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Yang, Mufan

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Mesophilic Submerged Anaerobic Membrane Bioreactor for Pulp and Paper Secondary Sludge treatment

By

MUFAN YANG

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List of Nomenclature and Abbreviations

AnMBR: Anaerobic Membrane Bioreactor

COD: Chemical Oxygen Demand

EPS: Extracellular Polymeric Substances

F: Full scale

HRT: Hydraulic Retention Time

L: Laboratory/ bench scale

LB-EPS: Loosely Bound-Extracellular Polymetric Substances

LBM: Liters Per minutes

MBRs: Membrane Bioreactors

MF: Microfiltration

MLSS: Mixed Liquor Suspended Solids

NF: Nanofiltration

OLR: Organic Loading Rate

PN: Protein

PPMSS: Pulp and Paper Mill Secondary Sludge

PSD: Particle Size Distribution

RO: Reverse Osmosis

R_t: Toral Resistance

SAnMBR: Submerged Anaerobic Membrane Bioreactor

SEM: Scanning Electron Microscopy

SMP: Soluble Microbial Products

SRT: Solid Retention Time

SS: Suspended Solids

TB-EPS: Tightly Bound-Extracellular Polymeric Substances

TMP: Transmembrane Pressure/Thermo-mechanical Pulping Pressate

TSS: Total Suspended Solids

UF: Ultrafiltration

VFAs: Volatile fatty acids

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Abstract

The production of pulp and paper is associated with the generation of large quantities of wastewater that has to be purified to avoid severe pollution of the environment. Wastewater purification in pulp and paper mills uses sedimentation, biological treatment, chemical precipitation, flotation and anaerobic treatment, and the specific combination of techniques is determined by the local conditions. Wastewater treatment generates large volumes of organic solid waste (primary and secondary sludge) that after dewatering can be incinerated and thus used for bio-energy production. Sludge is currently viewed as biofuel of poor quality due to its high water content, and some mills treat it solely as a disposal problem. In this study, a new technology Submerged Anaerobic Digestion Membrane Bioreactor (SAnMBR) was developed in order to treat pulp and paper mill sludge, which can not only improve the quality of effluent after pretreatment, but also can recycle the value of PPMSS (pulp and paper mill secondary sludge). In this thesis, a laboratory-scale SAnMBR was operated for 330 days under 37 °C to explore the feasibility of PPMS treatment at different hydraulic retention times (HRTs), besides, alkali pretreatment was adopted to PPMS in order to explore its effects on performance of SAnMBR for the treatment, included biogas production, biogas yield, solids destruction ratio and effluent COD. COD removal efficiencies were all excellent (over 95%). The solids reduction ratio was in the range of 20%-50% and there was no significant difference in solids reduction ratio under different HRTs and alkali pretreatment. The biogas production rate decreased with an increase in HRT before and after alkali pretreatment had no significant impact on biogas production rate, and these two factors also influenced extracellular polymeric substances (EPS), soluble microbial products (SMP) and solids destruction ratio. Membrane performance was affected by PSDs of supernatant and SCOD, alkali pretreatment caused sludge deflocculation and a larger amount of fine colloidal flocs, which resulted in increasing of membrane fouling rate. However, the results shown that the biogas production in lower HRT was better comparing with it in higher HRTs, and quality of effluent was kept excellent during the experimental period, the pretreatment increased membrane fouling rate, and it had no significant effect on biogas production. SAnMBR was feasibility from this study, but membrane fouling should be an issue.

Keywords: anaerobic digestion membrane bioreactor; pulp and paper mill sludge (PPMS); alkali pretreatment; biogas yield; biogas production; COD

1. Introduction

1.1 Current status of PPMS

According to the statistics, an estimated 400 million tonnes of paper and paperboard were produced globally in 2012 (FOEX Indexes Ltd), the production of 1 tonne of paper at a paper mill can generate around 40-50 of dry sludge (Hoyce Tw et al., 1979), and the pulp and paper industry in Canada produces about 7.1 dry Mt/year of sludge (Reid, 1997) and about 31 dry Mt/year of sludge worldwide (Cathie and Guest, 1991).

The global production in the pulp and paper industry was predicted to increase by 77% in 2020, with more than 66% of the paper would be recycled at the same time (Lacour, 2005). On average, most of the waste produced by paper production and as a by-product, PPMS can be recycled up to 23.4% per a unit of produced paper, the specific quantity depends on different processes of paper production (Miners, 1991). In addition, it is expected that the global production of PPMS will have 48 to 86% rises above the current level over the next 50 years (Mabee & Roy, 2003). This rise represents that the environment will bear a heavy burden due to more than 69% of PPMS treatment adopt by landfill. The generation process of PPMS is shown in Figure 1-1.

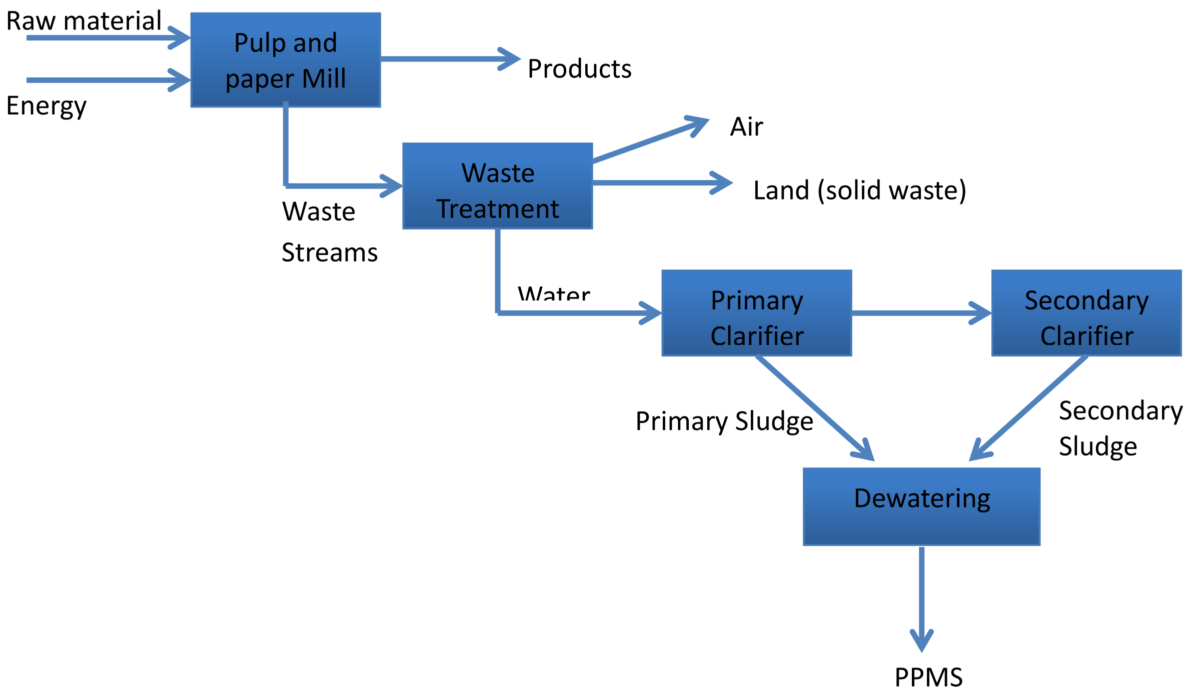

Fig.1-1. The generation process of PPMS

1.2 The kinds of PPMS

The process of pulp and paper wastewater treatment produces large amounts of sludge. The sludge comes from the sedimentation, which is produced during the process of papermaking. Depending on the different papermaking raw materials used and the stages of wastewater production, the sludge from wastewater can be classified as “primary sludge,” “secondary sludge,” and “deinking sludge.” Table.1 shows solid waste generated in pulp and paper mills.

Table 1-1. The Solid waste in pulp and paper mills

Deinking sludge
Deinking sludge is generated during the production of recycled fiber from recycled paper. This residue mainly includes short fibres or fine powders, coatings, fillers, ink particles (a potential source of heavy metal), extractions and deinking additives.
Primary sludge
This sludge is created during the first stage of the processing at the primary clarifier. Though Primary clarification is usually executed by sedimentation, it can also be carried out by dissolved air flotation. Primary sludge is mainly composed of fine particles and fillers, depending on the recycled paper which being processed, and is easier to dewater than the secondary sludge.
Secondary sludge
This sludge is produced in the clarification tank of the biological unit of the wastewater treatment which microorganisms convert the waste to carbon dioxide and water while consuming oxygen. The volumes of secondary sludge are lower than the relevant primary sludge because most of the heavy, fibrous or inorganic solids are removed in the original clarification tank. Secondary sludge is then mixed with primary sludge prior to dewatering and disposal.

Based on Monte et al. (2009), IPPC (2001), CANMET (2005)

1.3 The composition of pulp and paper mill sludge

The composition of solid wastes from pulp and paper mills depends on the process, type and grade of paper product, also the methods used for production of pulp, specific operating practices and type of equipment used in the main process or in wastewater treatment part can make the different compositions. Therefore, it is hard to explain their composition roughly. The following section will illustrate each kind of process.

1.3.1 Pulping

The solid waste removed from the mechanical pulping is mainly composed of bark and wood residues from debarking, washing and screening of chips, primary sludge, ash from biological sludge and energy production.

The main wastes associated with this operation, which is made up of different types of sludge, mainly fibers, containing primary sludge, and sludge from biological wastewater treatment. A chemical analysis of the primary or secondary sludge from a mechanical pulp industry is shown in Table 1-2.

Table 1-2. Composition of primary sludge and biological sludge from mechanical pulp mill (IPPC, 2001)

	Primary Sludge	Secondary Sludge
Dry solid content (%)	48	32
VS (% DS)	33	48
TOC (%)	19	23
Lead (mg/kg DS)	42	22
Cadmium (mg/kg DS)	< 0.7	< 0.7
Chromium (mg/kg DS)	24	17
Copper (mg/kg DS)	238	71
Nickel (mg/kg DS)	6	8
Mercury (mg/kg DS)	0.1	0.09
Zinc (mg/kg DS)	141	135

VS: Volatile Sludge, DS: Dry Sludge, TOC: Total Organic Carbons

The kraft pulping process is the most common pulping process worldwide. The main solid by-products contain lime mud, green liquor sludge (dredge), recovery boiler ash, bark, ashes, grits and wastewater treatment sludge. If bark and other wood residues do not burn for energy recovery, they would stand for the main composition of the residues (Axegard and Backlund, 2002; Demir et al., 2005; Martins et al., 2007).

Green liquor, lime and sludge are mainly made of $CaCO_3$. Recovered boiler produces ash, which is mainly composed of sodium sulfate (about 85%) and a small amount of sodium carbonate (15%). Most of the recovery boilers fly ash and ESP dust come back to the chemical cycle. About 5 kg / ton of these residues are removed to control the sulfur balance. Bark ash is mainly composed of CaO / CaCO3 and potassium salts. Grits is mainly composed of CaCO3.

During the kraft pulping process, green liquor sludge, dredger and lime mud are often mixed and constitute the largest part of the entire solid waste. The composition of this mixed waste varies widely, including different amounts of metals such as barium, chromium, copper, lead, nickel or zinc.

The sulfite pulping production is associated with the production of different types of manufacturing-specific wastes, the most of which can be further used. Waste is produced at different stages of the production process, such as debarking, chipping, screening and cooking liquor clarification operations, in the maintenance of the equipment, as well as in the treatment of fresh water and wastewater.

1.3.2 Papermaking using virgin fiber

Compared with recycled paper production and pulp production, the waste produced by paper mills producing paper from virgin pulp is quite small. Waste from paper production consists of rejects (from stock preparation), and sludge from water treatment. These rejects usually cause the effluent treatment (IPPC, 2001), but they may directly lead to sludge dewatering as well. Most of the solids will eventually be in the primary sludge.

Sludge from fresh water and wastewater treatment is the main source of waste in many mills. Different types of sludge are:

- Sludge from chemical pre-treatment of surface water to obtain process water by means of chemical precipitation/flocculation. This residue is only produced in mills that use surface water with low quality. In this case, the amount of sludge may be significant.

- Most of the mills produced sludge from primary clarification. It consists mainly of fiber, fines and inorganic materials in mills that use fillers in their products.

- Biological treated sludge contains a high percentage of organic matter. This sludge and the sludge from the primary clarification stand for the amount of the wastes when using virgin fibers.

- Sludge from chemical flocculation is produced in mills with tertiary effluent treatment. This treatment produces a lot of sludge. The amount of organic / inorganic material in the sludge varies from mill to mill, depending on the dosage and type of flocculants used.

1.3.3 Papermaking using recovered paper

The use of recycled paper as raw material brings some economic and environmental advantages, although many cleaning processes are needed to remove contaminants that this feedstock introduces into the papermaking process (Blanco et al., 2004). Most of the impurities in the recycled paper will eventually become waste. When the paper mill has an on-site waste incineration system, the main wastes are rejects, different types of sludge and ashes. According to the level of raw materials, process design, manufactured product and wastewater treatment, resulting in different amounts and qualities of wastes.

The residues can be roughly divided into heavy and coarse rejects, light and fine rejects and sludge. Depending on its origin and nature, sludge may be subdivided into deinking sludge, primary sludge and secondary sludge.

Rejects are impurities present in the recycled paper, consisting essentially of fibers, staples, metals from ring binders, sand, glass and plastic, representing about 6.5% of the purchased paper. In the earliest stages in the preparation section, rejects are removed as much as possible.

In general, the paper sludge contains very high levels of dry solids because it is rich in fiber, so dewatering is easy. All pulp and paper sludge is a mixture of cellulosic fibers (40-60%

dry solids), printing inks and mineral components (40-60% dry solids: kaolin, talc and calcium carbonate). Paper sludge is mainly carbon (about 30% C dry solids) and minerals (clay and calcium carbonate, 5-25% dry solids) with a high C/N ratio (50 to 200). It has low levels of constituent to be considered as fertilizing elements and low metal content (European Commission, 2001).

Deinking sludge mainly contains fines, fillers, coatings, ink particles, extractive material and deinking additives. In general, their pollutant emissions are comparable and loads as biological sludge with lower values of BOD. The contaminant content of recycled paper has a considerable change, and, consequently, in deinking sludge (IPPC, 2001).

From the white water and physical wastewater treatment process, the process of fiber recovery produces clear water sludge. It includes the main fine and the filler (two about 50%), however the proportions of main fine and filler depend on the recycled paper being processed. Typical composition of sludge is given in Table 1-3.

Table 1-3. Composition of the sludge from process water clarification (IPPC, 2001)

Component	Process water clarification
Dry solid content (%)	29-53
Volatile solids (% DS)	26-76
Lead (mg/kg DS)	10-210
Cadmium (mg/kg DS)	0.01-0.98
Chromium (mg/kg DS)	9-903
Copper (mg/kg DS)	20-195
Nickel (mg/kg DS)	<10-31
Mercury (mg/kg DS)	0.1-0.9
Zinc (mg/kg DS)	34-1320
Chlorophenols (µg/DS)	------
PCBs (µg/DS)	-------

Paper mill waste, no matter primary, biological or deinking origin, is heterogeneous in nature from viscous pastes to a solid material. Depending on the degree of dehydration, the dry solids content of the residue may vary from 20% to 60%. Therefore, the waste must be handled, usually mixed and treated (thickened and dehydrated), in order to obtain a residue with a high dry solid content.

To sum up, paper mill sludge tends to be highly fibrous. Chemical pulp mill sludge has a higher content of sulfur compounds; it comes from the process chemicals (Na_2S or H_2SO_3 and bisulphite ions, HSO^{3-}) specific to chemical pulping. Bleached pulp mill sludge may contain high concentrations of chlorinated organic compounds; it comes from bleaching agents (Cl_2, ClO_2 or NaOCl). Deinking plant sludge has high ash content, because of high inorganic filler content in the recycled paper. In terms of residual moisture content before treatment, bark and other abrasive scraps are easy to dehydrate and have a high solids content, which makes them suitable for large amounts of combustion in bark boilers. Deinking sludge also has low moisture content because a large part of the ash and reject materials in the flotation unit foams. As the higher concentration of biological solids and the hydrous material of latter, the sludge from the primary clarifier is easier to dewater than those of secondary clarifier.

1.4 Challenges of PPMS treatment, objective of studies and outline of this thesis

The production of Pulp and Paper is associated with the generation of large quantities of wastewater that has to be purified to avoid severe pollution of the environment. Wastewater purification in pulp and paper mills uses sedimentation, biological treatment, chemical precipitation, flotation and anaerobic treatment, and the specific combination of techniques is determined by the local conditions. Wastewater treatment generates large volumes of organic solid waste (primary and secondary sludge) that after dewatering can be incinerated and thus used for bio-energy production. Sludge is currently viewed as biofuel of poor quality due to its high water content, and some mills treat it solely as a disposal problem. Few traditional strategies have been identified as feasible options, such as landfill, land use, incineration or making building material, however, the limitations of these strategies are existing, land fill and land use are associated with secondary pollution and space limitation and incineration will leave toxic metals in residue ashes, it also will cause air pollution. Recently, anaerobic digestion of the wet sludge to produce methane as a novel option to solve the problem of sludge management, as the low operating cost, simple facilities and product can be used as fertilizer, fodder or raw materials of composting, anaerobic digestion has been researched widely, but anaerobic digestion of pulp and paper mill sludge (PPMS) has the limitations of a large reactor size, poor quality of effluent.

The overall objective of this study is to explore the performance of SAnMBR for pulp and paper sludge (PPMS) treatment with or without Alkali pretreatment, this includes efficient processing of sludge, effluent quality and energy recovery from sludge.

Specific objectives include:

1. To study the feasibility of using a mesophilic SAnMBR for PPMS treatment.
2. To investigate whether processing the anaerobic digestion in membrane bioreactor (decoupling HRT from SRT) can overcome the limitations (HRT=SRT) of conventional anaerobic digestion process.
3. To explore and evaluate the effect of different HRTs for the treatment of PPMS in SAnMBR.
4. To investigate whether it is an advantage to pretreat PPMS with alkali, which can improve methane productivity.
5. Study membrane fouling phenomena in SAnMBR for PPMS treatment

Chapter 1 summarizes the rational and objectives of the present study. A literature review of current treatment technologies for PPMS treatment has been conducted in the Chapter 2. In the third chapter of this thesis, setup of this experiment and methodologies are presented, then the fourth chapter will show results and discussion, which can prove the feasibility of this study for sludge management. The final Chapter 5 will summarize the findings from the present study and outlines the suggested future studies.

2. Literature review

The literature review will focus on the current practice and technologies for PPMS treatment and utilization; the gaps, challenges and opportunities of PPMS treatment for bioenergy and value-added products.

2.1 Traditional methods for PPMS treatment

Landfill disposal is the most common solution for pulp and paper mill sludge, some countries such as Germany, Spain and the Netherlands, waste streams cannot transport to landfill sites. Besides, the issues relating to the landfilling of the sludge and other wastes that are large volumes and hazardous substances, leaking into the environment, space limitation and increased taxes have lead to landfill disposal being gradually reduced.

The incineration of rejects and sludge generated power and steam, which is one of the most popular applied disposal methods currently. This technology can be applied to almost all types of sludge and its main achievement is decreasing 80-90% amount of sludge, which will be treated by landfill. After incineration, the left ashes can be applied depending on the different ash qualities. In some cases ash is directly landfilled, in others it can be used by the construction industry or added value applications. However, for incineration, the sludge firstly requires dehydration as the sludge contains various microorganisms, bacteria and dead viruses, while secondary sludge exists as a stable colloidal, so dehydration is very difficult and will consume large amounts of energy (Beauchamp CJ, 2002).

The composting solution through the action of microorganisms with lesser carbon loss, the waste or sludge sits until most of the paper fibers and organic materials have been stabilized. In order to increase the nutrient content, sometimes the fertilizer is added to the waste or sludge. This solution produces a humus-like substance that can be used for domestic plants and green houses. The composting is one of the most economical disposal methods, but large land demand in order to disperse the sludge will cause other additional costs (Jokela et al., 1997; Hackett et al., 1999; Christmas, 2002; Gea et al., 2005). In addition, composting sludge also takes up enormous amounts of space, and bulky organic matter in sludge can easily decay and release odor, its chemical constituents and heavy metals easily penetrate soil and water, which might result in secondary pollution. Thus, the above problems limit the generalized use of these methods.

2.2 Current sludge management

According to the current technical conditions, although the effluent standards of pulp and paper mill can be achieved, but now the problems are that the treatment of pulp and paper sludge will cause a series of issues, such as secondary pollution, energy consumption and storage space, whether to use landfill, incineration or compositing them. As reported by statistics, the treatment of wastewater and sludge costs more than 50% of totally waste material treatment fees in pulp and paper mill. However, if the properties of pulp and paper mill sludge can be changed, and consider as a resource then these problems will be resolved. Therefore, the resource utilization of paper mill sludge disposal will be future research direction. The literature review will summarize the recent researching progress on resource utilization of paper mill sludge worldwide.

2.2.1 Activated Carbon

Traditionally, activated carbon is produced from wood, peat, coal and wastes of vegetable origin (like nutshells, and fruit stones). Today, a promising way for production of cheap and efficient activated carbon is the recovering of waste sludge, such as solid waste from municipal or industrial wastewater treatment. As mass production and increasing space limitation for landfill, the reuse of waste sludge is becoming extremely important, recent studies showed that sludge from municipal wastewater treatment could be used for production of activated carbon (Walhof LK, 1998). The study built a procedure that successfully converted biological sludge to activated carbons with a surface area of 600-1000 m^2/g from two municipal wastewater treatment facilities and it also found that is possible to produce activated carbon from pulp and paper mill sludge, but failed due to the process of optimize the carbon production for this kind of sludge.

However, after constant attempts, the previous study has successfully developed a process where pulp and paper mill sludge can produce activated carbon (Nasrin R, 2000). The process involves drying pulp and paper mill sludge in an oven at 110 ℃ for 24 h and then crushing them to provide smaller particles with increased surface area and more efficient chemical activation of the sludge. After it has been crushed, it is mixed with Zinc, Zinc unites with degraded cellulose to form a porous structure, Zinc also can be used as a desiccant to promote decomposition of carbon-containing materials. Through above-mentioned treatment, the porous materials also have to be treated by UV-light and vapor, after surface oxidation, then through thermal decomposition (800 °C) to get the final product. This new technology can transform the waste into useful products, and compared to the traditional production method of activated carbon, it has significant environmental and economic benefits. For the activated carbon, increasing the amounts of ZnCI used for chemical activation resulted in a 600% increase in the mesopore volume.

2.2.2 Utilization in the cement and brick industry or other building material

In the cement industry, the material and energy content of paper residues can be recycled. For the cement industry, sludge from primary clarifier (or mixed with treated biological sludge) is particularly applicable (Ahmadi &Al-khaja, 2001; Cernec et al, 2005). However, its applicability depends on the amount and type of inorganic compounds present in the residues. Drying the sludge (about 50% moisture content) with the waste heat from the cement kiln pre-dryer can save energy, so that no extra heat is needed to reduce the moisture content of the sludge from 50% to 10-15%. Therefore, when the dry sludge is burned in the cement rotary kiln, the calorific value of the organic substance with high carbon content is used, and the residue of ash from the sludge incineration is retained in the product. The inorganic ash substance of the incinerated sludge is also a compound of cement clinker. When paper mills and brick-cement (or brick) manufacturing industries are in the neighboring area and the latter has the ability to use the sludge in its process, this sludge treatment scheme is feasible (IPPC, 2001).

In the case of brick production, adding 5-15% paper sludge as raw material can improve the final product and the process. First, because its fiber content increases the porosity of the substrate, making lighter bricks; second, it saves fuel in the oven, reduces the firing time, and makes the product more resistant to cracking during dry and firing stages (Cernec & Zule, 2005; Cernec et al, 2005). The same advantages can be applied to the building industry for producing light aggregates (Ducman and Mirtic, 2011).

2.2.3 Fertilizers

To use pulp and paper mill sludge to produce agricultural fertilizer can be an effective way for resource utilization. The sludge contains large amounts of organic matter and nutrients for plant growth, while it is also good for improving and culturing soil. Therefore, the sludge for agriculture use is a good resource, and also can save the problems of disposal and secondary pollution. However, before the sludge can be applied to the field, it has to process high-temperature composting or digestion treatment. The sludge contains a lot of nutrients, which means it can be a great source for composting. Composting is able to increase the content of N, and it is also able to increase soil structural stability. The recycling of the sludge composting means that mud cake from sludge dewatering workshop processed biochemical reaction, and then achieving material conversion, so as to achieve reduction, stabilization, detoxification and recycling of excess sludge.

Composting of pulp and paper mill sludge mixed with NPK (Nitrogen, Phosphorous, and Potash (Potassium)) fertilizer can be made into organic compound fertilizer. When examining corn potting with two kinds of fertilizers under the same rate of nutrients condition, the fertilizer efficiency of mixed organic fertilizer is better than single NPK fertilizers. Furthermore, the increasing rate of maize dry weight is more than 30%, and it also improves the quality of fertilizers, further advancing the efficiency of the mixed organic fertilizer. After the harvesting of corn potting, the soil (applied sludge organic fertilizer) still has high effective nutrient content. This demonstrates that composting of the sludge has good fertilizer conservation as carriers of fertilizer, besides, the efficiency of sludge organic fertilizer is long-lasting, which is conducive to the sustainable development of agriculture. Previous research showed that the composting of pulp and paper mill sludge as fertilizers would increase the content of Mg, K, Ca, and Na in soybeans (YX Kui, 2005).

The result of spectral analysis showed that the main components of pulp and paper mill sludge are lipid, alcohol, lignin, carbohydrate, and N-Containing compounds (Pabio S, 2000). After composting 17 days, the contents of C and N are reduced, but the content ratios of C and N remain the same. After composting, the content of lignin and carbohydrate are increased, lipid and alcohol are increased as well. The carbon nitride compound turns into a more stable and complex organic compound through various bacterial actions.

The study showed that nutrition and temperature are the key parameters for composting of pulp and paper mill sludge (Markjacksm, 1997). To add nutrients (N, P, K) before composting will result in the loss of nutrients and soil pollution, so in order to reduce the loss of nutrients, the nutrients should be added during the composting process. Temperature can affect the metabolism of the bacteria. The release amount of CO_2 and the uptake of O_2 under 55 °C are more than when it is under 35°C, while the temperature also reduces composting time from 35 days to 30 days. In addition, moisture content, organic content, pH value, and microbes also have an important influence on the composting of pulp and paper mill sludge.

The research showed that pulp and paper deinking sludge has high content ratios of C and N, which can limit the process of composting. The content ratios of C and N are main factors for the maintenance and proliferation of microbial cell, the content ratio of C and N in microorganisms (bacteria) is about 1: 5-10. If the ratio is about 5:6, the content of C will increase, the proliferation of microorganisms will be constrained due to the lack of N, thus slowing the decomposition of organic matter (M-H Charest, 2002).

In order for sludge to be used for composting in agriculture, it has to be treated (like heat drying, bio-compost, or chemical stabilization). Though the fabrication technique of pulp and paper mill is often enhanced, the structure of the sludge remains the same, so it can be used for composting (Nemati R, 2000). On the contrary, some scholars believed that the composting of pulp and paper mill sludge will not have any positive effect on improving the physical properties of the soil, as the sludge will increase released amounts of N_2O which is one of the greenhouse gases (B. Ahmadi, 2001).

2.2.4 Application in composite materials

The PPMS contained short plant fiber and inorganic substance that can enhance the performance of composite material, but their compatibility of hydrophilic group with plastic or resin is poor. Therefore, coupling agent or other promoters are usually added first, which can be used as a modification to improve the compatibility between PPMS and resin matrix, so as to enhance various property of composites material.

The research studied effects of particle size and extrusion temperature of PPMS on the dimensional stability, tensile, bending strength and impact strength of PPMS-thermoplastic resin matrix (PP, PE) while it also studied effects of sludge ratio, the types and concentration of coupling agent on mechanical property of PPMS-thermoplastic composites (PP, HIPP, HDPE, LDPE). The results showed that: with the increase in PPMS content, its density was increased, and melting index was decreased, the dimensional stability was improved slightly, the tensile and flexural modulus were increased, and the tensile and flexural strength of the material were improved obviously after adding coupling agent G-3003tm for modification (Jungil S, 2004).

Another research also studied the application of PPMS as filler or reinforcing agent in application of polypropylene (PP) composites, and the results showed that if the tensile properties were emphasized that PPMS could be used as filler, if the flexural properties were emphasized that PPMS could be used as reinforcing material (J Girones, 2007).

Due to the fact that PPMS contains parts of short plant fiber; it can be used in the production of Wood-based panel, which can not only widen the source of raw materials, but also alleviate the pressure of wood raw materials. Many studies on the production of PPMS-fiberboard have pointed out that the property of board is usually poor and also cannot reach the application requirement, if the PPMS was used as raw material of the production completely.

However, to use PPMS to replace parts of wood raw materials to produce Wood-based panel, the properties of the board can meet the requirements.

The research used MDI and UF respectively as tackiness agent, while using the sludge (produced by chemical pulp) and wood particulate as raw materials to prepare particle board, the results showed that: when the amount of the sludge is increased, the mechanical properties of the board is decreased (Asghar T, 2007). In addition, mechanical properties, water resistance and thickness swelling of particleboard (produced by UF tackiness agent) are better than the board (produced by MDI). However, when the sludge was added up to 10% and UF tackiness agent was applied at 12%, the production of the board can meet EN, ASTM D1073-99 (Performance evaluation method of wood fibreboard and particleboard).

S Migneault (2009) also tried to prepare PPMS-fiberboard without any adhesive, and the sludge was produced by mechanical pulping (TMP), mechanical-chemical pulping (CTMP) and sulfate pulping (KP), and PS: SS is 9:1, 8:2, 7:3 respectively. When the ratio of PS and SS in CTMP pulping sludge is 7:3, the performance of the plate can meet the requirements of hard plate. The physical and mechanical properties of fiberboard produced by CTMP pulping sludge were the best, the TMP was the second and the KP was the worst.

2.2.5 Lactic Acid

Due to the high content and sensitivity (for biological treatment) of carbohydrate in pulp and paper primary sludge, the carbohydrate can be invert into lactic acid as raw materials (S Marques, 2008). The conversion process consists of enzymatic glycosylation (Enzymatic Saccharification) of carbohydrates (cellulose and hemicellulose) and fermentation of Lactobacillus. At present, due to the dosages of lactic acid in the production of biodegradable polylactic acid are increased, thus people are becoming more interested in lactic acid. As polylactic acid break down naturally when it exposed in air, it is widely used in the production of disposable items and food packaging. Previous studies showed that pulp and paper primary sludge contains more than 60% carbohydrates (45% glucose, 10% xylose, mannose, arabinose), 20% lignin and 10% ash, the primary sludge (without any pretreatment) can be digested up to 70% by enzymic (S Marques, 2008).

Saccharification and fermentation are processing together, the carbohydrate is transformed into glucose first, and then transformed into lactic acid. When using cellulose and lactobacillus to process a variety of experiments under the different temperature, pH and nutrient concentrations, the conversion rate of lactic acid is over 90%, but only a small amount of acetic acid are produced. The xylose (main saccharides of hemicellulose) also can be transformed into lactic acid like glucose, however, different lactobacilli have different conversion effects.

2.2.6 Livestock bedding materials

As deinking paper sludge (DPS) has great water absorption capacity of approximately 250% (humid basis) to 700% (dry basis) (similar with absorption capacity of dry newspaper), some farmers are interested in using DPS as bedding material. The study used DPS to spread out barn, after 7-week experiment, the growth of animals was not affected by the DPS bedding, while compared with sawdust for detecting the content of Al, Cu and phenolic in pigs. Al and Cu are detected in the blood and bones; phenols are detected in the fat, meat, liver, and blood. The results showed that the sludge does not increase the content of Al, Cu and phenolic in pigs. The behavior and health of the pig is also similar to using sawdust. Therefore, using DPS as bedding material provides an alternative source of paper sludge treatment and animal manure (C.J.Beauchamp, 2002).

2.2.7 Anaerobic digestion

2.2.7.1 Principles of anaerobic digestion

Anaerobic digestion is a series of biological processes in which microorganisms break down biodegradable material in the absence of oxygen, for anaerobic digestion of organic material basically follows: hydrolysis, acidogenesis, acetogenesis and methanogenesis (shown in figure 2-1) (Gerardi MH, 2003; Deublein D etal., 2008; Reynolds TD, 1995).

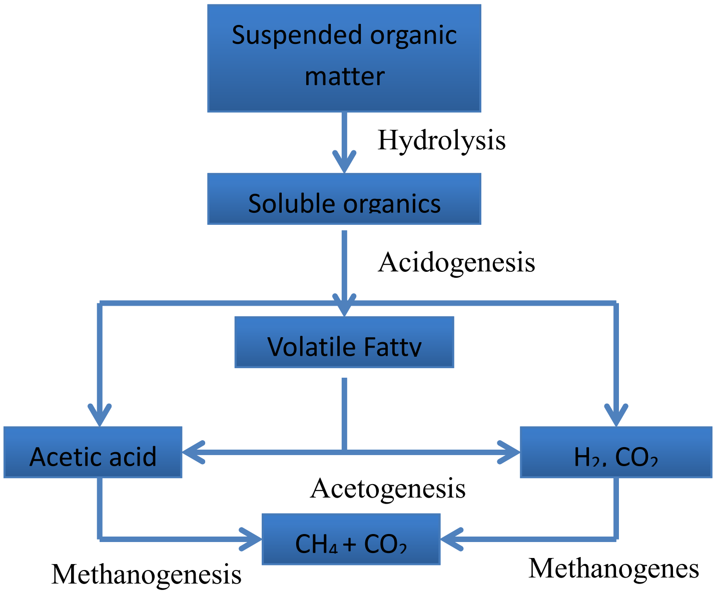

Figure 2-1. Subsequent steps in the anaerobic digestion process

AD is a complex process that requires the absence of oxygen (oxidation reduction potential (ORP) < −200 mV) and relies on several types of microorganisms to convert organic matter into CO_2 and methane (CH_4). Despite the continuous steps, hydrolysis is usually considered as rate limiting (David P, 1996).

Insoluble organic and high molecular weight compounds (such as lipids, polysaccharides, proteins and nucleic acids) are degraded into soluble organic matters (like amino acids and fatty acids). The components formed in the hydrolysis process are further separated in acidogenesis, the second step. The acidogenic bacteria produced VFA along with CO_2, H_2S, ammonia (NH_3) and other by-products.

The third stage of AD is acetogenesis, where acidogenesis produced higher organic acids and alcohols, which are further digested by acetogens to produce the mostly acetic acid, CO_2 and H_2. This conversion is controlled to a large extent by the partial pressure of H_2 in the mixture.

The final stage is methanogenesis, where acetates are converted into methane and carbon dioxide, while methanogenic bacteria consumed hydrogen (organisms capable of producing methane have been identified only from the Archaea).

The hydrolysis and acidification are more robust than acetogenesis and methanogenesis during anaerobic digestion. Due to the complex metabolic pathways of the anaerobic process, the symbiotic relationship of all these microorganisms is crucial to achieve process stability. If the balance is disturbed between acid forming and methane-forming microorganisms, it will result in reactor instability. Each group has their own sensitivity to environmental conditions, different physiologies and nutritional requirements. For example, methanogens need a proper pH range, usually between 6.8-7.2, and a more acid pH is better for acid forming microorganisms (Rajeshwari et al., 2000). It's necessary to adjust the pH value to create a proper acidic/basic environment to protect biological metabolism, and also inorganic fouling induced can be prevented, which are caused by mineral precipitation to some extent.

Anaerobic digestion has been widely used in wastewater treatment, such as various industries, agriculture and municipality. It has the potential to reduce the economic and environmental pressure at the same time, pulp and paper mill has gained increasing attention since late 1980s, and the reactors of anaerobic for pulp and paper mill are only treating selected in-mill stream, like paper mill effluents and evaporator condensates from chemical pulping, beyond which many other effluents are excluded. Compared to the application of mill wastewater treatment in the field of anaerobic digestion, the anaerobic digestion of pulp and paper mill sludge is still uncommon due to some limitations. (1) The organic fraction can be only decomposed partly. (2) The reaction is rather slow and large volumes and high costs of the anaerobic tanks. (3) The rather poor treated effluents produced. (4) HRT and SRT cannot be controlled respectively. (5) Due to the fact that organic fraction significant reduced during digestion, which left the mineral and non-degradable fraction untouched, the concentration of heavy metals and various industrial organics increased in the residual sludge.

2.2.7.2 Anaerobic digestion of pulp and paper mill sludge

In order to effectively improve the utilization value of PPMS, the stages of acetogenesis and methanogenesis are gaining increasing attention. The acetogenesis process can usually produce amounts of VFA (volatile organic acid) (WU Feng et al., 2010), and these VFA can be a good resource for methane production. In addition, the substrates in PPMS used for producing hydrogen are much smaller than the substrates for acid production; in other words, the hydrogen production is far less than methane production. Therefore, methane production is one of important evaluation for judging the performance of anaerobic digestion.

After anaerobic digestion, specific methane yields are usually between 30-200 mL/(g VS), and the volatile solids removal rate was 21%-55% (Park N D et al., 2012). VS can represent the concentration of organic matter much closer than COD, because the volatile solids have amounts of bound water, after dried at 104℃, it can be totally disappeared in high-temperature combustion (500-550℃). It is not clear whether the different kinds of sludge from different pulp and paper mills can influence efficiency of anaerobic digestion or not. Karlsson et al (2011) used a CSTR (continuous stirring tank reactor) to conduct anaerobic digestion under 37 ℃ for 20 days in sulfate pulp mill and TMP pulp mill. During the experiment, the organic content of sludge from each mill was 2-4 (g VS)/L, the VS removal rate of two kinds of sludge both reached at 40%, and the average methane yield of sludge from sulfate pulp mill was 120 mL/(g VS), and the methane production in TMP pulp mill was 180 mL/(g VS).

Bayr and Rintala (2012) used CSTR to digest primary sludge and a mixture of primary and bio-sludge generated in pulp and paper mills. Thermophilic anaerobic digestion of sole primary sludge resulted in higher methane yields (190-240 ml g VS fed) than that of the mixture (150-170 ml g VS fed), and it was feasible at HRTs of 16-30 days. Therefore, in that study, sole primary sludge is better than the mixture for producing methane, while experimental results indicate that cellulose and hemicellulose can be degraded during the process of anaerobic digestion, but lignin cannot be degraded. However, Mehdizadeh et al (2012) obtained another result from the anaerobic digestion of BCTMP pulp sludge, and the result showed that the methane yield of sole activated sludge is better than primary sludge.

Besides, some pretreatment methods of PPMS before anaerobic digestion are designed in order to improve methane production, which can increase accessibility and degradation of organic components in PPMS. The pretreatment can destroy the aggregation between cells, while can also destroy the cell walls, so as to ruin cell structure. Thereafter, the following hydrolysis will become much easier. Numerous pretreatment methods of PPMS have been investigated so far, they can roughly divided into mechanical pretreatment, thermal pretreatment, chemical pretreatment, bio-pretreatment and combined pretreatment.

Mechanical pretreatment was designed for breaking the cell membrane of microorganisms, so as to release the organic matter and increased the substrate concentration. The mechanical pretreatment mainly included high-pressure jet and ultrasonic method.

There were various operation modes that associated with the high-pressure jet, such as injection of high-pressure jet pump, high-pressure homogenization. Elliot A et al (2012) used a continuously anaerobic reactor to digest activated sludge in mechanical pulp mills. The sludge pretreated with high pressure homogenization after only 3 days, the methane production was as high as 20 days without pretreatment. Similarly, with high-pressure homogenization, Saha M et al (2011) observed an improvement in methane yield by 80% after digested 20 days.

A study conducted mesophilic anaerobic digestion of PPMS with ultrasonic pretreatment, the result shown that methane production increased by 40% to 80% in BCTMP pulp mills with 21 days. Wood N (2009) digested activated sludge in sulfite pulp mills with 34 days (≤55°C), and compared to untreated sludge, the results showed that ultrasonic pretreatment can reduce the time of the digestion, but the methane production was not increased, while the length of time of ultrasonic pretreatment did not have a significant impact on methane yield and sludge solubility.

Thermal treatment has been applied in pretreatment of PPMS. Wood N (2009) studied anaerobic digestion of activated sludge in sulfite pulp mill and kraft pulp mill by using three different pretreatments included thermal, caustic, and sonication. The results shown that thermal pretreatment was most efficient, Compared to untreated mill sludge, the methane production increased by 55% in sulfite pulp mill and 280% in kraft pulp mill after thermal pretreatment at 170 ℃. In another study, after thermal pretreatment at 150℃, the methane yield of pulp and paper mill activated sludge increased by 45% (Panter K et al., 2005). A Norwegian pulp mill digested activated sludge by anaerobic digestion with thermal pretreatment (30-60 min) and the temperature was 160-170℃, after 5-10 days, the VS removal rate can be reached at 60% and about 4000 tones of the sludge can be treated per year (Gordon D S, 2011).

Due to the high temperature effect of microwave treatment, the microwave pretreatment also can be considered as one of thermal pretreatments. Mehdizadeh S N et al., (2012) applied microwave pretreatment in activated sludge and mixed sludge (primary and secondary sludge) before anaerobic digestion in BCTMO pulp mill. (Heating rate: 1.35-4.47℃/min, pretreatment temperature range: 50-175℃). The results showed that if the heating temperatures microwave under 125 ℃, sludge solubility increased by increased temperature, while methane production also increased, when the temperature was higher than 125 ℃, methane production no longer increased by increased temperature. After microwave pretreatment, the sludge was treated at 35℃ (43 days), the methane yield can be reached at 290 ml/(g VS). Compared to untreated sludge, the yield increased by (63±3.2%).

Chemical pretreatment mainly consists of caustic and acid treatments. As the most general chemical pretreatment, caustic pretreatment can enhance the VS concentration, degradation of COD and methane yield, while it can also reduce the period of anaerobic digestion for PPMS. Lin et al (2008) conducted a mesophilic anaerobic digestion of PPMS by using different NaOH concentration to pretreat PPMS, after 42 days, the biogas yield was increased by 54-88%, compared to the untreated sludge, when the concentration of NaOH was

8g/ 100g TS, the biogas yield was highest, exorbitant Na^+ concentration can prevent metabolism of methane bacteria, so as to prevent the increase of methane yield. Acid pretreatment can also enhance the solubility of sludge. When pH of acid sludge pretreatment was at 2, the solubility of PPMS can be increased, but the increased sludge solubility did not mean that the methane yield could be increased as well (Devlin D C, 2011).

The experience from enzyme pretreatment of biosludge in municipal wastewater treatment mills have shown notable improvements in anaerobic digestibility (Parawira, 2012 and refstherein), whereas it was not very successful in pulp and paper mill sludge. In the study by Karlsson et al. (2011), a mixture of various hydrolases at a concentration of 40 mg/g TS were added to pulp and paper mill activated sludge, which resulted in an increase in methane yield by 35%. However, PPMS processed the digestion in a semi-continuously reactor at enzyme concentrations of up to 80 mg/g TS, the methane yield did not improve, the reason may be caused by an unfavorable sludge viscosity. However, the development of enzymatic sludge was limited by high production costs and low activities of enzymes in the past, now more enzymes are being discovered and production costs are dropping, and these factors may result in upswing in this field.

Due to the complex components of PPMS, more and more researchers have begun to combine two or more kinds of pretreatment for PPMS pretreatment. Park N D et al (2012) combined thermal and ultrasonic pretreatment for PPMS treatment, and the results shown that soluble COD, VS, TS increased 3-14 times, but the pretreatment only reduced the period of anaerobic digestion, not the methane production. Bayr S et al (2013) studied the effects of 12 different pretreatment methods (single or combined methods) on methane yield of pulp and paper mill activated sludge, which included thermal, enzyme, ultrasonic and chemical pretreatment.

Enzyme-ultrasonic pretreatment was found to be most effective pretreatment with a 31% increase in methane yield, compared to untreated mill sludge (108 mL/(g VS)- 141 mL/(g VS)). Wood N (2009) studied the performance of thermal, thermochemical (caustic) and ultrasonic pretreatment for activated sludge treatment in kraft pulp mill. The results shown that thermal pretreatment had the most significant influence on biodegradability, after the pretreatment, the methane yield increased by 50%, the production rate increased 10 times. According to the percentage of soluble COD and VS removal rate (after anaerobic digestion), the effect of ultrasonic treatment was inferior to thermal and chemical treatment. For the pretreatment of sulfate pulp mill sludge, the effects of thermal and caustic pretreatment were roughly equal. For kraft pulp mill sludge, the soluble COD in sludge (after caustic pretreatment) was higher than thermal pretreatment, but the VS removal rate had little different. In another study by Saha M et al (2011), compared to ultrasonic and chemical-mechanical pretreatment, the increase of methane production was biggest after microwave pretreatment, ultrasonic was second, and the increase of production was lowest among these three pretreatments after chemical-mechanical pretreatment. However, through comparing, thermal and thermochemical were more effective pretreatments and had a wide studying foreground, because the thermal energy can be directly gained through the production process of pulp and paper. Table 2.1 summarized the results of previous studies on anaerobic digestion of pulp and paper mill sludge.

Table 2.1- Results from previous experimental studies on anaerobic digestion of PPMS (Modified from Torsten M ta al., 2014)

Type of pretreatment	COD concentration g/l	TS %	VS %	VS loading rate [kg VS m^{-3} day^{-1}]	Detention Time [days]	Type of sludge	VS (or VSS, COD) removal %	Specific methane yield [ml g^{-1} VS fed]	Experimental setup
Hydrothermal (170℃, 1h)	12	0.9	0.7	Batch	34	Sulfite pulp mill WAS	65 (VSS)	185 (ml g^{-1} COD fed)	BMP assay
Hydrothermal (170℃, 1h)	27	1.8	1.4	Batch	34	Kraft pulp mill WAS	31 (VSS)	115 (ml g^{-1} COD fed)	BMP assay
Hydrothermal (150℃, 10 min)	1 (soluble COD)	4.7	3.9	Batch	20-23	Pulp and paper mill WAS	n.a.1	97	BMP assay (thermophilic)
Untreated control	12	0.9	0.7	Batch	34	Sulfite pulp mill WAS	n.a.	120 (ml g^{-1} COD fed)	BMP assay
Untreated control	27	1.8	1.4	Batch	34	Kraft pulp mill WAS	n.a.	30 (ml g^{-1} COD fed)	BMP assay
Untreated control	1 (soluble COD)	4.7	3.9	Batch	20-23	Pulp and paper mill WAS	n.a.	67	BMP assay (thermophilic)

Type of pretreatment	COD concentration g/l	TS %	VS %	VS loading rate [kg VS m^{-3} day^{-1}]	Detention Time [days]	Type of sludge	VS (or VSS, COD) removal %	Specific methane yield [ml g^{-1} VS fed]	Experimental setup
Caustic (NAOH, PH 12, 140℃, 1h)	12	0.9	0.7	Batch	34	Sulfite pulp mill WAS	62 (VSS)	145 (ml g^{-1} COD fed)	BMP assay
Caustic (NAOH, PH 12, 140℃, 1h)	27	1.8	1.4	Batch	34	Kraft pulp mill WAS	28 (VSS)	110 (ml g^{-1} COD fed)	BMP assay
Caustic (NAOH, PH 12)	1 (soluble COD)	4.7	3.9	Batch	20-23	Pulp and paper mill WAS	n.a.	11	BMP assay (thermophilic)
Acid (HNO_3, PH 3)	1 (soluble COD)	4.7	3.9	Batch	20-23	Pulp and paper mill WAS	n.a.	-3	BMP assay (thermophlic)
Untreated control	N.A	31	20	Batch	40	Mixture PS and WAS from pulp and paper	21-24 (COD)	~175 (ml g^{-1} VS removed)	Bench-scale
Untreated control	12	0.9	0.7	Batch	34	Sulfite pulp mill WAS	n.a.	120 (ml g^{-1} COD fed)	BMP assay
Untreated control	27	1.8	1.4	Batch	34	Kraft pulp mill WAS	n.a.	30 (ml g^{-1} COD fed)	BMP assay

Type of pretreatment	COD concentration g/l	TS %	VS %	VS loading rate [kg VS m^{-3} day^{-1}]	Detention Time [days]	Type of sludge	VS (or VSS, COD) removal %	Specific methane yield [ml g^{-1} VS	Experimental setup
Enzymatic (mixture of Hydrolases, 40 mg/g TS)	n.a	n.a.	n.a	Batch	20	WAS from six mechanical & chemical pulp and paper mills	n.a.	178	BMP assay
Enzymatic (mixture of Accelerases, 70 mg/g TS)	1 (soluble COD)	4.7	3.9	Batch	20-23	WAS from six mechanical & chemical pulp and paper mills	n.a.	66	BMP assay
Untreated control	n.a.	n.a.	n.a.	Batch	20	WAS from six mechanical & chemical pulp and paper mills	n.a.	43-155	BMP assay
Untreated control	1 (soluble COD)	4.7	3.9	Batch	20-23	WAS from six mechanical & chemical pulp and paper mills	n.a.	67	BMP assay (thermophilic)

Type of pretreatment	COD concentration g/l	TS %	VS %	VS loading rate [kg VS m^{-3} day^{-1}]	Detention Time [days]	Type of sludge	VS (or VSS, COD) removal %	Specific methane yield [ml g^{-1} VS fed]	Experimental setup
Combined caustic (NAOH at 0.21-0.26 g/g TS) and Ultrasound (40 kHz)	30	2.5	1.9	Batch	28	WAS from BCTMP/TMP pulp mill (raw)	30	67	BMP assay
Combined caustic (NAOH at 0.21-0.26 g/g TS) and Ultrasound (40 kHz)	88	6.5	5.5	Batch	28	WAS from BCTMP/TMP pulp mill (thickened)	27	96	BMP assay
Ultrasound (30 Wh/L) + Enzymatic	n.a.	n.a.	n.a.	Batch	20	WAS from six mechanical & chemical pulp and paper mills	n.a.	196	BMP assay
Untreated control	30	2.5	1.9	Batch	28	WAS from BCTMP/TMP pulp mill (raw)	21	85	BMP assay
Untreated control	88	6.5	5.5	Batch	28	WAS from BCTMP/TMP pulp mill (thickened)	23	88	BMP assay
Untreated control	n.a.	n.a.	n.a.	Batch	20	WAS from six mechanical & chemical pulp and paper mills	n.a.	43-155	BMP assay

2.3. Anaerobic Membrane Bioreactor (AnMBR)

Membrane is defined as a barrier in order to separate two fluids. Membrane filtration process is considered as the core part of membrane bioreactor. It has been successfully used for biological processes (Liao et al. 2006). Membrane can retain all biomass in the reactor while also increased the efficiency of biological removal by rejecting soluble organic matter (Ho and Song, 2009). Moreover, the membrane process can decouple SRT from HRT, keep biomass retention at its most due to elimination of the suspended solids in permeate and can treat higher biomass concentration and higher organic loading rates (OLRs).

The types of membrane processes can be divided into microfilitration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), electrodialysis (ED), dialysis and pervaporation (PV) (Beerlange et al. 2001), but only the first four types can produce permeate. Table 2-2 presents the characteristics of different membrane processes.

Table 2-2 Characteristics of different membrane process (Melamane, 2003)

Parameters	MF	UF	NF	RO
Operating pressure (bar)	1-4	2-7	10-40	15-100
Pore size (µm)	0.1-1.5	0.01-0.05	0.001-0.01	< 0.0002
MWCO range (Dalton)	> 300000	300000-100000	200000-20000	< 500
Size-cut-off-range (µm)	0.1-20	0.005-0.1	0.001-0.01	< 0.001

In recent years, the use of membrane technology in combination with anaerobic reactors (named anaerobic membrane bioreactor (SAnMBR)) has received considerable attention. In the anaerobic process, the membrane can be used as filtration part, so that the biomass can be completely preserved in the reactor, fully decoupling the hydraulic retention time (HRT) and SRT. With the combination of membrane technologies, complete biomass retention eliminates the effects of biomass separation. Methanogenic organisms or sulfate-reducing bacteria (Vallero et al., 2005) with slow-growth rate can be retained to achieve high biogas production and sulfate reduction rates. SAnMBR also offered very low suspended solids concentrations in treated effluents, promotion of effluent quality, greatly extends and further increases system productivity (Liao et al., 2006). Biomass concentrations can be improved in the reactor, thus the size of reactors can be reduced and relatively higher organic load rates can be allowed. These are attractive for treating effluents which containing relatively high levels of organic material, and produce good quality permeates that can be reused.

AnMBR systems can be roughly divided into two types: external/side-stream AnMBR (Figure 2-2) and submerged/immersed AnMBR (Figure 2-3). For external AnMBR, the membrane modules are placed outside of the bioreactor and a pump is needed to push the bioreactor effluent into the membrane unit and permeate pass over the membrane. So far, most of the previous AnMBR studies concentrated on side-stream AnMBR. However, this type of AnMBR requires high cross-flow rate to control membrane fouling, which may lead to the damage of sludge flocs, lower sludge activity, and high energy cost, thus increasing operating cost of whole system (Hu and Stuckey, 2006). With people realized the issues, An improved external MBR has been developed, which applies gas flushing in the separated membrane tank to create shear force to scour membrane surface to alleviate the membrane fouling.

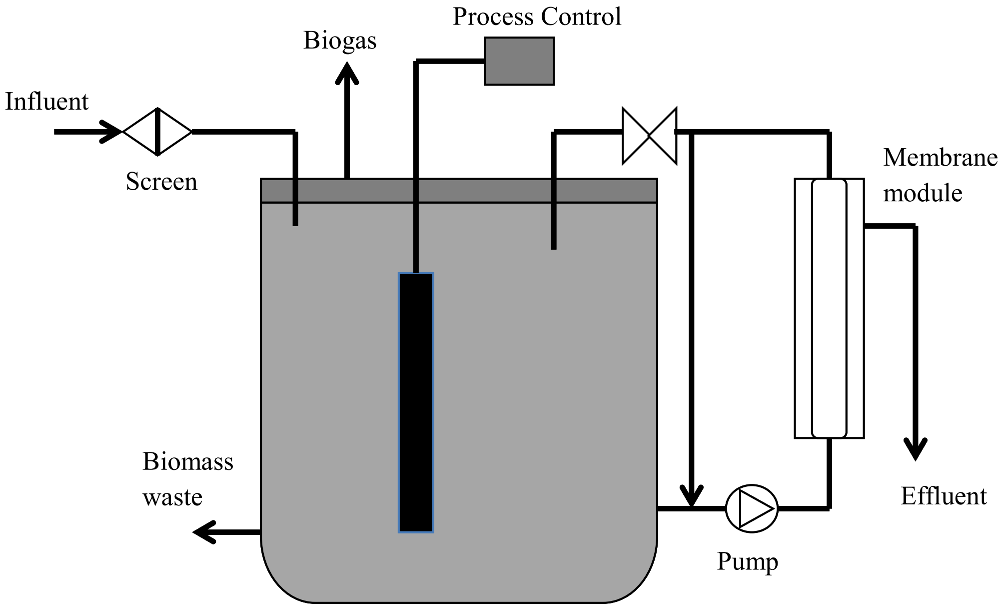

Figure 2-2 Schematic of External/side-stream SAnMBR

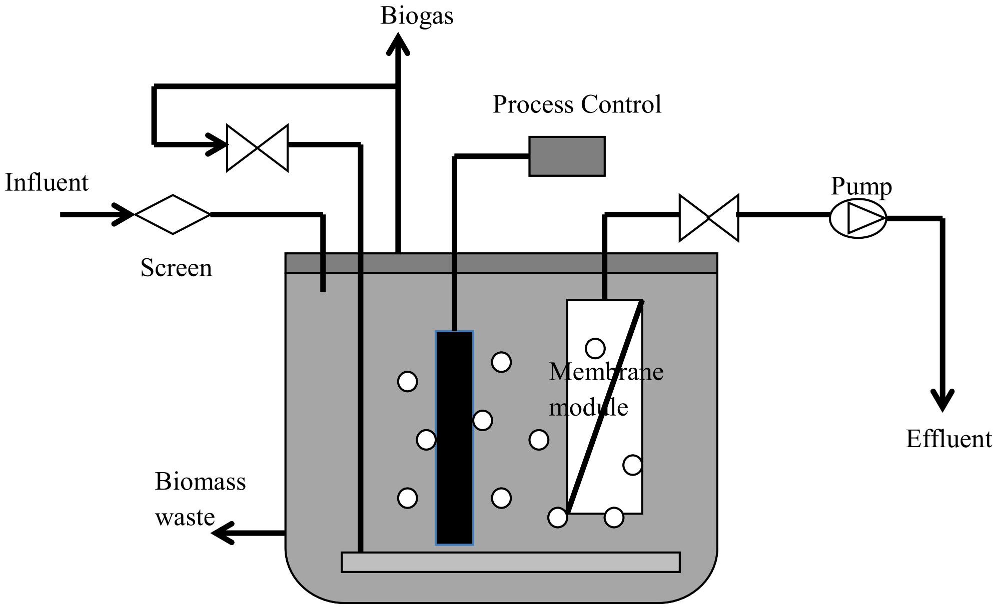

Figure 2-3. Schematic of Submerged/immersed SAnMBR

Submerged anaerobic membrane bioreactor (SAnMBR) is one interesting alternative to the conventional side-stream process, which submerged the membrane into the liquor. Also, the membrane is operated in a vacuum condition rather than direct pressure. As the lower tangential velocity, the operating conditions of SAnMBR are much milder than the conditions of external membrane systems. In fact, the energy requirements for this configuration may be two levels lower than that of the external systems (Chang et al., 2002), and the biomass pressure associated with recirculation can be reduced. In addition, the configuration of SAnMBR allows the membrane to be self-cleaning by recirculating the biogas produced (Liao et al., 2006).

3. Experimental Materials and Methods

3.1 Experimental setup and operation

3.1.1 Experimental setup

One An-MBR operated at 37 °C was used in this study (Fig.3-1). Circulating warm water offered constant temperature through the water jacket of the reactor, a flat sheet microfiltration membrane module (0.03 m^2) was submerged in the mix liquor. All membranes were made of polyvinylidene fluoride (PVDF) materials (pore size: 0.1 μm) using the phase inversion method in this study. Because of the longer durability and relatively lower fouling propensity compared to other kinds of membrane materials, PVDF membrane were applied (Yamato et al., 2006). Headspace biogas was recirculated by two sparging pumps (Masterflex L/S Precision Variable-Speed Console Drives), and the sparging loading rate was at 4 L/ min to provide mixing and to reduce the speed of the membrane fouling. A magnetic stirrer (Corning PC-611 Heavy Duty Stirrer) at the bottom of the reactor provided mixing for the sludge liquor. The pH was artificially controlled between 7.0 to 7.6 through adjust the influent pH by using 0.1 N NaOH solution.

The working volume of reactor was 6.024 L (diameter was 14.6 cm and height was 36 cm). PPMSS was pumped into the bioreactor automatically by a level sensor (Madison Co., USA) and sensor control box (Flowline, USA). Through a peristaltic pump (Masterflex C/L Variable-Speed Tubing Pump, 115/230 VAC) operated in the mode of 3-min-on and 2-min-off, the effluent can be obtained intermittently, and by adjusting the pump speed, the membrane flux can be controlled, which means that different HRTs can be achieved, in addition, so as to slow the speed of membrane fouling, which was needed by the mode of the on/off cycle. The anaerobic seed sludge was obtained from a previous study on synthetic municipal wastewater treatment using the same SAnMBR (Gu, 2016). The chemical oxygen demand (COD) of the feed was 17678 ± 3369 mg/L. During the operation of the reactor, the sludge was only removed for waste (166 ml/ per day) in order to maintain a sludge retention time of 36 days. The main operating conditions are shown in Table.3-1. However, as the membrane fouling, the HRT cannot be maintained constant for experiment demand all the time, so when the HRT was out of control, the reactor was opened and processed a physical cleaning (eg., cake layer or gel layer removal using a wet sponge).

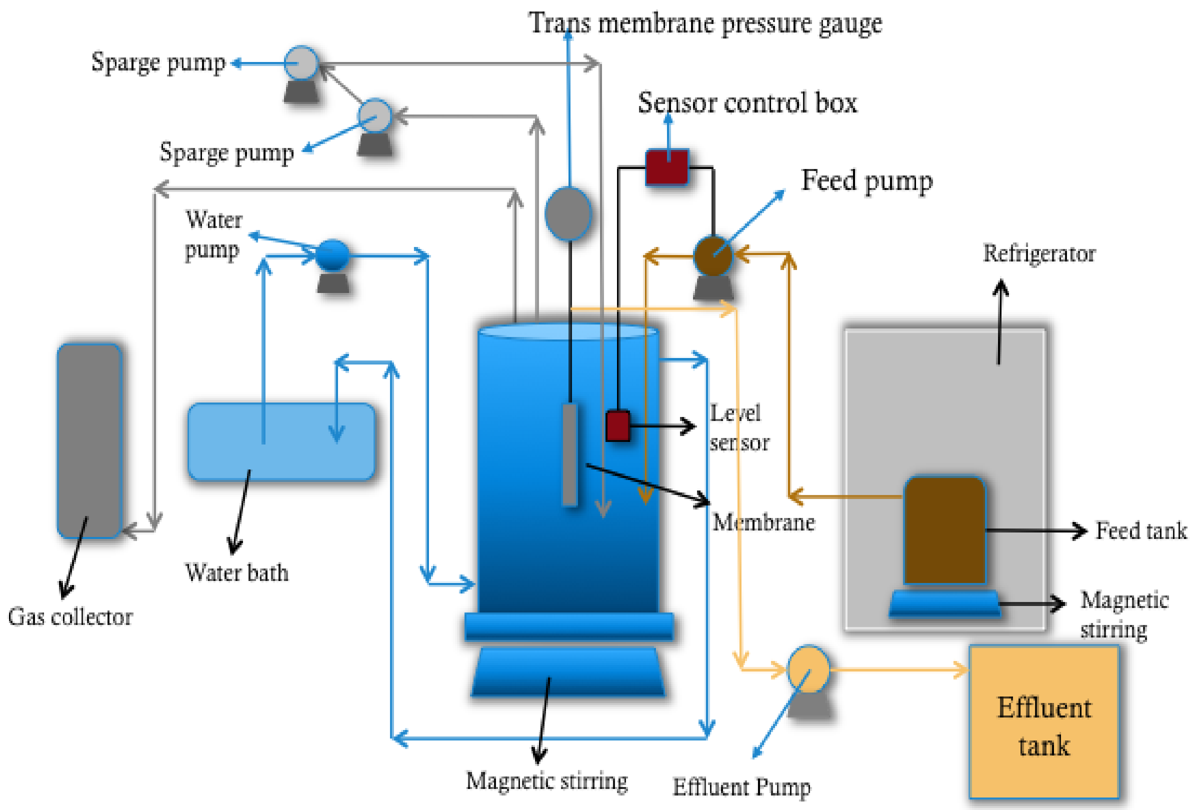

Figure. 3-1 Schematic of the submerged anaerobic membrane bioreactor and experimental setup

Table. 3-1 – Operational conditions of the experiment

	PPMSS without pretreatment		PPMSS with alkali pretreatment	
Temperature (℃)	37 (± 1)		37 (± 1)	
Working volume (L)	6.024		6.024	
pH of feed	7.0 - 7.3		7.3-7.6	
pH of reactor	6.9 -7.2		7.0 – 7.8	
Transmembrane pressure (kPa)	< 50		< 50	
Feed concentration (mg COD/L)	17766±3108	17850±131	19883±1072	12602±4550
Flux (L/m^2 h)	0.81-3.1	0.28-0.47	0.6-2.1	0.32-0.55
HRT (d)	7.5 ± 2.5	17.8 ± 1.9	8 ± 1.7	17.6 ± 1.2
SRT (d)	36		36	
Feed MLSS (g/L)	10.8 ± 1.6		12.8 ± 1.7	
Sparging Loading Rate	4 L/min		4 L/min	
Organic Loading Rate (Kg VSS/m^3 d)	1.61±0.3	0.65±0.17	1.73±0.21	0.74±0.13

3.1.2 Alkali Pretreatment

Various sludge pretreatment methods have been studied to achieve a significant result in a disintegration or lysis of sludge cell, which have the potential to improve the biogas production. Several methods (like thermal, chemical, ultrasonic, mechanical and biological) were already proved their feasibility. However, although thermal pretreatment of sludge has achieved an increase in biodegradability, compare to chemical consumption, it consumed more energy. Also, ultrasonic and enzyme pretreatment are concerned with the high cost to get the expected biodegradability rate. Previous studies have shown that alkali pretreatment was the best known method for improving the biodegradation of complex materials, and sodium hydroxide (NaOH) will usually be the first choice, because it can effective in solubilizing munitions-grade nitrocellulose into soluble organic carbon forms at relatively low dosage level (S. Tanaka, K. Kamiyama et al, 2002). From the previous studies on pretreat PPMSS, researchers have prepared to soak 0.3%, 0.6% and 1.2% sodium hydroxide solution in PPMSS, the dosages of them are 4g NaOH/ 100g TS_{sludge} , 8g NaOH/ 100g TS_{sludge} and 16g NaOH/ 100g TS_{sludge} respectively (J.G. Lin et al, 1997; Q.M. Luo et al, 2005; J.WU et al, 2006). Through estimated methane production of different dosages after retention time 42 days at 37 ℃, methane production has increased by 54%-88%,and 8g NaOH/ 100g TS_{sludge} has increased by 83% at a lower cost compared to other dosages. Therefore, in the last two phases of the present study, according to the concentration of PPMS, NaOH is dissolved into deionized water in proportion (8g NaOH/ 100g TS_{sludge}), then added to the PPMSS while stirring for 6 hours. The pretreated PPMSS is expected to be the new feed to the reactor, and the gained parameters in last two phases will be compared to the same parameters from phase 2-3, in order to explore whether alkali pretreatment can affect the performance of SAnMBR for PPMS treaement.

3.1.3 Operation of the study

The operation of the experiment can be divided into five phases: Phase 1(0 -44th day) as the start-up period with a thermomechanical pulping wastewater as influent; Phase 2 (44th – 134th day) is fed with PPMSS (no alkali pretreatment) and HRT is 7.5 ± 2.5 days; in Phase 3 (134th - 188th day) is fed with PPMSS (no alkali pretreatment) and HRT is 17.8 ± 1.9 days; in phase 4 (206th – 253rd day) is fed with PPMSS (with alkali pretreatment) and HRT is 8 ±1.7 days; in phase 5 (279th – 330th day) is fed with PPMSS (with alkali pretreatment) and HRT is 17.6 ± 1.2 days. The Fig.3-2 shows the variation of HRT with experimental operation.

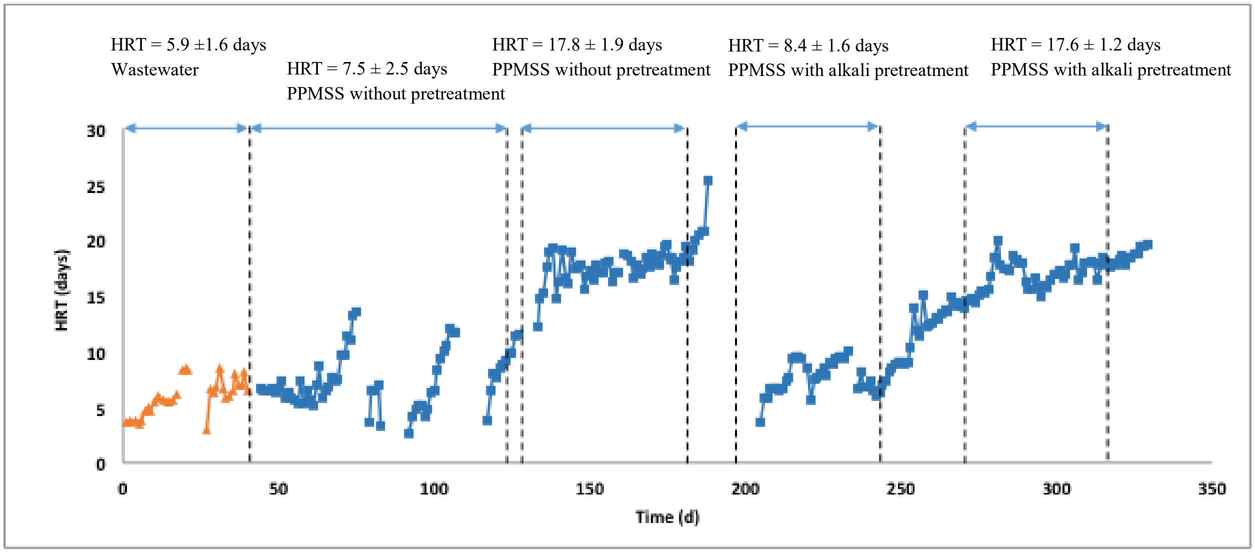

Figure. 3-2 Variations of HRT

3.2 Analytical methods

3.2.1 Water Quality Measurements

Sample of influent were collected every time before the preparation of the feed sludge. The mixed liquor and effluent samples were taken from the reactor 3 times per week during the stable operation. The supernatant samples were gained by centrifuging the mixed liquor for 20 minutes at 18700 x g. They were then filtered through 0.45μm membrane (Millpore) and stored in refrigerator (around 4 °C) for COD measurements. The effluent (permeate) COD were measured directly without further treated. Influent COD, soluble COD, effluent COD and Mixed liquor suspended solids (MLSS) were measured 2 or 3 times per week as defined in Standard Methods (APHA, 2005)

3.2.2 Measurements of the biogas composition and Production

This study collected biogas samples by using a syringe from the top space of the SAnMBR. The composition of the biogas produced by SAnMBR mainly included methane, nitrogen and carbon dioxide. The measurement of biogas compositions used gas chromatograph (Shimazu, GC-2014), which was equipped with a thermal conductivity detector and a silica gel packed column (5486 x 3.18mm). Helium gas was used as the carrier for the instrument, and the flow rate was 30 mL/min. The biogas composition was monitored throughout the whole study, twice a week.

The volume of biogas production is measured by using water displacement. The reactor was connected with rubber tubing in the top, which was then fed under the cylinder of water, as the methane was produced by the reaction in SAnMBR, it exited through the tubing and displaced the water in the cylinder (Xie et al. 2010; Gao et al, 2010).

3.2.3 Particle size distribution

The particle size distribution (PSD) of mixed liquor and supernatant were measured by a Malvern Mastersizer 2000 (Worcester Country), which ranged from 0.02 to 2000 microns. Based on volume or number of the particle, the detector in this instrument could detect the scattered light, and converted the signal to a size distribution. The PSD measurements were determined generally one time each week. Samples included mix liquor, suspension and influent (PPMS).

3.2.4 EPS (extracellular polymeric substances) extraction and measurement

Heat extraction method was divided into two steps for extracting LB-EPS (loosely bound EPS) and TB-EPS (tightly bound EPS) from sludge sample (Li XY et al., 2007). Compared to the heat EPS extraction method used by others, this procedure was improved (Drews A et al., 2006). In brief, 50 mL mix liquor was collected from the reactor, and then dewatered by centrifugation (IEC MultiRF, Thermo IRC, Needham Heights, MA, USA) at 18700 × g for 5 minutes. The gained supernatant was dumped while replaced with 0.05% NaCl (w/v) solution (room temperature), and after that the centrifugal tube immediately sheared for 1 minute with a vortex mixer (LP Vortex Mixer, Thermo scientific). Then the suspension was centrifuged at 18700 □ × g for 10 minutes, and the organic matter in gained supernatant liquor was considered as LB-EPS of the sludge mass. In order to further extract the TB-EPS, the sludge pellet was refilled again in 0.05% NaCl solution to its original volume 50 mL, then submerged it in a 60℃ water bath for 30 minutes. Thereafter, the sludge mixture was centrifuged at 18700 × g for 15 minutes. The organic matter in supernatant liquor was considered as TB-EPS.

Protein concentration within the EPS was measured by the colorimetric method (Lowry et al., 1951), which based on the Folin reaction. Firstly, 0.25 g $CuSO_4.5H_2O$ dissolved in 50 ml of 1% (w/v) aqueous solution of sodium tartrate, then mixed with alkali buffer (20 g Na_2CO_3 in 1 L of 0.1 N NaOH) in a ratio of 25:1, in addition, diluted Folin and Ciocalted’s phenol reagent, 1:1 with Millipore water. The EPS samples were removed from refrigerator while bovine serum albumin was used to prepare the standards, after that, 1 ml of each sample was added to test tubes, followed by 5 ml of the mixture (alkali buffer and Cu reagent) to the test tubes and vortex for 15 seconds, then allowed the mixture to react for 10 minutes at room temperature. Thereafter, added 0.5 ml the diluted Folin and Ciocalteu’s phenol reagent to the tubes and vortex immediately for 15 seconds, the samples should present various depths of blue and measure them with spectrophotometric at 750 nm.

The measurement of carbohydrate concentration depended on the Gaudy's method (1980). The needed reagent was Anthrone reagent, which dissolved 0.2 g Anthrone in 100 mL 95% H_2SO_4. The procedure of this method was as follow: firstly, prepare standards for calibration curve 0-100 mg/L D-glucose (6 with blank), standards in clean tubes (on ice for EPS), then 2 mL of each sample was added to the test tubes, follow added 5 mL of Anthrone reagent to each tube and vortex for 15 seconds, thereafter, the tubes should place in boiling water bath for 15 minutes immediately and then place the tubes in the ice bath in order to decrease temperature to room temperature quickly. Finally, the tubes were measured by spectrophotometric at 625 nm.

3.2.5 SMP Measurement

Soluble microbial products (SMP) represented the soluble EPS, which be released into solution during biomass growth, biomass decay and substrate metabolism (Barker & Stuckey, 1999), The SMP (Proteins and Carbohydrate) were measured using the methods of Drews A et al. (2006). Bovine serum albumin (BSA) was used as protein standards, while Carbohydrate standards used glucose.

3.2.6 Membrane filtration resistance

The membrane filtration characteristics were evaluated by using the resistance in series model ($R_t = R_m + R_f = R_m + R_c + R_p$).

Darcy's law analyzed membrane resistance as follows:

$$R_t = R_m + R_f = R_m + R_c + R_p = \frac{\Delta P_T}{\eta + \mathcal{J}} \qquad (1)$$

R_t- The total hydraulic resistance (1/m)

R_m- The new membrane resistance (1/m)

R_f - The total fouling resistance ($R_c + R_p$) (1/m)

R_c- The cake layer resistance caused by the cake layer deposition over the membrane surface during the process of filtration

R_p- The pore blocking resistance (1/m)

ΔP_T- The trans-membrane pressure (Pa)

η- The dynamic viscosity of the effluent (Pa s)

$\mathcal{T}$- The measured membrane flux (m^3/m^2 s)

Each resistance value was obtained from the same membrane module, and the membrane module was used in the laboratory-scale SAnMBR with an effective volume of 6.024 L, other researchers was also used a similar set-up to determine membrane fouling behavior (Huang et al., 2000; Wang et al., 2006). As the follow, each resistance value was determined by the experimental procedure:

1. R_m was evaluated by measuring the clean water flux of tap water;
2. R_t was estimated by the final flux of biomass microfiltration;

3. The membrane surface was then cleaned by tap water and removed the cake layer by a sponge. Thereafter, the tap water flux was measured again to determine the resistance of R_m+R_p.

With the steps described above, all the resistance values could be calculated. R_t and R_m were directly calculated by using Equation (2); then from step 3 and Equation (2), R_f, R_c, and R_p were calculated. This method was followed by previous studies (Jeison D et al., 2009; Lin HJ et al., 2009; Chang IS & Kim SN, 2009).

The inorganic fouling resistance, organic fouling resistance, and permanent (irremovable fouling) resistance were calculated by using the following equation:

$$R_p = R_{organic} + R_{inorganic} + R_{permanent} \qquad (2)$$

$R_{organic}$ – The organic fouling resistance (1/m)

$R_{inorganic}$ - The inorganic fouling resistance (1/m)

$R_{permanent}$ – The permanent fouling resistance (1/m)

After Step 3, in order to remove the organic foulants the chemical cleaning of the membrane was performed by submerging the membrane module in 200 ppm NaClO (sodium hypochlorite) at pH 9 for 2 h (Andreottola G & Guglielmi G, 2003).

4. The resistance (R_m + ($R_{inorganic}$ + $R_{permanent}$)) was calculated by executing a clean water flux test.

After step 4, the membrane module was submerged in a 2000 ppm citric acid solution at pH 2.1 for 2h in order to remove the inorganic foulants (Wang Z, Ma J, Tang CY, et al., 2014).

5. To process the clean water flux test to measure the resistance (R_m + $R_{permanent}$)

So $R_{inorganic}$ and $R_{permanent}$ could be gained from these steps.

3.2.7. Statistical Analysis

Statistical Analysis was gained by using T-Test in Microsoft Excel 2016. It was used to compare the means between two groups (one under the equal variance assumption and the other for unequal variance), for this study, it was different of the results between the two different HRTs or the different between the non-pretreatment and Alkali pretreatment under the similar HRTs. The statistically significant different was considered when the P-value was under 0.05 in this study.

4. Results and discussion

The experimental results are divided into three parts: biological performance, membrane performance and sludge properties, the first part includes: COD removal, OLR, Biogas yield, solids destruction ratio, Biogas production and Biogas composition. The second part includes: Membrane flux, TMP, Membrane resistance and Scanning Electron Microscopy (SEM) of Membrane pore. The final part includes: MLSS, PSD, SMP and EPS. The discussion will be presented after all the results.

4.1 Biological performance

4.1.1 COD removal and OLR

With the operational time in phases 1-5, the variations of influent, effluent, and supernatant chemical oxygen demand (COD) were presented in Figure.4.1.1. In phase 1, the influent COD of thermomechanical pulping wastewater was 4679 ± 207 mg/L, then the PPMSS was fed to reactor, starting from 17766 ± 3108 mg/L followed by 17850 ± 131 mg/L, 19884 ± 1072 mg/L and 12602 ± 4549 mg/L for phases 2-5, respectively, the concentration in last phase was lower than others, it probably due to the uneven concentration in different PPMS buckets. The permeate COD concentration were 667 ± 172, 429 ± 71, 597 ± 46, 605 ± 119 mg/L for phases 2-5, correspondingly. In addition, as presented in Figure.4.1.1, the supernatant COD in the bioreactor was higher than the permeate COD consistently, it shows that the retention of organic compounds by the membrane and the formed cake layer. The variation of supernatant COD concentrations before and after the pretreatment was observed. In phase 2, the average supernatant COD was 2801 ± 89 mg/L, then as the flux was gradually decreased (Figure. 4.2.1), the concentration of supernatant COD was decreased to 2291 ± 131 mg/L and kept constant throughout phase 3. In phase 4, due to the alkali pretreatment adopt to the PPMSS, the particle in supernatant became smaller (Figure. 4.3.4) and some sludge was solubilized, this resulted in an increased concentration of supernatant COD, the value was 3050 ± 274 mg/L, and it kept almost same until the end of phase 5. The same variation of supernatant COD was also found in previous study, Lin Yun qin et al (2009) conducted a study about effect of alkali pretreatment on biogas production in the anaerobic digestion of PPMSS. The results showed that supernatant COD of all bioreactors (processed different NaOH concentration for pretreatment) had increased in different degrees.

Figure. 4.1.2 illustrated the organic loading rate during the whole process. In phase 1, the average OLR of wastewater was 1.29 ± 0.28 kg VSS/m^3 d. then the PPMSS started to feed the system, due to the reactor was opened few times, the trend of OLR was not stable in this phase, the average OLR was 1.6 ± 0.3 kg VSS/m^3 d, thereafter, the average value was dropped to 0.65 ± 0.17 kg VSS/m^3 d by gradually decreasing the flux in phase 3. The same trend was appeared in the last two phases, at phase 4, the OLR was maintained at 1.73 ± 0.26 kg VSS/m^3 d, then it was expected to decrease the OLR by decreasing the flux, day 279 – day 330 with an OLR of 0.74 ± 0.13 kg VSS/m^3 d. However, before and after the pretreatment at the similar HRT, the changes of OLR were little different ($P=0.39>0.05$ between phase 2 and 4, $P=0.26> 0.05$ between phase 3 and 5).

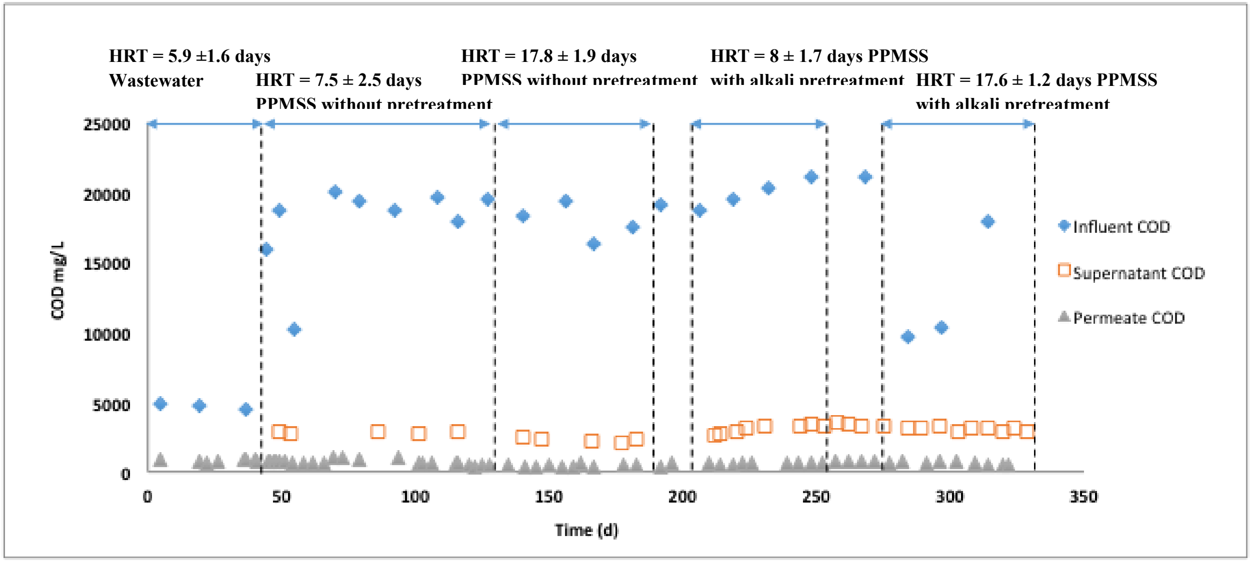

Figure. 4.1.1 Variations of the influent, supernatant, and permeate COD

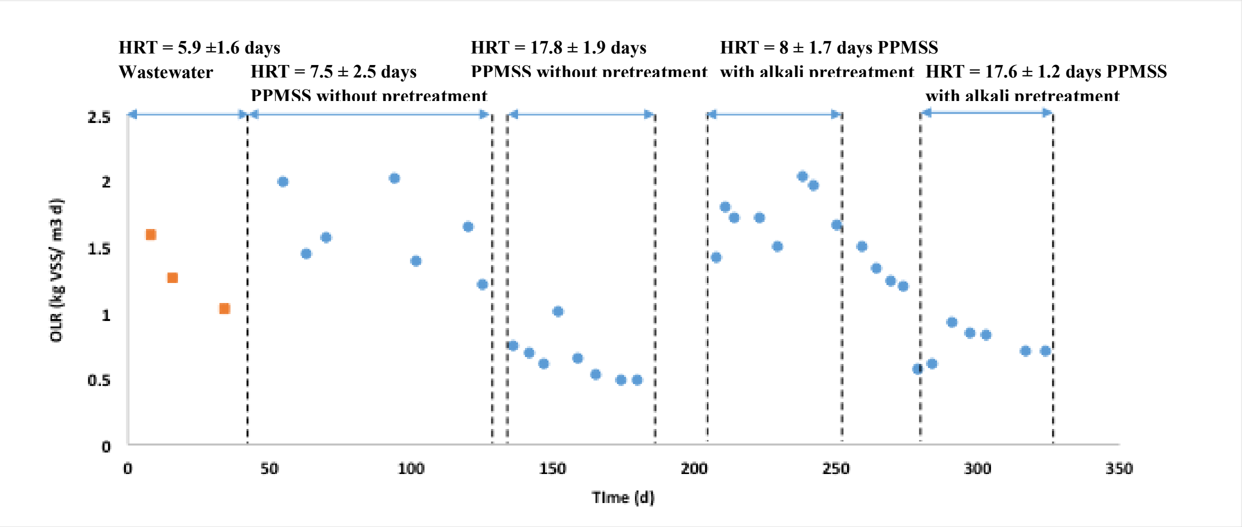

Figure. 4.1.2 Variation of Organic loading rate

4.1.2 Biogas yield and Solids Destruction Ratio

Figure.4.1.3 presented biogas yield (L/g VSS fed) in phase 2-5, it was affected by variation of the flux. In phase 2, the average biogas yield (L/g VSS feed) was 0.075 ± 0.02 (L/g VSS feed), then as the flux (Figure.4.2.1) was decreased at the same time, the biogas yield increased to 0.1 ± 0.012 (L/g VSS fed). The similar trend was observed in last two phases with alkali pretreated sludge as influent, the values were 0.0687 ± 0.017 (L/g VSS fed) and 0.09 ± 0.015 (L/g VSS feed), respectively.

Figure. 4.1.4 presented biogas yield (L/g VSS removed) with experimental time, after alkali pretreatment, the values of biogas yield (L/g VSS removed) had obvious decreased. In phase 3, it was 0.2 ± 0.039 (L/g VSS removed), and then it decreased to 0.14 ± 0.026 (L/g VSS removed) in phase 4. However, between phase 2 and 3 ($P=0.12 > 0.05$) or phase 4 and 5 ($P=0.79 > 0.05$), the biogas yield had little different, and with similar HRTs before and after, the different was significant ($P=0.000015 < 0.05$ between phase 2 and 4, $P=0.006 < 0.05$ between phase 3 and 5). The overall trend of biogas yield (removed) was decreased continuously. The value started with 0.23 ± 0.037 in phase 2, and in the last phase, it was 0.15 ± 0.012 (L/g VSS removed). The same results was also observed in the study by Bayr et al. (2013), the biogas yield decreased by 80% after alkali pretreatment, However, in another study by Wood et al. (2010), the biogas yield with a 20% and 270% increase compared to untreated PPMSS, the reason of this huge different is not clear. Solid destruction ratio was presented in Figure. 4.1.5, the solids reduction ratio was 26 ± 6% in phase 2, then with the biogas yield (L/g VSS removed) decreased, the destruction ratio was increased to 42.7 ± 4% in phase 3. However, after the alkali pretreatment, the values kept elevating in last two phases, the change was less ($P= 0.55 > 0.05$), the values were 43.2 ± 4.2% and 44.7 ± 3.2% in phase 4 and 5. The results of previous studies generally showed that anaerobic digestion of Pulp and paper bio-solids could reduce solid waste by 30-70% (A. Kowalczyk et al, 1989; A. Puhakka et al., 1988; J. Puhakka et al., 1991), the results before and after the pretreatment were in that range.

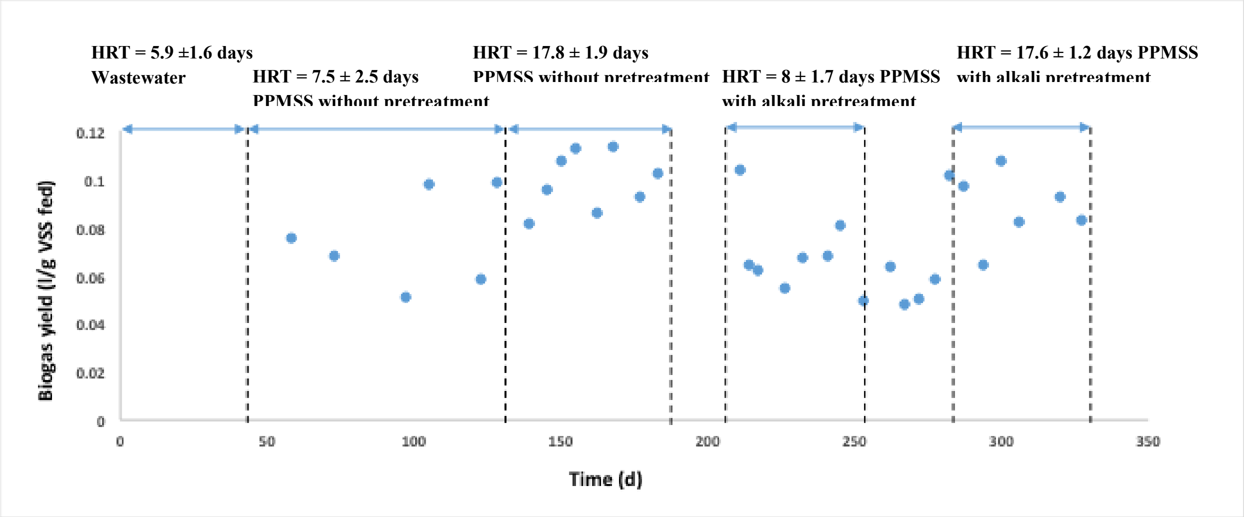

Figure. 4.1.3 Variation of Biogas yield (L/g VSS fed)

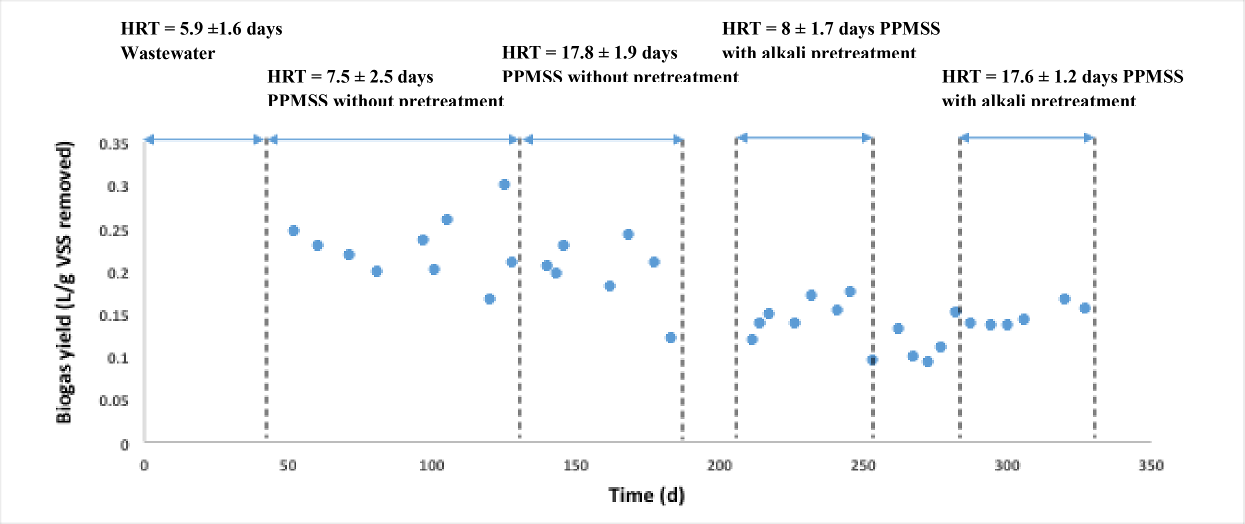

Figure. 4.1.4 Variation of Biogas yield (L/g VSS removed)

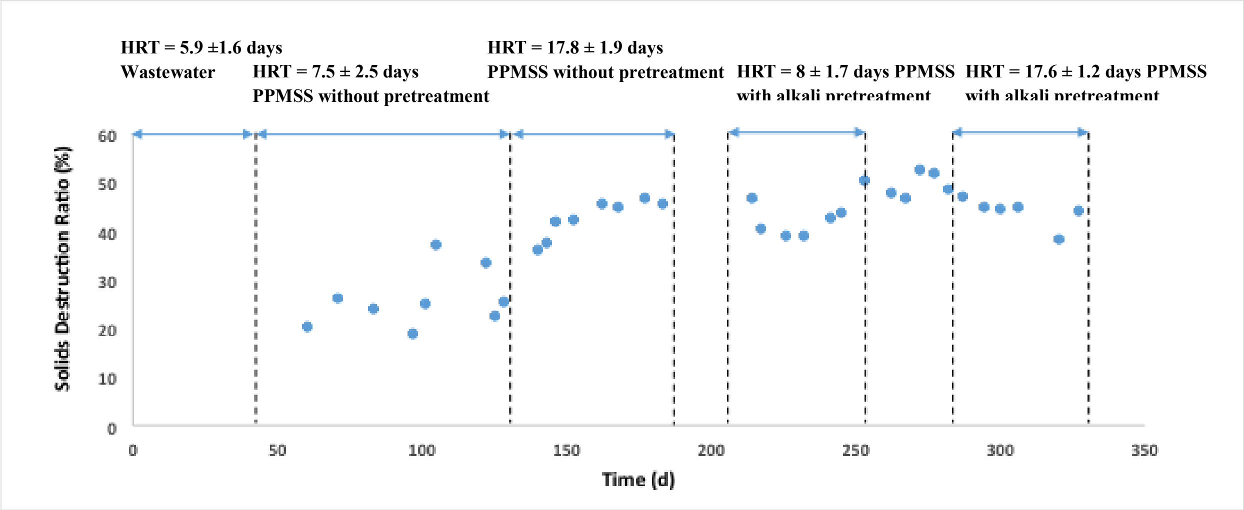

Figure 4.1.5 Variation of Solids Destruction Ratio

4.1.3 Biogas production and gas composition

Figure. 4.1.6 presented the biogas production during the whole process. In phase 1, the wastewater was fed to the reactor, as the wastewater was easily digested by the microorganisms, the average biogas production was 200.3 ± 66.55 L/m^3 d. Thereafter, the influent shifted to PPMS, at the beginning of phase 2, the biogas production had little different, by day 62 with the flux suddenly increased to 2.73 L/M^{2}H, which implied more organic matters pumped into the reactor, therefore, the biogas production also increased to 196.02 L/m^3 d, then due to the membrane fouling, the biogas production constant decreased by the decreased flux, and the average biogas production was 116.08 ± 41.02 L/m^3 d in phases 2. With respect to phase 3, the biogas production kept stabilization, and the average value was 58.81 ± 10.67 L/m^3 d. The different of biogas production was significant between phase 2 and 3 ($P=2.74E-18 < 0.05$), due the decrease in OLR in phase 3, as compared to phase 2. Whereafter, the PPMS was pretreated by NaOH in phase 4 and phase 5, the biogas production fluctuated frequently, which probably caused by positive change of membrane fouling rate, but the average production had little difference at the similar HRT before and after the pretreatment ($P=0.23> 0.05$ between phase 2 and 4, $P=0.06 > 0.05$ between phase 3 and 5). The values were 110.19 ± 37.19 and 54.3 ± 15.38 L/m^3 d in last two phases ($P=7.39E-15 < 0.05$), respectively. However, Y Lin at al (2009) employed 8g NaOH/100g TS_{sludge} to pretreat PPMS, the methane productivity increased by 83%, and in this study, the increase was not observed. The average of biogas production in each phase was shown in Figure. 4.1.7. However, the previous study by Nicholas W et al (2009) shown that the biogas production of pulp and PPMSS in anaerobic digestion after alkali pretreatment was increased 15%, and another study by Nathan D et al (2012) presented that the biogas production was slightly decreased after sludge pre-treated, the result suggested that addition of NaOH may solubilize recalcitrant compounds.

The gas composition was shown in Figure. 4.1.8. In phase 1, the gas was composed of 58.09 ± 3.25 % methane and 28.9 ± 4.8 % carbon dioxide, the remainder of the gas was mainly nitrogen, which was 7.06 ± 2.3 %. Thereafter, the figure presented that the gas composition was influenced by different OLRs. The content of N_2 in phase 3 was higher than it in phase 2, while the content of CO_2 was reduced from phase 2 to 3, the same trend was also appeared in phase 4 and 5: increased OLR resulted in an increase in content of N_2 and a decrease in the content of CO_2. However, the methane content was kept stabilization during the experimental time, the values were 53.33 ± 3.3, 54.2 ± 2.1, 56.4 ± 4.1 and 55 ± 2.8% for phases 2-5.

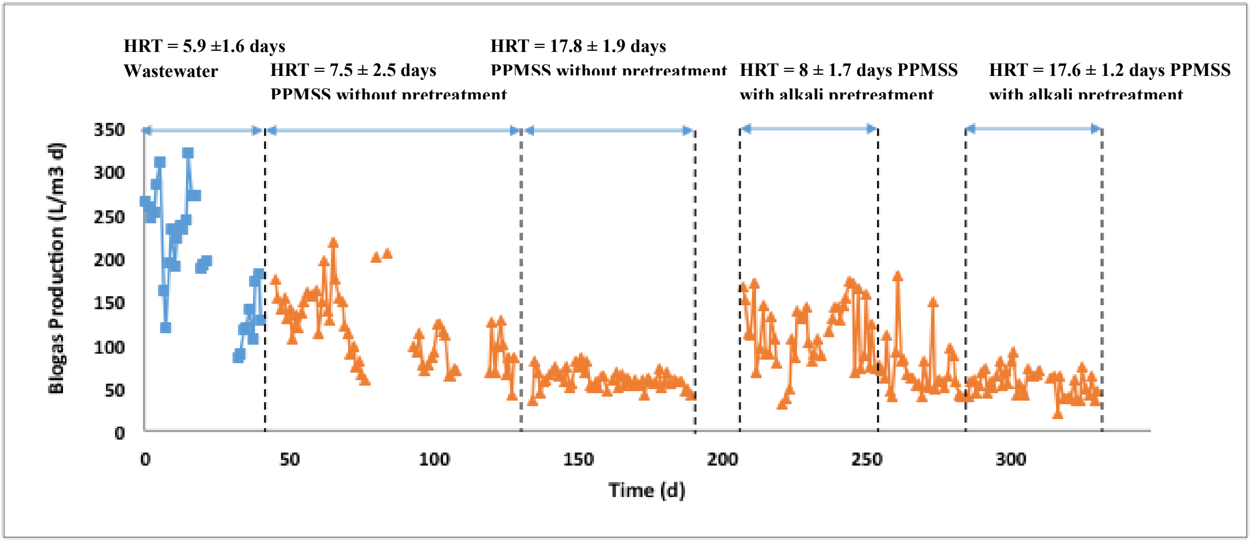

Figure. 4.1.6 Variation of biogas production

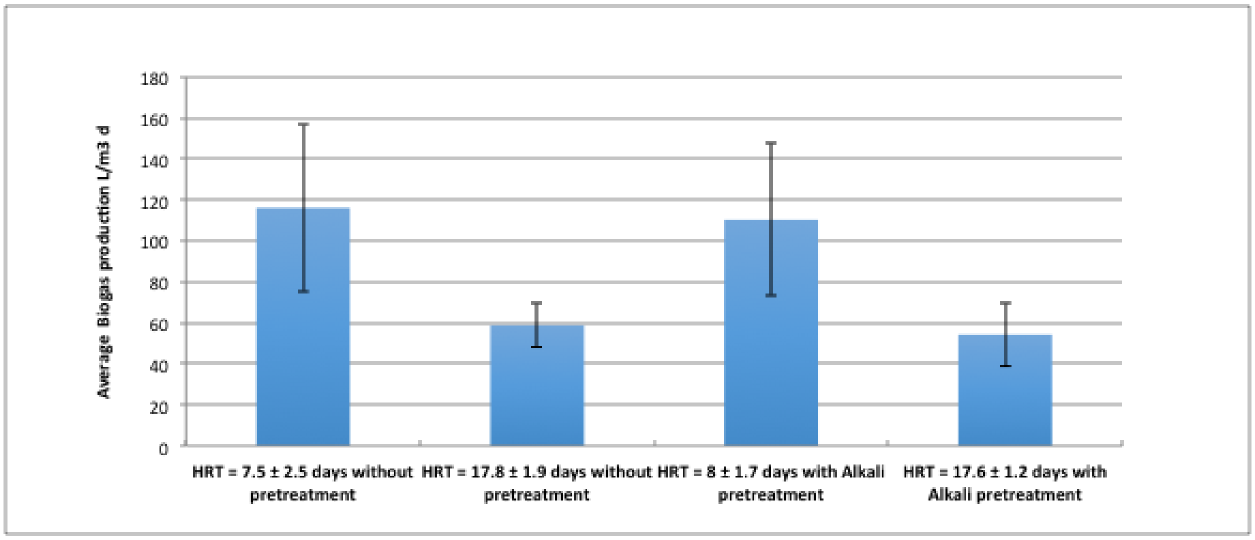

Figure. 4.1.7 Average of Biogas production in each phase

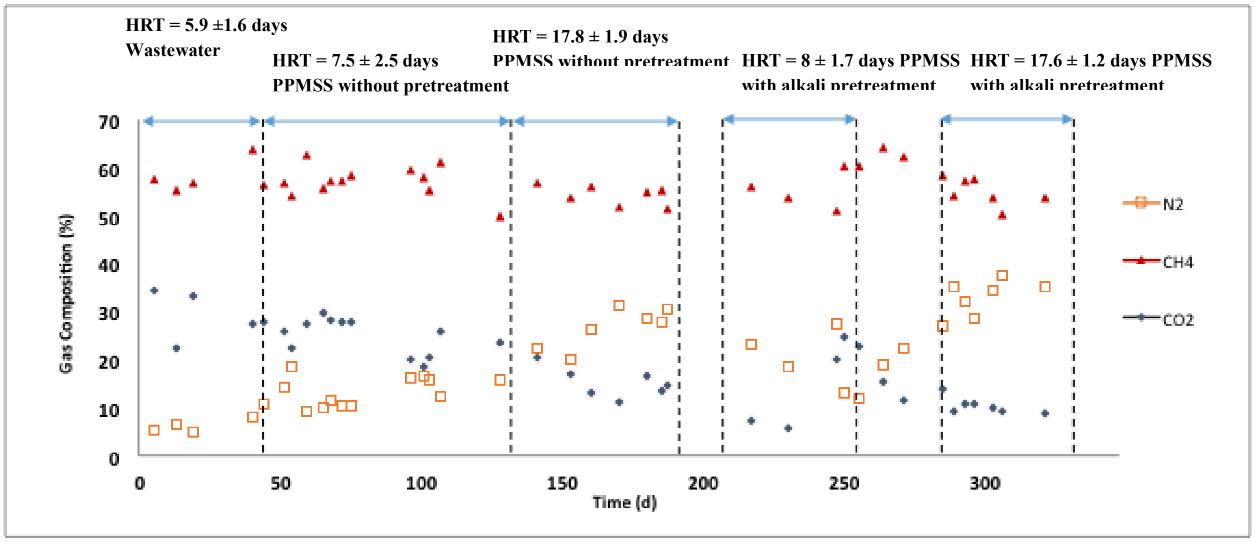

Figure. 4.1.8 Gas composition

4.2 Membrane performance

4.2.1 Flux and TMP (Transmembrane pressure)

The profiles of instant membrane flux and TMP were shown in Figure.4.2.1 and Figure.4.2.2, respectively. When the system operated at constant permeate flow rate, the rate of change in TMP can directly reflect the rate of membrane fouling, therefore, it was an important parameter, which can be used to evaluate the membrane performance in SAnMBR (Lin H-J et al., 2009). In phase 1 (HRT = 5.9 ± 1.6d), TMP and flux had obviously fluctuations, due to the high membrane fouling rates, the membrane flux decreased continually in first 20 days, the HRT cannot be maintained as expected, thus the reactor was opened for physical cleaning. With the TMP had no remarkable change after the cleaning, the flux was 2.56 ± 0.75 L/M^{2}H in the last days of phase 1. Compared phase 2 (HRT = 7.5 ± 2.5d) with phase 4 (HRT = 8 ± 1.7d), new membrane was used in the beginning of phase 4 in order to explore the effect of alkali pretreatment on PPMS treatment, and the alkali pretreatment was applied to PPMS in last two phases, as it was well known that alkali pretreatment caused sludge deflocculation and fine floc formation, which can improve the level of supernatant COD (Figure.4.1.1) and the amount of fine colloidal particles (Figure.4.3.4) (Chen YL et al., 2014). The high TMP jump appeared more earlier in phase 4 than it appeared in phase 2 (at the fifteenth day and fifth day respectively), this significant change can illustrate that supernatant COD and the amount of fine colloidal particles have positively affect on membrane fouling rate, it also reflected in the huge different between their TMP and flux, the average TMP in phase 2 was 14.42 ± 13.87 kPa, and in phase 4 the number reached at 31.59 ± 13.85 kPa (P=1.17E-0.5< 0.05), the fluxes were 1.66 ± 0.62 L/M^{2}H and 1.41 ± 0.33 L/M^{2}H (P= 0.002 <0.05). However, compared phase 3 (HRT = 17.8 ± 1.9d) to phase 5 (HRT = 17.6 ± 1.2d), the operation of system was in a relatively stable state, the average flux was 0.41 ± 0.08 L/M^{2}H and 0.41 ± 0.05 L/M^{2}H, respectively (P=0.36>0.05), and the TMP was 40 ± 6.3 kPa in phase 3 while in phase 5 it was slightly higher at 41.5 ± 10.8 kPa (P=0.19>0.05).

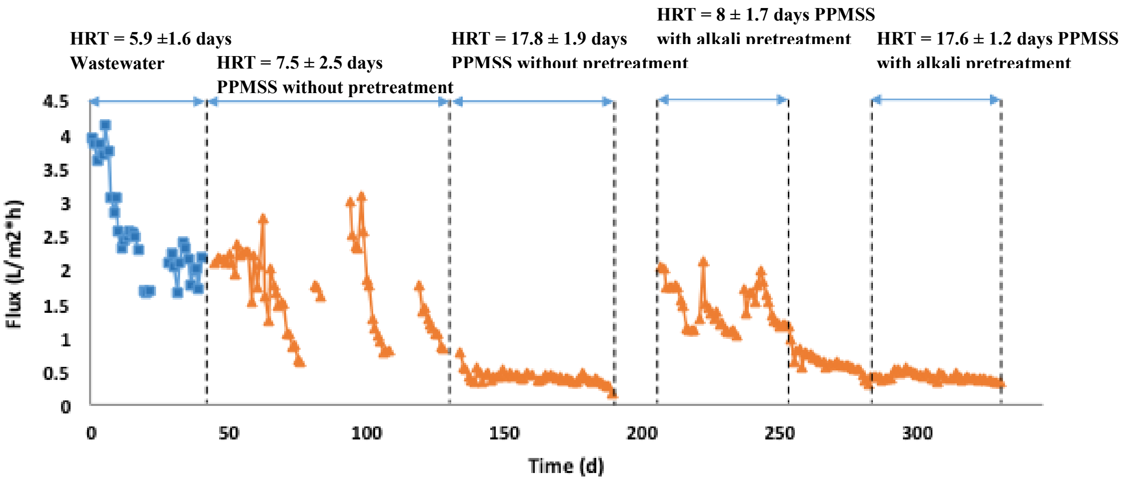

Figure.4.2.1 Variation of Membrane Flux

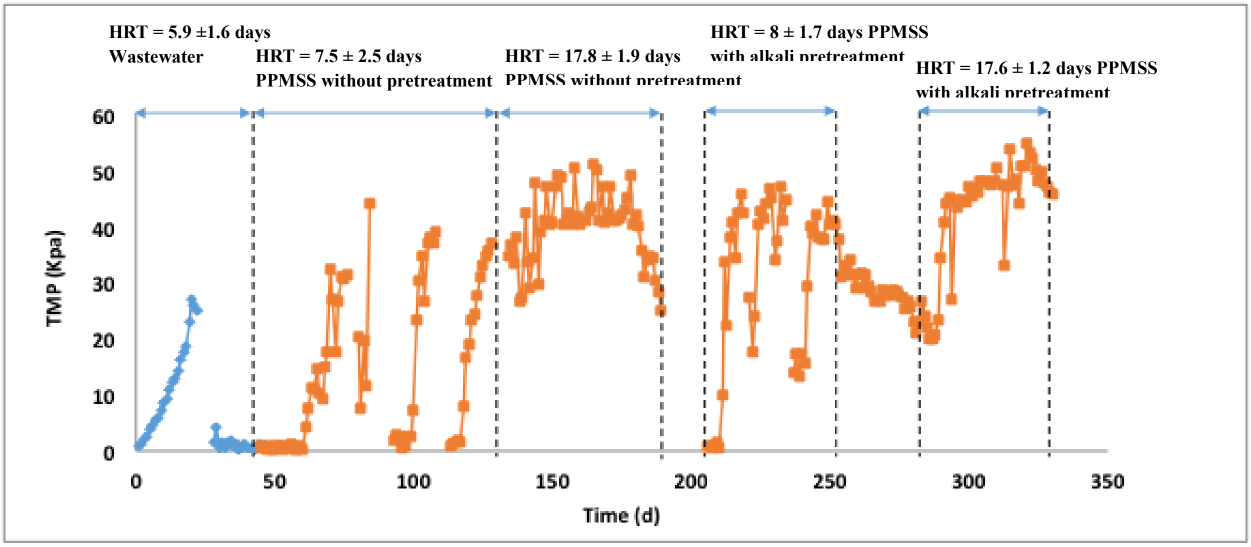

Figure.4.2.2 Variation of TMP

4.2.2 Membrane fouling characterization

In order to explored effects of the alkali pretreatment on the membrane performance, after end of Phase 3, the used membrane (membrane 1) was replaced by a new one (membrane 2), then processed physical and chemical cleaning, while calculated the membrane resistances, the same procedure will process on the membrane 2 at the end of experiment (phase 5). These two membranes were exactly alike, through the variation of each resistance, the effect of the alkali pretreatment can be found. Table.4.2.3 presented each resistance from these two membranes. R_c accounted for 99.24% and 99.31% of the total resistance, respectively, which indicated that the cake layer formation was the dominant fouling mechanism. R_m represented 0.53% and 0.51% of the total resistance (R_t), while R_p were 0.23% and 0.18%. On membrane 1, R_p were composed of $R_{organic}$ = 0.1%, $R_{inorganic}$ = 0.04%, and R_{perm} = 0.09%, the profiles of membrane 2 were $R_{organic}$ = 0.06%, $R_{inorganic}$ = 0.04% and R_{perm} = 0.08%. The results showed that $R_{organic}$ was slightly dominant on membrane 1 (44% and 33% of Rp, respectively), $R_{inorganic}$ and R_{perm} had little different.

Table. 4.2.3 resistances and percentage of the membrane

	Membrane 1	Percentage (%)	Membrane 2	Percentage (%)
R_t (1/m)	4.93366E+13	100	5.28171E+13	100
R_m (1/m)	2.50696E+11	0.53	2.77778E+11	0.51
R_f (1/m)	4.90859E+13	99.47	5.25394E+13	99.49
R_c (1/m)	4.90E+13	99.24	5.24149E+13	99.31
R_p (1/m)	8.83E+10	0.23	1.24457E+11	0.18
$R_{organic}$ (1/m)	2.73E+10	0.09	6.10E+10	0.06
$R_{inorganic}$ (1/m)	1.90E+10	0.04	1.45E+10	0.04
R_{perm} (1/m)	4.20E+10	0.1	4.90E+10	0.08

4.2.3 Scanning Electron Microscopy (SEM)

SEM images specifically presented the new membrane surface (Picture.4.2.4) and used membrane surface with alkali pretreatment in detail (Picture.4.2.5). The effective filtration area was slowly reduced by the accumulation of the organic and inorganic foulants, following a gradually increased TMP in order to maintain the same HRTs (Figure.4.2.1). Several possible mechanisms have been proposed for the TMP rise (Zhang et al. 2006), such as percolation theory, local flux effect, pore narrowing, and pore loss. Based on the present study, sludge cake formation could be the dominant mechanism of TMP jump for the reduction in effective membrane surface area.

The pore size distribution of new membrane and used membrane with alkali pretreatment (after physical and chemical cleaning) were shown in Figure.4.2.6, 10 images were randomly picked from the SEM images of new membrane (5 images) and used membrane with alkali pretreatment (5 images) by Google random number generator, then randomly calculated 100 pore areas from each image by using ImageJ (software), through the pore area, diameters of membrane pore can be gained, the membrane pore size distribution were presented in Figure.4.2.6. The main pore size distribution of used membrane with alkali pretreatment was between 15-20 nm, the number was almost two times of new membrane. The main pore size distribution of new membrane concentrated at 10-25 nm, which is larger than the used membrane. Although, the used membrane was cleaned by physical and chemical method in order to remove cake layer, organic and inorganic foulants, pore narrowing and pore loss were still existed due to irreversible loss during experimental period.

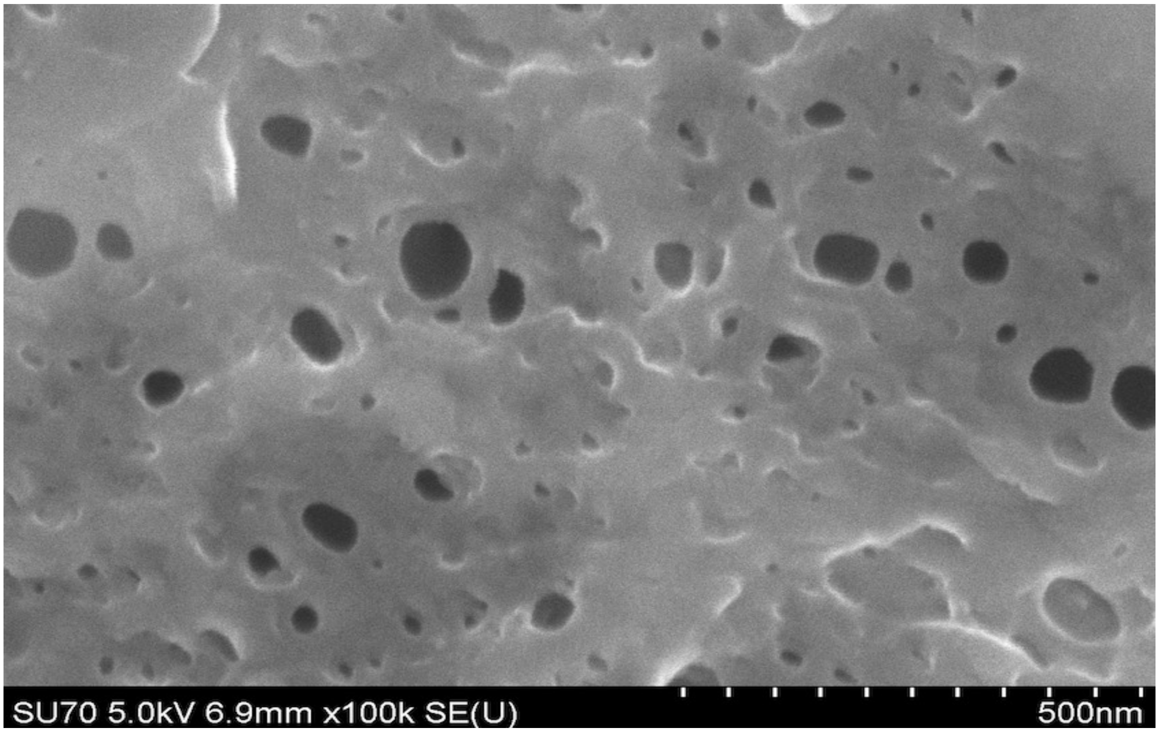

Figure. 4.2.4 SEM image of new membrane surface

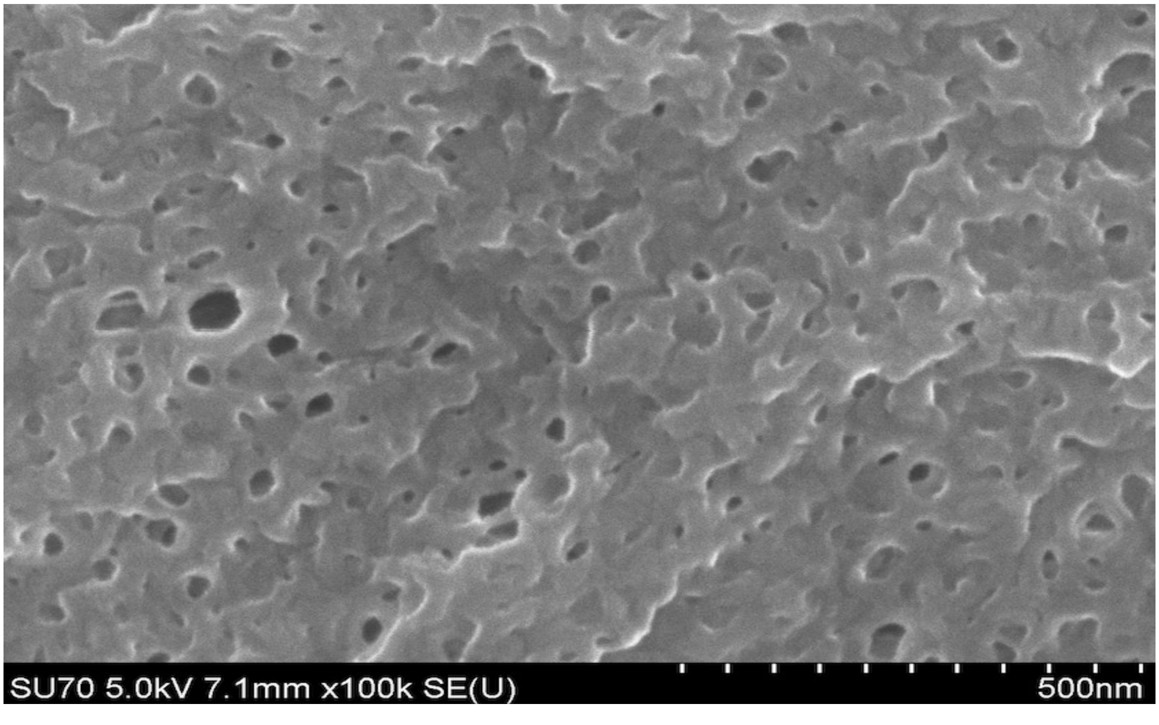

Figure. 4.2.5 SEM image of used membrane (with alkali pretreatment) surface

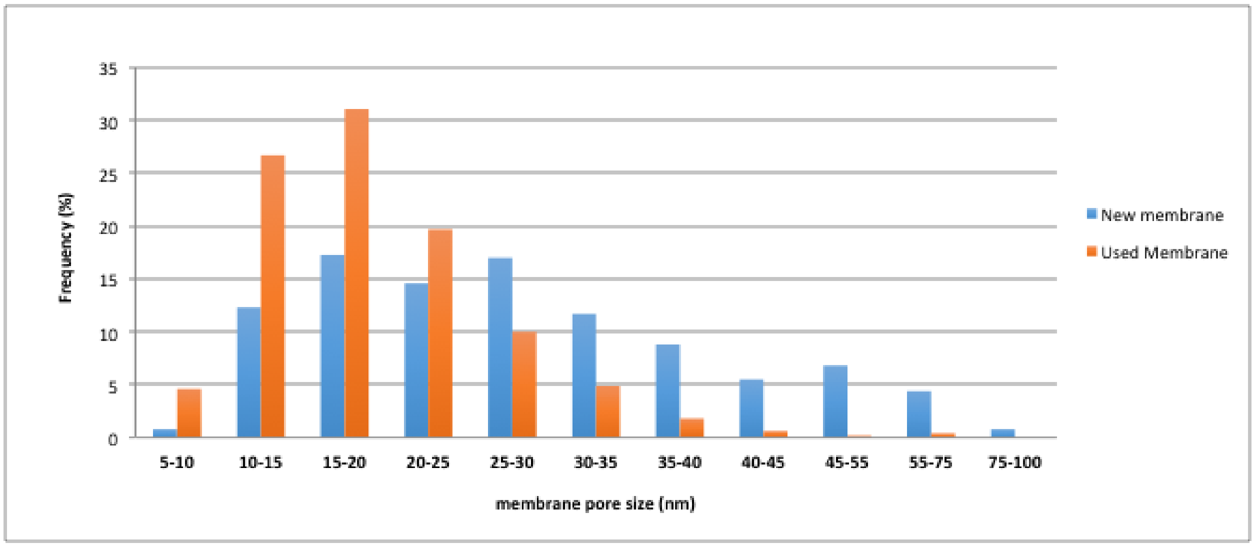

Figure. 4.2.6 Pore size distribution of new membrane and used membrane (with alkali pretreatment)

4.3 Sludge properties

4.3.1 MLSS concentration

The MLSS reactor/feed concentration in each phase was shown in Figure.4.3.1 (due to the influent of phase 1 was not PPMS, thus, the value of MLSS in that phase was not measured). The MLSS reactor concentration was 33.5 ± 3.3 g/L for the second phase, then with the flux decreased (Figure. 4.2.1), the concentration of MLSS also was gradually decreased, the value was 27 ± 2.8 g/L in phase 3. Thereafter, although the alkali pretreatment was used in PPMS, but the concentrations were no significant different before and after the pretreatment in phase 2 and 4 ($P=0.12> 0.05$), between phase 3 and 5, the different was significant ($P=0.0006 < 0.05$), the value was 31.8 ± 1.8 g/L in phase 4 and 22.8 ± 1.1 g/L in phase 5 ($P=2.91E-09 < 0.05$). The

MLSS concentration of feed had no remarkable change over the whole period. The values were 11 ± 1.7, 10.4 ± 1.4, 12.5 ± 1.2, 13 ± 2.1 for each phase.

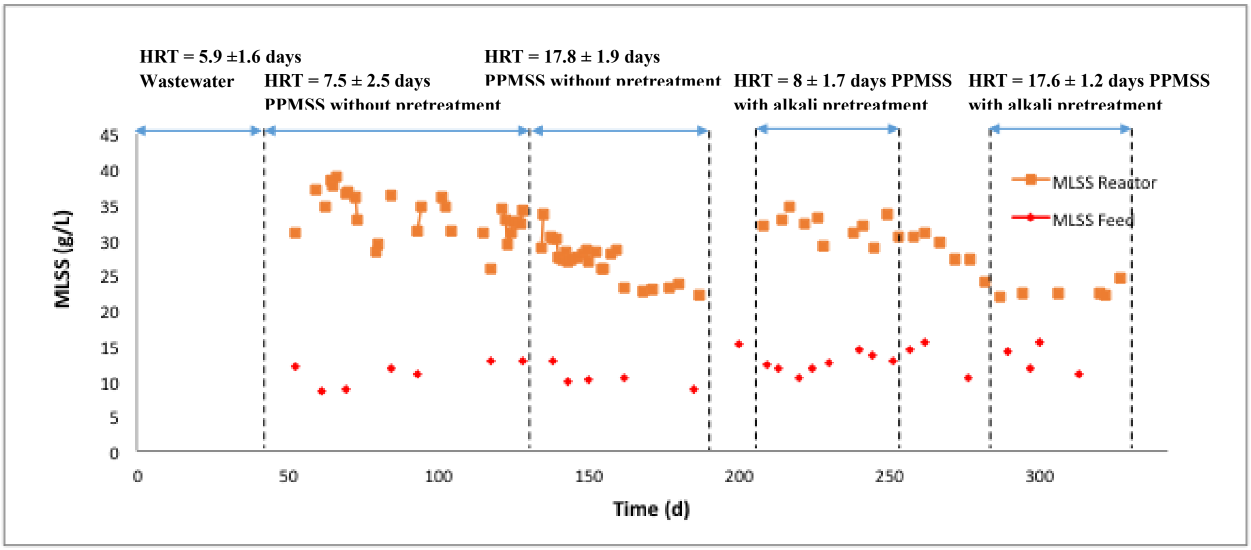

Figure. 4.3.1 Variation of MLSS reactor/feed concentration

4.3.2 Particle size distribution (PSD)

Figure. 4.3.2 shows PSDs of the feed before and after alkali pretreatment, it was interesting to note that was no obvious different between the two curves, it indicated that the alkali pretreatment had no significant impact on particle size distribution of PPMS. The PSDs of mix liquor in SAnMBR under different HRTs were presented in Figure.4.3.3. The curves in phase 2 and 3 had little different, but after the pretreatment, due to the pH of feed was increased (Table. 3.1), the pH of mix liquor in reactor also gained improvement (from 7 to 7.5), while the more big particles (between 10μm to 100μm) appeared in phase 4 and 5. Therefore, it could at least draw a conclusion that increased pH had some impacts on the PSDs of mix liquor in reactor.

The increased floc sizes after alkali pretreatment could be caused by a different batch of PPMS feed.

The PSDs of supernatant was shown in Figure.4.3.4. There was a significant change before and after the pretreatment. The main size of particles was less than 1μm after alkali pretreatment, further, it was concentrated at the range (0.1μm to 0.5μm) in phase 4, and concentrated at the range (0.5μm to 1.2μm) in phase 5. The results combined with the TMP jump (Figure.4.2.2), it could at least partially explain that the alkali pretreatment can induce more significant membrane fouling rate. Previous studies also showed that smaller particles had a strong tendency to deposit on the membrane surface and form a cake layer (Bae & Tak, 2005; Lin et al., 2009), and Gao et al (2010) also found that the particle size decreased by increased pH values.

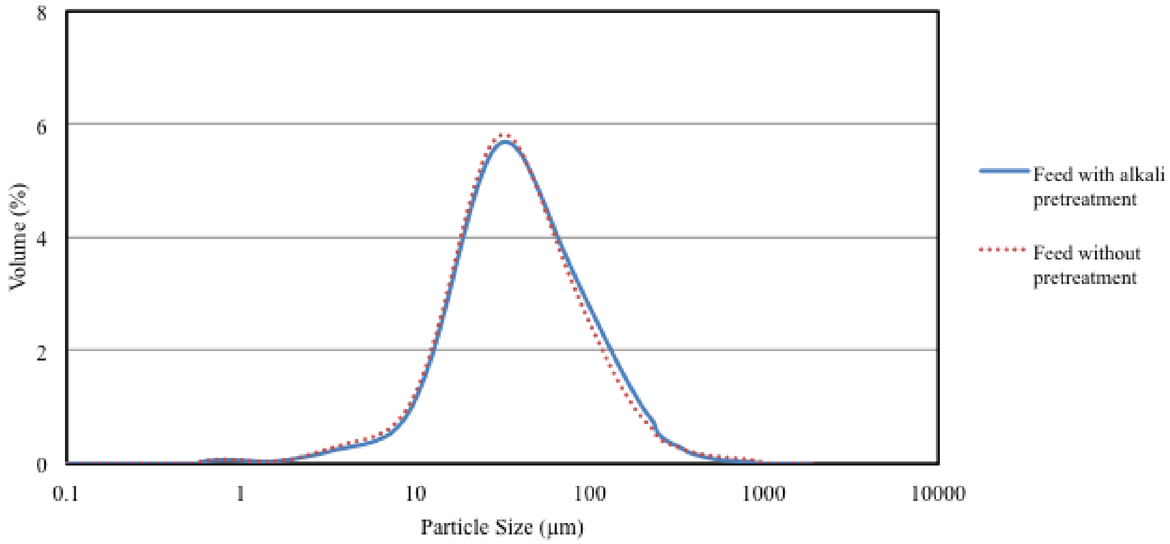

Figure. 4.3.2 Feed particle size distribution with/without alkali pretreatment

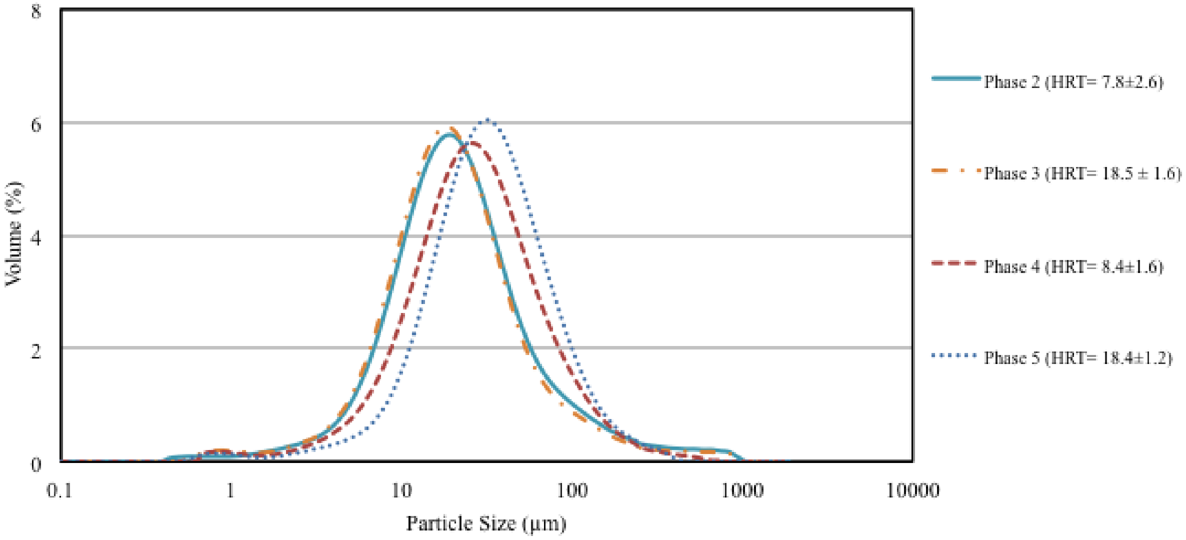

Figure. 4.3.3 PSDs of Mix liquor under different HRTs

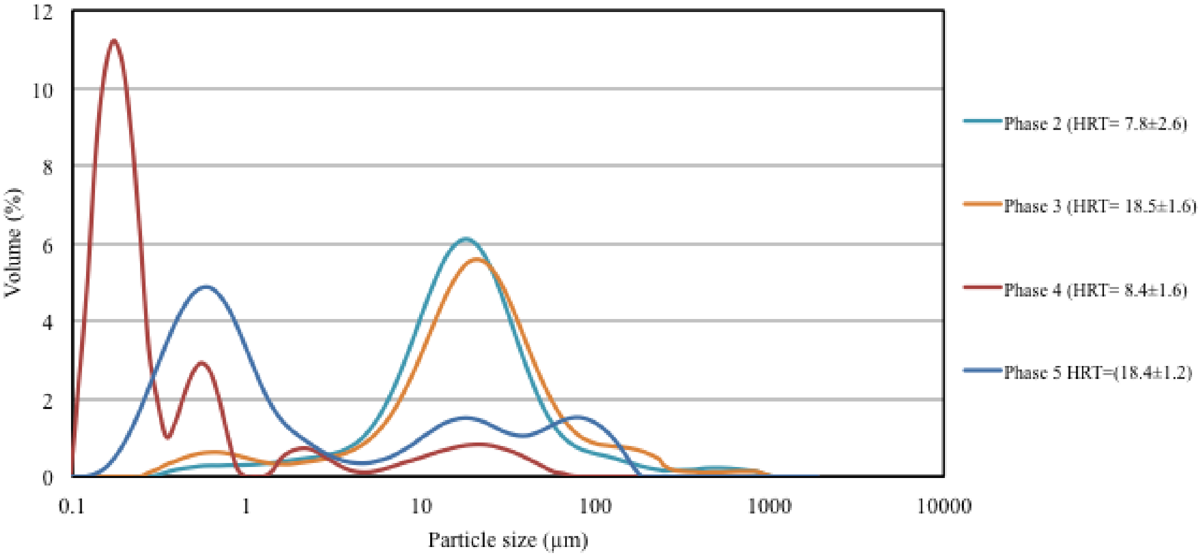

Figure. 4.3.4 PSDs of Supernatant under different HRTs

4.3.3 Extracellular Polymeric Substances (EPS)

Figure.4.3.5 presented LB-EPS (loosely bound) concentration normalized to biomass (as MLSS). Phase 3 had higher LB-EPS concentration (both protein and carbohydrate) than phase 2, this trend was also observed in phase 4 and 5, suggested that more EPS was produced at a lower HRT because LB-EPS production was in direct proportion to substrate utilization. On other hand, compared to the phases without pretreatment, phase 4 and 5 had higher LB-EPS concentration (both protein and carbohydrate) than that in phase 2 and 3, while between similar HRTs, the contents of LB-EPS were also increased. This indicated that the increased LB-EPS production could be attributed to the effect of alkali pretreatment. The result of previous study shown that an increase in LB-EPS had negative impacts on sludge sedimentation, compression and dewatering (S-f Yang et al., 2008), which can be a reason why the membrane fouling rate increased after alkali pretreatment in this study (phase 2 vs. phase 4).

Some different results were shown in TB-EPS (tightly bound) (Figure.4.3.6). The TB-EPS concentration (both protein and carbohydrate) in phase 3 was higher than it in phase 2, while similar result was also found in last two phases. However, compared to the results in LB-EPS, the protein concentration in TB-EPS was higher before the pretreatment, the values were 0.5721 and 0.7851 mg/g MLSS in phase 2 and 3, respectively. After the pretreatment, the values decreased to 0.5645 and 0.6079 mg/g MLSS, respectively. For carbohydrate concentration, the results were same to obtained finding in LB-EPS, the more carbohydrate content was produced at a lower HRT, phase 3 had higher concentration than phase 2, and it in phase 5 was higher than it in phase 4. However, effect of the pretreatment on content of carbohydrate was not clear, As Phase 4 had higher concentration than phase 2, and Phase 5 was lower than Phase 3.

Figure.4.3.7 presented the SMP (soluble microbial products) under different HRTs. The SMP concentration (both protein and carbohydrate) was decreased from phase 2 to 3 by decreased OLR, the value of protein was decreased from 76.95 to 48.87 mg/l, and the carbohydrate decreased from 125.05 to 78.81 mg/l. This variation was also found in phase 4 and 5, but the different was not obvious like previous phases. Compared to the SMP before and after alkali pretreatment, the SMP contents (both protein and carbohydrate) had obvious increase. The gap of protein and carbohydrate was small in phase 2 and 3, but after the pretreatment, the carbohydrate became the dominant component. The concentration of carbohydrate was increased from 125.05 to 224.14 mg/l between phase 2 and 4, also, between phase 3 and 5, the value increased from 78.81 to 219.99 mg/l. This fact can prove that the pretreatment had obviously influenced on the SMP concentration. The previous study shown that high SMP content had positive impact on filtration resistance, which means the membrane-fouling rate was also influenced (Lee at al., 2003; Meng et al., 2006)

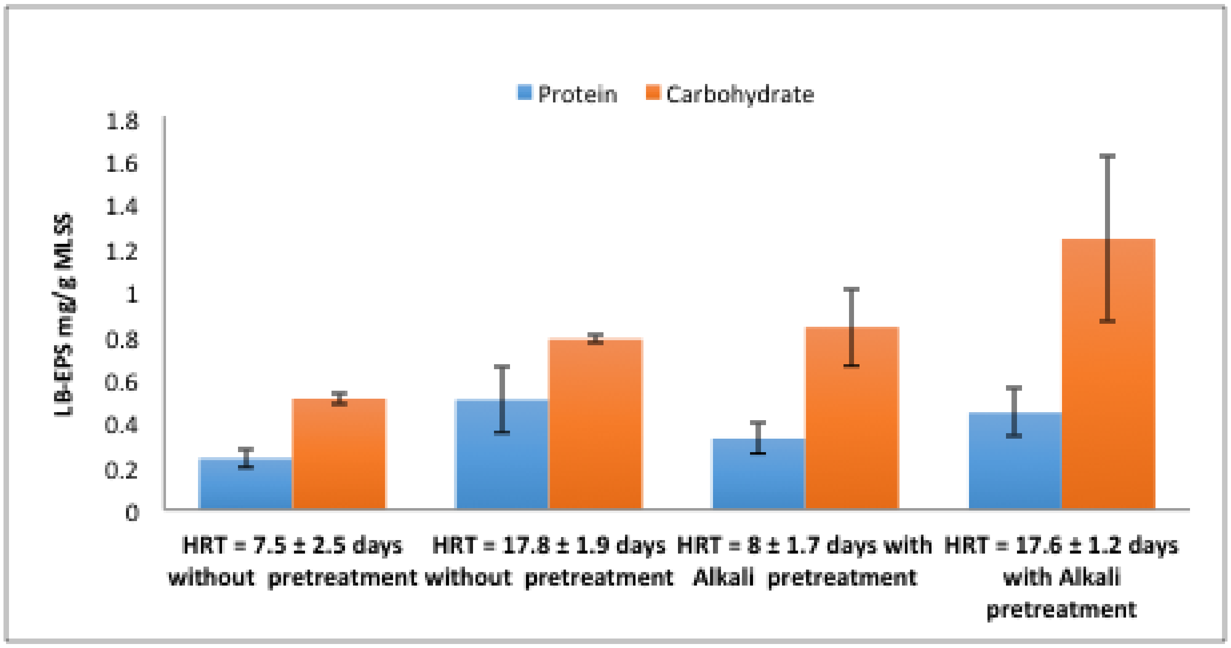

Figure. 4.3.5 LB-EPS (loosely bound) concentration under different HRTs

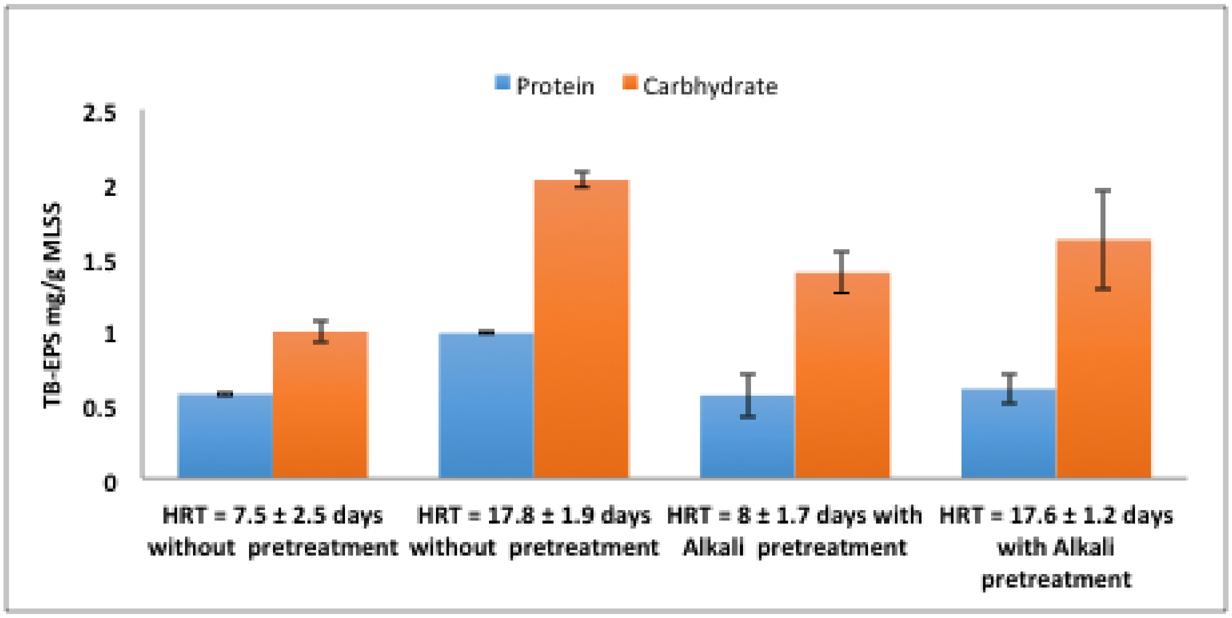

Figure.4.3.6 TB-EPS (tightly bound) concentration under different HRTs

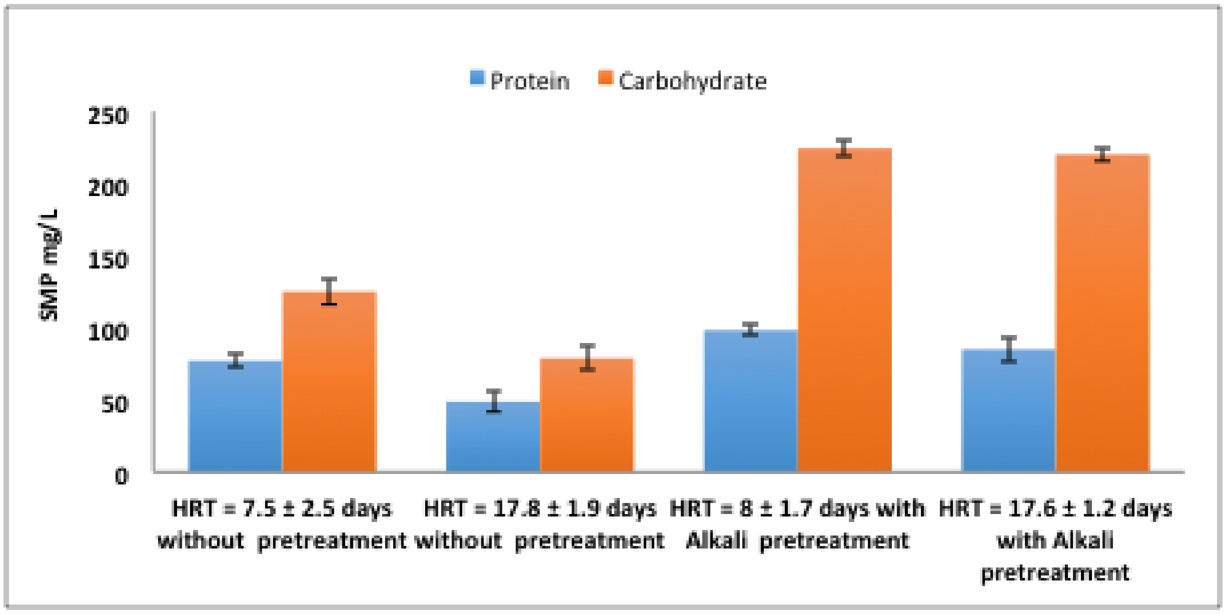

Figure. 4.3.7 SMP (soluble microbial products) concentration under different HRTs

4.4 Discussion

This study focused on the effects of alkali pretreatment on performance of SAnMBR for PPMS, and biogas production (Figure. 4.1.6) presented that no obvious change before and after the pretreatment under the similar HRTs. However, the conditions kept consistent during operating period (e.g. feed concentration, operation and environmental conditions), there still had something different after alkali pretreatment. Firstly, the particle of mix liquor became bigger, the more big particles (between 10μm to 100μm) were appeared in phase 4 and 5, while the particle size of supernatant became smaller, the main size concentrated at the range (0.1μm to 1μm) in last two phases, further, the supernatant COD (Figure.4.1.1) was increased from around 2500 (before the pretreatment) to 3000 mg/l (after the pretreatment). These facts indicated that alkali pretreatment caused sludge deflocculation and fine floc formation, and then resulted in membrane fouling rate increased. Secondly, Biogas yield (removed) (Figure.4.1.4) and destruction rate (Figure.4.1.5) were also affected by the pretreatment. The results of other parameters under similar HRTs presented same trend before and after pretreatment, but the value of biogas yield (removed) was kept elevating, while the destruction rate was decreased continuously during experimental period. Finally, LB-EPS (Figure.4.3.5) and TB-EPS (Figure.4.3.6) concentration both had more or less changes after pretreatment, and the carbohydrate (Figure.4.3.7) in SMP was increased obviously.

5. Conclusions and Recommendations

5.1 Conclusions

The thesis studied the feasibility of using a mesophilic SAnMBR for the treatment of PPMS and the effect of alkali pretreatment on performance of this study. The results shown that the SAnMBR was feasible for the treatment of PPMS, due to the high quality effluent (Figure. 4.1.1), the average influent (PPMSS) COD was 17026 ± 2233 mg/l, after the treatment of SAnMBR, the average effluent COD was decreased to 575 ± 102 mg/l. The solids reduction ratio was in the range of 20%-50%. There was an increase in solids reduction ratio with an increase in HRT for non-pretreated sludge but there was no significant difference for alkali-pretreated sludge. Alkali pretreatment led to an increase in solids reduction ratio at the lower HRT. On the other hand, the average biogas production was 0.68 ± 0.24 L/d in phase 2 and 4, 0.34 ± 0.08 L/d in phase 3 and 5, among them, around 55 % gas was methane. However, alkali pretreatment was no significant affect on performance of the treatment, compared with phase 2 and 3, the biogas production and quality of effluent had little different. Membrane fouling was still a problem associated with the SAnMBR system. Alkali pretreatment led to a more server membrane fouling (phase 2 vs. phase 4). The TMP profiles showed a two-stage behavior: rapid jump at the high OLR (phase 2 and 4), and steady TMP with subtle fluctuation at the low OLR (phase 3 and 5). The high OLR corresponding to a higher influent concentration caused steeper jumps of TMP. Besides, the pretreatment resulted in higher SMP concentration (Figure.4.3.7) and more small sludge particles (0.1- 1μm) (Figure.4.3.4), compared to phase 2, steeper jumps of TMP were appeared earlier in phase 4 (Figure.4.2.2). Based on the results presented in this study, the following conclusion can be drawn:

1. SAnMBR could be a promising alternative to treat PPMSS, due to the high quality effluent and biogas production.

2. High organic loading rate corresponded to a higher membrane filtration resistance and fouling rate in the SAnMBR.

3. Alkali pretreatment had no obvious effect on performance of SAnMBR for PPMSS treatment, but as alkali pretreatment can cause sludge deflocculation and fine floc formation, which have a negative effect on membrane fouling.

5.2 Recommendations for Future Work

The SAnMBR could be an alternative option for PPMSS treatment, compared to the traditional PPMSS treatment. There are several appealing benefits, such as excellent effluent quality, energy recovery, and high-treatment efficiency. Therefore, More studies are needed within this area. However, in order to enhancing its commercial feasibility, the design of system should be optimized, for instance, the method to collect the produced gas or the way to feed the reactor. Besides, the stabilization of system should be improved and the costs of the operating need to be reduced.

Membrane fouling can be a serious problem for the PPMSS treatment in SAnMBR, due to the increased filtration resistance can decrease the membrane flux, further affect the treatment efficiency. Small particle size was considered as the key factor to generate fouling resistance. On the other hand, cleaning strategies can also help to develop better fouling control. Therefore, the development of the particle size control and cleaning strategies should be the future study direction for solving the membrane fouling.

Although this study proved that SAnMBR can be an alternative method for PPMSS treatment, it cannot be scaled up directly from laboratory to plant dimensions, due to the problems like membrane fouling rate, and operation control, further studies of SAnMBR technology on an industrial scale should be needed.

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