**Optimization of Anaerobic Membrane Bioreactor Operation for
Brewery Wastewater Treatment**

by

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ABSTRACT

OPTIMIZATION OF ANAEROBIC MEMBRANE BIOREACTOR OPERATION FOR BREWERY WASTEWATER TREATMENT

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The micro-brewery business has been subjected to rapid growth within the last decade. Most brewers are facing expensive wastewater compliance bills and are seeking reliable on-site treatment methods. Anaerobic membrane bioreactor (AnMBR) treatment is favorable to the widely used upflow anaerobic sludge blanket (UASB) method. It offers high quality effluent free of solids, and has great stabilities under loading shocks. To date, there have been limited submerged AnMBR studies and none have been conducted on brewery wastewater. In this research, a state-of-the-art AnMBR laboratory scale system was used to investigate the performance and capability. The system was subjected to 230 days continuous operation with both synthetic and real brewery wastewater at organic loading rates (OLRs) ranging from 2 to 11.5 kg COD/m³/day. While the system demonstrated an excellent biological performance, the study found that the major limitation of AnMBR was the membrane fouling, which increased with the OLR and soluble microbial products (SMPs) in the mixed liquor.

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TABLE OF CONTENTS

Abstract	i
Acknowledgements	iii
Table of Contents	iv
Table of Tables	vii
Table of Figures	viii
Abbreviations	x
CHAPTER 1 - Introduction	1
1.1. Objectives of this study	3
1.2. Research Approach	4
1.3. Thesis Organization.....	5
CHAPTER 2 - Literature Review	6
2.1. Brewery Wastewater & Treatment.....	6
2.1.1. Brewery Wastewater Characteristics	7
2.1.2. Wastewater Treatment for Micro-breweries in Ontario.....	10
2.1.3. Anaerobic Treatment and Limitation of Conventional Methods	12
2.1.4. Introduction of AnMBR.....	15
2.2. AnMBR in The Food and Beverage Industry	19
2.2.1. AnMBR Developments.....	19
2.2.2. Laboratory Research	22
2.2.3. Commercial Applications	29
CHAPTER 3 - Synthetic wastewater	34
3.1. Abstract	34

3.2.	Introduction	35
3.3.	Material and Methods.....	38
3.3.1.	AnMBR System	38
3.3.2.	Wastewater Characteristics	39
3.3.3.	AnMBR Operation.....	40
3.3.4.	Bench Scale Filtration System	41
3.3.5.	Analytical Methods	42
3.4.	Result and Discussion	43
3.4.1.	System Performance	43
3.4.2.	Biomass Characteristics	46
3.4.3.	Soluble Microbial Product Characteristics	47
3.4.4.	Membrane Filtration Performance	50
3.4.5.	Bench Scale Filtration System	53
3.5.	Conclusion.....	54
3.6.	Acknowledgement.....	55
CHAPTER 4 -	Local Craft Brewery wastewater	56
4.1.	Abstract	56
4.2.	Introduction	57
4.3.	Materials and Methods	60
4.3.1.	AnMBR System	60
4.3.2.	Wastewater Characteristics	61
4.3.3.	AnMBR Operation.....	61
4.3.4.	Analytical Methods	62
4.4.	Results and Discussion.....	63
4.4.1.	Brewery Wastewater Characteristic.....	63

4.4.2.	COD Removal Efficiency	65
4.4.3.	COD in the Mixed Liquor.....	68
4.4.4.	Biogas Production.....	70
4.4.5.	Bicarbonate Dosage	71
4.4.6.	Nutrient Removal.....	72
4.4.7.	Biomass Characteristics	76
4.4.8.	Soluble Microbial Product Characteristics	77
4.4.9.	Membrane Filtration Performance	81
4.5.	Conclusion.....	85
4.6.	Acknowledgement.....	86
CHAPTER 5 -	Conclusion and recommendations.....	87
5.1.	Overall discussion and Conclusion	87
5.2.	Recommendations	89
CHAPTER 6 -	References	91
CHAPTER 7 -	Appendices	98
7.1.	Appendix I – AnMBR Operation Data	99
7.2.	Appendix II – Critical Flux Data.....	105

TABLE OF TABLES

Table 2-1 Main areas of wastewater generation (adopted from (Brewers Association, n.d.))	
.....	8
Table 2-2 Brewery wastewater characteristics	8
Table 2-3 Reported surcharge rates for some Southern Ontario municipalities (Stantec Ltd., 2012).....	11
Table 2-4 Comparison of aerobic and anaerobic treatment (Adopted from (Lin et al., 2013)).....	13
Table 2-5 Summary of lab scale AnMBR configuration and performance for treatment of food & beverage wastewater.....	23
Table 2-6 Summary of pilot and full scale AnMBR configuration and performance for treatment of food & beverage wastewater	32
Table 3-1 Composition of the synthetic wastewater.....	39
Table 3-2 Characterization of the synthetic brewery wastewater	40
Table 4-1 Operation conditions during the study	62
Table 4-2 Brewery wastewater characteristic	64

TABLE OF FIGURES

Figure 2-1 Schematic of AnMBR configurations. (a) External cross-flow AnMBR; (b) Fully submerged AnMBR; (c) Submerged AnMBR with membrane immersed in external tank.....	17
Figure 3-1 AnMBR system showing digester (centre) and membrane tank (right)	38
Figure 3-2 Bench scale filtration setup, digester showing in centre	41
Figure 3-3 COD concentration in the membrane permeate and COD removal efficiency for different organic loading rates.....	43
Figure 3-4 COD concentration in the membrane permeate, 1.5 μm and 0.45 μm filtrate of the mixed liquor	44
Figure 3-5 Biogas production for different OLR.....	46
Figure 3-6 MLSS and MLVSS change with time.....	47
Figure 3-7 EPS concentration in bulk sludge	48
Figure 3-9 EPS concentration in permeate	49
Figure 3-10 Protein and polysaccharide composition in mixed liquor	50
Figure 3-11 TMP and critical flux change over time.....	51
Figure 3-12 Relationship between EPS in bulk sludge and critical flux	52
Figure 3-13 Effect of gas scouring on critical flux	53
Figure 4-1 AnMBR system showing digester (centre) and membrane tank (right)	60
Figure 4-2 Influent COD and removal efficiency.....	65
Figure 4-3 Effluent COD and VFA concentration.....	66
Figure 4-4 Effluent BOD and COD concentration comparison.....	68
Figure 4-5 COD concentration in the 1.5 μm , 0.45 μm filtrate and membrane permeate ..	69

Figure 4-6 Biogas production under various OLR operation	70
Figure 4-7 Influent total alkalinity and sodium bicarbonate dosage over the study	71
Figure 4-8 Total nitrogen in feed, permeate and sludge filtrate	72
Figure 4-9 NH ₃ -N in feed, permeate and sludge filtrate	72
Figure 4-10 Total phosphorus in feed, permeate and sludge filtrate	74
Figure 4-11 Orthophosphate-P in feed, permeate and sludge filtrate	74
Figure 4-12 MLSS and MLVSS profile.....	76
Figure 4-13 Polysaccharide in bulk sludge filtrate and permeate.....	78
Figure 4-14 Protein in bulk sludge and permeate	79
Figure 4-15 Polysaccharide and protein composition in mixed liquor	80
Figure 4-16 TMP profile and measured critical flux	81
Figure 4-17 Relationship between critical flux and EPS in bulk sludge	83
Figure 4-18 Effect of gas scouring on critical flux	84

ABBREVIATIONS

AnMBR – Anaerobic Membrane Bioreactor

BOD – Biological Oxygen Demand

CIP – Cleaning-In-Place

COD – Chemical Oxygen Demand

CSTR – Continuous Stirred-Tank Reactor

TSS – Total Suspended Solid

VSS – Volatile Suspended Solid

HRT – Hydraulic Retention Time

LMH – Liter / m² / Hour

MLSS – Mixed Liquor Suspended Solids

MLVSS – Mixed Liquor Volatile Suspended Solids

MWCO – Molecular Weight Cutoff

ODFs – Over strength Discharge Fees

OLR – Organic Loading Rate

PABR – Periodic Anaerobic Baffled Reactor (PABR)

EPS - Extracellular polymeric substances

SRT – Solid Retention Time

TKN – Total Kjeldahl Nitrogen

TMP – Transmembrane Pressure

TN – Total Nitrogen

TP – Total Phosphorous

UASB – Upflow Anaerobic Sludge Blanket

VFA – Volatile Fatty Acids

WWTP – Wastewater Treatment Plant

CHAPTER 1 - INTRODUCTION

Over the last decade, the brewery industry structure has changed in Canada. The number of large operation plants has reduced while the number of micro-breweries has considerably increased (Bureau, 2009). With the large growth in the micro-brewery business, municipalities are paying more attention to the environmental issues associated with micro-breweries. Micro-breweries, like any other food and beverage business, must meet the wastewater compliances. Most micro-breweries do not have any dedicated on-site wastewater treatment system; they discharge untreated effluent to a municipal wastewater treatment plant (WWTP). This action results in an expensive wastewater surcharge bill. These surcharges, or over strength discharge fees (ODFs), are in addition to the regulatory sewerage and treatment charges. The surcharges are intended for the municipality to cover the extra cost on WWTP operation for treating the over strength discharges. Paying the bill for continuous high strength wastewater discharging is very costly, which limits the growth of the micro-brewery business. Therefore, many micro-breweries are seeking solutions for on-site treatment.

Anaerobic digestion is suitable for treating brewery wastewater, because the effluent from the brewery industry is high in strength and easily biodegradable with a high biological oxygen demand (BOD) to chemical oxygen demand (COD) ratio of 0.6-0.7 (Brito et al., 2007; Rao et al., 2007). Currently, upflow anaerobic sludge bed (UASB) reactors are widely used in the beverage industry. However, they still have a few major drawbacks, including a long start-up period and the requirement of highly skilled operation to prevent biomass loss. Organic loading rates (OLRs) or pH shocks from the

batch brewing operations can result in problems such as de-granulation and biomass washout.

Anaerobic membrane bioreactor (AnMBR) represents an advanced technology that has been revitalized by academia and membrane solution providers. With the integration of ultrafiltration (UF) membranes, the AnMBRs can retain all of the biomass and solids. Therefore, it offers a complete separation between solid retention time (SRT) and hydraulic retention time (HRT) as well as a high tolerance to pH and OLR shocks (Dereli et al., 2012a). The great stability under loading shocks and minimum labour requirement are argued to be the principal benefits compared to the UASB process. Quick start-up times for AnMBRs have been reported generally under 2 weeks (Lin et al., 2013). Although the AnMBR technology is more industrialized in some European countries, it remains in the developing stage in other parts of the world. There are limited pilot or full scale applications reported in available English publications.

There are two configurations used for AnMBRs, including the external cross-flow and the submerged membrane configurations. Most AnMBR studies to date have used an external cross-flow configuration, where it can operate at higher flux while providing direct hydrodynamic control of fouling through cross-flow velocity. However, this arrangement operates at high energy consumption and requires more frequent cleaning (Le-Clech et al., 2006). Further, multiple studies reported that high cross-flow velocity has a negative effect on the biomass activities due to the high shear stress on the microorganisms, and therefore destroys the sludge flocs (Brockmann and Seyfried, 1996; Choo and Lee, 1996).

Attributable to the submerged MBR concept developed by Dr. Yamamoto (Yamamoto et al., 1989) and the substantial revolutions in the membrane development over the last 20 years (Cote et al., 2012), submerged MBRs are able to operate with manageable energy requirements and pressures up to two orders of magnitude lower than external cross-flow processes. Advancements in membrane technology have presented great opportunities for the development of more effective AnMBRs. To date, there have been limited submerged AnMBR studies and none have been conducted on brewery wastewater.

Although the excellent COD removal efficiency and biogas generation of AnMBR are well proven, long HRTs and lower OLRs are applied under full scale applications for food processing wastewater (Christian et al., 2010). Several literatures have reported that the high biomass concentration and OLR puts stress on the membrane compartment (Ince et al., 1993; Saddoud and Sayadi, 2007). Low operation fluxes and high gas scouring requirements increase both capital and operation cost. Research on optimizing the OLR and biomass concentration in respect to both digestion and membrane performance would greatly help to shift AnMBR onto industrial-scale applications.

1.1. OBJECTIVES OF THIS STUDY

The general goal of this research is to evaluate the efficacy of submerged AnMBR technology in treating wastewater from micro-brewery applications and determine optimum operating conditions for the future commercial implementation. Detailed objectives of this research are:

- a) To demonstrate the efficacy of brewery wastewater treatment using a state-of-the-art laboratory scale submerged AnMBR unit, which is equipped with hollow fiber ultrafiltration membranes (GE Water & Process Technologies).
- b) To compare the effect of OLR on AnMBR performance, by evaluating the organic matter removal efficiency, effluent quality, methane yield, biomass growth, soluble microbial product (EPS) generation rate and membrane filterability.
- c) To evaluate the effect of biomass concentration in the mixed liquor on EPS generation and membrane fouling.
- d) To compare the strength and characteristics of synthetic and real wastewater from a local micro-brewery and assess differences in system performance.
- e) To determine the optimal OLR, MLSS and operation flux based on effluent quality and long term membrane performance.

1.2. RESEARCH APPROACH

In completing the study, a laboratory scale submerged AnMBR was continuously operated for 230 days. During the first 140 days, synthetic wastewater was applied to the system with OLR precisely controlled and step increased from 2 kg COD/m³/day to 10 kg COD/m³/day. The operation was then carried with real brewery wastewater from a local micro-brewery for another 90 days with uncontrolled OLR, which ranged from 3.5 to 11.5 kg COD/m³/day.

Feed, membrane permeate and sludge were sampled weekly and tested for TSS, VSS, COD, TN, TP, NH₄⁺-N, PO₄⁻³-P, VFA, Tot Alk, polysaccharide and protein. The treatment performance was predominantly evaluated by COD removal. Permeate COD

was tested every three days under controlled synthetic wastewater operation and was then closely monitored on a daily basis, after being switched with uncontrolled real wastewater. Total alkalinity, pH and VFA concentration were used as indicators for system stability. Biomass growth and yield were determined by daily MLSS and MLVSS monitoring. Methane yield was calculated from the continuous quantity data and the biogas composition was analysed by gas chromatography. Membrane filtration performance was evaluated through long term transmembrane pressure (TMP) monitoring and weekly critical flux testing.

A bench top bioassay membrane filtration system was built to investigate EPS production and membrane filterability on anaerobic sludge over different biomass concentrations. Short term (~ 1 week) constant flux filtrations were conducted within a controlled mesophilic environment. TMP and biogas production were monitored and sludge samples were taken for EPS quantification and prepared for advanced characterization.

1.3. THESIS ORGANIZATION

The research findings from this study are presented in manuscript format as two standalone publications. This thesis is organized into seven chapters. The research background and objectives are provided in Chapter 1. Chapter 2 covers the literature review on brewery wastewater characteristics and AnMBR case studies in the food and beverage industry. Chapter 3 and 4 present two related AnMBR studies on the treatment of precisely controlled synthetic wastewater and uncontrolled real brewery wastewater. Each chapter has its own conclusions. Chapter 5 compares and summarizes the two studies. References are listed in Chapter 6 and the Appendix is provided in Chapter 7.

CHAPTER 2 - LITERATURE REVIEW

This section will outline background information and earlier literatures that are fundamental to the thesis. Contents will be organized into three sub-sections. The first section will outline the significance of wastewater treatment in the brewery industry and introduce AnMBR technology, followed by a comprehensive review of the recent AnMBR applications in the food and beverage industry.

2.1. BREWERY WASTEWATER & TREATMENT

The structure of beer sales in Canada has slightly changed in the last few years. Instead of buying from popular brands, consumers are showing preference for craft beer. The number of large beer manufacturing plants has decreased while the number of micro-breweries has increased substantially (Bureau, 2009). There are over 47 micro-breweries in Ontario and most of them are facing an excessive amount of wastewater surcharge for discharging high strength wastewater to municipal sewer systems (MEDEI, 2012).

Recycling of the regenerated wastewater in the brewery industry is considered inappropriate for production purpose (Braeken et al., 2004). Therefore, many micro-breweries are seeking pre-treatment methods to reduce the organic load prior to sewer discharge.

This section will briefly discuss brewery wastewater strength and characteristics, and the driving force behind the sustainable development of micro-breweries in Ontario, as well as the conventional anaerobic treatments and their limitations. Further, this section will introduce the AnMBR technology, which can greatly improve the drawbacks of both conventional and UASB processes.

2.1.1. Brewery Wastewater Characteristics

Beer making involves multiple and complex processes, with major steps include mashing, filtering and boiling wort, as well as fermenting and packaging. Wastewater can be generated in each process by either discharging waste or rinsing equipment. Although each brewery will have different wastewater strength and characteristics related to their operation practices, the U.S. Brewers Association have summarized and published some typical wastewater characteristics from key processes in their Water and Wastewater Sustainability Manual. Table 2-1 shows some major areas of wastewater generation and the approximate wastewater strength. The quantity and quality of the wastewater being generated in each operation varies significantly. Effluent from rinsing fermenters, whirlpools and filters is extremely high in strength but low in volume. However, packaging and cleaning can generate large quantities of effluent containing mostly water and little organic content.

Table 2-1 Main areas of wastewater generation (adopted from (Brewers Association, n.d.))

Source	Operation	Composition	Strength
Mash Tun	Rinsing	Cellulose, sugars, amino acids	BOD ~3000 mg/L
Lauter Tun	Rinsing	Cellulose, sugars, spent grain	BOD ~10,000 mg/L, TSS~3000 mg/L
Spent Grain	Last run and washing	Cellulose, nitrogenous material	BOD ~100,000 mg/L, TSS ~30,000 mg/L
Boil Kettle	Dewatering	Nitrogenous residue	BOD ~ 2000 mg/L
Whirlpool	Rinsing spent hops and hot trub	Proteins, sludge and wort	BOD ~85,000 mg/L, TSS ~35,000 mg/L
Fermenters	Rinsing	Yeast	BOD ~100,000 mg/L, TSS ~6000 mg/L
Storage tanks	Rinsing	Beer, yeast, protein	BOD ~80,000 mg/L, TSS ~4000 mg/L
Filtration	Cleaning, start up, end of filtration, leaks	Beer, yeast, protein	BOD ~135,000 mg/L, TSS ~60,000 mg/L
Beer spills	Waste, flushing	Mostly water, beer	BOD ~1000 mg/L
Bottle/keg washing	Discharges	Beer, cleaning chemicals	High BOD and TSS, possibly high pH
Miscellaneous	Cleaning and sanitation. Floor washing, etc.	Detergents, cleaning chemicals	Low BOD, TSS, possibly low pH

Table 2-2 Brewery wastewater characteristics

Parameters	Survey U.S.	Survey	Opaque	Unicer	Craft	Large plant	China 1	China 2
pH	3 - 12	4.5 - 12	4.5 ± 0.6	6.5 - 7.9	6.27 ± 2.45	3 - 12	6.5 ± 0.2	7.5 ± 0.5
TSS (mg/L)	200 - 1500	200 - 1000	2840 ± 180		6300 ± 2700	2900 - 3000	480 ± 70	207 ± 53
COD (mg/L)	1800 - 5500	2000 - 6000	12500 ± 4300	800 - 3500	4000 ± 2100	2000 - 6000	2250 ± 420	1585 ± 170
BOD (mg/L)	600 - 5000	1200 - 3600		520 - 2300	2800 ± 1040	1200 - 3600	1340 ± 335	710 ± 150
BOD/COD	0.77	0.60		0.66	0.70	0.60	0.60	0.45
TN (mg/L)	30 - 100	25 - 80	0.023 ± 0.007	12 - 31	200 ± 30 ^a	25 - 80 ^a	54 ± 14 ^c	67 ± 15
TP (mg/L)	30 - 100	10 - 50	59 ± 52	9 - 15	95 ± 20	10 - 50 ^b	50 ± 35	10 ± 2
Reference	(Brewers Association, n.d.)	(Driessen and Vereijken, 2003)	(Parawira et al., 2005)	(Brito et al., 2007)	(Stadlbauer et al., 1994)	(Rao et al., 2007)	(Wang et al., 2008)	(Zheng et al., 2014)

^a TKN, ^b PO₄-P, ^c NH₃-N

Wastewater characteristics from two surveys and six case studies are shown in Table 2-2. The qualities of brewery effluents vary significantly among the different breweries. Moreover, in the same brewery, the effluent characteristic can fluctuate significantly as it depends on the different processes that are taking place within the brewery. In general, the brewery wastewater consists of sugar, starch, ethanol and volatile fatty acids (VFAs). The wastewater is slightly acidic and has low suspended solids, high organic matter as well as low nutrient contents. Many studies has reported that the brewery effluents are easily biodegradable with high BOD/COD ratio of 0.6-0.7 (Brito et al., 2007; Rao et al., 2007). Nitrogen and phosphorus levels mainly depend on the amount of yeast present in the effluent (Brito et al., 2007; Driessen and Verejiken, 2003).

Almost all micro-breweries combine wastewater streams together prior to discharge. Depending on the operation, the composition and characteristic of the discharged wastewater fluctuate momentarily. While most large breweries have their own wastewater treatment facilities either to meet municipal by-laws or to reduce the organic load (Simate et al., 2011), it is rare to find micro-breweries operate their own pre-treatment system. Some micro-plants have preliminary physical operations to remove coarse solid matter rather than dissolved contaminants. These operations include screening and sedimentation, but have yielded little success; the outcome of sedimentation was found unacceptable even with the addition of coagulants (Sheehan and Greenfield, 1980). Due to the high BOD level, almost no raw wastewater from the brewery industry meets sewer discharge standards, which will be discussed in the next section.

2.1.2. Wastewater Treatment for Micro-breweries in Ontario

Beer is composed mostly of water, yet the amount of water used in production is far greater than that within the beer itself. A study to benchmark water usage in the brewery industry was conducted in 2011 by the Beverage Industry Environmental Roundtable (BIER)(Brewers Association, n.d.). There were 211 breweries in the United States that participated in the study. The majority were larger brewers; however, the conclusions can be assumed to be representative for craft breweries. The study reported that in 2010, the water usage for 1 liter of beer production ranged from 3.26 to 7.44 liters. Conclusions were also drawn regarding the facility size, where larger facilities tend to have lower water use ratio. This was likely due to better management practices in the brewing and packaging processes. There are 47 micro-breweries in Ontario, with approximately \$190 million sales in 2010, equivalent to a 5% share of the Ontario beer market, and sales had grown 45% in 2011 (MEDEI, 2012). With the growth in production, some micro-breweries have started to look into environmental issues, especially wastewater management.

The largest driver has been wastewater compliance. Not many micro-breweries have a dedicated on-site wastewater treatment system, whereas most of them discharge untreated effluent to a municipal wastewater treatment plant (WWTP). Although the highly biodegradable wastewater being discharged is generally compatible with the municipal WWTP, it costs the plant more to treat high strength wastewater compared to treating discharge under the by-law limits. Municipalities charge these brewers over strength discharge fees (ODFs) in excess to the regulatory sewerage and treatment custody. These surcharges are usually based on the incoming water quantity, since only a few micro-

breweries have an effluent discharge metering system installed. The effluent quality is usually tested at the point to discharge by the municipality. The water quality results are then evaluated in according to the Sewer Use By-laws. In Ontario, almost all Sewer Use By-laws were based off the 1998 model provided by the Ministry of the Environment (MOE, 1998). The set discharge limits for major contaminants are 300mg/L for biochemical oxygen demand (BOD₅), 350 mg/L for total suspended solids (TSS), 100 mg/L for Total Kjeldahl Nitrogen (TKN) and 10 mg/L for total phosphorous (TP), respectively. The common ODF structure used in Ontario is based off Water Environment Federation (WEF) Financing and Charges for Wastewater Systems (3rd Edition) (Federation, 2004). Typically, the actual concentrations of the four surcharge-able parameters are compared with the Sewers By-law limits. The concentration difference is then used to calculate ODFs as $ODF = (\text{actual concentration} - \text{Sewer By-law limit}) * \text{volume} * \text{rate}$ and the surcharge of each parameter is addition to another. Surcharge rates for some municipalities in Southern Ontario are listed in Table 2-3, where the rate is with respect to the discharge load in kilograms.

Table 2-3 Reported surcharge rates for some Southern Ontario municipalities (Stantec Ltd., 2012)

Municipality	BOD5	TSS	TKN	TP
Toronto	\$0.62	\$0.60	\$1.18	\$1.69
York	\$0.53	\$0.53	\$0.53	\$2.65
Hamilton	\$0.67	\$0.53	\$2.03	\$1.43
Ottawa	\$1.44	\$0.77	\$5.75	\$2.31
Durham	\$0.48	\$0.48	\$0.48	\$0.48

In general, the intention of ODF is to recover the additional costs that are associated with the treatment of high strength wastewater and to upkeep a sustainable operation of the WWTPs (MOE, 1998). However, paying surcharge bills to municipalities for continuous discharging is very costly, especially to the brewery industry, which discharges high

strength wastewater with an excessive load in BOD₅. The surcharge bills often limit the growth of the micro-brewery business. Additionally, due to the development of cities and the capacity of WWTPs, some municipalities may enforce an on-site treatment system in case of expanding the existing brewery plant.

In addition to the regulatory surcharges, advertising a wastewater improvement program at craft breweries can positively impact their brand image and public recognition. Since most micro-breweries sell their products locally, having a good image in sustainable development and wastewater management can help with brand recognition and profits.

2.1.3. Anaerobic Treatment and Limitation of Conventional Methods

The brewery wastewater is highly biodegradable and has high organic strength; however it has insufficient nutrients for aerobic digestion. This leaves anaerobic treatment as an attractive alternative option. While the aerobic digestion requires intensive aeration and produces more microorganisms, there is no oxygen needed for anaerobic process and the sludge yield is much lower (Liao et al., 2006). These improvements can lower the operation costs dramatically. Furthermore, anaerobic microorganisms convert organic compounds into biogas, which can be utilized directly in a boiler. The biogas usually contains 55-75% methane and 25-40% carbon dioxide and traces of hydrogen sulfide (Briggs et al., 2004). A comparison between aerobic and anaerobic treatment on industrial wastewater is shown in Table 2-4. Anaerobic treatment shows an overall advantage over aerobic treatment. However, the widespread application of conventional anaerobic treatment is limited due to the intrinsic low biomass yield of anaerobic bacteria. A long start-up time and large reactor volume is required to provide sufficient solid retention time (SRT) for the methanogens. The large footprint becomes extremely

challenging as the on-site space arrangement is very crucial. Ince et al. (1993) reported that the OLR can be applied up to 6 COD/m³/day in a full scale conventional anaerobic digester. Any further increase would be restricted by an insufficient amount of biomass retained in the reactor.

Table 2-4 Comparison of aerobic and anaerobic treatment (Adopted from (Lin et al., 2013))

Parameters	Aerobic Treatment	Anaerobic Treatment
COD removal efficiency	High	High
Effluent quality	High	Moderate
Organic loading rate	Moderate	High
Sludge production	High	Low
Nutrient requirement	High	Low
Alkalinity requirement	Low	High (depends on strength)
Energy requirement	High	Low
Temperature sensitivity	Low	Moderate
Start-up time	2-4 weeks	2-4 months
Energy recovery	No	Yes

With the recognition of the crucial importance of bacterial immobilization, the high rate anaerobic digester was developed in the 1960s and early 1970s. These developments made the anaerobic treatment system feasible and brought public acceptance to anaerobic digestion in wastewater treatment. Two breakthrough developments were the anaerobic filter (AF) system developed in 1964 by McCarty and his co-workers at Stanford University and the upflow anaerobic sludge bed (UASB) reactor by Dr. Lettinga from Agricultural University in Wageningen, 1970 (Lettinga, 2011). Further developments include but are not limited to anaerobic fluidised bed (AFB), expanded granular sludge bed (EGSB) and internal circulation (IC) reactors. Up to date, UASB is still the most widely applied high rate anaerobic treatment process in the food and beverage industry.

In an UASB reactor, the wastewater flows vertically from the bottom, passes upwards through a dense bed of granular sludge and the anaerobic microorganisms degrade the

substrates as the wastewater come into contact. With the dense packing of granular sludge, the UASB configuration dramatically lowers space requirements and it is capable of treating high organic wastewater at higher hydraulic loads. The UASB technology made its first industrial appearance in the Dutch beet sugar industry (Klijnhout and Eerde, 1986). Through operation with granules at 2 – 5 mm in diameter, 60 – 75% removal in COD was found. The major limitation in UASB technology is the dependency on the large sludge globules with high settling velocity. It is challenging to have all anaerobic sludge staying in large globule form. Small granules and flocs tend to flush out sooner, causing biomass loss and low quality effluent. The full scale operation on opaque beer brewery wastewater has reported that there is a need to improve UASB performance in terms of organic removal (Parawira et al., 2005). Over a two year study period, a 500 m³ UASB reactor was operated under an average OLR of 6 kg COD/m³/day with influent COD ranged from 8250 to 20000 mg/L and TSS around 2800 mg/L. The overall COD and TSS removal efficiency were reported as 57% and 50% respectively, whereas the digester effluent had a high level of COD (~2000 mg/L), even under stable operation. The authors argued that the poor performance was mainly due to the presence of suspended solids in the influent and the removal efficiency could be improved based on other lab and pilot UASB studies.

A five month pilot study (Fang et al., 1990) on medium strength (avg. 2700 mg/L COD) brewery wastewater showed a better treatment efficiency. At OLR of 4.9 kg COD/m³/day, an average of 89% COD removal was achieved under stable conditions, however great fluctuations were observed following changes in organic loadings. The study indicated that the variability in strength and characteristics of the influent can have

disturbing effects on UASB performance. Due to changes in operation within the brewery plant, the effluent strength and characteristics fluctuate significantly, making it difficult to retain a constant organic loading rate. Therefore, maintaining a stable operation and consistent discharge quality through UASB treatment processes become challenging.

2.1.4. Introduction of AnMBR

While the granular formation represents the traditional high rate anaerobic bioreactor, use of membrane filtration represents an innovative and novel method to operator a bioreactor at high biomass concentration through complete biomass retention. With the use of membrane for liquid solid separation, the AnMBR is capable of completely retaining high concentrations of active biomass, thus minimizing the required reactor volume. Researchers suggested the digester volume can be scaled down to around 1/3 or 1/5 of conventional digesters, with biomass 3 to 5 times as concentrated (Kanai et al., 2010). In addition to delivering effluent free of solid, the membrane barrier also prevents any biomass loss in the effluent under organic load changes and variation in influent characteristics. Because of this, a quick system start-up can be achieved without worrying about granules breakdown or loss of biomass, thus preventing system acidification. Start-up times for AnMBRs were reported generally to be under 2 weeks (Lin et al., 2013). The great stability under loading shocks and minimum labour requirements are argued to be the principal benefits of AnMBRs compared to the UASB process. Furthermore, the complete separation of SRT from HRT allows the operator to change the treatment conditions without any adjustment made on the reactor configuration.

To date, AnMBR systems are based on two main configurations: external cross-flow membrane bioreactors (eAnMBR) and submerged membrane bioreactor (sAnMBR). In the eAnMBR configuration, the membrane modules are placed outside the digester in a cased membrane unit. A high rate pump is used to recirculate the sludge and create a forward driven pressure in the membrane unit, further pushing permeate through the membrane (Figure 2-1a). The external cross-flow configuration can operate at higher flux while providing direct hydrodynamic control of fouling by cross-flow velocity and ease of membrane maintenance. However, this arrangement operates at higher energy consumption and requires more frequent cleaning (Le-Clech et al., 2006). Further, various literatures reported that the high cross-flow velocity has a negative effect on biomass activities due to the high shear stress on the microorganisms, which destroy the sludge flocs (Brockmann and Seyfried, 1996; Choo and Lee, 1996).

Based on the submerged MBR concept developed by Dr. Yamamoto (Yamamoto et al., 1989), the submerged AnMBR (Figure 2-1b) employs membrane directly into the digester and operates under a vacuum pressure while scouring the membrane surface using recirculated biogas. Studies found this configuration operates at a much feasible pressure than the external cross-flow process, which is up to two orders of magnitude lower (Chang et al., 2002). Figure 2-1c shows the modified sAnMBR with membrane immersed in a separate tank, the biomass is being recirculated between the digester and membrane tank. This configuration is often used for full-scale MBR plants due to the ease of membrane cleaning and replacement (Cote and Thompson, 2000). The membrane tank can be easily isolated, instead of physically removing the membrane from a large sealed anaerobic digester, thus ensuring continuous operation during maintenance.

Figure 2-1 Schematic of AnMBR configurations. (a) External cross-flow AnMBR; (b) Fully submerged AnMBR; (c) Submerged AnMBR with membrane immersed in external tank.

Most membranes used in AnMBR applications are ultrafiltration membranes with pore sizes ranging from 0.03 to 1.0 μm . The pore openings are significantly lower than the size of most microorganisms and flocs in the mixed liquor; therefore, the membrane retains the biomass completely (Lin et al., 2013). Membranes are manufactured with three major classes of material including polymer, metal and ceramic. Previous AnMBR studies showed that ceramic and metallic membranes have a better hydraulic performance and fouling recovery, as well as a higher resistance to corrosion, abrasion and high temperature (Baker, 2002; Ersu and Ong, 2008; Zhang et al., 2005). However, due to the cost factor alone, the polymeric membranes have dominated commercial applications since economic plays an important role (Santos and Judd, 2010). In the current market, polyvinylidene fluoride (PVDF) and polyethersulfone (PES) membranes account for around 75% of total production. Owing to the high packing density and cost efficiency, hollow fiber membrane modules are more popular over flat sheet and tubular configurations (Lin et al., 2013).

2.2. ANMBR IN THE FOOD AND BEVERAGE INDUSTRY

Wastewater effluents from the food and beverage industry are characterized by their high organic strength (2000-180,000 mg/L COD) and are readily biodegradable, which is very suitable for anaerobic treatment. In this section, comprehensive reviews of AnMBR case studies in the food and beverage industries are presented. The reviews include the application of AnMBRs in the general food industry since 2000 and all available information on treating brewery wastewater. The source effluents range from field crop processing (potato, olive and palm oil) to food processing (whey, dumpling and snacks), as well as the beverage industry (brewery and distillery). There are 13 lab scale studies and 6 pilots along with two full scale applications presented in this review. In each case study, both reactors and membrane compartments are being reviewed regarding their configuration and performance. The review summaries are divided into two sub-sections: laboratory research and commercial applications.

2.2.1. AnMBR Developments

The AnMBR concept was first developed in 1978, where an external cross-flow membrane module was used to treat septic tank effluent (Grethlein, 1978). The trial achieved 85-95% reduction in BOD, 72% in nitrate and 24-85% in orthophosphate removal. However, due to the early stage of membrane development, very high external pressure (345 kPa to 1030 kPa) was applied. The filtration flux could be only maintained with high cross-flow velocity and frequent membrane cleaning. The study found the membrane separation method was not feasible to use in rural homes due to its high operation cost and labour attention. The technology was then commercialized by Dorr-Oliver in the early 1980s, while attempting to treat high strength whey processing

wastewater (Liao et al., 2006). The pilot system consisted of a continuous stirred-tank anaerobic reactor (CSTR) and an external cross-flow membrane module. Full scale application was not further pursued due to the high membrane cost. Starting in the 1980s, many studies including the significant Aqua Renaissance' 90 project have been conducted on AnMBR technology. Various membrane configurations including materials and module structures were intensively investigated over both suspended and attached film growth anaerobic bioreactors (Liao et al., 2006). With the concept of submerged MBRs was first developed by Professor Yamamoto in 1989, the membrane module was able to operate over a much lower vacuum pressure due to the lower tangential velocity. This configuration reduced the energy requirements potentially up to two orders of magnitude, and further reduced the shear stress on biomass associated with high cross-flow velocity (Hai et al., 2013).

Over the past 20 years, there were substantial revolutions in membrane development and manufacturing. Membrane manufactures increased from the two (Zenon and Kubota) in early the 1990s to over dozen today. With the GE Zeeweed membrane alone, there have been new releases introduced every 3-4 years (Cote et al., 2012). Further to the development of cyclic aeration (Cote et al., 2000) and sequential aeration (Breitner, 2013), the air scouring cost has been successfully reduced to a quarter without lowering the filtration performance (Cote et al., 2012). Overall, though the significant increase in flux, packing density and savings in aeration cost, the membrane product today has a volumetric cost of lower than 10% compared to 15 years ago (Buer and Cumin, 2010). The current commercial submerged hollow fiber membrane cassette can achieve a packing density of $162 \text{ m}^2/\text{m}^3$. At an average flux of 27 LMH, a total permeation capacity

of $104 \text{ m}^3/\text{m}^3_{\text{module}}/\text{day}$ can be achieved (Buer and Cumin, 2010). The continuous revolution in membrane technology has led to rapid development in AnMBRs as well, in both research and commercial applications. Considerable efforts have been made to improve energy efficiency, promoting biogas recovery as well as water reuse. Advancements in membrane technology introduces tremendous opportunity for the development of more effective AnMBRs.

2.2.2. Laboratory Research

By far the most common AnMBR design has been the continuous stirred-tank reactor (CSTR) configuration, due to the ease of construction and operation. In the review of 19 case studies, there are 15 CSTR, 3 UASB (or hybrid) and 1 baffled configuration. The dominance of CSTR is also likely due to the exclusive use of external cross-flow membrane, where the cross-flow velocity is achieved by high mixed liquor recirculation rate, resulting a well-mixed flow regime (Brockmann and Seyfried, 1996; Cote and Thompson, 2000). Further, a shorter start-up period was also observed with the CSTR configuration in comparison to the UASB process (Fuchs et al., 2003).

A summary of 13 lab scale studies are shown in Table 2-5. Most AnMBR studies have used external cross-flow membranes, with the exception of the submerged flat sheet UF membrane that was used during the Kraft evaporator condensate study conducted by Lakehead University (Lin et al., 2009). Early researchers have explained that the high cross-flow velocity usually put high shear stress on the biomass, and on average AnMBRs had a lower microbial activity compared to UASB systems, further restricting the maximum OLRs on AnMBR systems (Brockmann and Seyfried, 1996). In contrast, Yushina and Hasegawa (1994) reported that over a high particulate soybean wastewater study, the shear stress may promote the breakdown of complex particulates and improved methane yield. Studies on vacuum driven submerged membrane AnMBRs have been limited to date.

Table 2-5 Summary of lab scale AnMBR configuration and performance for treatment of food & beverage wastewater

Source	Reference	Configuration	Membrane Config.	Membrane type	Reactor Volume (L)	TEMP °C	HRT (d)	SRT (d)	ORR (g/L/d)	MLR (g/L)	Influent COD (mg/L)	Effluent COD (mg/L)	COD Removal (%)	CH ₄ yield (m ³ CH ₄ /kg COD)	Flux (LMH)	TMP (kPa)
Alcohol fermentation	(Kang et al., 2002)	CSTR	External	Tubular MF 0.14 µm	5	55	1	inf.	3-3.5	2	38,400		93-97%	0.187	140-180	60
Brewery	(Torres et al., 2011)	CSTR	External	Ceramic, 0.2 µm and polymeric 0.03 µm	4.5	30			12	12-25 ^a	200,000	200	>97%		4-8	
Brewery	(Strohwald and Ross, 1992)	CSTR	External	Tubular UF PES MWCO 40kDa	50	35	0.5-0.8		15	30, 50	3550-14800	180	96-99%		6-18	180
Brewery	(Ince et al., 1993)	CSTR	External	Tubular UF Polymer MWCO 200kDa	120	36	2.5-4.2	inf.	7.5-28.5	8-50 ^a	80,000-90,000	200-650	97%	0.28		240
Cheese whey	(Saddoud and Sayadi, 2007)	CSTR	External	Tubular ceramic, 0.2 µm	15	37	1-4	30-79	3-20	6.4-10	10,000-80,000		98.5%	0.3	140	125-175
Kraft evaporator condensate	(Lin et al., 2009)	UASB hybrid	Submerged	Flat sheet PVDF UF, MWCO 70kDa	10	55	5.8	230	3.1 ± 0.8	8.3 ± 1.6	10,000 ± 500	197 ± 54	97-99%	0.35 + 0.05	2.4 ± 0.6	<30
Kraft evaporator condensate	(Lin et al., 2009)	UASB hybrid	Submerged	Flat sheet, MWCO 70kDa	10	37	1.9	230	12.2 ± 1.1	8.2 ± 1.5	10,000 ± 500	151 ± 28	97-99%	0.35 + 0.06	7.2 ± 0.9	<30

Oilve-mill	(Stamatelatou et al., 2009)	PABR	External	Tubular ceramic UF, MWCO 25kDa	15	35	3.7-5-17.5	1.5-8.9	12.8 VS	147,000 ± 17000		72-80%	0.34-0.58	80-450	150	
Palm oil mill	(Abdurahman et al., 2011)	CSTR	External	Tubular UF, MWCO 200kDa	50		6.8-600	12-1000	1-11	11.8-20.8	60,000-87,000	1400	96.6-98.4%	0.25-0.57	150-200	
Slaughterhouse	(Saddoud et al., 2007)	CSTR	External	Hollow fiber UF, MWCO 100kDa	50	37	1.2-3.3		3-16	10.1 ^a	7150-20,400	265-1980	>94%	0.2-0.31	2.22	100
Slaughterhouse	(Siegrist et al., 2005)	CSTR	External	Ceramic UF 0.06 µm, Metal MF 3 µm	17	37	35	30-40	5-17		300,000 - 500,000		> 90%		40-100	
Slaughterhouse	(Fuchs et al., 2003)	CSTR	External	Ceramic MF 0.2 µm	7	30	1.2		3-7.4	20-28	5800-20150	100-400	>90%	0.12-0.32	5-10	
Tofu processing	(Kim et al., 2011)	CSTR	External	Hollow fiber MF	5	60				5.5 ^a	26,500 ± 2200	< 2 g/L carbo			4.32	

^a MLVSS instead of MLSS

AnMBRs are often operated under mesophilic (35 C) or thermophilic (55 C) conditions. Maintaining the high temperature has not been reported as a challenge for treating high strength food wastewater, where the high quality biogas can be utilized to meet the heating requirement (Liao et al., 2006). Thermophilic conditions allow the system to perform under a higher organic loading (Skouteris et al., 2012). However, a parallel study of two lab scale AnMBRs (Lin et al., 2009) found that the membrane fouling under thermophilic conditions were much more severe than in the mesophilic environment.

Almost all AnMBRs operate in the pH range of 6.8 – 7.2, which refers back to the complicated metabolic pathway of the anaerobic process. The process of hydrolysis and acidogenesis are more robust than acetogenesis and methanogenesis. The optimal pH for methanogens and acid forming microorganisms are slightly different; while the acid forming microorganisms are more favorable to acidic environments, methanogenesis favors pH ranging from 6.8 -7.2. Early research discussed that the activity of methanogens are much lower than the other microorganisms. Therefore, to achieve an overall efficient environment, the AnMBRs usually target to operate at optimal pH range for methanogens (Rajeshwari et al., 2000). Any disorders in the balance between acid forming and methane forming activity will cause reactor instability. VFA/alkalinity ratio is an important parameter to be monitored during the operation. It is a direct indicator of whether the microorganisms are capable to the organic loading. Usually a peak in VFA concentration is observed after rising to a higher OLR and the new loading operation can be maintained if the VFA concentration returns to lower level. Otherwise, accumulation of VFA in mixed liquor indicates overloading of the system and organic loading should be reduced (Fuchs et al., 2003).

The HRT of a reactor directly affects the capital cost. A shorter HRT allows for smaller reactor volume and lower initial cost, and often results in a higher OLR and puts the anaerobic system in stress. In general, the HRTs have been reported in AnMBRs have been higher than UASB or other high-rate anaerobic reactors. Reported HRTs are generally in the range of 1 to 35 days depending on the biodegradability and influent solid content. The lowest HRT reported (12 hours) was used for low solid brewery wastewater (Strohwald and Ross, 1992), while in comparison, UASB reactors typically have HRTs of 4-8 hours (Liao et al., 2006).

With the complete retention of biomass, the MLSS concentration in AnMBR is typically much higher than conventional systems. Most laboratory studies demonstrated that MLSS values of 8-25 g/L and 50 g/L were achieved for brewery wastewater (Strohwald and Ross, 1992; Torres et al., 2011). However, the performance of anaerobic digestion is not limited to the high biomass concentration. Low MLSS of 2 g/L was used in treating complete soluble alcohol fermentation wastewater at around 40,000 mg/L COD (Kang et al., 2002). The authors argued that the microbial cell lysis was enhanced by the high shear induced by high rate recirculation pumping. Though 70 days operation, COD removal was maintained at more than 90%. Yet, a low methane yield at 0.19 m³ CH₄/kg COD_{removal} was detected due to the low biomass.

Organic loading rate is a key factor in AnMBR operation and a direct measurement of the system capacity. A wide range of OLRs have been evaluated, aside from the membrane performance, the highest successful OLR was reported at 28.5 kg COD/m³/day for high strength brewery wastewater (Ince et al., 1993).

A laboratory AnMBR study with slaughterhouse wastewater (Saddoud and Sayadi, 2007) reported a stable operation at OLR under 8.23 ± 2.6 kg tCOD/m³/day with a COD removal efficiency over 93%. However, with the increase of OLR, the removal efficiency decreased to 62% and 53% at OLR of 13.27 and 16.32 kg tCOD/m³/day, respectively. The poor performance was due to the destabilization of microbial populations from the higher OLR, causing accumulation of VFA, which further acidifies the reactor and therefore inhibits the methanogens activity. VFA concentration greater than 3000 mg/L was observed over high OLR, thus resulting in a low methane yield at 0.13 m³ CH₄/kg sCOD_{removal}. The problem was overcome by the integrated fixed bed reactor (FBR) system to separate the acidogenesis from methanogenesis process in the AnMBR.

Strohwald and Ross (1992) observed an organic overload after the start-up in a brewery wastewater treatment study. The COD removal dropped to 80% with a high VFA/Alkalinity ratio of 0.83. VFA accumulation was also reported in another slaughterhouse wastewater study (Siegrist et al., 2005), however due to the extremely low hydraulic loading (HRT=35 days), no substantial inhibition was observed. Nonetheless, in a similar study performed by Fuchs et al. (2003) at OLR of 7.4 kg COD/m³/day the VFA had increased to over 3000 mg/L. The feeding had to be shutoff for 4 days in order to recover the system. The system was later restarted at a lower OLR of 3.0 kg COD/m³/day and further increased to 4.3 kg COD/m³/day while maintaining stable system performance.

The early AnMBR application on brewery wastewater (Ince et al., 1993) used a cross flow ultrafiltration membrane anaerobic reactor (CUMAR) system treating high strength brewery wastewater with total a COD of 80,000-90,000 mg/L and COD:N:P ratio at

400:0.7:0.4, which adjusted to 400:5:1 with addition of urea and KH_2PO_4 . A wide range of OLRs were studied (up to $28.5 \text{ kg COD/m}^3/\text{day}$) over a 15 month operation period. Biomass in the reactor increased from 5 g/L to 50 g/L MLVSS . Through no sudden increase in VFA was detected from increasing OLR, the reactor performance was very stable. The study suggested that the biological system did not reach its maximum loading capacity under OLR of $28.5 \text{ kg COD/m}^3/\text{day}$ and F/M ratio of $0.55 \text{ kg COD/kg VSS/day}$, with a COD removal efficiency of 97.3%. Even though the effluent BOD was found to be less than 130 mg/L at all times, effluent COD was detected over at 200, 440 and 650 mg/L at OLR of 7.5, 11.5 and $17.3 \text{ kg COD/m}^3/\text{day}$, respectively. Although there is a negligible amount of inert soluble COD in brewery wastewater (Ince, 1998), the authors proposed that the soluble inert fractions of COD were produced from microbial metabolism and the amount of EPSs may be linked to the microbial population within the MLSS. Methane yield was unchanged at $0.38 \text{ CH}_4/\text{kg COD}_{\text{removal}}$ up to OLR of $8 \text{ kg COD/m}^3/\text{day}$; further increases in OLR led to a decrease in both methane composition and methane yield, where $0.28 \text{ CH}_4/\text{kg COD}_{\text{removal}}$ was reported under $28.5 \text{ kg COD/m}^3/\text{day}$ operation. Through an energy balance, the potential corresponding energy recovery on the 120 L system was 87 MJ/day , which would account for all energy consumptions from the feed pump, mixer and heating. The generated energy provided 70% of the energy requirement for the high rate recirculation at 108 MJ/d . Constant pressure cross-flow filtration configuration was used in the study. A significant decrease in flux was observed corresponding to an increase of digester biomass concentration. An initial flux of 115 LMH was achieved in the early stage of operation at biomass concentrations as low as 4 g/L MLVSS . The flux dropped to 26 LMH in the later stage as the MLVSS

increased to 50 g/L. The authors suggested that flux rate is in dependent upon the concentration of biomass.

The most recent brewery wastewater AnMBR study (Torres et al., 2011) used an external cross-flow AnMBR while recirculating a combination of biogas/liquid through the tubular membrane module. The two phase flow regime was generated through the combination of gas injection and cross-flow velocity, creating highly turbulent conditions to control surface cake layer formation. Although the study was successful in the biological component, where over 97% COD removal was observed under OLR of 12 kg COD/m³/day, the two phase flow regime failed to provide high filtration capacity. A low flux at only 4 LMH was obtained over long term operation. The authors concluded that the gas scouring did not provide enough shear stress to prevent single cell deposition over the membrane surface.

A cost analysis based on lab scale studies (Lin et al., 2011) showed that the operational cost of an AnMBR was at only one third of the aerobic treatment process. The energy produced from biogas generation and the membrane gas scouring energy requirement theoretically balances out.

2.2.3. Commercial Applications

Compared to laboratory studies of AnMBRs, the numbers of commercial applications have been very limited. From 2000 to date, there are 6 pilot studies and only two industrial applications reported in available literatures (Table 2-6). In contrast to laboratory studies, there are more submerged AnMBRs used in pilot and full scale applications, mainly due to economics, where large savings were generated by

eliminating the high rate sludge recirculation. In general, most systems removed over 92% COD; however, longer HRT and lower OLR were used under the pilot and full scale applications. The high MLSS and OLR put stress on the membrane compartment. A low operation flux and high cross-flow velocity and gas scouring intensity would increase both capital and operational cost.

A pilot study conducted on brewery wastewater (Fakhru'l-Razi, 1994) demonstrated that the AnMBR can achieve over 96% COD removal at high OLR up to 19.7 kg COD/m³/day. The study increased OLR from 12.1 to 19.7 kg COD/m³/day in steps while maintaining MLSS, HRT and decreasing SRT. An increase in VFA concentration (510 to 995 mg/L) was observed relative to an OLR increase, and the effluent COD increased at a greater rate (790 to 3100 mg/L). There was no difference in methane yield related to the organic loading change.

In industrial applications, the ratio between the digester and membrane tank is significantly larger than in laboratory setup. The full scale AnMBR at Ken's Food (Massachusetts, USA) processing wastewater consisted of a 8300 m³ anaerobic digester and 4 membrane tanks with working volumes of 100 m³ each, with a high organic strength influent of 475 m³/day. Over 20 months operation (Christian et al., 2010), the system demonstrated a stable operation under organic loading of 1.2 kg COD/m³/day, achieved COD removal efficiency over 99.4% and generated consistent effluents at 210 ± 40 mg/L COD. Due to the high influent solid (12 g/L) and high MLSS concentration (20-45 g/L), the operation flux remained in the range of 2.5 to 4.2 L/m²/hr (LMH). Operating AnMBRs at low flux requires more membrane modules to balance the hydraulic flow, which directly impacts the capital cost of the system. Based on the concept of the critical

flux, controlling the operation flux is still the most critical strategy to achieve long-term stable operation and therefore extend membrane lifetime. Operation fluxes ranging from 6.7 to 10 LMH were achievable for the treatment of the different wastewaters (Chang, 2014).

Table 2-6 Summary of pilot and full scale AnMBR configuration and performance for treatment of food & beverage wastewater

Source	Reference	Configuration	Membrane Configuration	Membrane type	Reactor Volume (m ³)	Temp (°C)	HRT (d)	SR T (d)	OLR (g/L/d)	MLS (g/L)	Influent COD (mg/L)	Effluent COD (mg/L)	COD Removal (%)	CH ₄ yield (m ³ CH ₄ /kg COD)	Flux (LMH)	TMP (kPa)
Animal waste	(Wong et al., 2009)	CSTR	External	Tubular PVDF 0.03µm	0.1	Mes.	9	28	2.4		31,800±6560	3440±700	92%			200
Brewery	(Fakhru'l-Razi, 1994)	CSTR	External	UF MWCO 10k	0.12	35	3.64-3.98	58-83	12-20	31-38	46,200-84,000	790-3100	96.3-98.2 %	0.26-0.29		100-200
Dumpling processing	(He et al., 2005)	CSTR	External	Flat sheet PES UF, MWCO: 20-70 kDa	0.4	37	0.67-4.17	50	0.88-4.83	6-8	2000-15,000	141-3600	73-94.2 %	0.13-6	13.1-18.9	200
Ethanol thin stillage	(Dereli et al., 2012)	CSTR	Submerged	Flat sheet PVDF 0.08 µm	12	37	17±4	300	4.5-7	24	98,000±16,200	1700±500	98%	0.31	4.3±1.1	10-20
Potato processing	(Singh et al., 2011)	CSTR	Submerged	Flat sheet PET 0.4 µm	3.3	35	3.5-14	80	2-12	40			99%	0.34	0.83-5	3-4
Salad dressing processing	(Christian et al., 2010)	CSTR	Submerged	Flat sheet PET 0.4 µm	8700	33	29		1.2	23	33,500±9350	209±39	99.4 %		2.5-4.5	3
Shochu Distillery	(Kanai et al., 2010)	CSTR	Submerged	Flat sheet MF		Therm.					57,000-182,400		75-92%			
Snacks factory	(Diez et al., 2012)	UASB	Submerged	Hollow fiber PVDF 0.4 µm	0.76	35			5.1	7.9-10.4	8200-22,000	110-250	97%		6.5-8.0	18-51

Some industrial application demonstrated successful conversion and utilization of energy from biogas through mass balance. Shochu manufacture in Japan has had an AnMBR treatment facility installed for its distillery wastewater since 2005. A study in 2010 reported that the treatment plant had an average of 12 GJ/day energy recovery from biogas, which is well above the electricity consumption and the membrane bioreactor heating requirement on site (Kanai et al., 2010). However, there was no energy utilization method reported. So far, little information is available regarding AnMBR the energy consumption or energy production, and almost no public research has been made on optimization or modelling. Conducting more research with respect to energy balance would greatly help to shift the AnMBRs onto industrial-scale applications.

Of the 13 laboratory studies and 8 commercial applications of AnMBR in the food and beverage industry were reviewed in this section, most of the applications used external cross-flow filtration configuration and reported high energy consumption. In this research, an advanced submerged AnMBR will be evaluated regarding to biological and membrane performance.

CHAPTER 3 - SYNTHETIC WASTEWATER

3.1. ABSTRACT

This study investigated the applicability of the anaerobic membrane reactor (AnMBR) technology for the treatment of high organic strength brewery wastewater. The AnMBR was subjected to a stable operation over various organic loading rates (OLRs) of 2, 5, 7.5 and 10 kg COD/m³/day. The system achieved over 99% COD removal efficiency, excessive methane yield (0.38 m³ CH₄/kg COD at 35 °C) and minor membrane fouling. Greater microbial growth rates were observed over a shorter solid retention time (SRT), and more extracellular polymeric substances (EPSs) were released into bulk sludge at a higher organic loading rate, likely due to a higher metabolic rate. Results showed that the ultrafiltration (UF) membrane retained all suspended solids, rejected over 95% soluble polysaccharides and played an important role in improving the effluent quality. The study also found the EPS in bulk sludge was significantly correlated to membrane fouling when the polysaccharide and protein concentrations were below 200 mg/L and 800 mg/L. This research confirms the efficacy of using AnMBR with high strength brewery wastewater treatment, achieving high energy recovery while producing excellent quality effluent.

Keywords: Anaerobic membrane bioreactor, brewery wastewater treatment, membrane fouling, organic loading rate, anaerobic digestion, specific growth rate

3.2. INTRODUCTION

The beer brewing industry discharges high organic strength wastewater, which can present challenges for the municipal wastewater treatment plants if being discharged into the sewer system. It can also cause severe environmental impacts if discharged directly into water bodies. Economic and social pressure has been placed on breweries to treat effluent onsite for reuse or prior to discharging. Early research (Ince, 1998) has found that brewery wastewater has a negligible amount of non-biodegradable soluble COD, where it makes the biological treatment feasible.

Anaerobic treatment is a fast growing application, especially for high organic strength industrial wastewater. It offers many advantages over the commonly used aerobic treatment, such as lower sludge production and the ability to withstand high organic load and lower operation cost due to no aeration requirements (Skouteris et al., 2012). More importantly, anaerobic digestion can convert the organic contents in the wastewater into an usable energy source by producing biogas. Van Zyl et al.(2008) reported a 2.02 kWh energy per kg COD removed, about 7 times higher than the amount required for the system operation.

Since anaerobic microorganisms take significantly longer time to grow, immobilizing bacterial sludge for uncoupling the solid retention time (SRT) and hydraulic retention time (HRT) becomes important, which makes conventional systems unfavourable.

Currently, there are several types of anaerobic bioreactors to treat brewery wastewater.

The upflow anaerobic sludge blanket (UASB) is the most common (Brito et al., 2007).

The UASB retains biomass by forming dense granules with high settleability, and the wastewater degrades as it flows vertically upward through the dense bed of granular

sludge (Rajeshwari et al., 2000). Some drawbacks of UASB include long start-up periods and the requirement of highly skilled operation to prevent biomass loss. The organic loading rate (OLR) or pH shocks from the batch brewing operations can result in degranulation and washout of the biomass.

Anaerobic membrane bioreactor (AnMBR) is an advanced anaerobic wastewater treatment technology and is lately being revitalized by academia and membrane solution providers. AnMBRs are commonly configured with microfiltration (MF) or ultrafiltration (UF) membranes, which can completely retain solid and biomass, further offer entirely separation between SRT and HRT. This technology offers an attractive option for brewery wastewater treatment, as the shocks in OLR or pH would no longer cause loss of biomass and upset the system (Dereli et al., 2012a). Earlier research (Ince et al., 2000) showed a successful treatment of synthetic high strength brewery wastewater by a conventional cross-flow ultrafiltration membrane anaerobic reactor (CUMAR). The system operated at a high SRT (70 to 100 days) and had high mixed liquor suspended solids (10-50 g/L MLSS). The researcher reported that the influent COD and operation OLR had a direct impact on the effluent soluble COD, where an average effluent COD of 220, 440 and 660 mg/L was observed over stable operation under various OLR of 7.5, 11.5 and 17.3 kg COD/m³/day, respectively. The study also found a methane yield of 0.35 m³ CH₄/kg COD_{removed} at stable operation, which the potential energy production would enable to maintain approximately 75% of the CUMAR system operation energy requirements (Ince et al., 2001). However, the major drawback of the external cross-flow type filtration system is a high operational cost of which over 90% of total operation energy was used for sludge recirculation.

The success of MBR technologies have resulted in substantial progress within membrane filtration technology for large-scale wastewater treatment applications (Buer & Cumin, 2010). The advancement in the recent membrane filtration has provided tremendous opportunity for the development of more effective AnMBR systems for high strength wastewater treatment. More recent work by Van Zyl et al. (2008) showed that high strength soluble petrochemical wastewater (18 g COD/l) can be treated effectively (>96% COD removal) at short retention times (17 h) and high loading rates (up to 25 kg COD/m³/day). Although there is existing research on the application of AnMBRs for other types of wastewater, recent research on AnMBR performance for brewery wastewater treatment is very limited.

This study evaluates the treatment of high strength brewery wastewater by an AnMBR system with the most advanced membrane filtration design. The results include the COD removal efficiency, biogas production rate and the critical flux achieved under different organic loading rates by the AnMBR system. The study will also discuss the biomass growth rate, the extracellular polymeric substances (EPS) production and the role of the membrane filtration in improving effluent quality. These results are significant for understanding the treatment capacity of AnMBRs for brewery wastewater treatment.

3.3. MATERIAL AND METHODS

3.3.1. AnMBR System

Figure 3-1 AnMBR system showing digester (centre) and membrane tank (right)

As shown in Figure 3-1, the lab-scale AnMBR used in this study consisted of a complete mix anaerobic digester and a membrane tank. Continuous mixing was performed in the anaerobic reactor by using a mechanical mixer (Eurostar, IKA). The mixed liquor was recirculated from the anaerobic reactor to the bottom of the membrane tank and overflowed from the top portion of the membrane tank back to the reactor. A submerged hollow fiber membrane module with a total surface area of 0.047 m^2 (GE Water and Process Technologies, Oakville ON) was used for liquid-solid separation. A peristaltic pump (Miniplus 3, Gilson) was installed to extract permeate at a constant flux and biogas was recirculated to the membrane tank for membrane scouring. Pressure sensors

(Cerabar T, Endress Hauser) were installed on the digester tank and permeate line to monitor the system pressure and TMP, respectively. Level sensors were used to control the feed pump to maintain a working volume of 15 L in the system. The bioreactor temperature was maintained at 15°C by recirculating hot water in the water jacket. System pH was controlled by dosing sodium bicarbonate using a diaphragm metering pump (Stepdos 08, KNF). Biogas production was measured on-line by a mass flow meter (Burkert 8700). A PLC system was used to control the MBR system and for the collection of operation data.

3.3.2. Wastewater Characteristics

This study used synthetic brewery wastewater that was supplemented to provide a COD:N:P ratio of approximately 260:4:1 with the macronutrient and micronutrient compositions slightly modified from the ones given in Scampini (2010). Table 3-1 shows the main composition of macronutrients and micronutrients for the synthetic wastewater used at an OLR of 10 kg COD/m³/day, and Table 3-2 shows the corresponding concentration of COD and nutrients contained in the wastewater.

Table 3-1 Composition of the synthetic wastewater

Macronutrients	Conc. (g/L)	Micronutrients	Conc. (mg/L)	Micronutrients	Conc. (mg/L)
Beer (mL/L)	27.54	FeCl ₂ *4H ₂ O	11.66	AlCl ₃ *6H ₂ O	0.52
Glacial acetic acid (mL/L)	11.50	MnCl ₂ *4H ₂ O	2.92	(NH ₄) ₆ Mo ₇ O ₂₄ *H ₂ O	0.29
Yeast extract	1.50	CoCl ₂ *6H ₂ O	11.66	CuCl*2H ₂ O	0.22
NH ₄ Cl	0.38	NiCl ₂ *6H ₂ O	0.83	H ₃ BO ₃	0.29
K ₂ HPO ₄	0.24	ZnCl ₂	0.29	HCl	0.01
MgSO ₄	0.11	Na ₂ SeO ₃	0.72	EDTA	5.83

Table 3-2 Characterization of the synthetic brewery wastewater

Parameter	Unit	Value
COD	mg/L	17,000 ± 600
TN	mg/L	268 ± 18
NH ₄ -N	mg/L	101 ± 5
TP	mg/L	66 ± 2
PO ₄ -P	mg/L	55 ± 2

3.3.3. AnMBR Operation

The reactor started from an inactive state inherited from a previous study (David Hufnagel, 2014) with an initial MLSS and MLVSS concentration of 2.8 g/L and 1.8 g/L, respectively. The operation periods of the reactor in this study included a start period by batch feeding at an OLR of 2 kg COD/m³/day and continuous feeding operation with OLR at 2, 5, 7.5 and 10 kg COD/m³/day. In order to enhance biomass build up, there was no sludge wasting under OLR of 2, 5 and 7.5 kg COD/m³/day operation periods. For the OLR of 10 kg COD/m³/day operation period, there was no sludge wasting in the first 16 days, followed by an average of 500 ml/day sludge wasting, in order to stabilize the MLSS concentration at 11 ± 1 g/L, corresponding to a SRT around 30 days. The AnMBR was operated at pH ranges from 6.8 to 7.3 and temperature of 35 ± 1 °C. An online alkalinity dosing system was used to maintain the desired pH condition and the total alkalinity in the mixed liquor during the operation period. Membrane operation flux was set at 8 liter/m²/hour (LMH) and the operation cycle involved 10 minute permeation and 1 min relaxation during the entire study. Maintenance cleaning using 2000 mg/L citric acid and 2000 mg/L sodium hypochlorite was implemented only after constant SRT operation at OLR 10 kg/m³/day. The maintenance cleaning operation involved a 15 minute backwash cycle at permeation flux with each cleaning reagent.

3.3.4. Bench Scale Filtration System

Figure 3-2 Bench scale filtration setup, digester showing in centre

Bench top bioassay membrane filtrations were performed to investigate the EPS production and membrane filterability over anaerobic sludge with the different biomass concentration. The system (shown in Figure 3-2) consisted of a cylindrical heated vessel (1 L effective volume), a magnetic stir (350 rpm, Isotemp, Fisher Scientific) and a loop shaped hollow fiber membrane module (effective filtration area = 0.00179 m^2 , GE Water). Anaerobic sludge were taken from the AnMBR and the concentration were adjusted to 10, 15, 20 g/L MLSS prior to each filtration test. Each filtration test was operated continuously for 7 days with 3 stages constant flux filtration at 10, 11.5, 13 LMH and other operation conditions were the same as AnMBR. Pressure sensors (Cole-Parmer) were installed on the digester tank and permeate line to monitor the system pressure and TMP, respectively. Biogas productions were monitored with a volumetric gas meter

(MilliGascounter MGC-1, Ritter). Clean water tests were performed before and after the filtration experiments. The fouling resistance (R_f) were calculated as following:

$$R_f = R_t - R_m = \frac{\Delta P_t}{\mu * J(t)} - \frac{\Delta P_m}{\mu * J(t)}$$

Where R_t is the total membrane resistance (m^{-1}) from the post filtration clean water test, R_m is the intrinsic membrane resistance (m^{-1}), ΔP the TMP (Pa), μ the viscosity of water at 35°C (Pa*s) and J is the permeate flux ($m^3/m^2/h$). All membranes were soaked in deionized water before the test and washed with deionized water after each filtration experiment to ensure surface cake layer was removed. Sludge samples were taken for EPS characterization.

3.3.5. Analytical Methods

Membrane permeate samples as well as the sludge samples from the digester and membrane tank were taken regularly for analysis. The supernatant of the mixed liquor was obtained using the centrifugation/filtration procedure with centrifugation at 8000 rpm for 15 min at 4 °C followed by filtration through a 1.5 μm filter paper. Soluble samples were further filtered through 0.45 μm disposable membrane filters.

The Standard Methods (APHA-AWWA-WEF, 2005) were used for the measurements of MLSS and MLVSS concentration. Other parameters including COD, total nitrogen (TN), total phosphours (TP), ammonia nitrogen (NH_4^+-N), nitrate nitrogen (NO_3^-N), nitrite nitrogen (NO_2^-N), phosphate phosphorus ($PO_4^{3-}P$), and volatile fatty acids (VFA) were measured using Hach methods (HACH, 2008). Protein and polysaccharides concentration of EPSs were determined with the Bradford method (Bradford, 1976) and

the phenol-sulphuric acid method (DuBois et al., 1956), respectively. Bovine serum albumin (BSA) and glucose were used as standard references and the absorbance was taken by a spectrophotometer (DR5000, Hach). Total alkalinity was measured using an automatic titrator (TitraLab 870, Radiometer analytical). Biogas composition (N_2 , CH_4 and CO_2) was analysed using gas chromatograph (6890n, Agilent Technologies).

3.4. RESULT AND DISCUSSION

3.4.1. System Performance

Figure 3-3 COD concentration in the membrane permeate and COD removal efficiency for different organic loading rates

Figure 3-3 shows the COD concentration in the membrane permeate and the COD removal efficiency during the 140 days operation period. The reactor started from an inactive state with batch feeding at OLR 2 kg COD/m³/day. During the start-up period, the soluble COD removal increased from 20% to 80% in 20 days, indicating a quick recovery from the inactive state. After the start-up, the reactor operation was then

switched to continuous feeding and upon day 140, it had gone through operation with different OLRs of 2, 5, 7.5 and 10 kg COD/m³/day. Whenever OLR was increased, a stable operation in terms of the COD concentration in the membrane permeate was reached in 2-8 days and persisted lower than 100 mg/L, which delivered an over 99% COD removal efficiency. These results indicated that the AnMBR has excellent ability to achieve a quick start-up and high tolerance to the change in organic strength of the wastewater. This is likely due to the complete retention of the active biomass by the membrane and independence of the sludge retention. (Skouteris et al., 2012).

Figure 3-4 COD concentration in the membrane permeate, 1.5 µm and 0.45 µm filtrate of the mixed liquor

The results obtained in this study showed that the membrane filtration played an important role in improving the treatment performance. As showed in Figure 3-4, significant difference was observed from the COD concentration in 1.5 µm sludge filtrate, 0.45 µm soluble filtrate and 0.04 µm ultrafiltration permeate, where the COD in permeate

was found to be significantly lower (< 100 mg/L). In addition, while the COD concentration of the permeate maintained low and stable for all the organic loading rates tested, the COD concentration in the $1.5\ \mu\text{m}$ and $0.45\ \mu\text{m}$ filtrate of the mixed liquor increased with the organic loading rate. These results suggested that the membrane filtration played an important role in improving the effluent quality of anaerobic digestion.

The effluent pH, VFA concentration and total alkalinity were found to be in favorable conditions for methanogenesis. During the OLR of 2, 5 and $7.5\ \text{kg/m}^3/\text{day}$ operation, a daily average of $30.0 \pm 2.2\ \text{g NaHCO}_3$ was dosed using an online chemical dosing system, pH was maintained at 6.85 ± 0.01 and the total alkalinity in the mixed liquor was maintained at $2500 \pm 150\ \text{mg/L}$ as CaCO_3 . At OLR of $10\ \text{kg/m}^3/\text{day}$, a dosage of $26.7\ \text{g NaOH/day}$ was used to maintain pH and total alkalinity at 7.24 ± 0.01 and $4500 \pm 300\ \text{mg/L}$, respectively. The observed VFA concentrations were lower than $50\ \text{mg/L}$ at all-time, the low VFA/alkalinity ratio (<0.02) ensures an active metabolism of the methanogens.

Figure 3-5 Biogas production for different OLR

The biogas production rate was very stable under continuous feeding operation (Figure 3-5), with production rate of 18 ± 1 , 52 ± 2 , 79 ± 3 and 86 ± 4 L/day for OLRs of 2, 5, 7.5 and 10 kg COD/m³/day, respectively. The methane content in the biogas was determined as 54% by GC analysis, corresponding to an average methane yield of 0.38 m³ CH₄/kg COD_{removed} (35 °C), which represented 96% of the maximum theoretical value at 0.395 m³ CH₄/kg COD_{removed} (35 °C). The performance indicated the efficacy of energy recovery by AnMBR technology.

3.4.2. Biomass Characteristics

Figure 3-6 shows the MLSS and MLVSS concentration during different operation periods. As shown in the figure, the MLSS concentration rapidly increased from around 2.8 g/L to 5 g/L in the first 10 days during the start-up and was then persisted relatively steadily through the 2 kg/m³/day operation period even without sludge wasting. The biomass concentration started increasing rapidly after the organic loading was increased

from 2 to 5 kg/m³/day and maintained a steady MLSS and MLVSS growth rate until the OLR of 10 kg/m³/day operation. The MLSS concentration in the reactor was increased up to 16.8 g/L on day 80. Thus, the MLSS concentration in the reactor was reduced to 10 g/L by one time sludge wasting and a daily sludge wasting protocol (SRT = 31 days) was implemented to stabilize the MLSS concentration in the reactor around 11 ± 1 g/L.

Figure 3-6 MLSS and MLVSS change with time

Biomass yield and specific growth under each operating condition were calculated and are shown in Figure 6. An average observed yield and specific growth were observed at 0.028 ± 0.004 gVSS/gCOD and 0.029 ± 0.002 gVSS/gVSS/day, respectively. Both yield and specific growth values are comparably lower than the typical values on the conventional anaerobic processes (Metcalf & Eddy, 2002).

3.4.3. Soluble Microbial Product Characteristics

Various studies reported that the EPSs were the main contributor to membrane fouling in MBRs (Dereli et al., 2012a; Skouteris et al., 2012; Stuckey, 2012). EPSs are polymeric

substances produced by microorganisms, mainly consisting of protein, polysaccharides and humic acid (Laspidou and Rittmann, 2002). EPSs are released during the cell metabolism as well as during starvation and stress as the cell metabolizes internal material and scavenges nutrients (Barker and Stuckey, 1999). Operating factors such as extended SRT and high organic loading rate can increase EPS production (Stuckey, 2012). In this study, protein and polysaccharide concentration in bulk sludge was analysed and it was found that both protein and polysaccharide increased gradually over the operation period at 2 and 5 COD kg/m³/day, and more rapidly at 7.5 and 10 COD kg/m³/day (Figure 3-7). This indicated that the amount of EPS in the bulk sludge was linked to both the metabolic activity of microbial populations and the accumulation of existing EPS. The analysis also showed that protein was the major component of EPSs, where the protein/polysaccharide ratio ranged from 2.7 to 4.6.

Figure 3-7 EPS concentration in bulk sludge

EPSs in the permeate were analysed at the same time (Figure 3-8), A general tendency of higher EPS concentration was observed in higher OLR operation. The polysaccharide concentrations were found to be lower than 10 mg/L in the membrane permeate at all time, whereas over 95% polysaccharide retention was achieved by the UF membrane. In contrast, protein concentration in the membrane permeate ranged from 40 mg/L to 310 mg/L and no correlation was observed in terms of membrane rejection. Earlier research (Ince et al., 2000) also reported that inert soluble COD in the effluent was mostly produced by the biomass and could not be removed with extended operation time.

Figure 3-8 EPS concentration in permeate

Replicated filtration and EPS experiments were conducted over the OLR of 10 kg/m³/day study period to investigate both protein and polysaccharide composition in the mixed liquor, shown in Figure 3-9. In the mixed liquor supernatant, it was found on average that 36% polysaccharide could pass the 0.45µm membrane filter, while only 16% of the

protein passed through. Further, the 0.04 μm membrane retained about 95% soluble polysaccharide, in contrast, over 75% soluble protein passed through the membrane. The results suggested that while most polysaccharide in soluble EPS has particle size larger than 0.04 μm , the distribution is bimodal with a peak in the colloidal region and a peak in the small particle size ($<0.04 \mu\text{m}$) region.

Figure 3-9 Protein and polysaccharide composition in mixed liquor

3.4.4. Membrane Filtration Performance

Constant biogas recirculation rate of 12 LPM was used in the entire study, corresponding to a scouring rate about $15.3 \text{ m}^3/\text{m}^2/\text{hr}$, similar to the reported value $17.6 \text{ m}^3/\text{m}^2/\text{hr}$ in the earlier hollow fiber AnMBR study over high strength industrial wastewater (Diez et al., 2012). Over the 140 days study period, the transmembrane pressure (TMP) had increased 2.0 kPa while maintaining constant flux operation at 8 LMH (Figure 3-10). The TMP gradually increased during OLRs of 2-7.5 $\text{kg COD}/\text{m}^3/\text{day}$ operation and had a

jump over 1.5 kPa over the 15 days OLR 10 kg/m³/day with no sludge wasting operation and stabilized under constant SRT operation.

Figure 3-10 TMP and critical flux change over time

Critical flux tests were performed weekly using the flux stepping method, by increasing the flux in a 15 min step-wise fashion while monitoring the corresponding TMP.

According to Le Clech et al. (2003), critical flux can be determined as the flux corresponding to an increase in TMP of 0.1 kPa over a 10 minute duration. It was found that the critical flux was inversely proportional to the OLR, shown in Figure 3-10. The average critical flux for OLR of 5, 7.5 and 10 kg/m³/day were 17.8 ± 0.3 , 14.8 ± 0.1 and 9.3 ± 0.3 LMH, accordingly.

Figure 3-11 Relationship between EPS in bulk sludge and critical flux

Combining the critical flux data and EPS concentration in the bulk sludge data, a strong correlation is shown in Figure 3-11. The critical flux had decreased rapidly while the polysaccharide and protein concentration increased to 200 mg/L and 800 mg/L, respectively. A more gradual drop in the critical flux was then observed at higher ranges of polysaccharide and protein concentration. Critical flux was affected by the EPS concentration in bulk sludge, where it was more sensitive when polysaccharide and protein concentrations were below 200 mg/L and 800 mg/L, respectively.

Figure 3-12 Effect of gas scouring on critical flux

Critical flux tests were conducted over different air scouring rates towards the end of study period. Four biogas recirculation rates were tested, corresponding to a normalized scouring rate of 10.2, 15.7, 21.1 and 26.5 $\text{m}^3/\text{m}^2/\text{hr}$. The results in Figure 3-12 indicated that the critical flux was very sensitive to the gas scouring intensity.

3.4.5. Bench Scale Filtration System

All three bench filtration experiments achieved over 99% COD removal efficiency. An inversely proportional relationship between biomass concentration and permeate COD was observed, where the average permeate COD was 61, 53 and 47 mg/L at 10, 15 and 20 g MLSS/L, respectively. There was no significant evidence showing a difference between biogas productions at different operation fluxes for the same OLR. Under the same mixing condition, the TMP profile was found to be moderately sensitive to the biomass concentration. Critical fluxes were determined before and after the 7 day filtration test, and found to be 17.7, 13.2 and 7.9 LMH, whereas the critical flux at 20 g/L MLSS was substantially lower. The critical flux was lower than the operating flux at 20

g/L condition. The filtration was not completed in full duration due to high TMP profile. After the 168 hour filtration period, the critical flux of 10 g/L and 15 g/L were found to be similar, at 8.8 LMH. It was found that the critical flux was strongly correlated with the EPS concentration found in bulk sludge. The fouling resistance was calculated from clean water testing. It was found that the 10 g/L and 15 g/L batch had an increase of 4% and 13% in filtration resistance, respectively. No physical irreversible fouling was observed in 20g/L due to insufficient operation time.

3.5. CONCLUSION

The applicability of submerged AnMBR technology for the treatment of high organic strength synthetic brewery wastewater was investigated in this study. The system achieved over 99% COD removal efficiency, excessive methane yield and minor membrane fouling. A greater biomass yield and specific growth was observed over shorter SRTs. More EPSs were released into bulk sludge at a higher organic loading rate, due to a higher metabolism rate. It was also found that the ultrafiltration membrane retained all the suspended solids, rejected over 95% soluble polysaccharides and improved the effluent quality significantly. Not only was the gas scouring intensity was found to be an important factor to the critical flux, it was also found that the EPS concentration in bulk sludge plays an important role on membrane fouling, whereas the correlation was more sensitive when polysaccharide and protein concentrations were below 200 mg/L and 800 mg/L.

Overall, this research further validates the efficacy of using AnMBR on high strength brewery wastewater treatment. The system achieved a great energy recovery while producing excellent quality effluent. However, the membrane fouling mechanism behind

the microbial metabolism is still not fully understood at this stage. More work is needed to ascertain the composition of the fouling layer as well as the factors that influence the EPS production.

3.6. ACKNOWLEDGEMENT

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CHAPTER 4 - LOCAL CRAFT BREWERY WASTEWATER

4.1. ABSTRACT

Succeeding the earlier synthetic wastewater study, the anaerobic membrane bioreactor (AnMBR) technology was further subjected to an operation with high strength brewery wastewater from a local craft brewery. The characteristics of brewery effluent were analyzed and found to be highly variable in both organic strength and composition, yet highly biodegradable. The AnMBR system had gone through an operation with organic loading ranging from 3.5 to 11.5 kg COD/m³/day. The system achieved over 98% COD, 54% TN and 28% TP removal efficiency and demonstrated a very stable methane yield of 0.31 m³ CH₄/kg COD at 35 °C. Effluent COD was observed at 150, 170 and 270 mg/L for organic loading rates (OLRs) of 5.0, 6.5 and 11.5 kg/m³/day, respectively. AnMBR effluent contains mostly non-biodegradable organic compounds, mainly soluble protein. The ultrafiltration membrane rejected approximately 85% of soluble polysaccharide, while no significant rejection on soluble protein was observed. In comparison to the earlier synthetic wastewater study, significantly higher concentrations of EPS were found in the mixed liquor. The study recommended running the AnMBR on high strength brewery wastewater at an organic loading of 6.5 kg COD/m³/day with an operation flux of 7 L/m²/hour (LMH). This research further validates the efficacy of AnMBRs for high strength brewery wastewater treatment. The system achieved great energy recovery while producing excellent quality effluent.

Keywords: Anaerobic membrane bioreactor, brewery wastewater treatment, membrane fouling, organic loading rate, anaerobic digestion, specific growth rate

4.2. INTRODUCTION

Over the last decade, the brewery industry structure has changed in Canada. Large operation plants have reduced in number while the number of micro-breweries has increased considerably (Bureau, 2009). There are 47 micro-breweries in Ontario, having approximately \$190 million sales in 2010, equivalent to a 5% share of the Ontario beer market (MEDEI, 2012). Beer brewing is a process that is highly water intensive. An average of about 7 litres of water is used per every litre of beer produced and about 70% of the intake water is discharged to the sewer (Brewers Association, n.d.). With the large growth in business, environmental impacts became a concern. In municipal by-law, there is a set maximum permissible contaminant level for the wastewater being discharged into the sewer system. The standard normally encompasses volume, pH, suspended solids, BOD, COD, nutrients and toxic substances in the discharge water. Discharging wastewater higher than the limit often leaves the owner with a large surcharge bill (Natural Resources Canada, 2012). Paying surcharge bills to municipalities or private contractors for continuous discharge are very costly and often limit the growth of the micro-brewery business. Municipality may enforce an on-site treatment system in case of expanding the existing brewery plant.

Wastewater characteristics vary significantly among different breweries, as well as in day to day operation. Driessen and Vereijken (2003) have summarized some of the most relevant parameters, where typical brewery wastewater consists of 200-1000 mg/L TSS, 2000-6000 mg/L COD, 25-80 mg/L nitrogen and 10-50 mg/L phosphorous. In general, brewery wastewater effluent consists of sugar, starch, ethanol and volatile fatty acids (VFAs). In general, the brewery wastewater is easily biodegradable with a high

BOD/COD ratio of 0.6 to 0.7. Instead of relying on the municipalities treating brewery wastewater aerobically, anaerobic systems have become a more attractive on-site treatment option. The advantages include a lower sludge production, smaller foot print and more importantly, the ability to produce valuable biogas. Anaerobic treatment in the brewing industry is a proven technology. There are several types of anaerobic systems currently being used to treat brewery wastewater, with the upflow anaerobic sludge blanket (UASB) being the most common (Brito et al., 2007). Since anaerobic bacteria require a longer growth period, immobilizing bacterial sludge is necessary. UASB retains biomass by forming dense granules with high settleability. The wastewater degrades as it flows vertically upward through the dense bed of granular sludge (Rajeshwari et al., 2000). However, sustaining the granules becomes a challenge as the organic loading or pH shock from the batch brewing operation can result in degranulation and biomass washout. Requirement of highly skilled operation and long restart periods are also major drawbacks. More advanced technology anaerobic membrane bioreactors (AnMBRs) are being revitalized by academia and membrane solution providers lately. With the integration of ultrafiltration (UF) membranes, the AnMBRs can entirely retain the biomass and solids, thus offering a complete separation between SRT and HRT as well as a high tolerance to pH and OLR shocks (Dereli et al., 2012a). Although the AnMBR technology is more industrialized in some European countries, it is still in the developing stage in other parts of the world. Recently, General Electric has announced their first full scale AnMBR installation at Dogfish Head Craft Brewery in Milton, DE to reuse their industrial wastewater, where the system is expected to reduce wastewater volume by 80% (GE Water & Process Technologies, 2014).

The performance of a state-of-the-art AnMBR system was evaluated earlier using synthetic brewery wastewater adopted from Scampini (2010), with a COD:N:P ratio of approximately 260:4:1. The pilot system had gone through an operation over various organic loading rates (OLRs) ranging from 2 to 10 kg COD/m³/day and sustained long term stable operation over 10 kg/m³/day at 11 ± 1 g/L MLSS with observed SRT of 31 days. The AnMBR had a quick start-up and demonstrated a high tolerance to the changes in wastewater organic strength. Overall, the system achieved over 99% COD removal efficiency, excessive methane yield at 0.38 m³ CH₄/kg COD and minor membrane fouling. Considering results from the synthetic wastewater study, the efficacy of AnMBR technology was further investigated in this study over high strength brewery wastewater sampled from a local craft brewery. The system was subjected to an operation with higher organic loading fluctuation and more complex wastewater composition. The performance and tolerance of the AnMBR was challenged. In addition, this study examined the extracellular polymeric substances (EPSs) production and membrane fouling mechanism under a low biomass concentration, to evaluate whether if the low biomass operation is more practical for AnMBRs.

4.3. MATERIALS AND METHODS

4.3.1. AnMBR System

Figure 4-1 AnMBR system showing digester (centre) and membrane tank (right)

As shown in Figure 4-1, the lab-scale AnMBR used in this study consisted of a complete mix anaerobic digester and a membrane tank. Continuous mixing was performed in the anaerobic reactor using a mechanical mixer (Eurostar, IKA). The mixed liquor was recirculated from the anaerobic reactor to the bottom of the membrane tank and overflowed from the top portion of the membrane tank back to the reactor. A submerged hollow fiber membrane module with a total surface area of 0.047 m^2 (GE Water and Process Technologies, Oakville ON) was used for liquid-solid separation. A peristaltic pump (Miniplus 3, Gilson) was installed to extract permeate at a constant flux and the biogas was recirculated to the membrane tank for membrane scouring. Pressure sensors (Cerabar T, Endress Hauser) were installed on the digester tank and permeate line to

monitor the system pressure and transmembrane pressure (TMP), respectively. Level sensors were used to control the feed pump to maintain a work volume of 15 L in the system. The bioreactor temperature was maintained by recirculating hot water in the water jacket. System pH was controlled by dosing sodium bicarbonate using a diaphragm metering pump (Stepdos 08, KNF). Biogas production was measured on-line by a mass flow meter (Burkert 8700). A PLC system was used to control the AnMBR system and for the collection of operation data.

4.3.2. Wastewater Characteristics

This study used high strength brewery wastewater from a local craft brewery. Weekly sampling of 4 x 20 liter wastewater was conducted. The 20 L container was placed in a bar refrigerator (6 °C) and was directly connected to an AnMBR feed pump. Excess wastewater was stored in a cooler room (4 °C) prior to use during the week. Characteristics of each batch were tested and will be further discussed in the results section.

4.3.3. AnMBR Operation

The reactor was started in an active state inherited from the previous synthetic brewery wastewater study, with initial MLSS and MLVSS concentrations of 11800 mg/L and 10200 mg/L, respectively. The reactor had gone through 90 days continuous operation at a constant HRT of 44 hours. The OLR varied from 3.5 to 11.5 kg/m³/day and a target active biomass concentration of 7000 mg/L MLVSS was maintained by changing the daily sludge wasting volume. An average SRT was then calculated for each OLR condition, shown in Table 4-1.

Table 4-1 Operation conditions during the study

Days	OLR (g/L/d)	SRT (d)
0-7	6.5	30
8-12	11.5	17
13-29	6.5	30
30-50	3.5	46
51-90	5.0	50

The AnMBR was operated at $\text{pH } 7.02 \pm 0.01$ and temperature of 35.5 ± 0.1 °C. An online alkalinity dosing system was used to maintain the desired pH condition and the total alkalinity in the mixed liquor during the operation period. Constant filtration flux was set at 8 LMH and the operation cycle involved 10 minute permeation and 1 min relaxation throughout the entire study. Weekly online maintenance cleaning using 2000 mg/L citric acid and 2000 mg/L sodium hypochlorite was implemented. The maintenance cleaning operation involved 15 minute backwash cycle at permeation flux with each cleaning reagent.

4.3.4. Analytical Methods

Samples were regularly taken from the digester, membrane tank and membrane permeate for analysis. The supernatant of the mixed liquor was obtained using a centrifugation/filtration procedure with centrifugation at 8000 rpm for 15 min at 4 °C followed by filtration through a 1.5 μm filter paper, and the soluble samples were further filtered through 0.45 μm disposable filters.

The Standard Methods (APHA-AWWA-WEF, 2005) were used for the measurements of total suspended solid (TSS), mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS). Wastewater parameters including chemical oxygen

demand (COD), total nitrogen (TN), total phosphours (TP), ammonia nitrogen ($\text{NH}_4^+\text{-N}$), nitrate nitrogen (NO_3^-N), nitrite nitrogen (NO_2^-N), phosphate phosphorus ($\text{PO}_4^{3-}\text{-P}$), and volatile fatty acids (VFA) were measured using Hach methods (HACH, 2008). Protein and polysaccharide concentrations of EPS and EPS were determined with the Bradford method (Bradford, 1976) and the phenol-sulphuric acid method (DuBois et al., 1956), respectively. Bovine serum albumin (BSA) and glucose were used as standard references and the absorbance was taken by a spectrophotometer (DR5000, Hach). Total alkalinity was measured using an automatic titrator (TitraLab 870, Radiometer analytical). Biogas composition was analysed using gas chromatograph service from a commercial lab (ALS Environmental).

4.4. RESULTS AND DISCUSSION

4.4.1. Brewery Wastewater Characteristic

Wastewater quality indication parameters including pH, Total Alkalinity, TSS, VSS, BOD, tCOD, sCOD, TN, TP, $\text{NH}_3\text{-N}$ and $\text{PO}_4\text{-P}$ were analyzed on every batch, shown in Table 4-2. Due to the batch brewing operation, the wastewater strength and characteristic fluctuated significantly from batch to batch. BOD/COD ratio observed to the range from 0.5 to 0.77, indicating the efficacy of biological treatment (Metcalf & Eddy, 2002).

Based on the average analysis readings, the craft brewery wastewater had a C:N:P ratio of 200:3.2:1 with an average COD of 11000 ± 2800 mg/L and over 90% was soluble COD. The wastewater contained suspended solids at 950 ± 450 mg/L, primarily from mash tun and filter cleaning, with a VSS/TSS ratio ranged from 48 to 97%. Due to the high protein content in the wastewater, over 95% nitrogen and over 50% phosphorus was

organic. The wastewater was slightly acidic, with pH 5.7 ± 0.5 and has a total alkalinity of 270 ± 80 mg/L as CaCO_3 .

Table 4-2 Brewery wastewater characteristic

Batch	TSS	VSS	tCOD	sCOD	TN	TP	NH3- N	PO4- P	pH	Alk
Unit	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	-	meq/L
1	1380	1200	18140	17000	372.0	136.0	6.9	107.4	5.2	3.6
2	1270	1130	12080	10980	145.2	36.2	5.5	17.1	6.6	49.1
3	680	560	11500	10380	131.0	31.2	15.5	15.8	6.0	9.9
4	310	250	19140	15720	156.0	36.7	5.8	17.5	7.2	43.4
5	625	298	11180	10660	89.5	25.3	8.5	12.0	4.9	2.3
6	301	293	5950	5420	74.5	22.3	11.3	11.8	5.7	6.4
7	1395	1242	6580	5940	560.0	35.1	11.6	11.5	5.8	5.4
8	2614	2131	8900	8480	92.9	37.4	6.9	21.0	5.5	7.2
9	674	384	8950	8870	70.5	14.5	2.3	8.1	4.9	4.0
10	266	232	8410	8430	77.6	186.0	3.3	39.7	5.5	4.0
Avg	950	770	11080	10190	180	55	8	26	5.7	13.5
	± 450	± 390	± 2760	± 2320	± 100	± 35	± 3	± 19	± 0.5	± 10.8
Min	266	232	5950	5420	71	15	2	8	4.9	2.3
Max	2614	2131	19140	17000	560	186	16	107	7.2	49.1

4.4.2. COD Removal Efficiency

Figure 4-2 Influent COD and removal efficiency

The AnMBR system was continuously operated for 90 days on 10 batches of brewery wastewater, excluding day 71 to 74, during which the recirculation pump was failed, but a new pump was installed on day 75 and the operation was resumed. Figure 4-2 shows the influent COD concentration in black lines and the overall system COD removal efficiency. Figure 4-3 shows the effluent COD and VFA concentration. The influent COD varied from 6000 mg/L to 19100 mg/L which corresponded to OLRs from 3.5 to 11.5 kg/m³/day. The effluent COD fluctuated with OLR, but the maximum effluent COD observed during the operation was below 300 mg/L at all time. An average effluent COD of 149 ± 7 mg/L and 172 ± 15 mg/L was observed under the OLR of 5 and 6.5 kg/m³/day operation, respectively, with VFA concentration under detection limit (50 mg/L). A high

effluent COD concentration at 268 ± 21 mg/L with a detectable VFA concentration at 81 ± 5 mg/L was observed during OLR $11.5 \text{ kg/m}^3/\text{day}$ operation. The VFA residual in the mixed liquor at OLR $11.5 \text{ kg/m}^3/\text{day}$ indicated an incomplete biodegradation. The fluctuation in effluent COD was significantly smaller than the changes in the influent COD and operation OLR, indicating that the AnMBR had a high tolerance to organic loading changes from batch brewing operations, while maintaining good quality effluent free of solid. This was likely due to the retention of the suspended solids and colloidal substances by the membrane, compared to the conventional high rate anaerobic reactors.

Figure 4-3 Effluent COD and VFA concentration

In all of the above OLR operations, the AnMBR system has achieved over 98% COD removal efficiency, with the exception from day 30 to day 44, where the removal efficiency dropped below 98%. During day 30 to 35, the removal efficiency dropped to

97%, which was caused by the decrease of influent COD concentration thus resulting in a higher effluent/influent COD ratio in the removal efficiency calculation. During day 37 to day 44, the effluent COD concentration increased to 250 mg/L, dropped the removal efficiency down to 96%. The cause was argued to be the abnormal wastewater being fed into AnMBR during day 30 to day 37. The TSS and COD concentration of that batch of wastewater was comparably lower; however, the influent wastewater potentially contained cleaning detergent or other compounds, which could be toxic to the biomass. The toxic effect on the biomass had a delay of approximately 6 days and the bioreactor recovered in 7 days after the feed batch was switched on day 38. On day 45, the effluent COD concentration dropped below 150 mg/L and maintained overall removal efficiency above 98% for the rest of the study. With no acidification observed, the CSTR design of AnMBR established a high tolerance to toxic load and demonstrated a quick recovery, while suspended biomass was believed to be more susceptible for toxicants than granular sludge (Dereli et al., 2012a).

Figure 4-4 Effluent BOD and COD concentration comparison

Figure 4-4 shows the BOD and COD concentration in the effluent. The BOD concentration remained in the range of 30 to 40 mg/L, while the effluent COD fluctuated with the operation OLR. The low BOD/COD ratio (0.20 ± 0.05) suggest that the AnMBR effluent mostly contains non-biodegradable soluble substance, likely EPSs, which will be further discussed in the later section.

4.4.3. COD in the Mixed Liquor

The results demonstrated that the membrane filtration played an important role in improving the treatment performance of anaerobic digestion and the effluent quality. As shown in Figure 4-5, a significant difference was observed between the COD concentration in 1.5 μm sludge filtrate, 0.45 μm soluble filtrate and 0.04 μm ultrafiltration permeate. The permeate COD was found to be significantly lower (170 ± 36 mg/L), with the ratios to 1.5 μm and 0.45 μm sludge filtrate calculated to be 0.06 ± 0.01 and 0.16 ± 0.03 , respectively.

Figure 4-5 COD concentration in the 1.5μm, 0.45μm filtrate and membrane permeate

In addition, while the permeate COD remained relatively low and stable for all the organic loading rates tested, the COD concentration in the 1.5 μm filter paper and 0.45 μm membrane filtrate of the mixed liquor increased with the organic loading rate. With the exemption on day 35 and 41, while the operation OLR was at 3.5 kg/m³/day, the 1.5 μm sludge filtrate COD was abnormal and comparably higher, which does not reflect the relationship between feed wastewater organic strength and sludge COD. The higher colloidal COD (cCOD) to soluble COD (sCOD) ratio during this period suggested the increase in COD was not due to incomplete degradation of influent wastewater, rather a larger presence of colloidal organic substances released from the biodegradation process. This argument is also supported by the protein and polysaccharide data shown in the later EPS section. This phenomenon may perhaps relate to the abnormal intake wastewater from day 30 to day 37, which potentially caused a greater release of microbial products.

4.4.4. Biogas Production

Figure 4-6 Biogas production under various OLR operation

The biogas production rate was very stable under each organic loading rate (Figure 4-6). Daily biogas production for OLR 3.5, 5.0 and 6.5 kg COD/m³/day was measured at 27.1 ± 1.8 , 40.7 ± 1.6 and 44.0 ± 0.9 l/day, respectively. Gas chromatography analysis reported a biogas composition of 59% CH₄, 31% CO₂, 10% N₂ and no significant detectable CO and O₂, which demonstrated a feasible energy recovery, having an overall methane yield of 0.31 ± 0.01 m³ CH₄/kg COD_{removed} (35 °C), at 79% of the maximum theoretical value.

4.4.5. Bicarbonate Dosage

Figure 4-7 Influent total alkalinity and sodium bicarbonate dosage over the study

The pH and total alkalinity of the mixed liquor in the reactor were controlled to have favorable conditions for methanogenesis. Figure 4-7 shows the influent wastewater total alkalinity in black lines and the sodium bicarbonate dosage over the study. Excluding two batches from earlier stage of study, the influent wastewater was slightly acidic in general, with a low alkalinity of 270 ± 80 mg/L as CaCO_3 . With the intention of maintaining a favorable pH and total alkalinity in the mixed liquor at 7.02 ± 0.01 and 2800 ± 150 mg/L as CaCO_3 , respectively, sodium bicarbonate was added to the digester. An average of 30 ± 2 g NaHCO_3 was dosed per day, corresponding to a bicarbonate dosing rate of 3.7 ± 0.3 kg $\text{NaHCO}_3/\text{m}^3$ wastewater or 0.47 ± 0.03 kg NaHCO_3/kg COD treated.

4.4.6. Nutrient Removal

Figure 4-8 Total nitrogen in feed, permeate and sludge filtrate

Figure 4-9 NH₃-N in feed, permeate and sludge filtrate

Figure 4-8 and Figure 4-9 show the total nitrogen and ammonia nitrogen in feed, permeate and mixed liquor filtrate. The total nitrogen in the effluent slightly fluctuates with the intake nitrogen from batch to batch, with an average of 43 ± 10 mg/L. The system had an overall nitrogen removal efficiency of $54 \pm 13\%$. In contrast, the inorganic portion of nitrogen in feed wastewater was insignificant, with 7 ± 3 mg/L ammonia nitrogen, roughly only $7 \pm 4\%$ of the total nitrogen. The anaerobic digestion had then converted most organic nitrogen into ammonia, where 36 ± 11 mg/L $\text{NH}_3\text{-N}$ was found in both sludge filtrate and permeate due to the complete soluble of ammonia. The ammonia nitrogen made up $81 \pm 7\%$ of the total nitrogen in the effluent. Organic nitrogen accumulation was observed in the mixed liquor, 185 ± 45 mg/L was calculated from the difference in TN and $\text{NH}_3\text{-N}$. This can be further explained by the accumulation of protein EPS, which matches the mixed liquor colloidal protein concentration over the study period.

Figure 4-10 Total phosphorus in feed, permeate and sludge filtrate

Figure 4-11 Orthophosphate-P in feed, permeate and sludge filtrate

Total and orthophosphate-phosphors were tested throughout the study and shown in Figure 4-10 and Figure 4-11. Note that all phosphorus concentrations were significantly higher in day 88, caused by the high concentration in the last batch of feed wastewater. The AnMBR system was capable of $28 \pm 11\%$ total phosphorus removal, with observed total phosphorus of 28 ± 5 mg/L in effluent. Similar to nitrogen, the inorganic phosphorus in feed solution was comparably low, about $44 \pm 7\%$ total phosphors was ortho-phosphors. The anaerobic digestion has further converted organic phosphors into ortho-phosphors, resulting in effluent composed mainly of ortho-phosphors at $92 \pm 4\%$. An accumulation of 21 ± 5 mg/L organic phosphors was observed in biomass.

Based on the results, the AnMBR did not achieve an excellent nutrient removal as expected, as the effluent contains higher amounts of inorganic nitrogen and phosphorous. However, it presents opportunities for recovering nutrients from wastewater by reuse in lawn watering, where the presence of nutrients from effluents can be substituted for those from commercial fertilizer.

4.4.7. Biomass Characteristics

Figure 4-12 MLSS and MLVSS profile

Figure 4-12 shows the MLSS and MLVSS concentration during the different operation periods. The study started by using active anaerobic sludge inherited from the previous synthetic brewery wastewater study, with an initial MLSS and MLVSS concentration of 11800 mg/L and 10200 mg/L, respectively. One of the research scopes was to investigate the system and membrane performance under low biomass concentrations. The target was to stabilize MLVSS around 7000 mg/L by adjusting daily sludge wasting. During the earlier stage, the biomass concentration was gradually decreased by having high sludge wasting operation. The average wasting for OLR 6.5 and 11.5 kg/m³/day operation period were 500 ml/day and 900 ml/day. The set target was achieved after the OLR 6.5 kg/m³/day operation on day 29; however, the stabilization failed. The biomass further

decreased in the next 20 days, due to a combination of toxic influent wastewater on day 30 to 37 and low organic loading of $3.5 \text{ kg/m}^3/\text{day}$. Excessive wasting of 325 ml/day on average was observed during day 30 to 50, corresponding to an average SRT of 46 days. On day 32, an immediate decline in MLVSS was observed followed by MLSS reduction in the next few days. The MLSS was found to be less sensitive to condition changes. The lowest MLSS and MLVSS observed were 4825 mg/L and 4250 mg/L before increased OLR to $5.0 \text{ kg COD/m}^3/\text{day}$.

During the final organic loading $5 \text{ kg/m}^3/\text{day}$ stage, sludge was wasted at $300 \pm 50 \text{ ml/day}$, corresponding to SRT of 50 days. A stable biomass concentration was achieved at $7600 \pm 200 \text{ mg/L}$ MLSS and $6700 \pm 200 \text{ mg/L}$ MLVSS. The observed yield and specific growth were calculated to be $0.029 \pm 0.001 \text{ gVSS /gCOD}$ and $0.022 \pm 0.001 \text{ gVSS/gVSS/day}$. Both yield and specific growth values are comparably lower than the typical values on conventional anaerobic processes (Metcalf & Eddy, 2002). Comparing to the earlier AnMBR study on synthetic wastewater, the biomass yield was identical but specific growth was found to be 25% lower. Over the entire study, a very high and stable VSS/TSS ratio of 0.86 ± 0.04 was observed, indicating very active biomass.

4.4.8. Extracellular Polymeric Substances (EPSs) Characteristics

Various literatures reported that the EPSs were the main contributor to membrane fouling in MBRs (Dereli et al., 2012a; Skouteris et al., 2012; Stuckey, 2012). EPS are polymeric substances produced by microorganisms, mainly consisting of protein, polysaccharides and humic acid (Laspidou and Rittmann, 2002). EPSs are released during cell metabolism as well as during starvation and stress as the cell metabolizes internal material and scavenges nutrients (Barker and Stuckey, 1999). Operating factors such as

extended SRT and high organic loading rate can increase EPSs production (Stuckey, 2012). In this study, weekly analysis was done on both colloidal and soluble protein and polysaccharide in the bulk sludge, as well as the protein and polysaccharide in the membrane permeate. Figure 4-13 shows the polysaccharide concentration and Figure 4-14 shows the protein data in the mixed liquor and membrane permeate.

Figure 4-13 Polysaccharide in bulk sludge filtrate and permeate

Figure 4-14 Protein in bulk sludge and permeate

High EPS concentrations were observed in both polysaccharide and protein during the earlier high organic loading (day 11 at $11.5 \text{ kg/m}^3/\text{day}$), as well as after the toxic feeding during day 30 to 37. The toxic substance stimulates the production of colloidal protein and polysaccharide in the bulk sludge, since only colloidal polysaccharide and protein increased while soluble substances were maintained. Further, high colloidal protein in mixed liquor explained the higher concentration in colloidal COD and organic nitrogen on day 35 and 41 which has been reported earlier. Aside from the high organic loading $11.5 \text{ kg/m}^3/\text{day}$ operation (on day 11) and intoxication period (on day 35 and 41), the EPSs in bulk sludge were relatively stable, but may display a decreasing tendency. The observation is different than the earlier synthetic wastewater study, where a rapid increasing tendency or a bulk accumulation of EPS was found.

Overall, a very stable protein/polysaccharide ratio was found in the bulk sludge, with 3.7 ± 0.4 in $1.5 \mu\text{m}$ filtrate and 2.2 ± 0.3 in $0.45 \mu\text{m}$ filtrate. Protein was dominated in permeate, having a high protein/polysaccharide ratio of 16.2 ± 2.7 . Earlier research (Ince et al., 2000) also argued that the inert soluble COD in the effluent was mostly produced by the biomass and could not be removed even with the extended HRT. In this study, it was found that the soluble protein at $325 \pm 25 \text{ mg/L}$ in permeate could not be further biodegraded by anaerobic digestion, which makes up the majority of the COD in effluent.

Figure 4-15 Polysaccharide and protein composition in mixed liquor

Based on the above results, polysaccharide and protein composition were analysed by rejection pore size, shown in Figure 4-15. The observation was comparable to the earlier study. The majority of polysaccharide in the bulk sludge were colloidal, while most of the soluble ones had particle sizes larger than $0.04 \mu\text{m}$. Protein expressed a bimodal distribution, with a peak in the colloidal region and a peak in the small particle size ($<0.04 \mu\text{m}$) region. The ultrafiltration membrane rejected $85 \pm 3 \%$ soluble polysaccharide, and there was no significant soluble protein being rejected by the membrane.

4.4.9. Membrane Filtration Performance

Constant flux filtration at 8 LMH with continuous biogas recirculation rate of 12 LPM was operated over the entire study, corresponding to a scouring rate of approximately $15.3 \text{ m}^3/\text{m}^2/\text{hr}$, similar to the operation scouring at $17.6 \text{ m}^3/\text{m}^2/\text{hr}$ in an earlier lab scale hollow fiber AnMBR operation study (Diez et al., 2012). Over the 90 day study period, the TMP was monitored, and average daily cycle TMP, as well as the determined critical fluxes are reported in Figure 4-16. Critical flux tests were performed weekly using the flux stepping method (Cho and Fane, 2002), by increasing the flux in a 15 min step-wise fashion while analysing the corresponding TMP. According to Le Clech et al. (2003), critical flux was determined as the corresponding flux where in a 10 minute duration, the observed TMP had increased by 0.1 kPa or greater.

Figure 4-16 TMP profile and measured critical flux

A rapid increase in TMP at a daily rate of 0.28 kPa was observed in the first 11 days, when operating at OLR of 11.5 kg COD/m³/day. The critical flux test conducted on day 11 showed that the operation flux was higher than the critical flux that was found at 7.2 LMH. The EPS measurement conducted on the same day showed that the protein and polysaccharide concentrations were 2550 ± 35 and 600 ± 7 mg/L in 1.5 μ m sludge filtrate and 550 ± 21 and 210 ± 2 mg/L in 0.45 μ m membrane filtrate, respectively.

Organic loading rate was then immediately adjusted to 6.5 kg/m³/day by diluting the wastewater, with the operation flux still maintained at 8 LMH. A sudden drop of 1.4 kPa in TMP was observed on day 12, followed by a gradual decrease over the next week, which stabilized at 6.9 ± 0.1 kPa from day 20 to 35. A comparatively high critical flux was observed on day 35, due to lower organic loading (3.5 kg/m³/day) and lower observed EPS concentration in the mix liquor. It was noted that the weekly chemical cleaning-in-place (CIP) was skipped on day 35 after the critical flux test, which resulted in a TMP jump of 0.9 kPa shown on day 36. A gradual decline in TMP was then witnessed after weekly CIP was back to schedule and it was maintained at 7.5 ± 0.1 kPa for the rest of 3.5 kg/m³/day operation.

After switching to organic loading of 5.0 kg/m³/day, the operation TMP gradually increased and a slight drop in TMP was observed after each weekly CIP. With the weekly cleaning protocol, an operation TMP of 8.7 ± 0.1 kPa was perceived during the organic loading. The critical flux measured on day 88 was below the operation flux. Thus, a gradual increase in TMP was observed at the end of study period, suggesting that a recovery cleaning of the membrane was necessary.

Over the 90 day study period, a TMP increase of 3.6 kPa was observed without performing any recovery cleaning. A sustainable operation of 8 LMH was achieved at organic loading of 3.5, 5.0 and 6.5 kg/m³/day, with detected critical flux at 8.8 ± 0.3 LMH. Lower critical flux below 8 LMH was identified under high organic loading 11.5 kg/m³/day operation, which caused a significant increase on operation TMP over a short time frame, thus a sustainable operation at 8 LMH could not be maintained. The study suggests the AnMBR should be running at an organic loading less than 6.5 kg/m³/day and more importantly, a lower operation flux at 7 LMH is recommended to achieve long term sustainable operation and extend membrane lifetime. Aside from the design flux and OLR, a weekly CIP protocol is essential to control the long term membrane fouling.

Figure 4-17 Relationship between critical flux and EPS in bulk sludge

In comparison to the earlier synthetic wastewater study, significantly higher concentrations of microbial products were detected in this study. Colloidal polysaccharide and protein greater than 285 and 950 mg/L with soluble polysaccharide and protein no less than 95 and 155 mg/L were detected, respectively. Combining critical flux data and the EPS concentration in bulk sludge, a moderate correlation was found

between the critical flux and EPS or more precisely soluble protein in bulk sludge, shown in Figure 4-17. A steady decrease in the determined critical flux was affected by the increase of soluble portion of microbial products. The earlier synthetic wastewater study found the critical flux was more sensitive to EPS in bulk sludge with colloidal polysaccharide and protein concentration less 200 mg/L and 800 mg/L; however, it does not apply to real brewery wastewater.

Figure 4-18 Effect of gas scouring on critical flux

At the end of the study period, critical flux tests were conducted over different air scouring rates. Five biogas recirculation rates were tested, corresponding to normalized scouring rates of 5.0, 10.2, 15.7, 21.1 and 26.5 m³/m²/hr. The results in Figure 4-18 indicated that the critical flux was greatly affected by the gas scouring intensity, where the critical flux increased when the gas scouring rate was increased and the difference was smaller as scouring rate got larger. Eventually the difference is insignificant after the

gas scouring rate increased to 17 LPM or above, suggesting after this point, a higher gas scouring rate would not reduce membrane fouling any further.

4.5. CONCLUSION

In this study, the efficacy of the submerged AnMBR technology was demonstrated over high organic strength wastewater from a local craft brewery. Due to the variance of influent wastewater strength over the batch brewing processes, the AnMBR unit was subjected to operation with highly variable organic loading from 3.5 to 11.5 kg COD/m³/day. Overall, the system achieved over 98% COD, 54% TN and 28% TP removal efficiency. Effluent COD was slightly increased with the organic loading, where observed permeate COD was at 149 ± 7 , 172 ± 15 and 268 ± 21 mg/L for OLR of 5.0, 6.5 and 11.5 kg/m³/day, respectively. The permeate contained mostly non-biodegradable EPS, mainly soluble protein, as the ultrafiltration membrane rejected 85% soluble polysaccharide with no significant rejection on soluble protein. A favorable pH and total alkalinity condition was maintained with an average dosage of 0.37 kg NaHCO₃/m³ influent. The methane yield was found to be very stable at 0.31 m³ CH₄/kg COD (35 °C). In comparison to the earlier synthetic wastewater study, significantly higher concentration of EPS were found in the mix liquor. Moreover, a moderate correlation was found between the critical flux and soluble protein concentration. An overall TMP increase of 3.6 kPa was observed over the 90 days period without any recovery cleaning. The study recommends running high strength brewery wastewater AnMBR on organic loading under 6.5 kg/m³/day with operation flux at 7 LMH, coupled with a weekly CIP protocol to maintain long term sustainable operation and extend membrane lifetime.

4.6. ACKNOWLEDGEMENT

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CHAPTER 5 - CONCLUSION AND RECOMMENDATIONS

5.1. OVERALL DISCUSSION AND CONCLUSION

Throughout this research, the efficacy of the submerged AnMBR technology on wastewater treatment was demonstrated over the high organic strength wastewater from the brewery industry. The AnMBR unit was subjected to a total of 230 days continuous operation, undergoing precisely controlled OLRs (2-10 kg COD/m³/day) with synthetic wastewater and uncontrolled OLRs (observed OLR of 3.5 – 11.5 kg COD/m³/day) operation through feeding with local micro-brewery wastewater having high variability in strength and characteristics.

The system achieved stable operation with no acidification was observed. Overall, the AnMBR achieved an excellent organic reduction at over 98% COD removal efficiency. In spite of the variability in feed strength and OLR, the AnMBR was capable of producing high quality effluent with COD concentrations lower than 300 mg/L throughout the study. The effluent COD concentration was a function of the OLR and found to be significantly higher in the real brewery wastewater operation. At OLRs of 5 kg COD/m³/day, the COD concentrations in effluent under synthetic and real brewery wastewater were 52 ± 2 and 149 ± 7 mg/L, respectively. The study found that the effluent contained mostly non-biodegradable soluble substances, since the effluent BOD concentration remained below 40 mg/L at all OLRs.

The EPS analysis further supported this argument. The membrane permeate contains mostly non-biodegradable protein which was likely being produced during cell metabolism. Significantly higher EPS concentrations were observed in both sludge

supernatant and membrane permeate while operating AnMBR on real brewery wastewater. During the real wastewater operation at OLR of 5 kg COD/m³/day, the EPS concentrations observed in 1.5 µm sludge filtrate and membrane permeate were 1500 ± 240 and 335 ± 45 mg/L, compared to 185 ± 15 and 80 ± 10 mg/L that were found in the synthetic wastewater study at the corresponding OLR.

The weekly EPS analysis also suggested that the UF membrane was capable of 85 -95% soluble polysaccharide rejection but no significant soluble protein rejection. The majority of polysaccharide in the bulk sludge was colloidal and most of the soluble matter has particle sizes larger than 0.04 µm. The protein EPSs were expressed in a bimodal distribution, with a peak in the colloidal region and a peak in the small particle size (<0.04 µm) region. Moreover, a moderate correlation was found between the critical flux and EPS concentration in bulk sludge. The correlation was more sensitive when polysaccharide and protein concentration were below 200 mg/L and 800 mg/L; however, it did not apply to real brewery wastewater operation, as the EPS concentrations were found to be much higher.

Overall, the AnMBR system achieved an excellent COD removal at all tested OLRs, produced high quality effluent free of solid and demonstrated great energy recovery, with stable methane yield over 0.31 m³ CH₄/kg COD at 35 °C. The study found the major limitation was the low membrane filtration flux. Low critical fluxes were observed under high organic loading. An average critical flux of 8.6 ± 0.1 was observed under real brewery wastewater operation at an OLR of 5 kg/m³/day. To achieve full capacity in the anaerobic digestion compartment, the AnMBR should have more membrane installed to increase the operation OLR. However, this would largely increase the capital cost.

In evaluating the system performance and taking the membrane cost into consideration, this study suggests running AnMBRs on high strength brewery wastewater at an OLR under $6.5 \text{ kg/m}^3/\text{day}$ with an operation flux of 7 LMH. A weekly CIP and semi-annual recovery cleaning protocol is recommended to maintain long term sustainable operation and extend membrane lifetime.

5.2. RECOMMENDATIONS

The following recommendations can be made based on this research,

1. The membrane module used in this study was at a different initial condition between the two operations. Thus, it is recommended that recovery cleaning should be conducted prior to each operation condition. With the membrane being restored to similar conditions, long term fouling rate can be easily compared.
2. Membrane autopsies should be conducted at the end of each operation; so that foulants can be directly characterized.
3. To better evaluate irreversible membrane fouling, more work is needed to characterize the EPS in the mixed liquor and membrane permeate.
4. A comprehensive GC-TCD analysis is strongly recommended to test the biogas composition at different operation phase. With more frequent biogas composition, methane yield at different OLRs or MLSS can be further investigated. Further, H_2S concentrations should be measured, creating strategy for biogas utilization.
5. The study found that the filterability of the sludge is highly dependent on the concentration of colloidal and extracellular polymeric substances, which increased with OLR. Thus, the OLR was limited by the filterability of the suspended biomass. Hybrid reactor configurations should be considered in future

research. With a combination of granules, biofilm or presence of GAC, the OLR can be potentially increased with minor decreases in filterability.

6. Higher operation fluxes require more frequent membrane cleaning; thus decreasing the membrane lifetime and increasing membrane replacement cost. Contrarily, the lower operation flux requires more module, which increases the capital cost. A systematic cost balance should be conducted between the initial installation and replacement membrane cost. Design flux and cleaning frequency can be recommended based on the results.

CHAPTER 6 - REFERENCES

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CHAPTER 7 - APPENDICES

Appendices include 1) AnMBR operation data summery 2) Critical flux determination

7.1. APPENDIX I – ANMBR OPERATION DATA

Accumulated days	Date	Average pH	Average ORP	Average MTK Temp (C)	Average AD Temp. (C)	Daily Biogas Prod. (L)	TMP (kPa)
0	Jan 21, 2014	7.25	-278.37	32.79	34.20	3.02	
1	Jan 22, 2014	6.95	-268.30	32.70	34.20		
2	Jan 23, 2014	6.38	-223.49	33.15	34.18		
3	Jan 24, 2014	6.15	-229.37	33.20	34.26	4.32	
4	Jan 25, 2014	6.03	-220.44	33.28	34.28	5.50	
5	Jan 26, 2014	6.41	-229.51	33.16	34.18	6.68	
6	Jan 27, 2014	6.79	-282.63	33.31	34.24	6.30	
7	Jan 28, 2014	6.67	-292.45	33.17	34.23	7.35	
8	Jan 29, 2014	6.53	-313.20	33.18	34.21	12.02	
9	Jan 30, 2014	6.48	-290.64	33.05	34.16	14.65	
10	Jan 31, 2014	6.39	-275.07	32.98	34.15	16.21	
11	Feb 01, 2014	6.66	-291.30	33.05	34.20	17.36	
12	Feb 02, 2014	6.79	-292.58	33.22	34.26	11.96	
13	Feb 03, 2014	6.93	-292.40	32.93	34.14		
14	Feb 04, 2014	6.95	-268.20	32.67	34.01		
15	Feb 05, 2014	6.96	-251.82	32.93	34.17		
16	Feb 06, 2014	6.81	-311.35	32.82	34.17		
17	Feb 07, 2014	6.48	-461.72	32.36	33.43	15.84	
18	Feb 08, 2014	6.53	-469.86	28.90	29.41	14.40	
19	Feb 09, 2014	6.64	-487.71	33.79	35.11	18.23	
20	Feb 10, 2014	6.65	-491.95	33.67	35.07	19.43	
21	Feb 11, 2014	6.80	-495.57	33.69	35.04		4.9
22	Feb 12, 2014	6.50	-482.77	33.46	34.92	18.93	5.0
23	Feb 13, 2014	6.63	-480.73	33.71	35.01	16.77	5.0
24	Blackout						
25	Feb 15, 2014	6.72	-487.57	33.74	35.01	19.00	4.9
26	Feb 16, 2014	6.88	-495.53	33.27	34.97	18.50	5.0
27	Feb 17, 2014	6.92	-498.29	33.39	34.96	19.59	5.0
28	Feb 18, 2014	6.91	-498.95	33.51	34.91	19.45	5.1
29	Feb 19, 2014	6.90	-498.89	33.54	34.93	20.91	5.1
30	Feb 20, 2014	6.93	-500.47	33.42	35.06		5.1
31	Feb 21, 2014	6.90	-501.23	33.89	35.19	20.80	5.0
32	Feb 22, 2014	6.80	-496.42	33.98	35.23	19.71	5.0
33	Feb 23, 2014	6.80	-493.32	33.97	35.27	27.54	5.1
34	Feb 24, 2014	6.91	-505.11	33.98	35.35	49.31	5.0
35	Feb 25, 2014	6.91	-506.53	34.00	35.37	51.55	5.0
36	Feb 26, 2014	6.91	-503.91	34.18	35.42	51.23	5.1

37	Feb 27, 2014	6.91	-501.44	34.40	35.52	51.51	5.1
38	Feb 28, 2014	6.91	-500.07	34.09	35.39	52.34	5.2
39	Mar 01, 2014	6.91	-499.05	33.98	35.36	52.72	5.2
40	Mar 02, 2014	6.89	-498.13	33.94	35.34	54.30	5.3
41	Mar 03, 2014	6.83	-494.95	33.94	35.34	54.49	5.2
42	Mar 04, 2014	6.83	-494.90	33.57	35.41	56.44	5.3
43	Mar 05, 2014	6.83	-493.82	33.10	35.53	54.11	5.3
44	Mar 06, 2014	6.82	-491.57	33.67	35.51	55.95	5.2
45	Mar 07, 2014	6.82	-490.87	34.17	35.46	54.56	5.2
46	Mar 08, 2014	6.83	-490.34	34.17	35.44	50.59	5.3
47	Mar 09, 2014	6.82	-489.34	34.16	35.42	50.83	5.2
48	Mar 10, 2014	6.82	-488.91	34.08	35.35	52.45	5.2
49	Mar 11, 2014	6.81	-488.04	33.47	35.12	52.52	5.2
50	Mar 12, 2014	6.81	-487.39	34.11	35.35	52.85	5.2
51	Mar 13, 2014	6.81	-487.15	34.31	35.40	53.30	5.4
52	Mar 14, 2014	6.82	-486.88	34.31	35.38	49.59	5.3
53	Mar 15, 2014	6.82	-486.86	34.25	35.41	52.28	5.2
54	Mar 16, 2014	6.81	-486.42	33.93	35.28	52.38	5.4
55	Mar 17, 2014	6.81	-485.23	33.54	35.10	51.86	5.3
56	Mar 18, 2014	6.81	-480.71	34.08	35.37	55.27	5.3
57	Mar 19, 2014	6.82	-468.53	33.49	35.19	63.53	5.4
58	Mar 20, 2014	6.82	-469.62	33.55	35.22	79.08	5.4
59	Mar 21, 2014	6.91	-473.07	33.59	35.19		5.4
60	Mar 22, 2014	6.85	-476.50	33.59	34.97	81.64	5.4
61	Mar 23, 2014	6.85	-475.53	33.66	35.00	82.16	5.4
62	Mar 24, 2014	6.82	-475.78	33.23	34.85	76.31	5.4
63	Mar 25, 2014	6.84	-475.63	33.39	34.98	81.98	5.4
64	Mar 26, 2014	6.83	-475.54	33.18	34.79	78.27	5.4
65	Mar 27, 2014	6.83	-475.12	33.81	35.21	80.09	5.4
66	Mar 28, 2014	6.82	-475.94	33.71	35.15	79.22	5.4
67	Mar 29, 2014	6.83	-474.60	33.63	35.18	77.55	5.3
68	Mar 30, 2014	6.84	-475.16	33.40	35.05	78.21	5.5
69	Mar 31, 2014	6.85	-475.91	32.60	34.15		5.7
70	Apr 01, 2014	6.83	-476.15	33.62	35.41	80.26	5.6
71	Apr 02, 2014	6.88	-475.38	33.66	35.44	74.89	5.7
72	Apr 03, 2014	7.22	-485.02	33.83	35.42	75.33	5.7
73	Apr 04, 2014	7.07	-484.94	33.78	35.42	91.80	5.7
74	Apr 05, 2014	7.37	-338.46	33.72	35.33	79.46	5.7
75	Apr 06, 2014	7.25	-310.77	33.21	35.12	84.80	6.0
76	Apr 07, 2014	7.23	-360.90	33.38	35.09	91.78	6.6
77	Apr 08, 2014	7.24	-387.09	32.78	34.91	90.90	6.2
78	Apr 09, 2014	7.23	-403.91	32.79	34.90	87.75	6.2
79	Apr 10, 2014	7.24	-417.06	33.00	35.04	89.70	6.2

80	Apr 11, 2014	7.25	-427.56	33.33	35.18	91.13	6.2
81	Apr 12, 2014	7.25	-435.36	32.95	35.18	91.39	6.6
82	Apr 13, 2014	7.36	-346.69	33.54	35.26	64.58	6.4
83	Apr 14, 2014	7.34	-316.53	33.25	35.23	76.31	6.5
84	Apr 15, 2014	7.23	-359.86	33.38	35.40	91.49	6.6
85	Apr 16, 2014	7.21	-264.09	32.53	34.86	33.76	7.1
86	Apr 17, 2014	7.22	-266.07	33.04	34.83	0.00	
87	Apr 18, 2014	7.22	-315.49	33.11	34.85	0.00	6.6
88	Apr 19, 2014	7.23	-346.08	33.03	34.85	0.06	6.5
89	Apr 20, 2014	7.23	-368.11	33.11	34.91	0.00	6.7
90	Apr 21, 2014	7.23	-385.80	33.33	35.03	0.00	6.7
91	Apr 22, 2014	7.24	-400.77	33.44	34.98	0.00	6.8
92	Apr 23, 2014	7.25	-408.47	33.11	34.84	89.90	6.7
93	Apr 24, 2014	7.24	-415.71	33.30	34.97	88.03	6.7
94	Apr 25, 2014	7.24	-420.15	32.78	34.73	87.61	6.8
95	Blackout						6.3
96	Apr 27, 2014	7.24	-417.30	33.29	34.70	33.62	6.5
97	Apr 28, 2014	7.23	-455.96	33.11	34.89	85.06	6.6
98	Apr 29, 2014	7.24	-470.13	32.76	34.75	94.05	6.6
99	Apr 30, 2014	7.24	-474.64	33.14	34.87	79.88	6.6
100	May 01, 2014	7.23	-476.23	32.95	34.78	26.26	6.6
101	May 02, 2014	7.23	-477.91	33.35	34.96	83.35	6.6
102	May 03, 2014	7.22	-478.12	33.06	34.85	81.70	6.7
103	May 04, 2014	7.25	-479.24	32.87	34.76	77.38	6.7
104	May 05, 2014	7.24	-478.80	33.50	35.03	0.08	6.7
105	May 06, 2014	7.24	-477.63	33.07	34.91	0.08	6.7
106	May 07, 2014	7.22	-476.72	32.91	34.85	0.08	6.8
107	May 08, 2014	7.22	-476.08	32.96	34.89	0.07	6.8
108	May 09, 2014	7.21	-476.81	33.46	35.15	0.06	6.8
109	May 10, 2014	7.21	-477.16	33.46	35.11	0.06	6.8
110	May 11, 2014	7.21	-477.40	33.85	35.24	0.07	6.9
111	May 12, 2014	7.21	-478.14	33.48	35.08	0.07	6.9
112	May 13, 2014	7.21	-440.29	33.42	35.11	0.07	6.9
113	May 14, 2014	7.23	-432.97	33.62	35.16	0.07	6.8
114	May 15, 2014	7.23	-447.35	33.24	35.03	0.07	7.0
115	May 16, 2014	7.23	-454.48	32.54	34.74	0.08	7.1
116	May 17, 2014	7.25	-458.58	32.71	34.93	0.08	7.0
117	May 18, 2014	7.27	-462.41	33.08	35.12	0.07	7.0
118	May 19, 2014	7.26	-464.94	33.11	35.13	0.07	6.9
119	May 20, 2014	7.24	-465.89	33.25	35.18	0.07	6.8
120	May 21, 2014	7.24	-466.38	33.29	35.22	0.07	6.9
121	May 22, 2014	7.23	-467.49	33.37	35.25	0.10	6.9
122	May 23, 2014	7.23	-466.96	33.22	35.17	89.91	6.9

123	May 24, 2014	7.22	-467.60	33.38	35.23	0.03	6.8
124	May 25, 2014	7.22	-469.56	33.29	35.21	0.07	6.9
125	May 26, 2014	7.24	-469.93	33.63	35.46	44.55	6.8
126	May 27, 2014	7.22	-467.33	33.89	35.69	82.72	6.8
127	May 28, 2014	7.22	-467.60	33.57	35.55	25.13	6.9
128	May 29, 2014	7.21	-469.45	33.67	35.55	87.64	6.7
129	May 30, 2014	7.20	-470.35	33.59	35.55	84.70	6.8
130	May 31, 2014	7.21	-470.91	33.26	35.42	81.54	6.8
131	Jun 01, 2014	7.23	-471.14	33.62	35.58	83.04	6.9
132	Jun 02, 2014	7.24	-472.00	33.57	35.57	72.66	7.1
133	Jun 03, 2014	7.26	-470.05	33.08	35.29	77.08	6.9
134	Jun 04, 2014	7.24	-470.09	33.48	35.53	100.09	7.0
135	Jun 05, 2014	7.24	-471.13	33.81	35.61	82.63	6.8
136	Jun 06, 2014	7.24	-471.63	33.75	35.62	8.32	6.8
137	Jun 07, 2014	7.25	-460.11	34.03	35.72	0.07	6.8
138	Jun 08, 2014	7.25	-470.20	33.81	35.67	0.07	6.9
139	Jun 09, 2014	7.23	-471.88	33.89	35.70	21.15	6.9
140	Jun 10, 2014	7.25	-474.52	33.99	35.73	81.28	6.9
Switched to Real Wastewater							
0	Jun 11, 2014	7.25	-476.01	34.18	35.79		6.8
1	Jun 12, 2014	7.07	-471.13	33.97	35.77	43.28	7.2
2	Jun 13, 2014	7.00	-466.19	33.77	35.71	43.62	7.4
3	Jun 14, 2014	7.01	-464.96	33.36	35.55	43.59	8.0
4	Jun 15, 2014	7.01	-464.51	33.44	35.57	44.53	8.5
5	Jun 16, 2014	7.01	-463.38	33.24	35.49	44.67	8.4
6	Jun 17, 2014	7.02	-464.04	33.06	35.35	44.33	8.3
7	Jun 18, 2014	7.02	-464.24	33.32	35.42	42.36	8.4
8	Jun 19, 2014	7.03	-462.29	33.32	35.50	43.67	8.9
9	Jun 20, 2014	7.02	-462.40	33.36	35.56	73.73	8.6
10	Jun 21, 2014	7.04	-466.53	33.37	35.57	83.39	9.6
11	Jun 22, 2014	7.05	-465.69	33.81	35.69	71.02	9.2
12	Jun 23, 2014	7.03	-466.62	33.83	35.68	75.87	7.8
13	Jun 24, 2014	7.02	-464.90	32.96	35.30	62.21	7.6
14	Jun 25, 2014	7.02	-463.58	32.86	35.23	41.37	7.0
15	Jun 26, 2014	7.02	-462.83	33.36	35.49	42.97	7.4
16	Jun 27, 2014	7.02	-463.80	33.49	35.55	42.11	7.2
17	Jun 28, 2014	7.02	-463.31	32.93	35.31		7.0
18	Jun 29, 2014	7.00	-460.57	32.58	35.21		7.3
19	Jun 30, 2014	7.00	-458.17	32.52	35.21		7.2
20	Jul 01, 2014	7.02	-447.30	32.64	35.23		6.8
21	Jul 02, 2014	6.96	-450.15	33.12	35.37	44.78	6.9
22	Jul 03, 2014	7.02	-462.25	33.69	35.64	50.42	7.0
23	Jul 04, 2014	7.02	-463.78	33.73	35.64	41.88	6.9

24	Jul 05, 2014	7.05	-463.95	33.74	35.68		6.8
25	Jul 06, 2014	6.98	-463.06	34.02	35.77	43.45	6.8
26	Jul 07, 2014	7.02	-465.51	33.68	35.60	45.45	7.0
27	Jul 08, 2014	7.02	-465.21	33.13	35.34		6.8
28	Jul 09, 2014	7.02	-465.55	33.36	35.52	46.37	6.9
29	Jul 10, 2014	7.03	-466.26	33.79	35.73	42.86	7.2
30	Jul 11, 2014	7.01	-467.62	34.36	35.96	26.22	7.0
31	Jul 12, 2014	7.01	-469.31	34.25	36.00	26.37	6.8
32	Jul 13, 2014	7.01	-466.70	33.95	35.96	24.02	7.0
33	Jul 14, 2014	7.01	-467.53	33.81	35.90	22.93	7.0
34	Jul 15, 2014	7.01	-466.89	33.76	35.86	21.86	6.8
35	Jul 16, 2014	7.01	-467.05	33.61	35.79	24.75	6.9
36	Jul 17, 2014	7.01	-467.21	33.64	35.81	26.17	7.8
37	Jul 18, 2014	7.01	-468.20	33.71	35.84	26.41	7.9
38	Jul 19, 2014	7.00	-465.70	33.75	35.88	29.70	7.9
39	Jul 20, 2014	7.01	-469.16	33.83	35.92		7.6
40	Jul 21, 2014	7.02	-472.43	34.29	36.06		7.7
41	Jul 22, 2014	7.01	-471.41	34.21	35.73	29.82	7.8
42	Jul 23, 2014	7.01	-473.39	33.65	35.05	31.25	7.6
43	Jul 24, 2014	7.01	-474.07	33.05	34.94	30.49	7.4
44	Jul 25, 2014	7.02	-471.82	32.51	34.90	25.00	7.5
45	Jul 26, 2014	7.02	-472.18	32.63	34.93	24.47	7.5
46	Jul 27, 2014	7.02	-471.46	32.58	34.92	24.71	7.5
47	Jul 28, 2014	7.01	-472.07	32.86	35.05	24.90	7.5
48	Jul 29, 2014	7.01	-472.16	33.08	35.13	25.14	7.5
49	Jul 30, 2014	7.01	-469.82	33.04	35.13	31.38	7.2
50	Jul 31, 2014	7.01	-474.48	33.07	35.13	38.67	7.4
51	Aug 01, 2014	7.01	-473.69	32.92	35.09	39.27	7.9
52	Aug 02, 2014	7.01	-473.69	32.84	35.07	39.04	7.9
53	Aug 03, 2014	7.01	-473.41	32.64	34.99	37.34	8.2
54	Aug 04, 2014	7.01	-473.38	32.70	35.04	34.78	8.3
55	Aug 05, 2014	7.01	-472.58	32.66	35.05	34.90	8.2
56	Aug 06, 2014	7.01	-473.26	32.62	35.03	37.71	8.0
57	Aug 07, 2014	7.01	-473.32	32.74	35.10	37.59	8.4
58	Aug 08, 2014	7.01	-471.46	32.86	35.13	34.74	8.5
59	Aug 09, 2014	6.96	-468.92	32.79	35.04	39.40	8.5
60	Aug 10, 2014	6.91	-465.64	32.79	35.12	44.18	8.7
61	Aug 11, 2014	7.02	-473.06	32.79	35.12	43.83	8.7
62	Aug 12, 2014	7.02	-471.57	32.78	35.11	44.81	8.7
63	Aug 13, 2014	7.02	-472.40	32.77	35.11	37.15	8.7
64	Aug 14, 2014	7.02	-472.75	32.57	35.05	38.16	9.1
65	Aug 15, 2014	7.02	-472.92	32.68	35.07	40.94	9.3
66	Aug 16, 2014	7.02	-473.27	32.86	35.11	38.06	9.5

67	Aug 17, 2014	7.01	-472.30	32.95	35.14		8.6
68	Aug 18, 2014	7.01	-476.07	24.02	35.55		
69	Aug 19, 2014	7.02	-477.93	20.61	35.62		
70	Aug 20, 2014	7.03	-478.97	21.16	35.68		
71	Aug 21, 2014	7.08	-476.62	21.73	35.77		
72	Aug 22, 2014	7.09	-476.51	20.98	35.78		
73	Aug 23, 2014	7.12	-477.82	21.16	35.79		
74	Aug 24, 2014	7.16	-478.88	21.22	35.77		
75	Aug 25, 2014	7.14	-472.68	27.15	35.65		8.6
76	Aug 26, 2014	7.00	-474.61	35.71	35.51	43.19	8.6
77	Aug 27, 2014	7.01	-475.50	35.45	35.41	39.89	8.0
78	Aug 28, 2014	7.01	-474.89	35.44	35.38	38.05	8.3
79	Aug 29, 2014	7.01	-475.44	35.71	35.45	37.65	8.6
80	Aug 30, 2014	7.01	-474.41	35.92	35.53	37.53	8.7
81	Aug 31, 2014	7.04	-475.50	36.21	35.63	39.14	8.6
82	Sep 01, 2014	7.01	-474.13	36.67	35.75	42.23	8.7
83	Sep 02, 2014	7.02	-472.14	36.80	35.78	46.80	8.3
84	Sep 03, 2014	7.02	-473.98	36.81	35.61	48.92	9.0
85	Sep 04, 2014	7.02	-472.76	36.76	35.42	48.71	9.2
86	Sep 05, 2014	7.02	-471.51	37.28	35.58	50.13	9.3
87	Sep 06, 2014	7.02	-472.44	37.24	35.52	47.27	9.7
88	Sep 07, 2014	7.01	-472.15	37.32	35.53	40.02	10.2
89	Sep 08, 2014	7.03	-473.38	37.58	35.63	40.17	10.4
90	Sep 09, 2014	7.01	-473.03	37.79	35.57		10.6

7.2. APPENDIX II – CRITICAL FLUX DATA

Synthetic wastewater

42

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55

5-22

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Date: March 17, 2014

63

7.5-6

Date: March 25, 2014

71

7.5-14

80

10-9

91

10-20

99

10-28

105

10-34

Date: May 06, 2014

111

10-40

121

10-50

Date: May 22, 2014

127

10-56

132

10-61

Synthetic w.w.

135

10-64

Air scouring rate. (synthetic)

Date: May 12, 2014, 50%

Date: May 12, 2014, 65%

Date: May June 02, 2014, 50%

Date: May June 02, 2014, 65%

Date: May June 05, 2014, 50%

Date: May June 05, 2014, 65%

Date: May June 05, 2014, 80%

Real Brewery wastewater

D11

026

x

p35

X

B

041

Date: July 22, 2014

7

W48

Date: July 29, 2014

DS6

065

X

081

088

Air scouring effect. (Real)

Date: Sept 10, 2014, 35%

Date: Sept 10, 2014, 80%

Air scanning effect. (Real)

D91