Optimization of Thermal Hydrolysis Process for Co-digestion of Fermented Primary Sludge and Waste Activated Sludge

by

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A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

In

Environmental Engineering

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Abstract

This study focused on the optimization of the thermal hydrolysis process (THP) for co-digestion of fermented primary sludge (FPS) and thickened waste activated sludge (TWAS). For this purpose, lab-scale experiments were conducted under two different schemes with different combinations of pretreatment temperatures (140, 160, and 180ºC) and exposure times (15, 30, and 60 minutes); severity indices were ranged from 2.4 to 4.1. In scheme-1, a mixture of FPS and TWAS was subjected to THP, while in scheme-2, only TWAS was pretreated with THP. The biochemical methane potential (BMP) test was conducted for the evaluation of methane yields from sludge pretreated under different conditions. In scheme-1, the highest soluble chemical oxygen demand to total chemical oxygen demand (SCOD/TCOD) ratio of ~ 46% was achieved for FPS+TWAS pretreated at 180ºC for 15 minutes; volatile suspended solids (VSS) removal efficiency was 53%. In scheme-2, the maximum SCOD/TCOD ratio of ~ 58% was attained for TWAS pretreated at 180ºC for 30 minutes; VSS removal efficiency was 68%. Thus, 180ºC was the most effective temperature for sludge solubilization under both conditions. Severity indices showed a positive correlation with COD solubilization and VSS reduction efficiencies in scheme-2, while such relationships were not found in scheme-1. The increase in methane yields did not correlate with aggressive solubilization efficiencies achieved at 180ºC. In scheme-1, the maximum biomethane yield of 272 ± 24 mL/g COD was achieved for FPS+TWAS pretreated at 160ºC for 60 minutes, which was 161% higher than the control. In scheme-2, the highest biomethane yield of 182 ± 155 mL/g COD was achieved for TWAS pretreated at 140ºC for 30 minutes, which was 75% higher than the control. For both schemes, increases in severity indices negatively affected biomethane yields. Thus, the results suggested that higher severity indices could lead to solubilization of certain inhibitory or refractory organics.

Key words: Anaerobic digestion (AD); biomethane; thermal hydrolysis process (THP); solubilization; fermented primary sludge (FPS); thickened waste activated sludge (TWAS)

Preface

The findings in this thesis (Chapter 1, 3, 4, and 5) will be submitted as Zhou, P.; Meshref, M.N.A.; Dhar, B.R. (2020) "*Optimization of Thermal Hydrolysis Process for Co-digestion of Fermented Primary Sludge and Waste Activated Sludge*" to a journal for peer-review and publication. For this manuscript, Peijun Zhou was responsible for experimental design, literature review, laboratory experiments, data interpretation and analyses. M. Meshref assisted in processing of anaerobic biodegradation rate constant data. B.R. Dhar directed the study. All authors contributed to the manuscript preparation.

Acknowledgement

I would like to express my special thanks of gratitude to my supervisor, Dr. Bipro Dhar, for his expertise, guidance, dedication and the continuous support of my study and research work. His comments, suggestions and encouragement have substantially valorized my educational experience and enhanced the research's overall quality.

I would also like to thank my colleagues, Hok Joey Ting, Bappi Chowdhury, Basem Zakaria, Seyed Mohammad, Dr. Long Lin and Dr. Mohamed Meshref for providing me valuable assistance during research project with the lab techniques, equipment setup, literature review, discussion, and data analysis.

Finally, I am deeply thankful to my parents who helped and encouraged me throughout my life.

This research project was financially supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) and EPCOR.

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List of Abbreviations

AD – Anaerobic Digestion

BMP – Biochemical Methane Potential

COD – Chemical Oxygen Demand

FPS – Fermented Primary Sludge

PS – Primary Sludge

SCOD – Soluble Chemical Oxygen Demand

SCOD/TCOD – The ratio of soluble Chemical Oxygen Demand and Total Chemical Oxygen Demand

SI – Severity Index

SS – Suspended Solids

TAN – Total Ammonia Nitrogen

TCOD – Total Chemical Oxygen Demand

THP – Thermal Hydrolysis Pretreatment

TSS – Total Suspended Solids

TWAS – Thickened Waste Activated Sludge

VFAs – Volatile Fatty Acids

VSS – Volatile Suspended Solids

WAS – Waste Activated Sludge

WWTPs – Wastewater Treatment Plants

Chapter 1

Introduction

1.1 Background

Sewage sludge is a by-product generated from the operation of wastewater treatment plants (WWTPs), which consists of primary sludge (PS) and waste activated sludge (WAS). Sludge can be characterized in terms of where it is produced (Foladori, Andreottola, and Ziglio 2015). PS is generated from the primary clarifier. WAS, also known as secondary sludge, is typically produced from the secondary clarifier, where the effluent is separated from the activated sludge (Foladori, Andreottola, and Ziglio 2015). Sludge management and disposal is expensive and can cost range from 20% up to 60% of the total operational cost of a wastewater treatment plant (Grubel et al. 2014). Because of the rising concerns regarding energy and operating costs of sludge management, the minimization of volume and quantity of sewage sludge has become increasingly important (C. Eskicioglu, Kennedy, and Droste 2008).

Anaerobic digestion (AD) is a plausible and widely accepted approach for sludge solubilization, sludge volume reduction, and biogas production (Kim et al. 2003a). However, AD process has some challenges. Notably, due to the rate-limiting step of AD (hydrolysis), various pretreatment methods have been applied for the improvement of AD performance (Kim et al. 2003a). To date, various sludge pretreatment methods, such as mechanical (ultrasonic, microwave, electrokinetic and high-pressure homogenization), thermal, chemical (acidic, alkali, ozonation, Fenton, Fe(II)-activated persulfate oxidation, etc.), and biological options (temperature-phased anaerobic digestion and microbial electrolysis cell) have been investigated for improving anaerobic biodegradability of sewage sludge (Zhen et al. 2017).

Among different pretreatment technologies, thermal hydrolysis pretreatment (THP) has been the most extensively investigated and commercially implemented method (Barber 2016; Zhen et al. 2017). THP was originally used to enhance sludge dewaterability (Ødeby, Netteland, and Solheim 1996; Zhen et al. 2017). Subsequently, it was proven to be a successful approach to improve the dewaterability and solubilization of sludge, increase filterability, and viscosity of sludge (C. Bougrier et al. 2006), as well as enhance biogas production (Neyens and Baeyens 2003). Therefore, due to those proven benefits, various commercial thermal hydrolysis processes such as Cambi® Thermal Hydrolysis Process (CambiTHP® - Cambi Group AS) and BioThelys® (Veolia Waters Technologies) have been demonstrated in the pilot- and full-scale (Claire Bougrier, Delgenès, and Carrère 2008; Kor-Bicakci and Eskicioglu 2019). To date, there are over 75 facilities, either in operation or planning THP prior to the AD process (Barber 2016).

The performance of THP heavily relies on treatment temperature and retention/exposure time (Zhen et al. 2017). According to the literature review, the temperature of THP is typically conducted in the ranges of 60-180°C, while the treatment time normally varies from 15 minutes to 60 minutes. It is worth noting that most of the studies confirmed the previous conditions (temperature: 160-180°C, treatment times: 30-60 minutes) as the optimum conditions of THP (Dwyer et al. 2008; Claire Bougrier, Delgenès, and Carrère 2008; Kepp et al. 2000; Hélène Carrère et al. 2008).

Although thermal hydrolysis has been commercially employed for over 25 years, there remain numerous opportunities for the further evolution of this technology. Firstly, the destruction of volatile solids during anaerobic digestion of sludge remains relatively modest (at 60-65%), even with thermal hydrolysis (Barber 2016). Additionally, due to relatively higher temperature (160-180ºC) and longer retention time (30-60 minutes) to achieve the optimum conditions of THP (Kepp et al. 2000), research on advanced thermal hydrolysis (the combination of peroxidation and thermal hydrolysis) should be further developed and investigated to achieve similar or improved performance under milder conditions (Abelleira-Pereira et al. 2015). Moreover, many WWTPs have implemented fermentation of primary sludge for the production of sludge liquor enriched with volatile fatty acids (VFAs) that can be utilized as a readily biodegradable carbon source for biological nutrients removal process (Zheng, Chen, and Liu 2010). With the increasing interest in the adoption of primary sludge fermentation, previous studies provided very limited information on how THP should be retrofitted in WWTPs already adopted the primary sludge fermentation process.

1.2 Objectives

Based on the aforementioned research gaps, this study focused on the optimization of THP process conditions for WWTPs with PS fermentation. The specific objectives of this thesis are as follows:

1. To optimize THP process conditions (operating temperature, exposure time, and severity index).
2. To systematically evaluate two different schemes (FPS+WAS and WAS alone) for retrofitting THP in WWTPs with primary sludge fermentation.

1.3 Organization of thesis

The organization of this thesis contains five chapters. This chapter (Chapter 1) provides an overview of the research gaps and summarizes the specific objectives. Chapter 2 offers a literature review on the current status of THP studied on sewage sludge. The review pointed out the characteristics of sewage sludge, AD performance, and different pretreatment methods on sewage sludge. Amongst different pretreatment technologies, thermal hydrolysis pretreatment was mainly discussed in this review. Chapter 3 presents details on the materials used in the experiment, experiment design, and set-up configuration, analytical methods, and calculations throughout the study. Following this, Chapter 4 presents the results and discussions on the experimental work and data analysis. The influence of THP on chemical oxygen demand (COD) solubilization, solids removal, volatile fatty acids (VFAs), and ammonia nitrogen was interpreted. Additionally, the significance of severity index (SI) was also discussed. Finally, Chapter 5 summarizes the take-home messages and proposes recommendations for future research.

Chapter 2

Literature Review

2.1 Anaerobic digestion

Anaerobic digestion (AD) is a biological process that uses anaerobic microorganisms to degrade organic matters to biogas. AD process involves multiple steps: hydrolysis, fermentation (acidogenesis and acetogenesis) and methanogenesis (see Figure 2.1). The first two (or three) steps convert complex organic compounds (e.g. carbohydrate, proteins, and lipids) to volatile fatty acids (VFAs), carbon dioxide (CO_2) and hydrogen (H_2), while methanogenesis converts VFAs, CO_2, and H_2 to CH_4 and CO_2 (Lin, Yu, and Li 2017; Lin et al. 2018). Among these biochemical steps, hydrolysis is often considered as the rate-limiting step when digester is operated with feedstocks having high solids content (Kim et al. 2003b; Zhen et al. 2017; Dwyer et al. 2008; Xu et al. 2014), due to the complex floc structure of substrates (Zhen et al. 2017) and the formation of non-desirable by-products, such as complex heterocyclic compounds and VFAs (Ariunbaatar et al. 2014). Extensive research has been conducted on pretreatment methods to accelerate the hydrolysis step (Ariunbaatar et al. 2014; Zhen et al. 2017).

Based on temperature, anaerobic digestion can be classified into two major classes: mesophilic (35-40ºC, usually operated at 37ºC) and thermophilic (50-60ºC, mostly operated at 55ºC) (Lin et al. 2018). In terms of biogas production, the thermophilic condition is more advantageous compared to mesophilic operation, however, it requires high energy input for heating and may be limited by poor process stability (Lin et al. 2018).

The generated biogas is a mixture of methane and carbon dioxide while the proportion of CH_4 is around 60-65%, and the remaining 40-50% is CO_2 (Zheng et al. 2014). Biogas produced from AD is considered as an important renewable energy source to meet future energy demand (Lin et al. 2018), and thereby reduce the consumption of fossil fuel given that the reserve of fossil fuels is being depleted (Kim et al. 2003a). For instance, the biogas could be directly used for the generation of heat and electricity in which purified methane from biogas can be upgraded to compressed 'natural' gas (Bio-CNG) or liquefied 'natural' gas (Bio- LNG) for transportation fuels (Yang et al. 2015). Furthermore, residuals (known as digestate) from the AD process are rich in nutrients that can be potentially used as a soil amendment and organic fertilizer (Sheets et al. 2015). Compared to the aerobic treatment method, AD requires low nutrients and no oxygen needs. The process of AD also removes odors and pathogens; thus, stabilizes organic waste like sewage sludge (Zhen et al. 2017). Therefore, employing the AD process could provide significant environmental and economic benefits (Lin et al. 2018).

Nevertheless, the operation of AD has a few challenges, including relatively low methane production, longer residence times, potential of system instability, and low end-product values (Yang et al. 2015). The slowly biodegradable organic matter can lead to low methanogenesis rate and hence long retention time might be required. The imbalance of nutrients and accumulation of digestion intermediates (e.g. ammonia and VFAs), can cause system instability. Hence, the operation of anaerobic digestion requires appropriate control and management. Additionally, biogas and digestate, the two major end-products from AD, although they have potential values, still need additional treatment prior to usage (Yang et al. 2015).

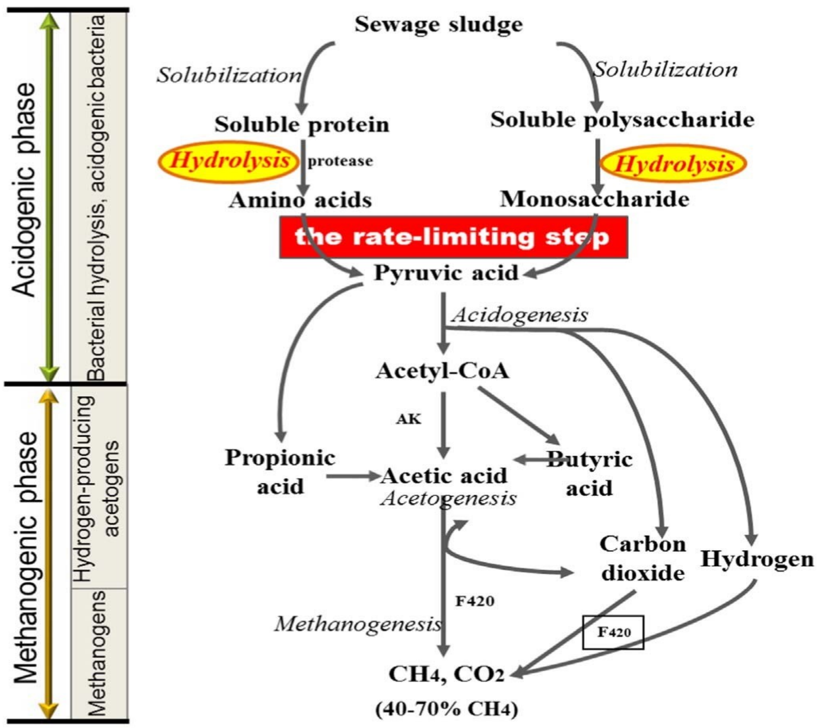

Figure 2.1. Metabolic pathway for anaerobic digestion adapted from (Zhen et al. 2017).

2.2 Sewage sludge

Sludge management is expensive and can cost up 60% of the total operational cost of a wastewater treatment plant (Grubel et al. 2014). Conversely, being an economically feasible and fairly safe alternative (Yang, Zhang, and Wang 2015), a renewable energy source, and a sustainable management choice for organic wastes and it by-products (Luste and Luostarinen 2010), AD is considered as one of the most effective methods to reduce the volume of sewage sludge (Pilli et al. 2015). Sewage sludge is a by-product of biological wastewater treatment while it is mainly characterized by a high content of organic compounds (Sosnowski, Wieczorek, and Ledakowicz 2003). Sewage sludge usually represents 1-2% of the wastewater volume (Zhen et al. 2017) and includes both primary sludge (PS) and waste activated sludge (WAS) (Sosnowski, Wieczorek, and Ledakowicz 2003).

PS is a result of the capture and settling down of large particles in the primary treatment process (i.e., gravity settling in primary clarifier). In contrast, WAS is generated at a result of secondary treatment (i.e., biological treatment) in the secondary clarifier. WAS mainly encompasses the excess biomass (Ji, Chen, and Chen 2010). PS and WAS are usually mixed in wastewater treatment plants (WWTPs) and utilized as a co-substrate for AD process. However, in recent years, many WWTPs implemented fermentation processes of PS in order to produce a sludge liquor with short-chain VFAs (see Figure 2.2). This generated VFAs can be used as an exogenous carbon source for biological nutrients removal process

(Zheng, Chen, and Liu 2010). It is well known that both biological phosphorus and nitrogen removal require organic carbon source (Yuan et al. 2020; Hu et al. 2020). Hence, polyphosphate accumulating organisms (PAOs) and denitrifying bacteria utilize readily biodegradable VFAs (Zheng, Chen, and Liu 2010). Hence, the VFAs-rich sludge liquor from the fermenter is pumped to BNR reactors, and fermented primary sludge along with the scum formed on the top of the fermenters is mixed with WAS for AD.

Both characteristics of PS and WAS are illustrated in Table 2.1. There are few similarities between PS and WAS in terms of having same concentration of total VFA (TVFA) and alkalinity (i.e., no significant difference in the concentration), having a low soluble chemical oxygen demand (SCOD) and low total chemical oxygen demand (TCOD). Also, they resemble in the smaller ratios of SCOD/TCOD, that demonstrates a large proportion of COD is derived from solids. Distinct from WAS, PS contains more easily biodegradable organic matters (Wu et al. 2010). This indicates that WAS is rich in organic solids limiting the hydrolysis step during AD (Mao et al. 2004). In terms of SCOD concentration and volatile solids/total solids (VS/TS) ratio, WAS has a lower soluble COD concentration and higher VS/TS ratio in relation to PS. However the mean particle size of PS is slightly larger compared to WAS (Valo, Carrère, and Delgenès 2004).

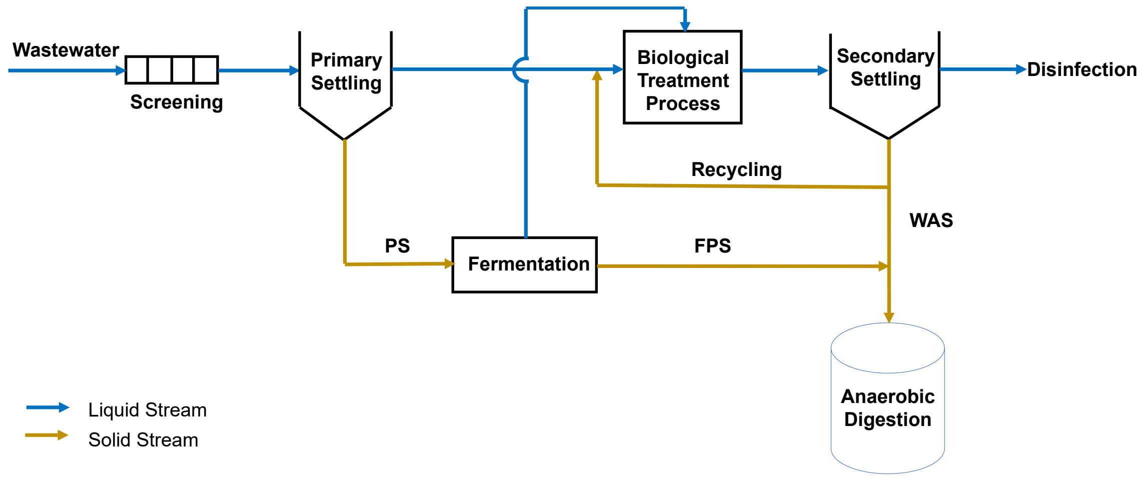

Figure 2.2. Schematic diagram of wastewater treatment process with primary sludge fermentation and anaerobic digestion process.

Table 2.1. Characteristics of primary sludge and waste activated sludge (WAS)

Parameter	Primary Sludge	WAS	References
pH	5.0-8.0	6.2-8.0	(Ji, Chen, and Chen 2010; Mao et al. 2004; Chen, Yue, and Mujumdar 2002; C. Eskicioglu, Kennedy, and Droste 2008; Koivunen and Heinonen-Tanski 2005)
TSS (g/L)	14.48-15.4	9.09-14.4	(Ji, Chen, and Chen 2010; Kiær 2007)
VSS (g/L)	9.05-10.4	5.42-10.6	(Ji, Chen, and Chen 2010; Kiær 2007)
TCOD (g/L)	12-175	10.0-65.7	(Ji, Chen, and Chen 2010; Wilson and Novak 2009; Kiær 2007; Mao et al. 2004; C. Eskicioglu, Kennedy, and Droste 2008)(Park and Ahn 2011)
SCOD (g/L)	0.4-6.3	0.3-2.4	(Ji, Chen, and Chen 2010; Wilson and Novak 2009; Kiær 2007; Mao et al. 2004; C. Eskicioglu, Kennedy, and Droste 2008)(Park and Ahn 2011)
TS (%)	3.0-7.0	0.5-6.0	(Wilson and Novak 2009; C. Eskicioglu, Kennedy, and Droste 2008)
VS (% of TS)	8.1-81	50-82.6	(Mao et al. 2004; Wilson and Novak 2009; C. Eskicioglu, Kennedy, and Droste 2008)(Park and Ahn 2011)
TVFA (mg/L) *	914	913	(C. Eskicioglu, Kennedy, and Droste 2008)
Alkalinity (mg/L as $CaCO_3$)	220-1500	580-1350	(Chen, Yue, and Mujumdar 2002; C. Eskicioglu, Kennedy, and Droste 2008)(Park and Ahn 2011)

*TVFA (summation of acetic, propionic, butyric acids)

2.3 Pretreatment methods for sewage sludge

Amongst various steps involved in AD, hydrolysis has been reported as the rate-limiting step (Kim et al. 2003b). Hence, in order to encounter this obstacle and ultimately improve the hydrolysis efficiency and overall process kinetics and maintain system stability, the pretreatment of feedstock prior to AD should be considered. Various pretreatment methods have been investigated to enhance the hydrolysis rates. For instance, the pretreatment methods include mechanical (ultrasonication, microwave, and high-pressure homogenizer), thermal, biological and chemical (ozonation, alkaline and acidic), and their combination (see Table 2.2).

As the focus of this mainly on AD of sewage sludge, the literature review will be limited to the studies and earlier investigations related to pretreatment methods for sewage sludge prior to AD.

2.3.1 Mechanical pretreatment

2.3.1.1 Ultrasonication

Ultrasonic pretreatment is a well-established mechanical pretreatment technique that acts on the disruption of microbial cell structures in order to release intracellular materials (Mao et al. 2004). The higher the sonication power employed, the more sludge particles are disrupted and the more completely the structure is deteriorated (Mao et al. 2004). Ultrasonication can improve the characteristics of sludge by the reduction of particle size and increase of SCOD yet an intensive energy will be required (Mao et al. 2004). Furthermore, ultrasonic pretreatment can significantly enhance the biogas production (i.e., >70%) (Cesaro et al. 2014) and improve the dewaterability (Toreci, Kennedy, and Droste 2009).

Ultrasonic pretreatment is influenced by the ultrasound density and solid concentration, in which a higher ultrasound density would require less specific energy. Once the optimal solids concentration is exceeded, the ultrasound is then attenuated (Mao et al. 2004). In terms of mechanisms associated with ultrasonication, there are two key mechanisms associated with the process. The first one is cavitation, which is favored at low frequencies (H Carrère et al. 2010). The mechanical shear forces caused by cavitation was confirmed as the dominant factor of the disintegration enhancement (Mao et al. 2004). Another mechanism, which tends to be occurred at high frequencies, is the chemical reactions due to the formation of of $OH^{\bullet}$, $HO_2^{\bullet}$ and $H^{\bullet}$ radicals (H Carrère et al. 2010).

Employing the ultrasonic on the pretreatment of a secondary sludge, Chiu et al. (1997) observed an increase in the rate of solubilizing particulate organic matter, a reduction in the pretreatment time and an enhancement in the production of VFA (i.e., a high recovery of TVFA is achieved) (Chiu et al. 1997). Kim et al. (2003) presented similar results in which ultrasonication of secondary sludge at 42 kHz greatly improved the SCOD removal and volatile solids (VS) reduction efficiency (Kim et al. 2003b). Overall, in terms of sludge pretreatment, low frequencies (20-40 kHz) are the most efficient (H Carrère et al. 2010).

In another investigation by Mao et al. (2004) wherein the researchers studied the effect of ultrasonication on PS and WAS. Based on their findings, more effectiveness was observed on ultrasonic pretreatment of WAS in comparison to ultrasonication of PS (Mao et al. 2004).

2.3.1.2 Microwave

Microwave irradiation is one of the most well-known sludge pretreatment methods (C. Eskicioglu, Kennedy, and Droste 2008). It was established as an alternative technique to conventional heating pretreatment method to conserve energy, destroy pathogens and increase VS reduction (Bordeleau and Droste 2011; Toreci, Kennedy, and Droste 2009).

Two mechanisms are most common in damaging sludge cells through microwave irradiation. The first pathway is athermal (non-thermal) effects. This pathway occurs during microwave and can cause a change in the dipole orientation of polar molecules. This change can then lead to a possible breakage of hydrogen bonds and unfolding and denaturing of complex biological molecules (Toreci, Kennedy, and Droste 2009). In contrast, the thermal effect as the second pathway is generated after a rotation of the dipoles under an oscillating electromagnetic field. Then the intracellular water is heated to the boiling point and microorganisms is ruptured (Tang et al. 2010).

Microwave irradiation can occur at wavelengths of 1mm-1m with equivalent frequencies of 300 Ghz-300 MHz. However, pretreatment of sewage sludge using microwave irradiation, a shorter wavelength (12.24 cm) with the corresponding frequency (2450 GHZ) is recommended (Bordeleau and Droste 2011; Tang et al. 2010).

The microwave effectiveness could be affected by various factors such as energy, temperature, contact time and etc. (Toreci, Kennedy, and Droste 2009; Tyagi and Lo 2013). For instance, Tang et al. (2010) indicated that the water content is the most important factor (Tang et al. 2010). However, other studies suggested that increasing the microwave energy input could enhance sludge solubilization efficiency (Zhen et al. 2017). In the same context of influencing factors, other investigations demonstrated occurrence of an adverse effect on solubilization as well as biogas yield during the higher power operations (Mehdizadeh et al. 2013). Consequently, given such conflicting results, proper optimization of power input is warranted for a successful operation and a wide application of microwave pretreatment method for sewage sludge (Tyagi and Lo 2013).

2.3.1.3 High-pressure homogenizer

In high-pressure homogenizers, sludge pressure often reaches up to 900 bar, then sludge passes through a pressure valve and get strongly depressurized (H Carrère et al. 2010). During high-pressure homogenization process, sudden pressure gradient, high turbulence, cavitation and strong shear forces are aroused. The sludge flocs and microbial membrane are then broken, which can result in the improvement of sludge biodegradation (Zhen et al. 2017).

Several processes are commercially available: The Crown® process, which is operated at 12 bars; Cellruptor process where sludge is compressed at pressures > 1 bar. In brief, soluble gas is introduced to sludge stream and then transported across the cell walls due to the rapid diffusion rate (H Carrère et al. 2010; Carrere et al. 2016). The other type is commercially called MicroSludge® process. In MicroSludge® process, chemical pretreatment (i.e., caustic materials) is also implemented to weaken cell membranes, while high-pressure (up to 830 bars) causes cell disruption. In this process, VS reduction is effectively enhanced (Stephenson et al. 2012).

2.3.2 Biological pretreatment

Compared to other pretreatment methods, biological pretreatment offers various advantages. First advantage is attributed to the main use of microorganisms and enzymes to treat sludge in biological pretreatment. Such microorganisms and enzymes demonstrate eco-friendly characteristic as they are more specific and effective. In addition, biological pretreatment could sustain a high flexibility in operation at different environmental conditions with a low special equipment (Parawira 2012).

Biological pretreatment could utilize either aerobic or anaerobic processes. Anaerobic processes are more commonly used in sludge pretreatment due to its effectiveness in pathogens and VS removal, as well as the increase in biogas production (Grubel et al. 2014). In his pioneer work, Parawira (2012) provided a comprehensive overview of the previous studies on biological pretreatments and summarized the advantages and disadvantages (Parawira 2012). However, in brief, the biological pretreatment can be classified into two key categories: (1) adding specific bacteria that could secret certain enzymes; and (2) adding industrial or endogenous enzymes prior to AD processes (Yu et al. 2013).

The importance of using lytic bacterial pretreatment was conducted by (Kavitha, Adish Kumar, et al. 2014). Their study revealed that the removal efficiency of extracellular polymeric substance (EPS) solubilization were highly enhanced. With regards to enzymes, Yu et al. (2013) studied the effects of endogenous amylase, protease and the combination of amylase with protease addition on sludge characteristic. Overall, their findings highlighted the improvement of sludge solubilization, biodegradability and biogas production after endogenous hydrolase pretreatments, apart from slight influence on floc disruption (Yu et al. 2013). Similarly, Liu et al. (2016) compared traditional protease hydrolysis (PH) with a modified protease/EDTA-2Na hydrolysis (PEH) method. In their results, they confirmed the potential of PEH to obtain large SCOD release and high SCOD utilization rate, as well as the fragmentation efficiency (Liu et al. 2016).

In summary, the use of high-cost commercial enzymatic preparations can cause the biological pretreatment procedure to be economically infeasible, and hence low-cost enzymatic pretreatments such as lipases, cellulases, proteases should be well-developed (Parawira 2012).

2.3.3 Chemical pretreatment

2.3.3.1 Ozone

Ozone is a powerful oxidant that could oxidize a wide range of organic and inorganic compounds (Chu et al. 2009). Ozonation was reported to improve sludge solubilization, floc disintegration and degradation of organic matters (Goel, Takutomi, and Yasui 2003; Campos et al. 2009). During the process of ozonation, microbial floc in sludge are broken into fine and dispersed particles, which leads to the increase in SCOD concentration (Chu et al. 2009).

Various factors impact the ozonation processes such as ozone transfer rate and ozone dosage (Linden and Mohseni 2014). For instance, high sludge solids concentration can lead to a limitation in ozone transfer rate and hence insignificant removal of solids. In a similar way, ozone dose significantly influences the effectiveness of sludge pretreatment by ozonation. The optimal ozone doses particularly for the enhancement of anaerobic biodegradability were reported as follows: 0.1 g O_3 g^{-1} COD, 0.2 g O_3 g^{-1} TSS, 0.15 g O_3 g^{-1} TS (H Carrère et al. 2010). It is worth mentioning that high ozone doses can result in a reduction of methane yield and sludge solubilization (H Carrère et al. 2010), while low ozone doses cannot activate biomass activity in sludge.

Goel et al. (2003) conducted an ozone pretreatment for WAS on the laboratory scale, where two ozone doses, 0.015 and 0.05 g O_3/g TS were studied. They observed that 0.05 g O_3/g TS were more effective on both solids solubilization and anaerobic digestion efficiency (Goel, Takutomi, and Yasui 2003). Furthermore, Dyrczak et al. (2007) recommended that ozonation could increase SCOD concentration in the sludge and reduce the excess volume of generated sludge in reactors (Dytczak et al. 2007). In the same concept of reducing sludge production, Campos et al. (2009) applied ozonation and demonstrated its effectiveness with a little requirement to increase the capital cost (Campos et al. 2009).

2.3.3.2 Alkaline and acidic pretreatment

Alkaline pretreatment is implemented using various alkaline solutions such as NaOH, KOH, Ca $(OH)_2$, Mg $(OH)_2$ and ammonia while the acidic pretreatment employs different and widely used regents and acids (e.g., HCl, H_2SO_4, H_3PO_4 and HNO_3). Distinct from other pretreatments, alkaline and acidic methods offer higher efficiency and the ease of performance (Waclawek et al. 2019).

The alkaline pretreatment could lead to an increase in the buffer capacity of the system as well as the specific methanogenic activities and process stability (Zhen et al. 2017). NaOH is the most effective alkaline regent in sludge solubilization, with a followed order of efficiency being NaOH >KOH >$Mg(OH)_2$ and $Ca(OH)_2$ (Kim et al. 2003b). However, too high concentrations of Na^+ and K^+ may cause subsequent inhibition of AD (H Carrère et al. 2010). Due to the high popularity of alkaline pretreatments of sludge, they are normally combined with thermal pretreatment. Valo et al. (2004) combined KOH addition with thermal pretreatment in which the study demonstrated a high enhancement of COD solubilization in thermal-chemical pretreatment compared to single chemical pretreatment (Valo, Carrère, and Delgenès 2004). Kim et al. (2003) reported similar results where the thermal-chemical pretreatment had the best effect on SCOD and VS removal in comparison of the individual thermal and chemical pretreatments (Kim et al. 2003b). In an assessment of three pretreatments: alkaline pretreatment, ultrasonic pretreatment and a combination of alkaline-ultrasonic pretreatment (i.e., alkaline followed by ultrasonic pretreatment), the combined pretreatment attained the best performance in terms of SCOD and nitrogen removal, while the individual alkaline pretreatment was less effective (Chiu et al. 1997).

Regarding the acidic pretreatment, it was reported its effectiveness for lignocellulosic biomass with a minimal impact on lignin hydrolysis (Zheng et al. 2014). However, the formation of toxic by-products and soluble non-biodegradable compounds may be observed after adding acidic additives. Furthermore, other drawbacks in acidic pretreatment is obvious in the impairment of bacteria activities and acceleration of equipment at extremely low levels of pH (Bordeleau and Droste 2011; Zhen et al. 2017). Consequently, special preparation and protection are necessary for such reactors during acidic pretreatment.

Table 2.2. Overview of different pretreatment methods.

Pretreatment		Conditions	Advantages	Disadvantages	References
Mechanical	Ultrasonication	low frequencies (20–40 kHz) are the most efficient	• Decreasing sludge bulking problems • Easy maintenance	• High energy demand	(H Carrère et al. 2010; Zhen et al. 2017)
	Microwave	wavelengths of 1 mm-1m with corresponding oscillation frequencies 0.3−300 GHz	• Quick and uniform heating • Easy to control	• High energy demand	(Zhen et al. 2017)
	high-pressure homogenizer	Sludge pressure is increased up to 900bar and under strong depressurization	• Easy to operate and relatively low cost • Suitable for large scale	• Sludge dewaterability diminished • High energy demand	(H Carrère et al. 2010; Zhen et al. 2017)
Thermal		Temperature between 60-180°C for 25min-1h	• Reducing sludge viscosity • Most efficient in terms of solubilization • Decreasing particle size Sanitation and odor removal	• Largely increased soluble inert fraction and final effluent color • Increased ammonia inhibition in the main digester due to increased performance • More thermal energy	(H Carrère et al. 2010; Kim et al. 2003b; Ferrer et al. 2008; Zhen et al. 2017; Bordeleau and Droste 2011)
Biological		In an additional stage prior to the main digestion process	• Reducing the organic matters of sludge • Eco-friendly	• Limited data in parameter optimization pH issues • Slow start-up	(H Carrère et al. 2010; Kavitha, Jayashree, et al.

					2014; Zhen et al. 2017)
	Ozonation	Optimal ozone dose is 0.1g O_3/g COD,0.2g O_3/g TSS, 0.15g O_3/g TS; Hydrogen peroxide (at 90°C with 2g H_2O_2/g VSS)	• Low energy consumption Improving sludge dewatering Pathogen removal Flexible operation	•Enhancement of biogas production is low • Corrosion problems	(H Carrère et al. 2010; Zhen et al. 2017)
Chemical	Alkaline	NaOH is most effective in sludge solubilization and biogas production, ranking with efficiency NaOH >KOH >Mg $(OH)_2$ and Ca $(OH)_2$	• Temperature is lower • Simple device and easy for operation • High methane conversion efficiency and low cost	• Too high concentration of Na^+ may inhibit AD process • Chemical cost	(H Carrère et al. 2010; C. Bougrier et al. 2006; Bordeleau and Droste 2011; Zhen et al. 2017)
	Acidic	Using HCl, H_2SO_4, H_3PO_4 and HNO_3 pH as low as 2	• Low temperature • Simple device and easy for operation • High methane conversion efficiency and low cost	• May produce toxic by-products • Causing corrosion • Chemical cost	(H Carrère et al. 2010; C. Bougrier et al. 2006; Bordeleau and Droste 2011; Zhen et al. 2017)

2.3.4 Thermal hydrolysis process (THP)

Thermal pretreatment is one of the most popular pretreatment methods for sewage sludge. Whilst other pretreatments (ultrasonic cavitation, ozonation, and high-pressure homogenization) are mainly targeted for WAS, the thermal pretreatment is applicable for both PS and WAS (Wilson and Novak 2009). In their investigations, Wilson and Novak proposed that both PS and WAS can have the same response and results after thermal hydrolysis pretreatment (THP) with regard to SCOD, protein and carbohydrate. Conversely, in terms of the impacts of the treatment on lipids, THP is more favorable to WAS than PS (Barber 2016). This can be attributed to the presence of more lipids in PS compared to WAS. PS produces more VFAs during THP as a result of the breakdown of unsaturated lipids. Furthermore, the production of ammonia from PS is lower than WAS, which correlates with the higher total protein content in WAS (Wilson and Novak 2009).

Overall, THP is more suitable for materials (i.e., sludge categories) that contain high concentrations of carbohydrates and proteins, and low amount of lipids. It is worth noting that THP will not only improve sludge dewaterability and solubilization (H Carrère et al. 2010), but also has the advantage of the increase of the filterability and viscosity of sludge due to the reduction of particle size (C. Bougrier et al. 2006). Additionally, THP can significantly increase the biogas production used to produce electricity and heat (Neyens and Baeyens 2003). Given this remarkable performance of THP, any subsequent AD processes will be surely enhanced.

2.3.4.1 Development of THP

According to (Ødeby, Netteland, and Solheim 1996), THP of sludge has been known since 1935 when Proteus originally developed the process. In brief, the sludge was hydrolysis occurs at temperature range of 160-210ºC and exposure time 30-90 minutes. In his early investigations, Proteus reported a high degree of hydrolysis for the COD (Ødeby, Netteland, and Solheim 1996). Subsequently, thermal hydrolysis process was implemented to dewater sewage sludges for many years (Ødeby, Netteland, and Solheim 1996).

Due to the limitations of experimental work done up until the beginning of 1967, a research program from the Department of Mechanical Engineering at the University College, Cardiff, UK was launched to explore the impact of temperature and time in THP on solubilization and dewaterability of sludge (EVERETT JG 1972). As a result, in 1975, Gossett and McCarty published their findings about improvement of sludge biodegradability after the thermal pretreatment (Haug 2016; Haug et al. 1978).

In the same regard of the thermal pretreatment but with the focus on gas production, Haug (1977) highlighted the improvement of potential of gas production under certain circumstances during the thermal pretreatment (Haug 1977). However, it was unfortunate that there were few deficiencies on their results (Haug 1977). Accordingly, due to the increased concerns about energy consumption and pathogen transmission in case of utilizing the pretreated sludge as fertilizer, a laboratory study at Stanford University was launched (Haug et al. 1978). The findings suggested that thermal pretreatment prior to AD could result in an increase in net energy production, as well as a decrease on odorous compounds. Nevertheless, with the growth of sludge biodegradability, gas production can be reduced if it exceeded an optimum thermal temperature near and beyond 175ºC. This was attributed to the formation of inhibitory substance (Haug et al. 1978).

Although Porteous's process revealed the concept of thermal hydrolysis and later many sites worldwide installed it, almost all the plants built afterwards (from 1938 to the seventies) was closed due to economic issues and technical reasons (i.e., odor problems) in thermal hydrolysis processes. Shortly, a new process called Cambi thermal hydrolysis was developed to minimize the amount of sludge and maximize biogas production (Cano, Pérez-Elvira, and Fdz-Polanco 2015). In 1995, a first full-scale plant using Cambi thermal hydrolysis was commissioned in Hamar, Norway (Kepp et al. 2000). In 1996, Ødeby et al. cooperated with the HIAS WWTP, Norway and verified the results of the improvement of gas production after thermal pretreatment regardless the sludge digestion (Ødeby, Netteland, and Solheim 1996). Based on their results, Cambi thermal hydrolysis solved the challenges occurred in the Porteous process (Kepp et al. 2000).

The interest of thermal hydrolysis pretreatment for sludge has been dramatically increased since the twentieth century, giving rise to a large quantity of research and publication (as depicted in Figure 2.3). To date, thermal hydrolysis has been commercially available for 25 years. In the meantime, Cambi® Thermal Hydrolysis Process (CambiTHP® - Cambi Group AS) and BioThelys® (Veolia Waters Technologies) are the most common pilot- and full-scale commercial thermal hydrolysis processes available on several continents (Kor-Bicakci and Eskicioglu 2019). CambiTHP® is a continuous process encompassing three steps and units. This design makes THP successful in eliminating corrosion, scaling problems, and difficult-to-degrade filtrate COD. In contrast, BioThelys® is vastly secure and mainly aims to improve sludge biodegradability. The two processes have similar operating conditions in which sludge is heated by direct steam for 20-30 minutes at 150-180ºC (Pilli et al. 2015). The systems' design allows a full energy integration to be achieved and recovered in both CambiTHP® and BioThelys® (Cano, Pérez-Elvira, and Fdz-Polanco 2015).

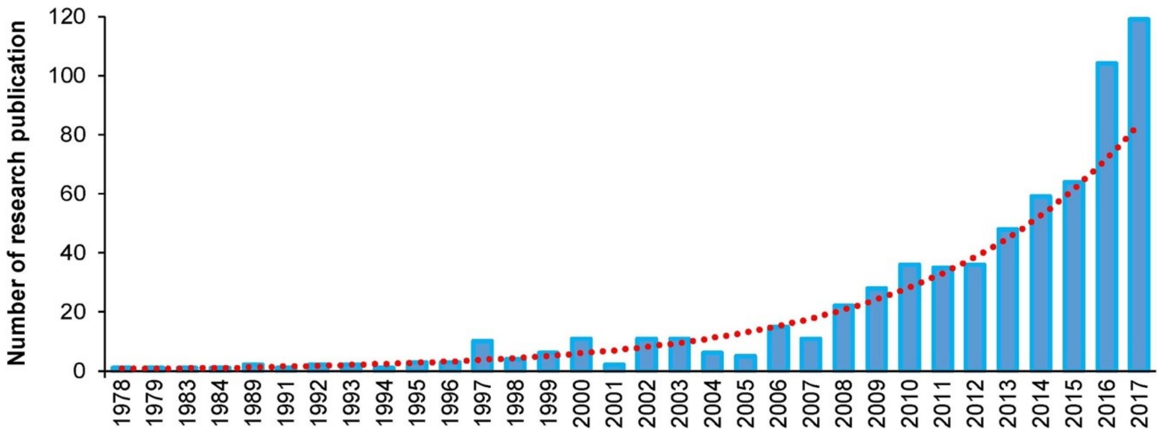

Figure 2.3. Number of scientific documents on the topic of "thermal pretreatment of sludge" published between 1978 and 2017 adapted from (Kor-Bicakci and Eskicioglu 2019).

2.3.4.2 Key influential factors

Both temperature and duration time play dominant roles in the thermal pretreatment. Various studies investigated the influence of different pretreatment conditions (see Table 2.3). The temperature of THP is typically conducted in the ranges of 60-180°C while the treatment time normally varies from 15 minutes to 60 minutes. It is worth noting that most of the studies confirmed the previous conditions (temperature: 160-180°C, treatment times: 30-60 minutes) as the optimum conditions of THP (Dwyer et al. 2008; Claire Bougrier, Delgenès, and Carrère 2008; Kepp et al. 2000; Hélène Carrère et al. 2008). Although THP process requires a high energy demand, it is still can be balanced by maintaining digester temperature through sludge residual heat (Bordeleau and Droste 2011).

In terms of temperature, two ranges can be defined: low temperature (50-90ºC) and high temperature (>100ºC). It was reported that the increase of the operating temperature (up to an optimum temperature), an increase of sludge solubilization and biodegradability, an enhancement of biogas production and a reduction of particle size could be observed (Barber 2016).

For the low temperature range (50-90 ºC), Appels et al. (2010) investigated the impact of three low temperatures (70ºC, 80ºC, 90ºC) on sludge characteristics. The authors observed that the temperature of 70ºC was too low to enhance biogas production, in comparison to a significant increase at 80 and 90ºC (Appels et al. 2010).

In the previous studies that examined operating conditions at extreme temperature (i.e., > 100ºC), mainly higher than 170-190°C, the sludge biodegradability was reduced in spite of attaining high solubilization efficiencies (H Carrère et al. 2010). Furthermore, no biogas production was observed beyond the optimal temperature range (160-180ºC) (Claire Bougrier, Delgenès, and Carrère 2008). Similarly, Pinnekamp (1989) reported an obvious decline of biogas production once condition temperatures > 180ºC, even below the biogas production of the control sludge. This was attributed to the formation of recalcitrant soluble compounds or toxic intermediates (i.e., dioxin) when temperature is typically raised above 175°C (Pinnekamp 1989). The increase of toxicity with the increase in temperature was previously reported (Stuckey and McCarty 1984; Dwyer et al. 2008; Claire Bougrier, Delgenès, and Carrère 2008), and can be elucidated by the “Maillard reaction” and “burnt sugar” reaction (Pinnekamp 1989; Claire Bougrier, Delgenès, and Carrère 2008; Mottet et al. 2009).

For the Maillard reaction, dark colored compounds (named melanoidins) are formed as a result of carbohydrate reaction with protein. These dark colored compounds are recalcitrant and hard to be degraded (Pinnekamp 1989; Dwyer et al. 2008). In contrast, the burnt sugar reactions occur if carbohydrate reacts with other carbohydrates and form compounds such as Amadori (Claire Bougrier, Delgenès, and Carrère 2008; Mottet et al. 2009). Amadori compounds are responsible for the dark brown color and inhibit the degradation of other organics (Pinnekamp 1989; Dwyer et al. 2008; Claire Bougrier, Delgenès, and Carrère 2008; Mottet et al. 2009).

It is worth noting that Maillard reaction occurs even at low temperature (<100ºC) for an extended duration of THP. Thus, a rapid (~1 min) thermal hydrolysis combined with a high pressure and temperature was typically used as a more preferable method of sludge disintegration and solubilization (Kor-Bicakci and Eskicioglu 2019).

Both Hiraoka et al. (1985) and Appels et al. (2010) studied the impact of low temperature and duration time on the thermal treatment. For Hiraoka's experiments at different temperatures (60ºC, 80ºC and 100ºC) and at different time (30, 60 and 120 minutes), the results exhibited a minimal increase in efficiency when the pretreatment time exceeded 60 minutes (Hiraoka et al. 1985). With respect to Appels' work, they examined three different temperatures (70, 80, 90ºC) with three corresponding heating time (15, 30, 60 minutes respectively), sludge solubilization was not effective at 70ºC even with 60 minutes treatment time. However, reducing the heating time to 15 minutes and maintaining the higher temperatures, same observation was obvious (Appels et al. 2010). Similar results were earlier reported at high temperature range (>100ºC) where the study highlighted the impact of both temperature and heating time on the solubilization of solids and dewatering of sludge (EVERETT JG 1972). In the study, the temperature range was 150-220ºC and conditioning time 1-500 minutes. Increasing both time and temperature caused more dissolution of organic matters. Additionally, at retention time > 30 minutes and temperature > 170ºC, a minimal effect on sludge solubilization was observed. The same trend of decline on solubilization was confirmed at temperature > 200ºC and time > 15 minutes. In an investigation of these two conditional parameters (i.e., temperature: 130, 150, and 170°C and time: 15, 30, 60 minutes) during WAS treatment, a slight change in solubilization was observed after 15 minutes (Valo, Carrère, and Delgenès 2004). Given the previous findings, a typical time of 15 minutes is therefore adequate for WAS solubilization.

2.3.4.3 Comparison with other pretreatments

Comparative studies were implemented to elucidate the relative effectiveness of various pretreatments on sludge solubilization and biodegradability (C. Bougrier et al. 2006) and biogas production and pollutant reduction (Kim et al. 2003a). For example, thermal, chemical and ultrasonic pretreatment were compared in terms of biogas production and pollutant reduction. In the study, the particle size, SCOD and VS were significantly decreased by thermal pretreatment, while methane production was slightly similar in the three methods (3390 L/m^3 WAS) (Kim et al. 2003a). Ultimately, in the overall improvement and the efficiency of sludge pretreatment in terms of methane production, SCOD removal and VS reduction, thermal pretreatment was the best alternative. Nevertheless, the combination of thermal pretreatment with other pretreatment could be a great option. Valo and other examined the thermal, chemical and thermal-chemical pretreatment of WAS. The authors supported the thermal-chemical pretreatment as the most efficient method particularly on COD solubilization (Valo, Carrère, and Delgenès 2004).

Therefore, in summary, to further increase sludge solubilization in particular cases, thermal pretreatment methods are more favorable to be combined with chemical pretreatment techniques (i.e. adding alkaline agents).

Table 2.3. Parameters of thermal pretreatment in different conditions

Substrate	THP conditions	Optimal condition	Solid removal (%)	Increase in solid removal (%)	Optimal CH_4 yield	Increase in CH_4 (%)	Reference
WAS	50°C, 30 min; 70°C, 30 min; 90°C, 30 min	70°C, 30 min	26 (VSS)	-	386 (mL CH_4/gm VSS)	19	(Dhar, Nakhla, and Ray 2012)
PS, WAS	70°C, HRT=2d	-	PS: 55 WAS: 43 (VSS)	PS: 55 WAS: 43	PS:162 WAS: 55 (mL/L/d)	PS: 11 WAS: 37.5	(Skiadas et al. 2005)
WAS	70°C, 15 min; 80°C, 30 min; 90°C, 60 min	90°C, 60 min	-	-	240 (mL/g ODS)	989	(Appels et al. 2010)
WAS	170°C, 30 min; 190°C, 60 min	170°C, 30 min	-	-	333 (mL CH_4/g COD_{added})	51	(C. Bougrier et al. 2006)
WAS	135°C, 30 min; 190°C, 15 min	190°C, 15 min	57 (VS)	46	217 (mL CH_4/g COD_{added})	25	(C. Bougrier, Delgenès, and Carrère 2007)
PS and WAS	130°C,140°C,150°C, 160°C,170°C; 30 min	170°C, 30 min	55 (VS)	-	361 (mL CH_4/g VS_{added})	-	(Higgins et al. 2017)
WAS	120°C,150°C,175°C, 30 min; 170°C, 60 min	170°C, 60 min	76 (VSS)	113	156 (mL CH_4/g COD)	108	(L. J. Wu et al. 2015)
WAS	180°C	-	-	-	22 (mL CH4/g VSS_{was})	27	(Tanaka, Kobayashi, and Kamiayama 1997)

Chapter 3

Methodology

3.1 Substrate and inoculum

For this study, fermented primary sludge (FPS), thickened waste activated sludge (TWAS), and anaerobic digester sludge were collected from the Gold Bar Wastewater Treatment Plant (Edmonton, Alberta, Canada). The anaerobic digester sludge collected from a full-scale continuous stirred tank reactor (CSTR)-type anaerobic digester (Gold Bar Wastewater Treatment Plant, Edmonton, Canada) was used as the inoculum for this study. The full-scale anaerobic digestion facility at the Gold Bar Wastewater Treatment Plant is operated at 37ºC and fed with a mixture of FPS and TWAS. The samples were stored at 4ºC in the cold room before use. Table 3.1 summarizes the characteristics of FPS, TWAS, and anaerobic digester sludge.

Table 3.1. Characteristics of substrate and inoculum

Parameters	Inoculum	Substrate	
	Digested sludge	Fermented PS	WAS
TSS (mg/L)	22,444±694	58,222±7,074	49,778±2,912
VSS (mg/L)	19,333±1,453	51,444±5,501	42,889±509
TCOD (mg/L)	25,375±1,431	68,189±4,185	47,716±1,277
SCOD (mg/L)	2,744±1,049	8,542±881	1,682±511
TVFA (mg COD/L)	42±42	3,411±79	160±48
Ammonia (mg/L)	1,122±11	121±10	45±12
pH	7±0	4.8±0	6.2±0

3.2 Thermal hydrolysis experiments

Fig. 3.1 shows the various experimental schemes investigated for thermal hydrolysis prior to the anaerobic digestion. In scheme-1, thermal hydrolysis was conducted for a mixture of FPS and TWAS (volume ratio of 1:1). In scheme-2, thermal hydrolysis was performed only for TWAS, and then mixed with FPS prior to anaerobic digestion. For both schemes, hydrothermal experiments were performed at different temperatures (140, 160, and 180ºC) and exposure times (15, 30, and 60 minutes). Moreover, untreated FPS and TWAS were used for the control test.

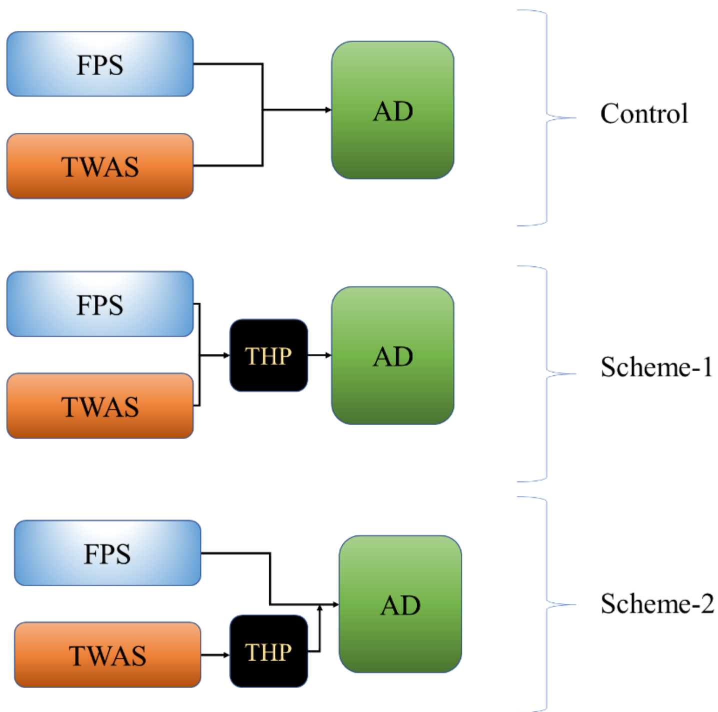

Figure 3.1. Schematic diagram showing the experimental set-up.

Table 3.2 shows the experimental design to investigate the effect of the hydrothermal pretreatment on the solubiliation of sewage sludge. In this study, the experimental design was done considering eight different severity index (SI) values (2.4, 2.7, 2.9, 3.0, 3.2, 3.5, 3.8 and 4.1). Severity index is a parameter widely adopted in industrial applications that combines the effect of the reacting temperature and retention time into one single parameter. It helps to evaluate different conditions of temperature and retention time with one single parameter during the hydrothermal pretreatment experiment (Razavi et al. 2019). The SI was calculated via Equation (3.3) further discussed in Section 3.6.

Table 3.2. Hydrothermal pretreatment design of this study

Temperature (ºC)	Exposure time (minutes)	Severity Index (SI)
140	15	2.4
140	30	2.7
140	60	3.0
160	15	2.9
160	30	3.2
160	60	3.5
180	15	3.5
180	30	3.8
180	60	4.1

The thermal hydrolysis of sludge was carried out using a 2 L bench-scale hydrothermal reactor (Parr 4848, Max. temperature: 350ºC, Max. pressure: 1900 psi, Parr Instrument Company, Moline, IL, USA). The hydrothermal reactor was equipped with an automated controller with auto-tuning capabilities that allows for accurate monitoring of both the heating and cooling parameters including target temperature, holding time (soak) as well as the heating/cooling rate (Lin et al. 2019). The reactor content was continuously mixed with the aid of a mechanical mixer connected to a speed controller (Lin et al. 2019). For each test condition, 450 mL of sludge was delivered into the reactor vessel. After sealing the vessel, the mechanical mixer was set and kept till the end of the cooling cycle. The heating rate was 2-3ºC/min before reaching 100ºC. Afterward, the heating rate was 0.5-1 ºC/min. After reaching the desired temperature, the temperature was maintained for the preferred exposure time (15/30/60 minutes). Then, the reactor was cooled down to room temperature by circulating cold water. In most cases, the entire cooling process took ~ 3 hours to lower the temperature below 50ºC.

3.3 Biochemical methane potential (BMP) test

The effectiveness of different pretreatment conditions was assessed with the biochemical methane potential (BMP) test. The BMP test was performed with a batch anaerobic bioreactor system (ISES-Canada, Vaughan, ON, Canada) (Figure 3.2). The system consisted of 500 mL glass anaerobic bioreactors equipped with mechanical stirrers and electrical motors. The gas outlet port of each reactor was connected to an absorption bottle for capturing acidic gases (e.g., CO_2, H_2S, etc.) from biogas. The gas outlet port of each absorption bottle was connected to a gasbag. The absorption solution contained 3 M NaOH with thymolphthalein as pH-indicator, which could allow capturing all acidic gases from the biogas (Ryue et al. 2019). Thus, pure methane gas could be collected in the gas bag. The volume of methane gas produced from each reactor was measured on a regular basis with a frictionless glass syringe. The BMP tests were conducted for three different conditions: control (untreated FPS and TWAS + inoculum), scheme-1 (treated FPS and TWAS + inoculum), scheme-2 (untreated FPS + treated TWAS + inoculum), and blank (DI water + inoculum). All experiments were conducted in triplicate. Based on the total working volume of 310 mL, the volumes of substrate and inoculum were estimated based on food to microorganism ratio (F/M) of 2 (g of COD of sludge/g of VSS of inoculum). Before starting the experiment, the reactors were purged nitrogen gas for 3 minutes to create an anaerobic condition. No trace nutrients were provided in the reactor. However, 5 g/L of sodium bicarbonate buffer was added to each reactor to avoid any pH drop during batch operation of BMP tests. During experiments, mesophilic condition (37 ±2°C) was maintained with water baths. The total duration of the experiment was 25 days.

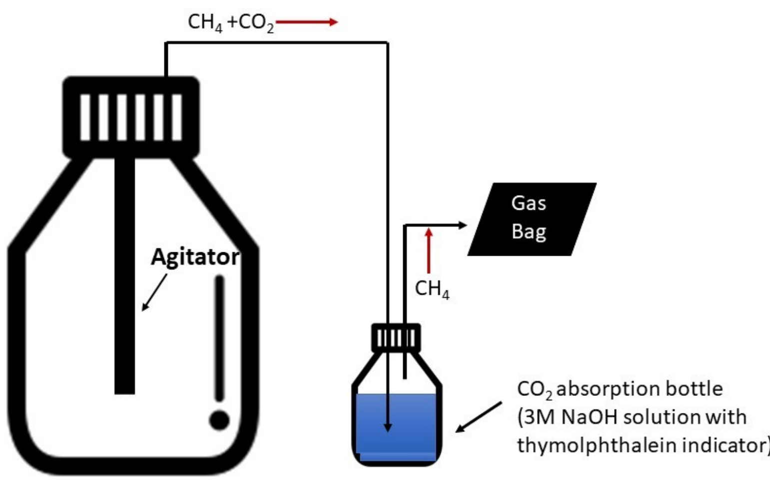

Figure 3.2. Schematic diagram of experimental set-up for biochemical methane potential (BMP) test and methane volume measurement.

3.4 Analytical methods

The chemical oxygen demand (COD) and total ammonia nitrogen (TAN) concentrations were measured using Hach reagent kits (Hach Co., Loveland, Colorado, USA). Samples were filtered with 0.45 μm membrane syringe filters for soluble chemical oxygen demand (SCOD) and TAN analysis. The volatile fatty acids (VFAs) concentrations were measured with an ion chromatograph (DionexTM ICS-2100, Thermos Scientific, USA) equipped with an electrochemical detector (ECD) and microbore AS19, 2 mm column. For analysis of VFAs (acetate, propionate, and butyrate), samples were filtered with 0.2 μm membrane syringe filters. Total suspended solids

(TSS) and volatile suspended solids (VSS) were determined according to a standard method (Bruno 2017). pH was measured using a bench-top pH meter (AR15 pH meter, Fisher Scientific, Pittsburgh, PA).

3.5 Estimation of kinetic parameter

To monitor the rate of methanogenesis from the methane (CH_4) experimental data production and in order to estimate the CH_4 production over time from the bioreactors, Equation (3.1) was used as illustrated (Li et al. 2015; Barua, Zakaria, and Dhar 2018):

$$V = V_m \cdot (1 - e^{-kt}) \qquad (3.1)$$

Where k = methanogenesis rate constant (d^{-1})

t = time (days)

V = the cumulative CH_4 volume at time (mL)

V_m = the ultimate CH_4 production (mL)

To estimate the values k and develop the best fit model of the CH_4 production, the relative least squares method in the Microsoft Excel Solver was initially implemented. While using the solver, the normalized errors were adjusted to be minimal ≤ 0.5. Due to the limited iterations in the Microsoft Excel Solver (5 iterations), further non-linear regression analyses using Minitab 19 software was performed to ensure generating the best model fit and values. The starting values estimated from excel solver was used in the first iteration in Minitab to minimize the standard error estimate and to attain best fit model of the data. In Minitab analyses, the Gauss-Newton Algorithm and maximum of 400 iterations was used and tolerance of 10^{-5}, and 95% confidence level for all intervals were preserved. It is noticed that the estimated values k from both excel solver and Minitab in most of the experimental data sets were matched (differences were 2-3%).

3.6 Calculations

VSS reduction efficiency (R) was calculated using Equation (3.2) (Azizi et al. 2019):

$$R\ (\%) = (VSS_B - VSS_A)/VSS_B \times 100 \qquad (3.2)$$

Where VSS_B = VSS concentration before the process (mg/L)

VSS_A = VSS concentration after the process (mg/L)

Severity index (SI) was calculated using Equation (3.3) (Razavi et al. 2019):

$$SI = \log \exp[\frac{T-100}{14.75} \times t] \qquad (3.3)$$

Where T = the pretreatment temperature (ºC)

t = the pretreatment retention time (minute)

Chapter 4

Results and Discussion

4.1 COD solubilization

Figure 4.1 shows the COD concentrations of untreated (control) and pretreated samples from two experimental schemes. In general, TCOD concentration in the pretreated sludge samples should remain almost constant after pretreatment (Dhar, Nakhla, and Ray 2012). However, in both two schemes (scheme-1 and scheme-2), TCOD concentrations slightly decreased after the pretreatment. This could be attributed to sludge being accumulated on the reactor's wall during transfer (C. Bougrier et al. 2006). Also, the volatilization of organics could also occur during thermal pretreatment (Mendez et al. 2014). In scheme-1, SCOD concentrations increased from 5112±185 mg/L (untreated FPS+TWAS) to a range of 15065±1021 to 26126±8488 mg/L, where the maximum SCOD concentration was achieved at the pretreatment condition of 160ºC, 30 minutes. Analogous to scheme-1, SCOD concentration increased for all pretreatment conditions in scheme-2. However, for scheme-2, the maximum increase in SCOD concentration was achieved at 180ºC, 60 minutes (24343±190 mg/L); SCOD concentration of untreated TWAS was 1682±511 mg/L. The increase of SCOD concentration after THP implies that THP promoted the solubilization of particulate organics in the sludge (Kakar et al. 2019). The disintegration of biomass and release of intracellular organic matters in sludge occurs during the thermal pretreatment, led to an increase of dissolved organics in the liquid phase. This could be related to SCOD increase (Park and Ahn 2011; Grubel et al. 2014).

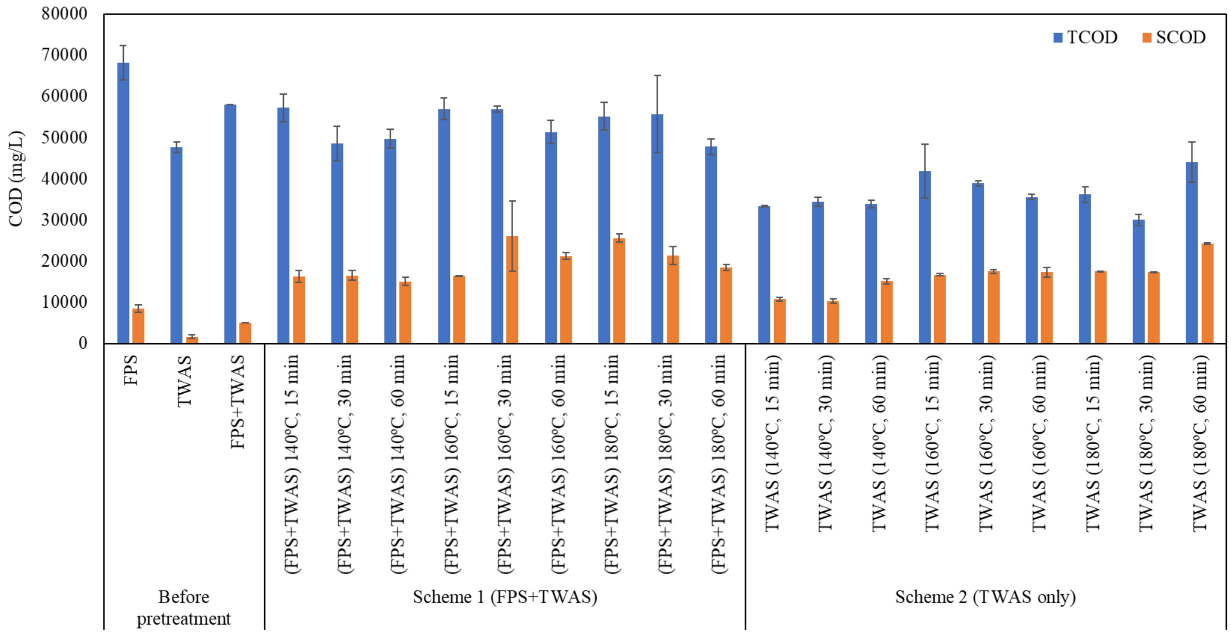

Figure 4.1. COD concentrations of raw and pretreated sludge samples.

The degree of solubilization and the extent of hydrolysis of the sludge can be reflected by the changes in SCOD/TCOD ratios (Park and Ahn 2011; Cigdem Eskicioglu, Kennedy, and Droste 2006). Fig. 4.2 shows the impact of different pretreatment conditions on the SCOD/TCOD ratios. As anticipated, all the pretreatment conditions caused considerable increases in the ratios of SCOD/TCOD relative to the corresponding control samples (i.e., FPS+TWAS and TWAS). In scheme-1, the highest SCOD/TCOD of 46% occurred at 160ºC, 30 minutes (see Fig. 4.2), which also showed a maximum increase in SCOD concentration (see Fig. 4.1). However, 180ºC, 15 minutes also showed a similar SCOD/TCOD ratio. In scheme-2, THP under the condition of 180ºC, 30 minutes showed the highest SCOD/TCOD ratio of 58%. It is worth noting that in scheme-2, COD solubilization was similar between the condition of 160ºC, 60 minutes and 180ºC, 15 minutes at ~ 49% ($p < 0.01$). It can be explained due to the fact that both these two conditions were under the same SI value of 3.5 (discussed later).

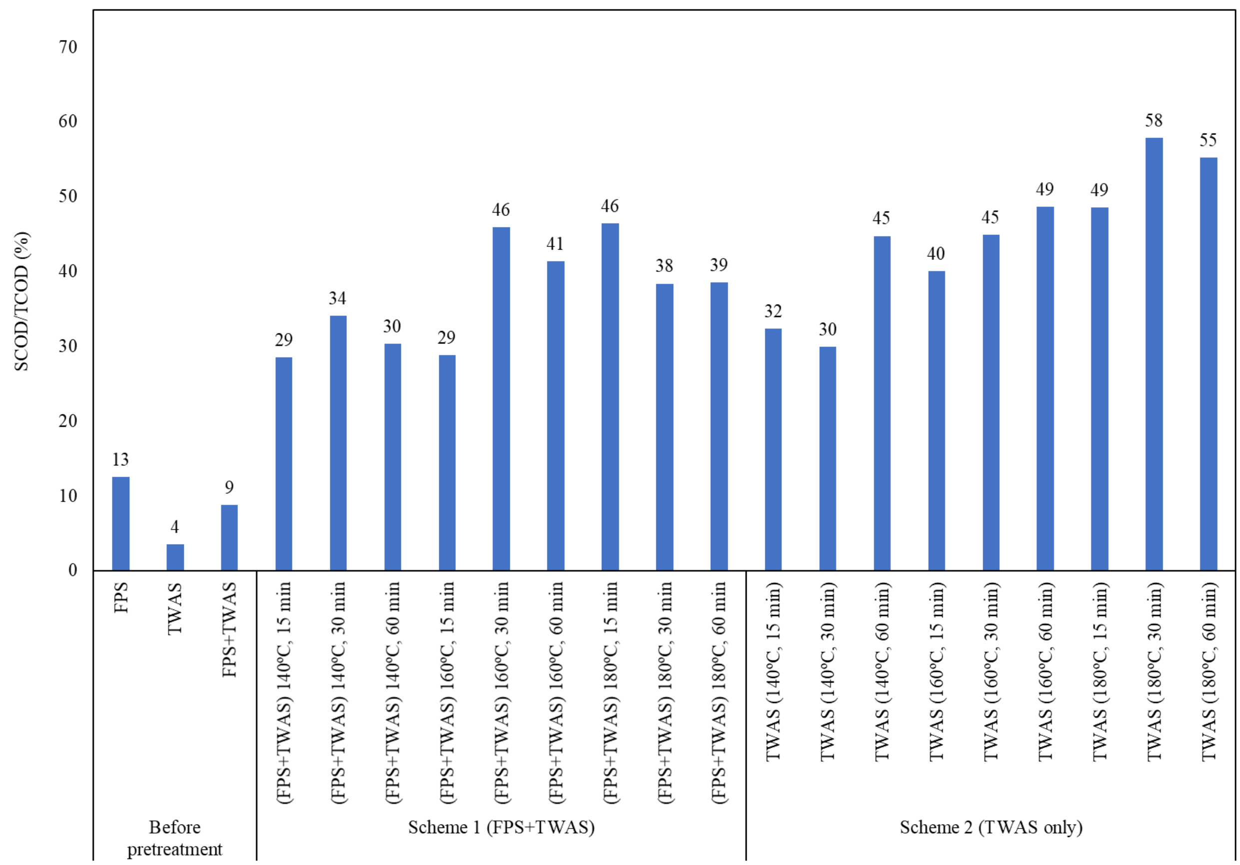

Figure 4.2. SCOD/TCOD ratios of the raw and pretreated sludge.

4.2 Solids removal

Figure 4.3 illustrates the TSS and VSS concentration of the untreated and pretreated sludge. The application of THP under different conditions led to a considerable reduction of TSS and VSS concentrations. For both schemes, the maximum decrease in TSS and VSS concentrations was achieved with 180ºC, 60 minutes (TSS: 24222 ± 2238 mg/L and 15056 ± 1584 mg/L, VSS: 20778 ± 3289 mg/L and 12389 ± 1711 mg/L, respectively). The decrease of TSS and VSS contents can be significantly correlated with the increase in temperatures, while the effect of pretreatment duration time on the SS reduction was less significant than that of the temperature. For example, in scheme-2, VSS concentrations remained almost the same for different exposure times at 140ºC.

According to the previous studies, it was reported that the solubilization efficiency at a constant temperature increased as the thermal treatment time increased, but it did not markedly increase at the thermal treatment time of over 30 minutes (L. J. Wu et al. 2015), which was comparable to the results in this study.

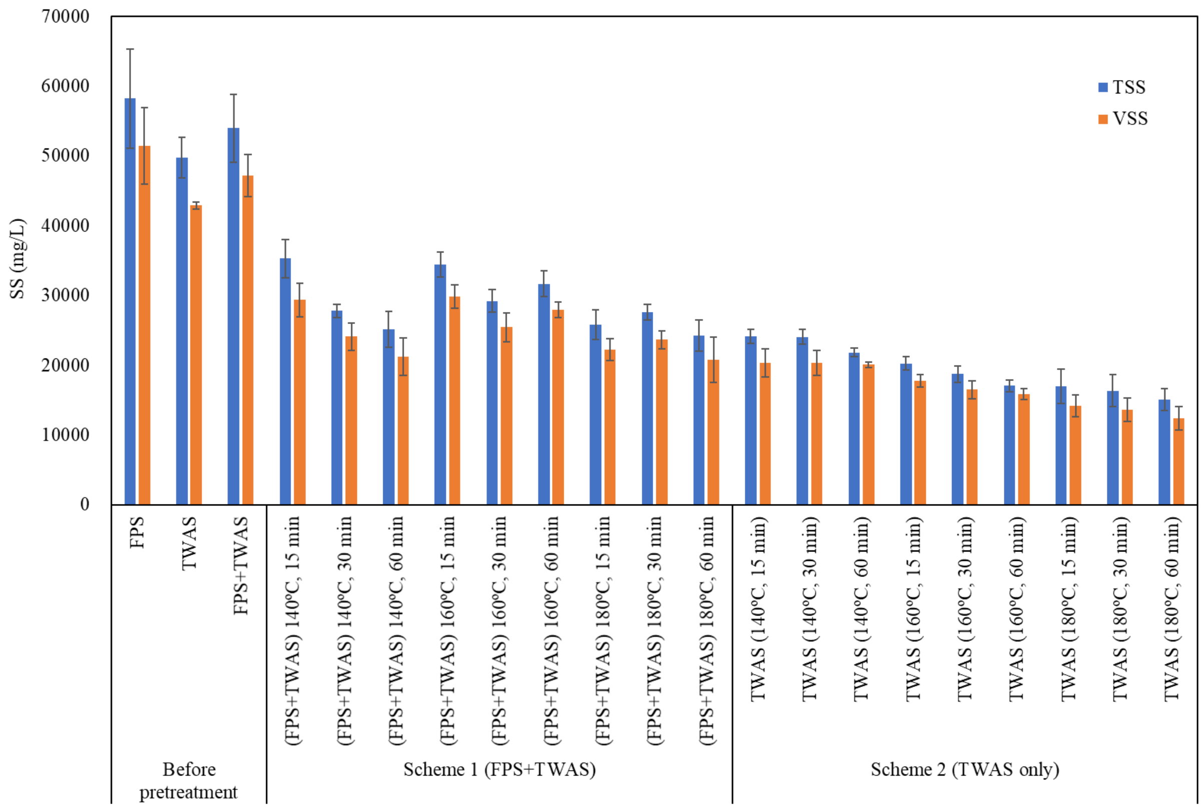

Figure 4.3. TSS and VSS concentrations of raw and pretreated sludge samples.

Since the hydrothermal pretreatment solubilizes particulate organic matters (Razavi et al. 2019), VSS removal efficiencies were calculated (see in Figure 4.4). The highest VSS removal efficiencies of 56% and 71% were observed at the condition of 180ºC, 60 minutes for scheme 1 and scheme 2, respectively. Bougrier et al. (2008) also reported the solubilization levels of 40% - 80% at the temperature range 170-190ºC in terms of solids reduction (Claire Bougrier, Delgenès, and Carrère 2008). It is noteworthy that a comparison of the results of the SS reduction tests with those of the COD solubilization study revealed that for a given scenario, the percentage of VSS reduction was higher than the degree of COD solubilization. For example, at the condition of 180ºC, 60 minutes in scheme-2, although the application of the THP resulted in 71% VSS reduction (Figure 4.4), it converted 16% of the particulate COD into SCOD. This observation can be explained by the fact that the suspended solids contents were analyzed by filtering the samples through 1.6 µm filter papers. However, for SCOD analysis, the samples were filtrated through 0.45 µm syringe filters. Thus, THP led to the solubilization of organics in the form of colloidal matters with a size range of 0.45–1.6 µm, which are often considered as slowly biodegradable. In terms of sludge solubilization (SCOD solubilization and VSS reduction efficiency), scheme-2 contributed to higher improvement in contrast with scheme-1. Therefore, THP had a better performance of sole TWAS rather than the mixture of FPS and TWAS on the sludge of solubilization, which is in agreement with the literature that THP is more effective on WAS than PS (Mottet et al. 2009; Ge, Jensen, and Batstone 2010; H Carrère et al. 2010; Wilson and Novak 2009).

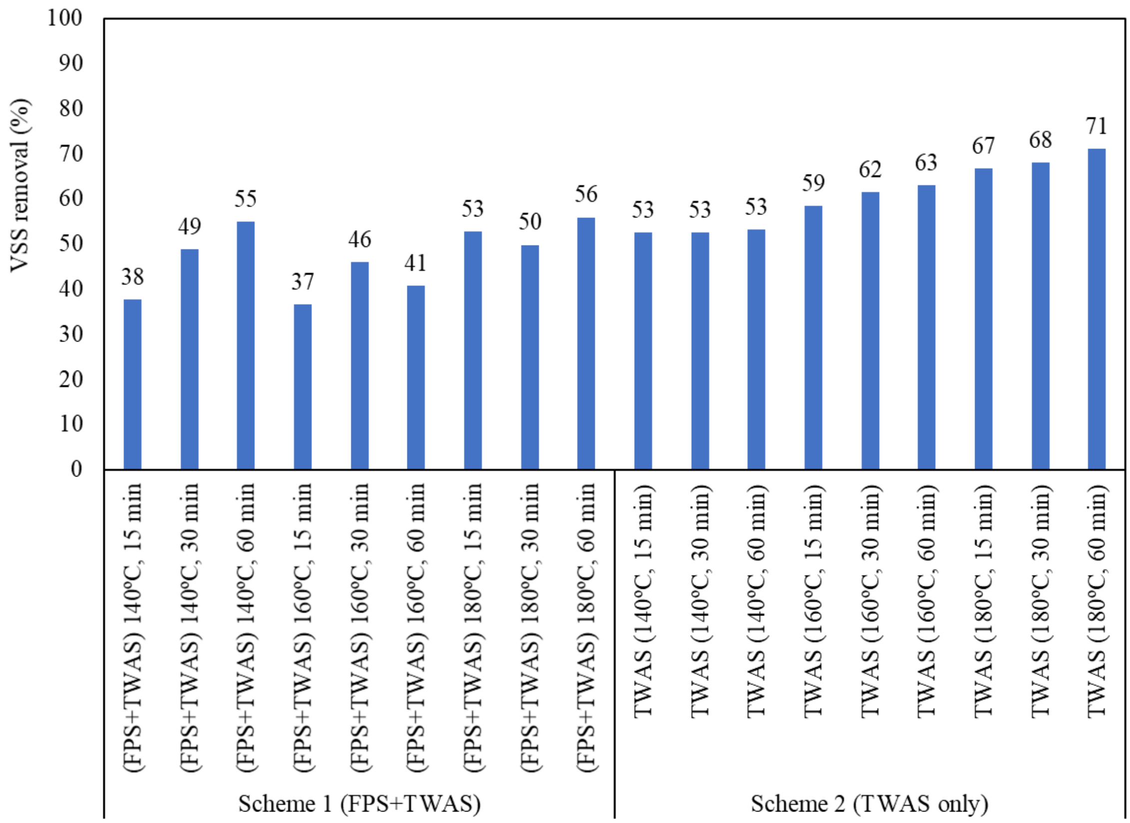

Figure 4.4. The effect of hydrothermal pretreatment on VSS removal efficiencies.

4.3 VFAs production

Figure 4.5. shows the concentrations of VFAs (acetate, propionate, and butyrate) in the raw and pretreated sludge. The overall trend showed an increase in VFAs concentration after all pretreatment conditions. Notably, VFAs concentrations increased with increasing temperature. In both schemes, pretreatment at 180ºC contributed to the highest increase in VFAs concentrations (acetate: 1693 ± 57 mg/L COD and 1157 ± 39 mg/L COD, propionate: 1134 ± 55 mg/L COD and 455 ± 36 mg/L COD, butyrate: 1001 ± 34 mg/L COD and 440 ± 23 mg/L COD, respectively). However, exposure times showed little impact on VFAs production; VFAs concentrations remained almost constant under different exposure times. The rise in VFAs

concentration was supposed to be linked to lipid degradation (Claire Bougrier, Delgenès, and Carrère 2008). Wilson and Novak (2009) performed a laboratory simulation of THP on PS and WAS in terms of proteins, lipids, and polysaccharides. In their study, more VFAs were produced from PS, and it was linked to the hydrolysis of unsaturated lipids (Wilson and Novak 2009).

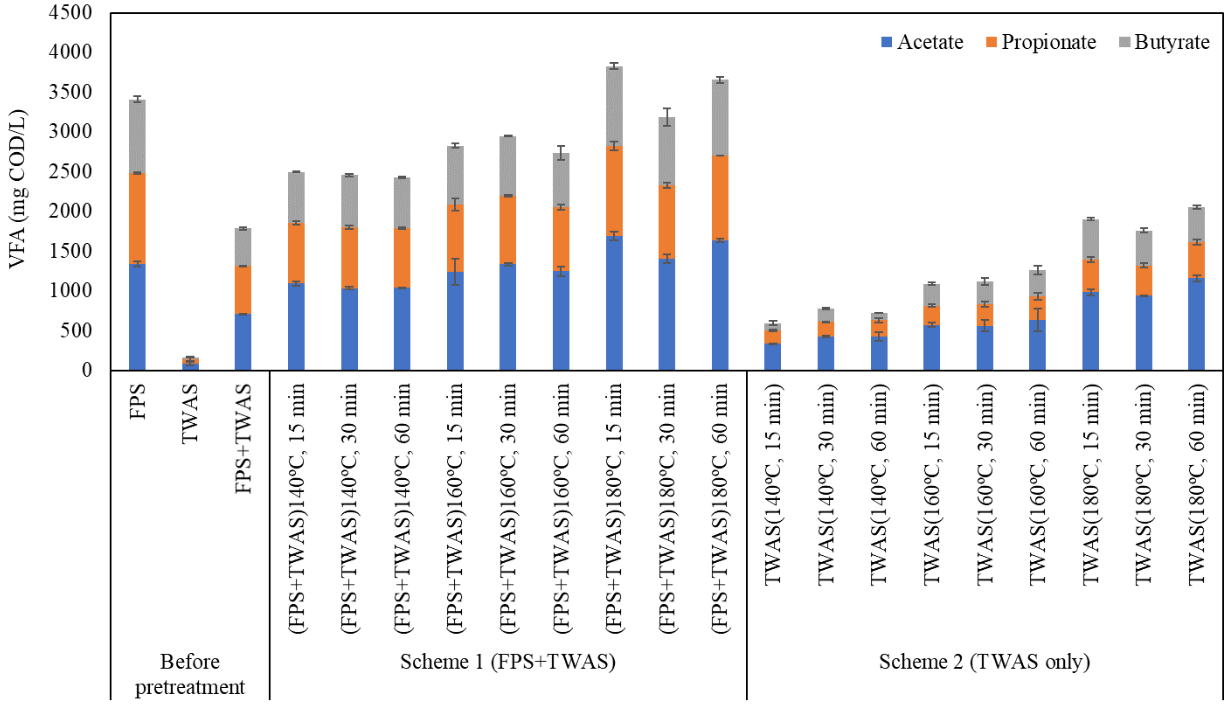

Figure 4.5. Impact of different pretreatment conditions on VFAs production.

4.4 Ammonia nitrogen

Ammonia concentration is of vital importance in the AD process to maintain system stability; proper ammonia concentration provides buffer capacity for active microbial activities (Angelidaki and Sanders 2004). However, high ammonia levels result in system toxicity and further inhibit AD performance (Lin et al. 2018). Figure 4.6 shows the concentration of total ammonia nitrogen (TAN) in the untreated and pretreated sludge. An obvious increase in TAN concentrations was observed after all the pretreatment conditions; TAN concentrations increased with the increase in temperature. The highest ammonia concentration occurred at the condition of 180ºC, 15 minutes at 361 ± 14 mg/L in scheme-1, and the condition of 180ºC, 60 minutes at 468 ± 12 mg/L in scheme-2. Also, increases in ammonia concentrations in scheme-2 (FPS+TWAS) was slightly higher than that observed for scheme-1 (TWAS). According to Wilson and Novak (2009), ammonia was produced from WAS, which correlates well with its higher total protein content relative to PS.

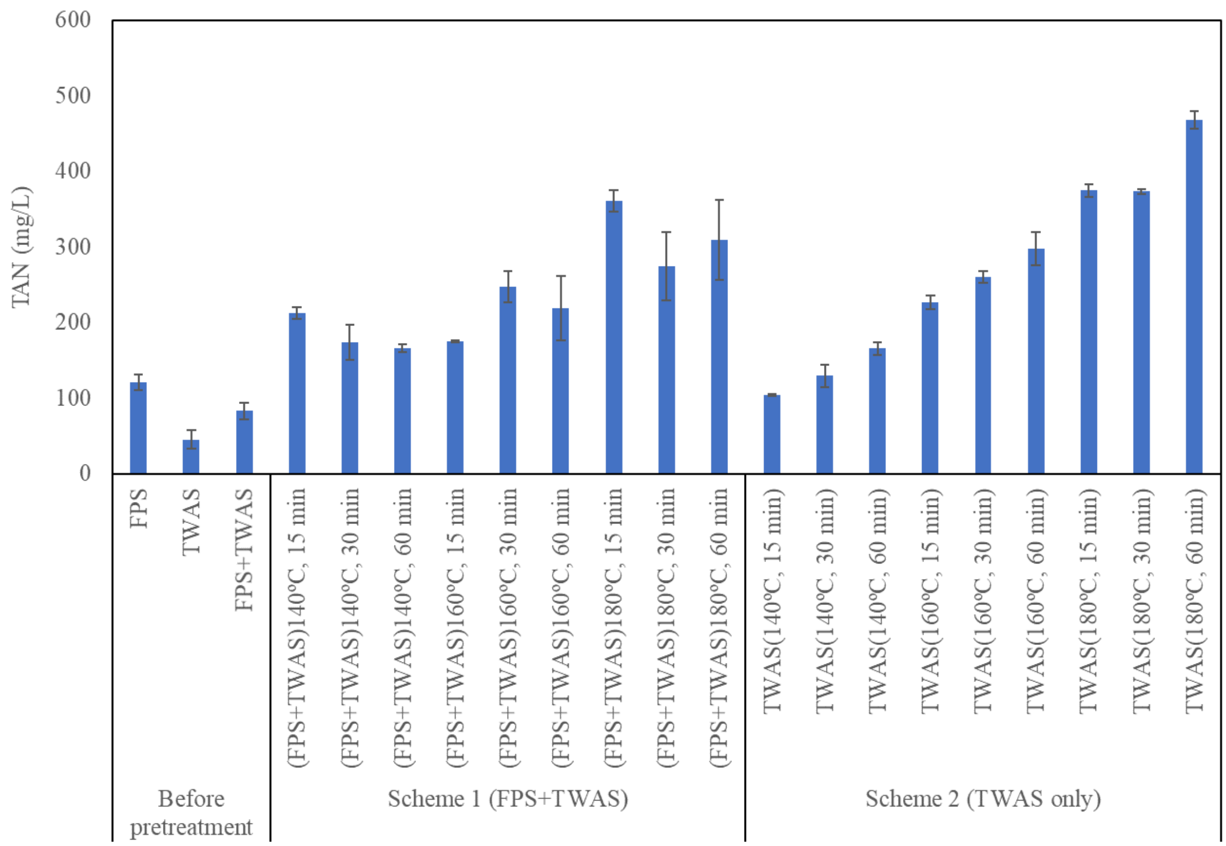

Figure 4.6. Effect of THP on total ammonia nitrogen.

4.5 Methane potential and kinetics

4.5.1 Biomethane yield

The BMP test was terminated after 25 days when the biogas production became nearly negligible except for the conditions of 140ºC, 30 minutes, and 160ºC, 15-60 minutes in scheme-1. The cumulative methane yields from raw untreated and thermally pretreated sludge are shown in Figure 4.7 (scheme-1) and Figure 4.8 (scheme-2). Different patterns of the cumulative methane yields were observed depending on the range of pretreatment temperatures and exposure times used. For both schemes, samples treated under 180ºC showed longer lag phases, as compared to samples treated at 140 and 160ºC. Interestingly, the lag phase for the untreated control sample was relatively shorter than most of the pretreated samples. However, except for samples treated at 180ºC, most of the pretreated samples ultimately provided higher methane yields, as compared to the control. A previous study also suggested that gas production increased as the increase of THP temperature until a threshold temperature is reached, above which the biogas production decreased (Higgins et al. 2017). Dwyer et al. (2008) found no increase in methane production while increasing THP temperature above 150ºC (Dwyer et al. 2008). Mottet et al. (2019) reported an optimal temperature of 165ºC through three different temperatures (110ºC, 165ºC, and 220ºC) (Mottet et al. 2009). Bougrier et al. (2018) reported the temperature lower than 190ºC enhanced methane production with a temperature range from 90-210ºC (Claire Bougrier, Delgenès, and Carrère 2008). Xue et al. (2015) observed a decrease in gas production at 180ºC (temperature: 120ºC, 140ºC, 160ºC and 180ºC) (Xue et al. 2015). This is usually ascribed to the Maillard reactions, where carbohydrates and amino acids in the formation of melanoidins, which are difficult or impossible to degrade (H Carrère et al. 2010). However, the reasons for the differences in the results are not clear but could be due to the specific testing conditions and the sludge properties (Higgins et al. 2017). Thus, further research would be needed to understand the underlying mechanism behind such observation.

According to the results, the methane yield was increased by 9–161% depending on the pretreatment condition. In scheme-1, the maximum methane yield of 272 ± 24 mL CH_4/g COD was obtained under a pretreatment condition of 160ºC, 60 minutes, 161% higher than that of the control digester (104 ± 127 mL CH_4/g COD). In scheme-2, the highest biomethane yield of 182 ± 155 mL CH_4/g COD was achieved at the condition of 140ºC, 30 minutes, which was 75% greater than that of the control one (104 ± 127 mL CH_4/g COD). Following the untreated sludge, the lowest methane production belonged to the condition of 180°C, 60 minutes for both these two schemes. It is worth mentioning that the different trends of the THP impacts on the sludge solubilization and biomethane production were observed. The increase of the SCOD and the decrease in the biogas production was found for a given condition of 180ºC. Previous studies suggested that some soluble non-biodegradable organics could be produced under severe conditions (i.e., high temperatures) such as melanoidins (Appels et al. 2010; Luo et al. 2019).

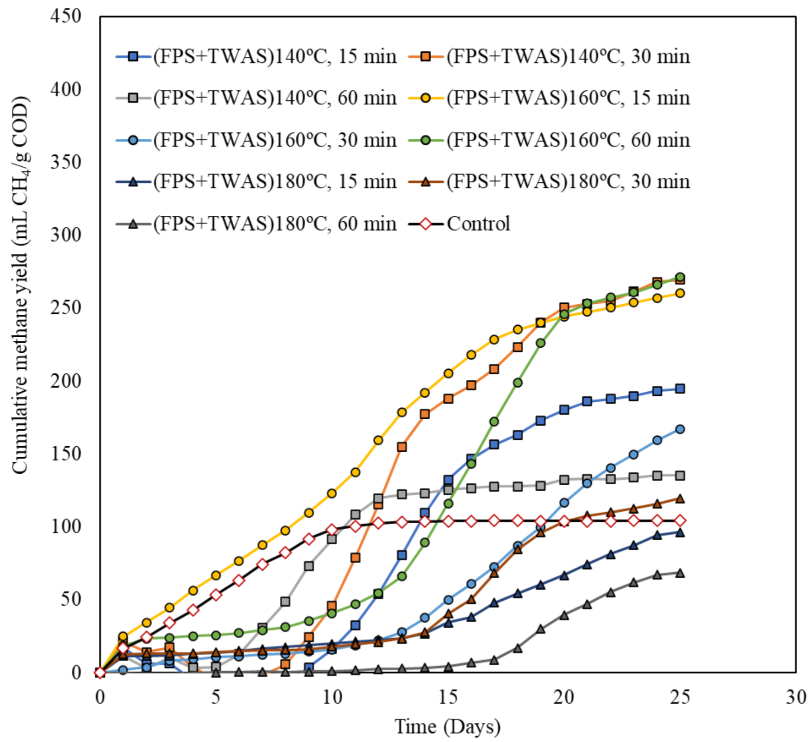

Figure 4.7. The time-course profile of cumulative methane yield for scheme-1.

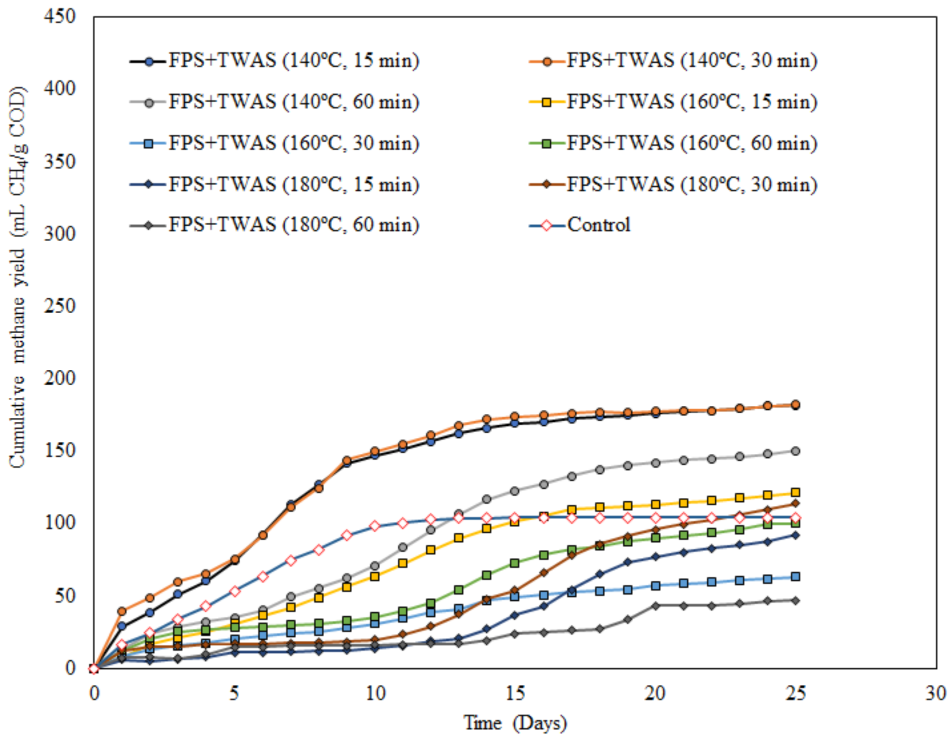

Figure 4.8. The time-course profile of cumulative methane yield for scheme-2.

4.5.2 Methanogenesis kinetics

Table 4.1 shows the best fit of the methanogenesis rate constant (k) for different experimental conditions. Interestingly, all the pretreatment conditions showed lower k values compared to the k value for the control. The maximum k value of 0.122 ± 0.005 /d was achieved for the condition of 140ºC, 60 minutes in scheme-1, followed by the second highest k value (0.090 ± 0.005 /d) at 160ºC, 15 minutes, and the third one (0.081 ± 0.006 /d) at 140ºC, 30 minutes. In contrast with scheme-1, two pretreatment conditions showed comparable methanogenesis rates with the control. The maximum k value of 0.165 ± 0.002 /d was observed for the condition of 140ºC, 30 minutes in scheme-2, followed by the second maximum k of 0.159 ± 0.003 /d at 140ºC, 15 minutes. These results were comparable with Figure 4.8 – 140ºC, 30 minutes and 140ºC, 15 minutes showed the highest and the second-highest methane yields after THP. It indicated that THP had a better influence on maintaining methanogenesis rates when only TWAS was pretreated at 140ºC (15-30 minutes). However, the pretreatment of a mixture of FPS and TWAS produced higher ultimate cumulative biomethane production while comparing with that of sole TWAS, which can be explained by the fact that fermented primary sludge already contained a higher level of readily biodegradable organics. However, thermal pretreatment adversely affected the methanogenesis rates for both schemes, except for two conditions in scheme-2 (140ºC; 15-30 minutes). Koupaie et al. (2017) applied microwave pretreatment to TWAS and found the k values for all the pretreatment conditions were higher than that of the untreated one (Hosseini Koupaie, Johnson, and Eskicioglu 2017). In another study, Azizi et al. (2019) reported an increase of k values after thermal pretreatment for source-separated organics (Azizi et al. 2019). This dissimilarity for the k values might be due to the nature of the substrates and the application of different pretreatment methods.

Table 4.1. The specific methanogenesis rate constant (k) of AD processes

Experimental conditions		Methanogenesis rate constant k (d^{-1})	Standard error for k
Scheme 1 (FPS+TWAS)	(FPS+TWAS) 140ºC, 15 min	0.077	0.006
	(FPS+TWAS) 140ºC, 30 min	0.081	0.006
	(FPS+TWAS) 140ºC, 60 min	0.122	0.005
	(FPS+TWAS) 160ºC, 15 min	0.090	0.005
	(FPS+TWAS) 160ºC, 30 min	0.045	0.005
	(FPS+TWAS) 160ºC, 60 min	0.055	0.006
	(FPS+TWAS) 180ºC, 15 min	0.054	0.004
	(FPS+TWAS) 180ºC, 30 min	0.055	0.006
	(FPS+TWAS) 180ºC, 60 min	0.041	0.005
Scheme 2 (TWAS only)	TWAS (140ºC, 15 min)	0.159	0.003
	TWAS (140ºC, 30 min)	0.165	0.002
	TWAS (140ºC, 60 min)	0.090	0.005
	TWAS (160ºC, 15 min)	0.094	0.005
	TWAS (160ºC, 30 min)	0.091	0.004
	TWAS (160ºC, 60 min)	0.080	0.005
	TWAS (180ºC, 15 min)	0.057	0.005
	TWAS (180ºC, 30 min)	0.061	0.005
	TWAS (180ºC, 60 min)	0.072	0.004
Control	Untreated FPS+TWAS	0.158	0.004

4.6 Significance of SI

As summarized in Table 3.2, depending on the pretreatment temperatures and exposure times, experiments were conducted under eight different SI values (2.4, 2.7, 2.9, 3.0, 3.2, 3.5, 3.8 and 4.1) for each scheme. Figures 4.9 and 4.10 show the SCOD/TCOD ratios and VSS removal efficiencies as a function of SI, respectively. In general, with increasing SI sludge solubilization also increased. For scheme-2 (TWAS only), COD solubilization and VSS removal efficiencies showed a strong linear correlation with SI ($R^2 > 0.9$). In agreement with the findings of this study, Kakar et al. (2019) reported five different SI values for sourced-separated organics, and it maintained a positive correlation between SI and COD solubilization (Kakar et al. 2019). However, such a strong correlation was not observed for scheme-1 (FPS+TWAS) in this study, which could be due to the difference in sludge characteristics. For instance, it is possible that a largerportion of readily biodegradable organics has already been solubilized and fermented in FPS than TWAS (see Table 3.1), THP may not improve it as much if samples have a high biodegradability (Higgins et al. 2017). Moreover, during the fermentation process, the liquid enriches with easily biodegradable organics (i.e., VFAs) is pumped to biological treatment process to enhance nutrients removal efficiency, the remaining particulate fractions of FPS might include more recalcitrant organics, which could also lead to a weak correlation between solubilization efficiencies and SI values.

Methane potential as a function of SI is shown in Figure 4.11. It was evident that higher SI values negatively affected methane yield for both scenarios. Although higher temperatures and longer retention time largely increased sludge solubilization, it did not show considerable improvement in terms of biomethane yields. Similar results were also found by Razavi et al. (2019). They investigated THP of source-separated organics under five SI values (3, 3.5, 4, 4.5 and 5). From their findings, the maximum methane production rate decreased with the increase of the SI intensity (Razavi et al. 2019).

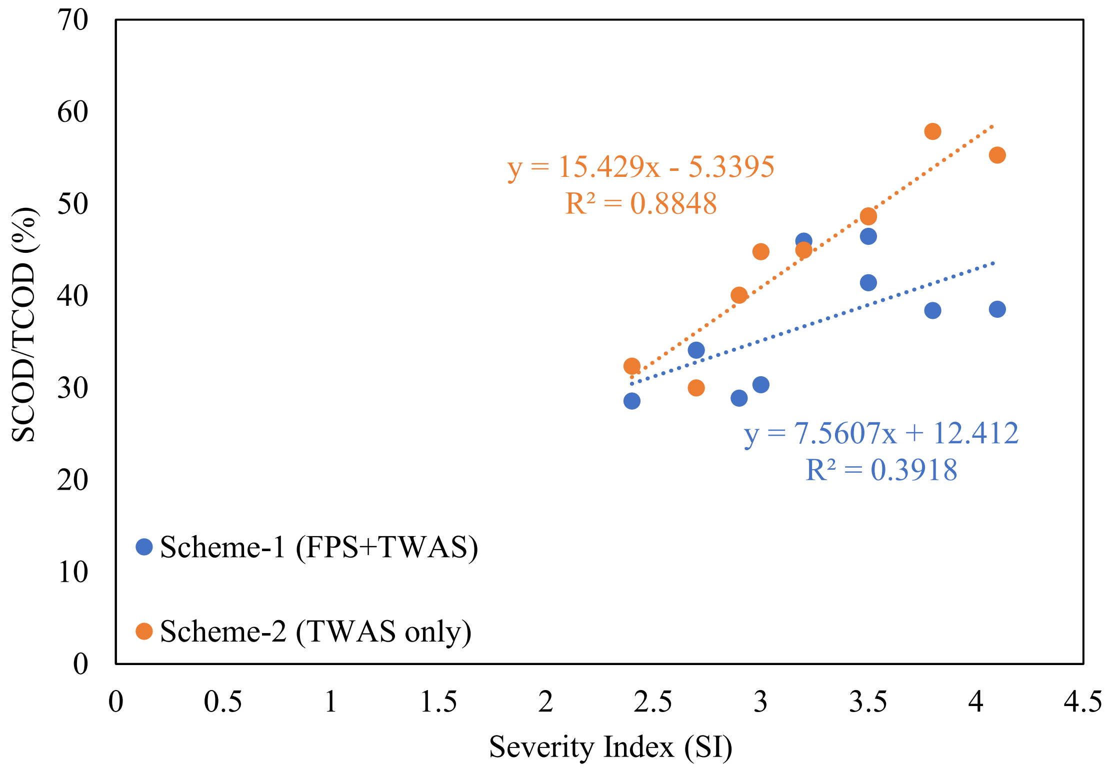

Figure 4.9. Sludge solubilization as a function of SI in terms of SCOD/TCOD ratios.

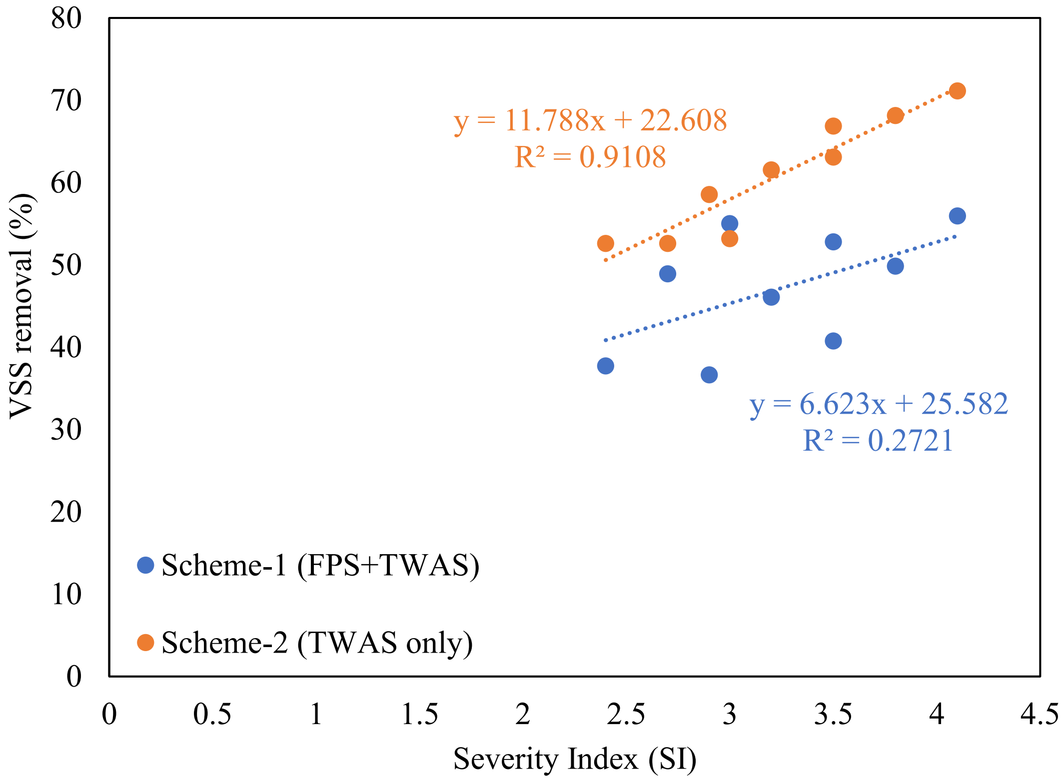

Figure 4.10. Sludge solubilization as a function of SI in terms of VSS removal efficiency.

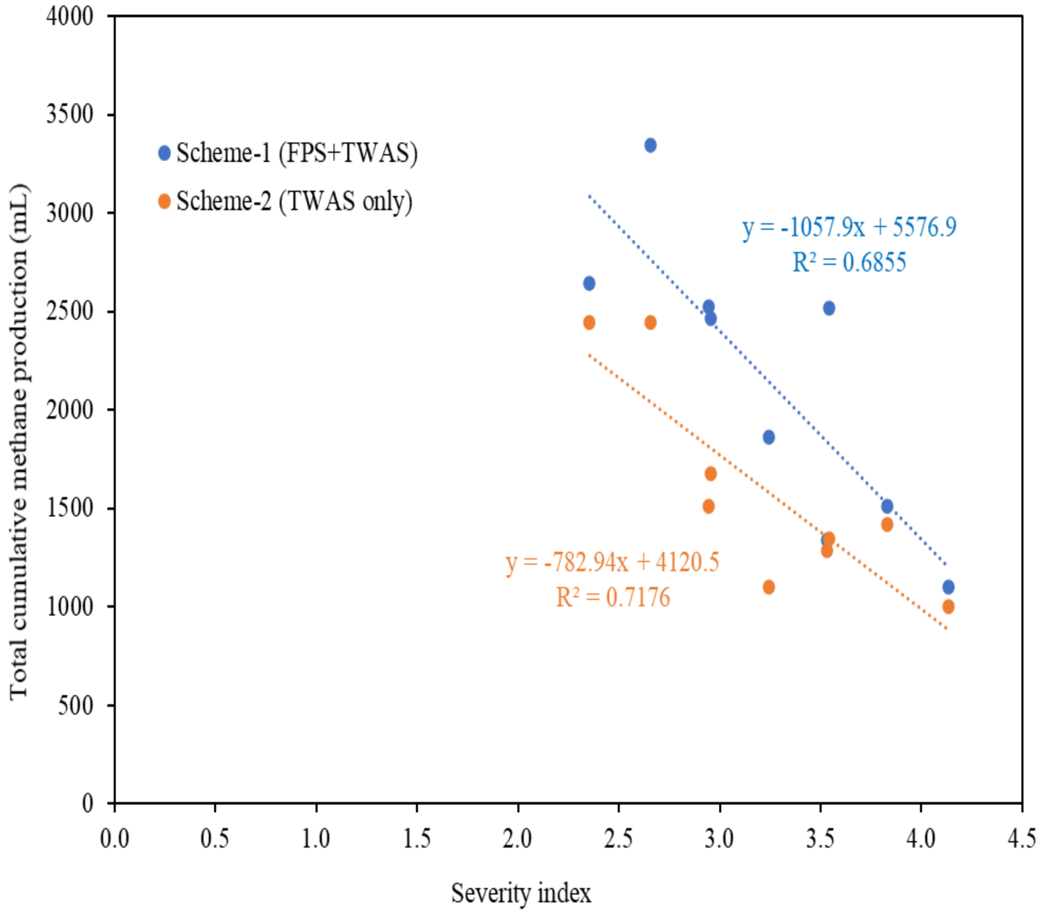

Figure 4.11. Methane potential as a function of SI.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

The major findings and take-home messages from this study are summarized below:

- THP enhanced the sludge solubilization in terms of COD solubilization, VSS reduction, VFA accumulation and TAN production for all conditions in both two schemes. The maximum degree of COD solubilization and VSS reduction were observed at the conditions of 160ºC, 30 minutes, 180ºC, 60 minutes for scheme-1, and 180ºC, 60 minutes for scheme-2. However, for scheme-1, the highest methane yield (272 ± 24 mg/L COD) and the maximum k values (0.122 ± 0.005 /d) occurred at the conditions of 160ºC, 60 minutes and 140ºC, 60 minutes, respectively. For scheme-2 both the highest methane yield (182 ± 155 mg/L COD) and the maximum k values (0.165 ± 0.002 /d) were found at 140ºC, 30 minutes.
- COD solubilization and VSS removal efficiencies showed a positive correlation with severity index in scheme-2. However, linear correlation was not found for hydrothermal treatment of scheme-1. It could be attributed to the larger fraction of readily biodegradable organics in FPS than TWAS.

- Although THP significantly promoted the sludge solubilization, pretreatment temperature >180ºC could lead to the release of inhibitory/refractory substances and a decreased in the biogas production. Higher severity index negatively affected methane yield for both cases, because the soluble sludge fraction that is converted to methane changes to the non-convertible-to-methane fraction under severe treatment.

5.2 Recommendations

- Further investigation of long-term continuous operation with pretreated sludge to evaluate the process performance is warranted.
- The techno-economic assessment for retrofitting different THP schemes needs to be conducted to evaluate feasibility of the process.
- A detailed energy balance and COD balance is recommended to evaluate the process application in full-scale.

References

Abelleira-Pereira, Jose M., Sara I. Pérez-Elvira, Jezabel Sánchez-Oneto, Roberto de la Cruz, Juan R. Portela, and Enrique Nebot. 2015. "Enhancement of Methane Production in Mesophilic Anaerobic Digestion of Secondary Sewage Sludge by Advanced Thermal Hydrolysis Pretreatment." *Water Research* 71: 330–40. https://doi.org/10.1016/j.watres.2014.12.027.

Angelidaki, Irini, and Wendy Sanders. 2004. "Assessment of the Anaerobic Biodegradability of Macropollutants." *Reviews in Environmental Science and Biotechnology*. https://doi.org/10.1007/s11157-004-2502-3.

Appels, Lise, Jan Degrève, Bart Van der Bruggen, Jan Van Impe, and Raf Dewil. 2010. "Influence of Low Temperature Thermal Pre-Treatment on Sludge Solubilisation, Heavy Metal Release and Anaerobic Digestion." *Bioresource Technology* 101 (15): 5743–48. https://doi.org/10.1016/j.biortech.2010.02.068.

Ariunbaatar, Javkhlan, Antonio Panico, Giovanni Esposito, Francesco Pirozzi, and Piet N.L. Lens. 2014. "Pretreatment Methods to Enhance Anaerobic Digestion of Organic Solid Waste." *Applied Energy* 123: 143–56. https://doi.org/10.1016/j.apenergy.2014.02.035.

Azizi, A., E. Hosseini Koupaie, H. Hafez, and E. Elbeshbishy. 2019. "Improving Single- and Two-Stage Anaerobic Digestion of Source Separated Organics by Hydrothermal Pretreatment." *Biochemical Engineering Journal* 148 (January): 77–86.

https://doi.org/10.1016/j.bej.2019.05.001.

Barber, W. P.F. 2016. “Thermal Hydrolysis for Sewage Treatment: A Critical Review.” *Water Research* 104: 53–71. https://doi.org/10.1016/j.watres.2016.07.069.

Barua, Sajib, Basem S. Zakaria, and Bipro Ranjan Dhar. 2018. “Enhanced Methanogenic Co-Degradation of Propionate and Butyrate by Anaerobic Microbiome Enriched on Conductive Carbon Fibers.” *Bioresource Technology* 266 (June): 259–66. https://doi.org/10.1016/j.biortech.2018.06.053.

Bordeleau, É L., and R. L. Droste. 2011. “Comprehensive Review and Compilation of Pretreatments for Mesophilic and Thermophilic Anaerobic Digestion.” *Water Science and Technology* 63 (2): 291–96. https://doi.org/10.2166/wst.2011.052.

Bougrier, C., C. Albasi, J. P. Delgenès, and H. Carrère. 2006. “Effect of Ultrasonic, Thermal and Ozone Pre-Treatments on Waste Activated Sludge Solubilisation and Anaerobic Biodegradability.” *Chemical Engineering and Processing: Process Intensification* 45 (8): 711–18. https://doi.org/10.1016/j.cep.2006.02.005.

Bougrier, C., J. P. Delgenès, and H. Carrère. 2007. “Impacts of Thermal Pre-Treatments on the Semi-Continuous Anaerobic Digestion of Waste Activated Sludge.” *Biochemical Engineering Journal* 34 (1): 20–27. https://doi.org/10.1016/j.bej.2006.11.013.

Bougrier, Claire, Jean Philippe Delgenès, and Hélène Carrère. 2008. “Effects of Thermal Treatments on Five Different Waste Activated Sludge Samples Solubilisation, Physical Properties and Anaerobic Digestion.” *Chemical Engineering Journal* 139 (2):

236–44. https://doi.org/10.1016/j.cej.2007.07.099.

Bruno, Latour. 2017. *Standard Methods for the Examination of Water and Wastewater , 23rd Edition*. *Journal of Chemical Information and Modeling*. Vol. 53.

Campos, J. L., L. Otero, A. Franco, A. Mosquera-Corral, and E. Roca. 2009. "Ozonation Strategies to Reduce Sludge Production of a Seafood Industry WWTP." *Bioresource Technology* 100 (3): 1069–73. https://doi.org/10.1016/j.biortech.2008.07.056.

Cano, R., S. I. Pérez-Elvira, and F. Fdz-Polanco. 2015. "Energy Feasibility Study of Sludge Pretreatments: A Review." *Applied Energy* 149: 176–85. https://doi.org/10.1016/j.apenergy.2015.03.132.

Carrère, H, C Dumas, A Battimelli, D J Batstone, J P Delgenès, J P Steyer, and I Ferrer. 2010. "Pretreatment Methods to Improve Sludge Anaerobic Degradability : A Review" 183: 1–15. https://doi.org/10.1016/j.jhazmat.2010.06.129.

Carrere, Hélène, Georgia Antonopoulou, Rim Affes, Fabiana Passos, Audrey Battimelli, Gerasimos Lyberatos, and Ivet Ferrer. 2016. "Review of Feedstock Pretreatment Strategies for Improved Anaerobic Digestion: From Lab-Scale Research to Full-Scale Application." *Bioresource Technology* 199: 386–97. https://doi.org/10.1016/j.biortech.2015.09.007.

Carrère, Hélène, Claire Bougrier, Delphine Castets, and Jean Philippe Delgenès. 2008. "Impact of Initial Biodegradability on Sludge Anaerobic Digestion Enhancement by Thermal Pretreatment." *Journal of Environmental Science and Health - Part A*

Toxic/Hazardous Substances and Environmental Engineering. https://doi.org/10.1080/10934520802293735.

Cesaro, Alessandra, Silvana Velten, Vincenzo Belgiorno, and Kerstin Kuchta. 2014. "Enhanced Anaerobic Digestion by Ultrasonic Pretreatment of Organic Residues for Energy Production." *Journal of Cleaner Production* 74: 119–24. https://doi.org/https://doi.org/10.1016/j.jclepro.2014.03.030.

Chen, Guohua, Po Lock Yue, and Arun S. Mujumdar. 2002. "Sludge Dewatering and Drying." *Drying Technology* 20 (4–5): 883–916. https://doi.org/10.1081/DRT-120003768.

Chiu, Ying-Chih, Cheng-Nan Chang, Jih-Gaw Lin, and Shwu-Jiuan Huang. 1997. "Alkaline and Ultrasonic Pretreatment of Sludge before Anaerobic Digestion." *Water Science and Technology* 36 (11): 155–62. https://doi.org/https://doi.org/10.1016/S0273-1223(97)00681-1.

Chu, Libing, Sangtian Yan, Xin Hui Xing, Xulin Sun, and Benjamin Jurcik. 2009. "Progress and Perspectives of Sludge Ozonation as a Powerful Pretreatment Method for Minimization of Excess Sludge Production." *Water Research* 43 (7): 1811–22. https://doi.org/10.1016/j.watres.2009.02.012.

Dhar, Bipro Ranjan, George Nakhla, and Madhumita B. Ray. 2012. "Techno-Economic Evaluation of Ultrasound and Thermal Pretreatments for Enhanced Anaerobic Digestion of Municipal Waste Activated Sludge." *Waste Management* 32 (3): 542–49.

https://doi.org/10.1016/j.wasman.2011.10.007.

Dwyer, Jason, Daniel Starrenburg, Stephan Tait, Keith Barr, Damien J. Batstone, and Paul Lant. 2008. “Decreasing Activated Sludge Thermal Hydrolysis Temperature Reduces Product Colour, without Decreasing Degradability.” *Water Research* 42 (18): 4699–4709. https://doi.org/10.1016/j.watres.2008.08.019.

Dytczak, Magdalena A., Kathleen L. Londry, Hansruedi Siegrist, and Jan A. Oleszkiewicz. 2007. “Ozonation Reduces Sludge Production and Improves Denitrification.” *Water Research* 41 (3): 543–50. https://doi.org/10.1016/j.watres.2006.11.009.

Eskicioglu, C., K. J. Kennedy, and R. L. Droste. 2008. “Initial Examination of Microwave Pretreatment on Primary, Secondary and Mixed Sludges before and after Anaerobic Digestion.” *Water Science and Technology* 57 (3): 311–17. https://doi.org/10.2166/wst.2008.010.

Eskicioglu, Cigdem, Kevin J. Kennedy, and Ronald L. Droste. 2006. “Characterization of Soluble Organic Matter of Waste Activated Sludge before and after Thermal Pretreatment.” *Water Research* 40 (20): 3725–36. https://doi.org/10.1016/j.watres.2006.08.017.

EVERETT JG. 1972. “Dewatering of Wastewater Sludge by Heat Treatment.” *Journal of the Water Pollution Control Federation* 44 (1): 92–100.

Ferrer, Ivet, Sergio Ponsá, Felícitas Vázquez, and Xavier Font. 2008. “Increasing Biogas Production by Thermal (70 °C) Sludge Pre-Treatment Prior to Thermophilic

Anaerobic Digestion." *Biochemical Engineering Journal* 42 (2): 186–92. https://doi.org/10.1016/j.bej.2008.06.020.

Foladori, Paola, Gianni Andreottola, and Giuliano Ziglio. 2015. *Sludge Reduction Technologies in Wastewater Treatment Plants*. *Sludge Reduction Technologies in Wastewater Treatment Plants*. https://doi.org/10.2166/9781780401706.

Ge, Huoqing, Paul D. Jensen, and Damien J. Batstone. 2010. "Pre-Treatment Mechanisms during Thermophilic-Mesophilic Temperature Phased Anaerobic Digestion of Primary Sludge." *Water Research* 44 (1): 123–30. https://doi.org/10.1016/j.watres.2009.09.005.

Goel, Rajeev, T. Takutomi, and H. Yasui. 2003. "Anaerobic Digestion of Excess Activated Sludge with Ozone Pretreatment." *Water Science and Technology* 47 (12): 207–14. https://doi.org/10.2166/wst.2003.0648.

Grubel, Klaudiusz, Alicja Machnicka, Ewelina Nowicka, and Stanisław Wacławek. 2014. "Mesophilic-Thermophilic Fermentation Process of Waste Activated Sludge after Hybrid Disintegration." *Ecological Chemistry and Engineering S* 21 (1): 125–36. https://doi.org/10.2478/eces-2014-0011.

Haug, R. T., D. C. Stuckey, J. M. Gossett, and P. L. McCarty. 1978. "Effect of Thermal Pretreatment on Digestibility and Dewaterability of Organic Sludges." *Journal of the Water Pollution Control Federation* 50 (1): 73–85.

Haug, R T. 2016. "Sludge Processing to Optimize" 49 (7): 1713–21.

Higgins, Matthew J., Steven Beightol, Ushma Mandahar, Ryu Suzuki, Steven Xiao, Hung Wei Lu, Trung Le, et al. 2017. “Pretreatment of a Primary and Secondary Sludge Blend at Different Thermal Hydrolysis Temperatures: Impacts on Anaerobic Digestion, Dewatering and Filtrate Characteristics.” *Water Research* 122: 557–69. https://doi.org/10.1016/j.watres.2017.06.016.

Hiraoka, M., N. Takeda, S. Sakai, and A. Yasuda. 1985. “Highly Efficient Anaerobic Digestion with Thermal Pretreatment.” *Water Science and Technology* 17 (4-5–5 pt 2): 529–39. https://doi.org/10.2166/wst.1985.0157.

Hosseini Koupaie, E., T. Johnson, and C. Eskicioglu. 2017. “Advanced Anaerobic Digestion of Municipal Sludge Using a Novel and Energy-Efficient Radio Frequency Pretreatment System.” *Water Research* 118: 70–81. https://doi.org/10.1016/j.watres.2017.04.017.

Hu, Haidong, Sijia Ma, Xuxiang Zhang, and Hongqiang Ren. 2020. “Characteristics of Dissolved Organic Nitrogen in Effluent from a Biological Nitrogen Removal Process Using Sludge Alkaline Fermentation Liquid as an External Carbon Source.” *Water Research* 176: 115741. https://doi.org/https://doi.org/10.1016/j.watres.2020.115741.

Ji, Zhouying, Guanlan Chen, and Yinguang Chen. 2010. “Effects of Waste Activated Sludge and Surfactant Addition on Primary Sludge Hydrolysis and Short-Chain Fatty Acids Accumulation.” *Bioresource Technology* 101 (10): 3457–62. https://doi.org/10.1016/j.biortech.2009.12.117.

Kakar, Farokh laqa, Ehssan Hosseini Koupaie, Ahmed Shabir Razavi, Hisham Hafez, and Elsayed Elbeshbishy. 2019. “Effect of Hydrothermal Pretreatment on Volatile Fatty Acids Production from Thickened Waste Activated Sludge.” *Bioenergy Research*, 1–20. https://doi.org/10.1007/s12155-019-10056-z.

Kavitha, S., S. Adish Kumar, S. Kaliappan, Ick Tae Yeom, and J. Rajesh Banu. 2014. “Improving the Amenability of Municipal Waste Activated Sludge for Biological Pretreatment by Phase-Separated Sludge Disintegration Method.” *Bioresource Technology* 169: 700–706. https://doi.org/10.1016/j.biortech.2014.07.065.

Kavitha, S., C. Jayashree, S. Adish Kumar, Ick Tae Yeom, and J. Rajesh Banu. 2014. “The Enhancement of Anaerobic Biodegradability of Waste Activated Sludge by Surfactant Mediated Biological Pretreatment.” *Bioresource Technology* 168: 159–66. https://doi.org/10.1016/j.biortech.2014.01.118.

Kepp, U., I. Machenbach, N. Weisz, and O. E. Solheim. 2000. “Enhanced Stabilisation of Sewage Sludge through Thermal Hydrolysis - Three Years of Experience with Full Scale Plant.” *Water Science and Technology* 42 (9): 89–96. https://doi.org/10.2166/wst.2000.0178.

Kiær, Birgitte. 2007. “Optimization of Anaerobic Digestion of Sewage Sludge Using Thermophilic Anaerobic Thermal Pre-Treatment of Primary and Secondary Sludge at 70 8 C Prior to Anaerobic Digestion,” 161–66.

Kim, Jeongsik, Chulhwan Park, Tak Hyun Kim, Myunggu Lee, Sangyong Kim, Seung

Wook Kim, and Jinwon Lee. 2003a. "Effects of Various Pretreatments for Enhanced Anaerobic Digestion with Waste Activated Sludge." *Journal of Bioscience and Bioengineering* 95 (3): 271–75. https://doi.org/10.1263/jbb.95.271.

———. 2003b. "Effects of Various Pretreatments for Enhanced Anaerobic Digestion with Waste Activated Sludge." *Journal of Bioscience and Bioengineering* 95 (3): 271–75. https://doi.org/10.1263/jbb.95.271.

Koivunen, J., and H. Heinonen-Tanski. 2005. "Peracetic Acid (PAA) Disinfection of Primary, Secondary and Tertiary Treated Municipal Wastewaters." *Water Research* 39 (18): 4445–53. https://doi.org/10.1016/j.watres.2005.08.016.

Kor-Bicakci, Gokce, and Cigdem Eskicioglu. 2019. "Recent Developments on Thermal Municipal Sludge Pretreatment Technologies for Enhanced Anaerobic Digestion." *Renewable and Sustainable Energy Reviews* 110 (January): 423–43. https://doi.org/10.1016/j.rser.2019.05.002.

Li, Li, Zihui Dong, Jianfeng Lu, Junping Dai, Qianru Huang, Chin-Chen Chang, and Ting Wu. 2015. "AN H.264/AVC HDTV Watermarking Algorithm Robust to Camcorder Recording." *Journal of Visual Communication and Image Representation* 26: 1–8. https://doi.org/https://doi.org/10.1016/j.jvcir.2014.08.009.

Lin, Long, Ehssan Hosseini Koupaie, Armineh Azizi, Amir Abbas Bazyar Lakeh, Bipro R. Dhar, Hisham Hafez, and Elsayed Elbeshbishy. 2019. "Comparison of Two Process Schemes Combining Hydrothermal Treatment and Acidogenic Fermentation of

Source-Separated Organics." *Molecules* 24 (8). https://doi.org/10.3390/molecules24081466.

Lin, Long, Fuqing Xu, Xumeng Ge, and Yebo Li. 2018. "Improving the Sustainability of Organic Waste Management Practices in the Food-Energy-Water Nexus: A Comparative Review of Anaerobic Digestion and Composting." *Renewable and Sustainable Energy Reviews* 89 (March): 151–67. https://doi.org/10.1016/j.rser.2018.03.025.

Lin, Long, Zhongtang Yu, and Yebo Li. 2017. "Sequential Batch Thermophilic Solid-State Anaerobic Digestion of Lignocellulosic Biomass via Recirculating Digestate as Inoculum – Part II: Microbial Diversity and Succession." *Bioresource Technology* 241: 1027–35. https://doi.org/10.1016/j.biortech.2017.06.011.

Linden, K G, and M Mohseni. 2014. "2.8 - Advanced Oxidation Processes: Applications in Drinking Water Treatment." In , edited by Satinder B T - Comprehensive Water Quality and Purification Ahuja, 148–72. Waltham: Elsevier. https://doi.org/https://doi.org/10.1016/B978-0-12-382182-9.00031-1.

Liu, Hongbo, Hang Xiao, Bo Yin, Yepin Zu, He Liu, Bo Fu, and Huijun Ma. 2016. "Enhanced Volatile Fatty Acid Production by a Modified Biological Pretreatment in Anaerobic Fermentation of Waste Activated Sludge." *Chemical Engineering Journal* 284 (November 2018): 194–201. https://doi.org/10.1016/j.cej.2015.08.121.

Luo, Kun, Ya Pang, Qi Yang, Dongbo Wang, Xue Li, Min Lei, and Qi Huang. 2019. "A

Critical Review of Volatile Fatty Acids Produced from Waste Activated Sludge: Enhanced Strategies and Its Applications." *Environmental Science and Pollution Research*, 13984–98. https://doi.org/10.1007/s11356-019-04798-8.

Luste, Sami, and Sari Luostarinen. 2010. "Anaerobic Co-Digestion of Meat-Processing by-Products and Sewage Sludge – Effect of Hygienization and Organic Loading Rate." *Bioresource Technology* 101 (8): 2657–64. https://doi.org/https://doi.org/10.1016/j.biortech.2009.10.071.

Mao, T., S. Y. Hong, K. Y. Show, J. H. Tay, and D. J. Lee. 2004. "A Comparison of Ultrasound Treatment on Primary and Secondary Sludges." *Water Science and Technology* 50 (9): 91–97.

Mehdizadeh, Seyedeh Neda, Cigdem Eskicioglu, Jake Bobowski, and Thomas Johnson. 2013. "Conductive Heating and Microwave Hydrolysis under Identical Heating Profiles for Advanced Anaerobic Digestion of Municipal Sludge." *Water Research* 47 (14): 5040–51. https://doi.org/https://doi.org/10.1016/j.watres.2013.05.055.

Mendez, Lara, Ahmed Mahdy, Marie Demuez, Mercedes Ballesteros, and Cristina González-Fernández. 2014. "Effect of High Pressure Thermal Pretreatment on Chlorella Vulgaris Biomass: Organic Matter Solubilisation and Biochemical Methane Potential." *Fuel* 117 (PART A): 674–79. https://doi.org/10.1016/j.fuel.2013.09.032.

Mottet, A., J. P. Steyer, S. Déléris, F. Vedrenne, J. Chauzy, and H. Carrère. 2009. "Kinetics of Thermophilic Batch Anaerobic Digestion of Thermal Hydrolysed Waste Activated

Sludge." *Biochemical Engineering Journal* 46 (2): 169–75. https://doi.org/10.1016/j.bej.2009.05.003.

Neyens, E., and J. Baeyens. 2003. "A Review of Thermal Sludge Pre-Treatment Processes to Improve Dewaterability." *Journal of Hazardous Materials* 98 (1–3): 51–67. https://doi.org/10.1016/S0304-3894(02)00320-5.

Ødeby, T., T. Netteland, and O. E. Solheim. 1996. "Thermal Hydrolysis as a Profitable Way of Handling Sludge." *Chemical Water and Wastewater Treatment IV*, 401–9. https://doi.org/10.1007/978-3-642-61196-4_38.

Parawira, Wilson. 2012. "Enzyme Research and Applications in Biotechnological Intensification of Biogas Production." *Critical Reviews in Biotechnology*. https://doi.org/10.3109/07388551.2011.595384.

Park, Woon Ji, and Johng Hwa Ahn. 2011. "Effects of Microwave Pretreatment on Mesophilic Anaerobic Digestion for Mixture of Primary and Secondary Sludges Compared with Thermal Pretreatment." *Environmental Engineering Research*. https://doi.org/10.4491/eer.2011.16.2.103.

Pilli, Sridhar, Song Yan, R. D. Tyagi, and R. Y. Surampalli. 2015. "Thermal Pretreatment of Sewage Sludge to Enhance Anaerobic Digestion: A Review." *Critical Reviews in Environmental Science and Technology*. https://doi.org/10.1080/10643389.2013.876527.

Pinnekamp, J. 1989. "Effects of Thermal Pretreatment of Sewage Sludge on Anaerobic

Digestion.” *Water Science and Technology* 21 (4-5–5 pt 1): 97–108. https://doi.org/10.2166/wst.1989.0214.

Razavi, A. S., E. Hosseini Koupaie, A. Azizi, H. Hafez, and E. Elbeshbishy. 2019. “Hydrothermal Pretreatment of Source Separated Organics for Enhanced Solubilization and Biomethane Recovery.” *Bioresource Technology* 274 (December 2018): 502–11. https://doi.org/10.1016/j.biortech.2018.12.024.

Ryue, John, Long Lin, Yang Liu, Wenjing Lu, Daryl McCartney, and Bipro Ranjan Dhar. 2019. “Comparative Effects of GAC Addition on Methane Productivity and Microbial Community in Mesophilic and Thermophilic Anaerobic Digestion of Food Waste.” *Biochemical Engineering Journal* 146 (March): 79–87. https://doi.org/10.1016/j.bej.2019.03.010.

Sheets, Johnathon P., Liangcheng Yang, Xumeng Ge, Zhiwu Wang, and Yebo Li. 2015. “Beyond Land Application: Emerging Technologies for the Treatment and Reuse of Anaerobically Digested Agricultural and Food Waste.” *Waste Management* 44: 94–115. https://doi.org/10.1016/j.wasman.2015.07.037.

Skiadas, I. V., H. N. Gavala, J. Lu, and B. K. Ahring. 2005. “Thermal Pre-Treatment of Primary and Secondary Sludge at 701 ??C Prior to Anaerobic Digestion.” *Water Science and Technology* 52 (1–2): 161–66.

Sosnowski, P., A. Wieczorek, and S. Ledakowicz. 2003. “Anaerobic Co-Digestion of Sewage Sludge and Organic Fraction of Municipal Solid Wastes.” *Advances in*

Environmental Research 7 (3): 609–16. https://doi.org/10.1016/S1093-0191(02)00049-7.

Stephenson, Rob, Scott Laliberte, Preston Hoy, Amanda Drew, and Diana Britch. 2012. "Full Scale and Laboratory Scale Results From the Trial of Microsludge At the Joint Water Pollution Control Plant At Los Angeles County." *Proceedings of the Water Environment Federation* 2007 (3): 272–99. https://doi.org/10.2175/193864707787975354.

Stuckey, David C., and Perry L. McCarty. 1984. "The Effect of Thermal Pretreatment on the Anaerobic Biodegradability and Toxicity of Waste Activated Sludge." *Water Research* 18 (11): 1343–53. https://doi.org/10.1016/0043-1354(84)90002-2.

Tanaka, Shuzo, Toshio Kobayashi, and Ken-ichi Kamiayama. 1997. "Effects of Thermochemical Pretreatment of the Anaerobic Digestion of Waste Activated Sludge." *Water Science and Technology*.

Tang, Bing, Linfeng Yu, Shaosong Huang, Jianzhong Luo, and Ying Zhuo. 2010. "Energy Efficiency of Pre-Treating Excess Sewage Sludge with Microwave Irradiation." *Bioresource Technology* 101 (14): 5092–97. https://doi.org/10.1016/j.biortech.2010.01.132.

Toreci, Isil, Kevin J. Kennedy, and Ronald L. Droste. 2009. "Evaluation of Continuous Mesophilic Anaerobic Sludge Digestion after High Temperature Microwave Pretreatment." *Water Research* 43 (5): 1273–84.

https://doi.org/10.1016/j.watres.2008.12.022.

Tyagi, Vinay Kumar, and Shang Lien Lo. 2013. "Microwave Irradiation: A Sustainable Way for Sludge Treatment and Resource Recovery." *Renewable and Sustainable Energy Reviews* 18 (71): 288–305. https://doi.org/10.1016/j.rser.2012.10.032.

Valo, Alexandre, Hélène Carrère, and Jean Philippe Delgenès. 2004. "Thermal, Chemical and Thermo-Chemical Pre-Treatment of Waste Activated Sludge for Anaerobic Digestion." *Journal of Chemical Technology and Biotechnology* 79 (11): 1197–1203. https://doi.org/10.1002/jctb.1106.

Waclawek, Stanislaw, Klaudiusz Grübel, Daniele Silvestri, Vinod V.T. Padil, Maria Waclawek, Miroslav Cerník, and Rajender S. Varma. 2019. "Disintegration of Wastewater Activated Sludge (WAS) for Improved Biogas Production." *Energies* 12 (1): 1–16. https://doi.org/10.3390/en12010021.

Wilson, Christopher A., and John T. Novak. 2009. "Hydrolysis of Macromolecular Components of Primary and Secondary Wastewater Sludge by Thermal Hydrolytic Pretreatment." *Water Research* 43 (18): 4489–98. https://doi.org/10.1016/j.watres.2009.07.022.

Wu, Haiyan, Junyan Gao, Dianhai Yang, Qi Zhou, and Wei Liu. 2010. "Alkaline Fermentation of Primary Sludge for Short-Chain Fatty Acids Accumulation and Mechanism." *Chemical Engineering Journal* 160 (1): 1–7. https://doi.org/10.1016/j.cej.2010.02.012.

Wu, Li Jie, Yu Qin, Toshimasa Hojo, and Yu You Li. 2015. "Upgrading of Anaerobic Digestion of Waste Activated Sludge by Temperature-Phased Process with Recycle." *Energy* 87 (34): 381–89. https://doi.org/10.1016/j.energy.2015.04.110.

Xu, Fuqing, Zhi Wu Wang, Li Tang, and Yebo Li. 2014. "A Mass Diffusion-Based Interpretation of the Effect of Total Solids Content on Solid-State Anaerobic Digestion of Cellulosic Biomass." *Bioresource Technology* 167: 178–85. https://doi.org/10.1016/j.biortech.2014.05.114.

Xue, Yonggang, Huajie Liu, Sisi Chen, Norbert Dichtl, Xiaohu Dai, and Ning Li. 2015. "Effects of Thermal Hydrolysis on Organic Matter Solubilization and Anaerobic Digestion of High Solid Sludge." *Chemical Engineering Journal* 264: 174–80. https://doi.org/10.1016/j.cej.2014.11.005.

Yang, Guang, Guangming Zhang, and Hongchen Wang. 2015. "Current State of Sludge Production, Management, Treatment and Disposal in China." *Water Research* 78: 60–73. https://doi.org/https://doi.org/10.1016/j.watres.2015.04.002.

Yang, Liangcheng, Fuqing Xu, Xumeng Ge, and Yebo Li. 2015. "Challenges and Strategies for Solid-State Anaerobic Digestion of Lignocellulosic Biomass." *Renewable and Sustainable Energy Reviews* 44: 824–34. https://doi.org/10.1016/j.rser.2015.01.002.

Yu, Shuyu, Guangming Zhang, Jianzheng Li, Zhiwei Zhao, and Xiaorong Kang. 2013. "Effect of Endogenous Hydrolytic Enzymes Pretreatment on the Anaerobic Digestion of Sludge." *Bioresource Technology* 146: 758–61.

https://doi.org/10.1016/j.biortech.2013.07.087.

Yuan, Chuansheng, Bo Wang, Yongzhen Peng, Xiyao Li, Qiong Zhang, and Tiantian Hu. 2020. "Enhanced Nutrient Removal of Simultaneous Partial Nitrification, Denitrification and Phosphorus Removal (SPNDPR) in a Single-Stage Anaerobic/Micro-Aerobic Sequencing Batch Reactor for Treating Real Sewage with Low Carbon/Nitrogen." *Chemosphere*, 127097. https://doi.org/https://doi.org/10.1016/j.chemosphere.2020.127097.

Zhen, Guangyin, Xueqin Lu, Hiroyuki Kato, Youcai Zhao, and Yu You Li. 2017. "Overview of Pretreatment Strategies for Enhancing Sewage Sludge Disintegration and Subsequent Anaerobic Digestion: Current Advances, Full-Scale Application and Future Perspectives." *Renewable and Sustainable Energy Reviews* 69 (September 2016): 559–77. https://doi.org/10.1016/j.rser.2016.11.187.

Zheng, Xiong, Yinguang Chen, and Chenchen Liu. 2010. "Waste Activated Sludge Alkaline Fermentation Liquid as Carbon Source for Biological Nutrients Removal in Anaerobic Followed by Alternating Aerobic-Anoxic Sequencing Batch Reactors." *Chinese Journal of Chemical Engineering* 18 (3): 478–85. https://doi.org/10.1016/S1004-9541(10)60246-7.

Zheng, Yi, Jia Zhao, Fuqing Xu, and Yebo Li. 2014. "Pretreatment of Lignocellulosic Biomass for Enhanced Biogas Production." *Progress in Energy and Combustion Science* 42 (1): 35–53. https://doi.org/10.1016/j.pecs.2014.01.001.

Appendix

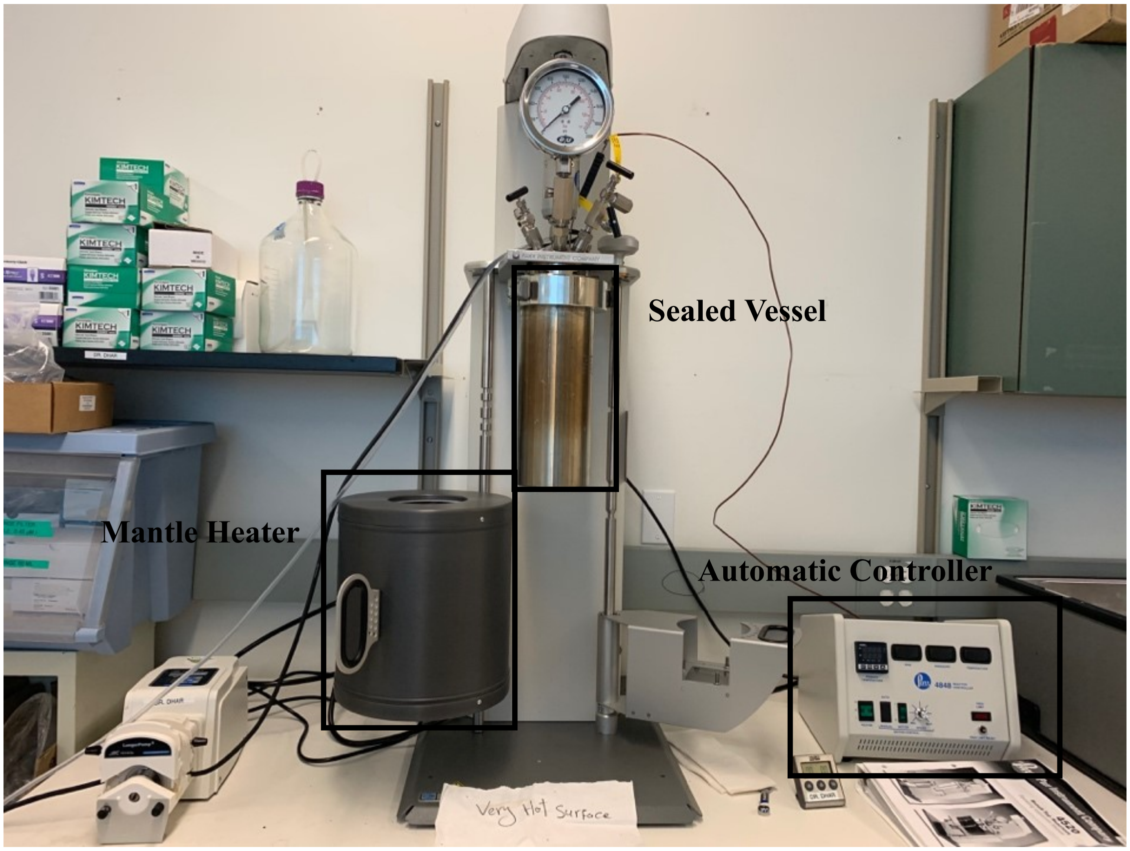

Figure A1. Parr Hydrothermal Reactor.

Figure A2. BMP setup during AD process.

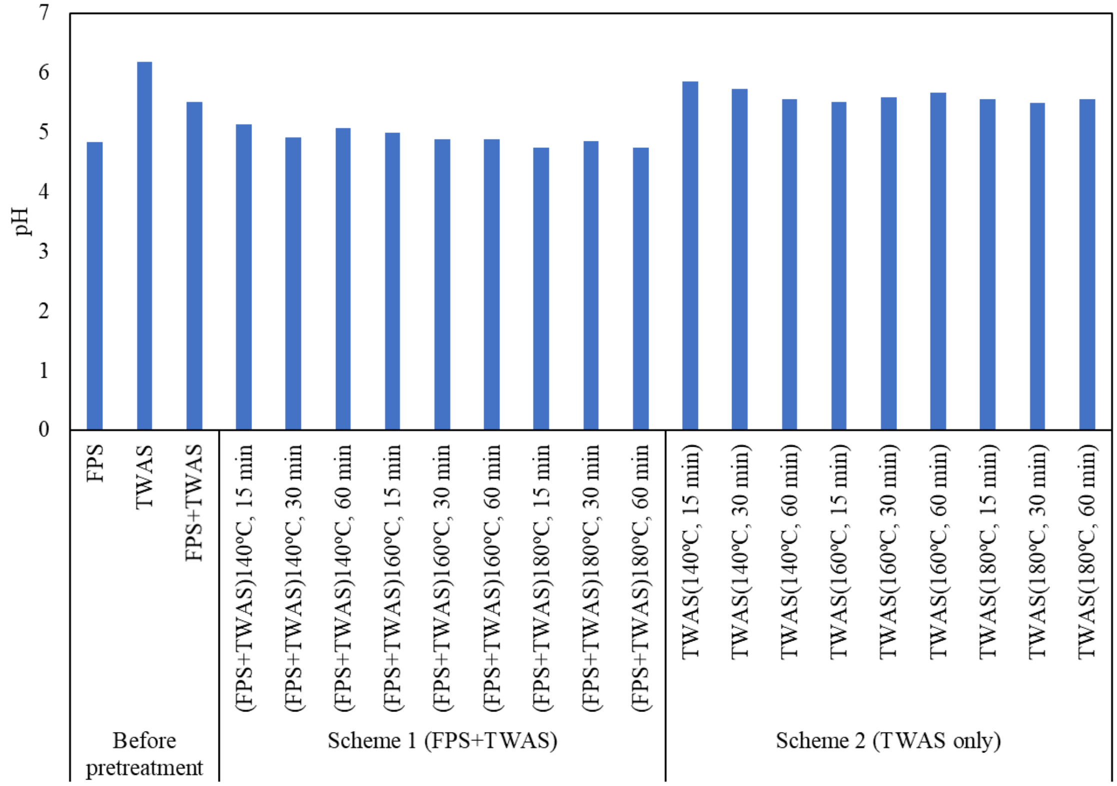

Figure A3. The comparison of pH changes before and after pretreatment.

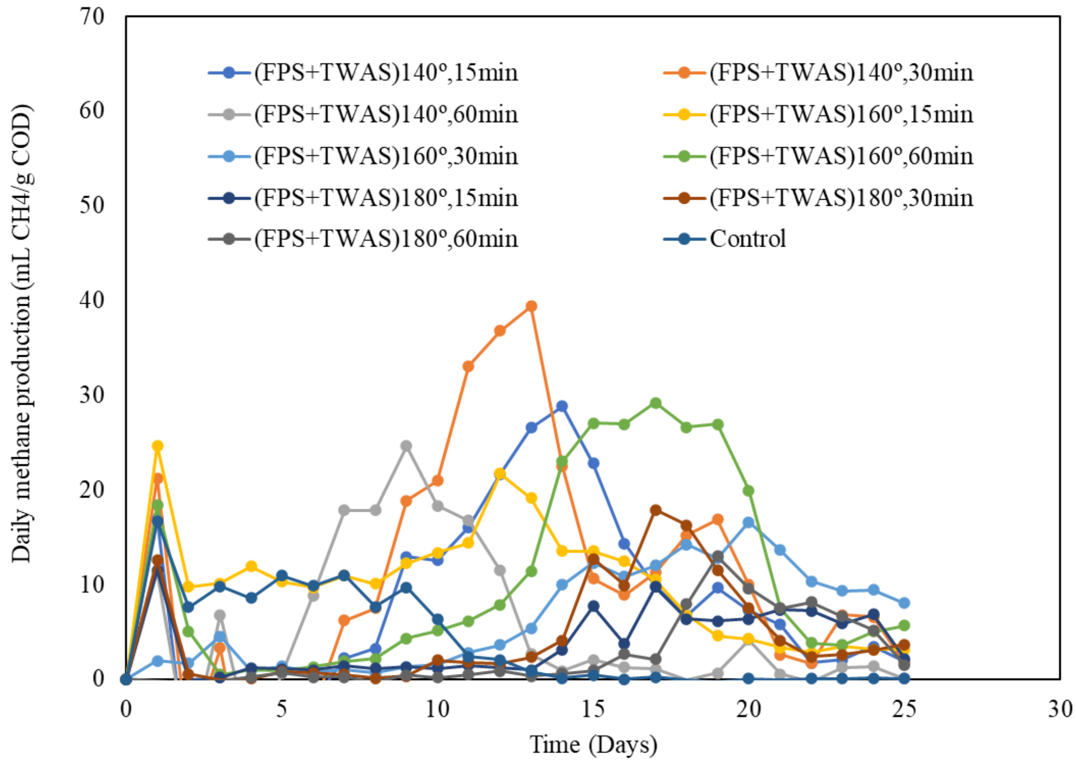

Figure A4. Daily methane production for scheme-1.

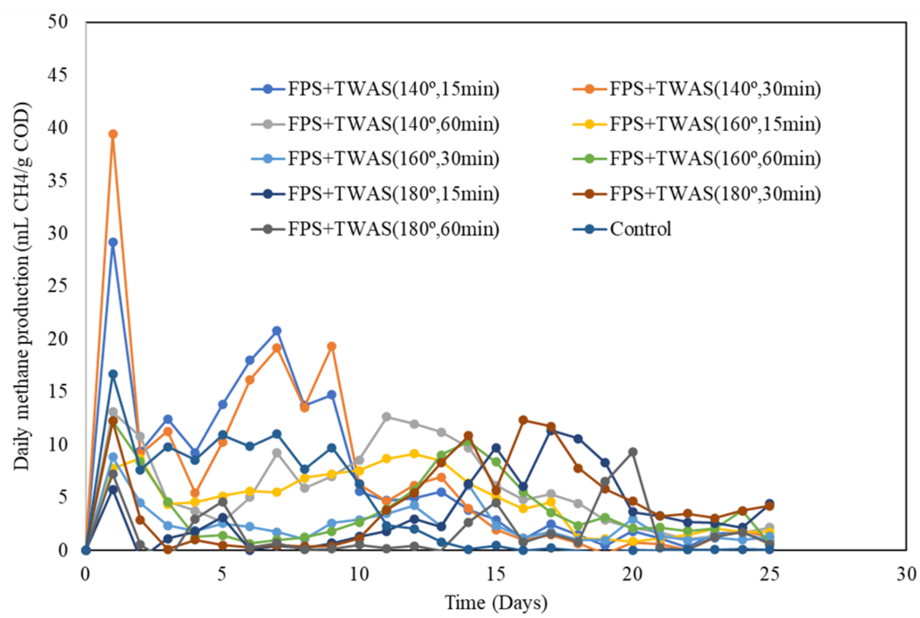

Figure A5. Daily methane production for scheme-2.