, these membranes were amenable to high temperature and extreme pH conditions (Table 4-1) that made them attractive for anaerobic sludge digestion which is often conducted at an elevated temperatures of 35 and/or 55^{o}C. The membranes also had mechanical and chemical resistance properties that made them the preferred membranes for challenging situations such as those created when chemical cleaning was conducted. The specifications and operating conditions of the ultra-filtration units are presented in Table 4-1(KOCH product literature).

Table 4-1 Specifications of the membranes (source: KOCH product datasheet)

	Neutral membrane (M1)	Negative membrane (M2)
Material	PVDF	PVDF
MWCO	100,000 Dalton	120,000 Dalton[1]
Diameter × length	2.54 × 25.4 cm	2.54 × 25.4 cm
Max. operating temperature	60 ^{o}C	60 ^{o}C
pH: continuous operation	2-10	2-10
pH: short term operation	1.5-10.5	1.5-10.5
Max. inlet pressure	90 psi	90 psi
Max. pressure on permeate side	5 psi	5 psi

[1]This is approximately equal to 0.02 μm

The membranes were operated at constant trans-membrane pressure, TMP (equation 4-3) and cross-flow velocity, CFV (equation 4-4) and the permeation flux, J (equation 4-5) was monitored to describe its performance. Constant TMP and CFV were maintained by manually regulating the membrane feed flow rate through throttling the bypass valve, V5 (Figure 4-4).

$$TMP=\left(\frac{P_f+P_c}{2}\right)-P_p, \quad \text{Equation 4-3}$$

$$CFV=\left(\frac{Q_r}{A_{cross\text{-}section}}\right), \quad \text{Equation 4-4}$$

where TMP, P_f, P_c and P_p are trans-membrane, feed, concentrate and permeate pressure in KPa. CFV stands for cross-flow velocity in ms^{-1}, Q_r is recycle flow rate to the membrane (m^{3}s^{-1}) and $A_{cross\text{-}section}$ is the membrane's cross sectional area in m^2.

$$J=\left(\frac{Q_p}{A_{surface}}\right), \quad \text{Equation 4-5}$$

where J is the permeation flux ($Lm^{-2}h^{-1}$ often referred as LMH), Q_p is the permeate flow rate (Lhr^{-1}) and $A_{surface}$ is the membrane surface area (m^2).

4.2.2 Bench scale membrane setup

A bench scale membrane apparatus was assembled to conduct short term filtration tests under controlled conditions. A schematic of the bench scale membrane setup is shown in Figure 4-5. A similar type of membrane and mode of operation to that of the pilot plant was adopted. The bench scale system consisted of three 50 L tanks that were employed for the feed digested waste activated sludge, clean water and backwash solutions respectively, a 30 cm long by 2.5 cm diameter horizontally mounted KOCH tubular ultra-filtration membrane, a centrifugal pump to re-circulate the feed continuously through the loop and a peristaltic permeate suction pump. The membrane module was operated at room temperature with a constant cross flow velocity that was adjusted by regulating the flow from the centrifugal pump. The feed, concentrate and permeate pressures were recorded using a digital pressure gauge. The permeate flow rate was recorded using a balance and/or graduated cylinder and stopwatch. The temperature was also monitored using a mercury thermometer. The concentrate from the loop and the permeate were returned to the feed tank to keep the feed volume and composition constant.

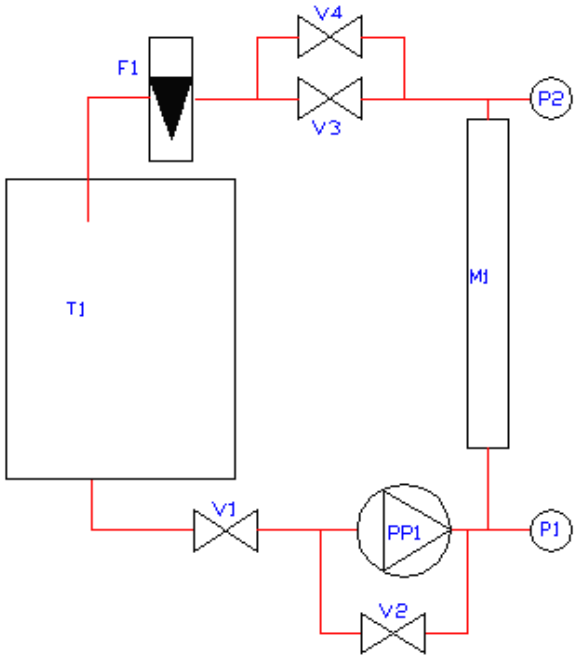


Figure 4-5 Schematics of bench scale membrane setup

4.2.3 Short term filtration experimental plan

Short term filtration tests were carried out to assess the influence of feed concentration, membrane type, and membrane flux and filtration time on membrane fouling in a controlled environment. Further studies were also conducted to identify foulants through fractionation and to characterize the impact of polymer addition on fouling. A methodology involving relaxation operation to control membrane fouling was also developed and introduced for the first time for tubular membrane operation. The details of the short term filtration tests used to evaluate membrane performance under different conditions are described below. The testing was completed in two phases (preliminary and detailed). In the preliminary phase the critical permeate flux was determined for the neutral and negatively charged membranes.

4.2.3.1 Preliminary test: Determination of critical flux in tubular membrane

Membrane flux is one of the most important parameter that determines the economic viability of membrane bioreactors. Elevated membrane fluxes allow for smaller membrane surface areas for a given hydraulic treatment capacity. However membrane fouling typically increases with flux and hence MBR's are typically operated below a critical flux region to minimize fouling. The critical flux is defined as the flux below which minimal fouling occurs. Since its introduction by Field et al. (1995) critical flux has become a widely accepted parameter for assessing the fouling behavior and comparing different operating conditions (Le-Clech et al., 2003). In sludge which consists of particulates and macromolecules, membrane fouling occurs even in a subcritical flux operation, but increases dramatically when the critical flux is reached (Le-Clech et al., 2006).

In this study, the critical flux was determined by operating the membrane in constant flux mode. The bench scale membrane setup was modified to allow constant flux operation by connecting a pump on the permeate side of the membrane that created suction to generate a prescribed flux. Figure 4-6a and b depict a classical tubular setup operating with constant pressure and the modified setup to operate with constant flux respectively. During constant flux operation: the feed was pumped through the membrane at a constant rate to keep a constant CFV, and the suction pump connected on the permeate side was set to deliver a

constant flux. In order to deliver the required flux, over a range of filtration resistance conditions, P_p changed and it was monitored over time.

(a) (b)

Figure 4-6 (a) Constant pressure operation (b) constant flux operation

The critical flux was determined by the flux step method (Le-Clech et al., 2003). The flux step method involved increasing the permeate flux in steps for a fixed duration and monitoring the TMP at each flux value. This is expected to result in a linear relationship between TMP and flux within the sub-critical flux region and an exponential increase in TMP indicating rapid accumulation of foulants at fluxes beyond the critical flux value. For each flux step, the increment in flux was 4 LMH. The duration of the test was 30 minutes and this was followed by a 2 minute relaxation time to eliminate built up of reversible foulants before the next flux value was implemented. The test was conducted with the neutral and negatively charged membranes using a relatively dilute feed (feed concentration of approximately 6 g TS/L) that consisted of digested WAS from the pilot AnM digesters.

4.2.3.2 Detailed testing

Detailed testing was carried out to assess the influence of feed concentration, permeate flux, membrane type and filtration time on membrane fouling. The impact of key operating factors was examined systematically following a 2^4 factorial experiment (Table 4-2). The main factors consisted of feed concentration (approximately 6 g/L and 18 g/L of TS), permeate flux (lower and upper end of the sub critical flux range) and membrane type (neutral vs. negatively charged). In addition, to assess whether conditions varied with the duration of membrane operation, data was collected over two different filtration times (30 and 120 minutes) resulting in a total of 16 runs. A few of the experiments were conducted with a virgin membrane while most of the runs were conducted with previously-used membranes. In these latter cases, the

membrane was backwashed with water for 20 minutes and a clean water TMP measurement was obtained prior to and at the end of each experiment.

Table 4-2 A 2^4 Factorial design setup

Factors	Levels	
	Plus (+)	Minus(-)
Membrane type	Neutral	Negative
Feed concentration	High (18 g/L TS)	Low (6 g/L TS)
Flux	Lower end of sub-critical flux	Higher end of sub-critical flux
Filtration time	Short (30 minutes)	Long (120 minutes)

Statistical analysis was performed to screen the experimental factors (feed concentration, membrane type, operating flux and test duration) and determine which had a significant impact on the response variable (membrane fouling). Fouling in this case was represented by the change in trans-membrane pressure (ΔTMP) after the raw TMP data were first corrected for temperature. Room temperature fluctuations between 13 and 22^{o}C were observed during the experimental period, and hence for comparison purposes all raw TMP data were corrected to 20^{o}C using equation 4-6 (Pohland, 1988). The design of experiments (DOE)-Factorial option of Minitab® release 14.13 (2004) was used to create and analyze the factorial design. Factors were considered statistically significant at a 95% confidence interval ($p < 0.05$).

$$TMP_T = TMP_{20} * 1.025^{(20-T)}, \qquad \text{Equation 4-6}$$

where TMP_T is the TMP recorded at room temperature T (^{o}C).

4.2.3.3 Foulant identification through fractionation

Digested sludge is a complex mixture of organic and inorganic materials that are present in suspended solids, colloids and dissolved fractions. The extent of membrane fouling was expected to be impacted by the ratio between the different fractions within the digested sludge. An improved understanding and identification of the foulant origin was obtained by evaluating the contribution of the various sludge fractions generated in the AnM digester process.

To evaluate the contributions of various fractions present in digested sludge to the reduction of permeation flux, tests that initially separated the sludge into two fractions (cake and supernatant) with subsequent filtration under similar operating conditions were conducted. For this purpose sludges were obtained from the pilot AnM and control digesters that were operated at varying HRT and SRTs and had TSS concentrations of 20, 9.7 and 31.3 g/L respectively. The cake and supernatant fractions of the sludges were separated by centrifuging at 3000 xg for 10 minutes at 4^{o}C. Once the supernatant was separated from the cake, the latter was re-suspended to its original volume using permeate from the corresponding pilot digester. Then each of the components and the un-fractionated sludge were filtered by the bench scale membrane setup using a neutral membrane operated at a constant pressure and at cross-flow velocity of ~1.1 m/s at a temperature of 20^{o}C for 30 minutes to reach a stable permeation flux. Figure 4-7 summarizes the sample preparation and filtration procedure. The fractionation and filtration experiments were conducted in duplicate resulting in a total of 12 runs. Concurrently, duplicate samples were collected from the whole sludge, cake and supernatant fractions for analysis of total and suspended solids, and total, colloidal and soluble COD. The membrane was cleaned and the clean water flux was measured before and after each test.

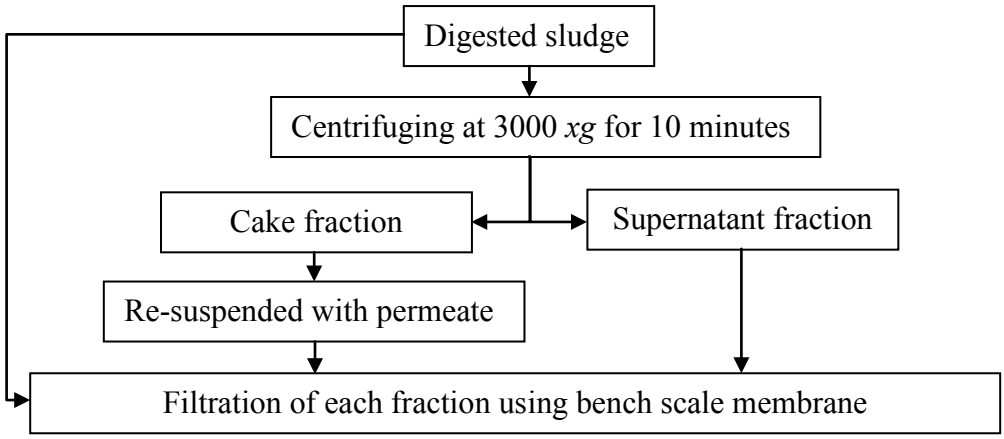


Figure 4-7 Fractionation and filtration of sludge components

To facilitate quantification of the contribution of the different components to the resistance to filtration, the filtration resistance of the different sludge fractions was computed and compared

with the filtration resistance of the un-fractioned sludge as per equations 4-7 and 4-8. The filtration resistance due to fouling is given by

$$R_f = R_t - R_m, \qquad \text{Equation 4-7}$$

where R_t, R_m and R_f denote the total, membrane and fouling resistances (m^{-1}). The membrane resistance was obtained as per Darcy's law using a flux and TMP values when filtering a clean (particle free) water through a virgin/washed membrane:

$$J = \frac{TMP}{\mu R_m}, \qquad \text{Equation 4-8}$$

where J is in $m^3m^{-2}s^{-1}$, TMP in Pa and μ is the absolute viscosity of the permeate (Pa s). The same equation was used to calculate the total filtration resistance (R_t) during sludge filtration using the steady state flux and the corresponding TMP data collected during the whole sludge run ($R_{whole\ sludge}$), re-suspended cake (R_{cake}) and supernatant (R_{sup}) runs respectively.

4.2.3.4 Relaxation operation of tubular membrane: a novel fouling control strategy

Membrane fouling in tubular membranes is characterized in general as a reduction of permeate flux through the membrane. The immediate effect is reversible fouling that leads to a reduction in membrane flux, while the long term impact may lead to irreversible fouling and reduction in membrane lifetime. To maintain economic viablity, membrane fouling should be kept to a minimum. Most fouling control in tubular membranes is achieved by increasing the CFV. Increasing CFV in the case of AnM digester operation has been reported to cause shear effects on the anaerobic biomass and subsequent reduction of digester performance (Brockmann and Seyfried, 1997; Ghyoot and Verstraete, 1997; Padmasiri et al., 2007). The mechanical stress due to excessive pumping can destroy the close relationship that is necessary for inter-species hydrogen transfer (Brockmann and Seyfried, 1997). Hence the concept of employing a relaxed operation as way of minimizing the rapid decline in flux without excessive CFV was explored.

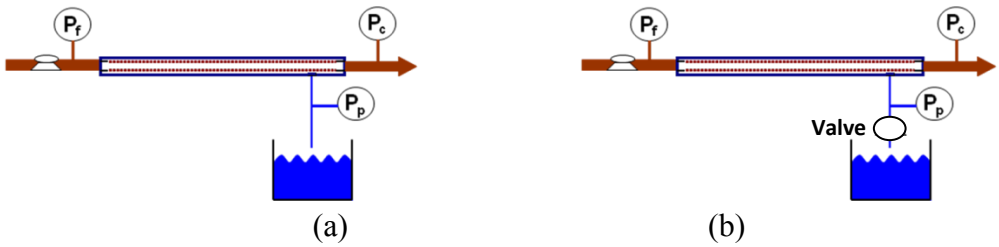
Membrane relaxation as a way of fouling control has been employed with other membrane configurations and therefore it was explored for this application. Relaxed operation involves periodic interruption of filtration by releasing the driving pressure and allowing most of the

materials accumulated on the membrane surface to relax and be removed by scouring. This is a common practice in hollow and flat sheet membrane modules where the configuration allows relaxation by releasing the suction pump and employing coarse bubble aeration for scouring. However it has not been implemented with tubular membranes due to some membrane safety restrictions such as de-lamination.

The polymeric tubular membranes consist of a membrane layer that is cast onto a stronger material or backing. This allows the module to withstand a strong inside-to-out pressure but results in a very weak resistance to outside–in pressure. When flow is restricted on the permeate side a partial reverse flow through the membrane surface could occur and this might result in de-lamination (separation of the membrane layer from the backing/ support material) (personal communication with vendor). For example, for KOCH tubular membranes, the maximum allowable pressure on the permeate side was specified as 5 psi (Table 4-1), and if exceeded de-lamination could be possible.

In this study the potential for fouling control through relaxation operation without compromising the membrane's integrity was evaluated. The relaxation of tubular membranes was conducted by periodically restricting the flux while the sludge was moving past the membrane. The scouring of the membrane surface by the moving sludge and the absence of the permeate flow towards the membrane was expected to result in a net positive force that would push the deposits away from the membrane surface.

In order to perform the relaxed operation, the bench scale membrane setup was modified by installing a valve connected to a timer on the permeate side. This modification is depicted in Figure 4-8b.



(a) (b)

Figure 4-8 Bench scale membrane setup during (a) continuous and (b) relaxed operation

As can be seen from Figures 4-8a and b, during continuous operation the permeate line is open hence the permeate pressure (P_p) =0 and the TMP is the average of the feed (P_f) and concentrate pressure (P_c). When relaxed, the valve is closed, hence the permeate pressure is equal to the average of P_f and P_c resulting in a TMP with a zero value. The use of 5 minute permeation followed by 1 minute relaxation was compared with continuous operation to control fouling when treating a high solids feed (18 g/L) at a high flux (30 LMH) with a neutral membrane. The relaxation interval was chosen based on preliminary experiments that showed that a minimum of 1 and 2 minutes were required to decrease the trans membrane pressure to zero following 5 and 10 minute production times respectively.

4.2.3.5 Polymer addition

Another approach evaluated as foulant control strategy was sludge pretreatment by addition of polymers. The sludge characteristics and filterability as a function of cationic polymer (Zetag, CIBA Specialties) doses were evaluated through jar and short term filtration tests. This polymer was selected as it was the thickening aid employed at the Skyway WWTP where the raw feed sludge was obtained. Digested sludges were collected from pilot AnM and control digesters. A series of coagulation tests was carried out using an apparatus with 1L beakers, in which the samples were mixed with smooth edged blades. Immediately after dosing the coagulant solutions into the sludge samples they were mixed at 250 rpm for 1 min followed by a slow mixing at 70 rpm for 15 minutes, samples were then taken to measure fCOD and time to filter through a 1.5 μ filter.

Once the optimum dose was selected based on its impact on decreasing the fCOD concentration and increasing the volume of water filtered per given period of time, the digested sludges obtained from the control and AnM digester were dosed with the optimum polymer concentration and further filtration experiments were conducted using the bench scale membrane apparatus shown in Figure 4-5. Sludge characteristics and membrane performance was evaluated by measuring the fCOD concentration of sludge before and after membrane filtration tests and membrane flux respectively.

4.2.4 Long term filtration experimental plan

4.2.4.1 Process conditions

Feed: A long term filtration study was conducted using the pilot AnM digester. The feed to the pilot reactor consisted of WAS obtained from the Skyway municipal wastewater treatment plant located in Burlington, Ontario, Canada. The Skyway plant is a conventional activated sludge facility operating at an extended SRT of 11 days. The facility employs dissolved air flotation (DAF) to thicken the waste activated sludge prior to stabilization with primary sludge in anaerobic digesters. The facility employs ferric chloride (about 20,000 kg of Fe per month, change to concentration) for phosphorus removal, and a variety of polymers in the secondary clarifier and DAF units to assist sludge settling and thickening.

The feed was transported to the Wastewater Technology Centre (WTC) twice per week and was kept in a chilled storage tank. To operate the pilot AnM digesters, a relatively constant feed total solids concentration of 2 ± 0.7% was maintained by mixing volumes of WAS with thickened waste activated sludge (TWAS) to make up the feed.

Experimental design: To evaluate membrane performance, fouling mechanisms, foulant types and fouling control strategies, three experiments that took into account the digester loading condition and the degree of solid's digestion were designed by varying and controlling the bioreactor's SRT and HRT. In addition, a control experiment was conducted in parallel with the other runs. The control experiment (run 4) didn't make use of a membrane to decouple the SRT and HRT and was conducted to assess the digester's performance under conventional conditions. Table 4-3 summarizes the AnM digester operating conditions.

Table 4-3 Pilot digester process conditions: a 2x2 factorial design

Experiments	Design conditions					
	OLR**	SRT, days	HRT, days	Sludge fed, L	Sludge wasted, L	Permeate volume, L
Run-1	1.13	30	15	36	18	18
Run-2	2.42	30	7	77	18	60
Run-3	2.42	15	7	77	36	47
Run-4	1.13	15	15	36	36	NA

* The two factors were HRT and SRT and each conducted at a high and low level. The high and low level were 30 and 15 days for SRT and 15 and 7 days for HRT

** Organic loading rate, kg COD $m^{-3}day^{-1}$

Runs 1 and 2 were conducted at extended SRTs of 30 days and at conventional and higher loading conditions with HRTs of 15 and 7 days respectively. Run 3 was performed at a conventional SRT (15 days) and higher loading condition (7 days HRT). The average COD loading rates in Runs 1, 2 and 3 were 1,13, 2.42 and 2.42 kg COD $m^{-3}day^{-1}$ respectively. The conventional operating conditions were chosen in ranges that are relevant for full scale operation of digesters. A conventional digester is a single pass reactor, with the solids residence time equal to the liquid residence time. Most WWTPs operate their digesters at SRT=HRT of greater than 15 days and average loading less than 1 kg COD $m^{-3}day^{-1}$. This type of operation was explored to provide a reference condition in the control experiment. The non-conventional operating conditions such as extended SRT and high solids loading were selected to assess conditions that would realistically and efficiently utilize the AnM digester's benefit of decoupling HRT and SRT and taking into account physical sizing restrictions of the pilot AnM digester. The three experimental AnM runs were conducted sequentially using the same bioreactor. In all cases the membrane was operated intermittently so as to obtain the desired amount of permeate under constant TMP and CFV conditions with an average membrane flow of 30 liters per minute (LPM).

4.2.4.2 Operational and Monitored Parameters

The fouling behavior of the membranes was studied using the experimental design presented in Table 4-3 during transient and steady state conditions of the digesters. The experiments were designed in a way to provide a range of SRT and HRT in the pilot scale AnM digester system. Hence, the biological, physical and chemical sludge properties were expected to vary which in turn was expected to impact the membrane performance. Thus these parameters were monitored at each condition and employed to interpret membrane performance.

For each run, the reactor was operated for a transient time of approximately 3 SRTs prior to considering that a quasi steady state had been reached. During the transient state, filtration was performed using the neutral membrane. Once the reactors had reached a quasi-steady state condition the membrane was cleaned in place (following the method discussed in section 4.2.3.3). Then for each run a comparative experiment was conducted to evaluate the performance of the neutral and negatively charged membranes under continuous and relaxed

operation. Using the pilot reactor the long term effect of relaxed operation of a tubular configuration for mitigating the decline in permeate flux was studied by relaxing the membrane for 1 minute followed by a 5 minute permeation. In addition, the critical flux was determined in-situ by the flux step method. The step duration was 10 minutes and the flux increment was 2 LMH. In between the flux steps the membrane was allowed to relax for 2 minutes to eliminate the reversible fouling built up before the next flux value was implemented. In all cases average daily membrane flux and flux after 30 minutes of filtration were used as measures of membrane performance. In some specific instances the fouling index which is the gradient of flux over time was also used to compare the membrane's performance.

To facilitate an understanding of the impact of the digested sludge composition on flux: feed, digested sludge and permeate samples were analyzed on a regular basis for total solids, volatile solids, total suspended solids and volatile suspended solids and COD (total, colloidal, soluble and permeate) fractions throughout the experiment.

Previous studies on aerobic MBRs and AnMBRs treating low strength wastewater have demonstrated the importance of biopolymers and cations as direct foulants and as stabilizing agents for biofilm formation on the membrane surface. However their exact composition and properties was expected to vary significantly with time in response to changes in the feed and continual evolution of the physiological environment in the digester. Thus in this research the biological sludge properties including polysaccharides and proteins corresponding to bound and loose biopolymer fractions were measured during the steady state conditions. Feed, digested sludge and permeate samples were also analyzed for Ca, Mg, Fe and Al cations. In addition the digested sludge and the raw feed sludge samples were analyzed for various physical sludge properties including particle size distribution, hydrophobicity and surface charge. The sampling protocol and analytical methods are discussed in sections 4.2.4.4 and 4.2.4.5. The selection of the physical, chemical and biological sludge properties that could potentially affect the membrane performance were based on literature findings.

4.2.4.3 Sampling

The three AnM experimental runs were conducted sequentially using the same bioreactor (Table 4-3). In all runs the membrane were operated intermittently (3 - 6 cycles/ day and 1 – 3.5 hours per cycle) to obtain the desired amount of permeate under constant TMP and CFV conditions with an average feed flow rate of 30 liters per minute (LPM). The average daily membrane flux after 30 minutes of filtration (flux at t=30 minutes) in a cycle, fouling index and the critical flux that was measured during steady state operation were used to characterize the long and short term membrane performances respectively. In some specific instances the filtration resistance (R_f) was also used to evaluate the resistance fractions corresponding to irreversible and reversible fouling.

During the transient and steady state periods, duplicate samples were collected from each digester and feed on a biweekly basis for total solids, volatile solids, volatile suspended solids, total suspended solids, total COD, filtered COD, permeate COD and soluble COD analysis (Table 4-4). During the steady state period weekly duplicate samples were also collected for biopolymer and cation fractions analysis following the method discussed below. To evaluate the amount of organic and inorganic deposits on the membrane surface samples were collected from spent chemical solutions during membrane cleaning and were analyzed for biopolymers and cations. Fouled, cleaned and virgin negative and neutral membrane samples were obtained for microscopic evaluation to further confirm if biopolymers were causing membrane biofouling.

Table 4-4 AnMBR process timeline and sampling strategy

Process condition	**15/30 H/SRT (Run 1)**	**7/30 H/SRT (Run 2)**	**7/15 H/SRT (Run 3)**
Transient period	Jan-June	Oct.-Jan	Mar-Apr
Steady state period	June- July	Jan- Feb	April- May
Solids fractions (TS, VS, TSS, VSS)		Twice per week	
COD fractions(TCOD, fCOD, sCOD, pCOD)		Twice per week	
Biopolymer fractions		Weekly during steady state	
Metal fractions		Weekly during steady state	
Particle size distribution		Weekly during steady state	
Relative hyrdrophobicity		Weekly during steady state	
Surface charge		Weekly during steady state	

4.2.4.4 Analysis of performance parameters

Duplicate raw feed sludge, digested sludge and permeate samples were collected for analysis. The sampling protocol is shown in Table 4-4. During sample collection, care was taken to obtain a representative sample. For example prior to sampling from the feed tank, the tank was mixed to obtain a homogenous sample and the first 2 L of sample that was in the pipe was discarded. When sampling permeate, it was noticed that, due to the free iron in solution there was precipitation of iron along the sampling pipes, and hence it was necessary to either frequently clean the line before sampling or disconnect the tube and directly sample from the membrane outlet. All digester samples were collected at the end of the digestion cycle and prior to feeding to avoid short circuiting. Most samples were analyzed immediately after sampling and for cases that required storage standard laboratory preservation and storage procedures were followed.

***Solids and COD fractions*:** Standard analytical methods (APHA, 1998) were adopted and slightly modified for solids (suspended, total and volatile) and COD (total and filtered) fractions in sludge samples. The modifications were required considering that most of the methods have been developed for a wastewater having relatively lower solids concentrations and highly biodegradable material. Direct application of them to sludge showed some inconsistencies and inaccuracies during preliminary experiments. The modifications included increasing the oven drying (105 ^{o}C) period from 2 hour to 24 hours in the case of solids analysis, disintegrating the sludge prior to digestion in the case of total COD analysis and centrifuging at 3000 xg and 4^{o}C for 30 minutes prior to 1.5 μm filtration for filtered COD analysis respectively. The detailed analytical procedures and modifications made during solids and COD fraction analysis are presented in Appendix H. The colloidal COD concentration was calculated by subtracting permeate soluble COD from the filtered COD (Fan et al., 2006). This approach was in agreement with the definition of colloidal particles as a portion of particles ranging from 0.01 to 1.0 μm by MetCalf and Eddy (2003). These were comparable to the nominal pore sizes of the pilot membrane unit (~ 0.02 μm) and the coarse glass fibre filters (1.5 μm) which were used to measure the permeate and filtered CODs respectively. In this thesis, the term "filtered" refers to samples that were obtained after centrifugation of sludge

samples followed by filtration through a 1.5 μm filter. The term "soluble" refers to a sample that was obtained from 0.45 μm filtration.

***Analysis of metal ions*:** Filtered, permeate and spent chemical solution samples were analyzed for dissolved metal ions (Mg, Ca, Fe, Al and S) by Inductively Coupled Plasma (OES PE Optima 5300DV) (method 3120B, APHA 1998). The metal ions associated with the flocs were analyzed for total metals after digesting the samples with HNO_3 (method 3120B, APHA 1998).

Loose and bound biopolymer extraction and analysis: In this study loose biopolymers represented the fractions of biopolymer that were able to move freely between sludge flocs and surrounding liquor while the bound biopolymers represented the fraction tightly bound to the floc (Poxon and Darby, 1997). The biopolymer extraction and analysis involved separation of the bound and loose fractions, extraction of bound biopolymers, filtration of each biopolymer fractions and subsequent analysis. The loose and bound fractions were separated by centrifuging 40 mL sludge samples at high speed (10,000 xg and 4^oC) for 45 minutes (SORVALL centrifuges). The supernatant of the centrifuged sample represented the loose biopolymer fraction. This fraction was further classified into filtered and soluble fractions. The filtered fraction consisted of the filtrate after filtration through 1.5 μm filters while the soluble fraction consisted of the filtrate after filtration through 0.45 μm filters. The colloidal fraction was calculated as the difference of the filtered and soluble fractions.

The bound biopolymers (floc associated biopolymers) were extracted from the cake remaining after the above mentioned centrifugation using a modified version of the cation exchange resin method employed by Froland et al. (1996). The method involved re-suspension of the cake fraction with phosphate buffer (2mM Na_3PO_4, 4mM NaH_2PO_4, 9mM NaCl and 1mM KCl) and extraction using Dowex® MARATHON® C, Na^+-form (Sigma-Aldrich 91973) cationic resin in an anaerobic environment under nitrogen gas. The extraction was performed by contacting 60 g of Dowex per gram of VS for 1 hour through stirring at 600 rpm and 4^oC in a custom-made extraction device equipped with rounded blades to minimize floc shearing during extraction. After extraction, the CER was separated from the sludge using a wire mesh and the sludge was again centrifuged for 45 minutes at 10,000 *xg* to separate the extracted biopolymers from the

floc. The extracted biopolymer was filtered with a 1.5 μm filter and the filtrate was kept in glass vials at 5°C for further analysis.

Duplicate filtered, soluble, and extracted biopolymer samples were analyzed for proteins and carbohydrates colorimetrically. Proteins and carbohydrates were determined according to the method described by Lowry et al. (1951) and Dubois et al. (1956) respectively. Bovine serum albumin (BSA) and glucose solutions with concentrations ranging from 0 to 100 mg/L were employed as protein and carbohydrate calibration standards respectively. Protein and carbohydrate samples were measured at wavelengths of 750 and 490 nm respectively. Biopolymer extraction and analysis steps are summarized in Figure 4-9.

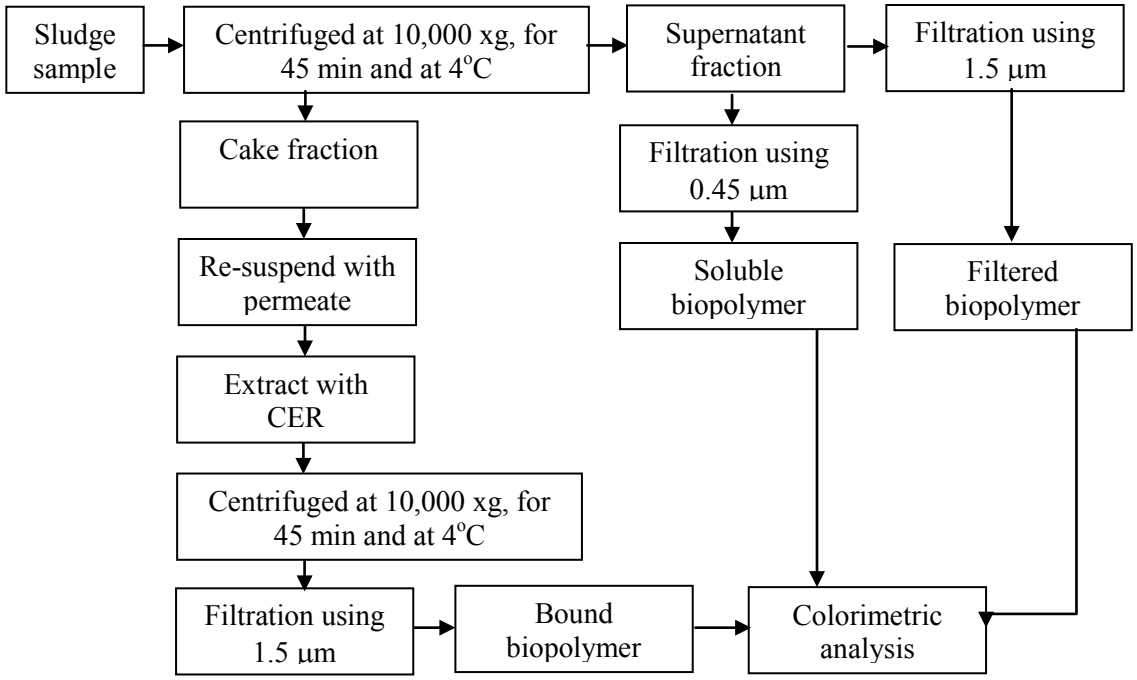


Figure 4-9 Summary of biopolymer extraction and analysis

Particle size distribution: Particle size distributions (PSD) were determined using a Beckman RapidVUE® particle size and shape analyzer. The size and shape of particles are obtained by analyzing digital images. The instrument is capable of detecting particles between 20-2500 μm and has capability of determining the shape of the particles as well.

Surface Charge: The surface charge of the flocs was measured by a colloid titration method (Morgan et al. 1990). This method is based on the change in color of an indicator such as cationic blue dye (toludiene blue, orthotoludiene blue, or methylene blue) used as an end point. The measurement process involves addition of excess cationic polymer into the digested sludge. The cationic polymer reacts with the negative surface charges on the sludge flocs. Anionic polymer is then titrated into the sample to react with the excess cationic polymer. After the entire excess cationic polymer has reacted with the anioinic polymer, the anionic polymer reacts with the indicator dye which resulted in the color changes from blue to purple.

Prior to analysis, samples were washed 2 times after centrifugation at 3000 xg for 10 minutes at 4^{o}C. The first wash was with distilled water and the second wash was with pH adjusted (pH=7.0) distilled water. Samples were then diluted to obtain a TS concentration of about 2000 mg/L. A volume of 2 mL of diluted sample was mixed with 43 mL of the pH adjusted (pH=7.0) distilled water and 1 mL of cationic polymer Polybrene (0.25 g/L) was added. The mixture was allowed to mix for 1 minute and 0.2 mL of toludiene blue (0.05 g/L) was subsequently added. The solution was then titrated with a 0.001 N (0.2027 g/L) solution of PVSK (Sigma-Aldrich®) until the color of the suspension changed from blue to purple. The same titration was employed with a blank sample by adding 2 mL of distilled water as opposed to the sludge sample to prepare the suspension. The surface charges of the samples were calculated as per equation 4-9.

$$C = \frac{(A-B)*N*1000}{V*VS}, \qquad \text{Equation 4-9}$$

where SC = surface charge in equ/gVS; A = volume of PVSK added to the sample (mL), B = PVSK added to blank sample (mL), N = normality of PVSK, V = volume of sample used (mL) and VS = volatile solids concentration of the sludge sample (g/L).

Hydrophobicity: The relative hydrophobicity was measured by a method called bacterial adhesion to hydrocarbons (BATH) using n-hexane as the hydrocarbon. The procedure included washing a 50 ml sample 3 times with a pH adjusted distilled water (pH=7.0) and then 1 mL of hexane was added to a 10 mL volume of the washed sludge sample. The mixture was agitated

for 30 s and then transferred into a separating funnel where it was allowed to stand for 10 minutes. After 10 min, when the two phases had separated completely, about 10 mL of the aqueous phase was transferred into a test tube and absorbance was measured at 400 nm wavelength. The relative hydrophobicity was calculated using equation 4-10:

$$RH=100*(1-\frac{S_e}{S_i}), \qquad \text{Equation 4-10}$$

Where S_e the aqueous phase concentration after emulsification and S_i is the initial sample concentration

4.2.4.5 Membrane cleaning

Cleaning strategies are typically specific to the type of application and operating conditions, membrane type and configuration. To determine an optimal cleaning strategy and to identify the possible mechanisms of fouling; mechanical, citric acid and sodium hydroxide cleaning were evaluated sequentially and/or individually once the membrane had reached a fouled condition. To assist in doing this the pilot AnM digester was equipped with a chemical cleaning tank that was heated and a pump that was dedicated to providing water from the tank to the membrane in the opposite direction of the feed flow. The sequential cleaning strategy involved:

1. Measurement of the flux corresponding to the fouled membrane (fouled flux) through a clean water (tap water) flux analysis that was conducted prior to cleaning
2. The fouled membrane was mechanically cleaned by a combination of high velocity water (53 LPM) and scrubbing with sponge balls that were supplied by KOCH. After the sponge ball cleaning was completed the clean water flux (sponge ball flux) was recorded.
3. A chemical cleaning that involved sequential use of basic and acidic solutions was then employed. The basic solution was prepared using NaOH to obtain a pH of ~ 9.5 and the acidic solution was prepared by adding citric acid solution to obtain a pH of about 2.7 and then adding hydrochloric acid to obtain a pH of 2. Both chemical washings were conducted with the cleaning solution at 50^{o}C. After each chemical cleaning the clean water fluxes was measured (base and acid fluxes respectively). All the clean water flux measurements were corrected for temperature to 20^{o}C.

4.2.4.6 Foulant layer characterization

A reduction of permeate flux through ultra-filtration (UF) and micro-filtration (MF) membranes as a result of increased flow resistance could be due to a combination of pore blocking and cake formation fouling mechanisms (Bai, 2002). The effect of each of these fouling mechanisms on flux decline and the characterstics of the fouling layer depends on factors such as membrane characterstics, feed characterstics and operating conditions. More efficient fouling mitigation methods can be implemented only when the phenomena occurring at the membrane surface are fully understood. However limited information is available on the fouling characterstics of AnM digesters stabilizing WAS. Membrane samples were submitted to Environmental Microbiology Laboratory, Guelph University for biofouling study. A variety of destructive and non-destructive tests were conducted to detect the mechanisms and types of fouling and characteristics of the fouling layer when the AnM digester was operated over a range of HRTs and SRTs.

4.2.4.6.1 Microscopic analysis of biofoulant layer

The nature of the biofoulant material on the fouled membranes was investigated in relation to virgin and cleaned membrane samples using attenuated total reflectance-fourier transform infra red spectroscopy (ATR-FTIR), scanning electron microscopy (SEM) and confocal laser scanning microscopy (CLSM). ATR-FTIR was used to detect functional groups on the surface and in the fouling layer of the membrane, thus providing information on the composition of organic foulants causing membrane fouling and the extent of organic foulant removal by cleaning agents. ATR–FTIR spectra were recorded on a IRP Restige-21 FTIR spectrometer (Shimadzu Corp., Tokyo, Japan) equipped with a deuterated triglycine sulphate detector and KBr beam-splitter. FTIR spectroscopy analysis was performed on triplicate virgin, fouled and cleaned negative and neutral membranes. The membranes were cut into small pieces and were analyzed immediately by ATR-FTIR. The recorded spectra were analyzed by IRsolution software. Several scans were conducted at different locations on each sample.

Coincidentally the structural properties of the cake layer on the fouled negative and neutral membrane surfaces were analyzed and compared with the virgin and cleaned membranes using scanning electron microscopy (SEM). Prior to analysis the membrane samples were fixed

using a phosphate buffer (pH 7.0) containing 2% gluteraldehyde by exposing them to the solution for 2 hours. The fixed samples were then washed with buffer three times. Samples were post fixed in 1% osmium teraoxide for 30 minutes, washed with buffer twice, and dehydrated through a series of ethanol washings with increasing concentrations of alcohol (50%, 70%, 80%, 90% and three rounds of 100%). The samples were then dried to the critical point and subsequently mounted on carbon tape and sputter coated with 20 nm gold with an Emitech K550 Sputter Coater. A Hitachi S-570 Scanning Electron Microscope (Tokyo, Japan) was used to capture micrographs. All images were acquired digitally and analyzed using Quartz PCI software (Vancouver, BC, Canada).

To understand the development of the biofouling materials on the membrane surface more specifically the relative distribution of proteins and carbohydrates along the cake layer profile were measured. Fouled membrane samples were examined microscopically by an upright confocal laser scanning microscopy (CLSM) (Leica DM RE microscope connected to a Leica TCS SP2) system with 3 different visible light lasers, covering 6 excitation wavelengths. Two probes, SYPRO orange and Concanavalin A tagged with Alexa Flour 633 conjugate, were collectively applied to target all proteins and α-Man and α-Glu polysacharides, respectively (Lin et al., 2009). The membrane specimens were stained in the dark at room temperature for 30 min. After staining, they were washed three times with a phosphate buffer to remove any unbound probes. After washing, the samples were immediately observed with the CLSM. Different objective lenses (i.e., 10x and 20x oil immersion and 63x water immersion lens) were used for imaging. Signals were recorded in the green channel (excitation 488 nm, emission 570 nm) for proteins and the red channel (excitation 633 nm, emission 647 nm) for polysaccharides. The confocal assistant software supplied by the manufacturer (Leica Confocal Software, version 2.61) was used to determine the distribution profile of proteins and polysaccharides in the cake layer.

4.2.4.6.2 Spent chemical solution analysis and geochemical modeling

The spent solutions that were generated from the mechanical and chemical cleaning were analyzed for calcium, magnesium, iron, aluminum and sulfur for identification of the type of inorganic materials deposited on the membrane surface. Permeate samples were also analyzed

for calcium, iron, magnesium, aluminum, sulfur, phosphorus and alkalinity to identify if the permeate was oversaturated and precipitation had either occurred or was likely to occur. The potential for precipitation and hence fouling propensity of the inorganic salts was determined by calculating the saturation index of the permeate using the geochemical equilibrium model PHREEQI Version 2 (USGS 2002). In this approach a saturation index of precipitates greater than zero indicated that the permeate was oversaturated and hence precipitation had occurred or there was the possibility of a compound precipitating within the digester and on the membrane surface (Zhang et al., 2007).

4.2.4.6.3 Fouling layer resistance fractions

Based on resistance fractions, possible mechanisms of fouling is classified as reversible fouling due to cake layer formation on the membrane surface and/or irreversible fouling due to pore plugging and/or adsorption of foulants directly onto the membrane surface that may be associated with biopolymers and/or cations. The pre- and post- cleaning water flux data collected during the sequential membrane cleaning outlined in section 4.2.4.5 was used to facilitate calculation of the fouling layer resistances corresponding to reversible and irreversible fouling as per the resistance in series model (equation 4-7 and 4-11).

$$J = \frac{TMP}{\mu R_t} \qquad \text{Equation 4-11}$$

$$R_t = R_m + R_f$$

$$R_f = R_r + R_i$$

where R_m, R_r and R_i refer to the intrinsic membrane resistance, filtration resistance due to reversible fouling and filtration resistance due to irreversible fouling respectively. In this case the clean water flux observed with the fouled membrane was used to calculate the total resistance (R_{tl}) that included the intrinsic membrane, reversible and irreversible resistances. Subsequently the membrane surface was cleaned with sponges to remove the cake layer. The clean water flux was measured after this procedure and was assumed to include the sum of the irreversible (R_i) and intrinsic membrane (R_m) resistances. The reversible fouling (R_r) was calculated as the difference of the resistances before and after cleaning with sponges. Finally clean water fluxes were measured after base and/or acid membrane cleaning was conducted to

remove organic and inorganic materials deposited in or on the membrane surface. The irreversible fouling (R_i) was calculated by subtracting the resistance values obtained before and after chemical cleaning.

4.3 Results and discussion

4.3.1 Bench scale short term filtration tests

The short term filtration tests were conducted to explore the interrelationships between operating flux, membrane type, sludge concentration and composition in a controlled environment at room temperature. In addition, fouling control strategies including implementation of relaxation and polymer addition were investigated. All tests were conducted at room temperature.

4.3.1.1 Critical flux

This section presents the results of preliminary tests that were conducted to identify the critical flux for the membranes when treating anaerobically digested waste activated sludge. Figure 4-10a depicts the flux steps employed and the TMP response at each step when filtering sludge with a TS concentration of 6 g/L. The flux was increased from 4 LMH to 44 LMH by increments of 10 LMH and with durations of 30 minutes and then decreased by steps back to the initial point i.e. 4 LMH (Figure 4-10a). A comparison of TMP obtained for the increase and decrease stage at each flux step showed no difference (Figure 4-10a), confirming that insubstantial fouling occurred during the flux-step test. Figure 4-10b summarizes the TMP versus flux profiles for the tests. The relationship between the TMP and flux was essentially linear for fluxes between 4 and 34 LMH and then increased exponentially for fluxes in the range between 34 and 44 LMH. The critical fluxes for the negative and neutral membranes lie in the same region. However as the flux was approaching the critical flux region the rate of particle accumulation on the neutral membrane surface appeared slightly higher than the negative membrane, as indicated by the relative increased rise in TMP of the former. Prior to reaching the critical flux region, *dTMP/dt* (fouling index) was almost zero, however in the region of critical flux (34 to 44 LMH) the *dTMP/dt* increased sharply to 0.37 and 0.21 bar/hour for neutral and negative membranes respectively (Figure 4-10b). The fouling index was calculated using TMP (t=30) minutes-TMP (t=1 min)/ (30-1) minutes.

From these results it was concluded that the critical flux was exceeded in the range of 30 to 40 LMH and operation of the membranes below this value was recommended. Operation at fluxes higher than this range could result in membrane fouling due to enhanced solids and organic loading and compaction of the cake layer on the membrane surface. The results from this portion of the study were used to select the lower (8 LMH) and upper (30 LMH) region of the sub critical flux for the detailed experimental testing.

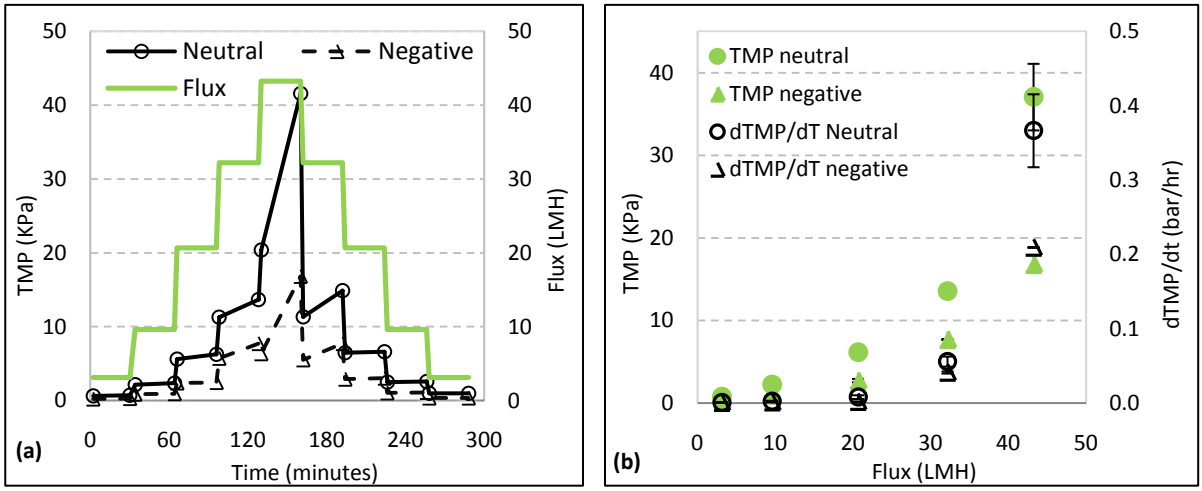


Figure 4-10 (a) Critical flux determination using flux step method (b) TMP (at t=30 min) and dTMP/dt versus flux (20^{o}C)

4.3.1.2 Detailed testing: impact of flux, sludge concentration and membrane charge on fouling

The detailed testing employed a factorial experimental design to assess the impact of feed solids concentration, membrane type, operating flux and test duration on membrane fouling in short term filtration tests. Figures 4-11a and b depict, as examples, the TMP versus filtration time for the negatively and neutral charged membranes respectively for runs with differing feed concentrations and operating fluxes.

From Figure 4-11a it can be observed that at a flux of 8 LMH the TMP response was similar for the lower and higher concentration sludge despite a three-fold increase in solids

concentration. However at the higher permeate flux of 30 LMH the TMP increased substantially faster for the concentrated sludge as compared to the dilute sludge. Similar trends in TMP profile were observed when operating the neutral charged membrane at different solids concentrations and flux levels (Figure 4-11b). However it can be clearly observed that the neutral membrane required an overall higher TMP to obtain the same permeate flux. This trend in membrane fouling was supported by the clean water TMP measurements that were performed prior to and at the end of each experiment (data not shown here). For example, the clean water TMP required for the virgin neutral membrane to obtain a flux of 30 LMH was 5.1 KPa. After low and high solids operation the clean water TMP increased to 6.1 and 9.8 KPa, respectively (data not shown).

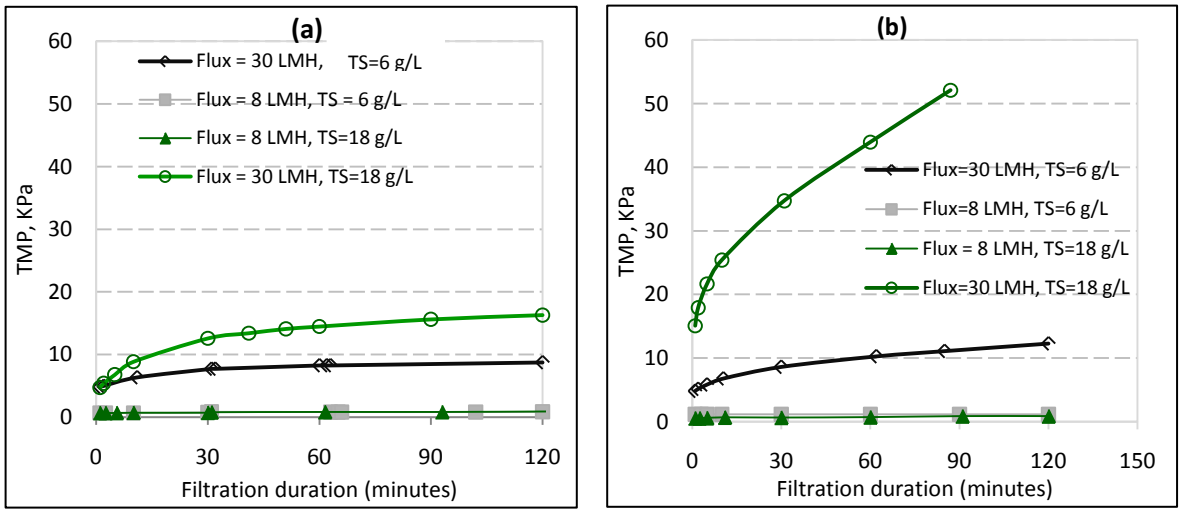


Figure 4-11 TMP versus time: (a) negative and (b) neutral charge membrane

The lower TMPs of the negatively charged membrane were likely due to electrostatic repulsion forces between the negatively charged colloids in the feed and the membrane surface charges. This would act to reduce the deposition and buildup of particles on the surface. In these tests both membranes were virgin membranes, and thus an effect of membrane charge on fouling rate was observed. The results are consistent with those reported by Shimizu et al. (1989) which showed that a negatively charged ceramic micro-filter made a greater flux improvement in the cross-flow filtration of anaerobic digestion broth than the non- or positive charged ones. Additional testing was conducted using the pilot AnM digester to further

examine whether the charge effect persisted during long term operation of the AnM digester and the results are discussed in section 4.3.2.2.

The influence of the test factors on the membrane fouling as indicated by the change of TMP were assessed statistically (ANOVA). The statistical analysis showed that the duration of filtration (30 minutes versus 2 hours) did not significantly affect fouling during the tests ($p < 0.163$). Sludge concentration ($p < 0.007$), flux ($p < 0.001$) and charge ($p < 0.026$) were found to have significant effects on membrane fouling. The effects of these parameters were complex as there was a significant interaction between solids concentration and flux ($p < 0.008$) and between flux and membrane charge ($p < 0.026$). An examination of the flux by charge interaction plots (not shown here), indicated that the charge of the membrane had no effect when the membrane was operated at the lower flux however the effect was significant when the flux was at the high level. For higher flux operations, neutral membranes showed a significant increase in fouling. A similar analysis of the flux by solids concentration interaction plot showed that at low permeate flux; an increase in solids concentration had no significant effect on fouling. However at the higher permeate flux, an increase in solids concentration resulted in a significant increase in fouling. The observed higher fouling at higher fluxes and solids concentrations could be due to either increased mass transfer of either suspended solids and/or colloids to the membrane surface and hence accumulation at the membrane surface. Both mechanisms could result in deposition of material at the membrane surface thereby increasing the fouling.

4.3.1.3 Contribution of individual sludge fractions to fouling

To describe the relative contributions of sludge fractions on membrane fouling, filtration tests were employed using sludges that were obtained from AnM and control digesters after separation into suspended solids and supernatant fractions. For the purposes of this discussion, the re-suspended cake from the centrifugation of the sludge is referred to as the cake fraction of the sludge. The TSS and COD values of the whole sludge, cake and supernatant fractions are presented in Table 4-5. The cake fraction contributed 84, 73 and 86 % of the total digested sludge COD obtained from the digesters operated at 15/30 (run 1), 15/15 (run 4) and 7/30 (run 2) days SRT/HRT, respectively. The supernatant fraction contributed 11% of the total COD

for run 1 and 4, and 8% for run 2 respectively. The cake fraction had a lower (~ 1 % for runs 1 and 4, and 2.4 % for run 2) colloidal COD (Table 4-5) while the supernatant fraction consist a higher fraction of colloidal COD (70%).

Table 4-5 Composition of fractionated sludge

Sludge source (HRT/SRT) days	TSS (g/L)	TCOD (g/L)	fCOD[1] (g/L)	cCOD[2] (g/L)
Run 1 (15/30)				
Supernatant	1.2	2.5	0.9	0.9
Cake	17.1	18.8	0.2	0.2
Whole	20.1	22.2	0.9	0.8
Run 2 (7/30)				
Supernatant	0.8	2.6	1.5	1.4
Cake	29.8	29.3	0.9	0.7
Whole	31.3	33.8	2.6	2.5
Run 4 (15/15)				
Supernatant	0.3	1.3	0.8	0.7
Cake	7.9	8.2	0.2	0.18
Whole	9.2	11.4	0.8	0.7

[1]fCOD (filtered COD)
[2]cCOD (colloidal COD) calculated by subtracting the permeate COD from fCOD

The results of the filtration tests are shown in Figures 4-12a, b and c respectively. The filtration resistance due to fouling (R_f) that was calculated as per equation 4-8 was employed to compare the fouling tendency of the different sludge fractions. In general the sludge obtained from runs 1 and 4 showed similar filtration characteristics where the R_f values of the supernatant had almost the same magnitude as that for the whole sludge, while those for the cake suspensions had kept at a much lower values (Figures 4-12a and b). These results confirm the hypothesis that colloidal particles play a critical role in increasing the hydraulic resistance in the filtration of digested sludge with TSS concentrations up to 20 g/L, although the contribution of this component was only 11% of the total COD. This fraction caused a significant decline in flux and contributed 70 and 84 % of the total resistance by the sludges with TSS concentrations of 20.1 and 9.2 g/L, respectively. These results are in agreement with

previous research that showed colloidal components of the solids fraction were the dominant contributor to AnMBR fouling (Choo and Lee, 1998).

The colloidal particles have been found to consist of both fine inorganic precipitates and many organic constituents such as loose EPS and other cell debris (Defrance et al., 2000). In a cross-flow mode of operation the tangential flow is expected to remove the cake layer that is derived from coarser particulate matter. However back transport of colloidal matter into the solution is typically limited due to the lower diffusion rates (Choo and Lee, 1998), thereby encouraging formation of a low-permeability and/or densified cake layer.

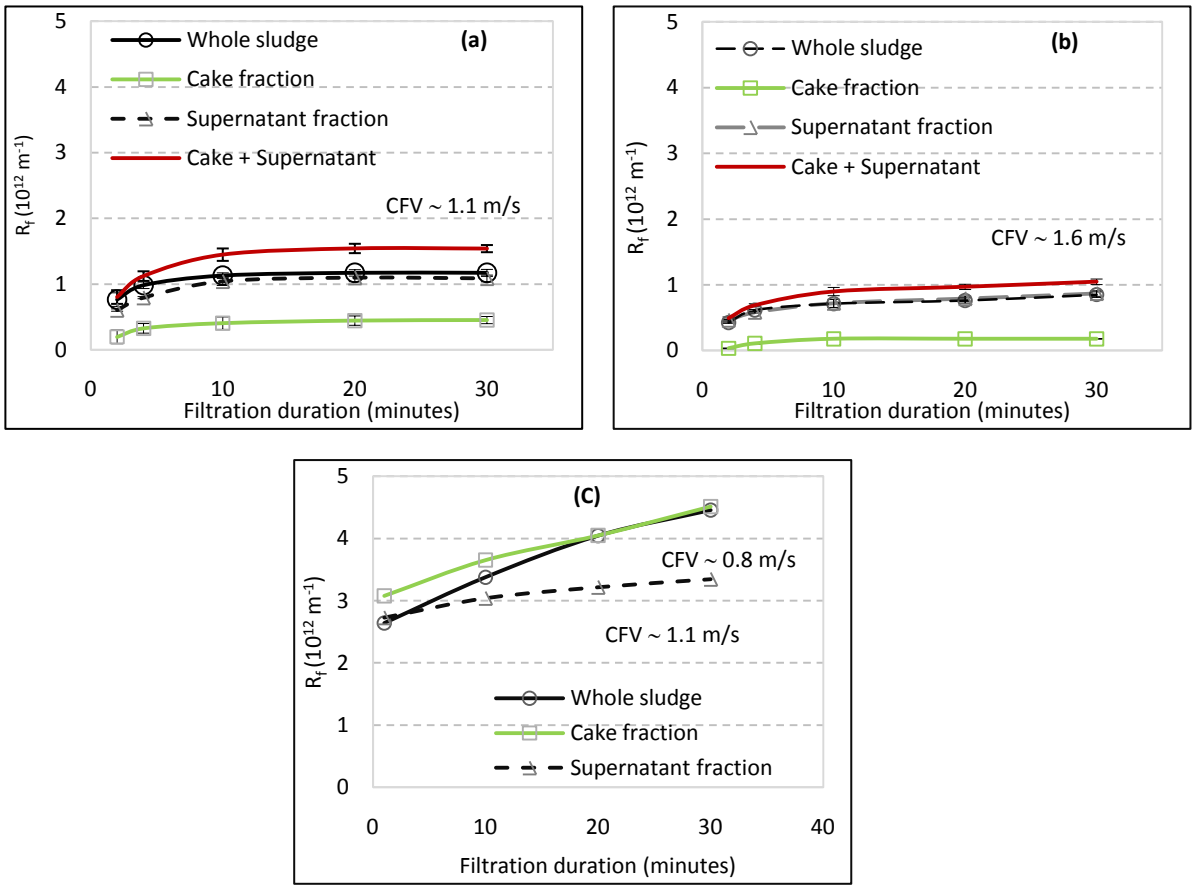


Figure 4-12 Filtration resistance due to fouling by digested WAS and its fractions obtained from digesters operated at (a) 15/30, Run 1 (b) 15/15, Run 4 (c) 7/30, Run 2 HRT/SRT

The cake fraction of the sludge obtained from runs 1 and 4 contributed only 30 and 16 % to the total resistance, respectively. These observation was however specific to runs 1 and 4 where the TSS concentrations were in the range of 10-20 g/L TSS. A greater impact of the cake fraction on R_f was observed for the sludge obtained from run 2 (TSS=31 g/L). In this case 57% of the total resistance was contributed by the cake fraction with 43% due to the supernatant fraction.

The increased contribution of the sludge fraction to the R_f could have been due to three factors. First, during the cake and whole sludge filtration of run 2 sludge, the pump flow rate dropped resulting in a reduction of the CFV to 0.8 m/s. This effect could be related to the complex relationship between sludge TSS concentration and viscosity. At increased TSS concentration, sludge becomes more viscous and difficult to pump. A study by Itonaga et al. (2004) showed sludge viscosity to remain the same with an increase in TSS concentration in the range of 10-17 g/L, while beyond this critical concentration the viscosity increased exponentially with TSS concentration. In addition to reducing the CFV, this increase in viscosity of the membrane feed would result in reduced turbulence (a change from turbulent to laminar flow) hence lowering scour that would act to remove the cake layer. This could result in a significant accumulation of particulate materials and formation of cake layer on the membrane surface. Second, at increased TSS concentration there is a possibility of increased convection of materials (mass flux) towards the membrane surface resulting in increased cake formation. Third, compared with the sludge samples from the runs 1 and 4, the cake fraction from run 2 also contained slightly higher percentage of colloids due to the difficulty in obtaining separation. Hence this might impact the filtration characteristics of the cake negatively.

Resistance additivity: The data was also used to compare the sum of the resistances to filtration associated with the supernatant, cake and whole sludge fractions. In this regard the sum of the resistances associated with the supernatant (R_{sup}) and cake (R_{cake}) was expected to be equal to the resistance in whole sludge (R_{whole}). However the sums of the fractions exceeded the whole sludge values by 40%, 56% and 28% for the sludges obtained from run 1, 2 and 4 respectively. The offset was proportional to the concentration of the sludge; run 2 > run1 > run 4. This result may have been due to the fact that during the filtration of the whole sludge, the

cake layer formed by the TSS prevented some colloids from being adsorbed onto the membrane surface hence minimizing formation of a compact fouling layer.

4.3.1.4 Fouling control strategies

Fouling control using either relaxation operation or addition of polymers was investigated in short term filtration tests using the bench scale membrane apparatus.

4.3.1.4.1 Relaxed operation

Relaxation is a fouling control strategy that involves periodic interruption of filtration by releasing the driving pressure and allowing materials that have accumulated on the membrane surface to relax and be removed by scouring. This approach has never been used with tubular membranes due to de-lamination that might result from outside-inside pressure gradients during relaxation. However, in the current study the operating pressure was low (< 40 KPa) and this reduced the likelihood of de-lamination. Hence the use of relaxed operation for removing the cake layer buildup was feasible from a membrane-integrity point of view. Figure 4-13 shows a comparison between TMP that was observed with relaxed (5 minutes operation followed by 1 minute relaxation) and continuous operation of the neutral bench scale membrane when treating high solids feed at a high flux (30 LMH) for 30 minutes. From Figure 4-13 it can be seen that relaxed operation resulted in extended operation with low TMPs. Hence the results from this study were adopted in the operation of the pilot AnM digester.

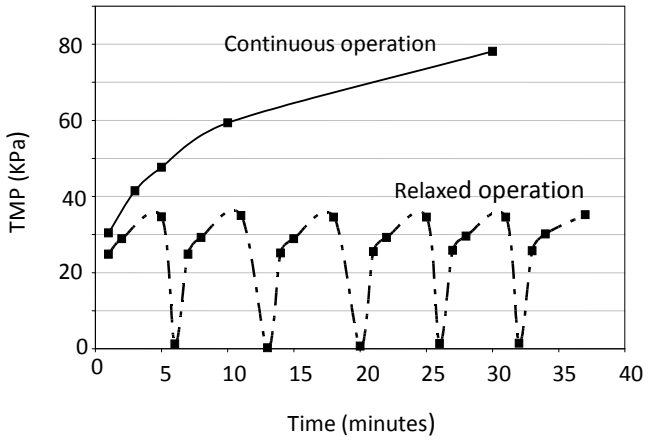


Figure 4-13 Relaxed versus continuous operation

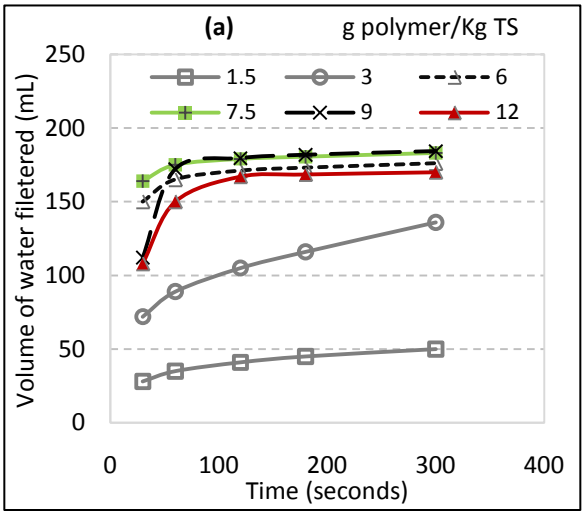
4.3.1.4.2 Polymer addition

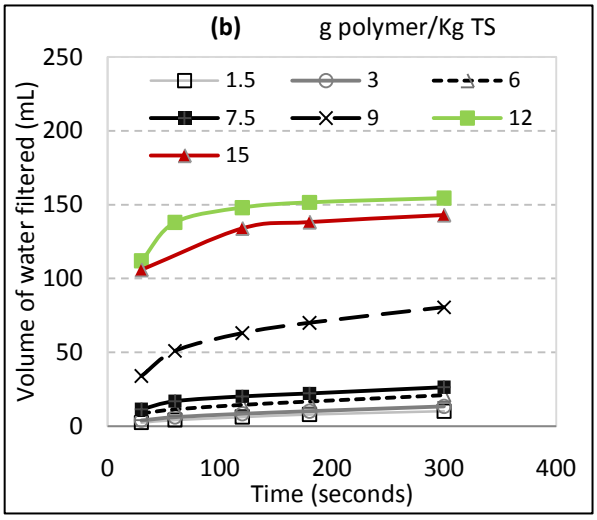
During the pilot AnM operation it was observed that the digested sludge filterability was poor when the raw feed sludge was thickened by gravity as opposed to the WWTP's typical practice that involved DAF thickening with the addition of a cationic polymer Zetag (92/7650, CIBA specialty chemicals) to aid in thickening. It was hypothesized that the polymer could potentially assist in formation of larger particles and could result in a better filtration. The addition of the cationic polymer (Zetag) was investigated as this was the type used at the WWTP for thickening the raw WAS. Thus the objective was to select the optimum polymer dose and evaluate the effectiveness of the polymer to control the fouling of the digested sludge.

Figures 4-14a and b compare the effects of polymer dose on the digested sludge fCOD concentrations and the volume of water filtered versus time in the jar tests. The fCOD concentration of the sludge obtained from run 4 decreased from 346 to 184 mg/L as the polymer dose increased from 1.5 to 12 g/kg of TS. Similarly the fCOD concentration of the sludge obtained from run 3 decreased from 1444 to 253 mg/L when the polymer dose was increased from 1.5 to 15 g/Kg of TS. This is in agreement with Murthy et al. (2000) that demonstrated ferric chloride and alum were effective at removing colloidal materials from digested sludge solids. For run 4 sludge, the volume of water filtered in 60 seconds increased from 35 to 175 mL with increase in polymer concentration from 1.5 to 7.5g/kg of TS. However a further increase to 12 g/kg of TS resulted in a decrease of the volume of water filtered to 150 mL. For the sludge with higher fCOD concentration (run 3 sludge), an increase in the volume of water filtered from 43 to 138 mL was observed with an increase in polymer dose from 1.5 to 12 g/Kg TS. A further increase of polymer dose concentration to 15 g/kg TS resulted in a slightly lower volume of water (126 mL) filtered over a 1 minute period. The observed poor filtration at higher polymer doses could be due to either the fouling effect of the excess polymer and/or due to an increase in interstitial water.

Based on the jar test results, and 7 and 12.5 g of polymer/kg of sludge TS were selected as the optimum polymer dose concentrations for the digested sludge obtained from runs 4 and 3 respectively. The sludge from both digesters were collected and dosed with the selected

optimum polymer concentration and filtration tests were conducted using the bench scale membrane setup. Figure 4-15 compares the filtration resistance due to fouling of the negative and neutral membranes during short term filtration for the raw and polymer dosed sludge. Overall the polymer dosed sludge exhibited a lower filtration resistance due to fouling.





fCOD (mg/L)	Polymer dose (g polymer/Kg TS of sludge) 1.5	3	6	7.5	9	12	15
Run 4, fCOD	346	292	237	200	200	184	-
Run 3, fCOD	1444	894	627	453	315	264	253

Figure 4-14 Effect of polymer dose on volume of water filtered (1.5µm) per time and fCOD for sludges obtained from (a) Run 4 and (b) Run 3

The degree of effectiveness of the polymer was substantial for the sludge that had the higher fCOD (2300 mg/L). In this case the fouling resistance decreased by 75% and 58% for neutral and negative membrane. By comparison, the resistances decreased by 12.5 and 10.4% for the sludge that had initial fCOD concentration of 445 mg/L. During the test, the fCOD concentrations were measured at the beginning and end of filtration period (Table 4-6). The fCOD concentration of the polymer dosed sludges from run 3 were about 325 and 257 g/L prior to filtration and increased to 501 and 896 g/L by the end of the filtration period using neutral and negative membranes respectively (Table 4-6). This may have been associated with

shearing of the flocs. Despite the shearing a significant improvement in membrane performance was observed as depicted in Figure 4-15b. The results showed that polymer addition can reduce fouling rates when AnM digesters were operated with a feed of higher fCOD concentration. In this case most of the fouling was controlled by the fCOD. Addition of the polymer could result in formation of larger particles hence reducing particle deposition and attachment on the membrane surface.

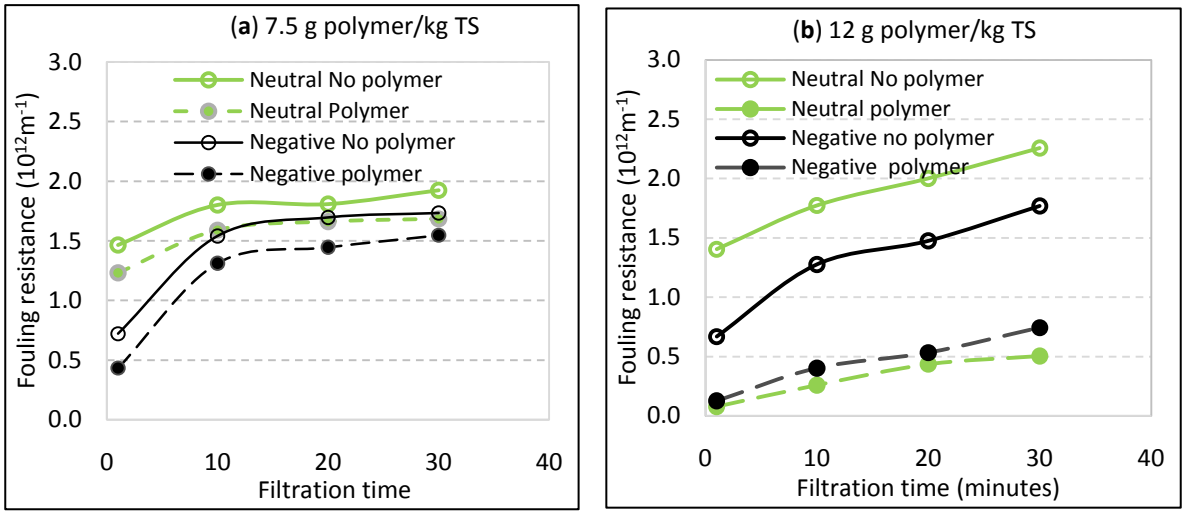


Figure 4-15 Filtration characteristics of polymer dosed and raw sludge obtained from (a) Run 4 (b) Run 3

Table 4-6 Filtered COD concentration of a polymer dosed sludge pre and post filtration process

Sludge condition, membrane type	Run 3 (fCOD, mg/L)		Run 4 (fCOD, mg/L)	
	Before filtration	After filtration	Before filtration	After filtration
Polymer, neutral	325	501	202	493
Polymer, negative	257	896	206	521

4.3.1.5 Summary of short term bench scale filtration results

The results obtained in this study provided clear indications of the feasible operating conditions for AnM digester membrane operation. The results suggested sustainable operation of an anaerobic membrane could be possible at fluxes below 30 LMH at 20^{o}C. The effects of flux, solids concentration and filtration duration on fouling of negatively charged and neutral membranes were identified. Flux and charge, showed a significant influence on the fouling. The effects of these parameters were complex and were a function of the operating flux region.

At a flux of 8 LMH, an increase in feed concentration from 6 g/L to 18 g/L showed no significant impact on the fouling parameter, where as the effect of solids concentration was found to be significant at higher flux (30 LMH). Similarly, while negatively charged membranes showed better performance at a higher flux condition, both showed similar performance at a lower flux. For operation of AnM digesters at higher fluxes, options such as feed pretreatment to lower the colloidal fraction and/ or intermittent filtration that could allow deposits to relax showed significant improvement on membrane performance and should be considered.

4.3.2 Long term pilot scale filtration characteristics

4.3.2.1 AnM digester raw feed characteristics: TSS and fCOD

The targeted total solids concentration of the feed sludge was 2%. This was achieved by mixing waste activated sludge with thickened activated sludge from the Skyway, Burlington Ontario WWTP. Figure 14-6 shows the TSS and fCOD concentration of the WAS fed to the AnM digester over the duration of this study. The actual average TSS concentrations were 16.6±2.7, 13.3±1.8 and 17.0±2.0 g/L and the average filtered COD (fCOD) concentrations were 1513±404, 616±137 and 1040±198 mg/L for runs 1, 2 and 3 respectively. On average the soluble COD was 541±133 and 849±129 mg/L for runs 2 and 3 respectively. The raw feed was found to contain very small amounts of colloidal materials (<20% of the fCOD corresponded to colloidal COD). Hence most of the fCOD in the feed was presented in the soluble COD fraction. Additional feed characteristics including biopolymer, cations, particle size distribution, surface charge and hydrophobicity are presented and discussed in sections 3.2.4 and 3.2.5.

4.3.2.2 Long term membrane performance: flux and permeability profile

The long term membrane performance, fouling mechanisms, foulant types and impact of fouling control strategies were investigated in relation to SRT, HRT and membrane type using the AnM digester. Runs 1 and 2 were conducted at an extended SRT of 30 days and conventional and high loading conditions with HRTs of 15 and 7 days respectively. Run 3, was performed at a conventional SRT (15 days) and higher loading condition (7 days HRT). In

all runs the membrane was set to operate at an average constant trans-membrane pressure (TMP) of 30 KPa and an average CFV of 1.0 m/s (Reynolds number ~ 2373).

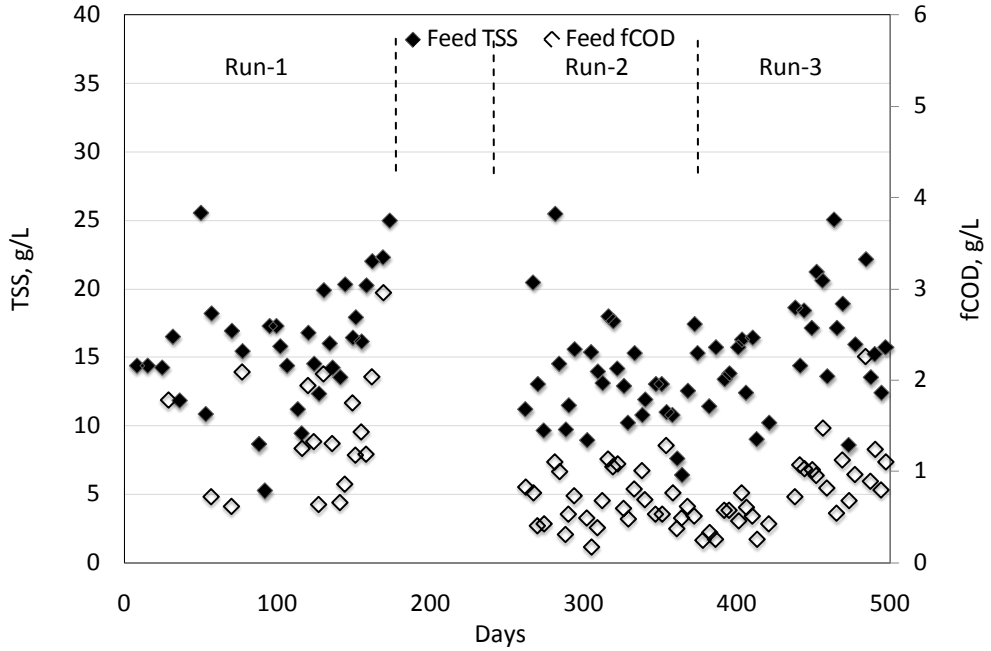


Figure 4-16 Feed sludge characteristics versus time

The TMP values and cross flow velocity were low when compared to conventional tubular membrane applications such as industrial wastewater treatment processes (CFV of 4.3 m/sec and TMP of 345 KPa, personal communication with the vendor). This might suggest that the membrane capacity was not fully utilized. However in the processing of high solids materials such as biosolids, this must be carefully examined. The choice of the applied CFV was within the recommended range of previous studies specific to high solids anaerobic treatment applications. Choo et al. (2000) evaluated the impact of CFV on flux when treating synthetic wastewater with an influent COD concentration of about 27 g/L and observed a remarkable decrease in filtration resistance when the Reynolds number increased from 1000 to 2000 (i.e. under quasi-turbulent condition). However, beyond a Reynolds number of 2000 no further significant reduction in filtration resistance was reported even with an increase of Reynolds number up to 18000. A similar result was reported by Kang et al. (2002).

Operation under a fully turbulent flow condition can scour the cake layer material from the membrane surface. However a potential outcome of this operation is that it may expose the membrane surface to more challenging foulants such as inorganic materials and/or smaller sized particles that will be deposited either on the membrane surface or within the pores thereby creating irreversible fouling and a severe decline in flux. Cakes formed at higher CFV were also reported to have higher specific cake resistances (Le-Clech 2006). In addition, from the bioreactor point of view high velocities can cause shearing of floc that could result in a reduction of microbial activity and ultimately the digestion efficiency (Brockmann and Seyfried, 1997; Ghyoot and Verstraete, 1997; Padmasiri et al., 2007). It has also been suggested that an increase in CFV might cause a breakup of biofloc causing cell lysis and release of soluble microbial products that could negatively affect membrane flux (Berube et al., 2006).

The literature also indicates that the function relating permeate flux to the TMP has two distinct zones. At low TMP, flux was proportional to the pressure while at high TMP the flux was independent of pressure (Beaubien et al., 1996; Ghyoot and Verstraete, 1997). Research by Pillay (1992) has shown that as the pressure increased beyond a certain limit, the cake layer that formed was compressed on the membrane surface making it less permeable and ultimately resulting in a reduction of the permeate flux. The results of the previously described short term tests indicated that the critical flux was close to 40 LMH when an average TMP of 20-40 KPa was employed at a CFV of approximately 1 m/s and hence the experiments were conducted within this range. Further the membrane fouling was managed by relaxing the membrane for a longer period (as oppose to increasing the CFV) between the filtration cycles (extended relaxation or semi continuous operation) and/or during the filtration cycle (referred here as to relaxed operation). In addition membrane fouling was controlled by developing and applying a cleaning methodology as required.

4.3.2.2.1 Conventional loading condition and extended SRT (15/30 days HRT/SRT-Run 1)

In Run 1 the AnM digester was fed with 36 Ld^{-1} of raw sludge, and about 18 Ld^{-1} of digested sludge was wasted while 18 L d^{-1} of permeate was filtered. During the experimental period, the recycle pump was operated at a constant flow rate of 30 LPM yielding a CFV of 1 m/s and

no fluctuation in pump performance was observed suggesting that the viscosity of the sludge was fairly constant. The filtration was performed intermittently with 4 cycles/day and 1 hour per cycle resulting in an extended relaxation mode of operation for four hours between the filtration cycles. This mode of operation is referred as a semi-continuous (extended relaxation) operation.

The membrane flux, permeability, TSS and fCOD profiles that were observed during the transient state are summarized in Figures 4-17a and b respectively.

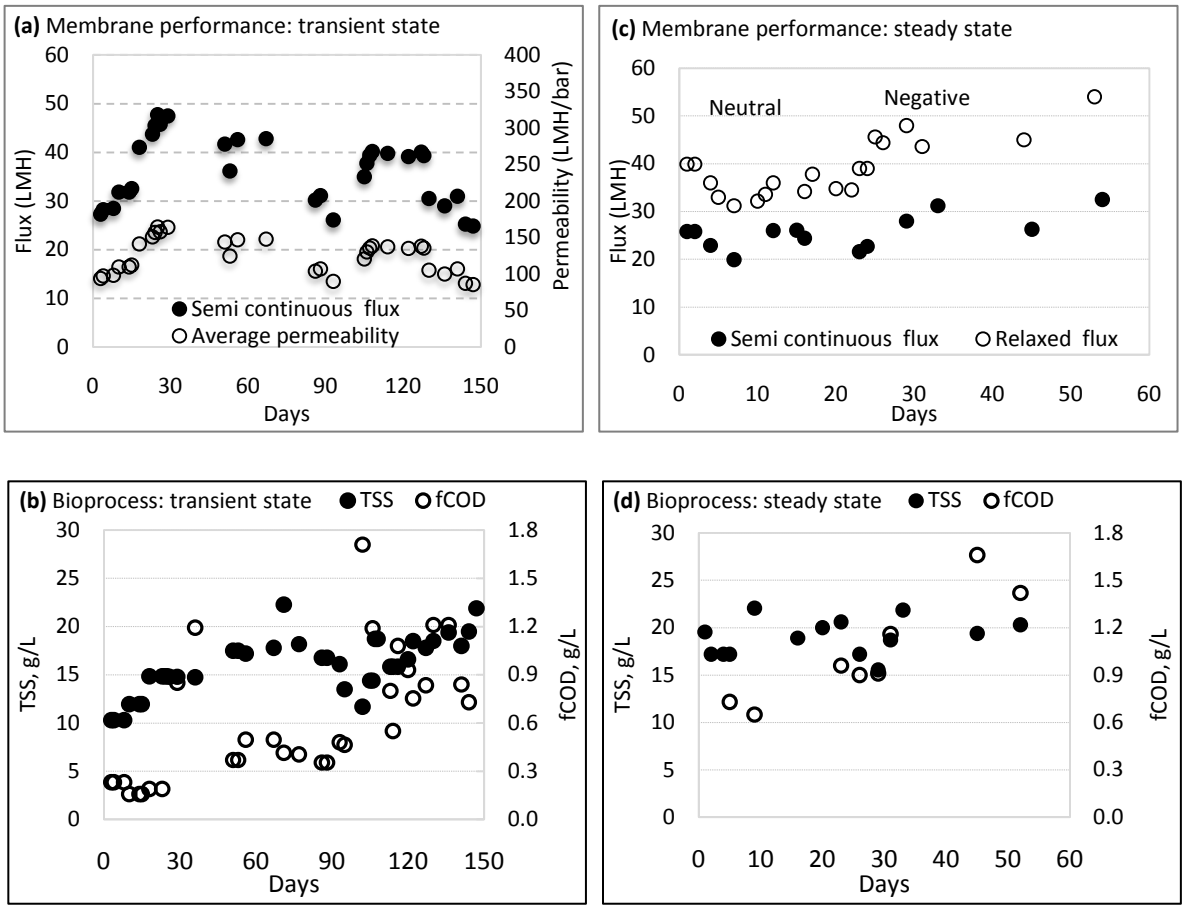


Figure 4-17 (a) Run 1 membrane flux and sludge characteristics versus time (a) & (b) transient state and (c) & (d) quasi-steady state condition

As shown in Figure 4-17b, the TSS concentration increased for the early part of the test (day 0 to 70) and stabilized at approximately 17 g/L. During the transient state operation, the flux and

permeability ranged from 30 to 55 LMH and 100 to 200 LMH bar^{-1}, respectively (Figure 4-17 a). The TSS and fCOD concentrations were in the range of 10 to 22 and 0.3 to 1.7g/L respectively. Between days 1 to 30 an increase in flux from 27 to 50 LMH was observed with increase in the TSS concentration from 10 to 15 gL^{-1}. This increase in flux could be due to the TSS acting as an external loose protective barrier to the membrane. During this period the fCOD concentration remained constant. After this initial period the flux remained constant at 45 LMH and the membrane flux did not decline over time with the exceptions of the period between days 86 to 93 which appeared to correspond to the time when the WWTP's thickener system, that makes use of cationic polymers, was inoperable and the feed sludge was thickened by gravity alone to about 1%. During this period the digester's TSS concentration decreased from 17 to 12 g/L and its fCOD concentration increased to 1710 mg/L. These results would suggest that the presence of the cationic polymer in the feed sludge may have enhanced the flux obtained in the AnM digester. Further a decline in flux was observed during the last part 125-150 days of the transient condition. This trend was coincident with the increase in TSS concentration from 17 to 22 g/L.

Figures 4-17c and d depict the flux and sludge characteristic profiles during pseudo steady state conditions that included operation with both of the membranes and when both semi continuous and relaxed operation were employed. During the quasi-steady-state condition a comparison was made between the membrane performance during semi continuous and relaxed modes of operation. To make this comparison, the membrane was operated for one cycle in a semi continuous mode and the second cycle in relaxed operation on a daily basis. The corresponding average digester TSS and corresponding fCOD concentrations were 19±1 and 1 ± 0.2 g/L respectively due to elevated TSS and fCOD concentrations in the feed. During the semi-continuous operation the average flux for the neutral and negatively charged membranes were 23.6±1.4 and 25.9±1.8 LMH respectively. This difference is not significant (P=0.12). Membrane cleaning was not required over the experimental period.

In the short term filtration tests, the membrane charge was observed to play a major role in membrane performance (section 4.3.1.2). Over the long term, the effect of the membrane charge may be masked by the multitudes of foulant species present in the digested sludge, thus

the benefits of membrane surface charge may have been obscured. In this case the formation of cake layer over the membrane surface probably determined the filtration properties of the system, since the deposited layer can act as a secondary membrane. In previous anaerobic and aerobic studies modification of the membrane filtration properties through formation of fouling layers has been reported (Harada et al. 1994; Pillay et al. 1994; Choi et al. 2005).

Membrane relaxation: During selected filtration events, the membrane was relaxed for 1 minute following every 5 minute filtration. With the relaxed operation the instantaneous flux increased significantly to 39.2±1.5 LMH and 47±2.4 LMH for the neutral and negatively charged membranes respectively. This result suggests that in a long term operation and at TSS and fCOD concentrations of 19 g/L and 1,200 mg/L respectively the negatively charged membrane resulted in a significantly improved ($p=0.003$) performance over the neutral membrane when the membrane was operated in a relaxed mode. In a relaxed mode of operation, while the sludge still moves past the membrane, the filtration has been stopped. This could result in a net positive force to push the cake layer away from the membrane surface. In the case of the negatively charged membrane, the electrostatic repulsion force between the membrane surface and the negatively charged sludge particles may have caused them to be more loosely attached to the membrane surface thereby making the relaxation process more effective.

4.3.2.2.2 Higher loading condition: Extended SRT (Run 2)

In Run 2 the AnM digester was fed with 77 Ld^{-1} of raw sludge, while the volume of biosolids that was wasted was the same as that wasted in Run 1 (18 Ld^{-1}) and the volume of permeate was 3 times that of Run 1 (59 Ld^{-1}). The filtration was performed with 6 cycles/day and 3 to 4 hours per cycle. Semi-continuous operation of the membrane was not possible due to the rapid decline in flux and the inability of the membrane to deliver the flux required to sustain the target HRT and SRT conditions. Therefore all data for this run was obtained using relaxed operation. In this case the membrane was operated with extended relaxation between cycles for 2 hours for the first 2 weeks, however the membrane soon started to foul and a rapid decline in flux was observed. The decline in flux resulted in an increase of the time required to permeate

the daily volume of 59 liters hence the extended relaxation time between cycles was shortened to 30 to 60 minutes.

The flux, cross-flow velocity and sludge characteristics profiles during transient conditions are summarized in Figures 4-18a and b. The membrane was operated for the first 20 days with no cleaning. Once the membrane failed to meet the target permeation flux of 12 LMH the membrane was cleaned in-place as per the sequential cleaning methodology presented in section 4.2.2.4 and operation was resumed. Subsequently the membrane was further operated for 2 months with a weekly cleaning schedule. After being operated in this fashion, the accumulation of solids in the system (TSS= 34 g/L) caused a significant increase in sludge viscosity which led to severe fluctuations and significant reductions of the recycle pump flow and associated trans-membrane pressure. The elevated solids concentrations resulted in a significant decrease of the cross-flow velocity to 0.56 m/s (50% reduction) and hence resulted in a laminar flow condition that likely resulted in a build-up of the cake layer on the membrane and a significant decline in membrane flux. As a result, daily mechanical cleaning was required in order to achieve the target permeate volume (59 Ld^{-1}) and to maintain the bioprocess at steady state conditions. The efficiency of the daily mechanical cleaning was reduced gradually with operating time hence it was necessary to incorporate chemical cleaning of the membranes on a weekly base. It could be hypothesized that over a period of membrane operation the sticky cake layer formed on the membrane surface becomes more and more dense. Besides the simple densification of the biomass cake layer, membrane fouling from the gradual precipitation/deposition of inorganic species was probably responsible for the poor flux recovery when using only mechanical cleaning method.

To deal with the concentrated and viscous sludge, in addition to cleaning of the membranes, the CFV was increased by switching the centrifugal pump with a Continental progressive cavity pump (CPM 44-CSQM) during the quasi-steady state condition. The pump made it possible to maintain a constant CFV of 0.95-1.1 m/s. Subsequently in order to maintain the design CFV, the feed flow rate to the membrane was monitored and adjusted in response to the change in solids concentration.

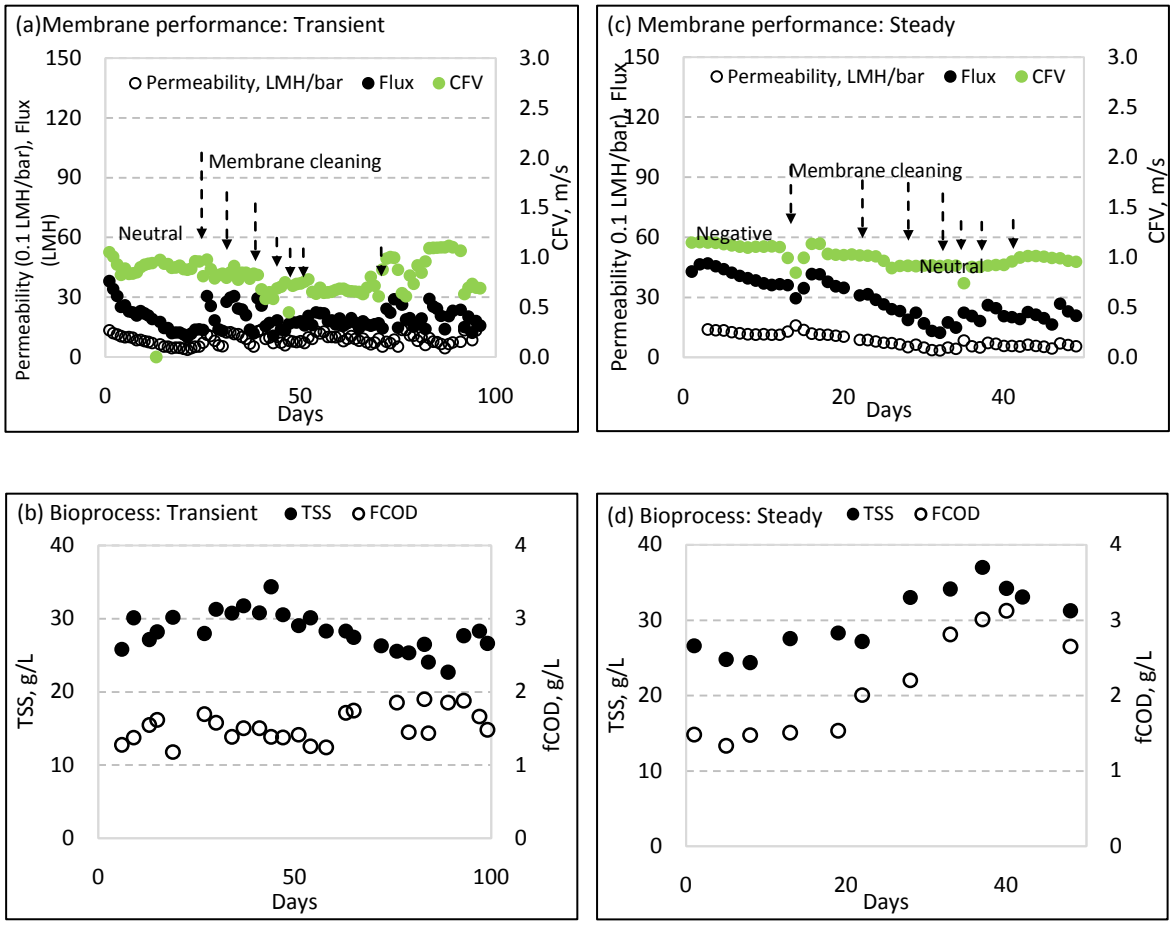
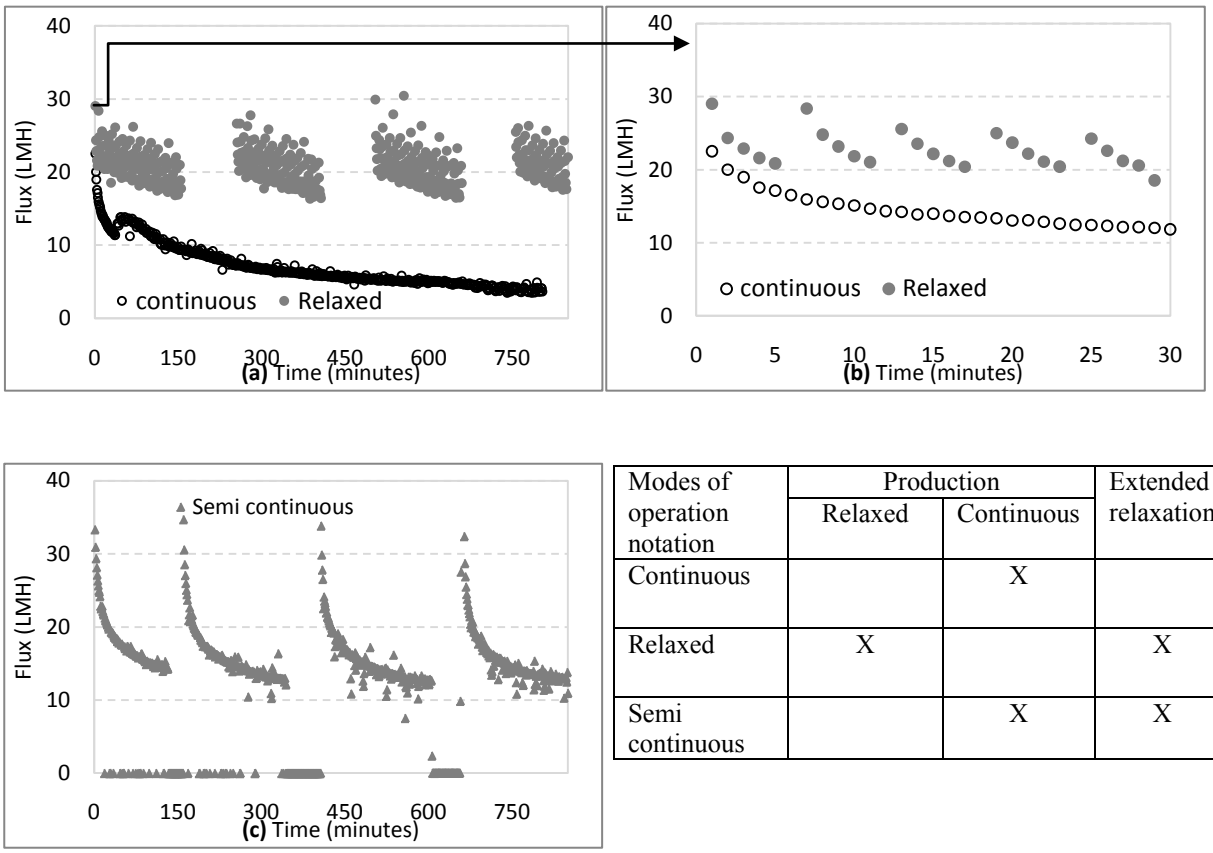


Figure 4-18 (a) Run 2 membrane flux and sludge characteristics versus time (a) & (b) transient state and (c) & (d) quasi-steady state condition (mechanical, base acid cleaning (- - - - →), mechanical and acid cleaning (- - →) and mechanical cleaning (- ▸)

Figures 4-18c and d depict the flux and CFV profile and digested sludge characteristics during quasi-steady state conditions. The negative and neutrally charged membranes had average instantaneous fluxes of 36.8±3.3 LMH and 20.6±2.0 LMH respectively. Both membranes showed a significant decline in flux versus time (Figure 4-18c). Relatively elevated TSS and fCOD concentrations of 34±3 g/L and 2900±105 mg/L respectively were recorded during the neutral membrane operation (Figures 4-18c and d). The average TSS and fCOD concentrations were 27.4±1.4 g/L and 1650±161 mg/L during negative membrane operation (Figures 4-18c and d). The lower instantaneous flux observed during the neutral membrane operation (20.6 LMH) in comparison to the flux of negative membrane (36.8 LMH) could have been due to the higher TSS and fCOD concentrations present during neutral membrane operation.

Membrane relaxation: The concept of relaxing the membrane for 1 minute followed by 5 minutes during filtration cycle, extended relaxation between the filtration cycles (semi continuous operation) and continuous modes of operation were evaluated with respect to their effect on membrane performance. Figure 4-19a compares the permeate flux when the membrane was operated in a relaxed and continuous modes during a 13 hours filtration. Figure 4-19b depicts a magnified view by taking subset of the filtration data showed in Figure 4-19a. In continuous mode the filtration was conducted continuously for 13 hours. In the case of relaxed operation two modes of operation cycles referred as production and extended relaxation cycles were incorporated. During production cycle, permeation was conducted for 5 minutes followed by a 1 minute relaxation. In addition an extended relaxation for a period of 40 minutes was incorporated in between the production cycle during the 13 hours operating period of the membrane. Figure 4-19c shows flux profile when the membrane was operated in a semi continuous mode. Similar to the relaxed mode, production and extended relaxation cycles were incorporated. However in this case, permeation was conducted continuously during the production cycle.

It was observed that having a relaxed operation resulted in better membrane performance. During continuous membrane operation for 13 hours the flux changed from 17 LMH (at t=2 min) to 4 LMH (at t=800 min). During the semi continuous operation the flux changed from 27 LMH (at t=5 min) to 13 LMH (t=830 min). In the case of relaxed mode the flux changed from 21 LMH (t=5 min) to 18 LMH (t=830 min). The results indicate that sustainable operation of the membrane under higher loading and extended SRT condition could be achieved when the relaxation incorporates both a short term relaxation (such as 1 min relaxation following every 5 minutes filtration) and an extended relaxation.



Modes of operation notation	Production		Extended relaxation
	Relaxed	Continuous	
Continuous		X	
Relaxed	X		X
Semi continuous		X	X

Figure 4-19 Membrane flux profile (a) continuous and relaxed operation (b) relaxed and semi-continuous operation

4.3.2.2.3 Higher loading: conventional SRT (Run3)

In Run 3 the AnM digester was fed with 77 Ld^{-1} of raw sludge, and about 36 Ld^{-1} of digested sludge was wasted while 41 L d^{-1} of permeate was filtered. During the experimental period, an average CFV of 1.01±0.02 m/s and TMP of 33.7±1.17 KPa were maintained. Figures 4-20a to d show the filtration and associated sludge characteristics profiles. As with runs 1 and 2, the neutral membrane was employed during the transient state. The run employed a relaxed mode of operation from the start (Figure 4-20a). The instantaneous flux and permeability during this period ranged from 27.5 to 33 LMH and 79 to 101 LMH/bar respectively. After two weeks of operating in a relaxed mode, semi continuous operation was initiated and this resulted in a decrease of flux to 17 LMH. With the semi continuous operation a further gradual decline in the membrane permeability at a rate of 1 LMH/bar*day was observed (Figure 4-20a). However

the membrane was able to deliver the target flux (13 LMH) and hence cleaning was not initiated.

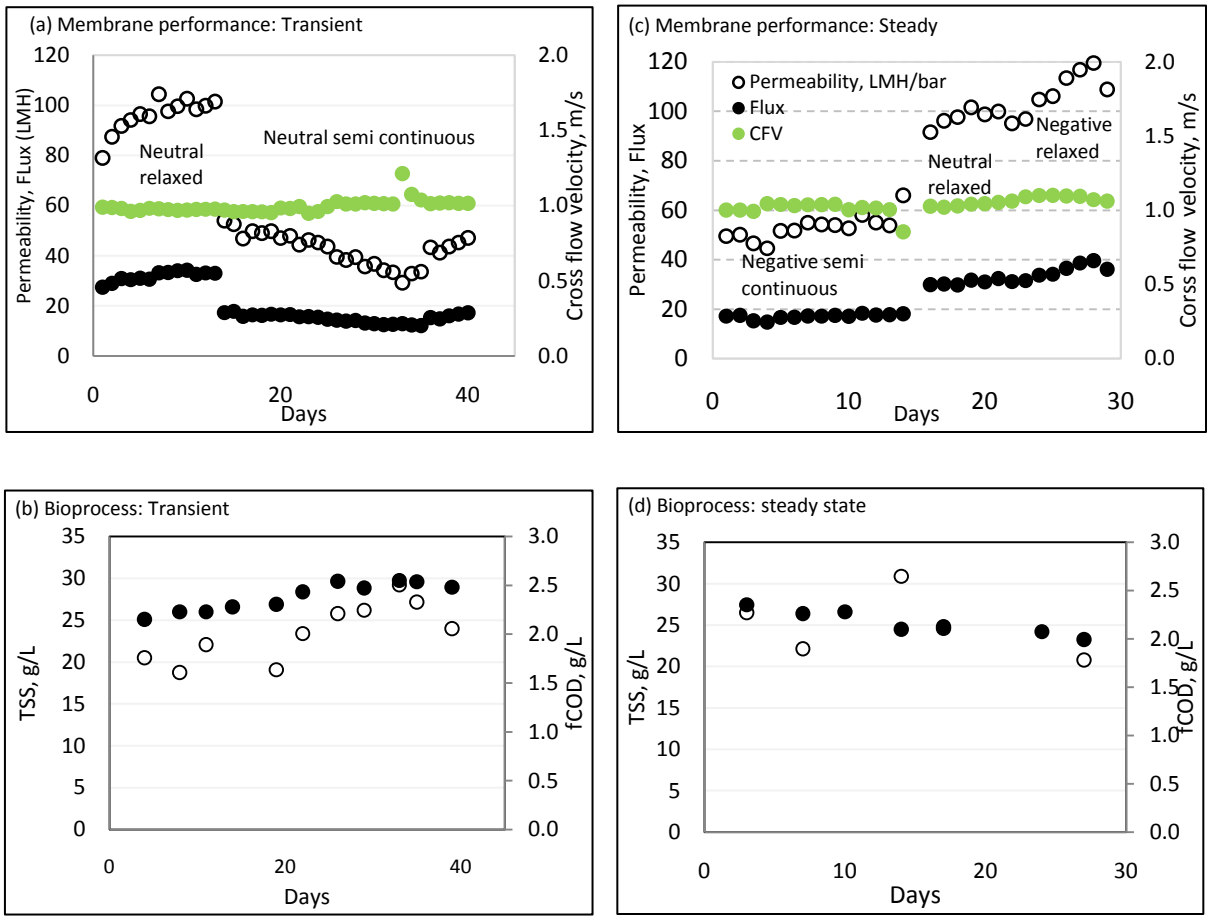


Figure 4-20 (a) Run 3: Transient and steady state (a) & (c) filtration characteristics and (b) & (d) sludge characteristics

Figures 4-20b and d depict the flux and sludge characteristic profiles during pseudo steady state conditions. Similar to the previous runs no significant difference was observed between negative and neutral membrane operation in semi continuous mode. An overall increase in instantaneous flux was observed when the membrane operation was relaxed.

4.3.2.2.4 Comparison of membrane performance between the runs

In general, the fluxes obtained during this experiment were within the typical design fluxes for AnM digester that have ranged between 10-40 $Lm^{-2}hr^{-1}$. The average fluxes in runs 1 and 3 were 32.3 and 14.1 LMH respectively under a semi-continuous mode of operation and 32.9, 18.7 and 31.1 LMH for runs 1, 2 and 3 under relaxed mode of neutral membrane operation

(Table 4-7). During the semi-continuous operation, no significant decline in flux was observed for run 1 and membrane cleaning was not required. In case of run 3 a gradual decrease in permeability at a rate of 1 LMH/bar*day was observed and a monthly sequential membrane cleaning was required. In run 3, it was only possible to operate the membrane in relaxed mode with mechanical cleaning every 4 to 7 days and sequential (mechanical and chemical) cleaning on a monthly basis was required to manage the fouling. On the contrary runs 1 and 3 when operated under relaxed condition showed no significant decline in flux. In all cases no significant difference was observed between neutral and negative membranes when operated under a semi-continuous condition, however the latter showed a better performance under relaxed condition (Table 4-7).

Table 4-7 Comparison between average daily flux between the runs

Experiment	**Semi-continuous mode**			**Relaxed mode**		
	Flux	**TSS**	**fCOD**	**Flux**	**TSS**	**fCOD**
Neutral						
Run-1	23.6±1.4	19.6±1.2	0.9±0.1	33.4±1.6	19.6±1.2	0.9±0.1
Run-2				15.6±0.6	32.6±0.8	2.6±0.2
Run-3	14.1±1.1	28.6±0.6	2.1±0.1	24.7±0.9	24.8±0.3	1.8±0.1
Negative						
Run-1	25.9±1.8	19.4±1.1	0.9±0.1	39±2.3	18.1±1.1	0.9±0.1
Run-2				27.7±1.3	26.2±0.4	1.7±0.1
Run-3	16.8±0.9	26.2±0.6	2.5±0.3	28.8±1.9	23.7±0.3	1.8

[1]Steady state condition
[2]Flux under relaxed condition are true flux not instantaneous

The observed membrane performance variations as indicated based on average daily flux (Table 4-7) between the different runs could be as a result of not only changes in sludge properties but also because of the difference in volume of water being permeated. In the conventional loading condition (Run 1) the membrane was subjected to relatively lower suspended and colloidal solids concentrations (Table 4-7). The relatively dilute sludge concentrations coupled with a lower volume of required permeate resulted in a condition where the membrane size was greater than that required for operation. Hence, the membrane was only permeating for about 3 to 4 hours per day and the rest of the time it was on an extended relaxed condition. However in Run 2, the membrane was permeating about 56 Liters of water per day. In this case the membrane initially permeated for about 12 hours at the beginning of a cycle (2-3 days from starting) and the permeation period increased to about 18-

20 hours after one to two weeks operation. In Run 3 the membrane was permeating 41 Liters of water per day. The fact that the membranes were permeating different volumes of water for the three experimental conditions could make a comparison of the membrane performance between the runs difficult.

To better understand the filtration characteristics independent of the volume of filtrate, further comparison was made using flux data after 30 minutes of filtration and corresponding fouling index (Table 4-8) and critical flux (Figure 4-21 and Table 4-9) that was measured when the reactors were operated in the steady state condition.

Table 4-8 compares the flux at t=30 minutes and fouling index between the different runs for the neutral and negative membrane. The trend of calculated flux at t=30 minutes were similar to average flux except the magnitude was smaller. Under all conditions, the run 1 flux at t=30 minutes were substantially higher than runs 2 and 3. However no difference was observed between runs 2 and 3 for the negatively charged membrane. The TSS and fCOD concentrations were also similar (Table 4-8). Despite this, under run 2 conditions frequent cleaning was required. This might be associated with the difference in the amount of permeate filtered per cycle. Contrarily substantial difference was observed in sludge TSS and fCOD and membrane performance between runs 2 and 3 for the neutral membrane operated under relaxed mode (Table 4-8). Further explanation on the relationship of sludge properties and membrane performances are given in sections 4.3.3.3 to 4.3.7.2.

Table 4-8 Comparison between flux at t=30 minutes and fouling index between the runs

Experiment (HRT-SRT)	**Semi-continuous mode**			**Relaxed mode[2]**		
	Flux, 30 min (LMH)	**FI[1] (LMH/min)**	**TSS (g/L)**	**Flux, 30 min (LMH)**	**FI (LMH/min)**	**TSS (g/L)**
Neutral						
Run-1 (15-30)	23.2±1.1	0.73±0.06	19.6±1.2	29.2±1.8	0.24±0.02	19.6±1.2
Run-2 (7-30)				11.0±1.3	0.06±0.01	32.6±0.8
Run-3 (7-15)	14.8±0.8	0.34±0.01	28.6±0.6	16.5±0.5	0.06±0.01	24.8±0.3
Negative						
Run-1 (15-30)	26.4±1.2	0.80±0.04	19.4±1.1	34.5±2.5	0.12±0.04	18.1±1.1
Run-2 (7-30)				20.2±1.3	0.08±0.02	26.2±0.4
Run-3 (7-15)	17.6±0.4	0.36±0.01	26.2±0.6	19.2±0.6	0.09±0.01	23.7±0.3

[1]Fouling index calculated: flux (t=30) minutes-flux (t=1 min)/ (30-1) minutes
[2]Fluxed under relaxed condition are true flux not instantaneous

Critical flux: The critical flux value is a function of sludge characteristics, operating conditions and membrane type (Le-Clech et al. 2006). In this case the operating conditions (cross flow velocity, trans-membrane pressure and temperature) and membrane characteristics were held constant and the only change was in the sludge characteristics that resulted from the change in the reactor loading conditions, degree of digestion and thickening. Figure 4-21 and Table 4-9 and show the critical flux and TMP of a neutral and negative membrane during runs 1, 2 and 3. From Table 4-9 it can be seen that the critical flux decreased by 65% (from 40 to 16 LMH) when switched from the conventional to high loading conditions. A modest decrease from 20 to 16 LMH was observed when the digester was operated at an equal HRT but at extended SRT.

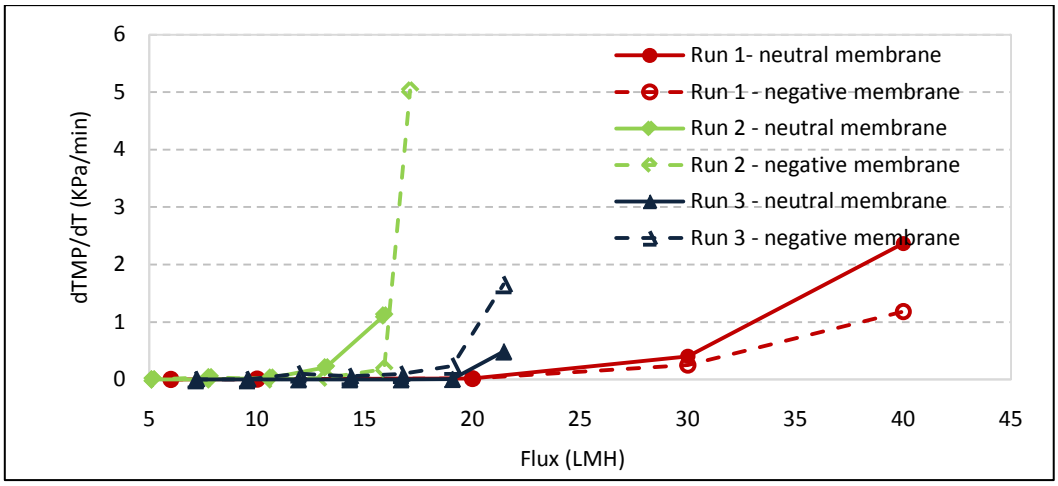


Figure 4-21 Change in TMP versus flux

Table 4-9 Critical flux comparisons

Membrane parameters	Run 1	Run 2	Run 3
Critical flux (LMH)[a]	30-40	15.9-17.0	20-22
TMP (KPa), Neutral membrane	13-29	7.6-14.5	11.0
TMP (KPa), Negative membrane	6.9-11.7	0.5-0.9	8.3
TSS, g/L	15.5	32.2	25

[a]Initial membrane conditions were similar

4.3.2.2.5 Membrane cleaning

Flux recovery of fouled neutral and negative membrane was compared within the runs following a sequential cleaning. During run 2, the combined effect of mechanical and chemical cleaning versus just chemical or mechanical cleaning was compared. In addition the sequence of chemical versus mechanical cleaning and sequence of acid versus base chemical cleaning on flux recovery were also investigated.

During run 1, the membrane was not fouled to the point that membrane cleaning was required throughout the experimental period. Cleaning was conducted only at the end of the experiment. Figure 4-22a shows the flux recovery of the negative and neutral membrane employed in run 1 post sequential cleaning. The negative and neutral membranes were cleaned after being used for 4 and 2 months and filtering ~ 2.2 and 1.1 m^3 of water respectively. The fouled flux was 21 and 42 LMH; after just rinsing with water the flux increased to 40.5 and 163.4 LMH up by ~ 10 and 45% (relative to the virgin/clean membrane flux), respectively. This showed that foulant removal from the negative membrane surface was easier. Then after a sequential scrubbing and chemical cleaning (NaOH followed by citric acid) the clean water flux was recovered by 93 and 98%.

Figure 4-22b shows an example of the neutral and negative membranes cleaned after just filtering ~ 0.35 m^3 during run 2. The mechanical cleaning (rinsing and scrubbing) recovered 28 and 53% of the flux. After chemical cleaning the flux recovered to 85 and 88% respectively (Figure 4-22b). Similarly in run 3, 48 and 89% recovery of the original flux was observed following mechanical cleaning of the neutral and negative membrane cleaning respectively. The final flux recovery after a subsequent chemical cleaning was 88 and 98% respectively.

The cleaning efficiency was also observed to depend on the sequence of cleaning. For example citric acid cleaning of the membrane surface prior to mechanical cleaning resulted in poor recovery -5% as oppose to 52% when the sequence was reversed (Figure 4-22d). Addition of chemical solution prior to scrubbing the membrane surface could have two problems: one the citric acid solution could not penetrate through the cake layer to result in solubilizing and removing inorganic materials deposited on the membrane surface. Second it might also result

in weakening the cation biopolymer bond and releasing of soluble biopolymers that were present on the cake layer. This might have caused further fouling on the membrane surface.

Likewise the sequence in the chemical cleaning were also found to be important; cleaning the membrane with NaOH prior to a citric acid cleaning were often found detrimental. In this case it can be reasoned that addition of NaOH would result in an increase on the pH hence causing further precipitation of the inorganic materials that already existed on the membrane surface. However, citric acid cleaning followed by NaOH cleaning were found to be effective (Figure 4-22d).

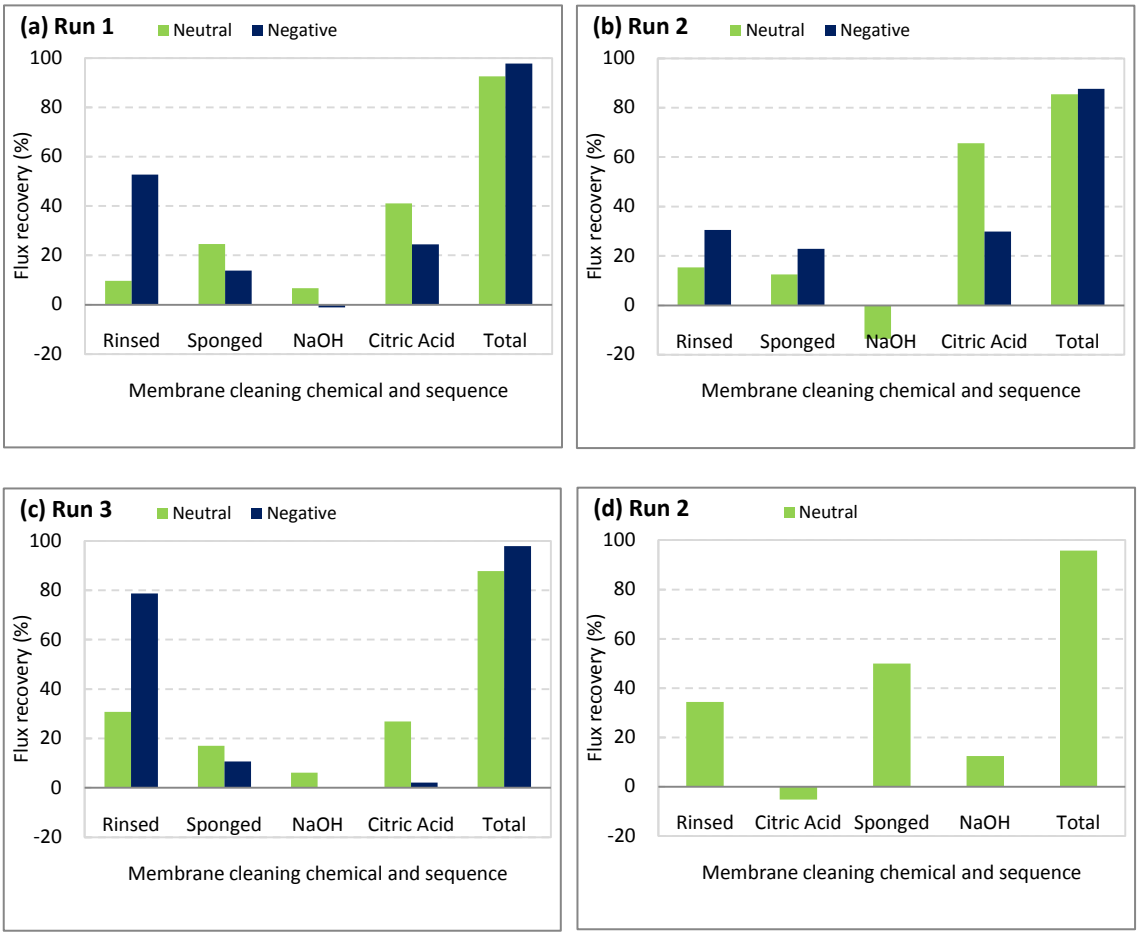


Figure 4-22 Membrane cleaning and recovery (a) Run 1 (b) Run 2 (c) Run 3 and (d) Run 2 with different chemical sequence.

4.3.3 Change in TSS and VSS with HRT-SRT and their effect on membrane performance

Change in solid fractions: Figures 4-23a and b show the average steady state total suspended solid (TSS), volatile suspended solids (VSS), fixed suspended solids (FSS) concentrations and VSS/TSS ratios in the sludge fed to the digesters and in the digested sludge. The average bound feed sludge TSS concentrations were 14.8±2.0, 13.6±1.8 and 18.1±3.7 during runs 1, 2 and 3 respectively and the corresponding VSS concentrations were 11.4±1.6, 11.2±1.0 and 15.1±2.8 g/L. Upon digestion and co-thickening the average digester TSS concentrations increased to 17.2±1.2, 28.4±2.0 and 25.7±1.0 g/L in the digester mixed liquor. The average corresponding VSS concentrations increased to 11.2±0.8, 18.5± 1.2 and 17.6±0.6 g/L during runs 1, 2 and 3 respectively. The FSS concentrations of the raw feed sludge were 3.5±0.5, 2.4±0.5 and 4.4±1.1 g/L. The digesters FSS concentrations were 5.9±0.6, 9.8±1.0 and 8.6±0.5 for runs 1, 2 and 3 respectively. Upon digestion the VSS/TSS ratio decreased from 0.76±0.02, 0.83±0.03 to 0.80±0.02 to 0.65±0.02, 0.65±0.02 and 0.8067±0.01 for runs 1, 2 and 3 respectively. However the change was independent of variations in SRT and/or HRT.

The significant increase in TSS and VSS concentration with a decrease in HRT from 15 to 7 days was mainly associated with the increased loading which resulted in accumulation of solids within the AnM digester. Figure 4-21 also depicts an increase in TSS, VSS and FSS concentrations with increase in SRT from 15 to 30 days while maintaining the HRT at 7 days (runs 2 and 3). The increase in SS concentrations of AnM digesters in this case was due to effect of thickening by membrane that resulted in accumulation of the slowly growing anaerobic biomass, slowly biodegradable and non biodegradable materials from the feed. Also the FSS follows the same trend to that of TSS and VSS indicating slight accumulation of inert materials. The accumulation factor of FSS was 1.7, 4.1 and 1.9 times for runs 1, 2 and 3, and was proportional to SRT to HRT ratio. The SRT to HRT ratio of runs 1 and 3 was 2; and the ratio for run 2 was 4.

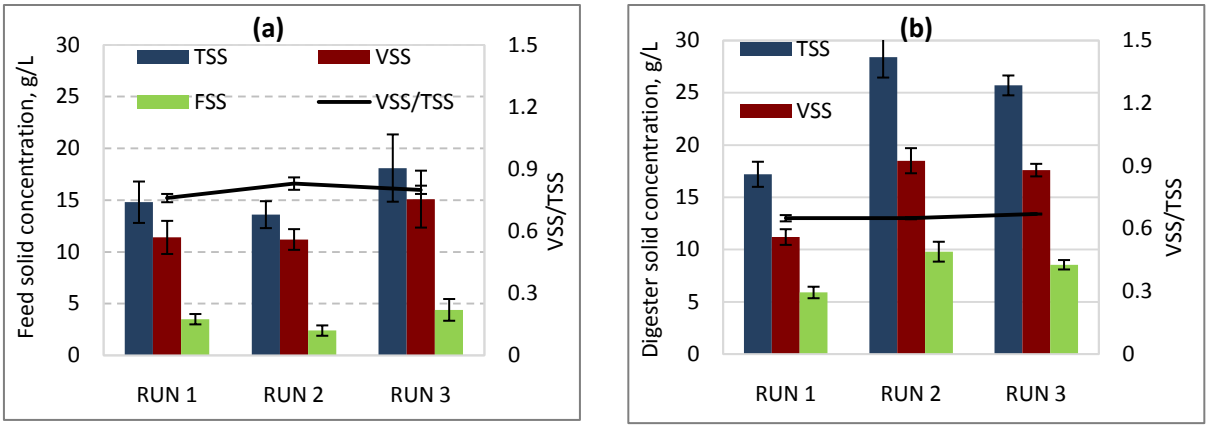


Figure 4-23 TSS, VSS, FSS concentrations and VSS/TSS in (a) raw feed sludge (b) digested sludge: The mean values based on 8 to 16 duplicate samples collected twice a week during steady state operation of run 1, run 2 and run 3

TSS impact on membrane fouling: Figure 4-24a shows the membrane flux at t=30 versus TSS concentration for all the three runs. The TSS concentration ranged between 10.3 to 34.9 g/L and corresponding flux ranged from 10.5 to 46.5 LMH. The results show that the impact of TSS on flux depends on the TSS concentration. Figure 4-24a shows that the flux increased with an increase in TSS concentration from 10 to 15 g/Lt (R^2=0.84). Figure 4-24aalso shows as TSS concentrations between 15 to 17 g/L no obvious relationships between TSS and flux was observed (R^2=0.19). However a significant decline in sludge's filterability with an increase in the TSS concentration beyond 17 g/L was observed (R^2=0.83). This suggests that the critical TSS concentration was in this range. Once the TSS concentration exceeded the critical range, a strong relationship between TSS and flux was observed: where an increase in TSS resulted in a decrease of membrane performance.

It has been hypothesized that at the lower range of TSS concentration, increases in TSS concentrations might reduce fouling by acting as an external loose protective barrier to the membrane. The negative effect of increased TSS concentrations on the pilot tubular membrane performance could have been due to either the increased viscosity that would attenuate the cross-flow scouring effect and/or due to increased mass transfer of solids to the membrane surface at higher concentration. In this study the impact of TSS on CFV was controlled by maintaining a constant recycle flow irrespective of variations in sludge viscosity. It was observed that during increased periods of TSS, the pump flow tended to drop resulting in

decreased CFV. To minimize this impact and have a constant CFV, the mixing pump flow was constantly monitored and the flow was kept constant by adjusting the throttling valve in response to changes in TSS concentration. Hence it could be speculated that the main mechanism of the TSS effect on the membrane's performance was through increased mass transfer and thick cake layer formation on the membrane surface.

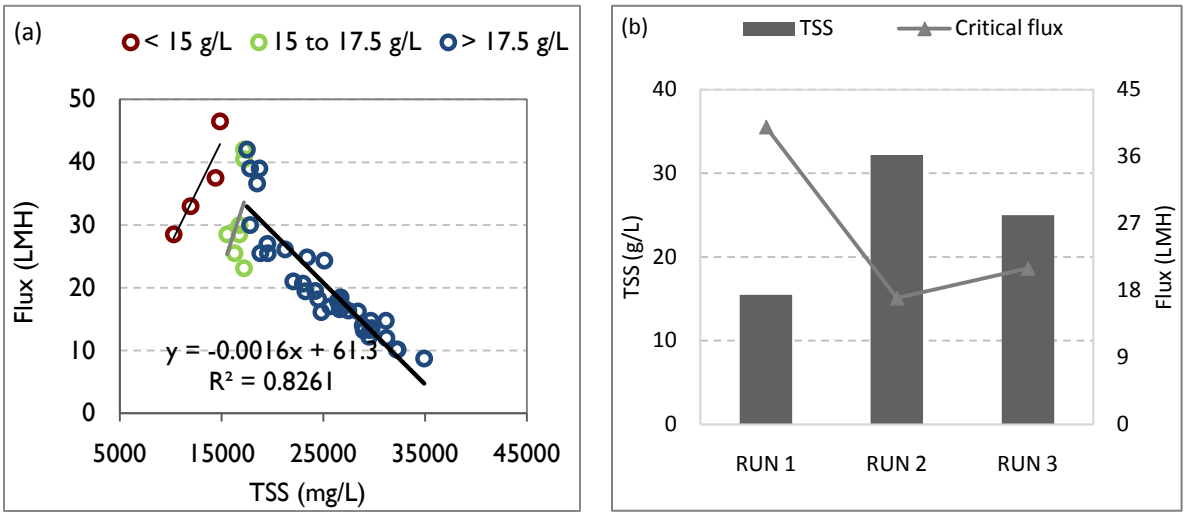


Figure 4-24 (a) TSS versus flux (after 30 minutes filtration) (b) TSS and critical flux relationship

The plot of critical flux values versus the corresponding TSS concentration showed a similar trend (Figure 4-24d) where a significant decline in critical flux was observed with an increase in sludge's TSS concentration. The results of this study agree with previous studies. For example, TSS concentrations below 10 g/L showed little impact on the fouling of a membrane (Le-Clech et al. 2006). However, as the concentration increased beyond a critical suspended solids concentration which was identified as 12 g/L by Le-Clech et al. (2006) and Meng et al. (2006) a significant decline in flux was observed as TSS concentrations increased. In these previous studies the MBRs were operated at a TSS concentration of less than 12 g/L to minimize the effect of TSS on fouling. Considering that most sludge digestion applications are conducted at solids concentration greater than 20 g/L, it is reasonable to assume that the TSS concentration in the digester will be a significant factor in the design and optimization of membrane performance.

4.3.4 Change in filtered and soluble COD with HRT-SRT and their effect on membrane performance

Change in filtered and soluble COD: The short term filtration tests indicated that a majority of the foulants in the digested sludge were also present in the supernatant after centrifugation. The filtered and soluble fractions of the sludge were investigated to explore the relationship between these sludge properties and the sludge filterability. Quantification of these fractions in sludge is difficult and highly dependent on the methods used to fractionate the different sizes. In this study the components in the filtered fraction were quantified by initially centrifuging the sludge samples and subsequently filtering them with a 1.5 μm filter. The truly soluble components were determined by subsequently filtered them using a 0.45 μm filter. Comparable results for the soluble and permeate fractions (pore size of 0.02 μm) were observed when a high speed centrifuge was employed prior to filtration through the 0.45 μm filter.

The average TCOD, fCOD, cCOD, sCOD and pCOD associated with the digested and raw feed sludges during the AnMBRs steady state conditions are presented in Table 4-10. The raw feed sludge consisted mainly of particulate material with the soluble fraction averaging 4.3±0.8 % of the total COD (Table 4-10). The colloidal fraction of the feed sludge (fCOD-sCOD) was on average 162±72 mg/L and 0.8±0.3% of the total COD. In general, upon digestion and concurrent thickening an increase in colloidal COD and an overall reduction in the soluble COD were observed (Table 4-10). The average AnM digester permeate COD concentration over all runs was 190 mg/L. The soluble COD concentration in the digester was 390 mg/L and on average 1.2±0.1% of the total COD (Table 4-10). A significant variation in colloidal COD concentration was observed between the runs. The average colloidal COD concentration in the digesters were 679, 2045 and 1970 mg/L and represented 3.7, 6.5 and 7% of the total COD (Table 4-10). A comparative factorial analysis using the raw steady state cCOD data from all the digesters showed significantly higher cCOD generation associated with decreasing HRT (P value <0.000) and increasing SRT to HRT ratio of the digester (P=0.004).

Understanding and quantifying the source of variations in colloidal concentration between the runs was not straightforward. It was found that the variation in the digester's colloidal COD was not associated with the concentration in the feed. Despite variations in the filtered COD of the feed, colloidal COD concentrations were small and the feed colloidal concentration was not significantly different. The colloidal concentrations in the digester in run 1 were significantly lower in comparison to runs 2 and 3. The generation and/or consumption in the digester's colloidal concentration were related to the loading rate, SRT to HRT ratio (thickening) and SRT (hydrolysis and decay).

Table 4-10 Average steady state digested and raw feed sludge COD fractions

Feed	TCOD (g/L)	cCOD (g/L)	fCOD (g/L)	sCOD (g/L)	pCOD (g/L)	cCOD /TCOD	sCOD /TCOD
RUN 1	20.3±3.0		1.2±0.3		NA		
RUN 2	17.3±2.4	0.06±0.03	0.4±0.1	0.37±0.1	NA	4.0±0.5	30±5
RUN 3	21.4±2.9	0.11±0.04	1.1±0.3	0.87±0.1	NA	5.0±2.0	40±4
RUN 4	21.4±2.9	0.11±0.04	1.1±0.3	0.87±0.1	NA	5.0±2.0	40±4
Digester							
RUN 1	18.0±1.2	0.6±0.1	0.9±0.1	NA	0.21±0.05	4±1	3±1
RUN 2	29.2±1.9	1.9±0.3	2.0±0.3	0.43±0.04	0.20±0.03	6±1	1±0.2
RUN 3	27.4±0.9	2.1±0.3	2.3±0.3	0.35±0.05	0.17±0.01	8±1	3±2
RUN 4	12.3±0.5	0.3	0.62±0.1	0.31±0.1	NA		

*The fCOD, sCOD and pCOD during critical flux measurement was (2652, 389 and 211 for Run 2); (2648, 296 and 169 for Run 3)

Impact of colloidal and soluble COD on fouling: Figures 4-25a and b show the membrane flux versus digested sludge colloidal and soluble COD concentrations. The results showed an overall decrease in flux with an increase in the colloidal and soluble COD concentration in the AnMBR digesters (R^2 =0.88 and R^2=0.46 respectively). These results were also observed during short term filtration study which demonstrated a significant (70%) decline in flux was related to the supernatant fraction of the digested sludge (section 4.3.1.3).

In previous studies the colloidal fraction of sludge has been identified as a dominant factor controlling membrane fouling (Wu et al. 2009; Fan et al. 2006). However most of the previous studies were conducted at lower TSS concentrations and often operated at a flux substantially lower than the critical flux. Hence cake formation and the effect of TSS under

these conditions was minimal and most of the fouling was associated with soluble and colloidal materials. In this study the TSS concentration was much higher, even then it was found in the short term and long term test that the cCOD sludge fraction had a significant effect on the membrane performance. Different mechanisms have been speculated in literature as to how colloids decrease the membrane performance including by adsorption on the membrane surface, blocking membrane pores, physical retention and formation of a gel structure on the membrane surface (Rosenberger et al. 2006).

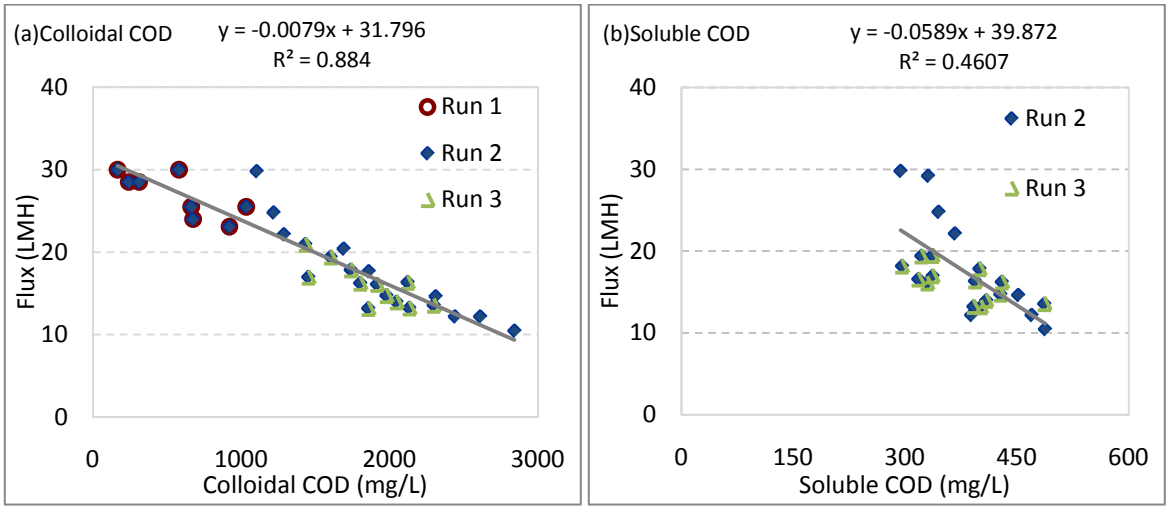


Figure 4-25 (a) Colloidal and (b) soluble COD versus flux

4.3.5 Impact of digestion on biopolymers and cations

Previous studies on AnMBRs treating low strength wastewater have demonstrated the importance of proteins, carbohydrates and cations as direct foulants and as stabilizing agents for biofilm formation on the membrane surface (Liao et al., 2006; An et al., 2009). Thus in this research the changes in composition and concentration of floc associated and solution biopolymers and cations during digestion under varying SRT and HRT conditions were monitored and subsequently related to the membrane performance and fouling. Proteins and polysaccharides were monitored and compared as they are the most abundant components of biopolymers in sludge and could potentially affect membrane performance.

4.3.5.1 Protein and carbohydrate fractions

Figures 4-26a and b and Figures 4-27a and b show the bound, colloidal and soluble protein and carbohydrate concentrations in the sludge fed to the digesters and the corresponding changes in these values during the digestion process. The feed data in Figures 4-26a and b suggest substantial seasonal variability in bound and soluble proteins and carbohydrates, respectively. In general, the WAS feed obtained during the winter season showed higher bound and relatively lower soluble protein concentrations (run 2, Figure 4-26a) and lower soluble carbohydrate concentration (Figure 4-26b). Conversely the raw feed sludge obtained during summer had a lower bound protein but increased soluble protein concentrations indicating hydrolysis of bound to soluble EPS. A similar seasonal dependence of higher bound biopolymer production in activated sludge at low temperatures was observed by Al-Halbouni (2008) and Barker and Stuckey (1999). This was attributed to a shift in microbial population in colder temperature towards more biopolymer producing bacteria and/or environmental stress initiating production of extracellular enzymes.

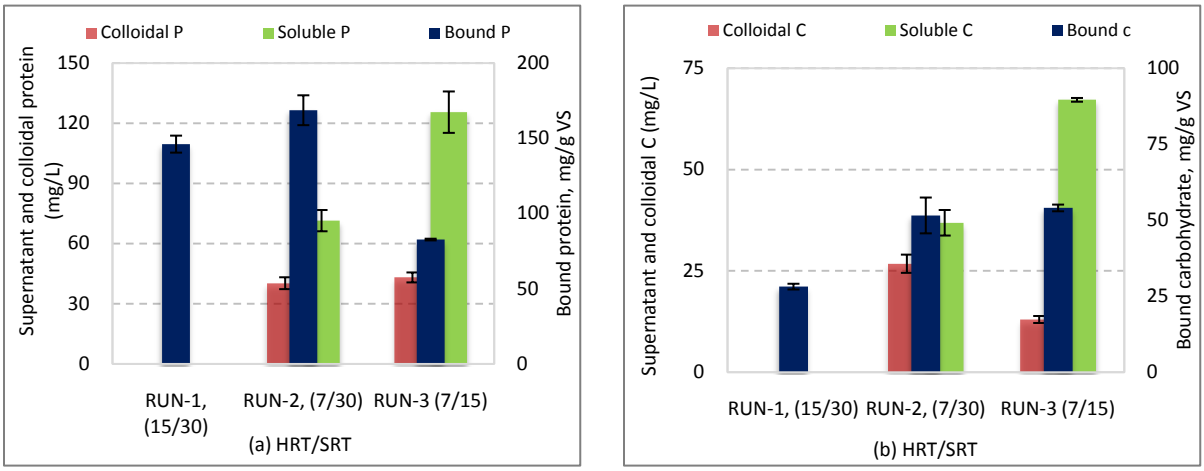


Figure 4-26 Colloidal, soluble and bound (a) protein and (b) carbohydrate concentrations in raw feed; mean values of 3 separate duplicate samples collected weekly during steady state operation

Upon digestion an overall reduction in the mass of bound biopolymer was observed for both proteins and carbohydrates (Figures 4-27a and 4-27b). The percent reductions in bound biopolymers (proteins + carbohydrates) were 74% at longer SRTs and 63% at shorter SRTs and preferential biodegradation was not observed. This showed that increasing the SRT

increased the amount of bound proteins and carbohydrate hydrolysis and their subsequent release into solution. The effect of SRT was similar to the pattern observed in VS destruction. Considering that typically 10% of the WAS is composed of active cells and a large fraction of the cell is composed of biopolymers, it can be deduced that a significant portion of the WAS destruction was contributed by the biodegradation of the biopolymers. This result is in accordance with the work of Park et al. (2006), Murthy et al. (1999) and Nielsen et al. (1996). Nielsen et al. (1996) found that both bound proteins and carbohydrates in sludge decreased rapidly within the first 2 days under anaerobic condition. Comparatively, varying the HRT didn't affect the change in the biopolymer fraction of the solids. However the digesters with shorter HRT had a relatively higher total bound biopolymer concentration (mg/L) within the digester that was mainly due to the increased SRT to HRT ratio which resulted in solids accumulation.

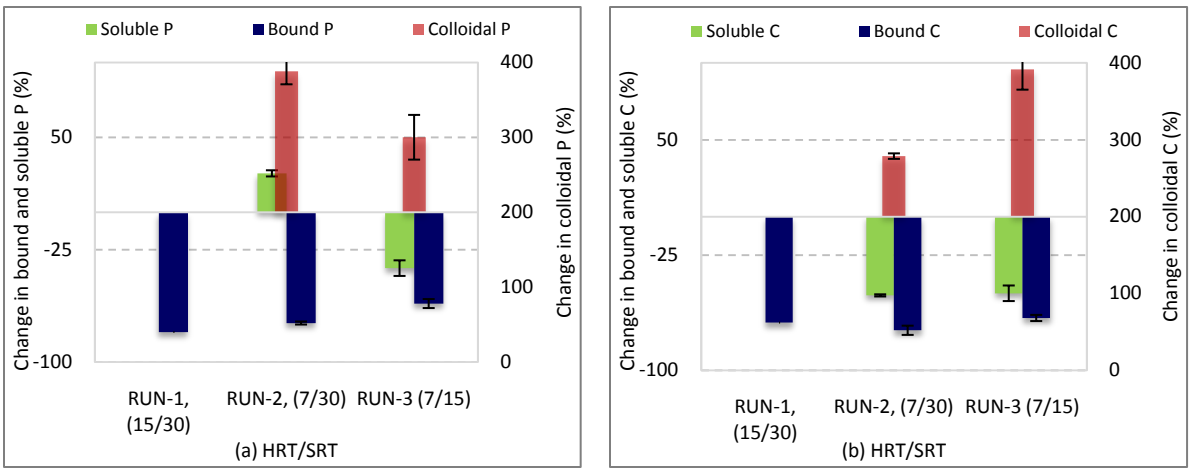


Figure 4-27 Changes in bound, soluble and colloidal (a) protein and (b) carbohydrate concentrations upon digestion (calculated based on mass balance); mean values based on 3 duplicate samples collected weekly during steady state operation

Overall, the bound biopolymer that was present appeared to be dependent on the digester feed biopolymer composition. Higher protein and carbohydrate mass fractions in the solids in the digester were associated with high protein and carbohydrate fractions in the feed.

Conversely, process parameters appeared to have a more substantial impact on the concentration of colloidal and soluble biopolymers in the digester than the feed composition (Figures 4-27a and b). The colloidal feed protein concentration was 40 and 43 mg/L for runs 2 and 3, respectively corresponding to only 24 and 37% of the total supernatant protein concentration (Figure 4-26a). During AnMBR digestion, the colloids were selectively retained by the membrane that resulted in an increase in protein concentration to 186 and 150 mg/L, respectively. This accounted for 69 and 68 percent of the total supernatant protein concentrations in the digester, respectively. Similarly the percentage colloidal carbohydrate concentration of the total supernatant increased from 28 and 26% to 78 and 60% for run 2 and 3 respectively.

The soluble proteins and carbohydrates showed different responses to changes in SRT. At both 15 and 30 day SRTs an overall 50% reduction in soluble carbohydrate concentration was observed (runs 2 and 3, Figure 4-27b). In contrast soluble protein concentrations were observed to increase with an increase in SRT (run 2, Figure 4-27a). The production mechanisms and/or definitions of the soluble biopolymers have varied between reports. For an anaerobic process digesting waste activated sludge, the possible sources of soluble biopolymers include: products associated with anaerobic biomass growth and substrate metabolism products, often referred to as utilization associated products (UAPs) and decay of anaerobic biomass that is often referred to as biomass associated products (BAPs) (Barker and Stuckey 2001). The UAPs during sludge digestion would mainly consist of the soluble biopolymer fraction of the WAS feed and the products released into solution due to metabolism/shear of bound biopolymers in the WAS feed. Barker and Stuckey (2001) indicated that the UAPs were more biodegradable than BAP and that BAPs accumulate in most systems. In the reactor at extended SRT, it appeared that the anaerobic bacteria released intracellular proteins due to increased cell lysis and possible endogenous respiration resulting in release and accumulation of non biodegradable protein.

4.3.5.2 Carbohydrate to protein ratios

Recently the fouling of membranes had been associated with the carbohydrate to protein ratio however the results vary between different authors. Haung et al. (2009) observed an increase in the fouling propensity of sludges with increased soluble carbohydrate to protein (C:P) ratios. Conversely, Lin et al (2009) observed an increase in fouling propensity of sludges with a decrease in the bound carbohydrate to protein ratios respectively.

Figures 4-28a and b show carbohydrate to protein ratios of the bound, colloidal and soluble fractions of the raw feed and digested sludge. A comparison of the protein and carbohydrate fractions showed the protein fraction as the dominant organic fraction of the bound and loose biopolymers in both raw and digested sludges (Figure 4-28a and b). These findings were in agreement with the work of Morgan et al. (1990) and Houghton et al. (2000).The carbohydrate to protein ratio (C:P) ranged between 0.2 and 0.6 depending on the feed composition and process conditions.

The bound C:P ratio appeared to be similar prior to and after anaerobic digestion and was independent of any variation in SRT and/or HRT indicating no preferential degradation of bound protein and/or carbohydrates (Figures 4-28a and b). These results were contrary to the observations made by Houghton et al. (2000). The authors reported a preferential degradation of carbohydrates over proteins and a decrease in the bound C:P ratio after anaerobic digestion of primary sludge. The current study may differ from those of Houghton et al. (2000) because of the difference in the type of carbohydrate materials in primary versus secondary sludge where low molecular weight carbohydrates could be present in the former that would be easier to digest than proteins. On the other hand an overall reduction in soluble C:P ratio was observed upon digestion, and the magnitude was higher with increase in SRT (Figure 4-28a and b).

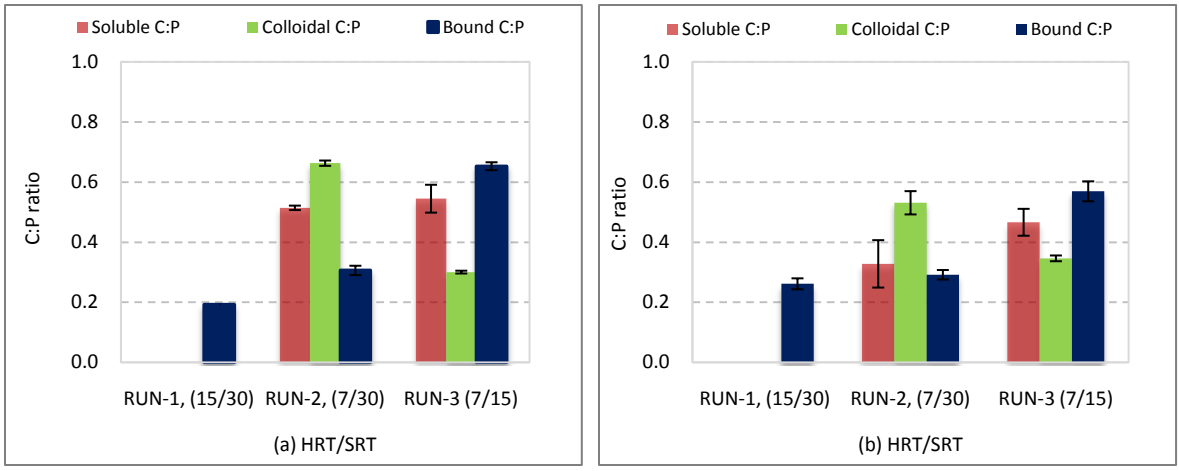


Figure 4-28 (a) Bound, colloidal and soluble C:P ratio in raw feed (b) digested sludge

4.3.5.3 Fate of floc associated and solution cations

Cations are part of the floc structure and an improved understanding of the behavior of floc-associated and solution metal fractions might provide useful information on their potential impact on membrane fouling. The average floc-associated, soluble and permeate calcium, magnesium and iron concentrations are depicted in Table 4-11. The floc-associated calcium and magnesium content was observed to be quite constant between the raw feed and digested sludge. In contrast a significant increase was observed in floc-associated iron content upon digestion.

Studies by Park and Novak (2007) have suggested that the organic fractions associated with iron degrade anaerobically while ones associated with divalent cations degrade aerobically and not anaerobically. In their study the iron was reduced resulting in a weakening of the iron-organic fraction bonds thereby releasing organic materials and making them available for microbial consumption. Hence with the destruction of the solids the iron was accumulated within the digester increasing the iron concentration in the solids during digestion. However in the current study no significant difference was observed in floc-associated iron concentrations at 15 and 30 day SRT. The dissolved magnesium was present at similar concentrations in the feed and digested sludges. In contrast a decrease in the dissolved calcium and iron concentrations was observed (Table 4-11). The decrease in dissolved Ca and Fe concentration

could be due to mineral precipitate formations such as FeS, $CaCO_3$ and $Ca_5OH(PO_4)_3$ either on the membrane surface, in the membrane pores and/ or on the surface of the flocs and biofilms.

Table 4-11 Total, filtered and permeate cation concentration in digested and raw feed sludge

Condition	***Floc associated, mg/gTS***			***Dissolved, mg/L***			***Permeate, mg/L***		
Concentration in feed	Ca	Mg	Fe	Ca	Mg	Fe	Ca	Mg	Fe
Run 1: 15 HRT, 30 SRT	NA[b]	NA	NA	106	23	-	NA	NA	NA
Run 2: 7 HRT, 30 SRT	11	3	66	327	63	604	NA	NA	NA
Run 3: 7 HRT, 15 SRT	23.5	5	94	139	35	100	NA	NA	NA
Concentration in digester									
Run 1: 15 HRT, 30 SRT	19±0.2	5±0.1	115±7	88±11	39±4	19±3	77±6	36±1	44±4
Run 2: 7 HRT, 30 SRT	17±1.4	3±0.2	130±8	250	62	28	120	38	33
Run 3: 7 HRT, 15 SRT	25	5	130	94	39	49	86	36	38

[a]mean values based on 3 separate duplicate samples collected weekly during steady state operation
[b]NA = not available

4.3.6 Relationship between membrane performance and biopolymer fractions

Previous studies on AnMBRs treating low strength wastewater have demonstrated the importance of proteins, carbohydrates and cations as direct foulants and as stabilizing agents for biofilm formation on the membrane surface (Liao et al., 2006; An et al., 2009). Figures 4-29a and b show the membrane flux at t=30 minutes versus the bound biopolymer concentrations that were observed in the digester contents. In general a decrease in the membrane performance was observed with an increase in bound protein (Figure 4-29a) and bound carbohydrate (Figure 4-29b) concentrations. However the relationship was not strong (R^2=0.32 and 0.42 for bound proteins and carbohydrates respectively).

Researchers have observed positive (Chang and Lee 1998 and Huang et al. 2009), negative (Lin et al. 2009) and no relationship (Yamato et al. 2006) between bound EPS and membrane fouling. A recent study by Wu et al. (2009) on filtration of aerobically digested WAS using flat sheet membranes showed no relationship between the critical flux and bound EPS. In earlier studies of sludge dewaterability and settling it has been identified that EPS and cations promote bioflocculation which assists in aggregation and improving the settlability and/or

dewaterability of sludge flocs (Raszka et al. 2006). However excess EPS was reported to have a negative impact on these responses.

The bound biopolymer composition could affect membrane performance positively by affecting the size and/or strength of flocs and negatively by enhancing the development of biofilms on the membrane surface by serving as a source of substrate and/or serving as a site for inorganic sorption. The bioflocculation effect of EPS may be dependent on the concentration of EPS present. Houghton et al. (2001) observed enhanced dewaterability of digested sludge with an increase in EPS up to 30 mg EPS/gSS and a further increase in EPS reduced sludge dewaterability. They concluded that the increase of dewaterability with EPS at low concentrations was due to the enhancement of flocculation at low EPS level. However an increase in EPS content further increased the amount of surface water bound by EPS thus lowering dewaterability. In this study the concentration of EPS found in all the experiments was higher than that reported for flocculation hence its possible positive effect on the observed membrane performance was minimal.

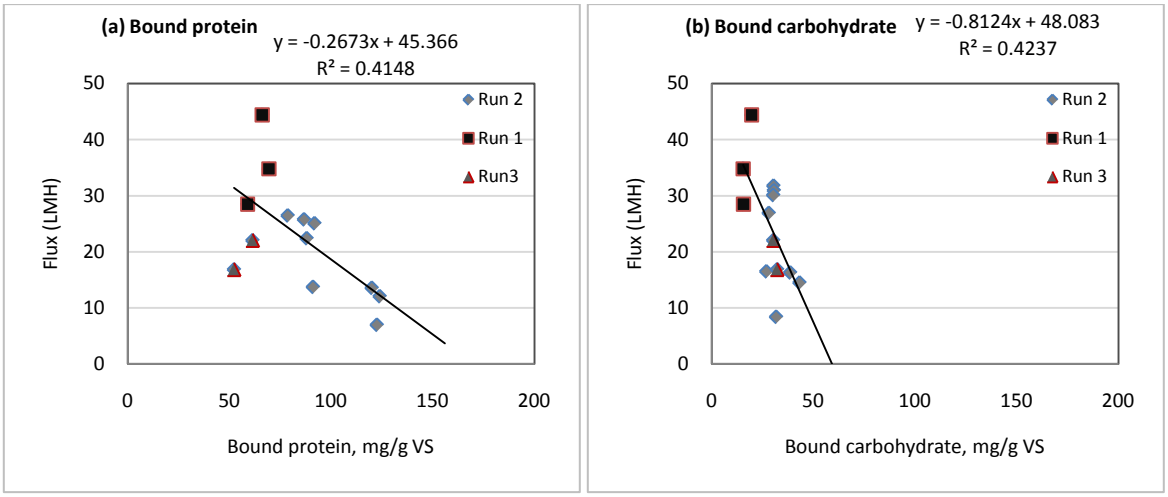


Figure 4-29 (a) Bound protein (b) bound carbohydrate versus flux (after 30 minutes of filtration) (c) Biopolymer concentration during critical flux measurement for run 1 (15/30 HRT/SRT), run 2 (7/30 HRT/SRT) and run 3 (7/15 HRT/SRT)

Figure 4-30a to d show membrane flux versus digested sludge colloidal and soluble biopolymer concentrations. With an increase in colloidal protein and soluble carbohydrate

concentration, a decrease in membrane flux was observed. (R^2=0.89 Figure 4-30a and R^2=0.91 Figure 4-30d respectively). There was no apparent relationship between flux and soluble protein and colloidal carbohydrate concentrations (Figures 4-30b and c). It was noted that the colloidal protein and carbohydrate concentrations had wider ranges (between 25-200 and 40-100 mg/L respectively) and the corresponding range of membrane fluxes were also wide (14-33 LMH). In contrast, the soluble protein and carbohydrate concentrations had narrow ranges (between 60-90 and 10-45 mg/L respectively). The colloidal protein and soluble carbohydrate components of the biopolymer appeared to be most important in determining the membrane performance. The former could be attributed to the formation of physically stable metal-colloidal protein complex resulting in dense cake layer whereas the impact of soluble carbohydrate could be through direct deposition on the membrane surface and/or by filling the void spaces between the cell particles in the cake layer.

Previous studies (Huang et al., 2009, Lee et al., 2003; Meng et al., 2006; Liang et al., 2007) have reported that soluble biopolymers had a considerable influence on membrane fouling. The studies that showed a significant effect of soluble carbohydrates on flux however have shown no significant relationship between soluble protein and flux. The impact of colloidal proteins and carbohydrates on membrane performance has not been previously reported. However, the impact of the colloidal COD fraction on flux has been documented (section 4.3.1.1). For example during the short term filtration study, a significant fraction (70%) of the decline in flux was related to the supernatant fraction of the digested sludge. The results of colloidal protein are supported by work done by Higgins and Novak (1997) where a decreased dewaterability and an increased demand for conditioning chemicals was observed with an increase in the solution protein fraction.

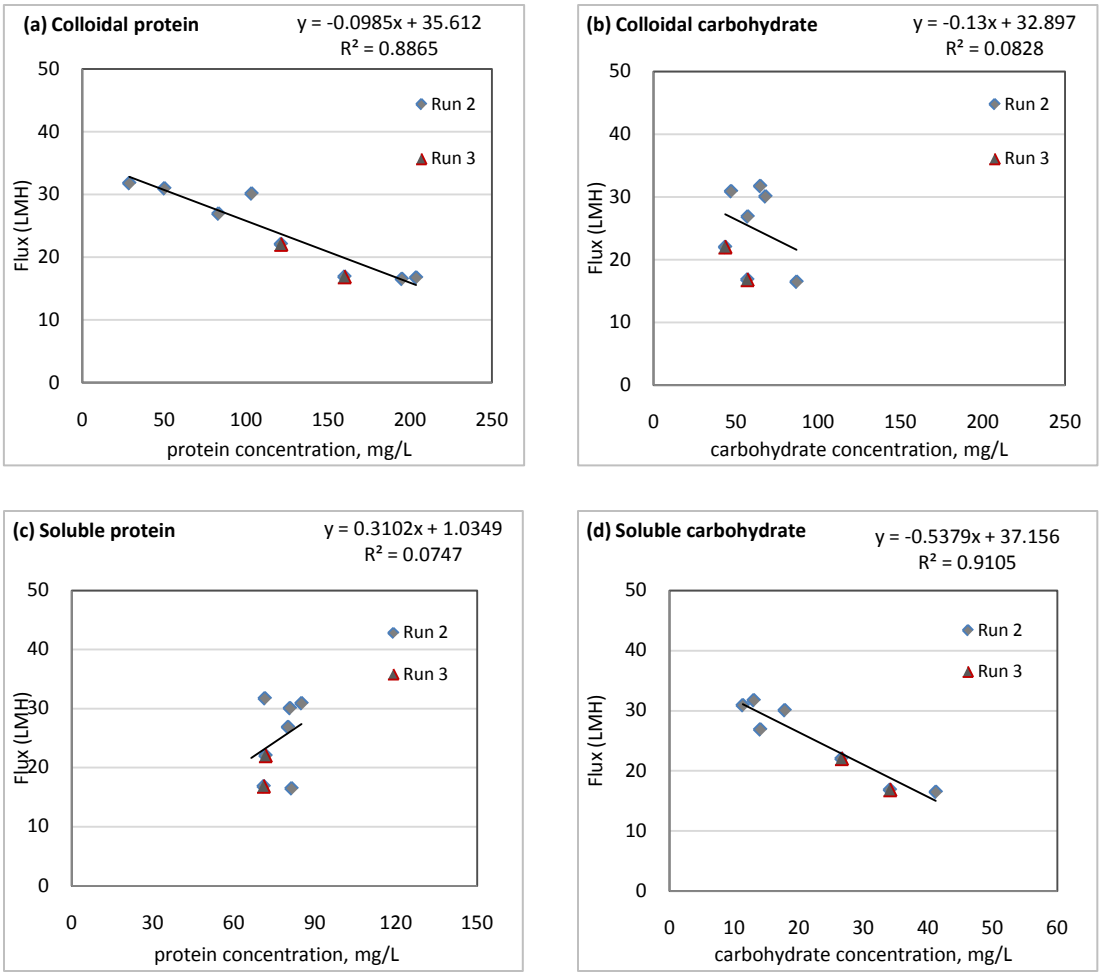


Figure 4-30 Filtered (a) proteins (b) carbohydrates and soluble (c) proteins (d) carbohydrate versus flux

A decrease in membrane flux was also observed with an increase in the soluble C:P ratio (R^2=0.92) and colloidal C:P (R^2=0.72) (Figures not shown). The plot of flux versus bound C:P ratio showed no significant relationship (R^2=0.17). The fouling of membranes has been associated with the carbohydrate to protein ratio however the results vary between different authors. Huang et al. (2009) observed an increase in the fouling propensity of sludges with increased soluble carbohydrate to protein (C:P) ratios. Conversely, Lin et al (2009) observed an increase in fouling propensity of sludges with a decrease in bound carbohydrate to protein ratios respectively. These variations could have been related to the different forms of biopolymers being investigated by the authors.

4.3.7 Changes in physical sludge characteristics and relationship with membrane performance

The physical characteristics of sludge are affected by the organic and inorganic composition of sludge that can be influenced by loading and/or SRT and operating conditions such as pH and temperature. The sludge's physical characteristics as described by particle size distributions, relative hydrophobicity and surface charge were examined and compared with the membrane performance.

4.3.7.1 Particle size distribution (PSD)

The particle size distribution of sludges has been identified as an important parameter affecting their filterability. Variations in particles sizes of the digested and raw feed sludge were studied using a RapidVUE particle shape and size analyzer. The instrument determines PSD based on image analysis. The particle size was characterized on the basis of both the volume and number distributions.

Figure 4-31a and b depict average cumulative volume and cumulative number distribution versus particle diameter of digested sludge and raw feed sludge flocs. The volume and number distributions were observed to characterize two ranges of particles sizes in the same sample and were found to provide complementary data. The volume distribution quantified the particle size distribution through a volume percent of each size range of particles on the total volume of particles. As a result the measurement is skewed towards larger size particles where most of the volume is concentrated. In a heterogeneous material such as sludge, PSD information from volume percentile can be used to characterize the distribution of larger size particles. The PSD based on number percentile gave information about relatively smaller sized particles which were less than 100 microns (Figure 4-31b).

All PSD measurements showed a significant difference between the particle sizes for the feed and digested sludges. The mean particle size of the raw feed sludge floc was considerably larger in than the digested sludges (Table 4-12 and Figure 4-31). According to the cumulative percentile data, about 90% of the volume was occupied by particles with an average size of 100 and 150 microns for the digested and raw feed sludges respectively (Figure 4-31a). The

number percentile data indicated that 90% of the digested and raw feed sludge particles had a size of less than 40 and 70 microns respectively (Figure 4-31b). Table 4-12 compares the mean particle size of particles between the runs. Overall the sludge from the digester operated at the extended SRT and shorter HRT (run 2) had slightly smaller sized particles.

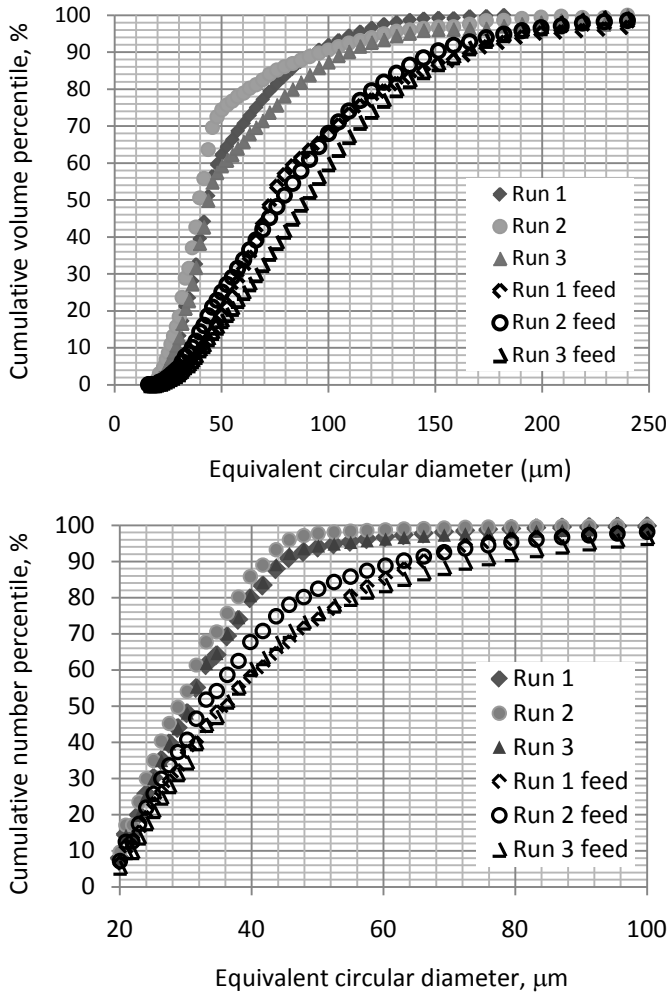


Figure 4-31 (a) Cumulative volume and (b) cumulative number percentile versus particle size in sludge

Table 4-12 Mean particle size comparisons

Nominal diameter (μm)	Digested sludge			WAS (raw feed)
	Run 1 mean(SD)	Run 2 mean(SD)	Run 3 mean(SD)	
Mean particle size	32.6 (1.1)	30.2(0.1)	32.5 (1.2)	40.3(3.5)

Investigation on the relationship of PSD with sludge composition such as soluble, colloidal and bound biopolymers showed a significant decrease in particle size with an increase in the colloidal biopolymer fraction (R^2=0.94). Also the PSD showed correlation with RH, where an increase in relative hydrophobicity (RH) is associated with an increase in size of particles (R^2=0.71). A plot of surface charge against PSD showed however a trend of increase in size of particles with an overall decrease on the negativity of surface (R^2=0.22) (Data shown in Appendix G)

Figures 4-32a and b show the interrelationships between flux and the PSD measurements (D50 volume and number percentile. PSD data derived from the volume and number percentile showed significant difference in terms of correlation with membrane flux. The results showed no relationship between PSD data based on volume percentile (d50) (R^2=0.0012). However significant increase in flux with an increase in the particle size based on number percentile was observed (R^2=0.87). This suggests that when characterizing PSD of sludge particles impact on filterability, measurement based on particle number should be considered as opposed to particle volume. This could mainly be because of the impact of smaller particles on sludge filterability.

In general particle size can impact on membrane fouling either by directly contributing through internal and/or external pore blocking as is the case where the size of the particle is close to or smaller than the pore size (Bai and Leow, 2002). Another mechanism where the size of a particle matters is through formation of a cake with higher specific cake resistance (Kuberkar and Davis, 2000). In this study the particle size instrument only measured particles as small as 15 microns. Hence based on this result it is difficult to comment on the participation of the particles in either pore blocking or constriction. However the observed relationship could be due to impact on cake layer resistance and increasing interstitial water held between particles. In general a decrease in the PSD of a sludge will result in an increase in surface area. This leads to increased frictional resistance to the movement of water, increased attraction of water to the particle surface due to more adsorption sites and greater electrical repulsion between sludge particles due to a large area of negatively charged surface. In addition with smaller sized particles back-transport of particles away from membrane

surface becomes difficult. All this could result in the deposit of particles on the membrane surface and increased resistance to filtration.

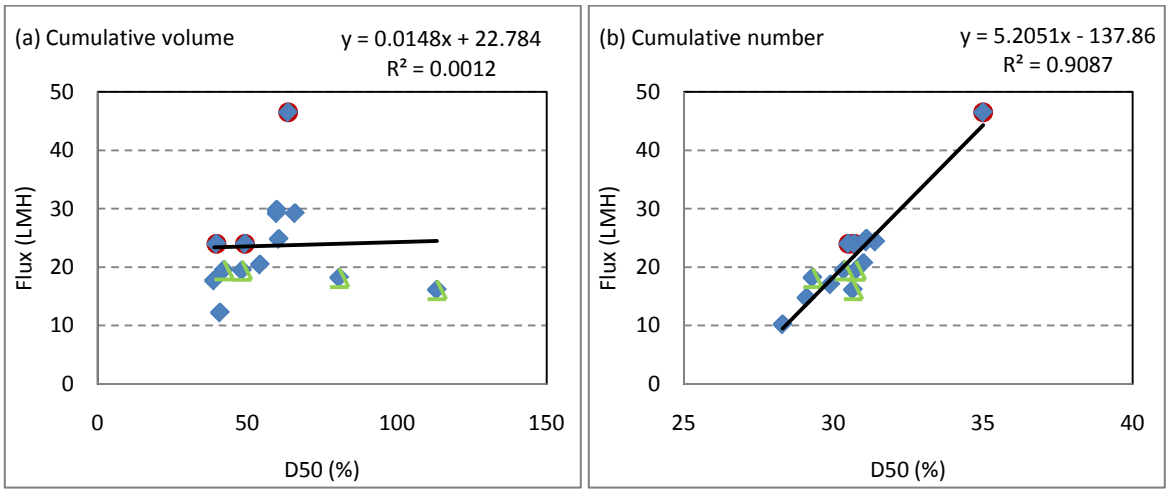


Figure 4-32 Flux versus cumulative (a) volume and (b) number percentile PSD

4.3.7.2 Relative hydrophobicity (RH) and surface charge (SC)

The RH and SC of floc are dominant surface properties that affect floc stability and flocculation ability and are thought of to have an effect on the filterability of the sludge. A sludge with a higher negative surface charge and subsequently increased repulsion between particles resulted in lower floc strength and smaller particle sizes (Wilen et al. 2003). Similarly an increase in sludge hydrophobicity would be expected to result in better floc formation due to hydrophobic interaction hence resulting in bigger size flocs. The RH and SC of the digested and raw feed sludge floc were measured using MATH (microbial adherence to hydrocarbons) and colloid titration methods respectively for the various runs at their quasi steady state condition and the results are shown in Table 4-13. The mean RH values of the digested sludges were 78.2±2.3, 74.2±2.3 and 79.6±1.4% for runs 1, 2 and 3 respectively. The mean RH values of the raw feed sludge were 83.7±1.7 and 81.2±3.2% for runs 2 and 3 respectively. In general it was observed that upon digestion sludge becomes less hydrophobic (75.5±4.7%) in comparison to the raw feed sludge (83.1±3.1%) (P=0.002). Plots of the RH versus supernatant and soluble proteins showed inverse relationship (R^2=0.6 and 0.4, respectively). It appeared that the change in the hydrophobicity of the sludge during digestion was related to the ratios of HRT to SRT. The RH seemed to increase with decrease in the HRT:SRT ratio of the digester

(run 2 versus 3; and run 1 versus 2) (P=0.096). An increase in RH was reported by Frolund et al (1996) and Liao et al (2001) with decrease in food to micro organism ratio that corresponds to higher SRTs.

Both the digested and feed sludge were observed to be negatively charged. Wilen et al. (2003) attributed the negative charge to ionization of functional groups such as carboxylic, sulphate and phosphate associated with the polymer in the EPS. The analysis showed that charge of the sludge flocs appeared to be more negative upon digestion. The corresponding measured average SCs corresponding to digested sludge flocs were -1.2±0.1, -1.5±0.03 and -1.2±0.1 for runs 1, 2 and 3 respectively. Similar to the RH, the floc obtained from the digester operated at a lower HRT: SRT appeared to be less negatively charged. The observed SC and RH trends with among the AnM digesters are negatively correlated and inversely proportional to the bound protein concentrations found in the digested sludge flocs (Data in Appendix G).

Table 4-13 Relative hydrophobicity and surface charge

Surface properties	**Digested sludge, (mean±SD)**			**WAS (feed sludge), mean±SD**		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
RH (%)	78.2±2.25 N=3	74.2±2.34 N=5	79.56±1.37 N=3		83.7±1.7 N=6	81.2±3.2 N=3
SC (meq/gVS)	-1.22±0.08 N=3	-1.51±0.03 N=5	-1.24±0.1 N=5	-0.65 N=1	-0.86±0.04 N=5	-0.68±0.01 N=5

Hydrophobicity and surface charge appeared to affect filterability (membrane filtration characteristics) as indicated by the critical flux and overall observed long term pilot filtration measurements (Figures 4-33a and b). The digested sludge with a decreased hydrophobicity (sludge from run 2) tended to have poor filterability characteristics. In previous studies increased hydrophobicity was reported to enhance flocculation through adhesion of flocs (Liu and Fang 2003), resulting in a larger more permeable flocs and reduced fouling (Wisniewski and Grasmick 1998). However Geng and Hall (2007) found no correlation and Le Clech et al. (2006) negative correlation between hydrophobicity and membrane fouling.

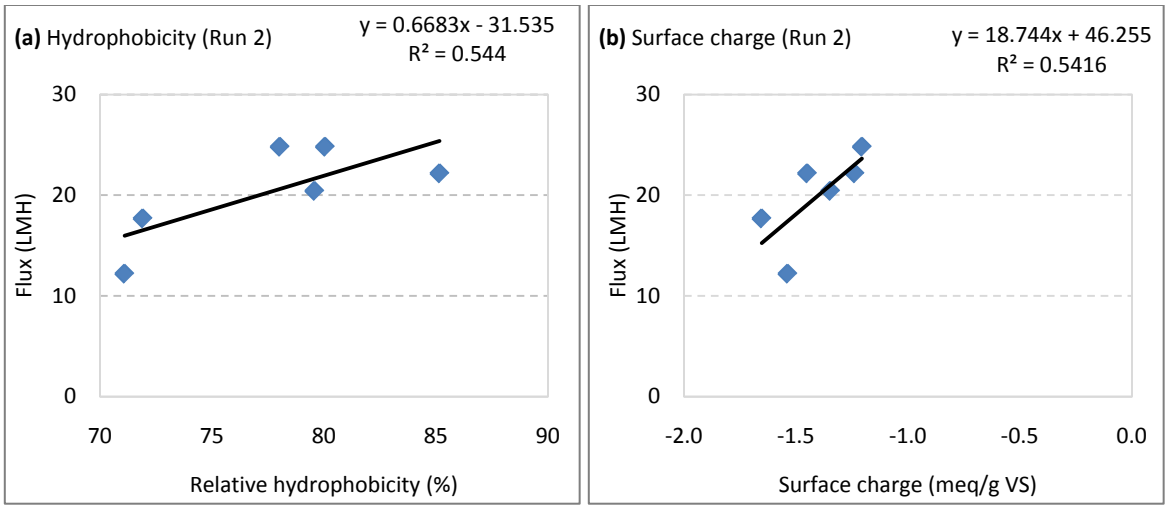


Figure 4-33 (a) Relative hydrophobicity and (b) surface charge versus flux

4.3.8 Fouling mechanism and foulant layer characteristics in AnM digester

4.3.8.1 Biofoulant layer characterization

To better characterize the fouling layer, surfaces and cross sections of new, fouled and cleaned membranes were examined using microscopic techniques (FTIR spectroscopy, CLSM and SEM). The FTIR spectrometry was used to probe the characteristics of functional groups and discover which chemical bonds were responsible for the adhesion of the foulants onto the membrane surface. In general, the FTIR spectral analysis of the cake layer on fouled membrane samples showed the appearance of additional peaks when compared to virgin membrane spectra indicating that organic foulants were present on the membrane surface.

The negative and neutral membrane spectra are shown in Figures 4-34a and b respectively. The FTIR of the virgin neutral and negative membranes demonstrated similar band contours and intensity of the absorption bands. The main absorption bands of these spectra were: a broad band at 3000-3400 cm^{-1} and sharp peaks at 835cm^{-1}, 869cm^{-1}, 1170 cm^{-1} , 1271cm^{-1}, 1377cm^{-1}, 1419cm^{-1} and 1627cm^{-1}. The fouled neutral and negative membranes also showed similar absorption intensity and bands. In this case most of the contour bands that were characteristic of the membranes were not observed or were observed with very low intensity. However additional sharp peaks at 720cm^{-1}, 960cm^{-1}, 1030cm^{-1}, 1080 cm^{-1}, 1232 cm^{-1}, 1336

cm^{-1}, 1505 cm^{-1}, 1627cm^{-1} and 1707cm^{-1} were observed. Further, a higher intensity broad band at 3000-3400cm^{-1} was recorded.

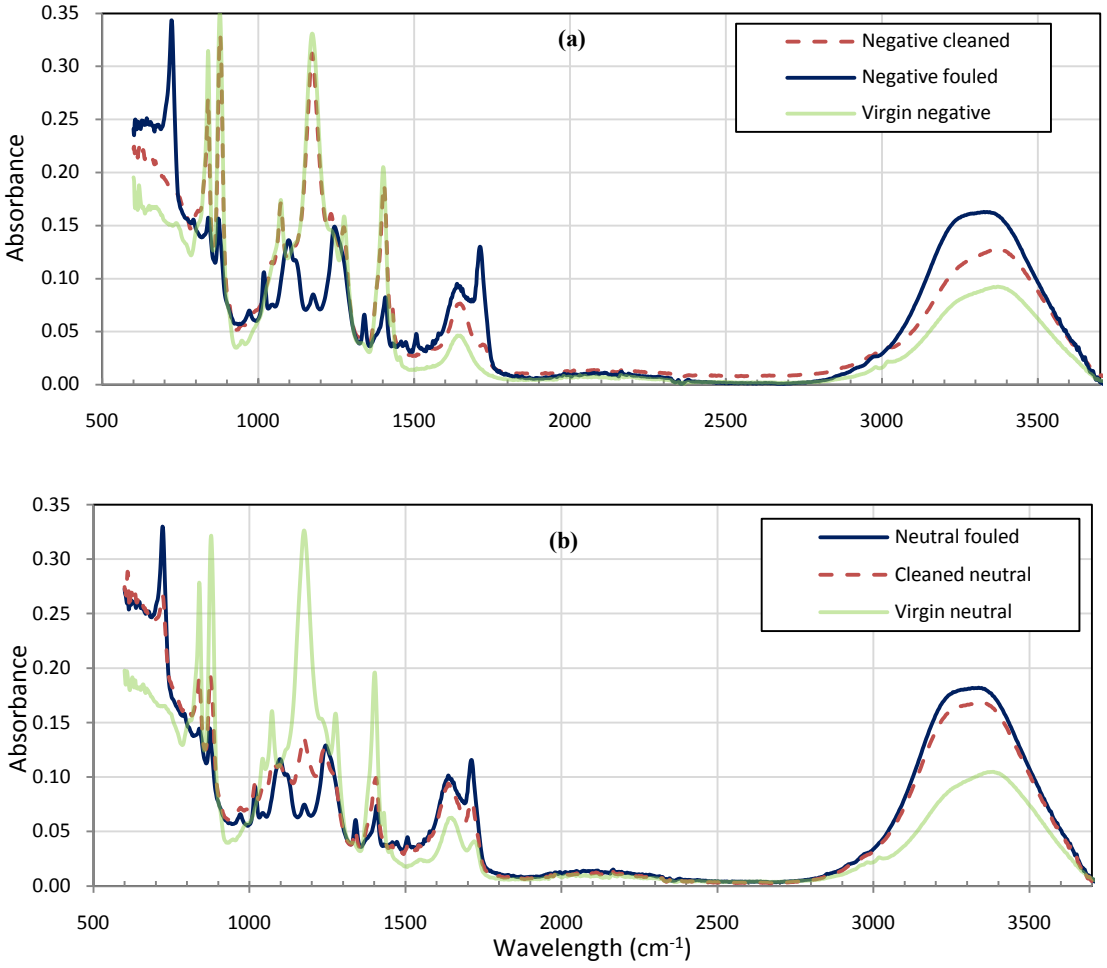


Figure 4-34 Membrane FTIR analysis of (a) negative membrane (b) neutral membrane

The observed additional peaks on the fouled membrane correspond to characteristic protein and polysaccharide bands. Moderate and strong peaks at 570 to 700 (N-H out of plane bending, C-H in aromatic ring or C-H deformation of carbohydrates), near to 1000 to 1150 cm^{-1} (symmetric and asymmetric C-O stretch in polysaccharide and carboxyl), 1450-1560 (-NH_3+ or –NH_2+ bending, amide II) and with sharp peak at 1600-1700 (stretching C=O (carbonyl) and N-H (amide I) bending) were identified as indicative of carbohydrate and protein characteristics respectively (Kimura et al. 2004, Kim and Jang 2006, Zhou et al. 2001). The

peak at 3338 cm^{-1} indicates an O-H bond. The cleaned negative membrane showed similar band contours and intensity of the absorption bands to that of the virgin negative membrane. However the entire spectrum of the cleaned neutral membrane was similar to the fouled neutral membrane with lower intensity of the characteristics foulant peaks clearly indicating presence of organic foulant materials on the neutral membrane surface even after the sequential mechanical and chemical cleaning. These results agreed with the clean water flux results where the negative membranes showed a relatively higher recovery than the neutral membranes.

Scanning electron micrograph (SEM) analysis: SEM micrographs of the negative and neutral virgin and cleaned membrane specimens that were collected at a 20x magnification are shown in Figures 4-35a to f. The images (Figures 4-35a and b) show that virgin neutral and negative membranes had a similar morphology containing a network of ridges and valleys, which could conceivably trap microbes, macromolecules and inorganic colloids. SEM micrographs of the fouled membranes (Figures 4-35c and f) were considerably different from those of the virgin membrane. On the active layer in contact with the sludge, bacterial cells embedded in a complex matrix were observed (Figure 4-35c and f). The SEM taken after rinsing the fouled negative membrane with water to remove any loosely bound components is shown in Figure 4-35f. The physical structure of this fouling layer was porous and with relatively fewer bacterial cells. Upon cleaning the negative membrane surface shows distinct pores on the membrane surface and organics washed out from the membrane surface (Figure 4-35d) however the neutral membrane surface after washing shows organics on the membrane (Figure 4-35e). The SEM analysis supported the FTIR results (Figure 4-34) and the observed post cleaning membrane resistance (Figure 4-37) trends for negative and neutral membranes.

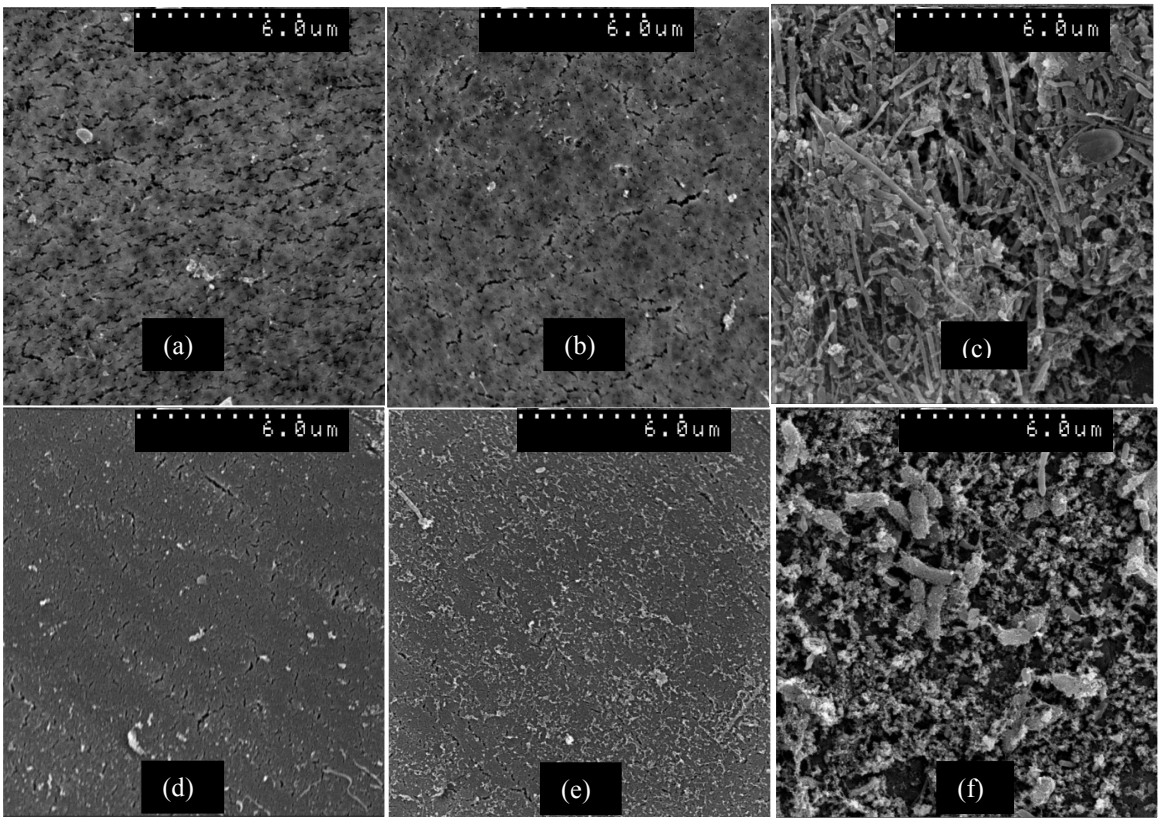


Figure 4-35 SEM micrographs of the (a) virgin negative (b) virgin neutral (c) fouled negative (d) mechanically and chemically cleaned negative, (e) mechanically and chemically cleaned neutral and (f) fouled and backwashed with water negative membrane specimens

Confocal Laser Scanning microscope (CLSM) analysis: An examination of the CLSM imaging of Concanvalin A and SYPRO orange stained fouled membrane samples revealed that proteins were a dominant feature of the foulant than polysaccharides. Further examination of the signal along the fouling layer profile however indicated that the relative distribution of proteins and polysaccharide varied with the depth of the cake layer. The profile in Figure 4-36 shows the CLSM analysis of the fouled negatively charged membrane with both loosely and well attached foulant materials present. The region closest to the membrane surface (referred to as bottom) was predominantly occupied by polysaccharides and the protein content increased with distance away from the membrane surface and was dominant at the outer region of the fouling layer. At the exterior of the fouling layer the ratio of surface area covered by proteins to carbohydrates was significantly higher. This was consistent with the biopolymer analyses on the sludge. Based on the observations made in this study, it appears that the

proteins were a more important biopolymer in the outer most fouling layer and carbohydrates in the inner most layer.

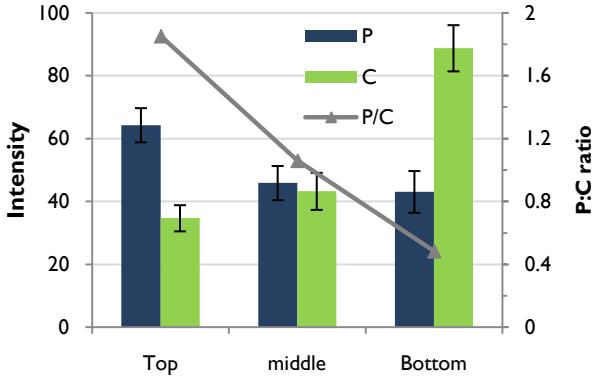


Figure 4-36 Localization of biopolymers (a) loosely and (b) tightly attached on negative membrane

Spent chemical solution analysis: In addition to the microscopic observation of fouled membranes, the spent chemical cleaning solution was analyzed for metals to identify the type of inorganic materials deposited on the membrane surface and/or membrane pores. The results from the neutral membrane in runs 2 and 3 are shown in Figures 4-37a and b respectively. Calcium, iron, magnesium and sulfur were the major inorganic deposits on the membrane surface (Figure 4-37). The cation deposits were released during both mechanical and chemical (NaOH and citric acid) cleaning, with iron released more effectively by citric acid than NaOH or mechanical cleaning. It is assumed that most of the sulfur would be expected to be associated with iron as a precipitate.

A similar observation was made by Welch et al. (2002) where the citric acid solution was regarded as an iron selective extraction method using the strong iron chelating properties of this acid. As the metals were removed in both mechanical and chemical cleaning, it is possible that the inorganic materials either had formed precipitates on the membrane surface and/or sorbed to the biopolymers resulting in consolidation of the biofouling. More cations were removed in run 2 than run 3, and this could partially explain the differences in filtration behavior (i.e. flux reduction at longer SRT) between the sludge from a longer and short SRT

respectively. From Figure 4-37a it can also be observed that additional release of cations was obtained with mechanical cleaning. This could be attributed to the cations that were sorbed on associated with the cake layer solids. With long term continuous operation the presence of these cations could lead to consolidation and hardening of the cake layer on the membrane surface shortening membrane life span (Choo and Lee, 1996 and Seidel and Elimelech 2002).

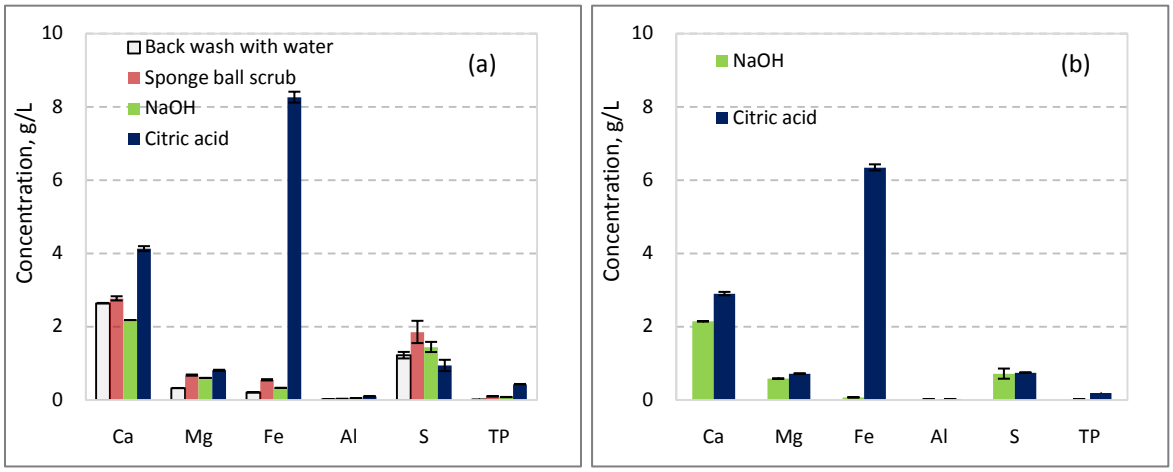


Figure 4-37 Metal concentrations in spent chemical solution (a) Run 2, 30 days SRT (b) Run 3, 15 days SRT after cleaning neutral membrane

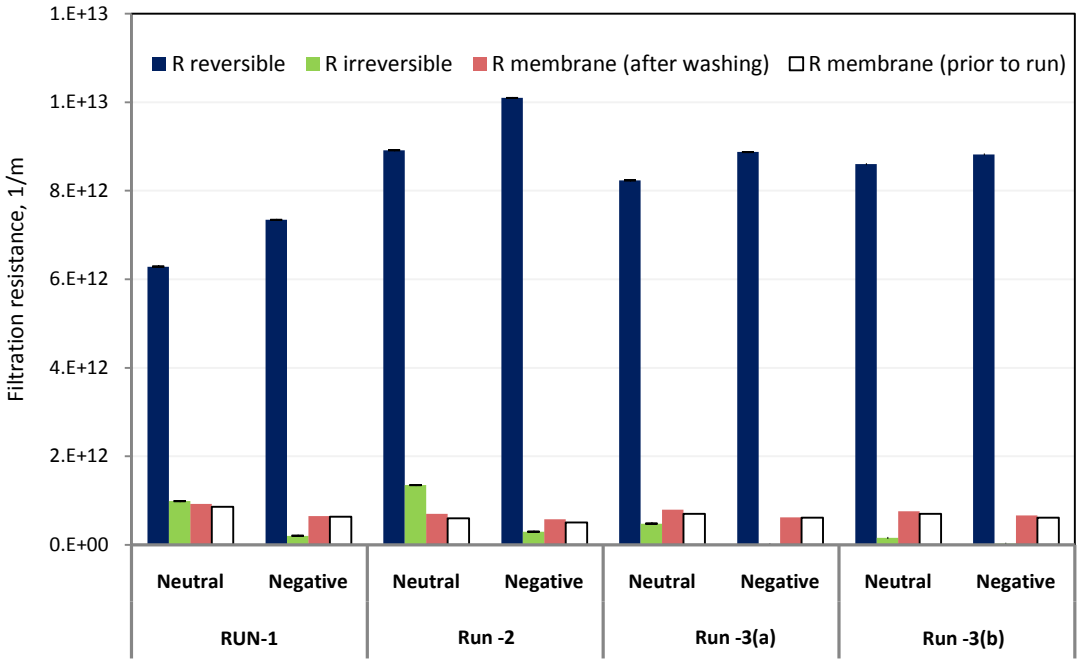
Chemical modeling: Permeate samples were analyzed for inorganic ions such as calcium, iron, magnesium, aluminum, sulfur, phosphorus, alkalinity to identify if the permeate were oversaturated and hence precipitation had occurred or was likely to occur. The potential for precipitation and hence fouling propensity of the inorganic salts was determined by calculating the saturation index of the permeate using PHREEQI Version 2 (USGS 2002). In this approach a saturation index of precipitates greater than zero indicated that the permeate was oversaturated and hence precipitation had occurred or there was the possibility of a compound precipitating within the digester and on the membrane surface (Zhang et al., 2007).

The precipitation of inorganic salts such as struvite ($MgNH_4PO_4$), hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), dolomite ($CaMg(CO_3)_2$) and Calcite ($CaCO_3$) were identified as the major contributors of inorganic precipitates within a digester and on the membrane surface when treating manure with an AnMBR (Zhang et al, 2007). Contrary to this previous study, in the

present study iron minerals were predicted by geochemical modeling with PHREEQI to be the dominant precipitates. Iron minerals such as siderite ($FeCO_3$), pyrite (FeS_2) and vivianite ($Fe_3(PO_4)_2{:}8H_2O$) showed possibility high likelihood of precipitation with saturation indices of 2.2, 5.83 and 3.62, respectively based on data from run 1. The predominance of iron precipitates was attributed to the composition of the WAS that was fed to the digester which was obtained from the Burlington Skyway WWTP that uses ferric chloride for phosphorus removal and sludge thickening. Hence the results from the metal analysis showed a significant concentration of iron in the liquid phase that would suppress the formation of other precipitates like struvite.

4.3.8.2 Reversible versus irreversible fouling

Fouling was divided into reversible and irreversible categories. The former type of fouling is typically attributed to a cake layer on the membrane surface and can be controlled as long as efficient physical membrane cleaning is carried out. Irreversible fouling is typically assumed to be due to pore plugging and/or solute adsorption onto the membrane surface and can be removed by chemical cleaning. Figure 4-38 shows the contribution of the reversible and irreversible type of fouling to filtration resistance during the various process conditions and membrane types examined. In all the runs it can be observed that both reversible and irreversible fouling contributed to the total fouling resistance. The contribution from the reversible resistance was significantly higher (>85% of R_{total}) in all cases. A comparison of the resistance fractions between the different runs showed that as the HRT decreased, the $R_{reversible}$ increased (Run 1 versus Run 2) however with an increase in SRT $R_{irreversible}$ increased (Runs 1 and 2 versus Runs 3). This could be associated with the increase in concentration of organic materials with decreases in HRT (runs 2 and 3) and increase in release of cations and increased solution biopolymers for the reactors operated at extended SRTs. The latter condition would result in adsorption of the organics either on the membrane surface and/or pores.



	RUN-1 (15, 30 HRT, SRT)		RUN-2 (7, 30 HRT, SRT)		RUN-3(a) (7, 15 HRT, SRT)		RUN-3(b) (7, 15 HRT, SRT)	
	Neutral	Negative	Neutral	Negative	Neutral	Negative	Neutral	Negative
Permeate vol. (L)	2160	1080	354	354	1728	714	308	308
$R_{reversible}$ (%)	76.7	89.6	81.3	92.1	87.3	93.3	89.4	92
$R_{irreversible}$ (%)	12.0	2.5	12.3	2.7	4.8	0.1	1.8	0.3

Figure 4-38 Filtration resistances due to reversible and irreversible fouling

The relative contributions of $R_{irreversible}$ to R_{total} also varied with the total amount of liquid permeated through the membrane. For example, in Figure 4-38, a comparison of the resistance fractions for the reactor after volumes of 308 and 1728 L of permeate were filtered (Run 3b and Run 3a respectively) indicated a shift of $R_{irreversible}$ from 1.8 to 4.8% (p=0.018). However the $R_{reversible}$ showed no difference.

The negative membrane consistently demonstrated a relatively lower contribution of irreversible fouling compared to the neutral membrane possibly due to charge repulsion effect. This also made cleaning of the negative membranes very effective. The fouling resistances were consistent with all the microscopic analyses that showed the presence of foulant on the neutral surface even after chemical cleaning.

4.3.9 Summary of pilot study

The results of the long term filtration study showed that it is feasible to employ AnMBR processes for sludge digestion applications and operation of the membrane was possible with a flux range of 11 to 40 LMH depending on bioprocess parameters (HRT and SRT). The study compared two different types of membranes, introduced fouling management strategies including various relaxation techniques that are unique to tubular membranes as well as developed in situ mechanical and chemical cleaning procedures that significantly improved the flux without impacting the bioreactor's performance.

The study also compared the impacts of process parameters, SRT and HRT on biological, chemical and physical sludge properties during the digestion process and assessed if they impacted the membrane flux. The investigation of the different sludge characteristics and comparing with membrane performance showed that changes in selected parameters through digestion and their impact on membrane performance was complex. The sludge properties were observed to be affected by the process parameters: both HRT and SRT (which were the test conditions). However the characteristics were observed to be affected by other conditions such as the changes in the raw feed sludge. These and possibly the difference in the volume of water filtered amongst the different runs introduced additional effects on the membrane performance.

Overall it was observed that sludge generated by the AnMBR process operated at an extended SRT of 30 days and a shorter HRT of 7 days had a very high fouling propensity with a significantly higher TSS, fCOD, less hydrophobic solids, having smaller PSD and elevated colloidal biopolymer content. Whereas the digested sludge with 30 days SRT and 15 days HRT was observed to have a better filterability resulting in a relatively higher critical flux value and lower fouling rate. As both these digesters were operated at an equal SRT, it can be concluded that changing HRT significantly impacted the filtration process. On the other hand the study also showed that with increased loading but reducing the SRT to a conventional condition resulted in a slight improvement in membrane performance. The most significant difference between operating the digesters at varying SRT were observed with the TSS

concentration, relative hydrophobicity (RH), particle size distribution and colloidal biopolymers which resulted in a slight decline in membrane performance.

Based on the data extracted from all the experiments, significant relationships were identified between the membrane flux and the TSS, fCOD, colloidal protein, and soluble carbohydrate, PSD, RH and SC. Most of these sludge characteristics were also found to be inter-correlated. For example, it was found that a decrease in RH led to a decrease in floc size due to less aggregate cohesion. On another note an increase in colloidal proteins through digestion at increased SRT was found to be associated with a decrease in relative hydrophobicity. While these in-depth investigations of the sludges physical, chemical and biological sludge properties help to understand the mechanism behind membrane fouling, their measurement on a routine basis is very difficult. Hence this study also showed a rather simplified monitoring tool such as analysis of TSS and fCOD to indicate fouling potential. These parameters were found to be negatively correlated with flux and could be used as design and monitoring tools to indicate impact of sludge characteristics on membrane flux.

In addition to regression investigation, a series of microscopic and membrane cleaning studies were conducted to confirm the presence of organic and inorganic foulants on the membrane surface. The FTIR results showed the presence of carbohydrate and protein functional groups on the fouled membrane. A further profile study by CLSM on fouled negative membrane surface proved that the region closest to the membrane surface was predominantly occupied by carbohydrates and the protein content increased with distance away from the membrane surface and was dominant at the outer region of the fouling layer. At the exterior of the fouling layer the ratio of surface area covered by proteins to carbohydrates was significantly higher. This was consistent with the biopolymer analyses on the sludge. Based on the observations made in this study, it appears that the proteins were a more important biopolymer in the outer most fouling layer and carbohydrates in the inner most. The characterization of inorganic materials on the membrane surface showed Ca, Fe and S as the dominant metals deposited in and/or on the membrane surface. Saturation indices analysis also showed the likelihood of formation of siderite ($FeCO_3$), pyrite (FeS_2) and vivianite ($Fe_3(PO_4)_2{:}8H_2O$) either on the membrane surface and within the digester.

Membrane cleaning studies also showed that effective cleaning requires targeting both reversible and irreversible type of fouling using mechanical (using sponge balls) and chemical cleaning (citric acid) respectively. The degree of severity in reversible and reversible type of fouling were found to be depend on the SRT, HRT, membrane type and volume of water filtered through the membrane. Overall, fouling control strategies for minimizing reversible fouling included membrane relaxation for tubular membrane and/or operating membrane below the critical flux. To minimize irreversible fouling negatively charged membranes can be used. Another strategy would be to control the bioprocess conditions by selecting optimum HRTs and SRT conditions that could result into a lower generation of biofoulants and inorganic foulants.

Chapter 5

5. CONCLUSIONS

The general conclusions are as follows:

By integrating membranes into conventional CSTR systems a reduction of digester volume by 75%, production of thickened digested sludge and a particle free permeate suitable for nutrient recovery can be obtained. Bioprocess performance was primarily a function of SRT while the digested sludge properties were a function of the SRT and the ratio of SRT to HRT that amplified the solids concentrations in the AnMBR systems.

The sludge produced in AnMBR process was found to have smaller particles with increased colloidal and suspended solids fractions and had a higher fouling propensity. Thus successful operation of AnMBR processes for WAS digestion requires choosing a lower flux relative to MBR processes treating wastewater. Considering the relatively lower daily volume of feed that needs to be treated during WAS digestion, the governing factor in choosing the flux should depend on its impact on membrane fouling. In addition to the bio and organic fouling present in MBR systems, the AnMBR process is impacted by inorganic fouling. Relative to AnMBR processes treating low strength wastewater, the presence of relatively higher particulate material in the digested WAS minimized the impact of the latter. However the particulate material increases the cake formation hence reversible fouling dominates AnMBR processes digesting WAS. This type of fouling is relatively easier to control making AnMBR applications for particulate wastewater attractive relative to their application for soluble wastewaters.

The specific conclusions are as follows:

Digestion performance of AnMBR stabilizing WAS: In this study it was confirmed experimentally that integrating membranes with anaerobic digesters increased the volumetric throughput of the digester and the SRT. This resulted in a significant improvement of the percent COD and VS removal efficiency and associated increase in gas production and improvement in the energy balance of the process. A pilot scale AnMBR operating at a 15 day

HRT and 30 day SRT demonstrated 35% more solids destruction than a conventional digester operating at 15 days when fed with 1.34 kg COD/m^3day. The net energy balance for the AnMBR was positive (22 GJ/m^3) as compared to that of the conventional digester that was negative (-40.8 GJ/m^3). When the HRT of the AnMBR was decreased to 7 days (COD loading of 2.35 kg COD/m^3day) an increase in the VS removal by 100% and net energy balance by 60 % was observed.

The increase in solids residence time appeared to increase degradation of protein containing materials as shown by an increase in the NH_4-N concentration. However increasing the solids retention time didn't impact the degree of pathogen destruction.

The AnM digesters produced thickened digested sludge that had solids concentrations that were 2 to 4 times higher than that of the control thereby minimizing the volume of sludge generated per digester volume for downstream processing. Analysis of the fixed suspended solids concentration revealed an accumulation of inert materials within the digester proportional to the SRT to HRT ratio. The accumulated inert material contributed only to 1 - 2% of the digester volume.

Membrane performance of AnMBR stabilizing WAS: The results of the long term filtration study indicated that it is feasible to employ AnMBR processes for sludge digestion applications. Stable operation of the membrane was possible at a constant transmembrane pressure of 30 KPa, cross flow velocity of 1 m/s and by incorporating a unique tubular membrane relaxation technique developed in this study. The average flux range was between 11 to 40 LMH depending on the bioprocess parameters (HRT and SRT) and the digested sludge characteristics. Membrane cleaning was not required to achieve this under normal loading conditions (15 days HRT). A monthly cleaning was required at a higher loading (7 days HRT) and when a 15 days SRT was kept. However when the SRT was extended to 30 days, weekly cleaning was required.

A relaxation cycle consisted of 1 minute relaxation of the membrane following every 5 minute filtration enhanced the sustainable flux. The sustainable flux (average flux at t=30 minutes) were 29.2, 11.0 and 16.5 LMH at HRT-SRTs of 15-30, 7-30 and 7-15 days respectively. The

corresponding TSS concentrations were 19.6, 32.6 and 24.8 g/L. In addition, incorporating an extended relaxation in between filtration cycles was found to significantly enhance the membrane performance and minimize the need for membrane cleaning.

A long term comparison of neutral and negative membrane performance indicated no significant difference during semi-continuous mode of operation. However the negative membrane showed a better flux recovery upon cleaning and relaxation.

Impact of cake and colloidal sludge fractions on membrane fouling: A study on the impact of the supernatant and solid (cake) sludge fractions on fouling resistance revealed that the supernatant fraction caused a significant decline in flux and contributed 70 to 84% of the total fouling resistance for sludge with solids concentrations less than 20 g/L TSS. The cake fraction contributed between 16 and 30% of the total resistance. A greater impact of the cake fraction on fouling resistance was observed for sludges with a relatively higher solids concentration (TSS=31 g/L). In this case 57% of the total resistance was contributed by the cake fraction with 43% due to the supernatant fraction.

Changes in sludge properties and their effect on membrane fouling: Changes in sludge properties were found to be complex and were associated with SRT, HRT and SRT to HRT ratios. The TSS, fCOD and the total concentration of biopolymers and/or cations in the digester increased with a decrease in HRT and increase in SRT to HRT ratio. Overall the sludge generated by the AnMBR process operated at an extended SRT of 30 days and a shorter HRT of 7 days showed a very high fouling propensity. The digested sludge that was generated at a 30 day SRT and 15 day HRT was observed to have better filterability. As both these digesters were operated at an equal SRT, it was concluded that changing HRT significantly impacted the filtration process.

The study also showed that reducing the SRT to a conventional condition resulted in an improvement in membrane performance. With reduction in SRT the composition of the sludge such as its colloidal protein, colloidal carbohydrate, soluble protein, floc associated iron and

calcium fractions decreased. On the contrary, the masses of bound carbohydrate and protein, soluble carbohydrate concentration, and soluble C:P ratios increased.

Significant relationships were identified between the membrane flux and the colloidal protein, and soluble carbohydrate concentrations, PSD, RH and surface charge (SC). While these in-depth investigations of the sludge physical, chemical and biological sludge properties helped to understand the membrane fouling, their measurement on a routine basis is very difficult. For design and control this study showed a rather simplified monitoring tool such as analysis of TSS and fCOD to indicate the impact of sludge characteristics on membrane flux could be employed.

Foulant types and mechanism of fouling in AnMBR digesting WAS: FTIR and SEM examination of the foulant layer confirmed the presence of proteinaceous and carbohydrate materials. Based on the CLSM profile study, it appeared that the proteins the more important biopolymer in the outer most fouling layer and carbohydrates in the inner most. The characterization of inorganic materials on the membrane surface showed Ca, Fe and S as the dominant metals deposited in and/or on the membrane surface. A saturation indices analysis also showed the likelihood of formation of siderite ($FeCO_3$), pyrite (FeS_2) and vivianite ($Fe_3(PO_4)_2{:}8H_2O$) either on the membrane surface or within the digester.

Both reversible and irreversible fouling contributed to the total fouling resistance. The degree of severity in reversible and irreversible type of fouling were found to depend on the SRT, HRT, membrane type and volume of water filtered through the membrane. The contribution of the reversible fouling was found to be significantly higher (>85%) and its magnitude increased with a decrease in HRT. The irreversible fouling increased with SRT.

Fouling control strategies for AnMBR digesting was: Strategies to control fouling included membrane relaxation (as concluded earlier), an optimum cleaning strategy, addition of cationic polymer and selection of optimum bioprocess parameters (HRT and SRT) were identified.

Membrane cleaning studies indicated effective cleaning requires simultaneously targeting both reversible and irreversible type of fouling using mechanical (using sponge balls) and chemical cleaning (citric acid and sodium hydroxide) respectively. The best flux recovery was obtained when mechanical cleaning preceded the chemical cleaning. Among chemical cleanings, citric acid was the most effective. The effectiveness of NaOH cleaning was minimal and it had an adverse effect when it preceded acid cleaning.

Addition of polymers enhanced sludge filterability and flux when the sludge contained elevated concentrations of colloidal COD. This study indicated that at a filtered COD concentration of 2300 mg/L, addition of 12.5 g of cationic polymer/kg of sludge decreased the fouling resistance by 75%. However excess cationic polymer addition was observed to have an adverse effect on fouling.

The bioprocess conditions of SRT and HRT were found to have a significant effect on the fouling behavior of the membrane. Conditions that were found to be optimum for the bioprocess in terms of VS removal and biogas production per feed and given digester volume were found to have a negative impact on the membrane's performance. Hence selection of optimum HRTs and SRT conditions that could result into a lower generation of biofoulants and inorganic foulants without significantly affecting the bioprocess should be further examined.

Chapter 6

6. RECOMMENDATIONS FOR FUTURE RESEARCH

The following recommendations are suggested for future AnMBR studies and/or applications for wastewater sludge stabilization.

The study showed the feasibility of integrating membrane to anaerobic digesters for sludge stabilization and indicated how bioprocess parameters impact efficiency of bioprocess and membrane performance. During the course of the study the concentrations of raw feed sludge varied making it difficult to attain stable sludge characteristics during a steady state at a given HRT and SRT conditions. This ultimately made accurate characterization of the membrane and digestion process as a function of the test process parameters difficult. For future studies mechanisms should be devised to keep a reasonably constant feed concentrations.

The low pressure and low cross flow velocity AnMBR process was characterized at HRTs of 7-15 days and SRTs of 15 to 30 days. By decreasing the HRT further it could be possible to increase the volumetric throughput. Also by increasing the SRT, further enhancement in digestion efficiency can be achieved. For example according to the VS destruction equation developed in this study it is possible to obtain a VS destruction up to 62% by increasing the SRT to 60 days. However under this condition digester mixing and membrane performance could be an issue. Therefore future research that could identify a reasonable minimum HRT and maximum SRT would be beneficial.

This study characterized the AnMBR process for WAS stabilization. The rationale behind this being, WAS is very slow to be hydrolysed and longer SRTs are detrimental for effective stabilization. However, most existing WWTPs mix primary and waste activated (secondary) sludges and it would be beneficial to investigate how the AnMBR process handles such types of feed streams. From this study a slight accumulation of inert materials was observed. However with the addition of primary sludge significant amounts of inert materials are expected to be introduced to the digester hence screening of the raw feed could be considered.

From an energy point of view the ability to increase the digester solids concentrations to 8-10% would be beneficial.

This study was conducted under mesophillic condition where the biosolids remained as Class B type. In order to produce Class A biosolids having a thermophillic digestion is required. Thermophillic digesters can have problems in CSTRs due to the potential for an imbalance between acidogenesis and methanogenesis processes. Due to the ability of decoupling the SRT and HRT, the AnMBR process could be a feasible choice. In this case high temperature could clearly increase the flux. However the thermophillically digested sludge characteristics are expected to differ from mesophillically digested sludge hence affecting membrane fouling differently. Future studies that investigate the AnMBR process under thermophillic condition during waste water sludge stabilization would be beneficial.

In the current study relaxation during the filtration cycle and extended relaxation between filtration cycles was introduced to mitigate membrane fouling. Further study is required to determine the impact of the extended relaxation time on the membrane performance.

The current study characterized tubular membrane performance in an anaerobic environment. Tubular membranes are designed to handle higher solids concentration and high temperature (up to 60^{o}C) which are desirable conditions for most anaerobic sludge digestion applications. However due to their wide application for municipal wastewater treatment (MBRs) and relatively less space requirement, most of the advances in membrane technology are on flat sheet and hollow fibre membranes. Hence the potential of these configurations under conditions desirable for sludge digestion applications should be examined.

The study identified colloidal materials and TSS materials as the main foulants. The development of online monitoring tools and/or modeling of the bioprocess to indicate the potential of foulant generation could be beneficial for process control applications.

REFERENCES

Akram A. and Stuckey D. C. (2008). Flux and performance improvement in a submerged anaerobic membrane bioreactor (SAMBR) using powdered activated carbon (PAC). *Process Biochemistry*, 43, 93-102.

Al-Halbouni, D., Traber, J., Lyko, S., Wingens, T., Melin, T., Tacke, D., Janot, A., Dott, W., Hollender, J. (2008). Correlation of EPS content in activated sludge at different sludge retention times with membrane fouling phenomena. *Water Research*, 42, 1475-1488.

An, Y., Wang, Z., Wu, Z., Yang, D. and Zhou, Q. (2009). Characterization of membrane foulants in an anaerobic non-woven fabric membrane bioreactor for municipal wastewater treatment. *Chemical Engineering Journal*, 155, 709–715.

APHA–AWWA–WEF. (1998). Standard methods for examination of water and wastewater, 20th ed. APHA, AWWA and WEF, Washington, DC.

Aquino, S.F., Stuckey, D.C. (2007). Bioavailability and toxicity of metal nutrients during anaerobic digestion. *J Environ. Eng., ASCE*, 133, 28-35.

Bai, R. and H.F. Leow, H.F. (2002). Microfiltration of activated sludge wastewater-the effect of system operation parameters, *Separation and Purification Technology,* 29. 189-198.

Baier, U. and Schmidheiny, P. (1997). Enhanced anaerobic degradation of mechanically disintegrated sludge. *Water Science and Technology,* 36(11), 137-143.

Barker, D.J. and Stuckey, D.C. (1999). A review of soluble microbial products (SMP) in wastewater treatment systems. *Water Research*, 33(14), 3063-3082.

Barker, D.J. and Stuckey, D.C. (2001). Modeling of soluble microbial products (SMP) in anaerobic chemostats. *Biotechnol. Bioeng*., 44, 1040-1047.

Beaubien, A., Bâty, M., Jeannot, F., Francoeur, E. and Manem, J. (1996). Design and operation of anaerobic membrane bioreactors: Development of a filtration testing strategy. *Journal of Membrane Science, 109*(2), 173-184.

Bérubé, P. R., & Hall, E. R and Sutton, P. M. (2006). Parameters governing permeate flux in an anaerobic membrane bioreactor treating low-strength municipal wastewaters: A literature review. *Water Environment Research, 78*(8), 887-896.

Bialey, A.D., Hansford, G.S. and Dold P.L. (1994). The enhancement of upflow anaerobic sludge bed reactor performance using crossflow microfiltration. *Water Research,* 28, 291-301.

Bolzonella, D., Pavan, P., Battistoni, P. and Cecchi, F. (2002). Mesophillic anaerobic digestion of waste activated sludge: influence of the solid retention time in the wastewater treatment process. *Process Biochemistry*, 40, 1453-1460.

Brockmann, M., & Seyfried, C. F. (1997). Sludge activity under the conditions of crossflow microfiltration. *Water Science and Technology, 35*(10), 173-181.

Brookes, A., Judd, S., Reid, E., Germain, E., Smith, S., Alvarez-Vazquez, H., LeClech, P., Stephenson, T., Turra, E. and Jefferson, B. (2003). Biomass characterization in membrane bioreactors. *in: Proceedings of the IMSTEC*, Sydney, Australia.

Chang, I.S. and Lee, C.H. (1998). Membrane filtration characteristics in membrane coupled activated sludge system – the effect of physiological states of activated sludge on membrane fouling. *Desalination*, 120, 221-233.

Cho, B.D. and Fane, A.G. (2002). Fouling transients in nominally sub-critical flux operation of a membrane bioreactor, *Journal of Membrane Science,* 209, 391-403.

Choi, H., Zhang, K., Dionysiou, D. D., Oerther, D. B., & Sorial, G. A. (2005). Effect of permeate flux and tangential flow on membrane fouling for wastewater treatment. *Separation and Purification Technology, 45*(1), 68-78.

Choo, K., & Lee, C.H. (1996a). Membrane fouling mechanisms in the membrane-coupled anaerobic bioreactor. *Water Research,* 30, 1771.

Choo, K., & Lee, C.H. (1996b). Effect of anaerobic digestion broth composition on membrane permeability. *Water Science and Technology,* 34(9), 173.

Choo, K., & Lee, C.H. (1998). Hydrodynamic behavior of anaerobic biosolids during crossflow filtration in the membrane anaerobic bioreactor. *Water Research,* 32(11), 3387-3397.

Choo, K.H, Kang, I.J., Yoon, S.H., Park, H., Kim, J.H., Adiya, S. and Lee, C.H. (2000). Approaches to membrane fouling control in anaerobic membrane bioreactors. *Water Science and Technology,* 41(10), 363-371.

Cicek, N., Macomber, J., Davel, J., Suidan, M.T. Audic, J. and Genestet, P. (2001). Effect of solids retention time on the performance and biological characteristics of a membrane bioreactor. *Water Science and Technology*, 43(11): 43-50.

Dagnew, M., Parker, W. and Seto, P. (2008). Anaerobic membrane bioreactors for digestion of WAS: Short term membrane fouling Tests. *WEFTEC 2008*, Chicago, IL.

Dagnew, M., Parker, W. and Seto, P. (2009). Digester performance of a pilot scale AnMBR digesting WAS under normal and higher VS loading condition. *5th Canadian Residuals and Biosolids Conference*, Niagara Falls, Ontario

Dagnew, M., Parker, W. and Seto, P. (2010). A pilot study of anaerobic membrane bioreactors for concurrent thickening and digestion of WAS. *Water Science and Technology*, 61 (6), 1451-1458.

Defrance, L., Jaffrin, M. Y., Gupta, B., Paullier, P. and Geaugey, V. (2000). Contributions of various constituents of activated sludge to membrane bioreactor fouling. *Biores. Technol*. 73, 105-112.

De la Rubia, Perez, M., Romero, L.I. and Sales, D. (2006). Effects of solids retention time (SRT) on pilot scale anaerobic thermophillic digestion. *Process Biochemistry*, 41, 79-86.

Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A. and Smith, F. (1956). Colorimetric method for determination of sugar and related substances. *Analytical Chemistry,* 28, 350–356.

Ekama, G.A., Sotemann and Wentzel, M.C. (2007). Biodegradability of activated sludge organics under anaerobic conditions. *Water Research*, 41, 244-252.

Fan, F., Zhou, H., & Husain, H. (2006). Identification of wastewater sludge characteristics to predict critical flux for membrane bioreactor processes. *Water Research,* 40(2), 205-212.

Farizoglu, B. and Keskinler, B. (2006). Sludge characteristics and effect of crossflow membrane filtration on membrane fouling in a jet loop membrane bioreactor (JLMBR). *Journal of Membrane Science,*279, 578–587.

Field, R. W., Wu, D., Howell, J. A. and Gupta, B. B. (1995). Critical flux concept for microfiltration fouling. *Journal of Membrane Science,* 100, 259-272.

Frølund, B., Palmgren, R., Keiding, K. and Nielsen, P.H. (1996). Extraction of extracellular polymers from activated sludge using a cation exchange resin. *Water Research*, 30 (8), 1749–1758.

Fuchs, W., Binder, H., Mavrias, G. and Braun, R. (2003). Anaerobic treatment of wastewater at high organic content using a stirred tank reactor coupled with a membrane filtration unit. *Water Research,* 37, 902.

Geng, Z. and Hall, E.R. (2007). A comparative study of fouling-related properties of sludge from conventional and membrane enhanced biological phosphorus removal processes. *Water Research*, 41(19), 4329-4338.

Ghosh, S. (1981). Kinetics of acid-phase fermentation in anaerobic digestion. *Biotechnol. Bioeng. Symp.* 11, 301-313.

Ghyoot, W.R. and Verstraete, W.H. (1997). Coupling membrane filtration to anaerobic primary sludge digestion. *Environmental Technology*, 18 (6), 569-580

Giraldo, E. and LeChevallier, M. (2006). Dynamic mathematical modeling of membrane fouling in submerged membrane bioreactors. *WEFTEC 2006.*

Grelier, P., Rosenberger, S. and Tazi-Pain, A. (2006). Influence of sludge retention time on membrane bioreactor hydraulic performance. *Desalination, 192*(1-3), 10-17.

Gossett, J.M. and Belser, R.L. (1982). Anaerobic digestion of waste activated sludge. *J. Environ. Eng. ASCE,* 108, 1101–1120.

Gujer, W. and Zehnder, A.J.B. (1983). Conversion processes in anaerobic digestion. Water Sci. Technol. 15(8/9) 127-167.

Harada, H., Momonoi, k., Yamazaki, S., & and Takizawa, S. (1994). Application of anaerobic-UF membrane reactor for treatment of a wastewater containing high strength particulate organics. *Water Sci. Technol.* 30(12), 307-319.

He, Y. Xu, P., Li, C., Zhang. B. (2005). High-concentration food wastewater treatment by an anaerobic membrane bioreactor. *Water Research,* 39, 4110–4118.

Hernandez, A.E., Belalcazar, L.C., Rodrigouez, M.S. and Giraldo, E. (2002). Retention of granular sludge at high hydraulic loading rates in an anaerobic membrane bioreactor with immersed filtration. *Water Science and Technology*, 45(10), 169.

Higgins, M.J. and Novak. J.T. (1997). Characterization of exocellular protein and its role in bioflocculation. *J. Environ. Eng*., 123, 479-485.

Ho, C.C. and Zydney, A.L. (2006). Overview of fouling phenomena and modeling approaches for membrane bioreactors. *Separation Science and Technology,* 41, 1231-1251.

Ho, J. and Sung, S. (2009). Anaerobic membrane bioreactor treatment of synthetic municipal wastewater at ambient temperature. Water Environment Research, 81(9), 902-928.

Ho, J., Khanal, S.K. and Sung, S. (2005). Application of anaerobic membrane bioreactor to treat low strength wastewater using non-woven filter and polytetrafluoroethylene (PTFE) composite membrane, *WEFTEC 2005,* 13, 2163-2175.

Hogetsu, A., Ishikawa, T., Yoshikawa, M., Tababe, T., Yudate, S. and Sawada, J. (1992). High rate anaerobic digestion of wool scouring waste water in a digester combined with membrane filter. *Water Science and Technology*, 25(7), 341-350.

Houghton, J.I. Quarmby, J. and Stephenson, T. (2001). Municipal wastewater sludge dewaterability and the presence of microbial extracellular polymer. *Water Science and Technology*, 44(2-3), 373-379.

Houghton, J.I., Quarmby, J. and Stephenson, T. (2000). The impact of digestion on sludge dewaterability. *Process Safety and Environmental Protection*, 78(2), 153-159.

Huang, Z., Ng, H.Y. and Ong, S.L. (2009). The Impact of Sludge Retention Time (SRT) on Submerged Anaerobic Membrane Bioreactor for Low-strength Wastewater Treatment. *WEFTEC 2009*, 2761-2770.

Hulse, C.A., Singh, K.S. and Grant, S.R. (2009). An innovative submerged anaerobic membrane bioreactor treatment for potato solids and bioenergy production. *WEFTEC 2009*, 2216-2230.

Imasaka, T., Kamekini, N., So, H. and Yoshino, S. (1989). Cross-flow filtration of methane fermentation broth by ceramic membranes. *Journal of Fermentation and Bioengineering,* 68, 200-206.

Itonaga, T., Kimura, K. and Watanabe, Y. (2004). Influence of suspension viscosity and colloidal particles on permeability of membrane used in membrane bioreactor (MBR), *Water Science and Technology,* 50, 301–309.

Jeison, D., van Betuw, W. and van Lier, J.B. (2008). Feasibility of Anaerobic Membrane Bioreactors for the Treatment of Wastewaters with Particulate Organic Matter. *Separation Science and Technology,* 43: 13, 3417-3431.

Jones, R., Parker, W., Khan, Z., Murthy, S. and Rupke, M. (2008). Characterization of sludges for predicting anaerobic digester performance. *Water Science and Technology,* 57(5), 721-726.

Judd, S. (2006). The MBR Book: Principles and applications of membrane bioreactors in water and wastewater treatment, Elsevier, Oxford.

Kang, I.J., Yoon, S.H. and Lee, C.H. (2002). Comparison of the filtration characteristics of organic and inorganic membranes in a membrane coupled anaerobic bioreactor. *Water Research*, 36, 1803-1813.

Kim I.S. and Jang N. (2006). The effect of calcium on the membrane biofouling in the membrane bioreactor (MBR). *Water Research,* 40, 2756–2764.

Kimura, K., Hane, Y., Watanabe, Y., Amy, G. and Ohkuma, N. (2004). Irreversible membrane fouling during ultrafiltration of surface water. *Water Research,* 38, 3431-3441.

Kuberkar, V.T. and Davis, R.H. (2000). Modeling of fouling reduction by secondary membranes. *J. Membr. Sci.* 168, 243.

Le-Clech, P., Jefferson, B. and Judd, S.J. (2003). Impact of aeration, solids concentration and membrane characteristics on the hydraulic performance of a membrane bioreactor. *Journal of Membrane Science*, 218,117-129.

Le-Clech, P., Chen, V. and Fane, T.A.G. (2006). Fouling in membrane bioreactors used in wastewater treatment. *Journal of Membrane Science,* 284(1-2), 17-53.

Lee, S., Jung, J. and Chung, Y. (2001). Novel method for enhancing permeate flux of submerged membrane system in two-phase anaerobic reactor. *Water Research,* 35(2), 471-477.

Lee, W., Kang, S. and Shin, H. (2003). Sludge characteristics and their contribution to microfiltration in submerged membrane bioreactors. *Journal of Membrane Science,* 216, 217-227.

Liang, S., Liu, C. and Song, L. (2007). Soluble microbial products in membrane bioreactor operation: behaviors, characteristics and fouling potential. *Water Research*, 41, 95-101.

Liang, S., Song, L., Tao, G., Kekre, K.A. and Seah, A.H. (2006). Modeling study of fouling development in membrane bioreactors for wastewater treatment. *Water Environ. Res.* 78(8), 857-863.

Liao B.Q., Jeremy T. K. and David M. B. (2006). Anaerobic membrane bioreactors: applications and research directions. *Environ. Sci. Technol.* 36, 489-530.

Liao, B. Q., Allen, D. G., Droppo, I. G., Leppard, G. G. and Liss, S. N. (2001). Surface properties of sludge and their role in bioflocculation and settleability. *Water Research*, 35, 339–350.

Liao, B.Q., Bagley, D. M., Kraemer, H.E. Leppard. G.G. and Liss, S.N. (1994). A review of biofouling and its control in membrane separation bioreactors, Water Environment Research, 76, 425.

Lim, A.L., Bai, R. (2003). Membrane fouling and cleaning in microfiltration of activated sludge wastewater. *Journal of Membrane Science,* 216, 279–290.

Lin, H.J., Xie, K., Mahendran, B., Bagley, D.M., Leung, K.T., Bagley, D.M., Liss, S.N. and Liao B.Q. (2009). Sludge properties and their effects on membrane fouling in submerged anaerobic membrane bioreactors (SAnMBRs). *Water Research,* 43, 3827-3837.

Liu, H. and Fang H.H.P. (2002b). Extraction of extracellular polymeric substances (EPS) of sludges. *J. Biotechnol.* 95 (3), 249-256.

Liu, Y. Fang, H.H.P. (2003). Influences of extracellular polymeric substances (EPS) on flocculation, settling and dewatering of activated sludge. *Crit. Rev. Environ. Sci. Technol.* 33, 237–273.

Lowry, O.H., Rosebrough, N.J., Farr, A.L. and Randall, R.J. (1951). Protein measurement with the folin phenol reagent. *J. Biol. Chem*., 193,265-275.

Lubken, M., Wichern, M., Schlattmann, M., Gronauer, A. (2007) Modeling the energy balance of an anaerobic digester fed with cattle manure and renewable energy crops. *Water Research*, 41, 4085-4096.

Meng, F.G., Zhang, G.M., Yang, F.L., Zhang, S.T., Li, Y.S and Zhang, X.W. (2006). Identification of activated sludge properties affecting membrane fouling in submerged membrane bioreactor. *Separation and purification technology*, 51(1), 95-103.

Metcalf and Eddy Inc. (2003). Wastewater engineering: treatment and reuse, 4th ed. McGraw-Hill, New York.

Miron, Y., Zeeman, G.Van Lier, J.B. and Lettinga, G. (2000) The role of sludge retention time in the hydrolysis and acidification of lipids, carbohydrates and proteins during digestion of primary sludge in CSTR systems. *Water Research,* 34(5), 1705-1713.

Morgan, J.W., Forester, C.F. and Evison, L.A. (1990). A comparative study of the nature of biopolymers extracted from anaerobic and activated sludge. *Water Research*, 24(6): 743-750

Murata, M., Kimuro, H., Kanekuni, N., Ohkuma, N., Ogasawara, H., Fujioka, T. (1994). Small-Scale sewage plant experiment by pretreatment and methanization of suspended Solids. *Desalination,* 98(1-3), 217-224.

Murthy, S.N. and Novak, J.T. (1999). Factors affecting floc properties during aerobic digestion: implications for dewatering. *Water Environ. Res*. 71, 197-202.

Nagaoka, H., Yamanishi, S. and Miya, A. (1998). Modeling of biofouling by extracelluar polymers in a membrane separation activated sludge. *Water Science and Technology*, 38, 497–504.

Nielsen, P.H., Frolund, B. and Keiding, K. (1996). Changes in the composition of extracellular polymeric substances in activated sludge during anaerobic storage. *Appl. Microbiol. Biotechnol*. 44, 823-830.

Novak, J. T.; Sadler, M. E.; Murthy, S. N. (2003). Mechanisms of floc destruction during anaerobic and aerobic digestion and the effect on conditioning and dewatering of biosolids. *Water Research,* 37, 3136.

Padmasiri, S.I., Zhang, J., Fitch, M., Norddhal, B., Morgenroth, E. and Raskin, L. (2007). Methanogenic population dynamics and performance of an anaerobic membrane bioreactor (AnMBR) treating swine manure under high shear conditions. *Water Research*, 41, 131-144.

Park, C. and Novak, J.T. (2007). Characterization of activated sludge exocellular polymers using several cation-associated extraction methods. *Water Research*, 41, 1679-1688.

Park, C., Abu-Orf, M.M. and Novak, J.T. (2006). The digestibility of waste activated sludges. *Water Environ. Res*. 78, 31-40.

Park, H., Choo, K.H. and Lee, C.H. (1999). Flux enhancement with PAC addition in the membrane anaerobic bioreactor. *Sep. Sci. Technol.* 34, 2781.

Parkin, G. F. and W. F. Owen. (1986). Fundamentals of anaerobic digestion of wastewater. *Adv. Microb. Ecol.* 9:1-55.

Pierkiel, A. and Lanting, J. (2005). Membrane-coupled anaerobic digestion of municipal sewage sludge. *Water Science and Technology,* 52(1-2), 253-258.

Pillay, V. L. (1992). Cake formation in cross-flow microfiltration systems. *Water Sci. Technol.* 25(10), 149-162.

Pillay, V. L., & Townsend, B. and Buckley, C. A. (1994). Improving the performance of anaerobic digesters at wastewater treatment works: The coupled cross-flow microfiltration/digester process. 30(12), 329-337.

Poggi–Varaldo, H. M., Oleszkiewicz, J. A. (1992). Anaerobic co-composting of municipal solid waste and waste sludge at high total solids levels. *Environ. Technol.* 13, 409–421.

Pohland H.W. (1988). Theory of membrane processes. *Proceedings of the AWWA Annual Conference*, Orlando, Florida.

Ponsa, S., Ferrer, S., Vazquez, F. and Font, X. (2008) Optimization of the hydrolytic acidogenic anaerobic digestion stage (55 ^{o}C) of sewage sludge: influence of pH and solid content. *Water Research,* 42, 3972-3980

Poxon, T. L. and Darby, J. L. (1997). Extracellular polyanions in digested sludge: measurement and relationship to sludge dewaterability. *Water Research,* 31(4), 749-758.

Psoch, C. and Schiewer, S. (2006). Anti-fouling application of air sparging and backflushing for MBR. *Journal of Membrane Science,* 283, 273–280.

Puchajda, B. and Oleszkiewicz, J. (2008) Impact of sludge thickening on energy recovery from anaerobic digestion. *Water Science and Technology,* 57-3, 395-401

Raszka, A., Chorvatova, M. and Wanner, J. (2006). The role and significance of extracellular polymers in activated sludge. Part I: Literature review. *Acta hydrochimica et hydrobiologica,* 34(5), 411-424

Rittman, B.E. and McCarty, P.L. (2001) Environmental Biotechnology: Principles and applications. McGraw-Hill, New York, NY, USA.

Rosenberger, S., Evenblij, H., Te Poele, S., Wintgens, T., & Laabs, C. (2005). The importance of liquid phase analyses to understand fouling in membrane assisted activated sludge processes - six case studies of different european research groups. *Journal of Membrane Science, 263*(1-2), 113-126.

Rosenberger, S., Laabs, C., Lesjean, B., Gnirss, R., Amy, G., Jekel, M. and Schrotter, J.C. (2006). Impact of colloidal and soluble organic material on membrane performance in membrane bioreactors for municipal wastewater treatment. *Water Research, 40*(4), 710-720.

Seidel, A. and Elimelech, M., (2002). Coupling between chemical and physical interactions in natural organic matter (NOM) fouling of nanofiltration membranes: implications for fouling control. *Journal of Membrane Science*, 203 (1–2), 245–255

Shimizu, Y., Rokudai, M, Tohya, S., Kayawake, E., Yazawa, T., Tanaka, H. and Eguchi, K. (1989). Filtration characteristics of charged alumina membranes for methanogenic waste. *J. Chem. Eng. Jpn.* 22, 635.

Siegrist, H., Renggli, D. and Gujer, W. (1993). Mathematical-modeling of anaerobic mesophilic sewage sludge treatment. *Water Science and Technology*, 28 (2), 25-36

Speece, R.E. (1996). Anaerobic biotechnology for industrial wastewaters, Archae Press, Nashville.

Tansel, B., Sager, J., Garland, J., Xu, S., Levine, L., Bisbee, P. (2006). Deposition of extracellular polymeric substances (EPS) and micro topographical changes on membrane surfaces during intermittent filtration conditions. *Journal of Membrane Science,* 285 (1–2), 225–231.

Trussell, R. S., Merlo, R. P., Hermanowicz, S. W. and Jenkins, D. (2006). The effect of organic loading on process performance and membrane fouling in a submerged membrane bioreactor treating municipal wastewater. *Water Research, 40*(14), 2675-2683.

Vavilin, V.A., Rytov, S.V. and Lokshina, L.Y. (1996). A descr.iption of hydrolysis kinetics in anaerobic digestion of particulate organic matter. *Bioresource Technology*, 56(2-3), 229-237.

Vavilin, V.A., Fernandez, B., Palatsi, J. and Flotats, X. (2008). Hydrolysis kinetics in anaerobic degradation of particulate organic material: an overview. *Waste Management,* 28(6), 939-951.

Verstraete, W. and Vandevivere, P. (1999). New and broader applications of anaerobic digestion. *Crit. Rev. Environ. Sci. Technol.* 28, 151.

Wallberg, O., Jonsson, A.S. and Wickstrom, P. (2001). Membrane cleaning—a case study in a sulphite pulp mill bleach plant. *Desalination,* 141 (3), 259–268.

WEF and ASCE. (2009). Design of municipal wastewater treatment plants, manual of practices, 5th ed.

Welch, K.D., Davis, T. Z. and Aust, S.D., (2002). Iron autoxidation and free radical generation: effects of buffers, ligands and chelators. *Arch. Biochem. Biophys.* 397(2), 360-369.

Wen, C., Huang, X. and Qian, Y.(1999). Domestic wastewater treatment using an anaerobic bioreactor coupled with membrane filtration. *Proc. Biochem.* 35, 335.

Wilen, B.M., Jin, B. and Lant, P. (2003). The influence of key chemical constituents in activated sludge on surface and flocculating properties, *Water Research*, 37, 2127–2139.

Wintgens, T., Rosen, J., Melin, T., Brepols, C., Drensla, K. and Engelhardt, N. (2003). Modelling of a membrane bioreactor system for municipal wastewater treatment, *Journal of Membrane Science,* 216 (1-2), 55–65.

Wisniewski, C. and Grasmick, A. (1998). Floc size distribution in a membrane bioreactor and consequences for membrane fouling. *Colloids Surfaces, A: Physiochem. Eng. Aspects*, 138, 403.

Wu, Z., Wang, X., Wang, Z., & Du, X. (2009). Identification of sustainable flux in the process of using flat-sheet membrane for simultaneous thickening and digestion of waste activated sludge. *Journal of Hazardous Materials, 162*(2-3), 1397-1403.

Yamato, N., Kimura, K., Miyoshi, T. and Watanabe, Y. (2006). Difference in membrane fouling in membrane bioreactors (MBRs) caused by membrane polymer materials. *Journal of Membrane Science*, 280, 911-919.

Yoon, S. H., & Kang, I. J. and Lee, C. H. (1999). Fouling of inorganic membrane and flux enhancement in membrane-coupled anaerobic bioreactor, *Separation science and technology,* 34(5), 709-724.

Zhang, J., Padmasiri, S. I., Fitch, M., Norddahl, B., Raskin, L., & Morgenroth, E. (2007). Influence of cleaning frequency and membrane history on fouling in an anaerobic membrane bioreactor. *Desalination, 207*(1-3), 153-166.

Zhang, T.C and Noike. T. (1994). Influence of retention time on reactor performance and bacterial trophic populations in anaerobic digestion processes. *Water Research*, 28(1), 27-36.

Zhou, L.X., Liang, J.R., Zhan, X.H. and Wong, J.W.C. (2001). Fractionation and characterization of sludge bacterial extracellular polymers by FT-IR, C-NMR and H-NMR. *Water Science and Technology*, 44(10), 71-78.

Zitomer D.H., Bachman, T.C., Vogel, D.S. (2005). Thermophilic anaerobic digester with ultrafilter for solids stabilization. *Water Sci. Technol.* 52:525–530.

APPENDICES

Appendix A Pilot AnMBR and control digester details

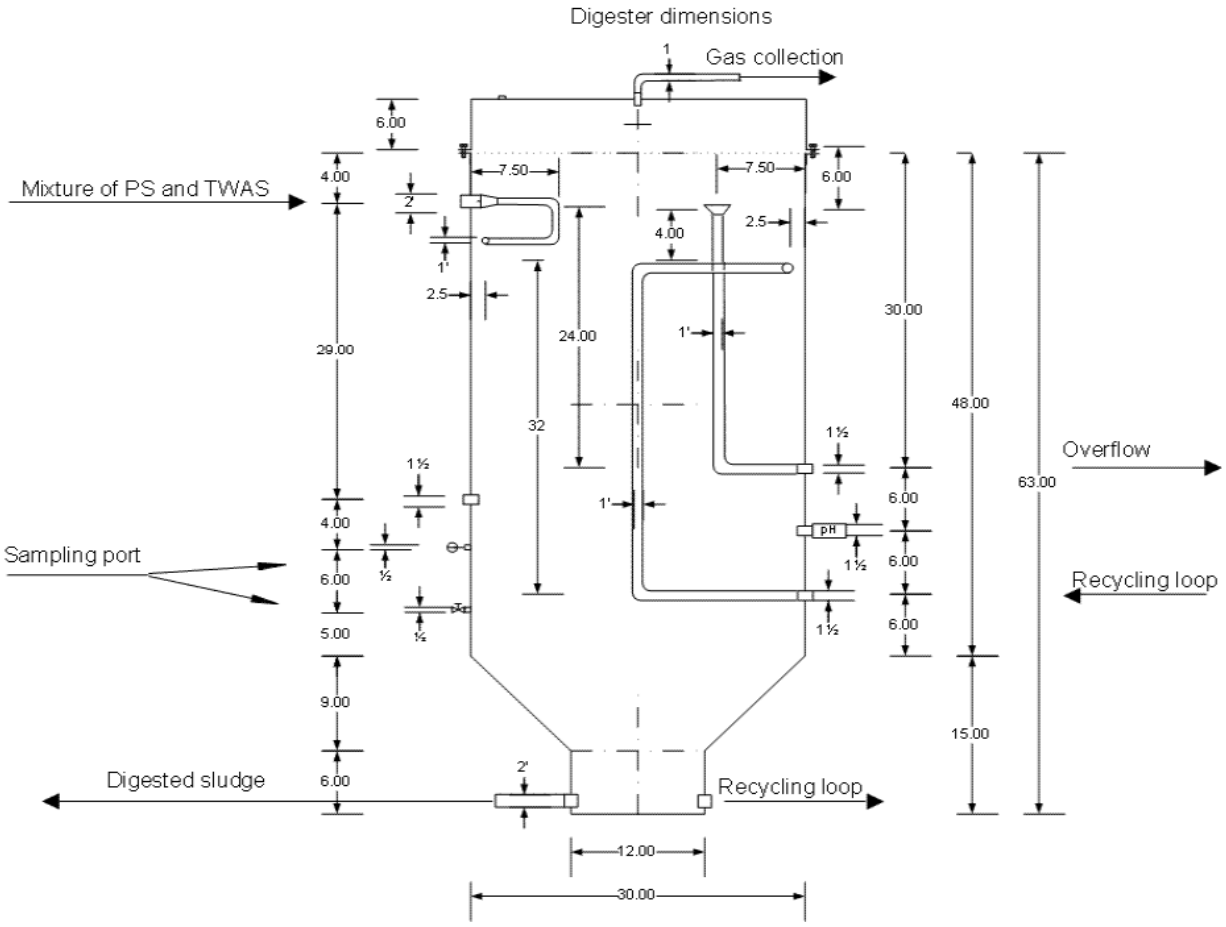


Figure A-1 Pilot anaerobic digestion tank dimension

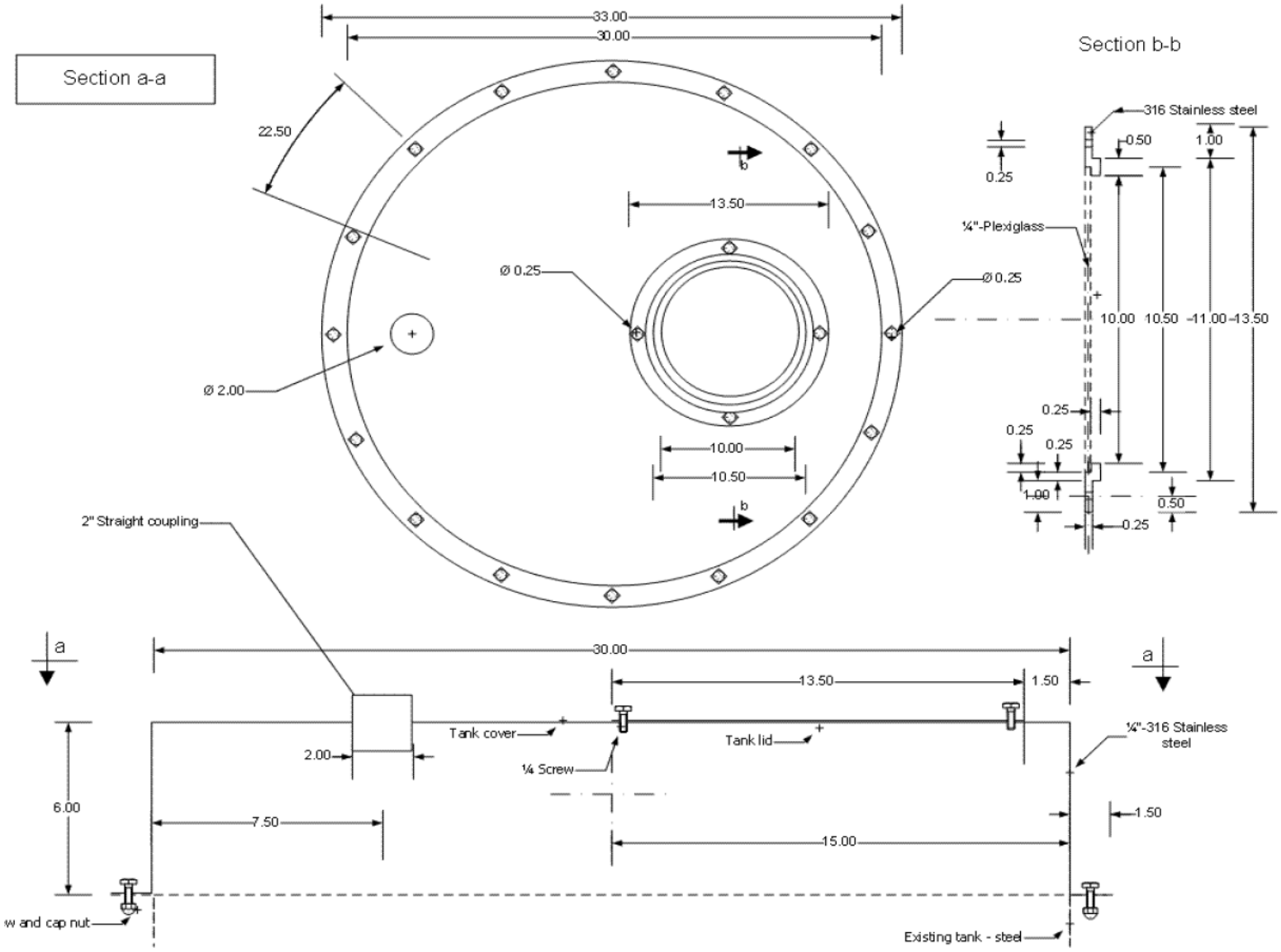


Figure A-2 Pilot anaerobic digester tank cover

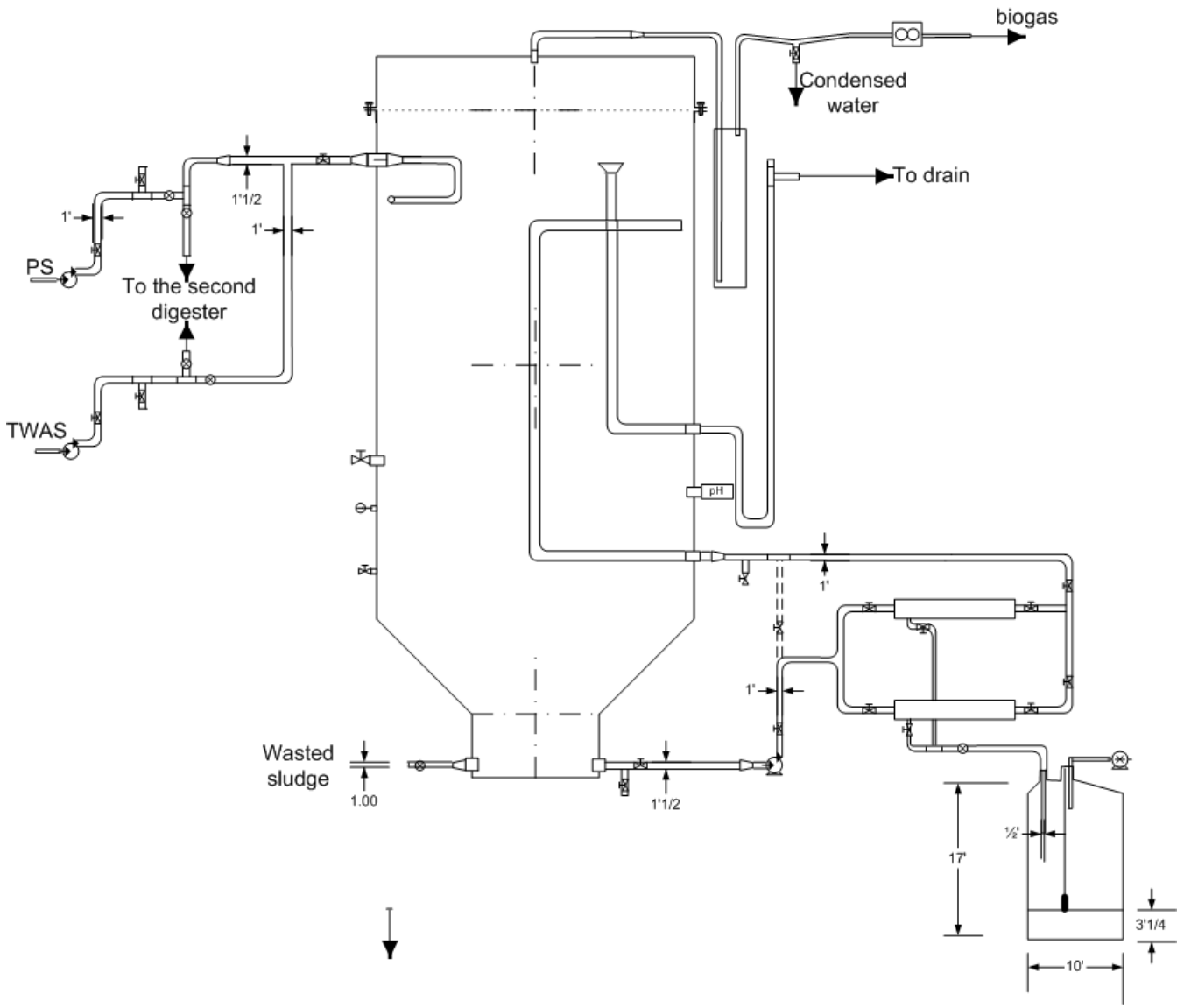


Figure A-3 Pilot membrane digester hydraulic design

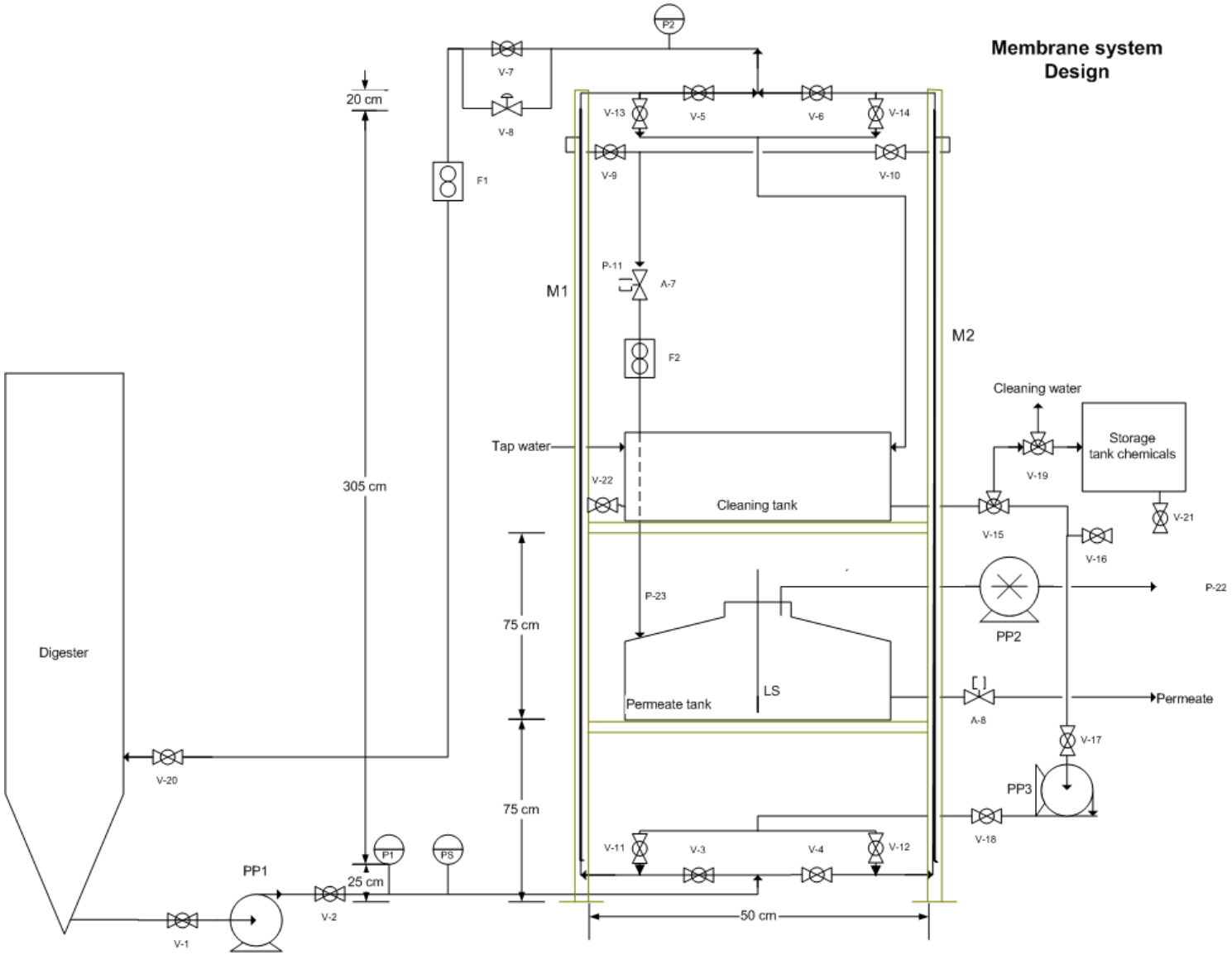


Figure A-4 Pilot membrane system design

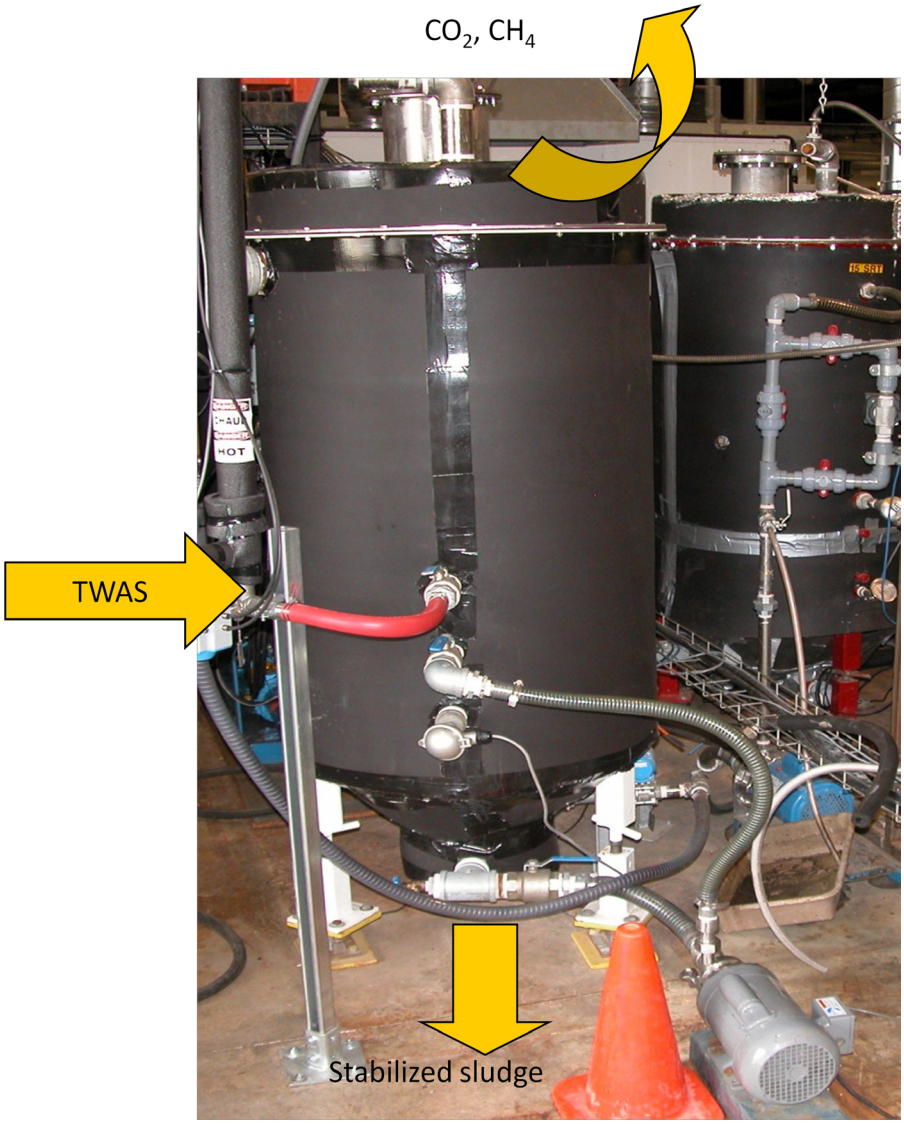


Figure A-5 Pilot control digester

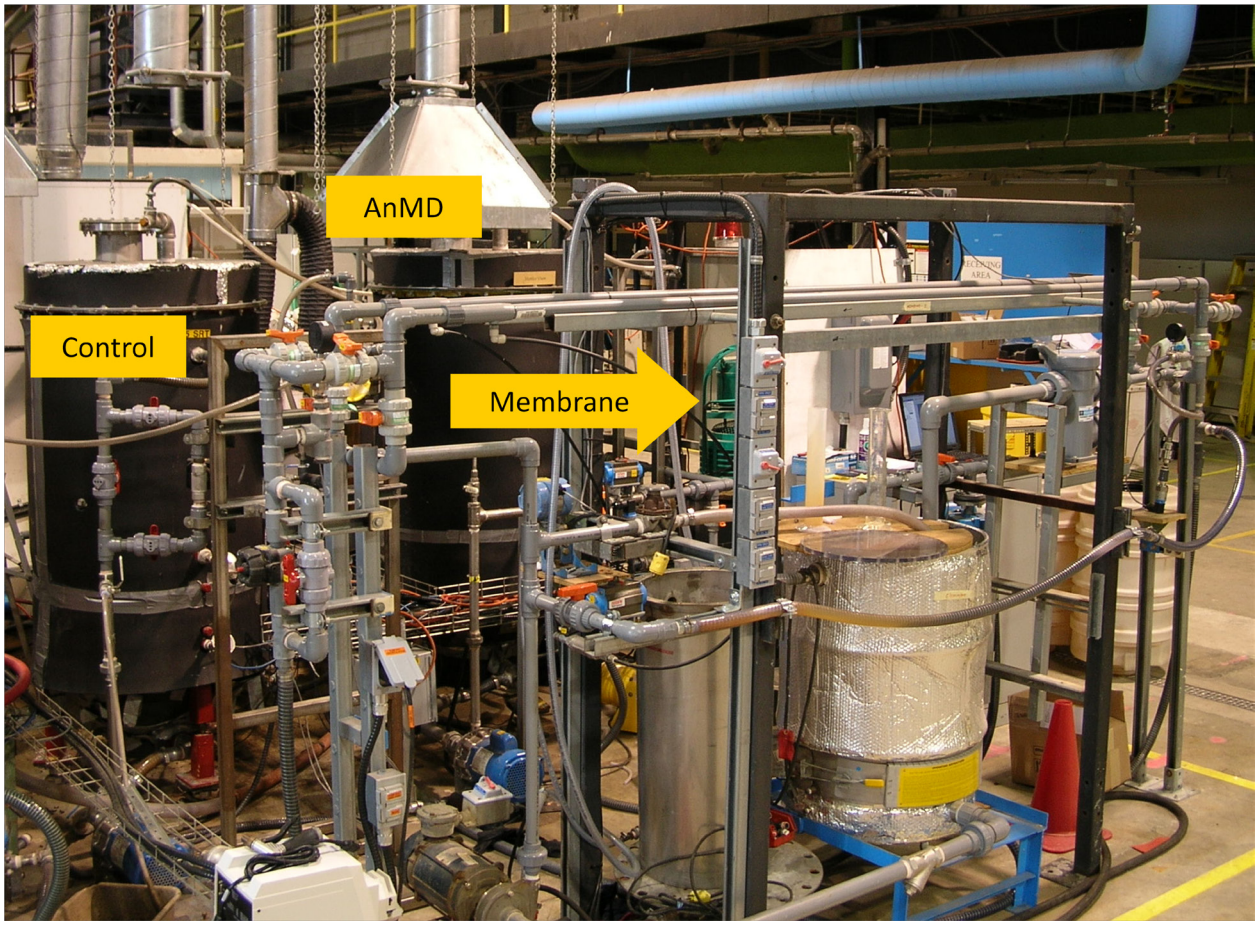


Figure A-6 AnM digester

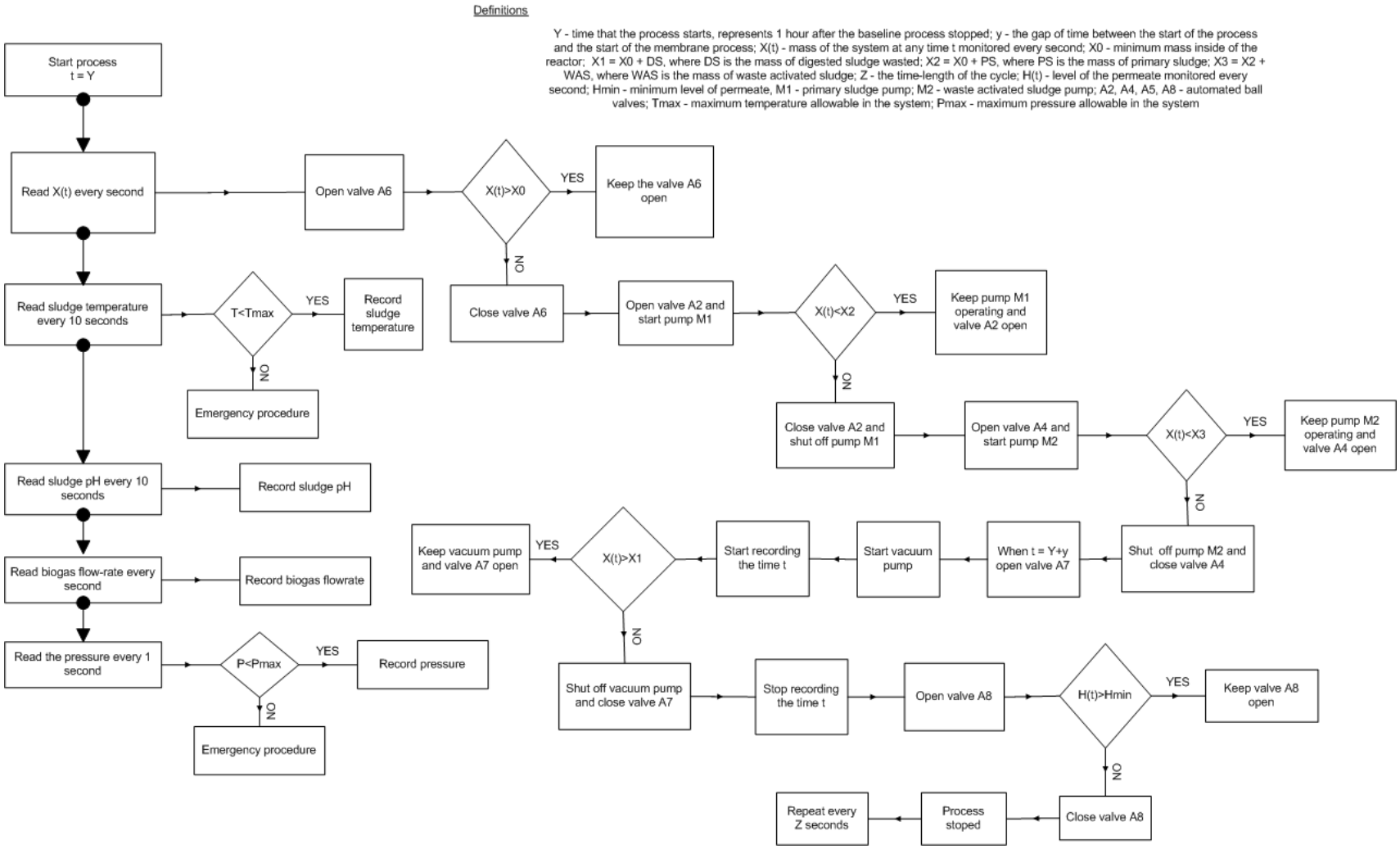


Figure A-7 Process logic

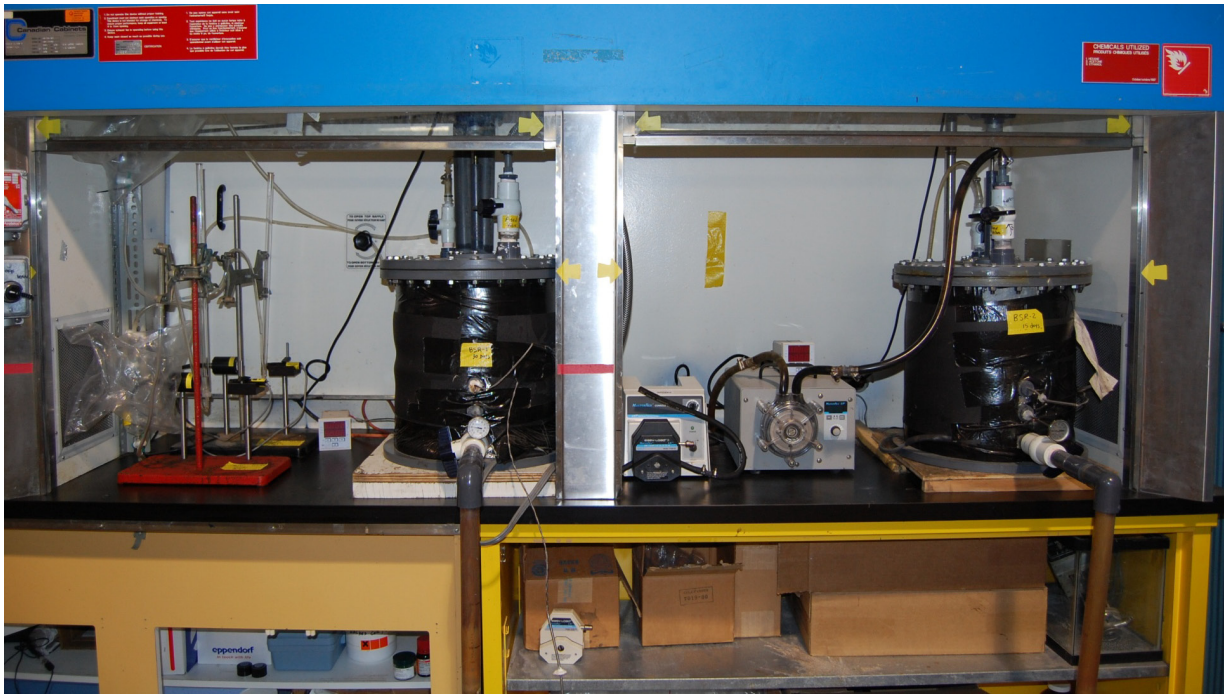


Figure A-8 Bench scale anaerobic digesters

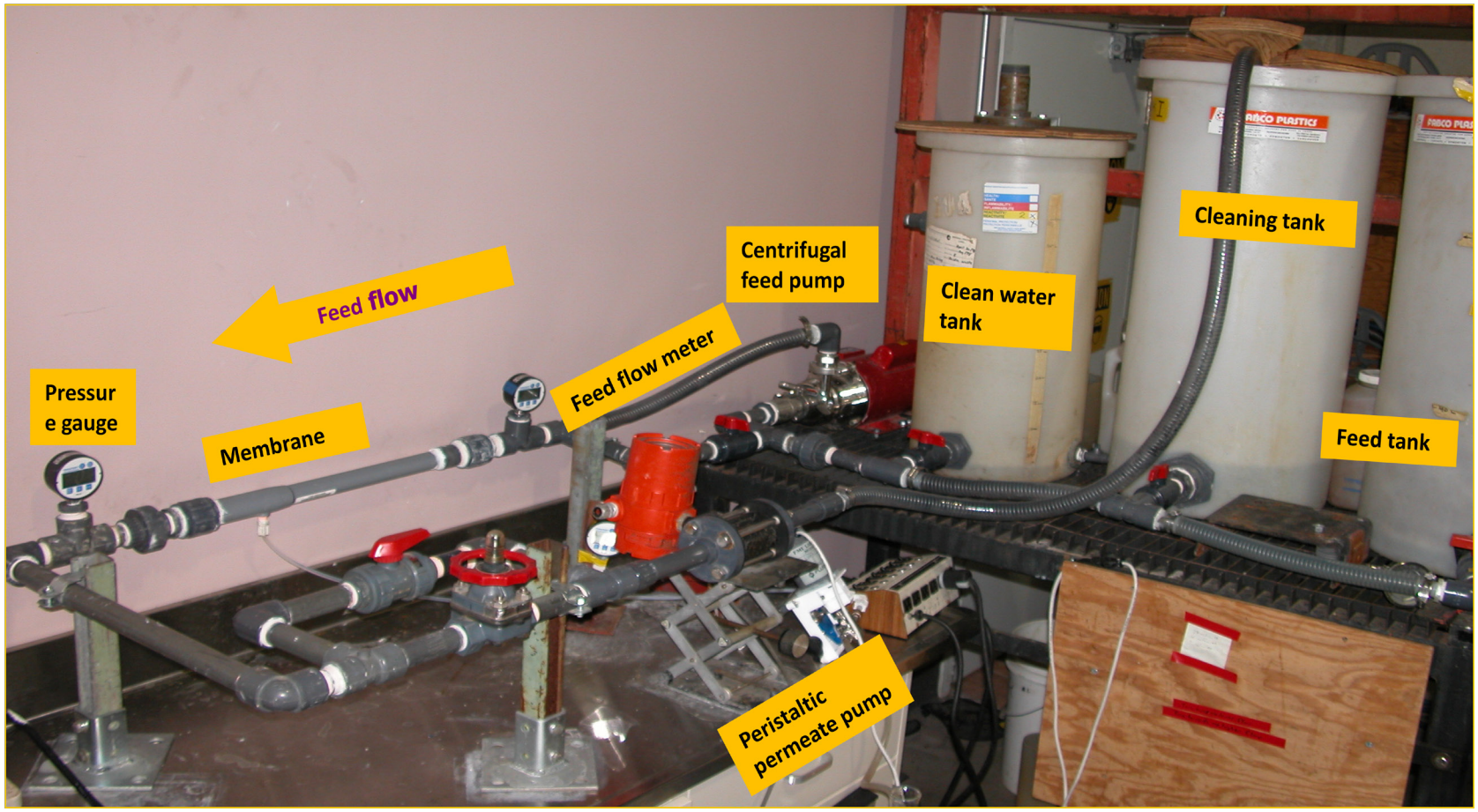


Figure A-9 Bench scale filtration unit

Appendix B Raw feed sludge characteristics data

Table B-1 Feed sludge TSS fraction steady state data

Experiment	Days	TS	VS	TSS	VSS	FSS	Statistics
Experiment -1 (Feed for AnM digester 15-30 and bench scale control digesters 15-15 and 15-30)	88	9540	6700	8640	6590	2050	
	92	6310	4040	5255	3850	1405	
	99	18650	13300	17300	12500	4800	
	102	19710	14300	15750	13350	2400	
	106	15150	12100	14380	10300	4080	
	113	12750	9090	11225	8500	2725	
	116	11500	10580	9400	7050	2350	
	120	20450	14950	16750	13050	3700	
	124	11850	8400	10600	7330	3270	
	127	13660	10150	12350	10120	2230	
	130	22240	16460	19850	15450	4400	
	134	17973	13068	15417	11483	3933	
	136	16220	11905	14250	11450	2800	
	141	19490	12185	13550	10600	2950	
	144	21420	15750	20300	15630	4670	
	149	18900	14000	16400	12700	3700	
	151	19635	14860	17900	14100	3800	
	155	17650	13200	16100	12300	3800	
	158	15620		21850	15050	6800	
		16.2	**11.9**	**14.6**	**11.1**	**3.5**	Average
		4.3	**3.3**	**4.3**	**3.3**	**1.2**	SD
		19	**18**	**19**	**19**	**19**	N
		0.315	**0.34**	**0.915**	**0.520**	**0.321**	P value

Experiment -2 (Feed for AnM digester 15-30 and bench scale control digesters 7-7	111	19320	13180	17400	12800	4600	
	113	16230	11400	15300	11400	3900	
	117	13340	9300				
	120	13610	9600	11400	9500	1900	
	125	17670	12720	15700	12700	3000	
	131	15645	11130	13400	10900	2500	
	134	16760	12160	13800	12500	1300	
	140	17050	13300	15700	12330	3370	
	142	18530	13800	16300	13480	2820	
	145	16080	11535	12400	10800	1600	
	149	18720	13400	16400	13170	3230	
	152	10650	6980	9000	6900	2100	
	160	13460	10000	10200	9420	780	
		15.9	**11.4**	**13.9**	**11.3**	**2.6**	Average
		2.5	**2.0**	**2.7**	**1.9**	**1.1**	SD
		13	**13**	**12**	**12**	**12**	N
		0.505	**0.390**	**0.383**	**0.185**		P value
Experiment -3 (Feed for AnM digester 7-15 and Pilot control digester 15-15	42	21410	15115	18900	15100		
	46	11595	7820		7750		
	50	19475	13665	15950	13150		
	57	25075	16935	22150	16850		
	60	16660	11730	13500			
	63	18280	15207	13900			
	67	14725		12400			
	70	18890	13400	15700	13380		
		18.3	**13.4**	**16.1**	**13.2**		Average
		4.1	**3.0**	**3.4**	**3.4**		SD
		8	**7**	**7**	**5**		N
		0.9	**0.4**	**0.412**	**0.331**		P value

Table B-2 Raw feed sludge characteristics during steady state

Experiment	Days	TCOD	fCOD	sCOD	cCOD	pCOD	Statistics
Experiment -1 (Feed for AnM digester 15-30 and bench scale control digesters 15-15 and 15-30)	88	10600					
	92	13575					
	95	12050	328				
	99	21450					
	102	37975	2050				
	106	15600	1310				
	113	13450	306				
	116	12325	1250				
	120	21950	1940				
	124	21000	1320				
	127	16825	630				
	130	21125	2060				
	134	21375	1300				
	136	17650	1300				
	141	22275	660				
	144	23175	860				
	149	22000	1750				
	151	21775	1170				
	155	22550	1430				
	158	27250	1190				
		19.8	**1.2**				Average
		6.3	**0.5**				SD
		20	**17**				N
		0.03	**0.3**				P value

Experiment -2 (Feed for AnM digester 15-30 and bench scale control digesters 7-7	111	19450	505	413	92	
	113	21625	> range	>range	> range	
	117	13375	241	61	180	
	120	18325	324	251	73	
	125	7800	255	257	0	
	131	16575	573	527	46	
	134	19725	566			
	140	23825	453			
	142	21400	760	635	125	
	145	17725	602	524	78	
	149	21625	504	462	42	
	152	10925	251	240	11	
	160	14500	418	380	38	
		17.4	**450**	**380**	**68.5**	Average
		4.7	**160**	**170**	**54**	SD
		13	**12**	**10**		N
		0.03	**0.03**	**0.03**		P value
Experiment -3 (Feed for AnM digester 7-15 and CD 15-15	42	21410	15115	18900	98	
	46	11595	7820		21	
	50	19475	13665	15950	64	
	57	25075	16935	22150		
	60	16660	11730	13500	201	
	63	18280	15207	13900	49	
	67	14725		12400	174	
	70	18890	13400	15700	133	
		21.3	**970**	**860**	**106**	Average
		5.7	**200**	**210**	**66**	SD
		8	**7**	**7**		N
		0.9	**0.9**	**0.4**		P value

Table B-3 Feed sludge nitrogen fraction, alkalinity, acetic and propionic acid steady state data

Experiment	Days	TKN	NH_4-N	Alkalinity	Acetic acid	Propionic acid	Statistics
Experiment -1 (Feed for AnM digester 15-30 and bench scale control digesters 15-15 and 15-30)	92	400	9.43	415	4.85	3.07	
	99	1,330	68.00	1,330	5	2	
	106	1,425	166.50	1,170	220	81	
	113	828	115.00	1,035	71	26	
	124	1,080	186.50	1,550	78	31	
	127	959	122.50	1,165	13.00	14.00	
	134	1,480	181.00	1,670			
	141	1,195	240.00	1,025	148	44	
	149	1,330	107.00		160.00	73.30	
	151	1,140	166.00	1,100			
	155	1,145	151.00	895	78	36	
		1119	**138**	**1136**	**86**	**34**	Average
		308	**63**	**349**	**78**	**28**	SD
		11	**11**	**10**	**9**	**9**	N
		0.3	**0.7**	**0.5**	**0.3**	**0.5**	P value
Experiment -2 (Feed for AnM digester 15-30 and bench scale control digesters 7-7	117	1,360	32.10	1,260	66.00	27.00	
	125	1,060		860			
	134	1,460	36.10	823	170.00	92.90	
	145	1,380	33.80	750	137.00	69.50	
	152	711	25.70	700	75.20	48.80	
	160	1,260	28.20	955	101.00	52.40	
		1205	**31**	**891**	**110**	**58**	Average
		249	**7**	**201**	**43**	**25**	SD
		6	**5**	**6**	**5**	**5**	N
		0.2	**0.8**	**0.2**	**0.6**	**0.8**	P value
Feed for Experiment -3	42	1630	112	1720	319	182	
	50	1620	113	1650	204	87	
		1625	**112**	**1685**	**261**	**134**	Average
				50	**81**	**67**	SD
		2	**2**	**2**	**2**	**2**	N
		0.2	**0.2**	**0.2**	**0.2**	**0.2**	P value

Transient and steady state feed characteristics profile

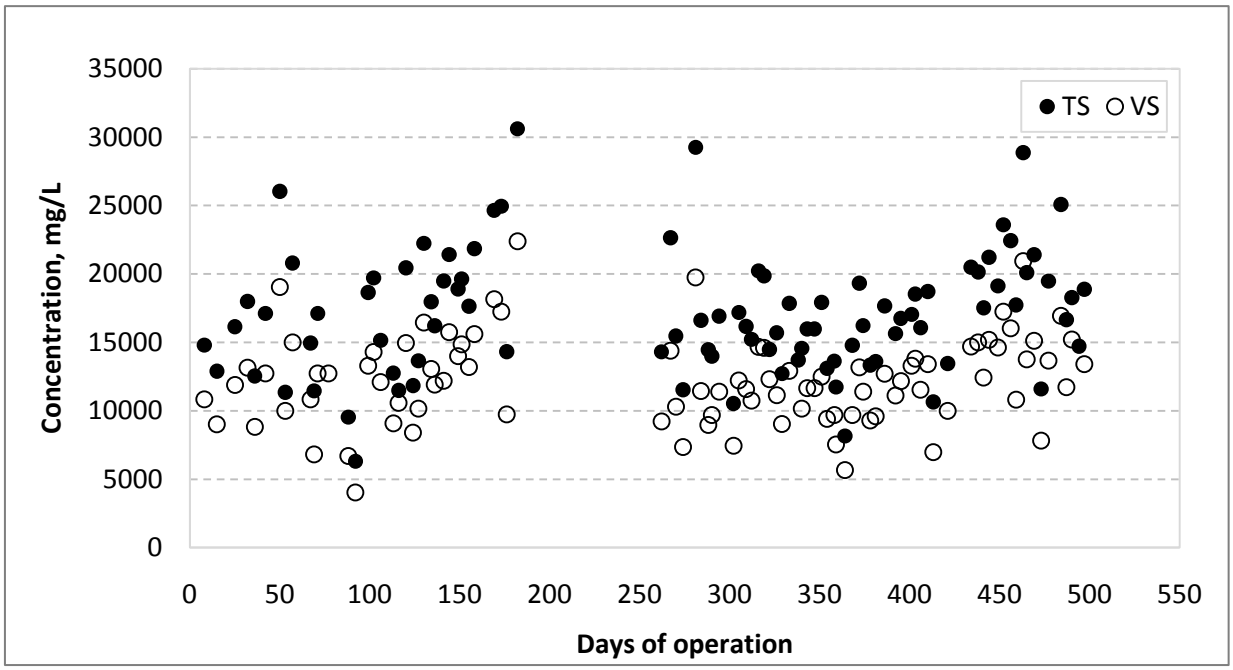


Figure B-1 Raw feed sludge TS and VS profile

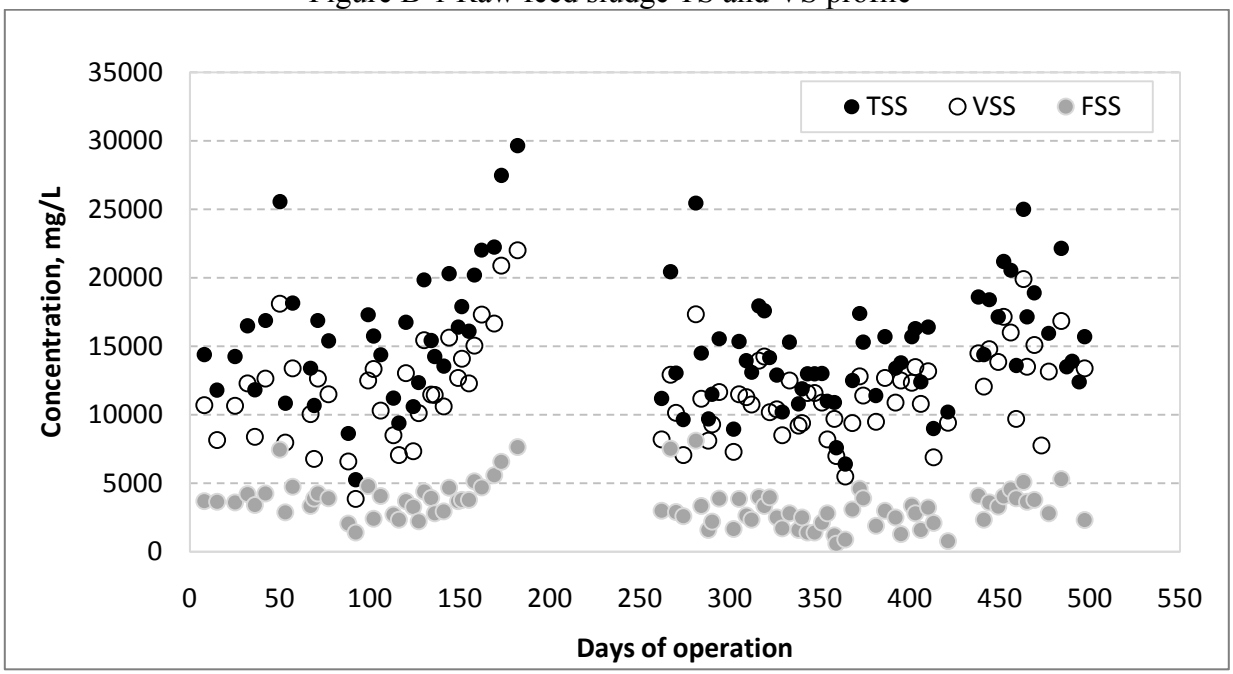


Figure B-2 Raw feed sludge TSS, VSS and FSS profile

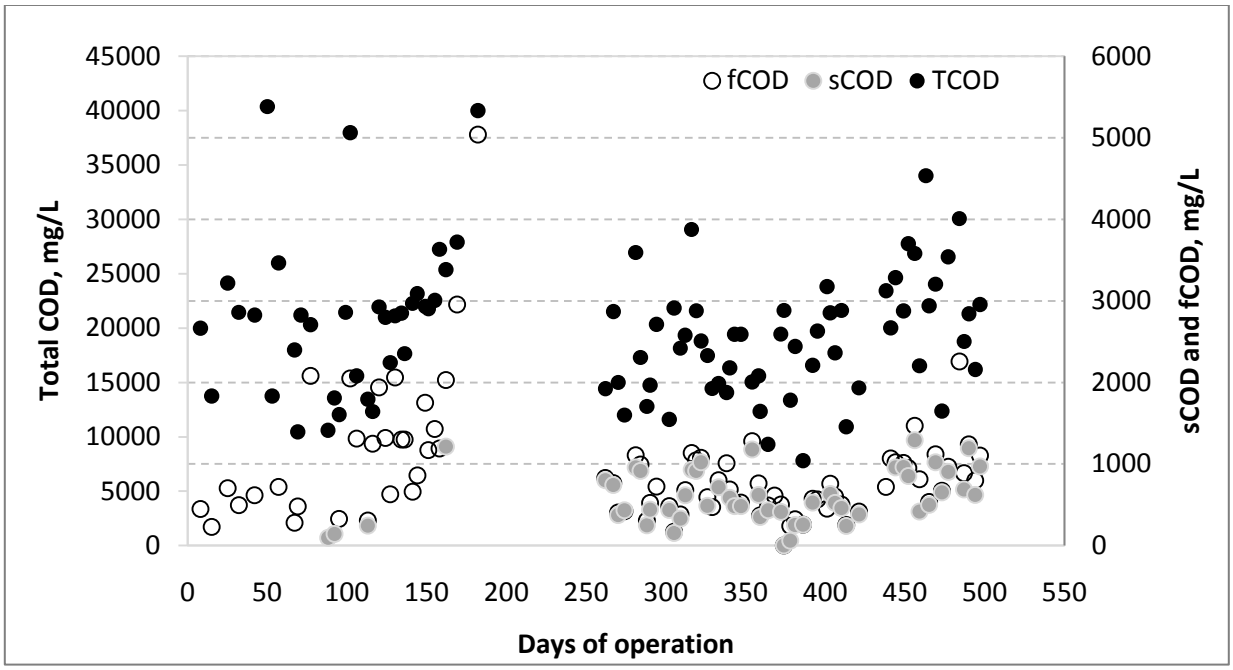


Figure B-3 Raw feed sludge COD fractions profile

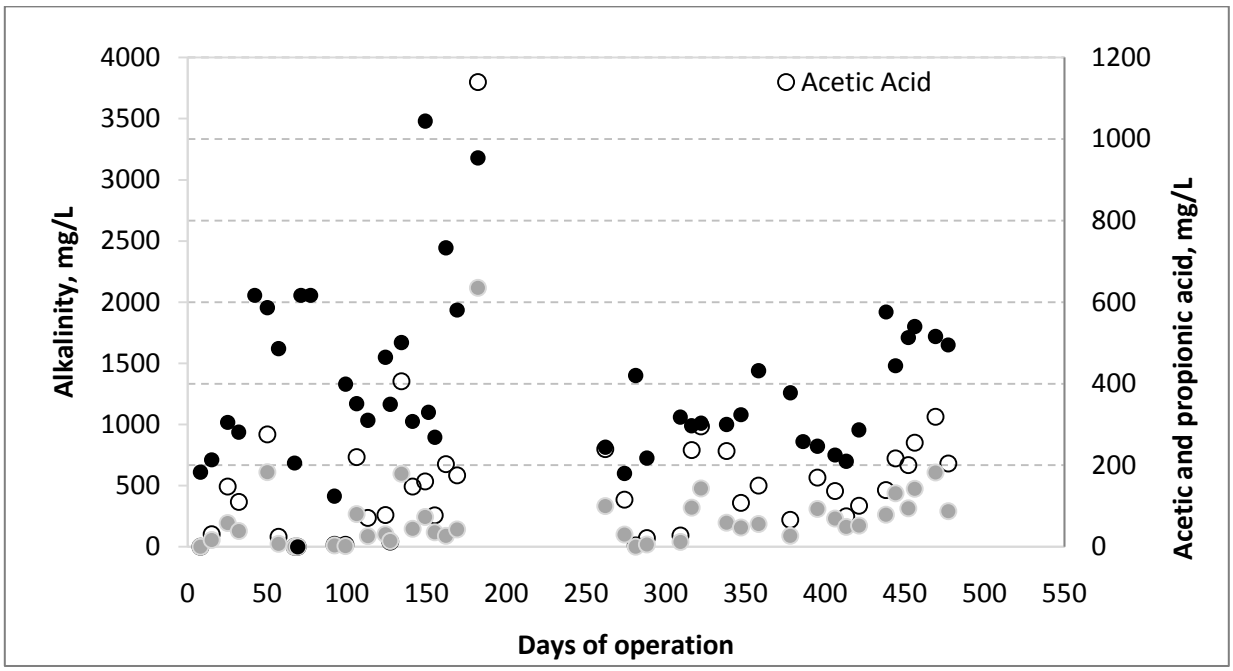


Figure B-4 Raw feed sludge alkalinity, acetic and propionic acid concentrations profile

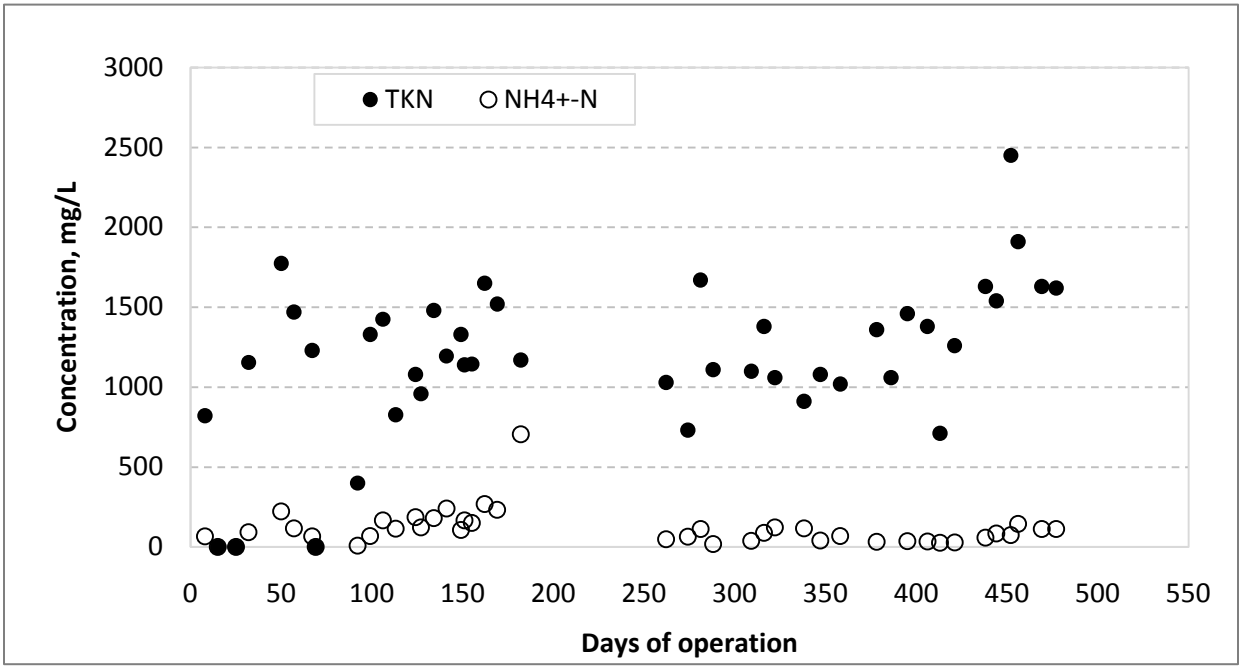


Figure B-5 Raw feed sludge TKN and NH4-N concentrations profile

Appendix C AnM digesters operational data

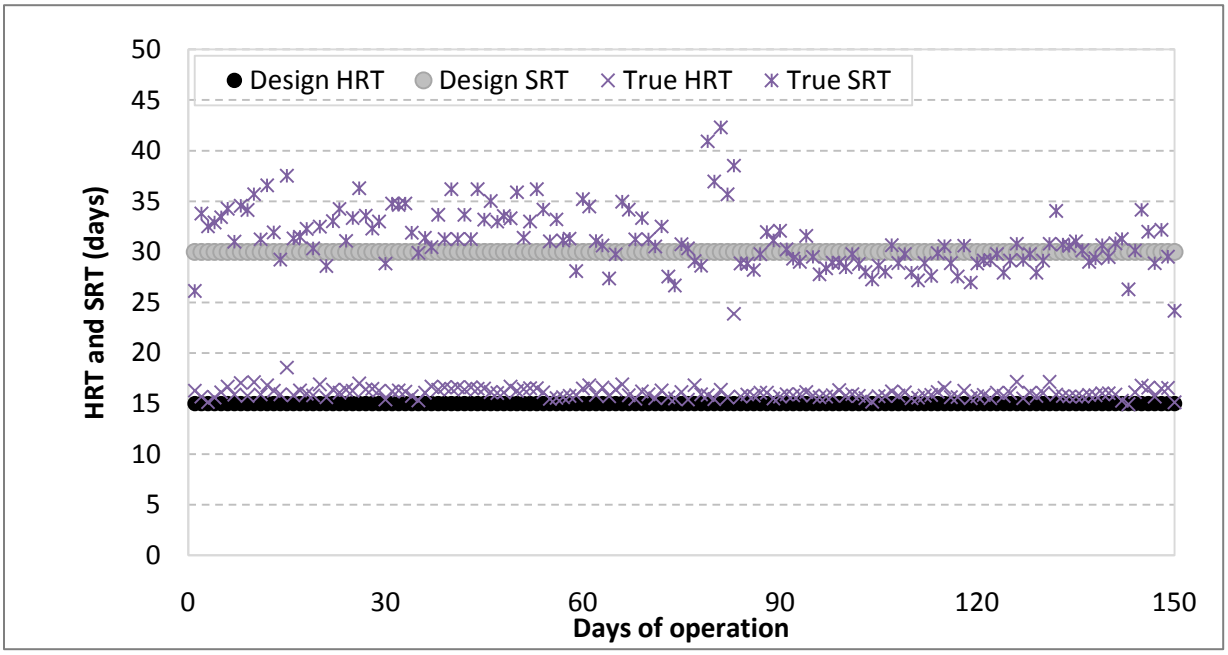


Figure C-1 AnM 15-30 digester true and design HRT and SRTs

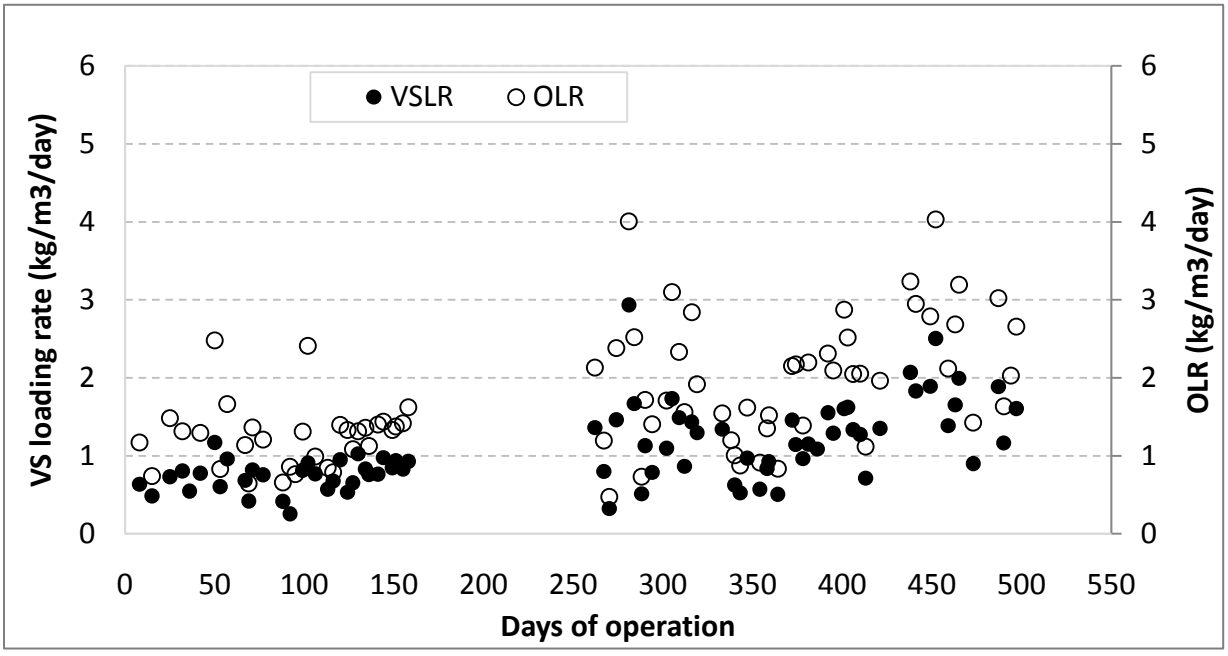


Figure C-2 AnM digesters volatile solids and organic loading rate profile

Table C-1 Density of digested sludge

Sampling date	Density of sludge (Pilot control digester 15-15)	Sampling date	Density of sludge (AnM digester 7-15)
1/26/2009	0.98	1/26/2009	0.98
2/2/2009	0.98	2/2/2009	0.96
2/11/2009	0.99	2/5/2009	
2/17/2009	1.01	2/10/2009	0.99
2/19/2009	0.99	2/17/2009	0.98
3/2/2009	0.99	3/9/2009	1.00
3/11/2009	0.99	3/11/2009	0.98
3/19/2008	0.99	3/18/2009	1.00
3/26/2009	0.98	3/25/2009	0.99
4/9/2009	0.99	4/1/2009	1.01
4/16/2009	0.99	4/8/2009	1.00
4/22/2009	0.99	4/16/2009	1.21
4/30/2009	0.99	4/27/2009	1.00
5/29/2009	1.00	5/1/2009	1.00
		5/11/2009	0.98
		5/19/2009	1.00
Average	**0.99**	**Average**	**1.01**
SD	**0.01**	**SD**	**0.06**

Appendix D Digested sludge solid fractions

Table D-1 Digested sludge solids fraction steady state data

Experiment	Days	TS	VS	TSS	VSS	FSS	Statistics
AnMBR 15-30 Experiment -1	88	17690	10690	16765	10535	6230	
	92	19170	11540	16277	10137	6140	
	99	15600	9310	13700	8200	5500	
	102	17040	10560	11700	8750	2950	
	106	14750	10000	14400	9040	5360	
	113	20100	12280	18725	11700	7025	
	116	18105	10645	15850	10000	5850	
	120	20090	12290	16600	10825	5775	
	124	18550	13000	18500	11350	7150	
	127	18530	12140	17800	12000	5800	
	130	19830	12000	17800	11950	5850	
	134	20500	12800	19400	12250	7150	
	136	20135	12500	16750	11150	5600	
	141	18000	11800	15550	11385	4165	
	144	20970	13250	19500	13050	6450	
	149	21900	14100	21250	13500	7750	
	151	20670	13340	18800	12850	5950	
	155	20600	13200	19550	12900	6650	
	158	18750	11440	17200	11150	6050	
		18999	**11941**	**17164**	**11196**	**5968**	Average
		1852	**1261**	**2307**	**1486**	**1082**	SD
		19	**19**	**19**	**19**	**19**	N
		0.318	**0.726**	**0.741**	**0.734**		P value

AnMBR 7-30 Experiment -2	111	26700	16600	27740	17120	10100	
	113	25100	16000	27640	16920	9100	
	117	23400	15600	25640	15645	7800	
	120	23000	15400	25960	16060	7600	
	125	26000	15850	27220	17240	10150	
	131	26700	17850	29430	18600	8850	
	134	25650	18050	29850	19075	7600	
	140	31150	19250	32980	20920	11900	
	145	32200	21850	34955	21910	10350	
	149	34910	21540	36500	23200	13370	
	152	32300	20600	34230	21320	11700	
	154	31200	20800	35495	22195	10400	
	160	29500	19800	34160	21290	9700	
		28293	**18399**	**30908**	**19346**	**9894**	Average
		3793	**2377**	**3921**	**2584**	**1747**	SD
		13	**13**	**13**	**13**	**13**	N
		0.129	**0.219**	**0.336**	**0.244**		P value
AnMBR 7-15 Experiment -3	42	32495	20095	28950	19700	9250	
	46	30360	18760	27450	18100	9350	
	50	30725	18830	26400	17650	8750	
	53	30130	18550	26600	17650	8950	
	57	27630	16760	24500	16600	7900	
	60	28615	17530	24800			
	67	27160		24200			
	70	26755	16595	23250	16150	7100	
		29234	**18160**	**25769**	**17642**	**8550**	Average
		2012	**1259**	**1904**	**1246**	**878**	SD
		8	**7**	**8**	**6**	**6**	N
		0.595	**0.525**	**0.728**	**0.538**		P value

Control digester: 30-30 Exp-1	99	10500	6220	8900	5200	3700	
	102	10730	6450		5450		
	106	9060		7600	5350	2250	
	113	12300	7380	10725	6850	3875	
	116	11220	6490	9500	5950	3550	
	120	11220	6490	9500	5950	3550	
	124	11050	6545	10100	8000	2100	
	127	11430	6960	9650	6600	3050	
	130	11610	6800	9650	6550	3100	
	134	12100	7265	10800	6575	4225	
	136	12330	7470		6900		
	141	12650	7985	10500	7300	3200	
	144	11920	7170	10850	7400	3450	
	149	12600	7650	11400	7100	4300	
	151	12525	7830	10450	7100	3350	
	155	12350	7630	11550	7375	4175	
	158	12050	7210	10000	6600	3400	
		11626	**7097**	**10078**	**6603**	**3418**	Average
		940	**549**	**1012**	**792**	**639**	SD
		17	**16**	**15**	**17**	**15**	N
		0.118	**0.494**	**0.487**	**0.347**		P value
Control digester: 15-15 Experiment 1	88	12,030	7,450	10,946	7,241	3,705	
	92	10,710	6,290	9,591	6,155	3,436	
	99	10,100	6,330	9,100	5,500	3,600	
	102	9,835	6,180	8,975	5,875	3,100	
	106	13,275	8,203	11,692	7,689	4,002	
	113	13,800	8,610	12,225	8,075	4,150	
	116	12,200	7,370	10,600	6,900	3,700	
	120	13,020	7,980	10,000	6,600	3,400	
	124	11,850	7,330	10,600	8,400	2,200	
	127	12,110	7,780	10,200	7,300	2,900	
	130	12,550	7,750	10,200	7,400	2,800	
	134	13,300	8,355	12,600	8,000	4,600	
	136	12,650	7,985	10,500	7,300	3,200	
	141	12,650	7,985	10,500	7,300	3,200	
	144	13,570	8,520	12,400	8,800	3,600	
	149	13600	8950	13200	8690	4,510	
	151	14000	9215	12750	8850	3,900	
	155	13850	9010	13150	8875	4,275	
		12506	**7850**	**11068**	**7497**	**3571**	Average
		1252	**910**	**1366**	**1031**	**622**	SD
		18	**18**	**18**	**18**	**18**	N
		0.098	**0.345**	**0.167**	**0.510**		P value

Control digester: 7-7 Experiment 2	20	15250	9585		10200	4350	
	23	14355	9010	12250	9500	2750	
	27	12550	7740	11400	8600	2800	
	29	15410	9300	11300	8900	2400	
	34	13750	8528	10875	8175	2700	
	41	12090	7755	10450	7450	3000	
	44	12950	8485	10400	7750	2650	
	48	13400	8910	11050	8400	2650	
	51	13520	8680	11350	8650	2700	
	55	13710	9145	11050	8350	2700	
	58	14880	9600	11800	9500	2300	
	61	12990	8380	11000	8700	2300	
	65	12720	8340	9200	7400	1800	
	68	12130	8050	10500	7900	2600	
	72	12770	8570	10700	8500	2200	
		13498	**8672**	**10952**	**8532**	**2660**	Average
		1067	**588**	**724**	**778**	**553**	SD
		15	**15**	**14**	**15**	**15**	N
		0.366	**0.867**	**0.449**	**0.632**		P value
Pilot control digester: 15-15, Experiment 3	7	10830	6815	8100	6500	1600	
	11	11930	7535	8800	6950	1850	
	14	11815	7210	9350	7250	2100	
	17	14825	9320	12000	8800	3200	
	22	12985	7305	10400	7850	2550	
	25	13915	8895	11000	8300	2700	
	29	13910	8615	12050	8700	3350	
	32	14410	8865	10950	8100	2850	
	36	15420	9845	12800	9800	3000	
	38	15355	9470	10350	9100	1250	
	42	15240	9530	12300	9750	2550	
	46	13020	8025	9700	7850	1850	
	50	13595	8380	9900	7750	2150	
	53	14610	9120	11300	9000	2300	
	57	13830	8515	9750	7600	2150	
	60	13130	8185	10800			
	66	12925		9750			
	70	13455	8390	10450	8300	2150	
		13622	**8472**	**10542**	**8225**	**2350**	Average
		1273	**879**	**1248**	**938**	**581**	SD
		18	**17**	**18**	**16**	**16**	N
		0.714	**0.811**	**0.901**	**0.962**		P value

Transient and steady state digested sludge solids concentrations profile

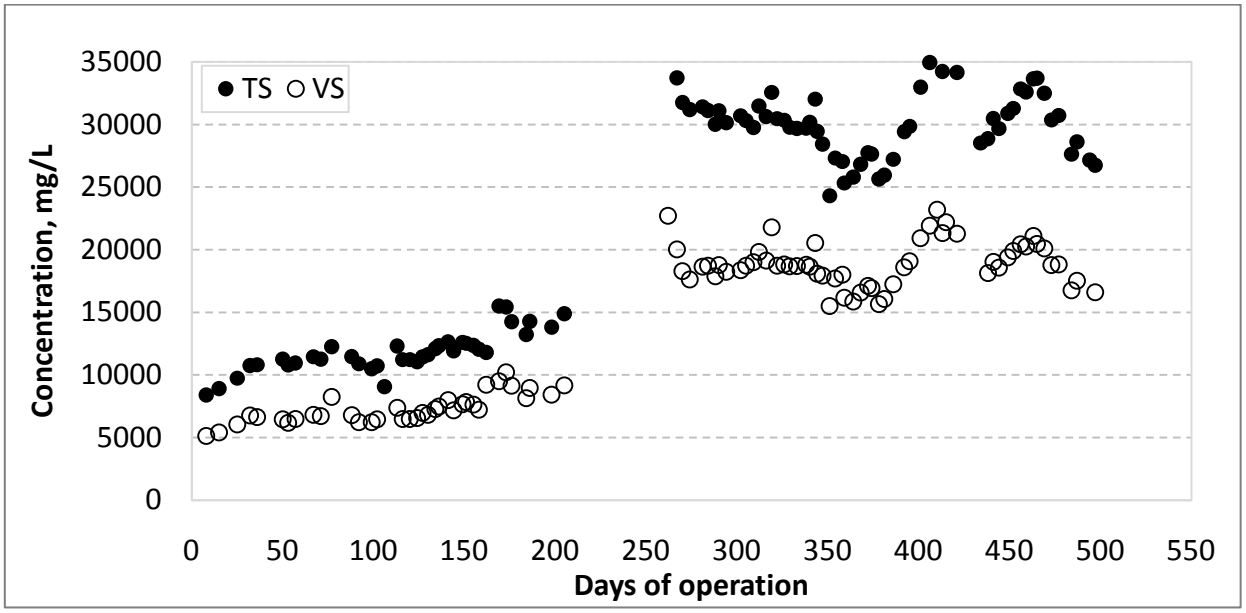


Figure D-1 TS and VS profile of sludge digested using AnM (test) digesters

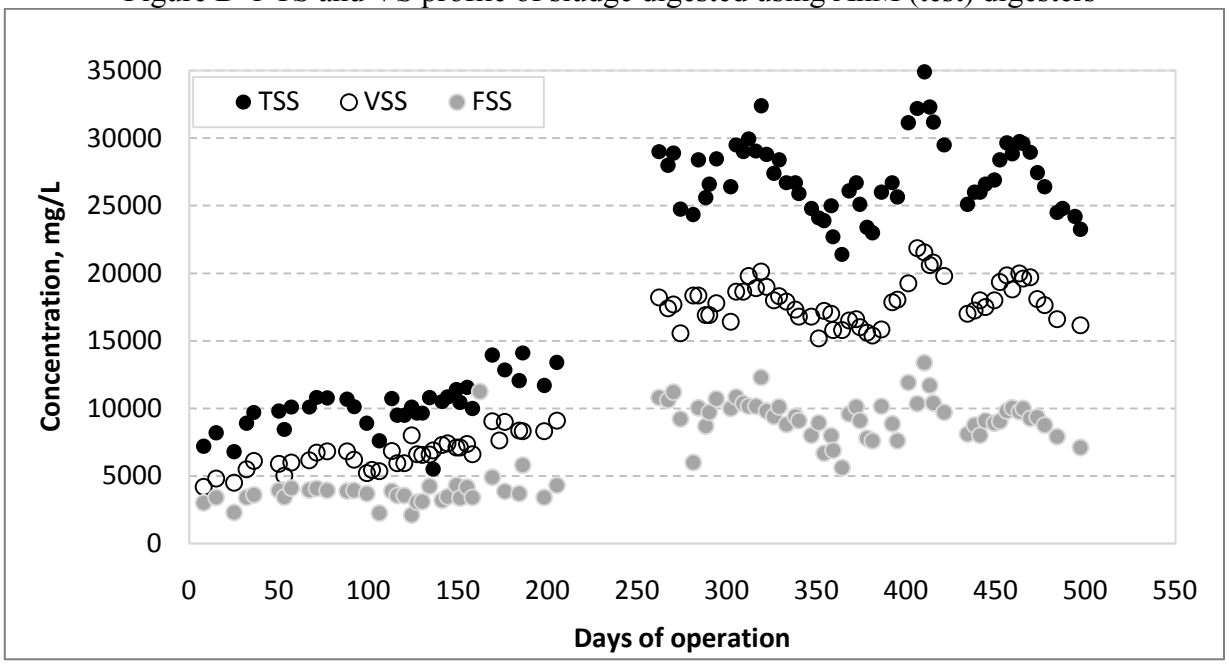


Figure D-2 TSS, VSS and FSS profile of sludge digested using AnM (test) digesters

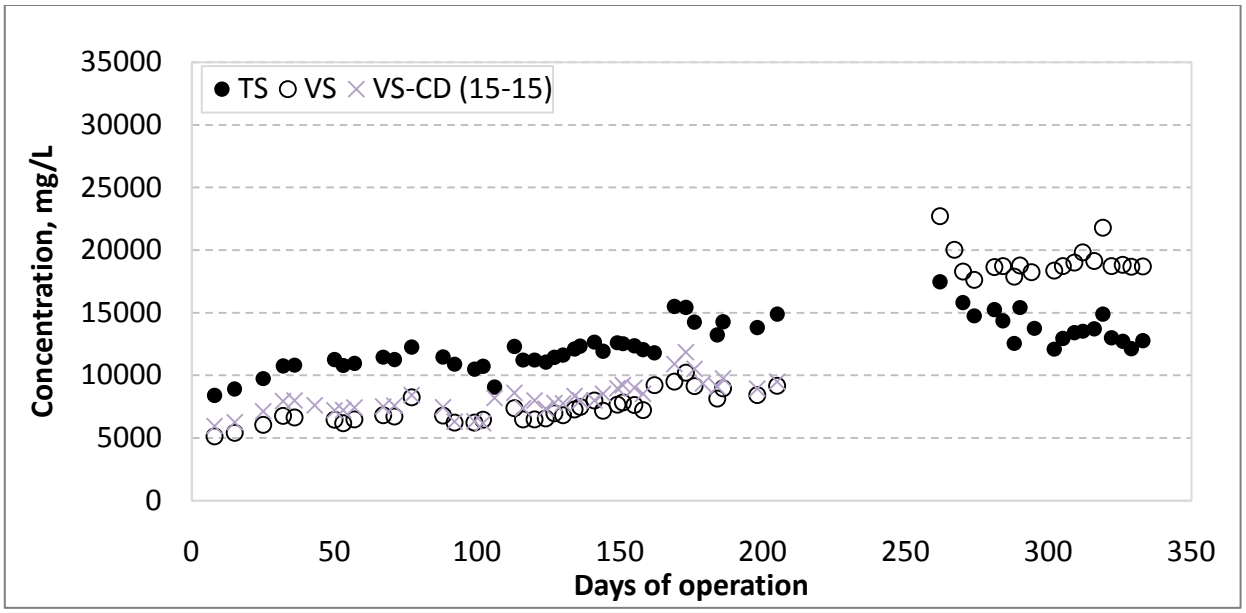


Figure D-3 TSS, VSS and FSS profile of sludge digested using AnM (test) digesters

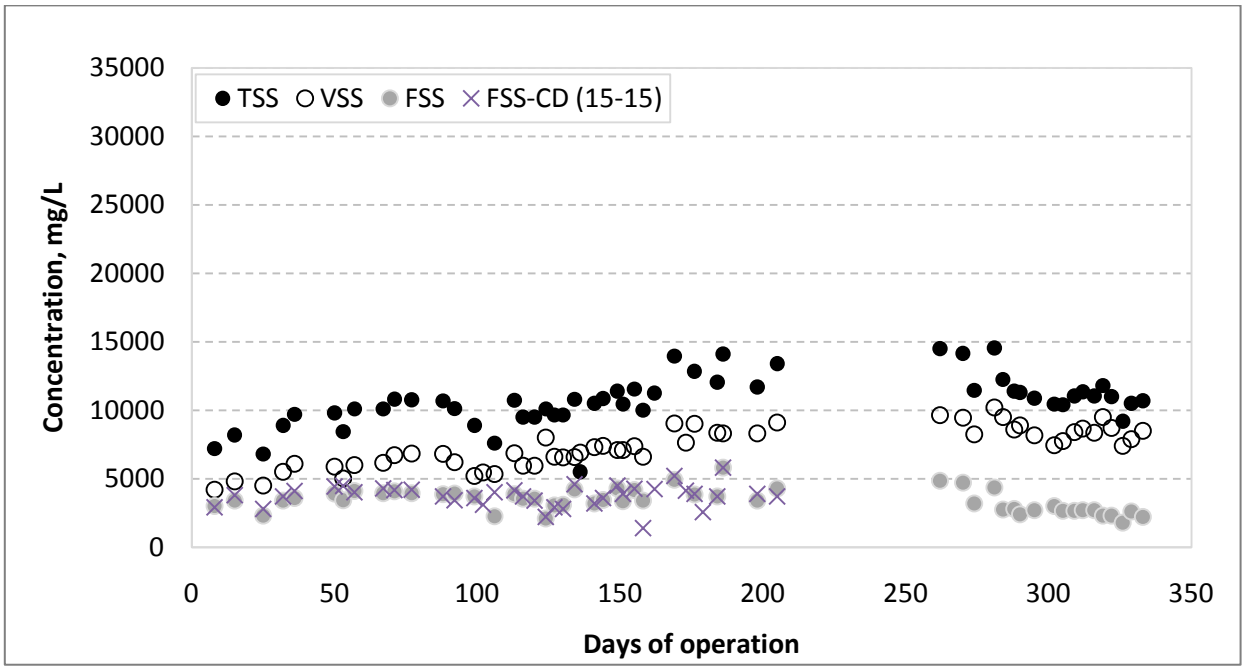


Figure D-4 TSS, VSS and FSS profile of sludge digested using conventional (control) digesters

VS removal calculations for AnM and control digesters based on mass balance

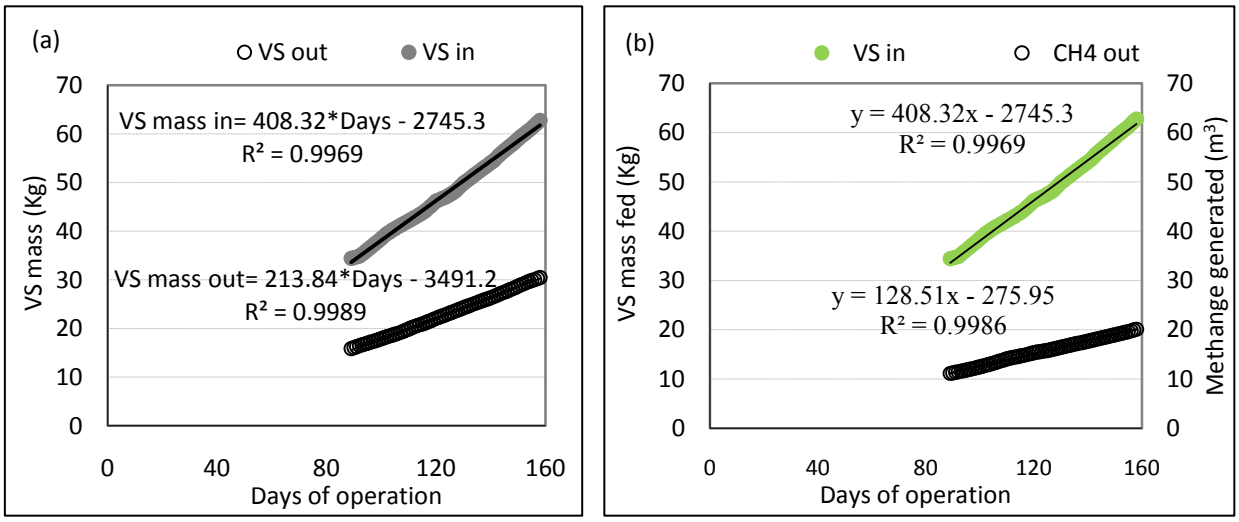


Figure D-5 AnM 15-30: (a) VS removal (b) Methane generated per VS fed

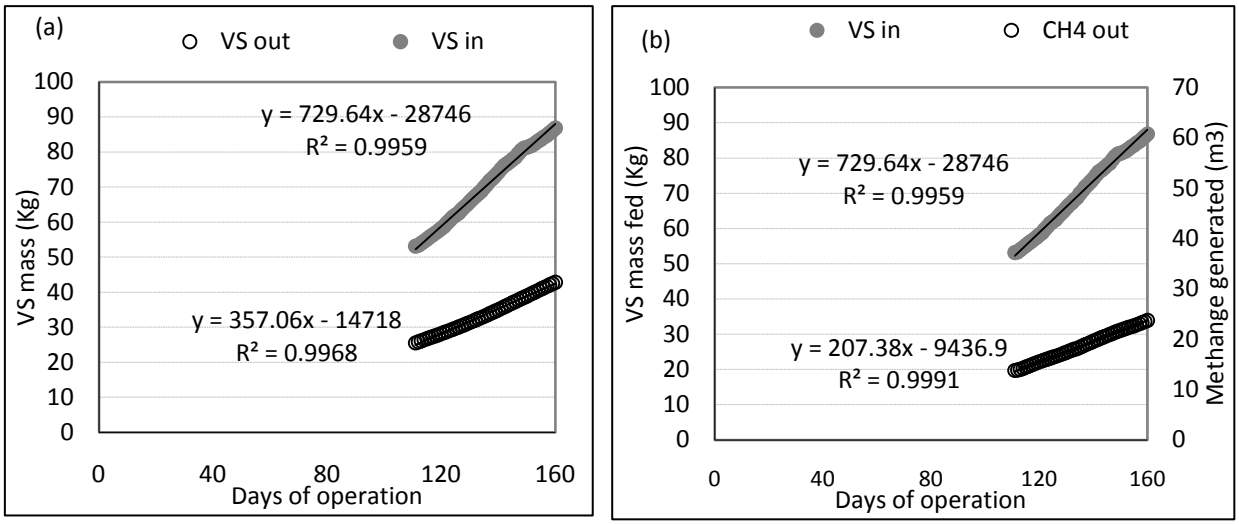


Figure D-6 AnM 7-30: (a) VS removal (b) Methane generated per VS fed

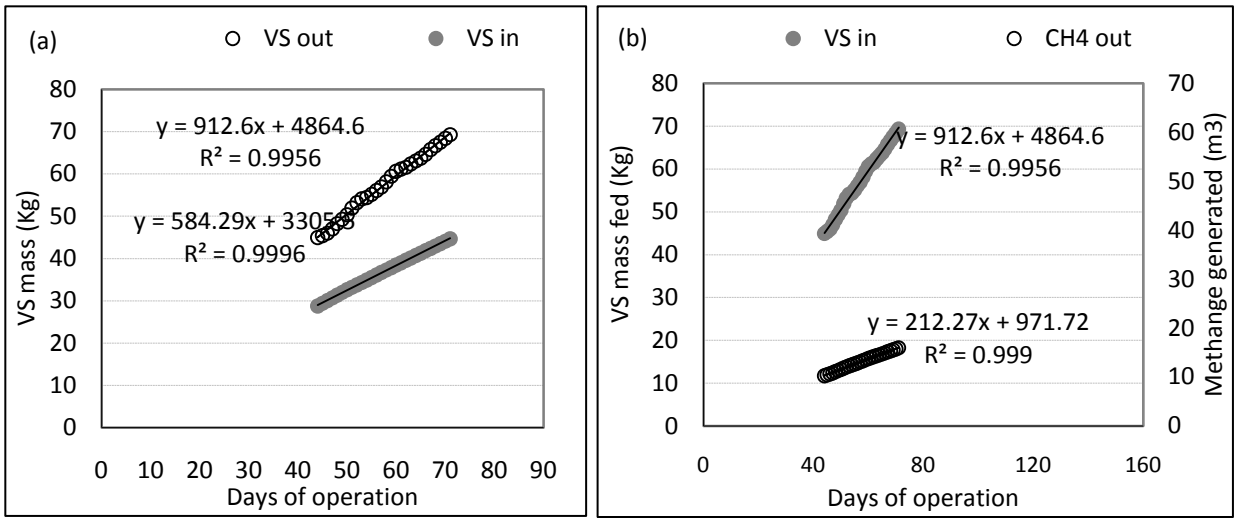


Figure D-7 AnM 7-15: (a) VS removal (b) Methane generated per VS fed

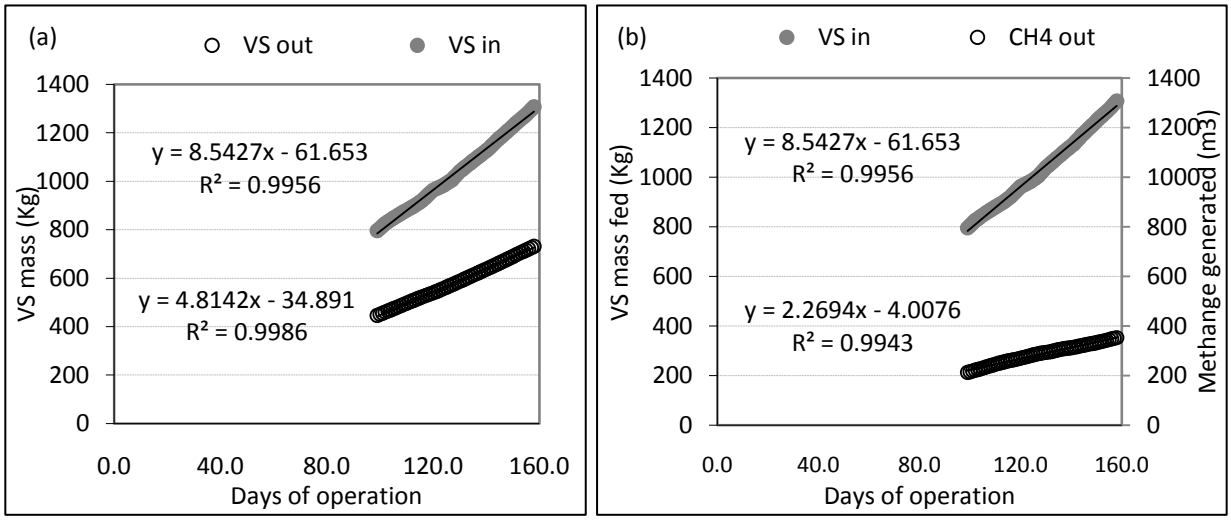


Figure D-8 Control digester 30-30: (a) VS removal (b) Methane generated per VS fed

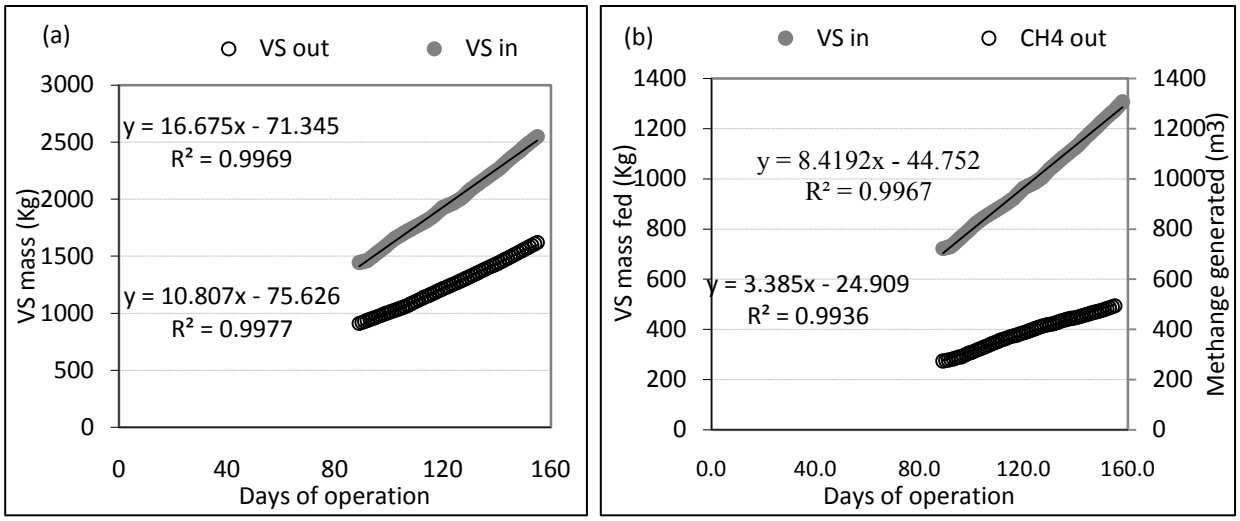


Figure D-9 Control digester 15-15: (a) VS removal (b) Methane generated per VS fed

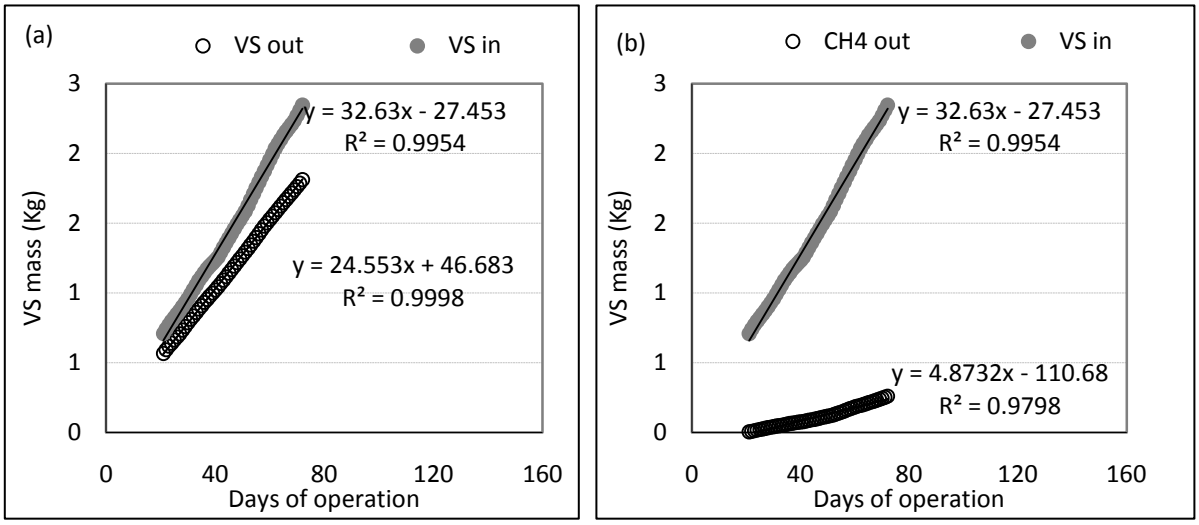


Figure D-10 Control digester 7-7: (a) VS removal (b) Methane generated per VS fed

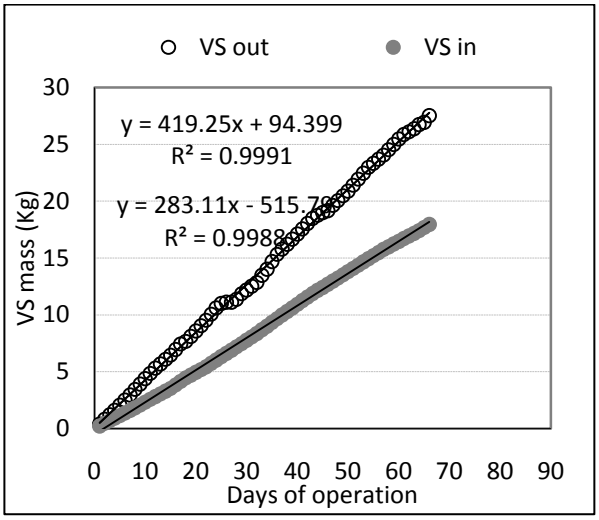


Figure D-11 Pilot control digester 15-15: VS removal

Appendix E Digested sludge COD fractions

Table E-1 Digested sludge COD fraction steady state data

Experiment	Days	TCOD	fCOD	sCOD	cCOD	pCOD	Statistics
AnM digester 15-30 Experiment-1	88	16150	354		168	187	
	92	16950	396		243	154	
	95	14575	464		313	152	
	99	14575					
	102	15075	1710		1710		
	106	13200	1190		1034	156	
	113	19000	800		663	138	
	116	15500	1080		921	159	
	120	18888	930		930		
	124	18800		754		239	
	127	18300	835		676	160	
	130	18800	690		690		
	134	20900				360	
	136	19675	1210		1210		
	141	18475	840		840		
	144	18500	730		581	150	
	149	19000		570		410	
	151	19750	840		840		
	153	19100		720			
	155	21950		655		290	
	158	18475	730		567	163	
		17888	**853**	**675**	**759**	**209**	Average
		2253	**349**	**81**	**393**	**89**	SD
		21	**15**	**4**	**15**	**13**	N
		0.03	**0.312**	**0.643**	**0.816**	**0.145**	P value

AnM digester 7-30 Experiment-2	111	25825	1570	375	1411	159	
	113	25787.5	1398	331			
	117	23787.5	1258	294	1105	153	
	120	27900	1393	345	1219	174	
	125	24162.5	1422.5	223	1284.5	138	
	131	26062.5	1448	367	1288	160	
	134	29550	1894			203	
	140	33325	2078			218	
	145	32300	2652	389	2441	211	
	149	33350	2842	488	2842		
	152	32925	2948	470			
	160	31850	2502	452	2311	191	
		28902	**1950**	**373**	**1738**	**179**	Average
		3730	**631**	**82**	**679**	**28**	SD
		12	**12**	**10**	**8**	**9**	N
		0.096	**0.05**	**0.843**	**0.556**		P value
AnM digester 7-15 Experiment-3	42	30738	2058	402	201	1857	
	46	28163	2272	394	150	2122	
	50	27775	1897	400	158	1739	
	53	27925	3182		172	3011	
	57	27363	2648	296	169	2480	
	60	26550	2108	330	192	1916	
	67	25375		337			
	70	25313	1781	322	178	1604	
		27400	**2278**	**354**	**174**	**2104**	Average
		1745	**487**	**43**	**18**	**490**	SD
		8	**7**	**7**	**7**	**7**	N
		0.425	**0.308**	**0.152**	**0.897**		P value

Control digester: 30-30 Experiment 1	102				
	106	8950	720		
	113	11400	500		
	116	9900	720		
	120		700		
	124	10600		616	
	127	10725	650		
	130	10550	650		
	134	12000			
	136	11800	910		
	144	12000			
	149	10400		460	
	151	11675	820		
	155	12750		423	
	158	12100	450		
		11142	**680**	**500**	Average
		1060	**143**	**103**	SD
		13	**9**	**3**	N
		0.373	**0.569**	**0.240**	P value
Control digester: 15-15 Experiment 2	88	11825	400		
	92	10263	321		
	95		360		
	99	10263			
	102	10263			
	106	13250	175		
	113	13250	535		
	116	11100	780		
	120	11325	650		
	124	13000	494		
	127	12325	580		
	130	12250	460		
	134	12600	510		
	136	12800	730		
	141	12800	510		
	144	12625			
	149	12100			
	150	13625	810		
	151	14800	638	440	
	154	14125	340		
		12347	**541**	**440**	Average
		1234	**177**	**0**	SD
		17	**14**	**1**	N
		0.369	**0.959**		P value

Control digester: 7-7 Experiment 2	20	13700	378	263	
	23	13550	410	243	
	27	13100	429	200	
	29	13550	424		
	34	12888	410	214	
	41	12225	396	214	
	44	14925	345	239	
	48	13950	432	245	
	51	15225	377	218	
	55	17175	396	280	
	58	14900	477	268	
	61	14625	402	222	
	65	12950	345	208	
	68		302		
	72	13450	354	243	
		14015	**392**	**235**	Average
		1263	**43**	**25**	SD
		14	**15**	**13**	N
		0.232	**0.752**	**0.454**	P value
Pilot control digester: 15-15 Experiment 3	7	10713	478		
	11	11775	531		
	14	11638	522		
	17	14350	555	265	
	22	12775	524	231	
	25	13125	590	264	
	29	12900	510	248	
	32	13200	430	228	
	36	14513	461	272	
	38	13925	544	346	
	42	14000	597	249	
	46	11513	541	224	
	50	11875	467	278	
	53	12788	878	805	
	57	12875	849	126	
	60	11913	566		
	66	11100	553	288	
	70	12450	395	230	
		12635	**555**	**290**	Average
		1109	**124**	**156**	SD
		18	**18**	**14**	N
		0.695	**0.459**	**0.154**	P value

Transient and steady state digested sludge COD concentrations profile

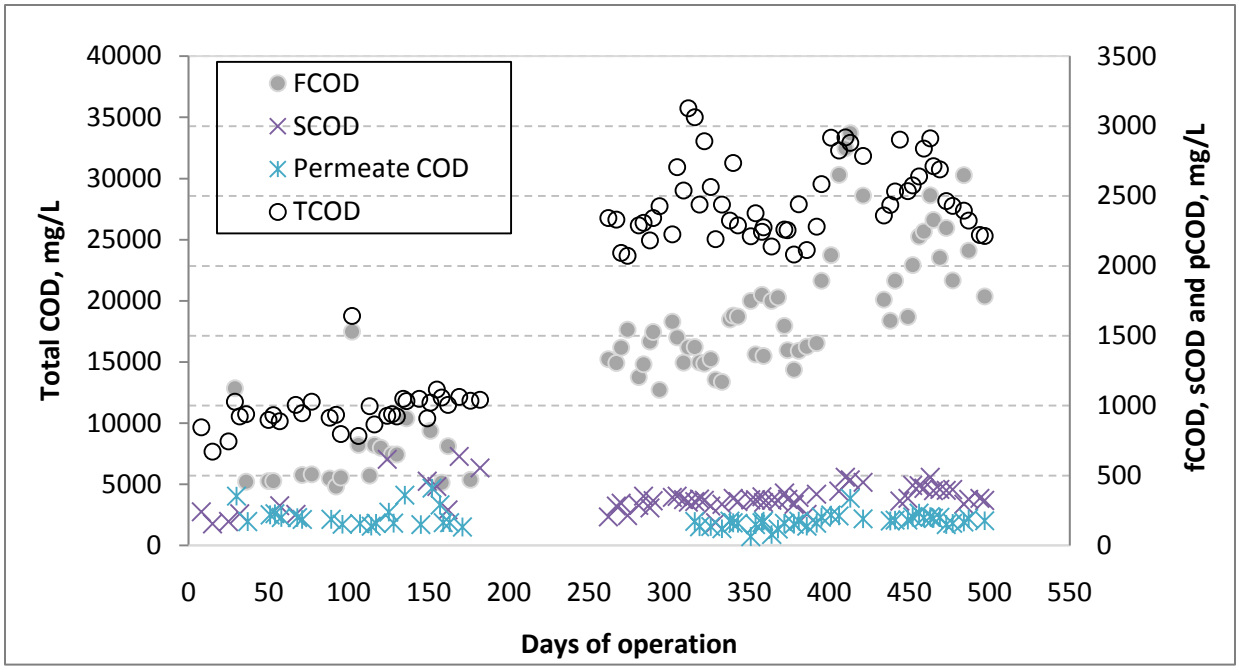


Figure E-1 COD fractions profile of sludge digested using AnM (test) digesters

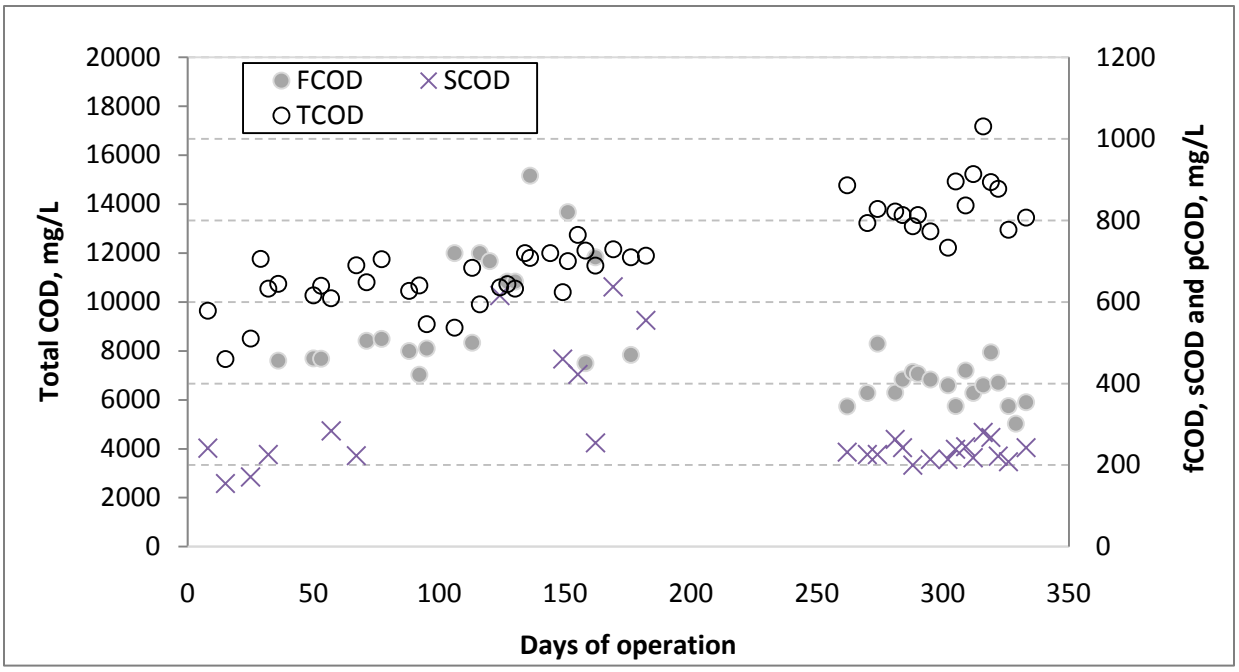


Figure E-2 COD fractions profile of sludge digested using control digesters

COD removal calculations for AnM and control digesters based on mass balance

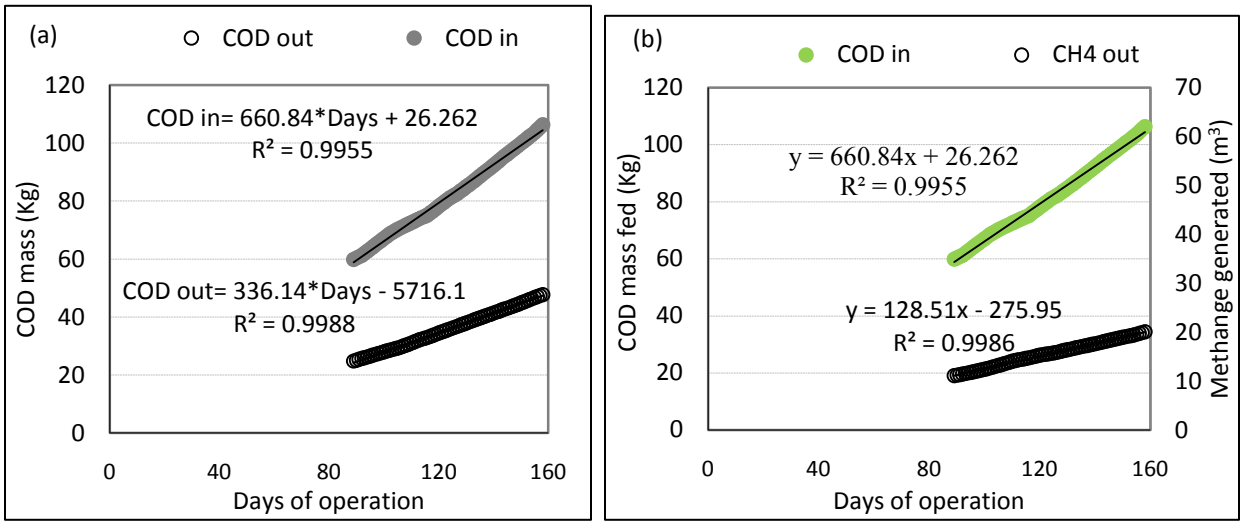


Figure E-3 AnM 15-30: (a) COD removal (b) Methane generated per COD fed

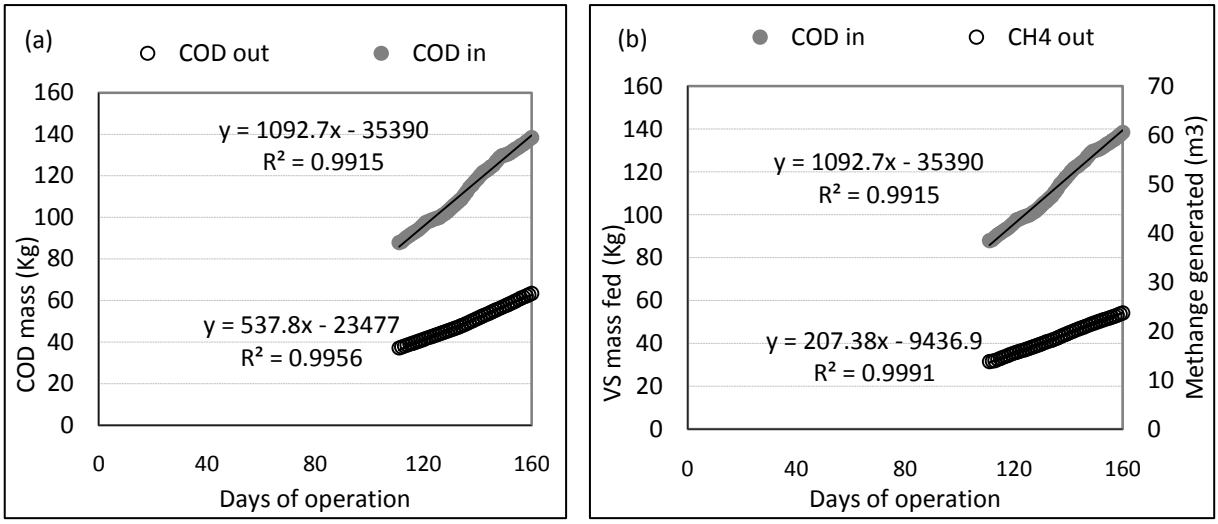


Figure E-4 AnM 7-30: (a) COD removal (b) Methane generated per COD fed

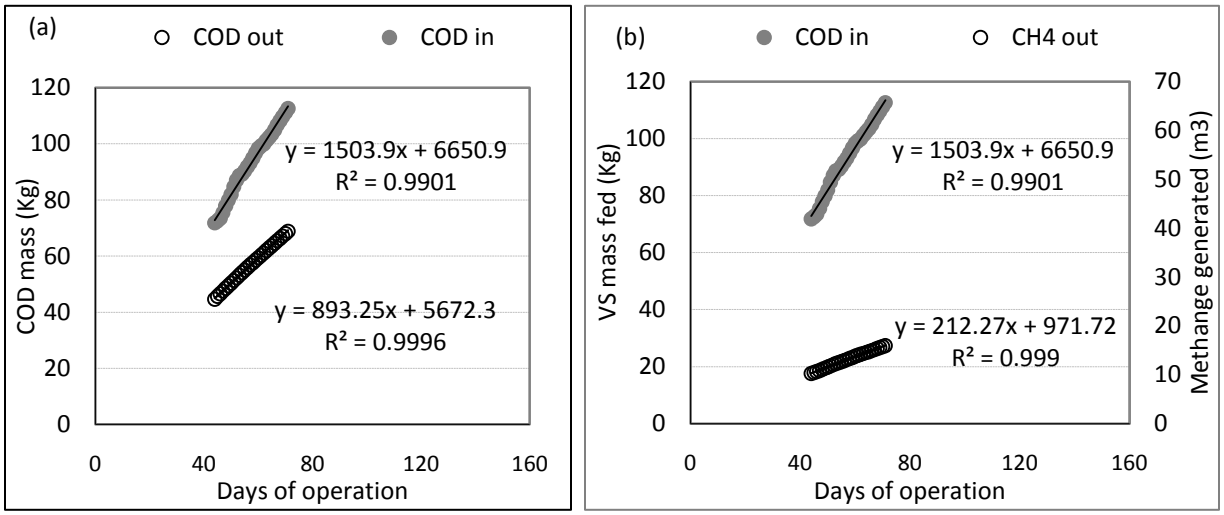


Figure E-5 AnM 7-15: (a) COD removal (b) Methane generated per COD fed

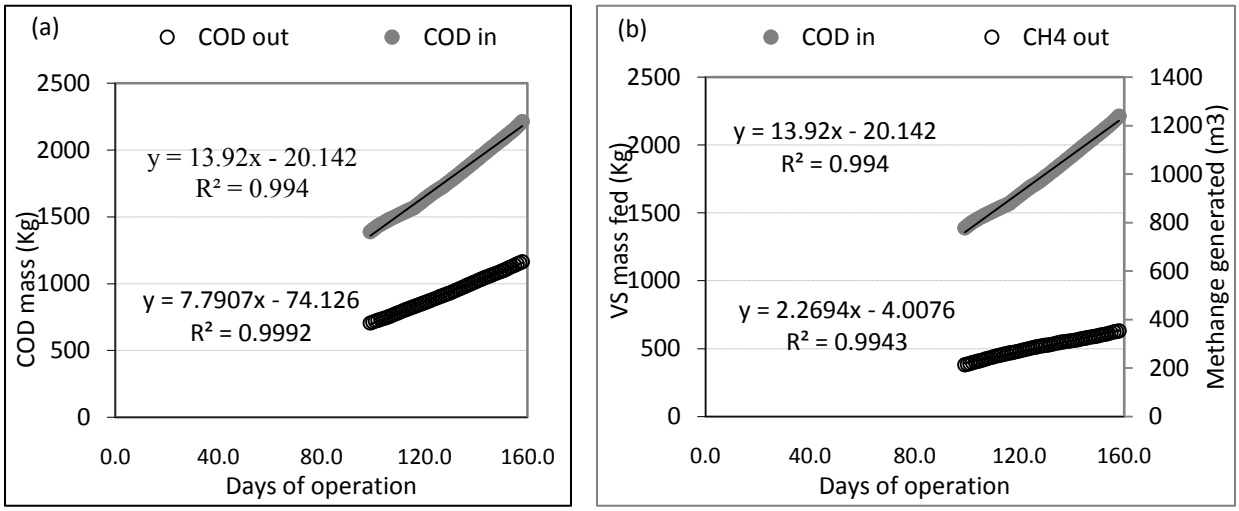


Figure E-6 Control digester 30-30: (a) COD removal (b) Methane generated per COD fed

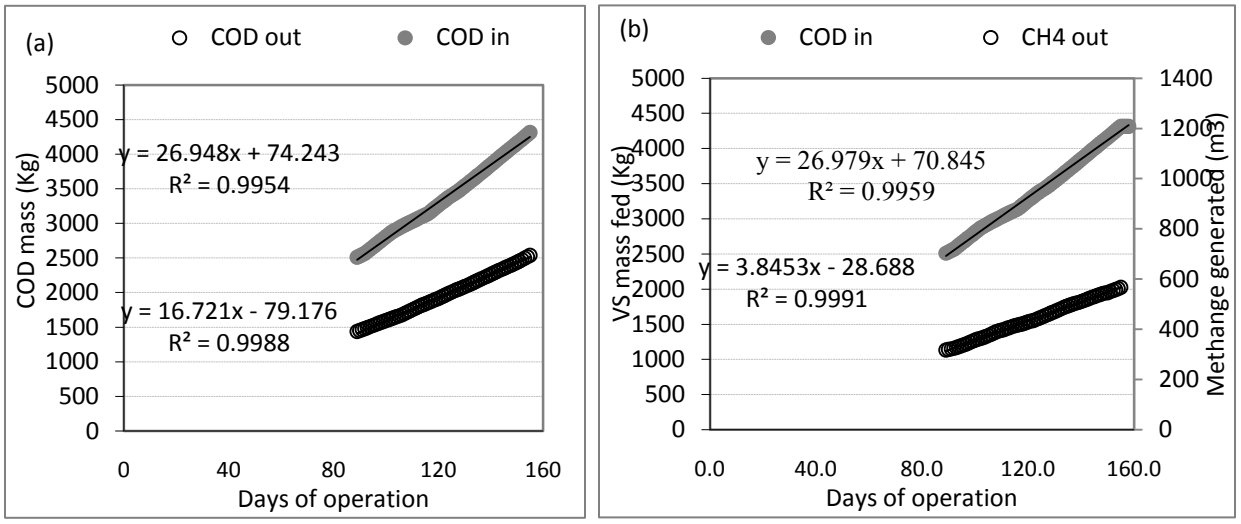


Figure E-7 Control digester 15-15: (a) COD removal (b) Methane generated per COD fed

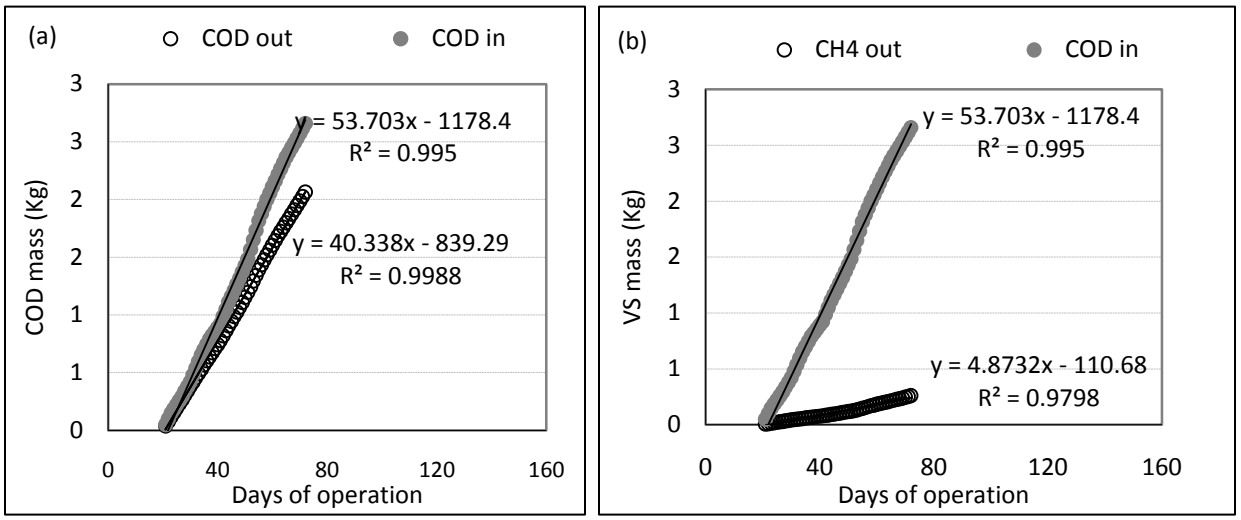


Figure E-8 Control digester 7-7: (a) COD removal (b) Methane generated per COD fed

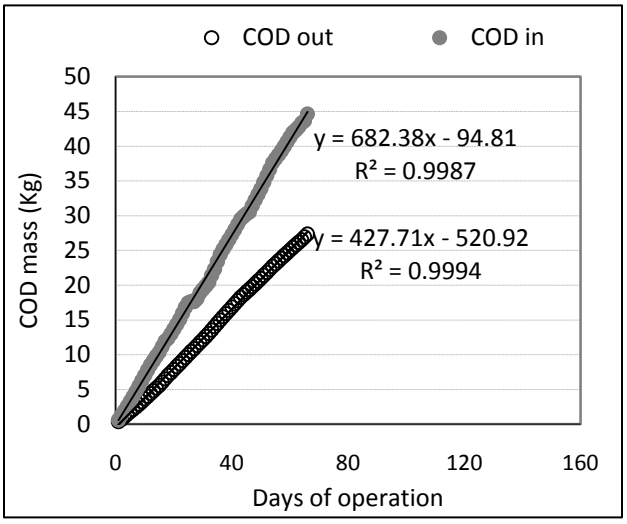


Figure E-9 Pilot control digester 15-15: COD removal

Appendix F Digested sludge nitrogen fractions, alkalinity and volatile fatty acids data

Table F-1 Digested sludge nitrogen fraction, alkalinity, acetic and propionic acid steady state data

Experiment	Days	TKN	NH_4-N	Alkalinity	Acetic acid	Propionic acid	Statistics
AnM 15-30 Experiment 1	92	1105	640	3140	2.5	0	
	99	1365	637	3145	3.3	0	
	106	1510	794	3085	4.5	0	
	113	1385	777	3620	1.9	0	
	124	1265	781	4615	2.2	0	
	128	1195	822	3685	2.9	0	
	134	1765	778	4145	12.2	2	
	141	1640	768	3825	24.5	2.1	
	149	1740	684	3835	19.3	2.8	
	155	1430	747	3910	8.8	1.6	
		1440	**743**	**3701**	**8**	**0.9**	Average
		224	**66**	**485**	**8**	**1.2**	SD
		10	**10**	**10**	**10**	**10**	N
		0.859	**0.067**	**0.431**	**0.012**	**< 0.005**	P value
AnM 7-30 Experiment 2	117	2010	489	4000	0	0	
	125		466	4500	2	0	
	134	2030	632	5290	3	0	
	145	2330	752	6970	8	0	
	152	2160	738	6150	4	0	
	160	2110	590	5300	4	0	
		2128	**611**	**5368**	**3**	**0**	Average
		128	**121**	**1078**	**2**	**0**	SD
		5	**6**	**6**	**6**	**6**	N
							P value
AnM 7-15 Experiment 3	2000	781	6400	6	0	2000	
	1940	712	5280	8	0	1940	
	1970	**747**	**5840**	**7**	**0**	**1970**	Average
	42	**49**	**792**	**2**	**0**	**42**	SD
	2	**2**	**2**	**2**	**2**	**2**	N
	0.227	**0.227**	**0.227**	**0.227**	**0.227**	**0.227**	P value

Control digester: 30-30 Exp-1	99	1105		2715	4	0	
	106	1105	758	2770	9	0	
	113	1200	754	3240	10	0	
	124	1065	784	3580	2	0	
	128	1060	777	3390	5	0	
	134	1385	762	2910	28	3	
	149	1250	797	3420	16	1	
	155	1170	738	3425	14	2	
		1168	**767**	**3181**	**11**	**0.8**	Average
		110	**20**	**334**	**8**	**1.2**	SD
		8	**7**	**8**	**8**	**8**	N
		0.306	**0.892**	**0.155**	**0.337**	**0.005**	P value
Control digester: 15-15 Experiment 1	92	984		2,360	89	8	
	106	1,090	648	2,660	97	5	
	113	1,265	788	2,665	50	6	
	124	1,130	743	3,755	35	8	
	134	1,450	737	3,235	176		
	136	1,340	727	3,075	36	8	
	141	1,340	727	3,075	36	8	
	149	1,290	656	3,140	30	16	
	155	1,195	696	3,160	51	10	
		1232	**715**	**3014**	**67**	**9**	Average
		145	**47**	**406**	**48**	**3**	SD
		9	**8**	**9**	**9**	**8**	N
		0.893	**0.455**	**0.306**	**0.05**	**0.1**	P value
Control digester: 7-7 Experiment 2	20	1130	436	2110	8		
	27		474	2040	4		
	48	1110	424	2020	6		
	55	1190	387	2150	9		
	61	1150	452	2260	10		
		1145	**435**	**2116**	**7.5**		Average
		34	**33**	**96**	**2.6**		SD
		4	**5**	**5**	**5.0**		N
		0.705	**0.868**	**0.612**	**0.510**		P value
Pilot control digester: 15-15 Experiment 3	11	1400	524	3850			
	17	700	1160	3900			
	25	1690	621	4420			
	29	1270	749	4790			
	42	1690	722	4950			
	50	1290	671	4300			
		1340	**741**	**4368**			Average
		365	**220**	**450**			SD
		6	**6**	**6**			N
							P value

Transient and steady state digested sludge nitrogen fraction, alkalinity and acetic concentrations profile

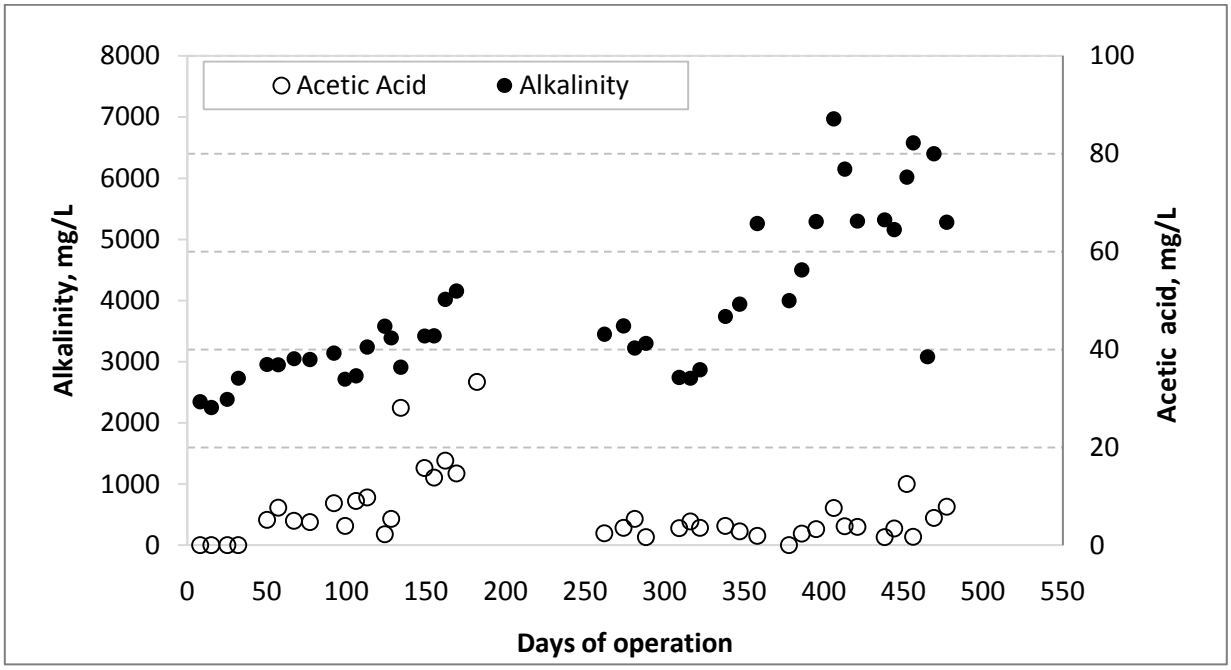


Figure F-1 Alkalinity and acetic acid concentrations profile of sludge digested using AnM (test) digesters

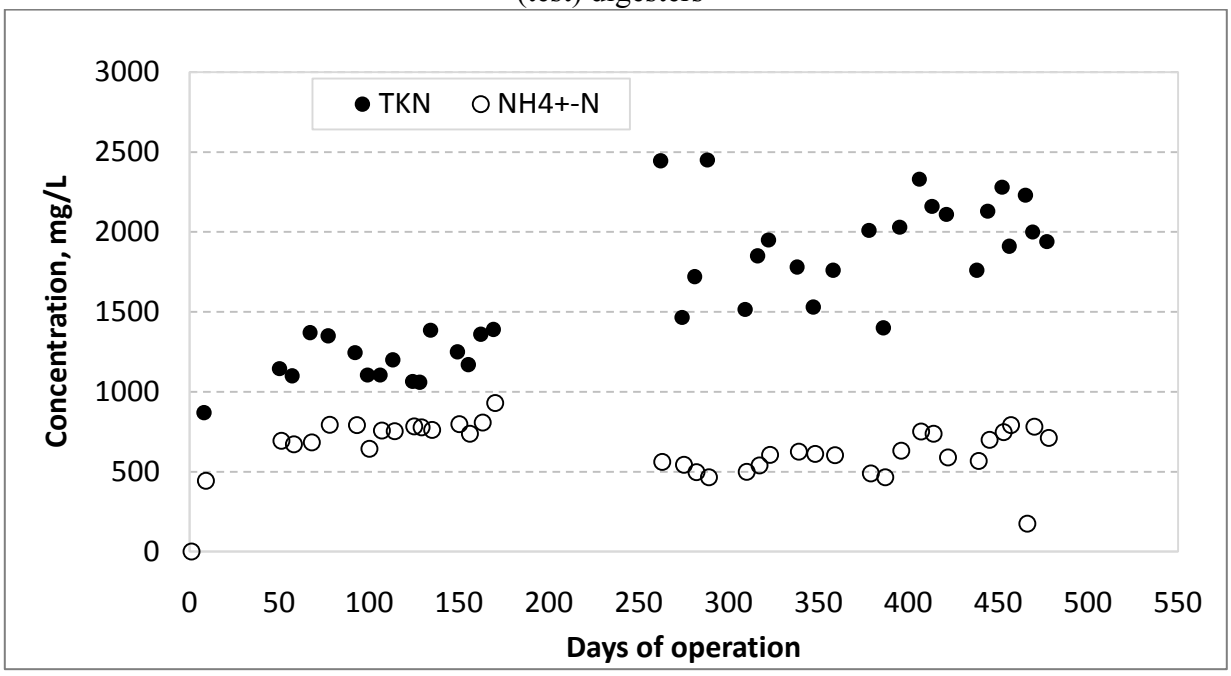


Figure F-2 TKN and NH4-N concentrations profile of sludge digested using AnM (test) digesters

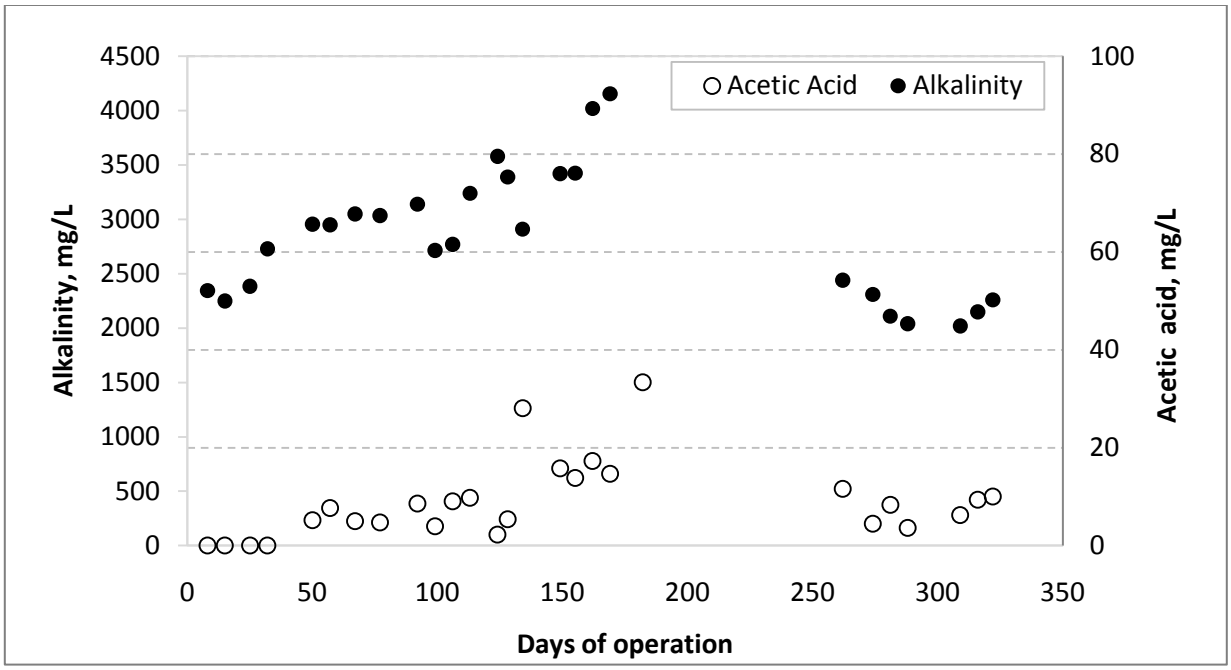


Figure F-3 Alkalinity and acetic acid concentrations profile of sludge digested using conventional (test) digesters

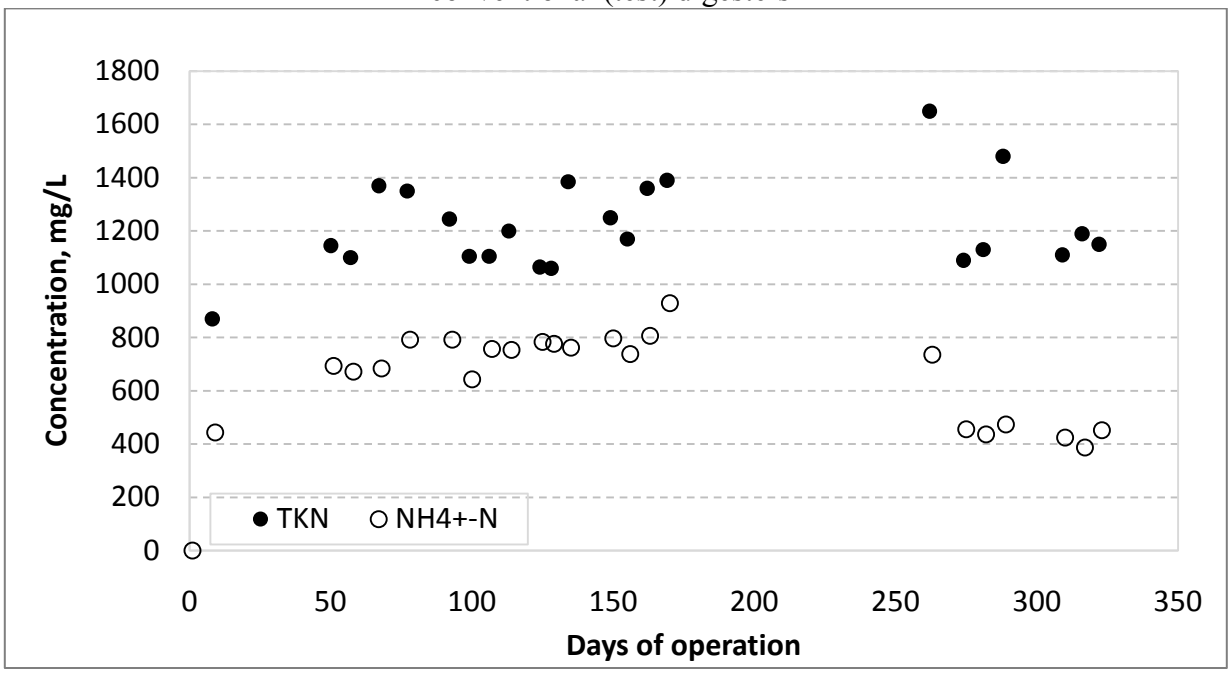


Figure F-4 TKN and NH4-N concentrations profile of sludge digested using conventional (test) digesters

Appendix G Relationship between particle size distribution, colloidal proteins and carbohydrates, and relative hydrophobicity

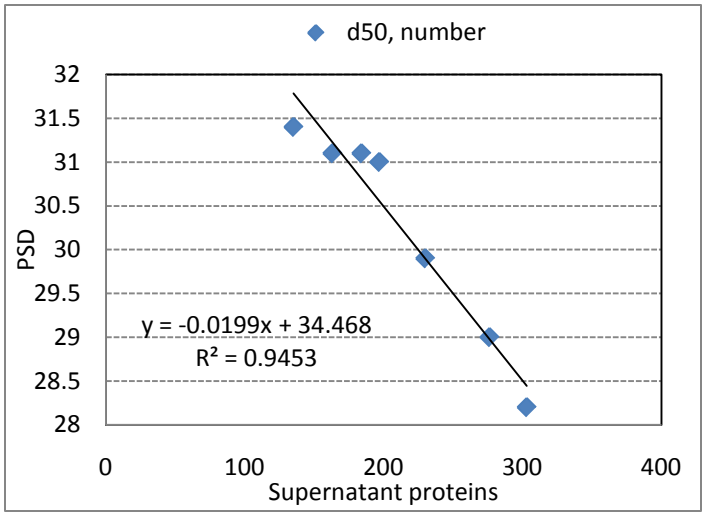


Figure G-1 Particle size distribution versus supernatant proteins

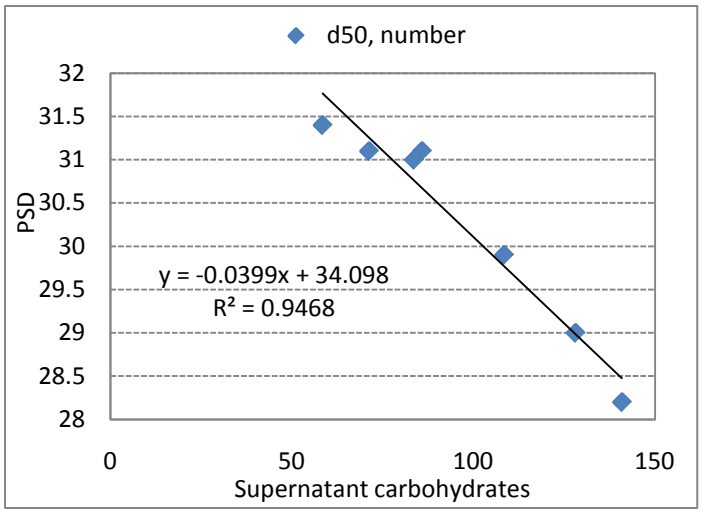


Figure G-2 Particle size distribution versus supernatant carbohydrate

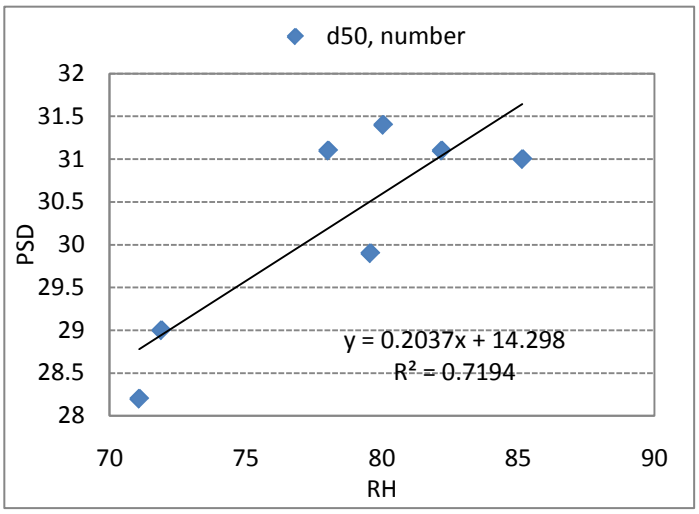


Figure G-3 Particle size distribution versus relative hydrophobicity

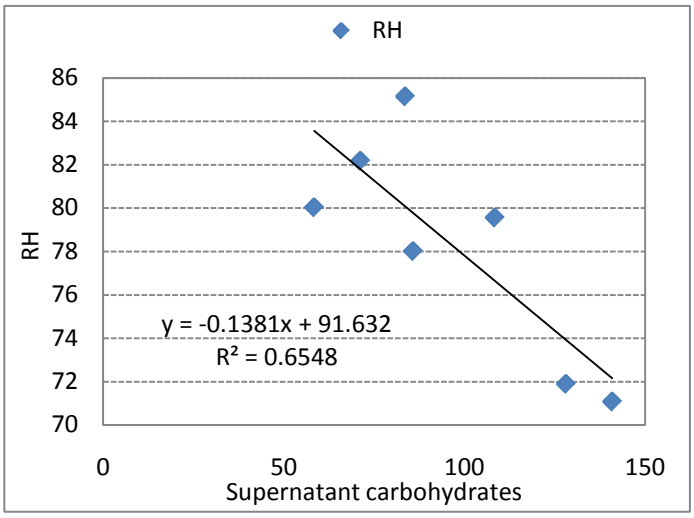


Figure G-4 Relative hydrophobicity versus supernatant carbohydrate

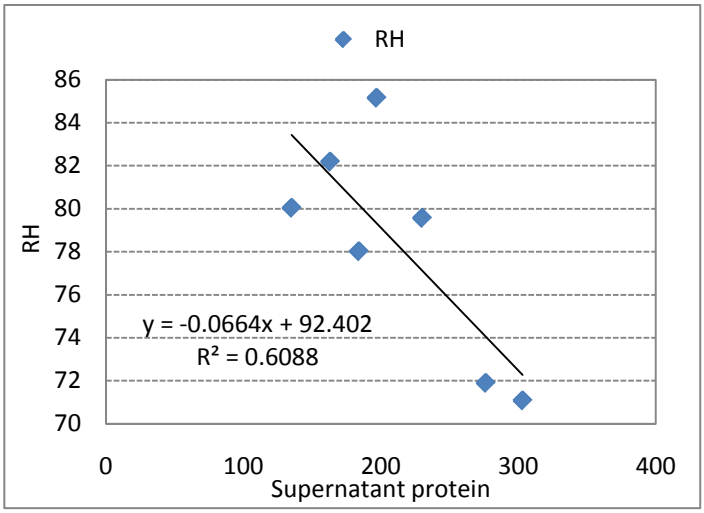


Figure G-5 Relative hydrophobicity versus supernatant protein