Thermophilic anaerobic membrane bioreactor for pulp and paper sludge treatment

By

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Abstract

Pulp and paper mills generate a significant amount of organic waste (primary and secondary sludge) that requires treatment and disposal. Currently, pulp and paper sludge (PPS) is either dried for incineration or used for landfilling. However, the dewatering and drying of sludge before incineration is an energy extensive process and landfilling is associated with a high cost and low public acceptance, the practices of landfilling will tend to decrease. Recently, anaerobic digestion is considered a cost-effective alternative to a small environmental footprint and has been researched widely. Similarly, anaerobic digestion of PPS has the limitations of a large reactor size, high capital cost, and reduced quality of effluent. Thus, it is highly desirable to search novel technologies for PPS treatment and disposal. In this study, a new insight was that thermophilic anaerobic membrane bioreactor (ThAnMBR) was developed for PPS treatment and disposal for biogas production because it can overcome some advantages of conventional anaerobic digestors.

In this study, a laboratory-scale ThAnMBR was operated for 328 days to assess the biological and membrane performance of the ThAnMBR at different hydraulic retention times (HRTs) and different types of pulp and paper secondary sludge. In the first part of this thesis, the biological performance of ThAnMBR are discussed by effluent, organic loading rate (OLR), chemical oxygen demand (COD), biogas production rate, biogas composition, biogas yield and suspended solid destruction. The results showed that the performance of a higher HRT is better than a low HRT, but the performance of ultrasonic pretreatment on PPS does not improve all properties. In the second part of this thesis, the membrane performance of ThAnMBR was discussed by: flux,

transmembrane pressure (TMP), membrane fouling, particle size distribution, extracellular polymeric substances (EPS), soluble microbial products (SMP), morphology and pore size distribution. The results suggest that ThAnMBR is feasible for PPS treatment, but the membrane fouling should be minimized. Operating ThAnMBR at a higher HRT is more attractive than at a lower HRT from the biological performance point of view.

Keywords: Thermophilic anaerobic membrane bioreactor; pulp and paper sludge; ultrasonic pretreatment; biogas production; organic loading rate

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List of Nomenclature and Abbreviations

AnMBR	Anaerobic Membrane Bioreactor
CHO	Carbohydrate
COD	Chemical Oxygen Demand
CSTR	Completely Stirred Tank Reactor
EPS	Extracellular Polymeric Substances
F/M	Food/Microorganisms
GC	Gas Chromatograph
HRT	Hydraulic Retention Time
LB-EPS	Loosely Bound- Extracellular Polymeric Substances
MBR	Membrane Bioreactor
MF	Microfiltration
MLSS	Mixed Liquor Suspended Solids
OLR	Organic Loading Rate
PN	Protein
PP	Pulp and paper
PPS	Pulp and Paper Sludge
PSD	Particle Size Distribution
PWW	Paper Wastewater
R_T	Total Resistance
SCOD	Soluble Chemical Oxygen Demand
SEM	Scanning Electron Microscopy

SMP	Soluble Microbial Products
SRT	Solid Retention Time
SS	Suspended Solid
TB-EPS	Tightly Bound- Extracellular Polymeric Substances
TCOD	Total Chemical Oxygen Demand
TCD	Thermal Conductivity Detector
ThAnMBR	Thermophilic Anaerobic Membrane bioreactor
TKN	Total K Nitrogen
TMP	Transmembrane Pressure
TSS	Total Suspended Solid
US	Ultrasonic
VSS	Volatile Suspended Solid

Table of Contents

Thermophilic anaerobic membrane bioreactor for pulp and paper sludge treatment 1

Abstract 2

Acknowledgements i

List of Nomenclature and Abbreviations ii

Table of Contents iv

1. Introduction 1

1.1 Current Problems 1

1.2 Objectives 3

1.3 Novelty 4

2. Literature Review 5

2.1 Anaerobic Digestion 5

2.1.1 Anaerobic digestion of PPS 7

2.1.2 Non-pretreatment and pretreatment of PPS 10

2.1.3 Pretreatment of PPS 11

2.2 Combustion/incineration 26

2.3 Fermentation (Ethanol) 26

2.4 Pyrolysis 28

2.5 Gasification 29

2.6 Liquefaction 30

2.7 Challenges and Opportunities of Pulp and Paper Sludge 31

3. Experimental Materials and Methods 32

3.1 Anaerobic Membrane Bioreactor Setup and Operation 32

3.1.1 Waste Sludge and Inoculum Sample 35

3.1.2 Pretreatment of PPS 37

3.2 Analytical Methods 37

3.2.1 Chemical Oxygen Demand (COD) 37

3.2.2 Biogas Determination and Quantification 38

3.2.3 Particle Size Distribution 39

3.2.4 Extracellular Polymeric Substances (EPS) Extraction and Measurement 40

3.2.5 Soluble Microbial Products (SMP) Measurement 41

3.2.6 Measurement of Feed Sludge and Mix-Liquor 41

3.2.7 Membrane Resistance Determination 42

3.2.8 Scanning Electron Microscopy (SEM) 44

3.2.9 Statistical Analysis 44

4. Results and Discussion 45

4.1 Biological Performance of ThAnMBR 45

4.1.1 Organic Loading Rate (OLR) 45

4.1.2 Chemical oxygen demand (COD) 48

4.1.3 Biogas production 52

4.2 Membrane performance 60

4.2.1 Flux and TMP 60

4.2.2 Membrane Fouling Characterization 62

4.2.3 Particle Size Distributions 65

4.2.4 Extracellular Polymeric Substances (EPS) and Soluble microbial products (SMP) 68

4.2.5 Morphology and pore size distribution of new and used membranes 70

5. Conclusions and Future work 73

5.1 Conclusions 73

5.2 Future work 74

6. Reference 75

1. Introduction

1.1 Current Problems

The pulp and paper industry has been considered the third largest industrial polluter affecting air, water, and land, and the severe situations have to face because of the globalized completion and legislations of a stringent environment. The global waste and wastewater treatment market is estimated to increase by 60% between 2012 and 2020 (Frost & Sullivan, 2013), even though the paper production will always be in decline. Currently, the aerobic membrane bioreactor and anaerobic membrane bioreactor are used to treat the pulp and paper wastewater. Anaerobic processes are increasingly used to treat pulp and paper industry wastewaters (Habets and Driessen, 2007). On the other hand, pulp and paper mills generate a large amount of organic solid waste (primary and secondary sludge) that needs to pay more attention for treatment and disposal. The production rate of pulp and paper sludge (PPS) is able to increase by 48-86%, as compared to the actual PPS production rate, which is estimated to 550 million tons by 2050 (Mabee and Roy, 2003).

The conventional treatment and disposal of PPS is landfilling, which has a number of disadvantages such as a large space is required, high cost, and leachate problems. As a result, the proportions of landfilling are decreased due to the public opinions and jurisdiction policies (Wang et al., 2008; Joo et al., 2015; Pervaiz and Sain, 2015). For example, in the U.S., the percentage of landfilling is decreased to 52% (2015), but the percentage was 87% in 1979 (Amberg, 1984; Pervaiz and Sain, 2015). In addition, in Quebec, Canada, 29% of 1.4

million tons PPS are treated by landfilling, and the Quebec's government predicted to decrease the percentage of landfill to zero (MDDEP, 2011; Gouvernement du Quebec, 2012; MDDELCC, 2015). Furthermore, except for landfilling, land application and energy recovery can be used to treat the PPS (Faubert et al., 2016). There are numerous uses for land applications, for example, agriculture, silviculture, land reclamation, composting. When the PPS was used by agriculture, some nutrients of PPS are recycled, but the land application have to be monitored to avoid soil and water contamination (Camberato et al., 2006; Rashid et al., 2006). Furthermore, most of the PPS cannot be directed to be used onto land applications due to the heavy metals (Camberato et al., 2006). In recent years, anaerobic digestion (AD) has been considered as one of the energy recovery approaches from PPS. AD is a biological process to produce bioenergy in which organic matters is broken down and converted into biogas by a microorganism consortium under the oxygen-free condition. AD process can convert the organic matter into biogas, and significantly reduce the production of solid wastes. Furthermore, Magnusson and Alvfors (2012) found that PPS can be used as a substrate for anaerobic digestion in Sweden to encourage anaerobic digestion technology development. However, anaerobic digestion of PPS remains in the initial stage. A few projects on a pilot or demonstration scale have been implemented on PPS, but a full-scale digestion of PPS is still rare. The most important reasons are the capital costs and the large size of bioreactors required due to a long hydraulic retention time (HRT) and a costly investment in conventional anaerobic digestors.

Anaerobic membrane bioreactor (AnMBR) combines the membrane separation and anaerobic treatment together; thus, it can solve some problems, such as the same HRT as

solids retention times (SRT) used, of the conventional anaerobic digestion. First of all, the SRT can be separated with the HRT in AnMBRs, and thus the HRT can be decreased to around seven days, while the SRT is in the range of 20-30 days and maintain a high biomass concentration in the AnMBRs (Liao et al., 2006). Consequently, the size of the bioreactor can be obviously reduced due to the decreased HRT. Also, the HRT of the reactor has the immediate impact on the capital cost. Thus, the ideal case is a shorter HRT and a smaller reactor size for PPS anaerobic digestion. Although membranes are combined with the AD process which is a good choice to solve the high capital costs and long retention time issues, membrane fouling is still a serious and tough problem for AnMBRs. Literature review shows that there is no known study of AnMBR for PPS treatment, although the distinct advantages of AnMBRs and several published studies of AnMBR for pulp and paper wastewater (PPW) treatment. However, membrane fouling is directly or indirectly affected by wastewater characteristics, sludge properties, operating conditions and hydrodynamic conditions (Drews, 2010; Meng et al., 2009). The common methods for membrane fouling control are: air/biogas scouring, relaxation, backwashing/backflushing, physical cleaning and chemical cleaning (Baker, R. W, 2012). To optimize the performance of AnMBR for wastewater and sludge treatment, membrane fouling mechanisms, characterization and its control should be further studied.

1.2 Objectives

The overall goal of this study was to test the feasibility of thermophilic anaerobic membrane bioreactor (ThAnMBR) for PPS treatment for solids reduction and biogas production. Specific objectives of this study were to:

1.) Test the feasibility of ThAnMBR for PPS treatment for biogas production

2.) Study the impact of HRT on the biological and membrane performance of ThAnMBR

3.) Study the impact of ultrasonic pretreatment and non-pretreatment of PPS on the biological and membrane performance of AnMBR

4.) Study the impact of sludge characteristics on membrane performance and membrane fouling.

1.3 Novelty

In this thesis, the ThAnMBR technology was developed for the first time to treat PPS for biogas production and solids reduction. ThAnMBR can overcome some disadvantages of conventional anaerobic digesters. The problem of membrane fouling in ThAnMBR has been improved.

2. Literature Review

The large amount of PPS generated in the PP industry has received much attention, due to its environmental problems. The PPS treatment technologies are limited by environmental legislation. PPS is a type of biomass, and there are a number of technologies that can valorize the PPS for biofuels and value-added products. More specifically, there are four major and mature technologies to obtain biofuels: direct combustion, gasification, pyrolysis, and anaerobic digestion (Demirbas, 2011). Furthermore, there are four primary kinds of bioenergy from PPS treatments: biogas, bioethanol, biohydrogen and biobutanol (Gottumukkala et al., 2016). PPS represents an attractive feedstock for biofuels, as currently, most of the sludge is disposed in landfills where it degrades to methane gas, a more harmful greenhouse gas than carbon dioxide (Demirbas, 2011). Through researches, biofuels can improve economic benefits, and reduce the carbon wastage and pollution problems, as compared to incineration or landfill. Besides, the amount of researches on primary sludge is more than that of secondary sludge from PP mills because secondary sludge contains a high microbial content which is more difficult to process (Gottumukkala et al., 2016).

2.1 Anaerobic Digestion

Anaerobic digestion has been used for municipal sewage and sludge treatment and industrial wastewater treatment for many years, due to its distinct advantages over aerobic processes (Rao et al., 2010). Anaerobic digestion is a biological degradation process that converts organic compounds into different end products: nitrogen (1%-2%), hydrogen (5%-10%),

carbon dioxide (25%-50%) and methane (50-75%) (Maghanaki et al., 2013), and it has been extensively operated on primary and secondary sludge treatment. The process of anaerobic digestion transpires in the serving four basic steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Demirbas, 2011). The sludge has inherent ability to produce high-quality biofuel such as methane (Saxena et al., 2009). The per unit production cost of biomass anaerobic digestion is less than other renewable energy sources such as solar, wind and hydro, and the capital investment is reduced (Rao et al., 2010).

In anaerobic digestion, the organic materials can be converted into biogas. The chemical composition of the biogas from bio-digesters, or a biogas plant is similar to that of natural gas (Demirbas and Balat, 2009). The biogas composition consists of a mixture of essential methane, carbon dioxide, and a small allocation of other gases, for example, hydrogen sulfide (Demirbas, 2011). In anaerobic digestion, the nutrition and temperatures play an important role, because the maintenance of steady temperatures can prompt that methanogen bacteria degrade the waste substrates (Demirbas, 2011). The main nutrients of sludge can be recirculated from anaerobic digestion (Stoica et al., 2009). Although anaerobic digestion has been widely used in wastewater treatment of various aspects, such as: chemical, municipal, agriculture and pulp and paper industries, a rapid growth of anaerobic digestion technology has not been observed until the late 1980s (Meyer and Edwards, 2014). Full-scale anaerobic digestion of pulp and paper sludge (PPS) is uncommon. However, from Hagelqvist research, the anaerobic digestion of PPS is more challenging than municipal sewage sludge because it may lack appropriate anaerobic digestion organisms (Saxena et al., 2009). As compared to other treatment technologies, secondary sludge is more suitable for anaerobic digestion than

incineration (Stoica et al., 2009), as dewatering and drying processes, which are energy intensive, are not necessary. Biosludge in anaerobic digestion is a fascinating choice; on the other hand, the pretreatment is needed to enhance anaerobic digestibility and dewaterability, and hydrolysis is a puzzle among the pretreatments (Meyer and Edwards, 2014). There are a number of studies concerning on municipal sludge and PPS treatment. The literature review will focus on the anaerobic digestion of PPS.

2.1.1 Anaerobic digestion of PPS

Nowadays, full-scale anaerobic treatment of pulp and paper wastewater has been successfully used for some effluents; however, anaerobic digestion of PPS is still in the preliminary stages. One of the major challenges in the anaerobic digestion of PPS is the rate-limiting process of hydrolysis of the: lignocellulose materials, microbial cells and associated complex organics (extracellular polymeric substances or EPS) (Elliott and Mahmood, 2007). Hydrolysis is slow and an incomplete process, and thus needs a high sludge retention time (SRT), a large reactor, and conclusively high capital cost (Elliott and Mahmood, 2007). The temperature of the bioreactor is one of the most important conditions; it will influence the result of anaerobic digestion. Moreover, various pretreatment methods of sludge, including numerous: chemical, thermal, biological and physical methods, have been developed to enhance digestibility of PPS.

Most studies used primary sludge, but there are some studies using biosludge from pulp and paper mills. There are major differences in composition of primary and secondary sludge. The primary sludge is composed of pulp fibers and kaolins, while the secondary sludge

(biosludge) is made of microbial cells. A focus should be made to the anaerobic digestibility of PPS (Meyer and Edwards, 2014). The average ratio of primary sludge to biosludge is expected to be approximately 7:3 in Canadian pulp and paper mills (Elliott and Mahmood, 2005), but the ratio various among individual pulp and paper mills (Stoica et al., 2009). Some pulp and paper mills produce only waste biosludge (i.e., secondary sludge) and without consuming primary sludge, and vice versa.

2.1.1.1 Primary Sludge

The primary sludge of pulp and paper mills consists of wood fibers, such as: cellulose, hemicellulose and lignin, papermaking fillers, for example pitch, kaolin and calcium carbonate, lignin by-products and ash. Moreover, Kim et al. (2000) noted that a kraft pulp mill primary sludge had hemicellulose (12 wt.%), klason lignin (20 wt.%) and cellulose (58 wt.%). In the few studies of anaerobic digestion of PPS, most of them are related to biosludge or sludge mixtures which include trivial fractions of primary sludge. It is worthy of mentioning that Bayr et al. (2012) used semi-continuously fed CSTRs (continuously stirred tank reactors) on primary sludge anaerobic digestion under thermophilic conditions, and the primary sludge is apparently available with the highest result of organic loading rate and biogas yield (Bayr and Rintala, 2012). It also mentioned that methane yields from the semi-continuous CSTR reactor are similar to that from the batch methane potentials evaluations, indicating that all the biodegradable material in the primary sludge were degraded under reactor conditions as observed in batch experiments. In addition, the optimal conditions of the anaerobic process were the use of a higher organic loading rates and continuous feeding for biogas production (Bayr and Rintala, 2012).

2.1.1.2 Secondary Sludge

The secondary sludge from a pulp and paper mill contains: cell-decay products, non-biodegradable lignin precipitates, and microbial biomass (Puhakka et al., 1992). Secondary sludge is already partially degraded in the aerobic process, but primary sludge is not (Bayr and Rintala, 2012). The majority of the reported studies on secondary sludge digestion were under mesophilic condition. Saha et al. (2011) studied the effects of different temperatures and pretreatments on anaerobic digestion of pulp and paper secondary sludge. The results of a comparative study between the secondary sludge and a mixture of the secondary sludge and primary sludge under mesophilic temperatures showed that the volatile solids (VS) removal of secondary sludge (23%) was higher than that of using mixed sludge (10%). However, the specific methane yield of secondary sludge was 50 mL g^{-1} $TCOD_{added}$, which was lower than that of the mixed sludge (55 mL g^{-1} $TCOD_{added}$) at 21 days (digestion time) (Saha et al., 2011).

2.1.1.3 Co-digestion of Primary and Secondary Sludge

In most of the studies, co-digestion of primary and secondary sludge was more common than an individual study of primary or secondary sludge alone. Lin et al. (2009) found that the mixture of primary sludge and secondary sludge consisted of: hemicellulose (9%), lignin (17%) and cellulose (23%). The presence of lignin and sulfur plus nutrient deficiency in PPS are some disadvantages and led to an incomplete anaerobic treatment of pulp and paper mill wastes (Kamli et al., 2016). According to the study of Bayr et al. (2012), anaerobic co-digestion of primary and secondary sludge could achieve a methane yield of 150-170 m^3/t VS fed with an HRT of 25-31 days and an OLR of 1 kg VS/m^3 under thermophilic temperature.

There are some studies about mixed PPS with other sludge, such as food wastes, cow manure and municipal sludge. According to Lin et al. (2013), a mesophilic anaerobic process was designed for co-digestion of PPS and food wastes, and the results of biohydrogen and biomethane were 64.48 mL/g VS fed for hydrogen and 432.3 mL/g VS fed for the methane production, respectively. In another study, Lin et al. (2016) compared the performance of primary and secondary PPS with mixed primary and secondary PPS and cow manure sludge. The methane yield of mixed PPS and cow manure is 269 $mLg^{-1}VS^{-1}$, while using PPS as the feed alone, the methane yield was only 14.7 $mLg^{-1}VS^{-1}$ which was much lower than the mixed sludge.

2.1.2 Non-pretreatment and pretreatment of PPS

There are a number of studies on the effect of pretreatment on PPS anaerobic digestion. The experimental setups are usually bench-scales. From Table 1, the VS (VSS) removal rates of non-pretreatment PPS were between 10%-33% under mesophilic condition; among them, the results of mixed PPS were higher than the result of only primary PPS. Moreover, the results of the untreated control PPS digestion, under mesophilic condition, showed that the methane yield of the 20 days SRT (77 $mLg^{-1}COD_{fed}$) was higher than that of the 12 days SRT (45 $mLg^{-1}COD_{fed}$), due to the different VS loading rate and detention time; however, the VSS removal rate of 20 days (SRT) (29%) was lower than 12 days (SRT) (33%) (Elliott and Mahmood, 2012).

From Table 2, under thermophilic temperature, the VS (VSS) removal rates of no pretreated PPS were in the range of 9%-40%. There was no clear relationship between the digestibility

of sludge and the type of mills studied. Furthermore, it is a challenge to compare the methane yields from different studies, because the unit of methane yield from different studies was different.

2.1.3 Pretreatment of PPS

Various pretreatment methods have been investigated to enhance the anaerobic digestibility of biosludge and dewatering properties of PPS. Although anaerobic digestion is successfully applied in municipal sludge digestion, it has not achieved success in PPS. One of the most important queries is that the HRT and SRT are in the range of 20-30 days. For large scales, the HRT, which determines the bioreactor size, is too long; hence, it is economically prohibitive for the large size digesters in PPS digestion (Elliott and Mahmood, 2007). Recent studies showed that, by using preprocessed technologies, sludge residence time (HRT and SRT) requirement could be reduced to 7 days, which could lead to a significant reduction in bioreactor size and thus the capital cost would be reduced. Also, the pretreated sludges were modified for a high methane yield and solids reduction. The different pretreatment technologies are summarized in the following sections.

2.1.3.1 Mechanical Pretreatment

2.1.3.1.1 Ultrasound treatment

Ultrasonic treatment can mechanically interrupt the cell structure and the flow matrix, and one of the mechanisms is cavitation that leads to sludge disintegration by sound waves of high frequencies (20-40 kHz) (Elliott and Mahmood, 2007).

According to Khanal et al. (2006), ultrasonic disintegration can significantly influence solids content of sludge and the input of specific energy and reduce the consumption of energy at higher solids content. In addition, sonication pretreatment could remove more soluble COD in digester receiving, enhance the destruction of volatile solids (VS) and make the digested biosolids stable by using an ultrasonic-treated digester. Muller et al. (2005) noticed that there is an association between gas production and energy utilized, and pretreatment of waste activated sludge required more energy (compared with non-pretreatment). From Sandino et al. (2005), the rate of reaction was also faster after pretreatment; however, the endpoint of VS reduction stayed the same because of some septic in the waste activated sludge.

Furthermore, some studies investigated the influence of ultrasound on PPS treatment. Saha et al. (2011) used microwave rather than ultrasound to pretreat PPS (Table 1), and the specific methane yield was increased by up to 63%. Both microwave and ultrasound utilize high-frequency waves to rupture cell walls, but the treatment of ultrasound applies acoustic waves, while microwave treatment uses electromagnetic waves (Meyer and Edwards, 2014). From Table 1, Tyagi et al. (2014) found under mesophilic temperature, the ultrasonic

improvement treatment was higher than microwaves on biogas yield. Meanwhile, the total cost for ultrasonic treatment was also higher than for microwaves. From Table 1, there are some studies used combined ultrasound and another pre-treatment. For example, Park et al. (2012) studied that when the alkaline and ultrasound treatments were combined, the methane yield was 222 $mLg^{-1}VS_{consumed}$ which was lower than the untreated control (404 $mLg^{-1}VS_{consumed}$); on the other hand, the VS removal of pre-treatment was higher than the untreated control.

However, Bayr et al. (2013) found, under thermophilic temperature, the methane yield of untreated control (67 $mLg^{-1}VS_{oringinal}^{-1}$) was similar to that (68 $mLg^{-1}VS_{oringinal}^{-1}$) of ultrasonic treated sludge (45 kHz, 30minutes) and no significant improvement in biogas yield was observed. The result of methane yield of sludge pretreated by ultrasound had no statistically significant difference as compared to untreated sludge (114 ± 6 $mLg^{-1}VS_{oringinal}^{-1}$ vs. 115 ± 6 $mLg^{-1}VS_{treated}^{-1}$) (Bayr et al., 2013).

As a result, using the ultrasound pretreatment under mesophilic temperature, the anaerobic digestibility could be significantly improved in most of the published studies; but under thermophilic condition, the results of ultrasonic pretreatment do not show a significantly increase in biogas yield from the limited two studies between pretreatment and non-pretreatment. There were some pilot-scale trials and full-scale installations using different ultrasound technologies to enhance the anaerobic digestion. For example, in Avonmouth, UK, the domestic and industrial mixed sludge was pretreated using Sonic^{TM}, which is a new technology and implements concentrated ultrasound with high-power for sludges (Brown et

al., 2003). In addition, there are four commonly used ultrasound systems, Sonix™, Sonolyzer™, MaXonics™ and Hielscher™ (Elliott and Mahmood, 2007). However, these technologies have not been applied for pretreatment of pulp and paper sludge yet.

2.1.3.1.2 Thermal treatment

The second commonly used mechanical pretreatment is thermal pretreatment, and the range of pre-treatment temperature is between 150 °C and 200°C (Elliott and Mahmood, 2007). If the waste activated sludge is exposed to high temperatures or associated with high pressures, it will achieve that cellular disintegration and decrease the required time for hydrolysis (Elliott and Mahmood, 2007).

Kepp et al. (2000) operated an anaerobic bioreactor to treat mill biosludge, which is found in full-scale application currently. Anaerobic digestion can retrieve energy from wet sludge by producing biogas, and the volume of methane is 60%-70%, so it is appealing process (Mahmood and Elliott, 2006). Before using the Cambi process, biosludge was usually pretreated with sodium hydroxide of alkaline hydrolysis, and this treatment was more expensive than the Cambi process (Cambi, 2013). The Cambi process, the one of the current commercially accessible thermal process, belongs to a Norwegian company. This process could produce more biogas, at the same time gain 60% VS reduction (Panter and Kleiven, 2005). Because of improved dewatering and increased digester capacity, the mass of biosolids was reduced. Before using the Cambi process, the PPS was pretreated by alkaline hydrolysis with sodium hydroxide, and it was more expensive than thermal pretreatment (Cambi et al., 2013). In addition, the other positive effect of thermal pretreatment is the

dewaterability of the digestate can improve (Panter and Kleiven, 2005). For pulp and paper mills, the thermal pretreatment may develop an opportunity toward anaerobic digestion economically feasible (Meyer and Edwards, 2014).

Wood et al. (2010) studied the effect of thermal pretreatment (170°C for an hour) on anaerobic digestion of two types of sludge, from a kraft pulp mill and a sulfite pulp mill, respectively, and found that the production of methane had increased significantly, especially for the kraft pulp mill sludge. Bayr et al. (2013) focused on thermophilic anaerobic digestion of PPS (Table 2) and found that, by using a thermal treatment under 150°C for 10 min, the methane production was increased by 45%. In addition, Kinnunen et al. (2015) compared the effect of different thermal treatment temperatures (80,105,121 and 134°C) on the performance of anaerobic digestion of PPS under mesophilic conditions and observed that the methane production also was increased by 77% (121°C, 20min). Moreover, the VS removal of a lower temperature pretreatment (80°C) was 9%, as compared to the 11% VS removal of the untreated control, indicating the low temperature pretreatment had no positive effective for VS removal (Kinnunen et al., 2015). Thus, thermal treatment could have obvious positive effects on production of methane for difficult digestion of biosludge, depending on the conditions used.

Thermal pretreatment is an acquirable economic process for anaerobic digestion, especially for PPS because excess steams and plenty of heat are available in pulp and paper mills. The heat could be easily used for thermal sludge treatment instead of discharging or releasing

them. Also, the thermal pretreatment could improve the dewaterability of anaerobically digested sludge (Panter and Kleiven, 2005).

2.1.3.1.3 Other mechanical treatment methods

Mechanical pretreatment uses rupturing methods to achieve the hydrolysis of cellular membranes and for improving the soluble COD content (Elliott and Mahmood, 2007). For example, the collision plate method applies a high-pressure (30-50 bar) force on the sludge, and squirts collide the plate and then goes into a nozzle (Nah, 2000). Liquid shear pretreatment relies on high liquid flows and using high-pressure way to implement mechanical splitting of cells and flocs (Carrère et al., 2010). In Elliott and Mahmmoods studies (Table 2), waste activated sludge was treated by mechanical shear mixing at 1500 rpm, the VSS removal was 32%, and the methane yield was decreased by 5.2% (Elliott and Mahmood, 2012).

For the high-pressure homogenizers, the sludge pressure was raised to 900 bar and then homogenization valve was used to depressurize quickly (Muller and Pelletier, 1998). This method has been used at full-scale plants for anaerobic digestion (Li et al., 2012). Digested sludge was treated in this study and the volume of sludge was reduced by 23% and the biogas production was increased by 30% (Onyeche, 2007), but the sludge dewaterability decreased (Barjenbruch and Kopplow, 2003). From Table 1, Elliott and Mahmood (2012) used a combined high-pressure homogenization and alkaline treatment to enhance the digestibility of waste activated sludge and observed an increase of 2.2% in methane production. Saha et al. (2011) mentioned that the specific methane yield was improved 34% (Table 1) and 16%

(Table 2) by a combined high-pressure homogenization and chemical pre-treatment and the biosludge digestibility was improved as well.

2.1.3.2 Chemical Treatment

2.1.3.2.1 Alkaline treatment

Alkaline treatment, also called caustic treatment, is the most commonly used chemical method for sludge pretreatment. Alkaline could be comparatively efficient in sludge solubilization (Kim et al., 2003), but anaerobic digestion might be prompted in the reverse direction because of the excessive concentrations of sodium and potassium ions (Mouneimne et al., 2003). Most of the studies used alkaline treatment combined with other pretreatments, and the use of thermal coupled with alkaline was common; for example, the study of Saha et al. (2011) as mentioned in the above sections.

From Table 1, Park et al. (2012) and Elliott and Mahmood (2012) used a combined caustic ultrasound and a combined caustic and high-pressure homogenization, respectively, to enhance anaerobic digestion of PPS. Both studies observed an increase in methane yields (9.1% and 2.2%, respectively). However, from Table 2, the study from Bayr et al. (2013) showed that alkaline treatment alone had a negative effect on the methane yield and the methane yield decreased by 84%. Furthermore, Wood et al. (2010) designed an efficient pretreatment by using alkaline (using NaOH to adjust pH to 12) and thermal pretreatment (140°C and an hour), and the methane yield was increased by 267% and 21%, respectively. The apparent contrariety has not been solved. Thus, alkaline pretreatment could be the supplementary to combine with other pretreatments. Moreover, there was a potential advantage to waste activated sludge by using alkaline pretreatment (Elliott and Mahmood,

2007). Because anaerobic decomposition floated the sludge by the small gas bubbles generated and gradually became a thickening sludge. It has some benefits for latter anaerobic digestion.

2.1.3.2.2 Ozone oxidation treatment

Ozone oxidation exposes sludge to highly oxidative conditions, and thus cell walls are ruptured and soluble COD is released (Goel et al., 2003; Weemaes, 2000; Yasui and Shibata, 1994). If the concentration of ozone is too high, apparent solubilization will be decreased because of further oxidation of the solubilized ingredients (Yeom et al., 2002). The methane yield may be influenced by the oxidative. Application of ozone may increase the overall cost to improve anaerobic digestibility of pulp and paper mill biosludge (Meyer and Edwards, 2014). Ozonation not only could be a pretreatment in anaerobic digestion, but also be posttreatment to recycle back, and the performance was better in the posttreatment (Goel et al., 2003).

2.1.3.3 Biological treatment

Enzyme treatment is a biological pretreatment, which can stimulate cellular degeneration upon lyses (Doha´nyos et al. 1997). Enzyme pretreatment could improve the anaerobic digestibility of municipal sludge but have not been success for pulp and paper mill biosludge. According to Bayr et al., the raw waste activated sludge was treated by enzyme and a mixture of accelerator (70 mg/g VS) (Bayr et al., 2013), the methane yield was decreased by 1.5%, and anaerobic digestion did not gain any improvement. Nonetheless, this process could be possible to enhance the digestibility of pulp and paper mill sludge (Meyer and Edwards,

2014). A wide application of enzymatic treatment depends on the further decrease in enzyme costs and the discovery of high efficient enzymes (Elliott and Mahmood, 2005).

Table 1 Anaerobic digestion performance for treatment of PPS under mesophilic condition

Type of sludge	pH	TS (or TSS) [%]	VS loading rate	Detention time (days)	Type of pretreatment	VS (or VSS, COD) removal [%]	Methane yield	Pretreatment improvement (%)	Scale[a]	Reference
BCTMP pulp mill WAS	6.5-6.9	2.44-2.5	1.98 g TCOD/L d	21	(1) Microwave (2450MHz, 1250W, 50-175 ℃)	(1) 23-34	50-120 ml/g COD fed	63±3.2	L	Saha et al., 2011
BCTMP pulp mill WAS	6.5-6.9	2.44-2.5	1.98 g TCOD/L d	21	(2) Ultrasound (20kHz, 400W, 15-90 min)	(2) 26-30	70-90ml/g COD fed	51±2.6	L	Saha et al., 2011
BCTMP pulp mill WAS	6.5-6.9	2.44-2.5	1.98 g TCOD/L d	21	(3) Chemo-mechanical (900mg/L NaOH, 83,000kPa)	(3) 26	90ml/g COD fed	34±2.2	L	Saha et al., 2011
BCTMP pulp mill WAS	6.5-6.9	2.44-2.5	1.98 g TCOD/L d	21	(4) Untreated control	(4) 23	50ml/g COD fed	n.a.	L	Saha et al., 2011
BCTMP pulp mill WAS + PS	6.2	2.21	1.71 g TCOD/L d	21	(1) Microwave (50-175 ℃, 2450 MHz)	(1) 16-24	60-90ml/g COD fed	46±2.7	L	Saha et al., 2011
BCTMP pulp mill WAS + PS	6.2	2.21	1.71 g TCOD/L d	21	(2) Ultrasound (20 kHz, 15-90 min)	(2) 15-23	50-890ml/g COD fed	43±3.5	L	Saha et al., 2011
BCTMP pulp mill WAS + PS	6.2	2.21	1.71 g TCOD/L d	21	(4) Untreated control	(4) 10	55ml/g COD fed	n.a.	L	Saha et al., 2011
WAS from BCTMP/TMP pulp mill (raw)	8.4	2.73	Batch	28	(1) Combined caustic (NaOH at 0.206g/g TS) and Ultrasound (40kHz)	(1) 30	222 mL/ gVSconsumed	-45.05	BMP assay	Park et al., 2012
WAS from BCTMP/TMP pulp mill (raw)	7.3	2.42	Batch	28	(2) Untreated control	(2) 21	404 mL/ gVSconsumed	n.a.	BMP assay	Park et al., 2012

Table 1 Anaerobic digestion performance for treatment of PPS under mesophilic condition (Continued)

Type of sludge	pH	TS (or TSS) [%]	VS loading rate	Detention time (days)	Type of pretreatment	VS (or VSS, COD) removal [%]	Methane yield	Pretreatment improvement (%)	Scale[a]	Reference
WAS from BCTMP/TMP pulp mill (thickened)	8.8	6.42	Batch	28	(1) Combined caustic (NaOH at 0.261 g/g TS) and Ultrasound (40kHz)	(1) 27	354 mL/ gVSconsumed	-7.81	BMP assay	Park et al., 2012
WAS from BCTMP/TMP pulp mill (thickened)	7.2	6.52	Batch	28	(2) Untreated control	(2) 23	384 mL /gVSconsumed	n.a.	BMP assay	Park et al., 2012
WAS from mechanical pulp mill	7.5	3.1 (TSS)	1.42 kg VSS/m3 day	20 (SRT)	(1) Mechanical shear (high-shear mixing at 1500 rmp)	(1) 32 (VSS)	(1) 73 mL/g COD fed	-5.19	B	Elliott and Mahmood, 2012
WAS from mechanical pulp mill	7.5	3.1 (TSS)	1.44 kg VSS/m3 day	20 (SRT)	(2) Ultrasound (20 kHz)	(2) 39 (VSS)	(2) 90 mL/g COD fed	16.88	B	Elliott and Mahmood, 2012
WAS from mechanical pulp mill	7.8	3.1 (TSS)	1.43 kg VSS/m3 day	20 (SRT)	(3) High-pressure homogenization (NaOH 0.1% by weight, 83 Mpa)	(3) 58 (VSS)	(3) 91 mL/g COD fed	18.18	B	Elliott and Mahmood, 2012
WAS from mechanical pulp mill	7.4	3.1 (TSS)	1.43 kg VSS/m3 day	20 (SRT)	(4) Untreated control	(4) 29 (VSS)	(4) 77 mL/g COD fed	n.a.	B	Elliott and Mahmood, 2012
WAS from mechanical pulp mill	7.2	3.1 (TSS)	2.06 kg VSS/m3 day	12 (SRT)	(1) Mechanical shear (high-shear mixing at 1500 rmp)	(1) 36 (VSS)	(1) 52 mL/g COD fed	15.56	B	Elliott and Mahmood, 2012

Table 1 Anaerobic digestion performance for treatment of PPS under mesophilic condition (Continued)

Type of sludge	pH	TS (or TSS) [%]	VS loading rate	Detention time (days)	Type of pretreatment	VS (or VSS, COD) removal [%]	Methane yield	Pretreatment improvement (%)	Scale[a]	Reference
WAS from mechanical pulp mill	7.5	3.1 (TSS)	2.02 kg VSS/m3 day	12 (SRT)	(2) Ultrasound (20 kHz)	(2) 32 (VSS)	(2) 82 mL/g COD fed	82.22	B	Elliott and Mahmood, 2012
WAS from mechanical pulp mill	7.7	3.1 (TSS)	2.07 kg VSS/m3 day	12 (SRT)	(3) High-pressure homogenization (NaOH 0.1% by weight, 83 Mpa)	(3) 45 (VSS)	(3) 99 mL/g COD fed	120	B	Elliott and Mahmood, 2012
WAS from mechanical pulp mill	7.1	3.1 (TSS)	2.06 kg VSS/m3 day	12 (SRT)	(4) Untreated control	(4) 33 (VSS)	(4) 45 mL/g COD fed	n.a.	B	Elliott and Mahmood, 2012
WAS pulp and paper mill effluent treatment plant	6.8	24576 (±373) mg/L	Batch	22	(1) Micorwave (50-175℃, 30-438s, 1200 W, 2.45 GHz)	8-39 (VSS)	4895mL	16	L	Tyagi, et al., 2014
WAS pulp and paper mill effluent treatment plant	6.8	24576 (±373) mg/L	Batch	22	(2) Ultrasonicator (15-60 min, 40 kHz, 500 W)	27-37 (VSS)	5175mL	46.75	L	Tyagi, et al., 2014
WAS pulp and paper mill effluent treatment plant	6.8	24576 (±373) mg/L	Batch	22	(3) Alkali (30-240 min, pH 9-12.5)	8.6-21.7 (VSS)	n.a.	n.a.	L	Tyagi, et al., 2014

Table 1 Anaerobic digestion performance for treatment of PPS under mesophilic condition (Continued)

Type of sludge	pH	TS (or TSS) [%]	VS loading rate	Detention time (days)	Type of pretreatment	VS (or VSS, COD) removal [%]	Methane yield	Pretreatment improvement (%)	Scale[a]	Reference
WAS pulp and paper mill effluent treatment plant	6.8	24576 (±373) mg/L	Batch	22	(4) Hybrid: microwave-alkali (pH 12, 30min, 50-175℃)	17-66 (VSS)	4490mL	6.27	L	Tyagi, et al., 2014
WAS pulp and paper mill effluent treatment plant	6.8	24576 (±373) mg/L	Batch	22	(5) Hybrid: ultrasonic-alkali (pH 12, 15-60min, 0.75W/mL)	38-49 (VSS)	6200mL	46.75	L	Tyagi, et al., 2014
WAS pulp and paper mill effluent treatment plant	6.8	24576 (±373) mg/L	Batch	22	(6) Untreated control	n.a.	4225mL	n.a.	L	Tyagi, et al., 2014
Pulp and paper watewater treatment plant	6.60	16.99	2.2g VS/L day	18 (HRT)	Enzyme (5 different brands)	n.a.	134.7-170.0 mL CH4/ g VS day	n.a.	5 L scale	Kolbl et al., 2017
Pulp and paper watewater treatment plant	6.60	16.99	2.2g VS/L day	18 (HRT)	untreated control	n.a.	121.9-147.3 mLCH4/ gVS day	n.a.	5 L scale	Kolbl et al., 2017
Pulp and paper watewater treatment plant	6.54	17.64	2.2g VS/L day	18 (HRT)	Enzyme (5 different brands)	n.a.	92.0-146.4 mL CH4/g VS day	n.a.	5 L scale	Kolbl et al., 2017
Pulp and paper watewater treatment plant	6.54	17.64	2.2g VS/L day	18 (HRT)	untreated control	n.a.	71.7-93.1 mL CH4/g VS day	n.a.	5 L scale	Kolbl et al., 2017

[a]L=laboratory scale, B=bench scale

Table 2 Anaerobic digestion performance for treatment of PPS under thermophilic condition

Type of sludge	pH	TS (or TSS) [%]	VS loading rate	Detention time (days)	Type of pretreatment	VS (or VSS, COD) removal [%]	Methane yield	Pretreatment improvement (%)	Scale[a]	Reference
BCTMP pulp mill WAS	6.5-6.9	2.44-2.5	1.98 g TCOD/L d	43	(1) Microwave (2450MHz, 1250W, 50-175 ℃)	(1) 19-26	90-110 ml/g COD fed	13±0.7	L	Saha et al., 2011
BCTMP pulp mill WAS	6.5-6.9	2.44-2.5	1.98 g TCOD/L d	43	(2) Ultrasound (20kHz, 400W, 15-90 min)	(2) 24-26	90-120ml/g COD fed	28±1.4	L	Saha et al., 2011
BCTMP pulp mill WAS	6.5-6.9	2.44-2.5	1.98 g TCOD/L d	43	(3) Chemo-mechanical (900mg/L NaOH, 83,000kPa)	(3) 26	90ml/g COD fed	16±2.2	L	Saha et al., 2011
BCTMP pulp mill WAS	6.5-6.9	2.44-2.5	1.98 g TCOD/L d	43	(4) Untreated control	(4) 21	50ml/g COD fed	n.a.	L	Saha et al., 2011
BCTMP pulp mill WAS + PS	6.2	2.21	1.71 g TCOD/L d	43	(1) Microwave (50-175 ℃, 2450 MHz)	(1) 12-21	55-75ml/g COD fed	38±2.0	L	Saha et al., 2011
BCTMP pulp mill WAS + PS	6.2	2.21	1.71 g TCOD/L d	43	(2) Ultrasound (20 kHz, 15-90 min)	(2) 10-18	60-70ml/g COD fed	38±2.2	L	Saha et al., 2011
BCTMP pulp mill WAS + PS	6.2	2.21	1.71 g TCOD/L d	43	(4) Untreated control	(4) 9	55ml/g COD fed	n.a.	L	Saha et al., 2011
Kraft pulp and paper mill PS (primary)	6.8-8.2	2.7-3.4	1	23-32	No pretreatment	30-37	240mL/g VS fed	n.a.	L	Bayr and Rintala, 2012
Kraft pulp and paper mill PS (primary)	6.5-8.0	2.7-3.4	1.4-2	14-16	No pretreatment	25-40	190mL/g VS fed	n.a.	L	Bayr and Rintala, 2012
Mixture kraft pulp and paper mill PS + WAS (VS ratio 3:2) (primary & secondary)	7.2-8.2	n.a.	1	25-31	No pretreatment	29-32	150-170 mL/g VS fed	n.a.	L	Bayr and Rintala, 2012

Table 2 Anaerobic digestion performance for treatment of PPS under thermophilic condition (Continued)

Type of sludge	pH	TS (or TSS) [%]	VS loading rate [kg VS/m3 day]	Detention time (days]	Type of pretreatment	VS (or VSS, COD) removal [%]	Methane yield	Pretreatment improvement (%)	Scale[a]	Reference
Kraft and paper mill WAS	n.a.	4.70	Batch	20-23	(1) Ultrasound (45 kHz, 30 min)	n.a.	68 ml/g VS original	1.49	BMP assay	Bayr and Rintala, 2012
Kraft and paper mill WAS	n.a.	5.10	Batch	20-23	(2) Alkali (NaOH, pH 12)	n.a.	11 ml/g VS original	-83.58	BMP assay	Bayr and Rintala, 2012
Kraft and paper mill WAS	n.a.	5.10	Batch	20-23	(3) Acid (HNO3, pH 3)	n.a.	-3 ml/g VS original	-104.48	BMP assay	Bayr and Rintala, 2012
Kraft and paper mill WAS	n.a.	3.90	Batch	20-23	(4) Enzymes (mixture of Accelerases, 70 mg/gVS)	n.a.	66 ml/g VS original	-1.49	BMP assay	Bayr and Rintala, 2012
Kraft and paper mill WAS	n.a.	4.50	Batch	20-23	(5) Hydrothermal (150 ℃, 10min)	n.a.	97 ml/g VS original	44.78	BMP assay	Bayr and Rintala, 2012
Kraft and paper mill WAS	n.a.	4.70	Batch	20-23	(6) Untreated control	n.a.	67 ml/g VS original	n.a.	BMP assay	Bayr and Rintala, 2012

[a]L=laboratory scale, B=bench scale

2.2 Combustion/incineration

Incineration of solid residues combined with power and steam generation can be applied to almost all the pulp and paper sludge, including primary and secondary or biological sludge (Monte et al., 2009). The minimum amount of PP solid waste is achieved by incineration of PPS (Stoica et al., 2009). Nevertheless, due to the high moisture and ash content of most sludges before incineration, thickening, dewatering and drying of sludge is needed, which is an energy intensive process. Thus, the overall energy balance can be energy deficient (Monte et al., 2009). Fluidized bed boiler technology is a promising solution for the final disposal of paper mill wastes (Porteous, 2005; Oral et al., 2005) Incineration can reduce 80-90% amount of material for the landfill (Monte et al., 2009). In the incineration process, the temperature needs to over 850°C for more than 2s. The temperature should be increased to 1100°C for more than 2s if the hazardous waste contains more than 1% halogenated organic substances (Monte et al., 2009). Moreover, the nutrients of phosphorus remain in the ash can be used in forest soil if the sludge is incinerated (Stoica et al., 2009). The main challenge for incineration is the high energy input for sludge dewatering and drying and air pollution.

2.3 Fermentation (Ethanol)

Fermentation can be used for PPS treatment to solve the severe sludge disposal problem for the pulp and paper industry (Lang, 1995; Solid Waste Treatment and Disposal, 2013). Bioethanol is a mature field in bioenergy processes from the paper sludge at bench scales, but rare studies are reported at the pilot scale. The sludges can be converted to additional value products, such as ethanol, by biological treatment, due to its good dispersed structure and

high carbohydrate content (Kang et al., 2010). Ethanol as a typical fermentation product has been investigated. The sludges were converted into sugar enzymatically by commercial cellulose enzymes, and the conversion was inefficient due to disturbance of the ash in the sludges. Besides, the change of pH level is a major concern, due to the constituent of $CaCO_3$ in sludge ash, which can cause a higher pH level (as much as twice the pH level) than the optimal pH for cellulase enzyme. SSCF (simultaneous saccharification and cofermentation), SSF (simultaneous saccharification and fermentation) and SHF (separate hydrolysis and fermentation) are three solutions to treat the sludges without any pretreatment (Marques et al., 2008). SSCF uses cellulase from recombinant *Escherichia coli*, and SSF applies cellulase from *Saccharomyces cerevisiae*. Furthermore, it was found that the sulphite sludge and kraft sludge are more suitable for ethanol production than thermo-mechanical mills sludge. However, the content of cellulose fibers is low in deinking sludge, due to the high efficiency of papermaking processes, so deinking sludge is not a suitable choice for bioconversion (Monte et al., 2009). Primary and recycle sludges were studied for ethanol production and the ethanol yields were in the range of 75-81% based on total carbohydrates by using SSCF, and 74-80% based on glucan by using SSF (Kang et al., 2010). Fan et al. (2003) found that paper sludge could be converted into ethanol by using SSF (simultaneous saccharification and fermentation) with a semi-continuous reactor. The percentage of conversion was between 74% and 92%, and the concentration of ethanol was 50g/L and 42 g/L, respectively (Fan et al., 2003). Chen et al. (2014) conducted an economic analysis for ethanol production from PPS and found that it is an acceptable expenditure, if the payback period is less than 4.4 years.

2.4 Pyrolysis

Pyrolysis, a destructive distillation, is a process of heating the organic waste in the inadequacy of oxygen, and the products are: gaseous, liquid fuels and some solid inert residue (Monte et al., 2009). Pyrolysis possibly can provide an advantage to handling PPS waste from thermal improved processes for a higher calorific value, such as: fuels, biogas, bio-oils, and charcoal (Strezov and Evans, 2009). Under the anaerobic condition, the PPS is broken-down into gaseous products approximately between 400-800°C by indirect heat, and at the same time ensure to take volatiles (Monte et al., 2009). The sludge will be broken down and fractionated into heavy/light oils, gases and tars under indirect heating (Monte et al., 2009). The process of pyrolysis has an obvious difference from incineration/combustion as no oxygen is involved. Although the pyrolysis technology can replace incineration and landfill of PPS, a consistent waste stream is usually required to produce a usable fuel product (Fytili and Zabaniotou, 2008). From Strezov and Evans (2009)' case, pyrolysis of paper sludge may provide an alternative option for managing this waste and alleviate the need for landfilling, and the energy potential of the produced biogas compounds can be utilized to recover the heat required for pyrolysis, hence reducing the requirement for external heat supply (Strezov and Evans, 2009). The bio-oils and charcoal produced from paper sludge pyrolysis have the potential to provide marketable feedstock and sources of energy (Strezov and Evans, 2009). From Ridour research, using fast pyrolysis treatment to convert the low and high ash paper waste sludge, because the reactor temperature and pellet size are influenced factor; thus, Ridout et al. (2015) studied the effect of pyrolysis temperature and pellet size on a fast pyrolysis process of a paper waste sludge and found that the maximum bio-oil yields are 59.9 ± 4.1 daf, wt.% and 44.5 ± 1.7 daf, wt.% at 340°C and 400°C,

respectively. The conversion yield of fermentation process followed by pyrolysis is higher than the pyrolysis process only (Ridout, 2016).

2.5 Gasification

The gasification process is a thermal process and has been used for a long time. This process requires air or oxygen to convert the combustible materials into inflammable gases and inert residues. For instance, gas can be converted from coal by using gasification. Both air and pure oxygen can be used in the gasification process; pure oxygen requires a much higher temperature which is between 1000˚C and 1400˚C, and air requires a temperature between 900˚C and 1100˚C (Monte et al., 2009). Oxygen is more common since it reduces the volume of flue gas. It generates CO_2, water, and the unwanted by-product N_2 can be completely avoided by using pure oxygen. According to the study of Gross et al. (2008), the available capacity range in gasification is between 1000 to 8000 tons of total solids per year.

Pyrolysis process which is mentioned in the previous sections is another kind of gasification process with no oxygen present. The two main differences between pyrolysis and gasification are the operating temperature and usage of air. In the biomass industry, these two processes can work together when processing sludge (Monte et al., 2009). The last is a very new concept; gasification process is being used right after the pyrolysis process to produce gas from the solid residue. Both digested and undigested sludge with no water content can be used as the resources in this process (CANMET, 2005). Since this process is still not well developed, there is not much information in the literature regarding it. In general, the subject of thermal gasification process is based on the selection of final products. Therefore, the

subject for pyrolysis process is to optimize the quality of char (Ridout, 2016), and the subject for gasification process is to optimize the production of gas (Monte et al., 2009).

Both processes have a very high capital cost (Monte et al., 2009). Estimating costs for these technologies can be very difficult. There are too many variables related when calculating the costs. For example, the magnitude of the destruction required, total volume, waste composition and their concentrations will all affect the costs. In addition, since both pyrolysis and gasification need a lot of energy to reach such a high temperature, and they all need flue gas equipment to prevent the air pollution. Costs are varied from case to case.

2.6 Liquefaction

High-pressure direct liquefaction, as a thermo-chemical process, is a treatment of converting the biomass feedstock to expensive liquid organic products such as: phenols, carboxylic acids, etc. The reaction temperature is in the range of 150-420°C (Behrendt et al., 2008). As the sludge can be solidified to reach a high solids content by vaporization or mechanical dewatering processes, pre-mixing and co-liquefied with other waste, such as municipal solid waste, are an excellent choice to reduce the cost associated with dewatering (Zhang et al., 2011). Furthermore, considering the ability to decompose lignin compounds and reaction rates, direct liquefaction has a higher reaction rate than anaerobic digestion (Bridgewater AV). Some studies found that the use of catalysts could improve the liquid products yield from the processes of biomass liquefaction and defeat the formation of chars (Zhang et al., 2011; Xu and Lancaster, 2008). Liquid oil products can be produced through direct

liquefaction treatment with and without catalyst from secondary pulp and paper sludge and have a heating value of higher than 18.3MJ/kg on a dry basis.

2.7 Challenges and Opportunities of Pulp and Paper Sludge

Renewable energy will reach the feasible for commercial usage prospectively by 2025 (Rao et al., 2010). Nowadays, the conversion energy of hydroelectric power has been widely used, but there still are a lot of kinds of renewable resources which have not been developed and utilized. Thus, a lot of challenges and opportunities are waiting for exploration in renewable resources fields. Although landfills are currently widely used for PPS disposal, the space limitation and pollutions are concerns for future landfills of PPS, thus the way of biorefinery should be considered after it has developed and improved. However, nowadays, the exploitations of renewable resources are still lack particularly on PPS field, and limited studies are conducted on pilot-scales. There are a huge number of opportunities to exploit and develop in this area. Combustion and incineration can decrease a great deal amount of landfill with only few seconds combustion. Anaerobic digestion has been explored, the routine to convert to biogas directly such as biomethane and biohydrogen, which are green fuels. Moreover, fermentation, pyrolysis, gasification, and liquefaction are worthy of studying for treatment and disposal of PPS. The product of biofuels can replace petrochemical products after upgrading. In addition, biorefinery of PPS can not only solve the incineration and landfill needs but also generate revenues from these renewable chemicals and biofuels and provide surplus income for pulp and paper mills.

3. Experimental Materials and Methods

3.1 Anaerobic Membrane Bioreactor Setup and Operation

The experiment system setup is shown in Fig 1. It was a submerged AnMBR equipment with a flat sheet microfiltration (MF) membrane module with two sides membranes (10cm×15cm×2, 0.03m^2) made by using phase inversion method. The membranes were made of polyvinylidene fluoride (PVDF) materials, and the pore size was 0.4μm (Dafu Membrane Technology, PRChina). The membrane module was set in the middle of the lid connected by a stainless steel tube. The reactor was a PVC column (20cm outer diameter ×H 50.5cm) with an external water jacket, and the working volume was 6 Liter (14.5cm inner diameter ×H 36.5cm). To maintain a thermophilic temperature, warm water was circulated through the jacket to keep the temperature of the bioreactor at 50±1°C. A magnetic stirrer (Thermolyne Cimarec, Model S47040) was placed at the bottom of the reactor to provide a gentle mixing to prevent sludge settling at the bottom. Two sparging pumps (Masterflex L/S, Model 07528-10, Cole-Parmer Instrument Company, LLC., Canada) were used to circulate the biogas from the top of the reactor to the bottom of the membrane module by using two stainless steel tube diffusers on either bottom side of the module. Therefore, bubbling was sent from the tubes to scour the membrane surfaces and mix the sludge adequately. Each sparging pump rate was maintained at 260 rpm (around 1.7L/min per pump). The experimental devices include a feed tank, the anaerobic digester, the membrane filtration module, an effluent tank and a water displacement cylinder for biogas collection.

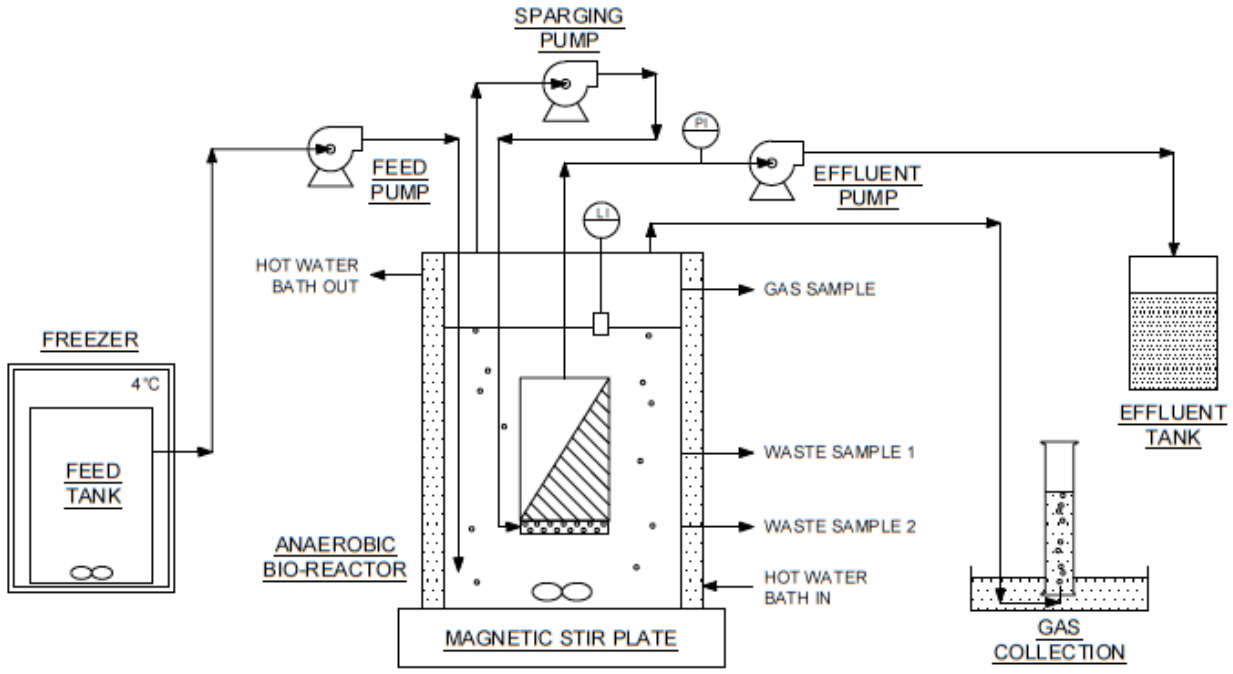


Figure 1 Schematic diagram of the submerged anaerobic membrane bioreactor setup

The pulp and paper secondary sludge from a local pulp and paper mill was stored in a cold room at 4°C in 20L buckets and then put in an 8 L feed tank in a refrigerator at 4°C and semi-continuously fed to the bioreactor with a feed pump (Iwaki Magnet Pump, Model MD-6L, Iwaki Co., LTD. Japan), which was controlled by a liquid level sensor (Madison Co., USA) and a controller (Flowline Standard controller, USA). The biogas collection was connected with the top of the reactor by a plastic tube to a water displacement cylinder, and the volume of gas was measured by water displacement method at ambient temperature (23-25°C). The effluent was obtained by a peristaltic pump (Masterflux, C/L, Model 77122-14, Cole-Parmer Instrument, Co., USA), which is connected to the membrane module. The permeate pump was controlled by a timer (GraLab Timer, Model 451, DimcoGray Corp.,

USA) with a suction cycle for 3 min running (on) by 2 min stop (no suction) (off); the flux of the membrane was controlled by adjusting the pump speed, and calibrations were done twice per day. The Trans-membrane pressure (TMP) was measured by a vacuum pressure gauge which is connected to the reactor and the permeate pump and located on the permeate line. When the trans-membrane pressure reached 50 KPa, the reactor was shut down and the reactor was opened to do a physical cleaning on the membrane module. Physical cleaning was accompanied by scraping of the cake layer from the surface of the membrane by using a plastic sheet and then using a soft sponge and tap water. After washing of the fouled membranes, the operation of the reactor was restarted. Because of the need of an anaerobic condition for the AnMBR, oxygen is prohibited; hence, nitrogen (99.998%) was bubbled for 5 min to purge out the air in the system before starting.

Semi-continuous AnMBR for the pulp and paper mill secondary sludge treatment was run using a completely sealed PVC stirred tank reactor (CSTR). The temperature of the reactor was maintained at 50±1°C. The operation of the reactor system was divided into five phases (Fig.2): Phase 1 (0-63rd day) used thermo-mechanical pulping mill wastewater as the feed to acclimate the sludge seed and the hydraulic retention time (HRT) is 4.5±0.7 day; Phase 2 (64th-123rd day) used the non-pretreatment pulp and paper secondary sludge as the feed and control the HRT at 7.9±1.3 day; Phase 3 (124th-173rd day) used the same feed as Phase 2, but changed the HRT to 17.2±1.4 day; Phase 4 (183rd-253rd day) used the pretreated pulp and paper sludge (ultrasonic treatment, 40 kHz, 30 minutes; GT Sonic, Model VGT-1620QTD, Guangdong GT Ultrasonic Co., Ltd, China) as the feed and control the HRT at 8.0±1.4 day; Phase 5 (259th-328th day) used the same ultrasonically treated feed as in Phase 4, but the HRT

was changed to 16.0±1.4 day. During the operation of Phases 2-5, solid retention time (SRT) was controlled at 36 days, and the volume of daily waste is 166 mL of sludge. The influent pH was adjusted to 7.8±0.1 by using 1 mol/L NaOH before being pumped into the reactor to maintain a desired pH (around 7) in the bioreactor. New membranes (two sides of the module) were used starting in Phase 1 and Phase 4.

3.1.1 Waste Sludge and Inoculum Sample

Thermo-mechanical pulping wastewater and the pulp and paper secondary sludge were collected from a local pulp and paper mill and its activated sludge treatment plant, respectively. The anaerobic seed sludge was from an internal circulation anaerobic reactor system at AV Cell, located in Atholville, New Brunswick, Canada.

Table 3 summarizes the characteristics of non-pretreated PPS and pretreated PPS. Among them, the concentration of dissolved aluminum, iron and zinc ions are increased after the pretreatment of PPS.

Table 3 The characteristics of feed of PPS with non-pretreatment and pretreatment

Description	Non-pretreated PPS	Pretreated PPS
TCOD (mg/L)	16666.7±861.4	17998.5±3452.1
SCOD (mg/L)	777.2-1460.1	1770.3-2150.1
Total Ammonia-N (mg/L)	106.2-126.2	121.6-176.8
Total K Nitrogen (mg/L)	111-133.5	117.5-130
Total Phosphorous (mg/L)	21.86-23.77	22.69-24.48
Chloride (IC) (mg/L)	294.39-342.62	277.05-296.72
Dissolved Aluminum (mg/L)	0.542-0.594	2.880-3.102
Dissolved Barium (mg/L)	n.a.	0.056-0.058
Dissolved Calcium (mg/L)	41.45-41.48	38.04-38.62
Dissolved Chromium (mg/L)	0.005	0.006-0.007
Dissolved Iron (mg/L)	0.056-0.075	0.165-0.177
Dissolved Potassium (mg/L)	72.04-77.02	68.12-72.31
Dissolved Magnesium (mg/L)	10.48-10.72	9.696-10.2
Dissolved Manganese (mg/L)	0.296-0.305	0.272-0.276
Dissolved Sodium (mg/L)	567.4-600.4	534.7-564.6
Dissolved Sulfur (mg/L)	91.52-94.7	83.5-84.67
Dissolved Silicon (mg/L)	9.679-10.19	9.308-9.728
Dissolved Strontium (mg/L)	0.132	0.123-0.124
Dissolved Titanium (mg/L)	0.013-0.014	0.015-0.017
Dissolved Zinc (mg/L)	0.006-0.009	0.016-0.022
Sulphate (SO4) [IC] (mg/L)	83.02-105.3	79.08-119.56

Note: other metals (Nitrite NO_2-N, Nitrate NO_3-N, dissolved Arsenic, dissolved Beryllium, dissolved Cadmium, dissolved Cobalt, dissolved Copper, dissolved Molybdenum, dissolved Nickel, dissolved Lead, dissolved Selenium, dissolved Thallium and dissolved Vanadium) are under determining limitation.

3.1.2 Pretreatment of PPS

Ultrasonic pretreatment was selected for pulp and paper secondary sludge treatment to enhance its digestibility and then compare the treatment efficiency between the non-pretreatment PPS and the ultrasonically pretreated PPS. Ultrasonic (US) pretreatment was performed using a professional ultrasonic cleaner (GT Sonic, Model VGT-1620QTD, Guangdong GT Ultrasonic Co., Ltd, China) to pretreat the PPS at 40 kHz for 30 min. The temperature of PPS during the treatment was kept below 30°C, and the pretreated feed was placed in 4°C after pretreatment.

3.2 Analytical Methods

The samples of effluent, the feed, and the mixed-liquor were taken routinely from the system 2-7 times every week during the steady state of every phase.

3.2.1 Chemical Oxygen Demand (COD)

Influent COD, effluent COD, and soluble COD were analyzed 2-4 times every week by Standard Methods (APHA, 2005). The influent was collected from the feed tank to be measured the influent COD. The effluent COD was measured directly and without any

further treatment. For the measurement of soluble COD, the samples of mixed liquor were centrifuged at 18,700×g for 20 min, so that supernatant of mixed-liquor can be obtained to analyze to get soluble COD.

3.2.2 Biogas Determination and Quantification

Samples of biogas were taken from the top one of three T-valves by using a syringe and determined and quantified by gas chromatography (Shimazu, GC-2014) equipped with a silica gel packed column (5486×3.18 mm) and a thermal conductivity detector (TCD). Helium was the carrier gas, and the flow rate was 30 mL/min.

The biogas production rate can be found by the Equation 1:

$$\text{Biogas production rate } \left(\frac{L_{biogas}}{\text{g}MLSS_{fed}}\right) = \frac{V_{biogas}}{MLSS_{fed} \times V_{influent}}$$

Equation 1

where the V_{biogas} is the volume of the biogas production per day (L), $MLSS_{fed}$ is the mix-liquor suspended solids of the feed (g/L), $V_{influent}$ is the volume of the effluent which is equal to the volume of influent (L) and V_{waste} is the volume of the waste per day (0.166 L).

The biogas yield can be found by the Equation 2:

$$\text{Biogas yield } \left(\frac{L_{biogas}}{gMLSS_{removed}}\right)$$

$$= \frac{\sum V_{biogas}}{\sum[V_{influent} \times MLSS_{feed}] - \sum(V_{waste} \times MLSS_{reactor}) - V_{reactor} \times (MLSS_{reactor2} - MLSS_{reactor1})}$$

Equation 2

where the V_{biogas} is the volume of the biogas production per day (L), $V_{influent}$ is the volume of the effluent which is equal to the volume of influent (L), V_{waste} is the volume of the waste per day (0.166 L), $MLSS_{fed}$ is the mix-liquor suspended solids of the feed (g/L), $MLSS_{reactor}$ is the mix-liquor suspended solids of the reactor (g/L) and the $V_{reactor}$ is the volume of the reactor which is 5.6 L.

The suspended solids destruction ratio can be calculated by Equation 3:

$$\text{Suspended solid destruction}(\%) = \frac{\sum[V_{influent} \times MLSS_{feed}] - \sum(V_{waste} \times MLSS_{reactor}) - V_{reactor} \times (MLSS_{reactor2} - MLSS_{reactor1})}{\sum[V_{influent} \times MLSS_{fed}]}$$

Equation 3

where the $V_{influent}$ is the volume of the effluent which is equal to the volume of influent (L), V_{waste} is the volume of the waste per day (0.166 L), $MLSS_{fed}$ is the mix-liquor suspended solids of the feed (g/L), $MLSS_{reactor}$ is the mix-liquor suspended solids of the reactor (g/L) and the $V_{reactor}$ is the volume of the reactor which is 6.0 L. The average solids destruction ratio was calculated based on the data of 7 days, in order to reduce experimental error.

3.2.3 Particle Size Distribution

The particle size distributions (PSD) of mixed-liquor, the non-pretreated and ultrasonically pretreated feed sludge were determined by a Malvern Mastersizer 2000 instrument (Worcestershire, UK) with a detection range of 0.02-2000μm. The scattered light is detected using a detector which converts the signal to a size distribution based on volume or number.

The mixing intensity of measuring is 2500±50 rpm for each sample during PSD analysis. Each sample was analyzed three times, and the measurements of PSD were routinely conducted 2-3 times every week.

3.2.4 Extracellular Polymeric Substances (EPS) Extraction and Measurement

EPS extraction was conducted by collecting the mixed-liquor sludge at the steady state period of time of Phases 2-5. The way of extraction was used a two-step heat extraction method (Morgan et al., 1990) to extract the loosely bound EPS (LB-EPS) and tightly bound EPS (TB-EPS) from the sludge sample. The method of the heat EPS extraction procedures was modified by others users (Li and Yang, 2007; Yang and Li, 2009). A sludge suspension sample was centrifuged at the 4000× g for 5 min to dewater by using a 50ml centrifuge tube. The sludge pellet was resuspended into 0.05% NaCl warm solution at 50°C and immediately sheared by a mixer (Vortex mixer, Fisher Scientific, USA) for 1 min, and the sludge suspension was centrifuged at 4000×g for 10 min. In the supernatant, the organic matter was regarded as the LB-readily extractable EPS or readily extractable EPS.

For the extraction of the TB-EPS, the sludge pellet was then resuspended once again in 0.05% NaCl solution to an initial volume of 50mL. Once mixed, the sludge suspension was heated to 60°C in a water bath for 30min, and the centrifugation of mixture was set at 4000×g for 15min. The supernatant of the tube was collected as the TB-EPS extraction of the sludge. For the LB-EPS and TB-EPS extraction solutions were analyzed for the carbohydrate (Gaudy, 1962) and protein (Lowry et al., 1951).

3.2.5 Soluble Microbial Products (SMP) Measurement

The mixed-liquor sludge was centrifuged at 18,700×g for 20 min to obtain the supernatant; and then, the supernatant was filtered through 0.45 μm membrane filters (Merck Millipore Ltd.). The filtered supernatant was analyzed for SMP. The measurement of SMP was similar to the measurement of EPS, according to Gaudy (1962) and Lowry et al. (1951).

3.2.6 Measurement of Feed Sludge and Mix-Liquor

The study was conducted using a lab-scale ThAnMBR and treated two types of PPS: the original PPS and pretreated PPS. The details of the operating conditions of the ThAnMBR are summarized in Table 4. The characteristics of mix-liquor and two kinds of PPS were characterized by the mix-liquor suspended solids (MLSS) by filtration of the mix-liquor through a membrane filter paper of 0.45 μm pore size. The soluble samples and colloids were obtained by centrifuging the feed sludge or mix-liquor at 18,700×g for 20 minutes and then filtered through membrane filter paper (0.45 μm pore size) (Merck Millipore Ltd.).

Table 4 Operating conditions of AnMBR under different operation conditions

Parameters	Anaerobic membrane bioreactor			
Temperature °C	50±1°C	50±1°C	50±1°C	50±1°C
Types of feed	Non-pretreatment PPS	Non-pretreatment PPS	Ultrasonic pretreated PPS	Ultrasonic pretreated PPS
HRT (days)	7.9±1.3	17.2±1.4	8.0±1.4	16.0±1.4
SRT (days)	36	36	36	36
pH	6.9-7.4	7.0-7.4	6.9-7.4	7.1-7.6
MLSS of feed (g/L)	10.34±1.30	10.64±0.77	10.93±1.61	14.49±1.88
MLSS of mix-liquor (g/L)	28.94±2.54	20.85±3.07	32.47±2.06	29.50±1.87

3.2.7 Membrane Resistance Determination

The series of resistances was used to obtain the characteristics of membrane filtration, and the membrane resistance was calculated by Darcy's law as follows:

$$J' = \frac{Q}{A} = \frac{\Delta P}{\eta_T \cdot R_{membrane}}$$

Equation 4

Thus, the total resistance can be found by the equation:

$$R_T = R_m + R_f = R_m + R_c + R_p = \frac{\Delta P_T}{\eta_T \cdot J'}$$

Equation 5

where R_T is the total membrane resistance (m^{-1}), R_m is the new membrane resistance (m^{-1}), R_f (m^{-1}) equals to R_c adds R_p which was the total fouling resistance, R_p is the pore blocking resistance (m^{-1}), R_c (m^{-1}) is the resistance of cake layer, ΔP_T is the TMP (Pa), η_T is the dynamic effluent viscosity (m^3/m^2 s). The organic, inorganic and irremovable (permanent) fouling resistance were calculated following the equation:

$$R_P = R_{Organic} + R_{Inorganic} + P_{permanent}$$

Equation 6

where $R_{Organic}$ is the organic fouling resistance (m^{-1}), $R_{Inorganic}$ is the inorganic fouling resistance (m^{-1}) and $P_{permanent}$ is the permanent fouling (irremovable fouling) resistance (m^{-1}). Each result of resistance was determined using the same module which was used in the AnMBR.

The measurement and calculation of the experiment was followed: (1) R_m was obtained by measuring the clean water flux of tap water; (2) R_T was assessed by measuring the final flux and corresponding TMP of the HRT=17.2 $\pm$ 1.4 days with non-pretreatment and HRT=16.0 $\pm$ 1.4 days with pretreatment and calculated from Equation 5; (3) by using Equation 5, the R_f can be calculated by R_T minus R_m; (4) R_c can be obtained by R_f minus R_p; (5) the pure water flux was measured to obtain the (R_m+R_p) by Equation 5 after a physical cleaning which was cleaning the membrane by using tap water and removing the cake layer with a sponge; (6) after the physical cleaning, the chemical cleaning was applied to the module in 200 ppm sodium hypochlorite (NaClO) solution at pH 9.86 for two hours so as to remove the organic foulants; (7) the resistance of R_m+$R_{Organic}$ + $R_{Inorganic}$ was measured by the clean water flux; (8) and then, the module was cleaned by the second chemical

cleaning which was submerging the module in a 2000 ppm citric acid solution at pH 2.9 for two hours so as to remove the inorganic foulants; (9) the $R_m+P_{permanent}$ can be measured by the clean water flux; (10) $R_{Organic}$, $R_{Inorganic}$ and $P_{permanent}$ can be calculated from Equation 6.

3.2.8 Scanning Electron Microscopy (SEM)

The new and chemically cleaned used flat sheet MF membrane specimens were fractured in liquid nitrogen for 10 minutes to obtain the cross-section, and coated with electric coat for SEM observation. The used membrane sample was obtained from the top, middle and bottom of the membrane for three sampling, respectively.

3.2.9 Statistical Analysis

Statistical analyses were used to identify the differences of the results between the different HRTs with the same type of sludge feeds and between non-pretreatment and pretreatment of sludge at the same HRT. The t-test (two-sample assuming equal variances and two-sample assuming unequal variances) of the two-tail results was used to determine if there are any significant differences between different HRTs and between control (non-pretreatment) and ultrasonic pretreatment using Microsoft Excel statistical analysis tools. Differences are considered statistically significant at a 95% confidence interval when the P results under 0.05.

4. Results and Discussion

The experimental results and discussion are presented in two categories: 1.) Biological performance of ThAnMBR, which includes: COD removal, OLR, biogas yield and composition, and solids destruction ratio; and 2.) membrane performance of ThAnMBR, which includes: membrane flux, TMP, resistances, and membrane pore sizes.

4.1 Biological Performance of ThAnMBR

4.1.1 Organic Loading Rate (OLR)

The results of organic loading rate (OLR) with experimental time are shown in Fig 2. The OLR was mainly controlled by the changes in HRTs and sometimes by changes in feed MLSS. At the start-up period of time, thermo-mechanical pulping wastewater was used as the feed to cultivate the anaerobic sludge seed from day 0-63 with an OLR of 1.82±0.12 $KgCOD_{fed}/m^3d$. After the thermophilic anaerobic sludge was developed with the thermo-mechanical pulping wastewater, the pulp and paper secondary sludge was fed to the bioreactor, the OLR of feed sludge was controlled at 1.27±0.26 $KgMLSS_{fed}/m^3d$ and 0.63±0.10 $KgMLSS_{fed}/m^3d$ at an HRT of 7.9±1.3 days and 17.2±1.4 days, respectively, for non-pretreated feed sludge. The results show that there was a significant difference between the two different HRTs with non-pretreated PPS (t-test, $p=0.000 < 0.05$). To compare the effect of ultrasonic pretreatment on anaerobic digestibility of PPS, similar HRT and OLR were used as that of the non-pretreated sludge. The OLR was maintained at 1.38±0.33

$KgMLSS_{fed}/m^3d$. and 0.94±0.12 $KgMLSS_{fed}/m^3d$ at an HRT of 8.0±1.4 days and 16.0±1.4 days, respectively. Similarly, there was a significant difference between the two different HRTs with pretreated PPS (t-test, p=0.000<0.05). Compared between the same or similar HRT for different kinds of PPS, there was no significant difference in OLR between non-pretreatment PPS and pretreated PPS at HRT of 7.9 ± 1.3 and 8.0 ± 1.4 days (t-test, p=0.09>0.05), but there was a significant difference in OLRs between non-pretreatment PPS and pretreated PPS at an HRT of 17.2±1.4 days and 16.0±1.4 days (t-test, p=0.000<0.05). The reason was that the flux of the HRT=16±1 days with pretreatment was slightly higher than similar HRT with non-pretreatment phase due to the low transmembrane pressure condition at the HRT=16.0±1.4 days with pretreatment, so the flux was difficult to control at a slow speed. Thus, the OLR was directly influenced by the HRT, and the MLSS of the feed could also affect the OLR, as shown in Figure 3.

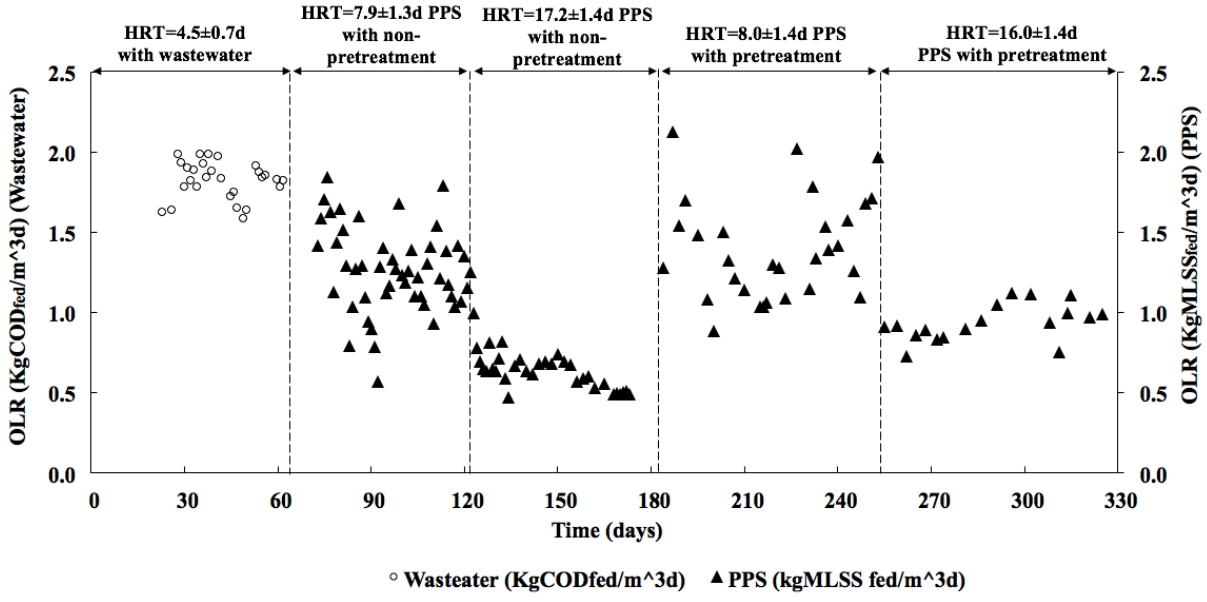


Figure 2 Variation of organic loading rate under different operating conditions

As shown in Figure 3, the reactor mix-liquor concentration (MLSS) was 11.52±0.12 g/L when the feed was wastewater. When the feed was changed to PPS, the feed sludge concentration (MLSS) was at 10.34±1.30 g/L, 10.64±0.77 g/L, 10.93±1.61 g/L, and 14.49±1.88 g/L at an HRT of 7.9±1.3 days and 17.2±1.4 days (non-pretreatment) and 8.0±1.4 days and 16.0±1.4 days (with pretreatment), respectively. No significant difference in feed sludge MLSS was observed among the first three phases of feed with sludge (t-test, p=0.20, p=0.09 and p=0.35>0.05, respectively). But there was a significant increase in feed sludge MLSS in the last phase (HRT=16.0±1.4 days, feed MLSS=14.49±1.88 g/L), because a new bucket of feed sludge was used. Moreover, the MLSS concentration in the ThAnMBR was controlled at 28.94±2.54 g/L, 20.85±3.07 g/L, 32.47±2.06 g/L, and 29.50±1.87 g/L at an HRT of 7.9±1.3 days and 17.2±1.4 days (non-pretreatment) and 8.0±1.4 days and 16.0±1.4 days (with pretreatment), respectively (Fig. 3). The variation in MLSS level in the bioreactor was achieved by variations in HRT and feed sludge MLSS.

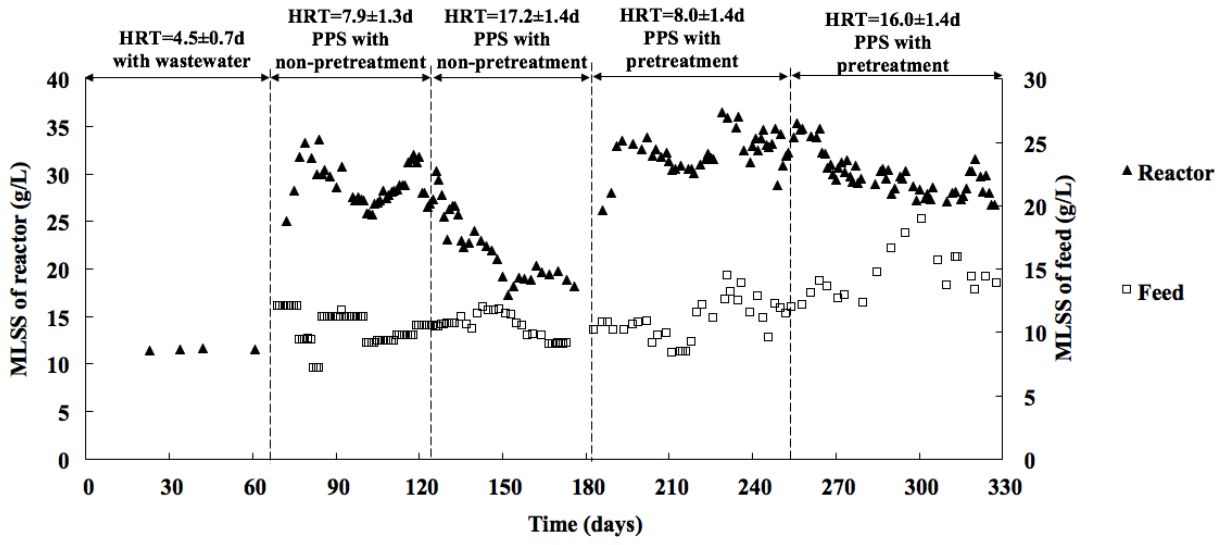


Figure 3 Variation of MLSS of reactor and feed under different operating conditions

4.1.2 Chemical oxygen demand (COD)

Fig. 4 shows the COD levels of the feed, permeate and supernatant. At the beginning, thermo-mechanical pulping wastewater was used as the feed to acclimate sludge, and after around 40 days, the permeate COD stabilized. At day 61, the COD removal was 79.91%. Thus, it was evident that thermophilic anaerobic inoculum was developed.

The total feed COD was at 16,879±1,065 mg/L, 16,427±526mg/L, 15,824±2,808 mg/L and 20,484±2,257 mg/L at an HRT of an HRT of 7.9±1.3 days and 17.2±1.4 days (non-pretreatment) and 8.0±1.4 days and 16.0±1.4 days (with pretreatment), respectively, as shown in Figure 4. The permeate characteristics under stable operation are summarized in Table 5. The stable operation average permeate COD was in the range of 425-1223 mg/L, which corresponded to a COD removal of 93.36% -97.34%, as compared to the total feed soluble COD. An increase in HRT led to a decrease in permeate COD for both non-pretreated sludge treatment and ultrasonically pre-treated sludge (t-test, $p=0.000$ and $p=0.000$, respectively). At similar HRTs, the permeate COD from the pretreated sludge treatment was generally higher than that of the non-pretreated sludge treatment (t-test, $p<0.05$). These differences could be explained by the fact that an increase in the HRT would enhance the biodegradation of slowly biodegradable compounds and thus led to a lower permeate COD at a higher HRT, and ultrasonically treatment of sludge ruptured cell structure to release intracellular compounds and extracted EPS into the aqueous phase and thus increased permeate COD. On the other hand, an increase in HRT for the same sludge used and

ultrasonically pre-treated sludge (as compared to the non-pretreated sludge at the same HRT) led to an increase total Ammonia-N in permeate (t-test, $p=0.047<0.05$). This is related to the fact that an increase in HRT to 16.0-17.2 days and ultrasonically pre-treated sludge would release proteins and DNA/RNA, which contain Ammonia-N and phosphorus, respectively, in the aqueous phase and thus increased the total Ammonia-N and total phosphorus in permeate. In the mesophilic anaerobic digestion of sludge, the concentration of Total Ammonia-N and total phosphorus increased by 10-15% and 77-88%, respectively, during the ultra-sonication period (McDermott et al., 2001). For the other ions measured, sodium, potassium, calcium and magnesium were the dominant cations and chloride and sulphate were the dominant anions but there were no general trends observed in terms of concentrations under different tested conditions. According to Turkdogan et al. (2013), when the HRT increased from 4h to 9h, the COD removals increased from 60% to 81%. Moreover, Sun et al. (2009) achieved 82% and 76% removals of COD when the HRT decreased from 40h to 19h. Apparently, compared the results of COD removal, the high HRT is more effective than the low HRT may because a high HRT can react more completely.

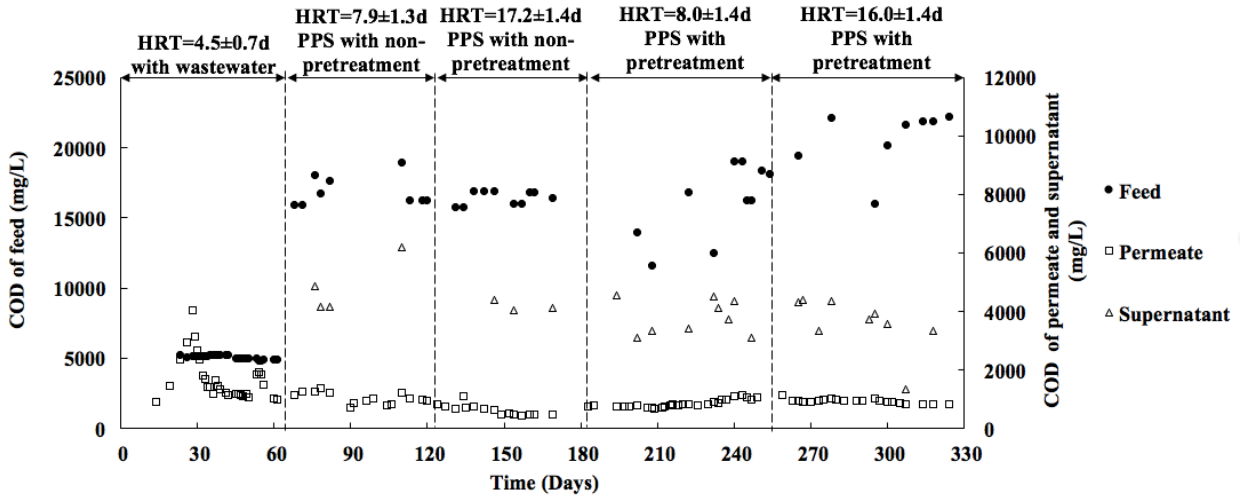


Figure 4 Variations of total COD variation of feed, permeate and supernatant under different operating conditions

Table 5 Characteristics of effluent under different operating conditions

Description	Effluent of HRT=7.9d±1.3 with non-pretreated PPS	Effluent of HRT=17.2d±1.4 with non-pretreated PPS	Effluent of HRT=8.0d±1.4 with pretreated PPS	Effluent of HRT=16.0d±1.4 with pretreated PPS
Permeate COD (mg/L)	985.66±39.61	456.43±27.26	1043.96±64.79	823.06±10.03
Total Ammonia-N (mg/L)	78.53±26.52	97.93±27.8	135.63±44.56	167.37±65.33
Total K Nitrogen (mg/L)	71.43±31.24	89.88±39.18	158.63±59.14	159.83±63.28
Total Phosphorous (mg/L)	10.97±2.96	11.68±1.51	20.88±6.71	21.26±5.01
Chloride (IC) (mg/L)	283.11-249	236.77-251.1	315.29-316.4	320.27-322.87
Dissolved Aluminum (mg/L)	0.12-0.214	0.344-0.34	0.732-0.827	0.642-0.649
Dissolved Calcium (mg/L)	18.32-28.64	32.86-33.54	30.33-31.24	31.97-32.61
Dissolved Chromium (mg/L)	0.005-0.006	0.006-0.007	0.008-0.009	0.007
Dissolved Copper (mg/L)	0.014-0.029	0.043-0.079	0.033-0.051	0.010-0.014
Dissolved Iron (mg/L)	0.105-0.323	0.052-0.064	0.030-0.036	0.025
Dissolved Potassium (mg/L)	38.09-39.30	38.74-41.16	78.57-80.68	81.66-82.59
Dissolved Magnesium (mg/L)	4.714-5.111	7.967-7.977	9.159-9.509	9.453-10.15
Dissolved Manganese (mg/L)	0.309-0.595	0.238-0.244	0.143	0.137-0.147
Dissolved Sodium (mg/L)	387.9-436.9	598.3-621.5	994.4-1079	637.2-645
Dissolved Nickel (mg/L)	0.043-0.050	0.043-0.046	0.078-0.087	0.080-0.089
Dissolved Sulfur (mg/L)	10.32-24.8	21.55-37.7	99.26-116.9	43.4-95.29
Dissolved Silicon (mg/L)	6.782-7.072	13.13-13.63	11.9-12.36	12.73-13.04
Dissolved Strontium (mg/L)	0.054-0.082	0.069-0.07	0.087-0.091	0.092-0.098
Sulphate (SO4) [IC] (mg/L)	28.3	31.6-69.09	9.62-17.7	58.95-178.83

Note: other metals (Nitrite NO_2-N, Nitrate NO_3-N, dissolved Arsenic, dissolved Barium, dissolved Beryllium, dissolved Cadmium, dissolved Molybdenum, dissolved Lead, dissolved Selenium, dissolved Titanium, dissolved Thallium, dissolved Vanadium and Zinc) are under determining limitation.

4.1.3 Biogas production

4.1.3.1 Biogas production per day

The overall biogas production per days is shown in Fig. 5. Using the average of 7 days biogas production can minimize experimental errors as compared to the daily data. The biogas production per day for feeding with wastewater was 1.28±0.57 L/days.

After changing the feed to non-pretreated PPS, the biogas production per day was 0.88±0.30 L/days, 0.62±0.16 L/days, 0.89±0.31 L/days 0.70±0.18 L/days at an HRT at an HRT of 7.9±1.3 days and 17.2±1.4 days (non-pretreatment) and 8.0±1.4 days and 16.0±1.4 days (with pretreatment), respectively. There was a significant difference in biogas production per day between HRT=7.9 ± 1.3 days and 17.2 ± 1.4 days with non-pretreated PPS (t-test, $p=0.009<0.05$). There was no significant difference in the HRT=8.0 ± 1.4 days and HRT=16.0±1.4 days with pretreated PPS (t-test, $p=0.16>0.05$). A comparison between the non-pretreated and pretreated PPS showed that there was no significant difference in the biogas production per days between the HRT (7.9±1.3 and 8.0±1.4) (t-test, $p=0.87$), but there was a significant difference in the similar HRT (17.2±1.4 days and 16.0±1.4 days) with different pretreatment (t-test, $p=0.005<0.05$). The biogas production decreased due to

the HRT and OLR could influence it at the same time. A high HRT could decrease the biogas production because the OLR was low. Besides, due to the OLR of the HRT=16.0±1.4 d (PPS with pretreatment) was higher than the HRT=17.2±1.4 d (PPS with non-pretreatment), the biogas production of the HRT=16.0±1.4d (PPS with pretreatment) was higher than the HRT=17.2±1.4 d (PPS with non-pretreatment).

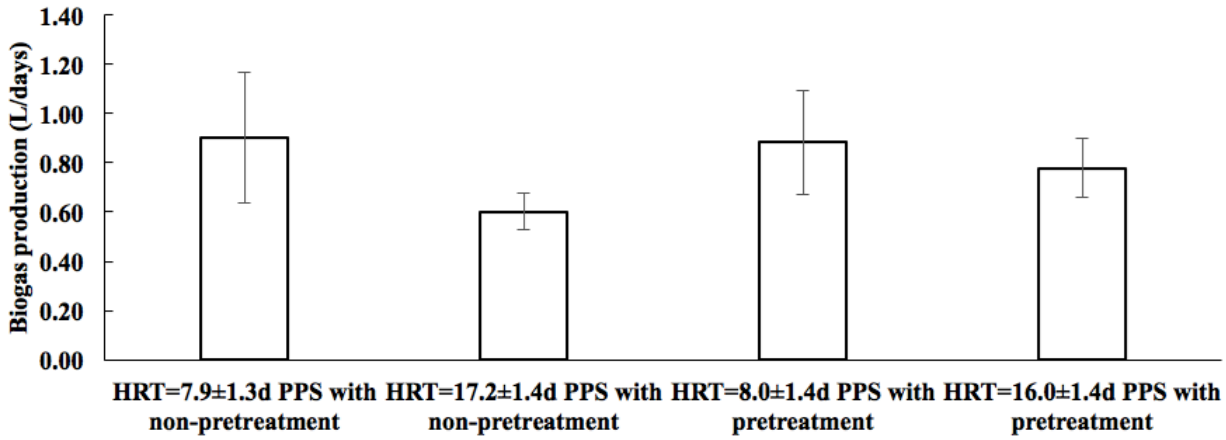


Figure 5 Comparison of the average of seven days biogas production per days under different operating conditions

4.1.3.2 Biogas production rate

The biogas production rate is shown in Fig. 6, and was calculated by Equation 1. The biogas production rate was found to be 0.10±0.01 L/gMLSS$_{fed}$, 0.14±0.01 L/gMLSS$_{fed}$, 0.12±0.02 L/gMLSS$_{fed}$, 0.16±0.03 L/gMLSS$_{fed}$ at an HRT of 7.9±1.3 days and 17.2±1.4 days (non-pretreatment) and 8.0±1.4 days and 16.0±1.4 days (with pretreatment), respectively. There was a significant difference in biogas production rate between an HRT=7.9±1.3 days and 17.2±1.4 days with non-pretreated PPS (t-test, $p=0.000<0.05$) and between an HRT=8.0±1.4

days and 16.0±1.4 days with pretreated PPS (t-test, $p=0.000<0.05$). Furthermore, there were significant differences in biogas production rate either between non-pretreated sludge and pretreated sludge either at the same low HRT (7.9±1.3 vs. 8.0±1.4 days) or the similar high HRTs (17.2 ± 1.4 days vs. 16.0 ± 1.4 days) (t-tests, $p=0.006<0.05$ and $p=0.044<0.05$), suggesting that ultrasonic pretreatment had a significant impact on biogas production rate and led to a slightly increase in biogas production rate. Elliott and Mohmood (2012) found that, when the HRT decreased from 20 days to 12 days, the biogas production rate was decreased from 77 mL/gCOD_{fed} to 45 mL/gCOD_{fed} under the mesophilic condition and fed with secondary PPS. Thus, the increased HRT had the positive impact on the biogas production rate.

Due to the fact that none study of using AnMBR for PPS treatment was conducted, the results of the present study are compared to results from the anaerobic digestion of PPS treatment of conventional anaerobic digestors under thermophilic condition. Bayr and Rintala (2012) found that the methane potential was 100 m^3CH_4/tVS_{added} for co-digestion of primary and secondary PPS under 55°C and an HRT of 25-30 days. Compared to the result of ThAnMBR at an HRT=17.2±1.4 days with non-pretreatment, the methane production was about 72 $m^3CH_4/tMLSS_{fed}$, which was at the same level as that reported by Bayr and Rintala (2012). Furthermore, Saha et al. (2011) found that the methane yield was 70 ml/g COD_{fed} (111.54ml/g VS_{added}) for pulp mill WAS under the mesophilic condition. Compared with the result of HRT=17.2±1.4 days with non-pretreatment (0.14 L/g$MLSS_{fed}$), the results are at the same level, the result under the mesophilic condition is lower than the thermophilic condition. Thus, the ultrasonic pretreatment can improve the biogas production rate.

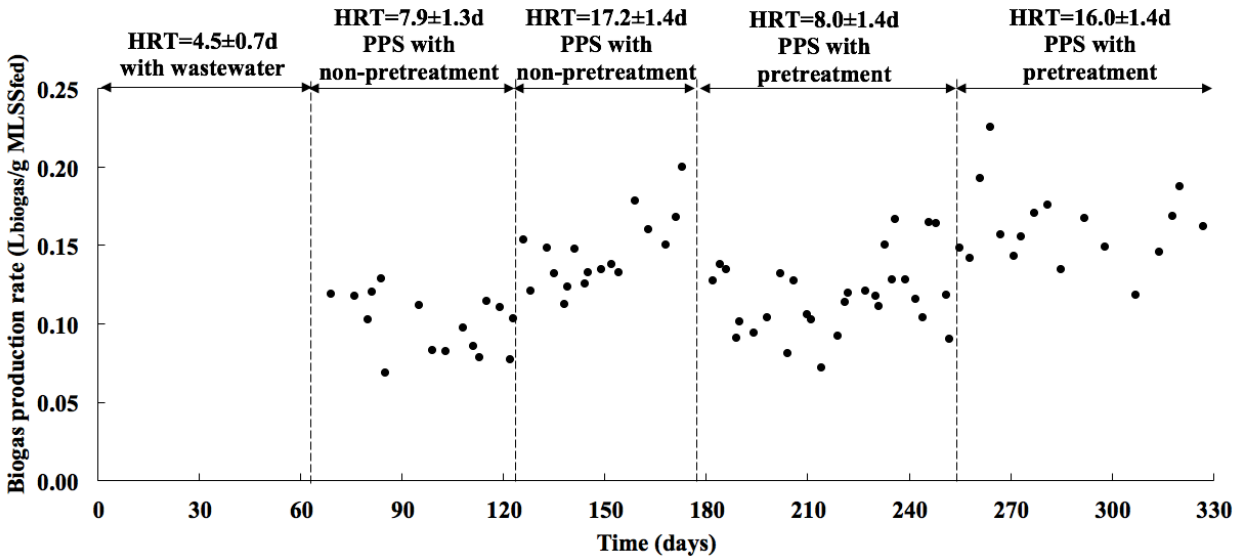


Figure 6 Variations of biogas production rate under different operating conditions

4.1.3.3 Biogas composition

The biogas composition is shown in Fig. 7. The methane content in biogas fluctuated between 48.21-71.4%. Among them, when the wastewater was used, the methane content was 45.42-64.51% when thermo-mechanical pulping wastewater was used at the beginning. After the feed was changed to PPS at day 63, the methane content was 56.57%±3.29%, 51.56%±2.46%, 61.22%±5.09%, and 56.24%±2.40% for an HRT of 7.9±1.3 days and 17.2±1.4 days (non-pretreatment) and 8. 0 ±1.4 days and 16.0±1.4 days (with pretreatment), respectively. There was a significant difference in the methane content between these two HRTs for both non-pretreatment and pretreated sludges (t-test, $p=0.000<0.05$ (non-pretreatment) and $p=0.001<0.05$ (pretreated sludge)). Furthermore, the results showed that, as compared to the non-pretreatment sludge at the same or similar HRT, the methane content

of biogas from pretreated sludge (61.22% and 56.24%) was much higher than that (56.57% and 51.56%) from non-pretreatment sludge (t-test, $p=0.002<0.05$ (HRT were 7.9±1.3 and 8.0±1.4 days) and $p=0.000<0.05$ (HRT=16.0-17.2±1.4 days)). The methane content of the biogas composition decreased continuously when the HRT increased. In the anaerobic digestion, the OLR and HRT could affect the methane yield (Menard et al., 2011). However, according to the Mahmoud et al. (2017) study, the biogas composition decreased continuously when the OLR was increased which was under mesophilic condition. The methane content in biogas (48.2-71.4%) from this study is similar to that observed result (50-75%) in previous study. (Maghanaki et al., 2013).

The composition of carbon dioxide was a fluctuation at the steady state between 17.96 – 31.36%. the CO_2 content in biogas was 27.36% ± 2.75%, 25.99% ± 1.11%, 21.76%±2.16% and 27.28%±1.18% for an HRT of 7.9±1.3 days and 17.2±1.4 days (non-pretreatment) and 8.0±1.4 days and 16.0±1.4 days (with pretreatment), respectively. There was no significant difference in the carbon dioxide content between the two HRTs for non-pretreated sludge (t-test, $p=0.087>0.05$). However, a significant difference in carbon dioxide content was observed between the HRT=8.0±1.4 days and 16.0±1.4 days with pretreated PPS as the feed (t-test, $p=0.000<0.05$). There were significant differences in carbon dioxide composition between non-pretreated PPS and pretreated PPS either at the same HRT (7.9±1.3 vs. 8.0±1.4 days) (t-test, $p=0.000<0.05$) or at a similar HRT (16.0-17.2±1.4 days) (t-test, $p=0.008<0.05$). At the low HRT (7.9±1.3 and 8.0±1.4 days), the methane content increased and the CO_2 content decreased with pretreated sludge. A similar trend was observed in a previous study (Rico et al., 2015). According to Mohmoud et al. (2017), most

of the CO_2 production was released into the gas phase; sequentially, decreasing the methane percentage in the biogas.

The nitrogen content of biogas was in the range of 12-20% in all the four phases of sludge as feed. An increase in HRT led to an increase in the nitrogen content for non-pretreated sludge (from 13.02%±3.56% to 19.04%±4.30%). This explained the decrease in the methane content with an increase in HRT for non-pretreated sludge. However, the decrease in the methane content of biogas with an increase in HRT for pretreated sludge was related to an increase in the CO_2 content but not the N_2 content (12.39%±4.57% for the HRT=8.0±1.4 days vs. 12.89%±2.75% for the HRT=16.0±1.4 days). There was no significant difference in nitrogen composition between the two HRTs with pretreated PPS as the feed (t-test, p=0.68>0.05). Furthermore, there was no significant differences in nitrogen composition between non-pretreated PPS and pretreated PPS at the similar HRT (7.9±1.3 and 8.0±1.4 days) (t-test, p=0.64>0.05), but there was a significant difference between non-pretreated PPS and pretreated PPS at an HRT of 16.0-17.2±1.4 days (t-test, p=0.001<0.05).

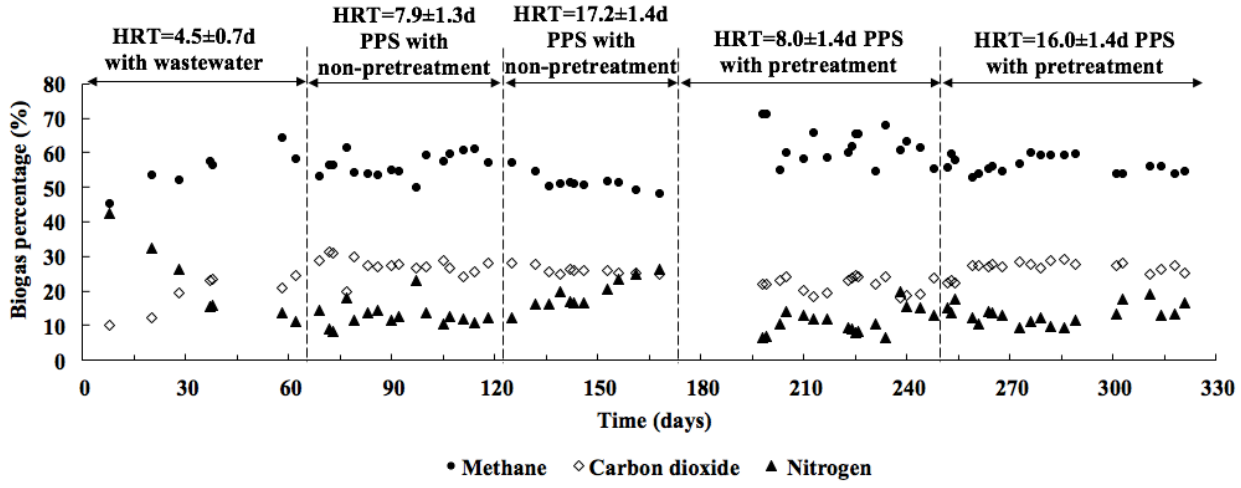


Figure 7 Variation of biogas composition under different operating conditions

4.1.3.4 Biogas Yield

The biogas yield was calculated by Equation 2 and shown in Fig. 8. At the steady-state of HRT=4.5±0.7 days feeding with wastewater, the biogas yield was 0.26±0.03 L/g COD removed, which was similar to that observed (0.20-0.27 L/g COD removed) by Gao et al. (2016). After the feed was changed to PPS, the biogas yield was 0.31±0.05 L/g $MLSS_{removed}$, 0.44±0.08 L/g $MLSS_{removed}$, 0.31±0.03 L/g $MLSS_{removed}$ and 0.38±0.05 L/g $MLSS_{removed}$ at an HRT of 7.9±1.3 days and 17.2±1.4 days (non-pretreatment) and 8.0±1.4 days and 16.0±1.4 days (with pretreatment), respectively. The results show that there was a significant difference in biogas yield between the two HRTs for the same sludge (either for non-pretreated PPS (t-test, $p=0.006<0.05$) or for pretreated PPS (t-test, $p=0.008<0.05$)). Thus, an increase HRT could increase the methane yield, based on solids destructed. The results are comparable to that in the literature. Park et al. (2012) found that the biogas yield of PPS treatment was in the range of 0.22-0.40 L biogas/g $VS_{consumed}$. However, there was no significant difference in biogas yield between the non-pretreated PPS and pretreated PPS at the similar HRT (7.9±1.3 and 8.0±1.4 days) (t-test, $p=0.85>0.05$) and or at a similar HRT (16.0-17.2 ± 1.4 days) (t-test, $p=0.13>0.05$), based on solids destructed, implying that ultrasonic pretreatment had no significant impact on biogas yield based on per unit solids destructed. A similar result was found from Bayr et al. (2012) that ultrasound could not improve the methane yield when the feed is secondary PPS.

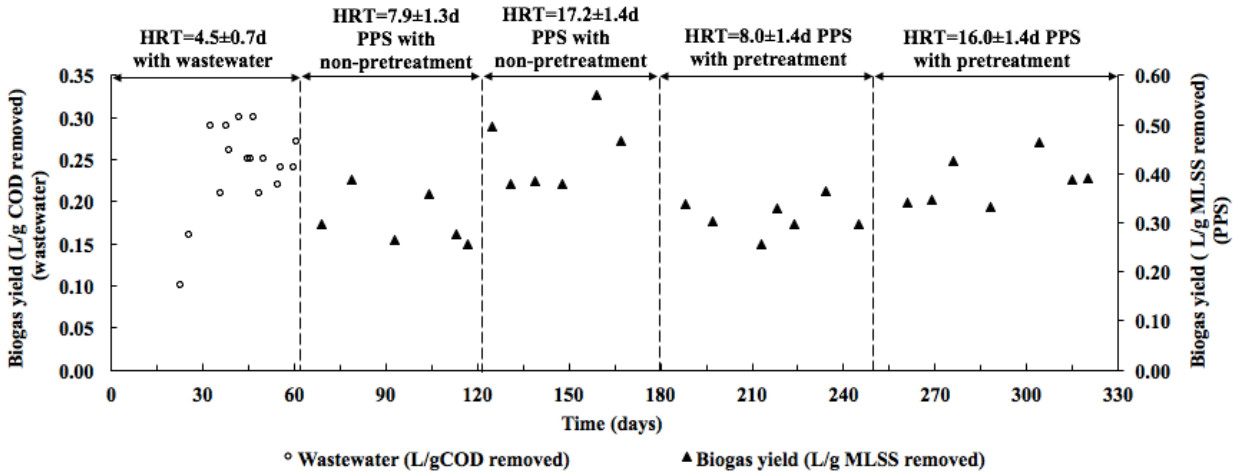


Figure 8 Variation of biogas yield under different operating conditions (ambient temperature 24±1°C)

4.1.3.5 Suspended Solid destruction

The result of suspended solid destruction was calculated by Equation 3 and is shown in Fig. 9, which were 36.77%±4.90% and 35.84±3.46% for non-pretreated PPS at an HRT of 7.9±1.3 days and 17.2±1.4 days, respectively. After switching to ultrasonically pretreated sludge, the suspended solid destruction were 33.57±5.35% and 37.51%±6.60% at an HRT of 8.0±1.4 days and 16.0±1.4 days, respectively. There were no significant differences in the suspended solid destruction either between the two HRTs used for non-pretreated sludge or pretreated sludge or between the two types of sludge (non-pretreated vs. pretreated) at the same or similar HRT (t-test, $p>0.05$). The results are comparable to that in the literature in that solids reduction of PP secondary sludge was in the range of 45.8% for the non-pretreatment and 50.3% for the ultrasonic pretreatment. (Mahmood and Elliott, 2006).

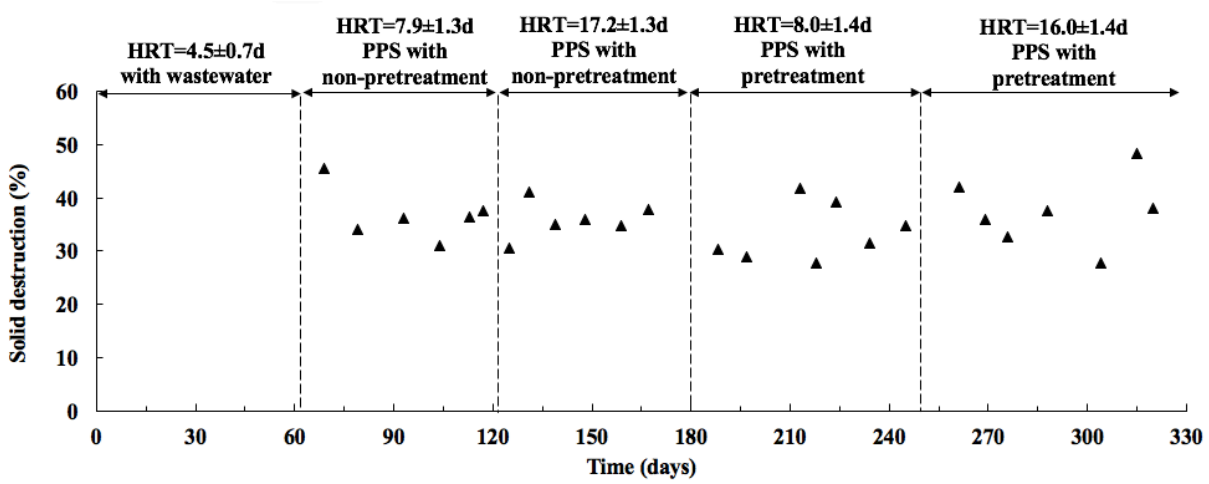


Figure 9 The variations of suspended solid destruction under different operating conditions

4.2 Membrane Performance

4.2.1 Flux and TMP

The flux of AnMBR is related to the operating HRT. The flux profile is shown in Figure 10. The initial membrane flux was maintained at 3.19±0.36L/m^{2}h at the HRT=4.5±0.7 days feeding with thermo-mechanical wastewater. After the feed was switched to PPS, the flux was changed to 1.41±0.37L/m^{2}h and 0.42±0.09L/m^{2}h for non-pretreated sludge to achieve an HRT of 7.9±1.3 days and 17.2±1.4 days, respectively. Due to the limitation of the smallest speed the permeate pump could achieve, the low flux (0.42±0.09L/m^{2}h) used for an HRT of 17.2±1.4 days was achieved by membrane fouling (no cleaning after membrane fouled at the end of the phase of HRT=7.9±1.3 days (i.e., flux=1.41±0.37L/m^{2}h). Two new pieces of membranes were used at day 180 when changing to the ultrasonic pretreated PPS. The flux was set at 1.36±0.37L/m^{2}h for an HRT of 8.0±1.4 days from day 180 to day 255.

Then the flux was decreased to 0.5±0.10L/m^{2}h for an HRT of 16.0±1.4 days with pretreated PPS.

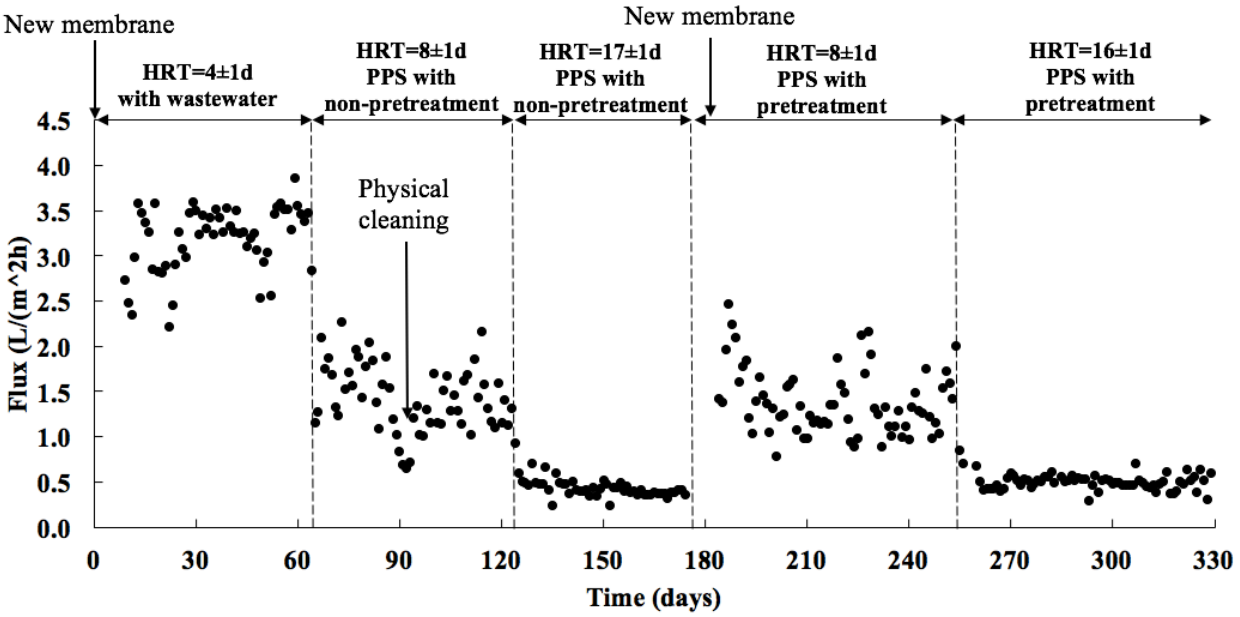


Figure 10 Variation of Flux under different operating conditions

The variation of transmembrane pressure (TMP) is shown in Fig 11. There was no membrane fouling (TMP<20kPa) during the first 63 days operation with thermophilic pulping wastewater as feed, and a bioreactor MLSS of 11.52±0.12g/L. However, membrane fouling (TMP jump) was observed about three weeks later after the feed was switched to PPS (with non-pretreatment) with a bioreactor MLSS of 28.94±2.54 g/L. Another membrane fouling (TMP jump) was observed on day 123, about one month later after physical cleaning of membrane to re-install membrane flux on day 92. In order to achieve a higher HRT (17.2±1.4 days), no physical cleaning was conducted after the second TMP jump and the relatively stable flux (0.42±0.09L/m^{2}h) was maintained for this phase study with a bioreactor MLSS of 20.85±3.07 g/L. No significant membrane fouling (TMP<5kPa) was observed at

the two tested HRTs (8.0±1.4 days and 16.0±1.4 days) for ultrasonically pretreated sludge, even though the bioreactor MLSS (32.47±2.06 g/L) was higher than that (28.94±2.54g/L) of the SAnMBR with non-pretreated sludge. These results suggest that membrane performance of the SAnMBR with ultrasonically pretreated sludge was much better than that of the SAnMBR with non-pretreated sludge at an HRT of 7.9±1.3 days.

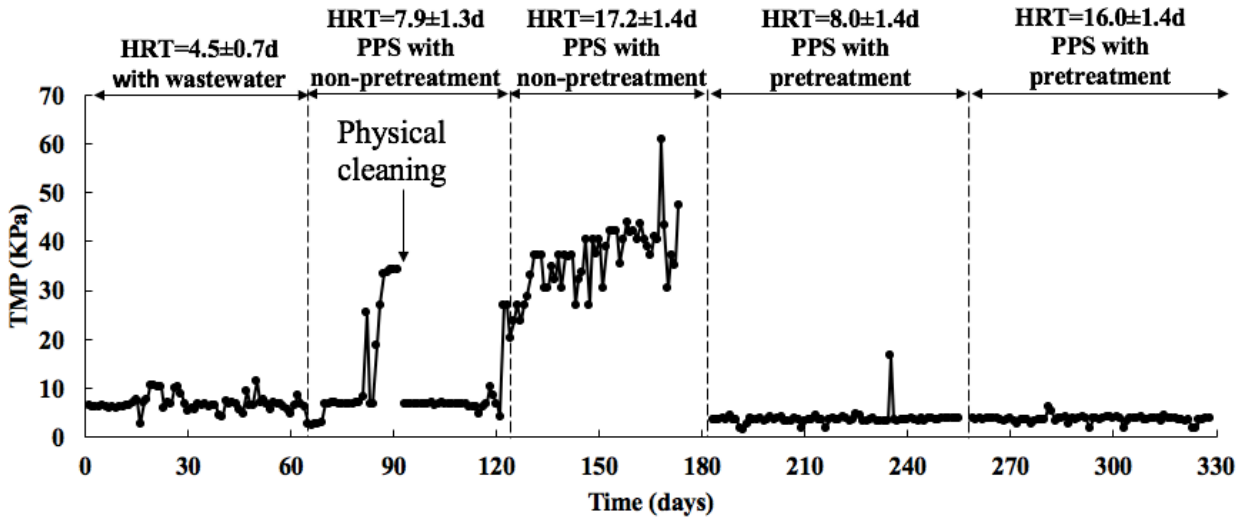


Figure 11 Transmembrane pressure (TMP) under different operating conditions

4.2.2 Membrane Fouling Characterization

Membranes at the end of the 3rd phase (non-pretreated sludge at an HRT of 17.2±1.4 days) and the 5th phase (pretreated sludge at an HRT of 16.0±1.4 days) were used to characterize membrane filtration resistances and identify the mechanism of membrane fouling. For the first set of membranes subjected to membrane cleaning studies, leaking of glued connections was observed during cleaning and thus the relative contribution of membrane resistances

caused by cake layer/or gel layer and chemical cleanings were not identified. But the permanent resistance formation was indeed observed and the results after chemical cleanings suggested permanent resistance only accounted 0.32% of the total filtration resistance. For the second set of membranes, physical and chemical cleanings suggested the relative contribution of resistances from gel layer formation, organic fouling, inorganic fouling and permanent fouling accounted for 98.89%, 0.16%, 0.17% and 0.00% of the total filtration resistances, respectively. Thus, gel layer formation occurred during the treatment of pretreated sludge and was the dominant mechanism of the limited membrane fouling. The gel layer formation was caused by the filtration of macromolecules released during ultrasonic pretreatment. The particle size distribution of supernatant (as shown in Fig.15 in later sections) suggested there were a significant amount of colloids or macromolecules in the size range of 0.1-1 μm presented in the supernatant of ultrasonically pretreated sludge, which could easily deposit on the membrane surfaces by the permeation to form gel layer.

Table 6 Different kinds of resistance and R/R_T of different membrane

Resistance (%)	Membrane 1		Membrane 2	
	Resistance (m^{-1})	R/R_T (%)	Resistance (m^{-1})	R/R_T (%)
Membrane resistance	3.72E+11	0.89%	3.08E+11	0.33%
Total resistance	4.18 E+13	n.a.	3.92E+13	n.a.
Organic resistance	n.a.	n.a.	6.08E+10	0.16%
Inorganic resistance	n.a.	n.a.	6.75E+10	0.17%
Cake layer resistance	n.a.	n.a.	3.87E+13	98.89%
Permanent resistance	1.35E+11	0.32%	3.06E+08	0.00%

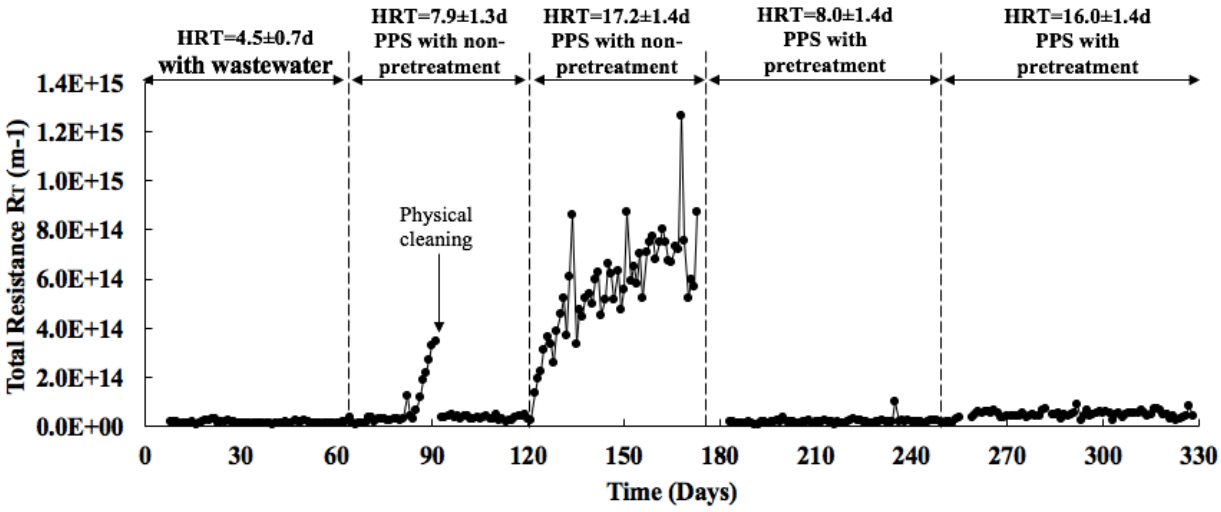


Figure 12 Typical total filtration resistance (R_T) profiles under different operating conditions

4.2.3 Particle Size Distributions

The particle size distribution (PSD) of mix-liquor in bioreactor at four different phases is shown in Fig 13. A log-normal distribution curve for PSD was observed. It appeared that HRT had no impact on the PSD of MLSS in bioreactor with either non-pretreated sludge or ultrasonically pretreated sludge as feed. However, the mean particle size of MLSS in bioreactor shifted from 21 μm to 30 μm when the feed was changed from non-pretreated PPS to pretreated PPS. The difference might be caused by the use of a different batch of feed sludge for phases 3 and 4. Although ultrasonic pretreatment led to a break-up of flocs in PPS feed, as shown in Figure 14. The mean particle size shifted from 43 μm to 21 μm when the feed was changed from non-pretreated PPS to pretreated PPS. The reason is that ultrasonic treatment can mechanically interrupt the cell structure and the flow matrix, and one of the mechanisms is cavitation that leads to sludge disintegration by sound waves of high frequencies (20-40 kHz) (Elliott and Mahmood, 2007). There was a significant difference of the shape with the feed of non-pretreatment and pretreatment. The PSD of non-pretreatment sludge was much narrower than the pretreated one, and the same result was observed by Cougrier et al. (2005).

The PSD of the supernatants at four different phases is shown in Fig 15. All of the supernatants contained a large number of colloidal particles with a size in the range of 0.1-1μm. The PSD curves had two peaks in every phase. The first peaks of PSD for supernatants from HRT=7.9±1.3 days and 17.2±1.4 days with non-pretreated PPS as feed were shown at 0.52 μm and 0.29 μm, respectively, and the second peaks were at 21.45 μm and 13.37 μm, respectively. Moreover, when the feed was changed to pretreated PPS, the first peaks of PSD

were shown with a smaller size at 0.20 μm and 0.18 μm for HRT=8.0±1.4 days and 16.0 ± 1.4 days, respectively, as compared to that with non-pretreated PPS as feed. Furthermore, a significant higher portion of colloids in the size range of 0.1-1μm was observed for supernatants from the bioreactor with ultrasonically pretreated sludge as feed. This might not be surprising, as ultrasonic treatment can mechanically interrupt the cell structure and the flow matrix, and lead to sludge disintegration and release of EPS and cellular compounds in the supernatants (Elliott and Mahmood, 2007).

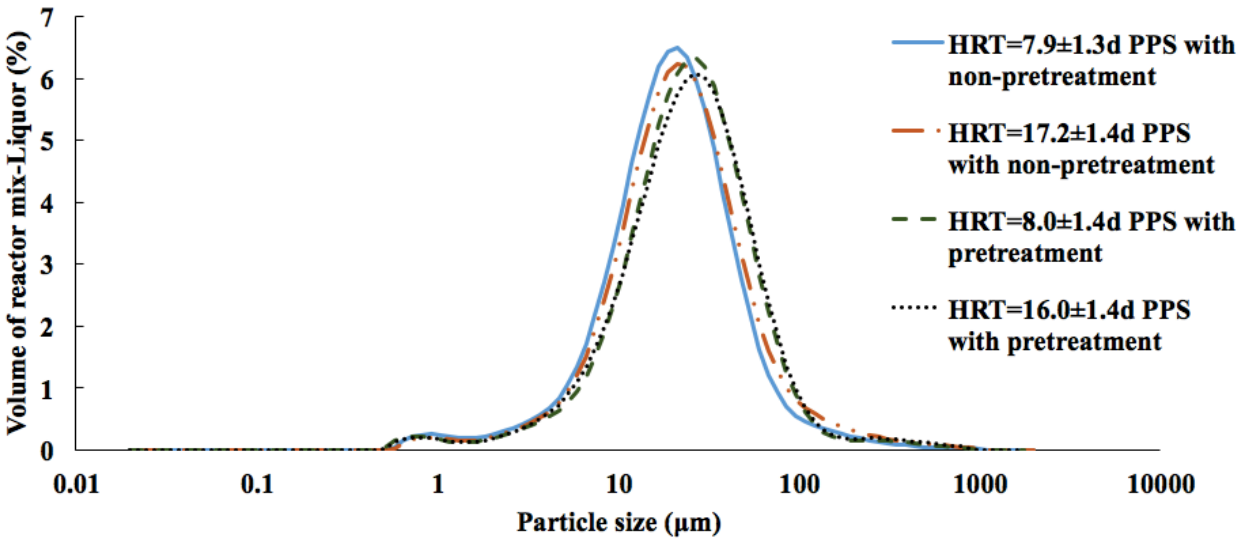


Figure 13 Particle size distributions of reactor mix-liquor under different operating conditions

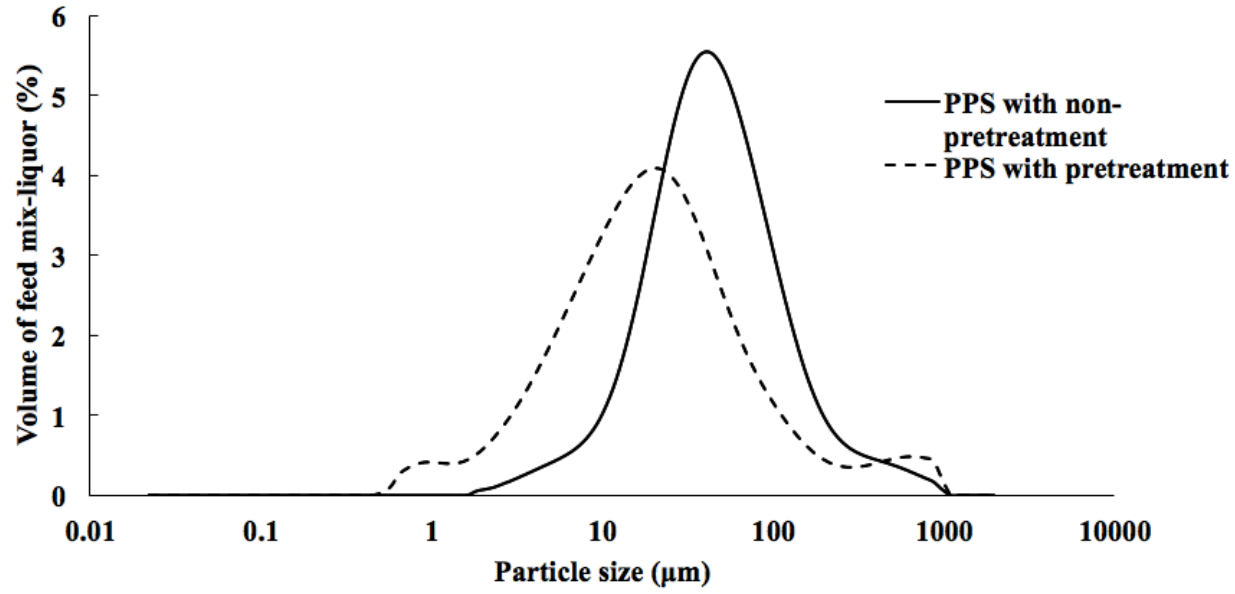


Figure 14 Particle size distribution of feed mix-liquor under different operating conditions

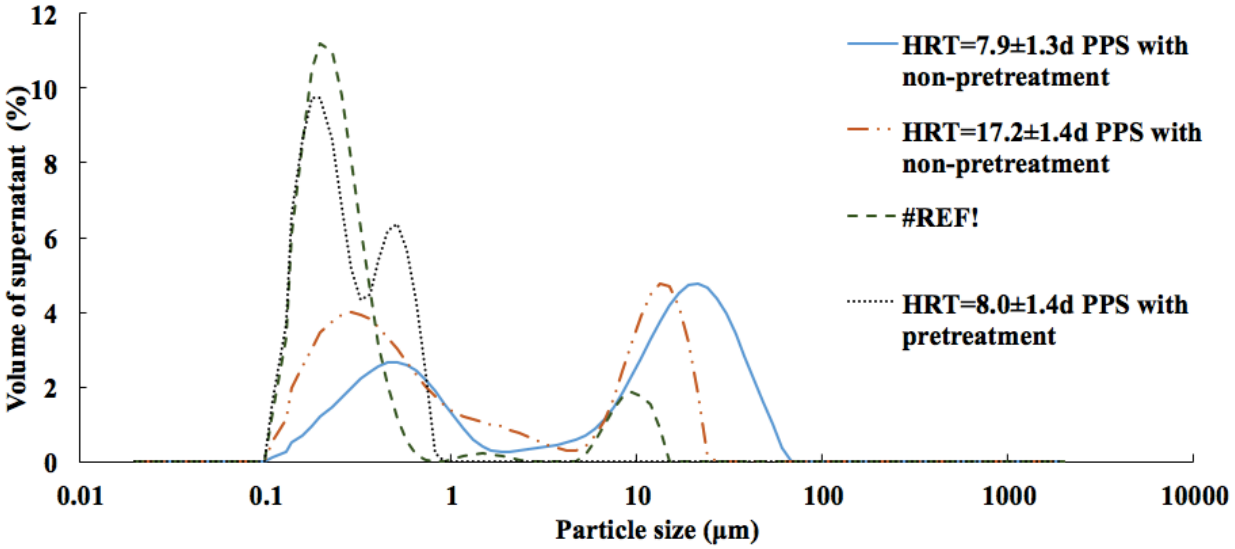


Figure 15 Particle size distributions of supernatant under different operating conditions

4.2.4 Extracellular Polymeric Substances (EPS) and Soluble microbial products (SMP)

The Protein and Carbohydrate ratio (PN/CHO ratio) is shown in Fig.16. The PN/CHO ratio was high in HRT=7.9±1.3 days and HRT=17.2±1.4 days with non-pretreatment and HRT=8.0±1.4 days with pretreatment. The PN/CHO ratio was low in HRT=16.0±1.4 days with pretreatment possibly because of the high food to microorganism (F/M) ratios. From the research of Lin et al. (2009), the low F/M ratios could decline the carbohydrate concentration. In addition, EPS was an identification of an important factor of membrane fouling parameter in the MBR system (Meng et al., 2009). Moreover, the PN/CHO ratio was more important for fouling resistance rather than the quantity of total EPS (Lee et al., 2003). Especially in thermophilic condition, the higher PN/CHO ratio could contribute to the membrane fouling in the AnMBR (Lin et al., 2009). Sludge with a higher PN/CHO ratio in bound EPS would have higher stickiness and thus favor the development of cake formation (Zhou et al., 2008; Lin et al., 2009). HRT=8±1 days with non-pretreatment and with pretreatment, the PN/CHO ratios were higher than high HRT phase. The membrane fouling happened in the phase of HRT=7.9±1.3 days. The PN/CHO ratio of high HRT was lower than PN/CHO ratio of low HRT. The total TB-EPS and LB-EPS are shown in Fig. 17. Among them, the TB-EPS of the phase of HRT=7.9±1.3 days with un-pretreatment PPS was the highest. The presence total LB of EPS had the significant negative effect on sludge settleability, dewaterability, bioflocculation and effluent clarification (Li and Yang, 2007). It may cause the membrane fouling during the HRT=7.9±1.3 days with non-pretreatment.

Although EPS was essential to the formation of sludge floc, excessive LB-EPS can weaken the cell attachment and deteriorate the floc structure, so that complicate the cell erosion and poor sludge-water separation (Li and Yang, 2007).

Compared the Fig.18, the protein and carbohydrate of SMP of the phase of HRT=16.0±1.4 days with pretreatment was higher than other phases. A high SMP content can increase the filtration resistance (Lee et al., 2003; Meng et al., 2006).

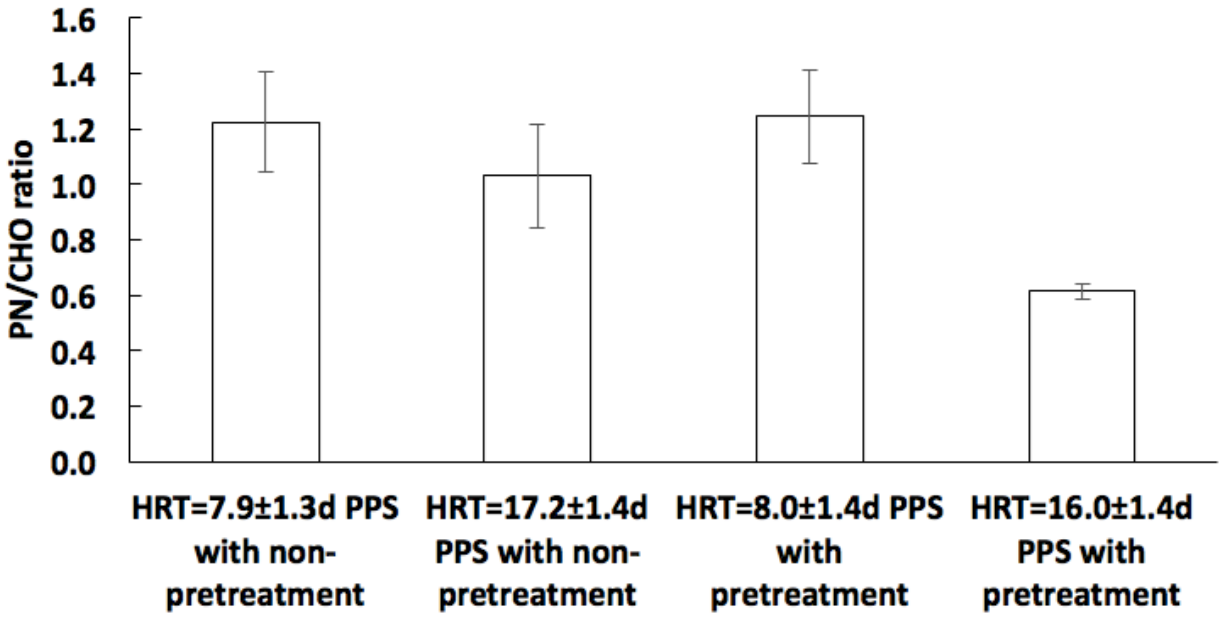


Figure 16 Comparison of Mix-liquor of PN/CHO ratio in four phases

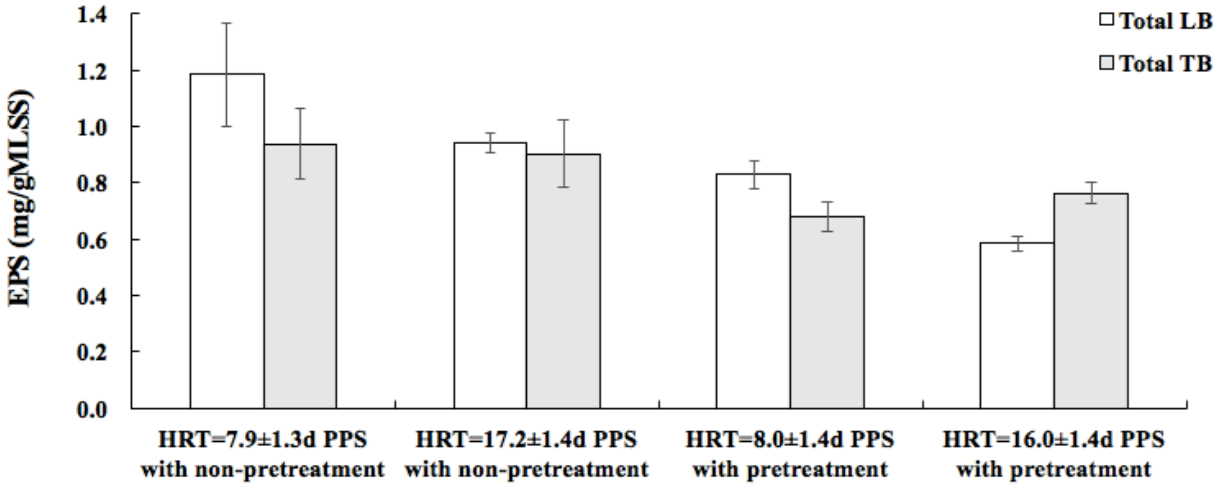


Figure 17 Comparison of Total LB and TB in different phases

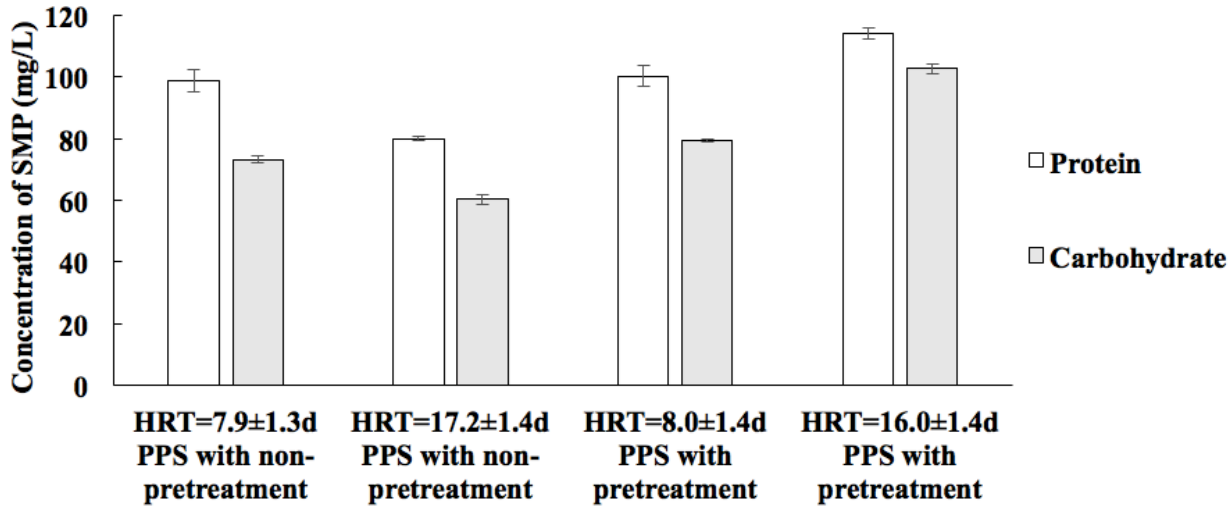


Figure 18 Comparison of SMP of TB and LB protein in four phases

4.2.5 Morphology and pore size distribution of new and used membranes

Scanning electron microscopy (SEM) was used characterize the morphology and pore sizes of the new and physically and chemically cleaned used membranes. Figure 19 shows a

typical image of pore size and morphology of the new and physically and chemically cleaned used membrane. There were no visual differences of morphology and pore sizes between the new and used membrane. However, a more in-depth study by accounting approximately 500 membranes pores of each membrane showed that significant differences in membrane pore size distribution were observed. Clearly, the used membrane has a greater amount of larger pores and less smaller pores, as compared to the new membrane. This could be explained by the impact of temperature. The used membrane was exposed to a thermophilic temperature of 50°C in the ThAnMBR for more than 150 days. The thermophilic temperature would lead to pore size expansions and thus more large pores were observed in the used membranes.

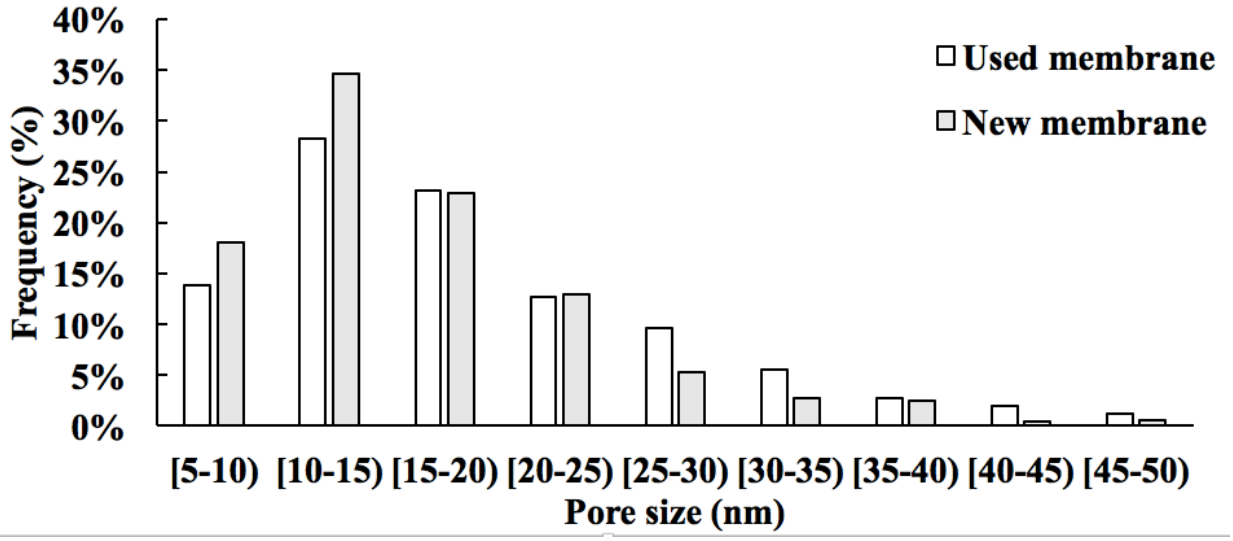
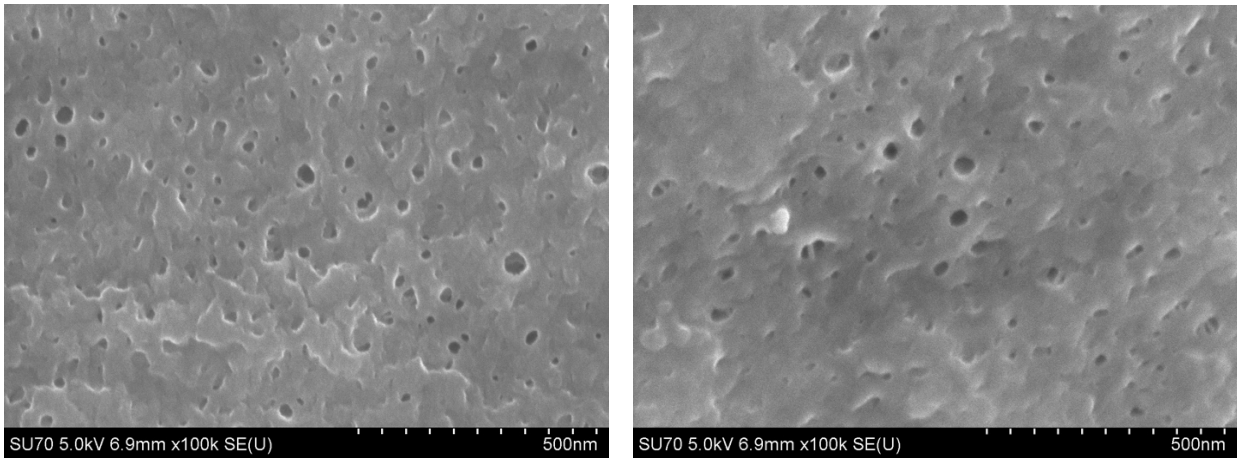


Figure 19 Comparison of the pore size distribution in the used membrane and new membrane



(a) New membrane (b) Used membrane

Figure 20 SEM of (a) new membrane and (b) used membrane

5. Conclusions and Future work

5.1 Conclusions

The feasibility of ThAnMBR for PPS treatment for biogas production was studied for about 330 days. The impacts of HRT and ultrasonic pretreatment of sludge on the biological and membrane performance of the ThAnMBR were systematically studied. The results show that the ThAnMBR is a promising new technology for PPS treatment for biogas production. As compared to the conventional anaerobic digestors, HRT was successfully separated from SRT and a low HRT (8 days) and high HRT (36 days) were used for PPS treatment. An increase in HRT led to an improved biogas yield (L_{biogas}/g $MLSS_{fed}$) for both non-pretreated and ultrasonically pretreated sludge. Ultrasonic pretreatment of PPS had a slight improvement of biogas yield (Lbiogas/g $MLSS_{fed}$), as compared to that of non-pretreated sludge, at the same or similar HRT. The solids destruction ratio was in the range of 32-40% and neither HRT nor pretreatment had a significant impact of solids destruction ratios. The ultrasonic pretreatment contributed to the higher concentration of: COD, total Ammonia-N, the total K nitrogen, the total Phosphorous in permeate.

Cake layer or gel layer formation was the dominant mechanism of membrane fouling. Physical and chemical cleaning could completely re-install membrane performance with limited or no permanent membrane fouling observed. The ThAnMBR with ultrasonically pretreated sludge had better membrane performance than that of the ThAnMBR with non-pretreated sludge. Changes in sludge properties could explain the difference in membrane

performance between non-pretreated and ultrasonically treated sludge. Thermophilic temperature led to an expansion of membrane pore sizes, as compared to the new membrane.

5.2 Future work

The use of AnMBR for PPS treatment for solids reduction and biogas production is a new technology. There was no one previous study that tested this novel technology. Consequently, there are a number of opportunities in exploring this new technology. More specifically, the impact of process conditions (like SRT) and environmental conditions (like temperature) and different pretreatment technologies to enhance the anaerobic digestability of PPS should be systematically investigated. The feasibility of AnMBR for PP primary sludge treatment and/or co-digestion of PP primary and secondary sludge should be investigated. Furthermore, the impact of process and environmental conditions and different pretreatment technologies on sludge properties and their impact on membrane performance should be systematically studied to optimize membrane performance. Moreover, the economic feasibility of the AnMBR technology for PPS treatment should be investigated and compared to that of the other practices currently being used. Toward that end, the scale of ThAnMBR can be enlarged from laboratory scale to pilot scale; ultimately, it could be used in the full scale applications.

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