Comparison of the Impacts of Thermal Pretreatment on Waste Activated Sludge using Aerobic and Anaerobic Digestion

by

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Author's Declaration

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

Abstract

Thermal pretreatment systems are typically employed to improve waste-activated sludge (WAS) dewaterability and to treat sludge prior to anaerobic digestion. It is important to understand how WAS properties are affected during pretreatment to be able to assess the performances of processes utilizing pretreated WAS (PWAS). However, there are no generally accepted means of characterizing and comparing pretreatment processes. A pretreatment model for high temperature thermal hydrolysis was developed previously for one pretreatment condition. The motivation for this project stemmed from the need to extend the range of thermal pretreatment conditions to span the range of conditions commonly employed in practice and to evaluate the impact of these pretreatment conditions on WAS chemical oxygen demand (COD) fractionation. The two main objectives of this study were to fractionate the COD of WAS before and after pretreatment for several high temperature thermal pretreatment conditions and to compare the impact of pretreatment on aerobic and anaerobic biodegradability. The secondary objectives were to investigate how pretreatment affected the rate and extent of aerobic and anaerobic digestion of WAS.

The data employed in this study was collected by others following the work of Staples-Burger (2012) and was generated by pretreatment of sludges at 125°C, 150°C, and 175°C for 10, 30 and 50 minutes. Physical and biochemical properties were measured for raw WAS (BR WAS) and PWAS. Offline and online respirometric data were used to evaluate the aerobic biodegradability of BR WAS and PWAS and to fractionate the COD of the BR WAS and PWAS. Biochemical methane potential (BMP) tests were conducted for BR WAS and PWAS to evaluate the anaerobic biodegradability of BR WAS and PWAS. BioWin® was used to aid in determining the WAS COD fractionation before and after pretreatment, and to determine whether pretreatment changed the aerobic and anaerobic biodegradability of the WAS.

It was found that the high pressure thermal hydrolysis (HPTH) pretreatment conditions employed substantially solubilized the COD, organic nitrogen and volatile suspended solids (VSS) in the range of 30 – 55%, 23 – 41% and 30 – 89% respectively. Total COD (TCOD) was however not reduced by pretreatment indicating that organics were not mineralized. These findings closely agreed with the conclusions made in the literature.

Pretreatment did not increase the overall extent to which WAS could be aerobically biodegraded. The fraction of non-biodegradable COD as represented by endogenous decay products (Z_e) in the BR WAS were not converted to biodegradable form by pretreatment. However, pretreatment increased the rate at which WAS could be aerobically biodegraded as indicated by an increase in the fractions of readily biodegradable COD (S_{bsc}) in the PWAS.

Pretreatment increased both the rate and extent of anaerobic biodegradability. The ultimate methane yield and the methane production rate were both increased when compared to the ultimate methane yield and methane production rate observed in BMP tests conducted on BR WAS.

The experimental results were combined with BioWin® modeling to determine that the BR WAS consisted of 79% Z_{bh} and 18% endogenous decay products (Z_e). The endogenous decay products fraction remained at 18% through pretreatment and the concentration of active biomass (Z_{bh}) in PWAS was deemed to be negligible. HPTH pretreatment at the employed temperatures and durations transformed the biodegradable fraction of BR WAS (Z_{bh}) to 16.5 – 34.6% S_{bsc} and 45.8 – 63.6% slowly biodegradable COD (X_{sp}) of the TCOD concentration. The same PWAS COD fractionations were employed in anaerobic biodegradability test modeling and it was concluded that the aerobic and anaerobic biodegradability of PWAS was different. Up to 50% of the endogenous decay products were converted to biodegradable substrate (X_{sp}) due to HPTH pretreatment.

It was determined that both pretreatment temperature and duration were important in solubilizing organic matter in the WAS. Increasing the pretreatment temperature and duration generally increased the organics solubilization. However, the impact of pretreatment temperature and duration on WAS COD fractions were inconclusive. The increase in organics solubilization did not correspond to how much of the biodegradable COD of BR WAS was converted to S_{bsc} by pretreatment.

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List of Abbreviations

AA	Amino Acids
AD	Aerobic Digester
ADM	Anaerobic Digestion Model
ASM3	IWA Activated Sludge Model Number 3
AS	Activated Sludge
ASM	IWA Activated Sludge Model
bCOD	Biodegradable COD
b_h	Aerobic Decay Rate of Z_{bh}
BR	Biological Reactor
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
EPS	Extracellular Polymeric Substances
ffCOD	Filtered and Flocculated COD
FPWAS	Filtered and Pretreated WAS
HPTH	High Pressure Thermal Hydrolysis
HRT	Hydraulic Retention Time
ISS	Inorganic Suspended Solids
IWA	International Water association
LCFA	Long Chain Fatty Acid
MLSS	Mixed Liquor Suspended Solids
MS	Monosaccharides
nbCOD	Non-Biodegradable COD
nbpCOD	Non-Biodegradable Particulate COD
nbsCOD	Non-Biodegradable Soluble COD
NH_3-N	Ammonia Nitrogen
NO_3-N	Nitrate Nitrogen
∑OU	Cumulative Oxygen Uptake
OUR	Oxygen Uptake Rate
PAO	Phosphate Accumulating Organism
PCOD	Particulate Chemical Oxygen Demand
PHA	Poly-hydroxy-alkanoates
PS	Primary Sludge
PWAS	Pretreated WAS
rbCOD	Readily Biodegradable COD
sbCOD	Slowly Biodegradable COD
SBR	Sequencing Batch Reactor
S_{bsa}	Readily Biodegradable COD (Acetate)
S_{bsc}	Readily Biodegradable COD (Complex)
SCOD	Soluble COD
sON	Soluble Organic Nitrogen
SRT	Solids Retention Time
SS	Sum of Squares

sTKN	Soluble Total Kjeldahl Nitrogen
S_{us}	Soluble Inert COD
TCOD	Total Chemical Oxygen Demand
TH	Thermal Hydrolysis
TKN	Total Kjeldahl Nitrogen
TP	Total Phosphorous
TS	Total Solids
TSS	Total Suspended Solids
VFA	Volatile Fatty Acids
VS	Volatile Solids
VSS	Volatile Suspended Solids
WAS	Waste Activated Sludge
WW	Wastewater
WWTP	Wastewater Treatment Plant
X_i	Particulate Inert COD
X_{sc}	Slowly Biodegradable COD (colloidal)
X_{sp}	Slowly Biodegradable COD (particulate)
X_{STO}	Stored COD
Y_h	Aerobic Yield of Z_{bh}
Z_{bh}	Heterotrophic Microorganisms
Z_e	Endogenous Products

1. Introduction

Sludge processing and disposal are significant operating costs for a wastewater treatment (WWTP) facility. They can range from 20 to 65% of the total operating costs for the entire WWTP. Sludge can be characterized in terms of where it is produced (Aboulfotoh & Monayeri, 2015; Foladori et al., 2010). Primary sludge (PS) is generated from primary settlers through physical separation of solids. Secondary sludge, commonly known as waste-activated sludge (WAS), is the by-product of activated sludge systems and is typically produced in the secondary clarifiers, where the effluent is separated from the activated sludge (Foladori et al., 2010). Agricultural use, landfill, or composting are popular options for sludge disposal. However, regulation limits, public opinion, and high costs places strains on each option. The cost of sludge disposal is expected to continue to rise due to increases in sludge production and development of more stringent regulatory limits for sludge disposal alternatives. There are two approaches when it comes to improving the sustainability of sludge processing. The first consists of recovering nutrients or energy from the sludge, wherein it is considered as a resource. The other option is to reduce the quantity of sludge produced, which treats it as a waste (Foladori et al., 2010).

There are various digestion pretreatment technologies that can improve sludge processing sustainability. Pretreatment technologies can be broadly classified as thermal (Bougrier et al., 2008; Haug et al., 1978; Li & Noike, 1992), chemical (Lin et al., 1997; Rajan et al., 1989; Valo et al., 2004), mechanical (Hwang et al., 1997; Nah et al., 2000), and biological (Neyens & Baeyens, 2003). Some pretreatments are a combination of different types such as thermos-chemical and ultrasonic-chemical (Liu et al., 2008).

Out of all of the different technologies, thermal hydrolysis systems have been the most extensively reported. Thermal pretreatment has been reported to decrease the amount of sludge to be disposed (Donoso-Bravo et al., 2011) and is usually coupled with anaerobic digestion to increase biogas generation that can be used as an alternative energy source. There are a number of full scale systems already in operation, which includes the CAMBI™ (Kepp et al., 2000), EXELYS™ (Gurieff et al., 2011), and Bio THELYS™ (Chauzy et al., 2008) configurations.

Anaerobic digestion encompasses four major processes that can be categorized as either cellular or extra-cellular. The first step, categorized as extra-cellular, involves disintegration of complex particulate matter into macro-constituents – carbohydrate, protein and lipid substrates – and inert material (Batstone et al., 2002). Extra-cellular hydrolysis of these macro compounds is typically coupled with physical disintegration to further break them down into monosaccharides (MS), amino acids (AA), and long chain fatty acids (LCFA). The processes succeeding hydrolysis are cellular and include acidogenesis, acetogenesis and methanogenesis. Acidogenesis, or fermentation converts monosaccharides and amino acids into various

forms of volatile fatty acids (VFA), including acetate, propionate, butyrate, and valerate. Acetogenesis then converts propionate, butyrate, and valerate to acetate and hydrogen gas. The last step, methanogenesis is performed by acetoclastic methanogens which produce methane by consuming acetate and hydrogenotrophic methanogens which produce methane using hydrogen gas.

Models can play an important role in assessing a system or technology for further research and application. The International Water Association (IWA) modeling group has developed several wastewater treatment models like the activated sludge model (ASM) and the anaerobic digestion model (ADM) to assist with understanding and predicting various process streams involved in wastewater treatment. These models can support the application of technologies such as thermal pretreatment and anaerobic digestion if the processes involved in these systems can be accurately represented. Staples-Burger (2012) conducted preliminary work on this topic by characterizing WAS before and after thermal pretreatment in terms of chemical oxygen demand (COD) fractions. A stoichiometric COD pretreatment model was developed to describe the impacts of thermal pretreatment for one pretreatment condition and using aerobic digestion to characterize the biodegradable fractions. There is however a need to extend the range of thermal pretreatment conditions to span the range of conditions employed in practice. In addition, the model needs to be examined with respect to its ability to predict anaerobic digestion responses to pretreatment.

1.1 Objectives

The objectives of this project were to:

- Fractionate the COD of raw and pretreated WAS for several high temperature thermal pretreatment conditions to evaluate how pretreatment temperature and heating time affect WAS composition
- Investigate how pretreatment affects the rate and extent of aerobic digestion
- Investigate how pretreatment affects the rate and extent of anaerobic digestion
- Compare the impacts of pretreatment on aerobic and anaerobic biodegradability

1.2 Scope

This project investigated the impacts of high temperature thermal pretreatment on waste activated sludge (WAS) properties and its subsequent aerobic and anaerobic digestion using data that was generated in the laboratory at bench-scale. The lab data was generated by others following methods by Staples-Burger (2012) and Kianmehr (2010). Therefore, the focus of the project was to conduct a detailed analysis of the provided data and assess the applicability of models. The scope of the project included:

- Physical and biochemical characterization of WAS before and after pretreatment

- Assessment of aerobic and anaerobic biodegradability of WAS before and after pretreatment using respirometry data
- Assessment of COD fractionation of WAS before and after pretreatment
- Simulation of bench-scale system using BioWin Integrated Model calibrated with measured data

2. Background

2.1 Thermal Pretreatment

2.1.1. Introduction

Thermal pretreatment systems were initially employed to improve sludge dewaterability (Haug et al., 1978; Li & Noike, 1992). More recently, it has been increasingly studied and employed to treat sludge prior to anaerobic digestion. It is widely acknowledged that the particulate compounds in the sludge are disrupted and lysed by thermal pretreatment, allowing organics to be released (Xue et al., 2015). Hydrolysis is the first step of anaerobic digestion and is known to be the rate limiting step. The studies on thermal pretreatment thus attribute improvements in methane production to the increased rate of hydrolysis (Bougrier et al., 2008; Donoso-Bravo et al., 2011; Morgan-Sagastume et al., 2011; Xue et al., 2015). The solubilized materials are more readily biodegraded by extracellular processes, thus accelerating the release of simple organics from complex organic matter such as protein, lipids and carbohydrates.

Thermal pretreatment can be generally classified into two categories, low temperature (LT) thermal pretreatment (<100°C) and high temperature thermal pretreatment (>100°C) (Pilli et al., 2015). The variables of thermal pretreatment most widely studied are pretreatment temperature and duration (Aboulfotoh & Monayeri, 2015; Appels et al., 2010; Bougrier et al., 2008; Donoso-Bravo et al., 2011; Wilson & Novak, 2009). Pressure is also an important factor in thermal pretreatment. However, the pressure in a thermal hydrolysis unit usually changes with temperature. As such, high temperature thermal hydrolysis is usually conducted at a more elevated pressure and is typically designated as high pressure thermal hydrolysis (HPTH). According to the literature, pretreatment temperature is considered more important in HPTH in terms of solubilizing organics (Donoso-Bravo et al., 2011; Valo et al., 2004). Comparatively, it has been reported that pretreatment duration was more important when assessing the efficacy of low temperature thermal pretreatment (Appels et al., 2010; Xue et al., 2015).

The main disadvantage of HPTH is the extensive energy requirement (Morgan-Sagastume et al., 2011). However, the energy can be recovered by coupling thermal hydrolysis with anaerobic digestion to produce biogas. Kepp et al. (2000) suggested that the energy balance may even be positive when coupled with anaerobic digestion. The improvements in biogas/methane production due to HPTH are well documented (Donoso-Bravo et al., 2011; Eskicioglu et al., 2006; Valo et al., 2004; Xue et al., 2015). Comparatively, LT pretreatment has been found to yield no improvements in total gas volume (Nielsen et al., 2004; Prorot et al., 2011; Xue et al., 2015). Further attesting to the reliability and high performance of HPTH pretreatment is the number of full-scale configurations in operation including CAMBI™ and BIOTHELYS® (Pilli et al.,

2015). Another advantage is that the HPTH pretreatment is able to generate Class A biosolids that can be used as fertilizer in land applications (Oosterhuis et al., 2014). As such, HPTH was the focus of this project.

2.1.2. Pretreatment Conditions

The typical HPTH temperature range is 120°C to 180°C and the duration of pretreatment is typically 30 or 60 minutes (Bougrier et al., 2008). A few studies have focused on the impacts of pretreatment duration alone using HPTH by varying the duration between 0 and 60 minutes (Aboulfotoh & Monayeri, 2015; Donoso-Bravo et al., 2011). These studies sought the optimal pretreatment condition based on maximizing either the methane/biogas yield during anaerobic digestion or the degree to which various organics were solubilized. On the basis of increasing methane production and organics solubilization, the optimal range has been found to be 160°C to 180°C with pretreatment durations lasting for 30 to 60 minutes. Operation at temperatures higher than 180°C tended to decrease the biodegradability of the sludge due to formation of toxic refractory compounds such as Amadori and melanoidins compounds (Neyens & Baeyens, 2003; Pilli et al., 2015). While the range of temperatures and durations that have been tested is wide, studies that analyze and compare all of the conditions are scarce. Many studies either changed the temperature at a fixed duration (Arakane et al., 2006; Bougrier et al., 2008; Ramirez et al., 2009; Wilson & Novak, 2009), or changed the duration at a fixed temperature (Braguglia et al., 2015; Donoso-Bravo et al., 2011). However, Xue et al. (2015) and Sapkaite et al. (2017) evaluated pretreatment temperatures that ranged from 120°C to 180°C with durations ranging from 0 to 60 minutes.

One of the main issues stemming from previous pretreatment studies is that the results are generally not directly comparable between studies. Some studies did not characterize the sludge being pretreated. If they were characterized, the sludge source and experimental conditions were often different between studies. An experimental condition that varied widely across literature was the time to reach the desired pretreatment temperature. Bougrier et al. (2008) found that the duration varied from 25 to 60 minutes depending on target temperature. Donoso-Bravo et al. (2011) only required 10 minutes to raise temperature to 170°C, while Xue et al. (2015) found that the rise in temperature took 90 to 120 minutes. There were also conflicting results from HPTH systems using a flash tank to release the steam immediately after pretreatment. Donoso-Bravo et al. (2011) showed that the decompression had a significant impact on COD solubilization, whereas Gurieff et al. (2011) showed that the absence of a flash period did not affect COD solubilization. Sapkaite et al. (2017) found that the number of flash periods (decompression) did not affect the COD solubilization, however, a single flash seemed to have a significant impact on increasing methane production during anaerobic biodegradability tests.

The temperatures selected in the current study were 125°C, 150°C and 175°C as part of extending Staples-Burger (2012) study. For each pretreatment temperature, the duration employed was 10, 30 and 50 minutes. This did not include the time to reach the desired temperature. Hence a wide range of pretreatment conditions was selected to assess and compare the impact of HPTH temperature and duration on WAS.

2.1.3. Physical Properties

Measurements of solids were conducted in the current project to assess the physical properties of WAS before and after pretreatment. This section presents a review of the impact of HPTH on solids concentrations.

Bougrier et al (2008) calculated TSS/TS ratios before and after thermal pretreatment of five different WAS samples. For WAS pretreated at 130°C, 150°C and 170°C, the decreases in TSS/TS ratio were 20 ± 4%, 32 ± 5%, and 44 ± 11% respectively. These findings showed that suspended solids were solubilized by pretreatment and that temperature influenced the extent of suspended solids destruction (Bougrier et al., 2008). Morgan-Sagasume et al. (2010) reported a 20-30% decrease in TSS concentration according to (2.1), using the CAMBI^{TM} process at three different WWTP plants

$$TSS\ \%\ decrease = \frac{TSS_i - TSS_f}{TSS_i} \times 100\% \tag{2.1}$$

in which, TSS_i and TSS_f are TSS concentrations before and after pretreatment respectively. When combined with COD solubilization results that were reported in the study, this indicated that a substantial fraction of the suspended solids were solubilized by HPTH pretreatment.

Volatile suspended solids (VSS) concentrations are a common indicator of particulate organic matter in sludges. As such, decreases in VSS are often used to represent the conversion of particulate organic fractions to soluble organic fractions (Liu et al., 2012). Liu et al. (2012) pretreated WAS at 175°C for 60 minutes and found that the VSS solubilization was 27.5%. Further attesting to the solubilization of VSS was the increase in volatile dissolved solids (VDS) concentration after pretreatment from 5.77 g/kg to 35.5 g/kg. Staples-Burger (2012) reviewed a study by Gurieff et al. (2011) that showed the average VSS solubilization for WAS pretreated at 165°C was 31%. The VSS solubilizations in both of these studies were calculated by (2.2) in which VSS_i and VSS_f were VSS concentrations before and after pretreatment and TS was the total solids concentration.

$$VSS\ \%\ Solubilization\ = \frac{VSS_i - VSS_f}{TS} \times 100\% \tag{2.2}$$

A constant ratio of VS/TS and stable TS concentration during pretreatment are indications that organics are not removed or degraded through pretreatment (Morgan-Sagastume et al., 2011). Morgan-Sagastume et al. (2011) reported that the VS/TS ratio and TS concentrations before and after pretreatment at 160°C for two different sludge were unchanged. Braguglia et al. (2015) pretreated WAS at 135°C at various durations and concluded that the VS/TS ratio, as well as TS concentration was unchanged by pretreatment. Xue et al., (2015) studied pretreatment temperatures ranging from 120°C to 180°C at various durations and also concluded that the VS/TS ratio was constant during pretreatment. Furthermore, the total solids concentration also remained relatively stable. Therefore, the findings from these studies indicated that pretreatment did not remove or degrade organic matter for WAS pretreated at 120°C to 180°C.

2.1.4. Biochemical Properties

Measurements of COD and nitrogen species were conducted in the current project to assess the extent of organic solubilization due to pretreatment. The solubilization of COD is one of the most common indicators employed in assessing the impacts of HPTH pretreatment on WAS. The equations used to assess the degree to which COD was solubilized were (2.3) (Bougrier et al., 2008; Braguglia et al., 2015; Donoso-Bravo et al., 2011; Graja et al., 2005) and (2.4) (Kim et al., 2003; Y. Y. Li & Noike, 1992; Xue et al., 2015).

$$COD\ \%\ Solubilization\ = \frac{SCOD_f - SCOD_i}{PCOD_i} \times 100\% \tag{2.3}$$

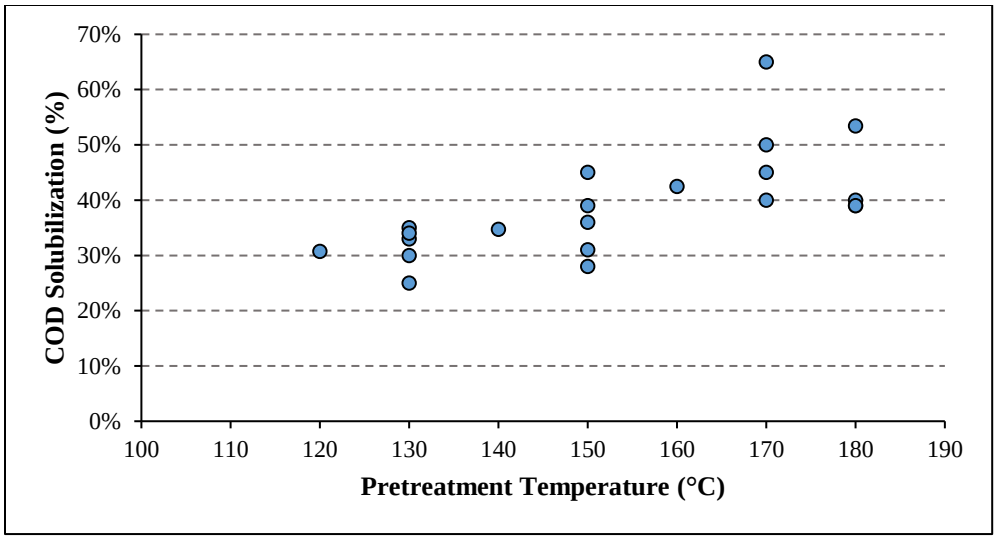
$$COD\ Soluble\ Ratio\ (\%) = \frac{SCOD_f}{TCOD_f} \times 100\% \tag{2.4}$$

In (2.3), $SCOD_i$ and $SCOD_f$ represented the soluble COD (SCOD) concentrations before and after pretreatment and $PCOD_i$ was the particulate COD (PCOD) prior to pretreatment. This formula calculated the amount of the initial PCOD in raw WAS that was converted to SCOD by pretreatment. Comparatively, the soluble fraction of the PWAS was calculated using (2.4). Suarez-Iglesias et al. (2017) noted that the equations became identical if the SCOD concentration of WAS prior to pretreatment was negligible and the total COD (TCOD) concentration remained constant through pretreatment. In all of the studies reviewed, the SCOD concentration was negligible in the raw WAS and significant removal of organics were not observed. Therefore, the calculation of COD solubilisation by both equations was deemed comparable.

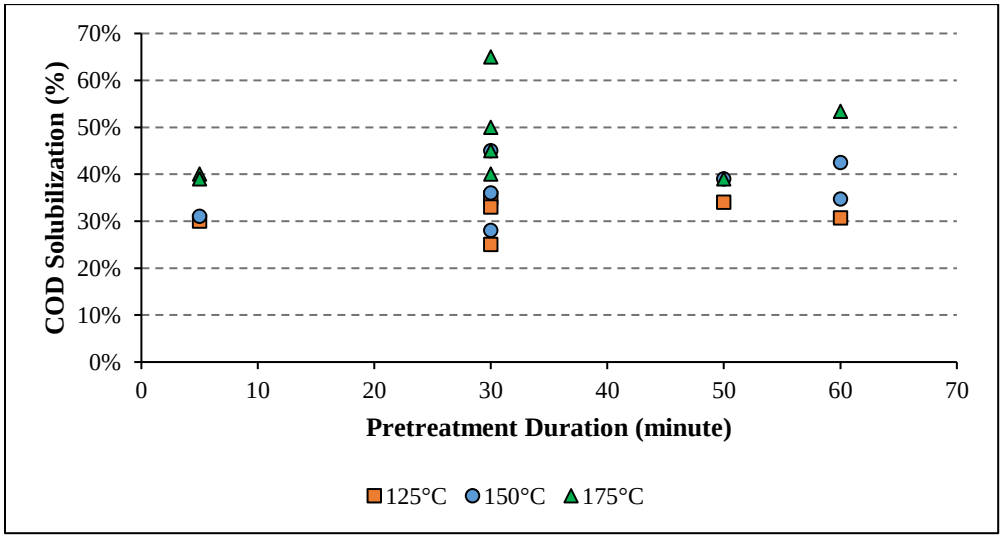
Xue et al. (2015) reported that the COD solubilization for WAS pretreated at 120°C, 140°C, 160°C and 180°C for approximately 60 minutes (not including time to reach desired temperature) was 30.7%, 34.7%, 42.5% and 53.4% respectively. Bougrier et al. (2008) pretreated 5 different sludge types at 130°C, 150°C and 170°C for 30 minutes and found that the range of COD solubilisation was approximately 25-35%, 30-

50% and 45-65% respectively. Donoso-Bravo et al. (2011) used a single temperature setting of 170°C to treat the sludge at different durations. Pretreatment durations of 5 to 30 minutes showed COD solubilisation ranging from 40 – 50%. It was noted that further increasing the duration from 10 minutes did not result in significant increases in COD solubilisation. Sapkaite et al. (2017) studied pretreatment temperatures of 130°C, 150°C and 180°C for 5, 30 and 50 minutes. The COD solubilization from this study ranged between 30% and 40%. The results of COD solubilization across the reviewed literature are summarized in Figure 2.1 (A). It can be seen that temperature has a greater influence on COD solubilization than pretreatment duration as evident by a distinct positive linear trend. It is widely accepted that temperature was important in solubilizing COD (Donoso-Bravo et al., 2011; Valo et al., 2004). However, conclusions on the effects of pretreatment duration were divided (Figure 2.1 (B)). Donoso-Bravo et al. (2011) reported that at high temperatures, increasing the duration from 10 to 30 minutes had minimal impact on COD solubilization. Conversely, Sapkaite et al. (2017) showed that pretreatment duration was also significant in increasing sludge solubility, albeit less than temperature. The COD solubilization results of the studies were comparable and ranged from 28% to 65% for pretreatment temperature range of 120°C to 180°C.

Staples-Burger (2012) reviewed three studies regarding the changes in the fractionation of nitrogen compounds due to pretreatment. The degree to which proteins were broken down and whether they were solubilized or mineralized was assessed. It was found that proteins may be ultimately broken down into amino acids by pretreatment, which then may be mineralized to release ammonia (Staples-Burger, 2012). Bougrier et al. (2008) and Donoso-Bravo et al. (2011) both demonstrated increases in ammonia concentrations were nominal, which showed that protein was not mineralized by HPTH. Morgan-Sagasume (2010) reported that the mass of total nitrogen per mass of total solids was constant throughout pretreatment at 160°C. Furthermore, the relatively low ratios of NH_4^+-N/TN indicated that pretreatment only partially mineralized amino acids.



(A)



(B)

Figure 2.1 COD Solubilization due to (A) Pretreatment Temperature (B) Pretreatment Duration

Xue et al. (2015) showed that pretreatment at 120°C and 140°C only showed a slight increase in ammonia concentrations. Park et al. (2014) also showed that ammonia concentration was unchanged by pretreatment at 121°C. However, the soluble total nitrogen (sTN) concentration increased, indicating that protein was solubilized rather than being degraded into amino acids. Comparatively, pretreatment at 160°C and 180°C increased the ammonia concentration (Xue et al., 2015). A similar finding was observed in an earlier study by Wilson et al. (2009) who found that ammonia concentrations increased quickly above 170°C. This

implied that at higher temperatures (>160°C), a portion of the proteins were degraded. However, in these studies the ammonia concentrations were not normalized to the total nitrogen (TN) concentration.

Morgan-Sagasume (2010) calculated the released ammonia concentration as a fraction of the TN and the ratio was relatively low indicating that mineralization of protein was not significant despite the increases in ammonia concentration. All previous studies that reported total nitrogen along with ammonia concluded that significant mineralization did not take place. Based on the review of the studies, it can be summarized that protein is solubilized rather than mineralized by pretreatment at temperatures in the range of 125°C to 175°C. However, at the higher range (160°C), proteins are increasingly mineralized albeit not to a substantial extent.

2.1.5. Biological Properties

HPTH pretreatment was expected to impact the activity of the biomass of the sludge (Staples-Burger, 2012). Donoso-Bravo et al. (2011) showed that the total coliform concentrations in pretreated sludge were undetectable indicating that bacteria were inactivated by pretreatment. Two approaches were reviewed and employed by Staples-Burger (2012) to estimate the activity of the biomass in WAS before and after pretreatment. Both of these methods utilized batch-mode respirometry in order to measure the concentration of active heterotrophic bacteria. From batch-mode respirometry, the oxygen uptake rate (OUR) due to consumption of substrate (WAS) was obtained. The first method employed a food to microorganism (F/M) ratio in the batch respirometric test that was high enough to observe an exponential increase in OUR with time as a result of biomass growth. Subsequent depletion of substrate resulted in a decrease in the OUR later in the tests. Staples-Burger (2012) followed the approach of Wentzel et al. (1998) to estimate the active heterotrophic bacteria concentration (Z_{bh0}) using (2.5)

$$Z_{bh0} = \frac{e^{y-intercept}}{\frac{1-Y_h}{Y_h} \times slope \times b_h} \tag{2.5}$$

in which, the y-intercept and slope values were estimated from the plot of the OUR curve that exponentially increased with time and was natural log transformed, Y_h was the aerobic yield of heterotrophic bacteria, and b_h was the aerobic decay rate. The aerobic decay rate (b_h) used by Staples-Burger (2012) was 0.24 d^{-1} at 20°C. A typical value of Y_h in activated sludge systems that is commonly cited (0.67 $gCOD_{produced}/gCOD_{removed}$) was employed (Henze et al., 2008). Hence, unless stated otherwise, the values for b_h and Y_h were 0.24 d^{-1} and 0.67 in the current study.

A low F/M ratio approach, where the OUR values reflected decay of WAS only was also employed when endogenous decay was the only oxygen consuming process (Staples-Burger, 2012). In this case, a nonlinear

regression of (2.6) to the measured OUR data could be employed to yield an estimate of the initial active biomass concentration in a sample (Jones et al., 2009)

$$OUR = (1 - f)b_h Z_{bh0} e^{-b_h t(\frac{1}{24})} \quad (2.6)$$

in which, OUR is the measured oxygen uptake rate (mg O_2/L/hr), f is the endogenous decay product fraction or organisms (0.2), Z_{bh} is the concentration of active biomass (mg COD/L), and t is time (days).

2.1.6. Indicators of Biodegradability

2.1.6.1. Rate and Extent of Aerobic Biodegradability

Staples-Burger (2012) demonstrated that the biodegradable fraction of WAS could be estimated using offline and online respirometry. This method involved calculating the oxygen consumption by substrate (WAS) from OUR curves derived using offline and online respirometry. The oxygen consumed was normalized by the TCOD mass of substrate in the samples to obtain an estimate of the biodegradable fraction of the COD.

The rate of aerobic biodegradability has been assessed by calculating the concentration of readily biodegradable COD (rbCOD) in samples. Both Musser (2010) and Kianmehr (2010) used the estimation of rbCOD to determine the impact of sonication and ozonation of WAS on the rate of aerobic biodegradability. The oxygen uptake for a sludge sample typically exhibits four distinctive successive phases. The first area (Area 1) corresponds to the oxygen uptake due to rbCOD. The second area (Area 2) corresponds to nitrification, however, distinguishing this area from Area 1 is usually difficult. Studies employing this method to determine rbCOD concentration typically inhibit nitrification such that Area 2 is not exhibited. The third area corresponds to the oxygen uptake due to consumption of slowly biodegradable COD (sbCOD) and the remaining area is due to endogenous respiration. Both studies (Kianmehr, 2010; Musser, 2010) estimated the concentration of rbCOD on the basis on the oxygen consumed during the initial oxygen uptake (Area 1).

Staples-Burger (2012) estimated the rbCOD concentration of WAS pretreated at 150°C for 30 minutes using a similar approach as Musser (2009) and Kianmehr (2010) and verified the results through modeling. Findings from all three studies showed that the pretreated WAS contained a substantial amount of readily biodegradable COD indicating that pretreatment increased the rate at which the WAS could be aerobically degraded.

2.1.6.2. Rate and Extent of Anaerobic Biodegradability

Kianmehr (2010) demonstrated that the rate and extent of anaerobic biodegradability could be evaluated using biochemical methane potential (BMP) tests. The initial rate of increase in methane concentrations in sealed serum bottles was determined to be indicative of the rate of anaerobic biodegradability. Comparatively, the ultimate methane yield at the end of a BMP test showed whether or not the biodegradability of the WAS changed for different samples. Kianmehr (2010) also investigated the ammonia generated during BMP tests. An empirical model was fit to the ammonia generation data ((2.7)) in order to determine the ammonification rate (k_{ammon}), which was assumed to represent the hydrolysis rate of proteins.

$$Ln\left(\frac{U_{Ult}^{ammon} - U_t^{Ammon}}{U_{ult}^{Ammon} - U_0^{Ammon}}\right) = -k_{Ammon} \times t \tag{2.7}$$

U_{Ult}^{ammon} denoted the ultimate ammonia yield (NH_4-N/TKN), U_t^{ammon} was the NH_4-N/TKN fraction at time t, U_0^{ammon} was the NH_4-N/TKN fraction at beginning of test, k_{Ammon} represented the ammonification rate constant (d^{-1}) and t was the digestion time (d).

Donoso-Bravo et al. (2011) and Pérez-Elvira et al. (2010) showed that the anaerobic biodegradability of WAS could be evaluated by fitting a Reaction Curve model to the cumulative methane production data ((2.8)). The maximum methane production (P) was used to assess whether pretreatment changed the extent of anaerobic biodegradability and maximum methane production rate (R_m) was used to assess the rate of anaerobic biodegradability.

$$B = P \cdot \left(1 - exp\left(\frac{-R_m(t-\lambda)}{P}\right)\right) \tag{2.8}$$

In the Reaction Curve, B was the methane production (mg/gCOD), P was the maximum methane production (mL/gCOD), R_m was the maximum methane production rate, λ was lag time (d) and t was the time of the assay (d).

2.1.7. Pretreatment Impact on Anaerobic Digestion

A common indicator of HPTH pretreatment performance is improvement in biogas/methane yield during anaerobic digestion of WAS. Bougrier et al. (2008) reviewed studies that reported improvements in biogas/methane generation due to thermal pretreatment. The results were presented in various ways. Some reported the improvements in terms of volume of methane (CH_4) produced per gram of COD entering an anaerobic digester. Others reported improvements in terms of volume of CH_4/biogas produced per gram of

VSS entering anaerobic digestion tests. Many studies also reported the improvement in terms of biogas/methane production (mL) without normalizing to the COD or VSS of the WAS. Despite the different responses, all studies reported the percentage increase in biogas/methane yield due to pretreatment according to (2.9). As such, this review on biogas/methane production improvements will be presented using changes in biogas/methane (%ΔCH_4) production. CH_{4i} and CH_{4f} denote the ultimate methane production before and after pretreatment.

$$\%\Delta CH_4 = \frac{(CH_4)_f - (CH_4)_i}{(CH_4)_i} \times 100\% \tag{2.9}$$

Sapkaite et al., (2017) pretreated WAS at 130°C, 150°C, and 180°C for 5, 30 and 50 minutes. These samples were used to conduct BMP tests for 50 days to measure methane generation. The increases in methane yield ranged from 30% to 63%. The average increase in methane yield for WAS pretreated at 130°C, 150°C and 180°C were 40%, 50% and 50% respectively. The average increase in methane yield for WAS pretreated for 5, 30 and 50 minutes were 44%, 47%, and 49% respectively. The authors used variance analysis to assess the influence of the pretreatment conditions on methane production. There were three factors studied: temperature, duration and flash (no. of decompressions). It was determined that the effect of temperature was linear and significant. The authors showed that there was an optimal range for improvement in methane yields for all three factors. Compared to temperature and number of flash periods, the impact of changing pretreatment duration was minimal for methane generation.

It should be noted that the results of previous studies described by Bougrier et al. (2008) were not comparable to Sapkaite et al. (2017). The duration of the digestion periods employed were typically less than 30 days. For example, Li and Noike (1992) reported an apparent 100% increase in biogas production for WAS pretreated at 175°C for 60 minutes. However, the increase was observed in the first 5 days of digestion. In these studies, it is likely that if digestion was allowed to continue, the improvements would have been lower. The substantial increase was likely due to the increased rate of methane production due to pretreatment rather than an increase in the ultimate biodegradability of the WAS. As such, comparison of improvements in methane production from the current study will be paired with results from Sapkaite et al. (2017) as digestion times employed in the current study were approximately 50 days.

3. Material and Methods

3.1 Experimental Setup and Operation Overview

The experimental setup used in this study was previously employed by Staples-Burger (2012), to evaluate a pretreatment condition of 150°C for 30 minutes. The bioreactors (BR) and thermal pretreatment reactors were used to generate a raw WAS (BR WAS) and pretreated WAS (PWAS) respectively and the PWAS was then aerobically digested in an aerobic digester. In the current study, a range of pretreatment conditions with temperatures and durations ranging between 125°C – 175°C and 10 – 50 minutes were evaluated as shown in Table 3.1.

Table 3.1 List of all Pretreatment Conditions Employed for Aerobic Digestion

Pretreatment Condition	Pretreatment Temperature (°C)	Pretreatment Duration (min)
125°C-10	125	10
125°C-30		30
125°C-50		50
150°C-10	150	10
150°C-30		30
150°C-50		50
175°C-10	175	10
175°C-30		30
175°C-50		50

In addition, the impacts of pretreatment on the anaerobic digestion of PWAS were investigated. All experimental data employed in this study were collected by others following the approach of Staples-Burger (2012). This section provides a broad overview of the experimental set-up and operation. The specific details of the operation can be found in Staples-Burger (2012).

Figure 3.1 provides an overview of the various stages of the experimental studies conducted to address the objectives of the project.

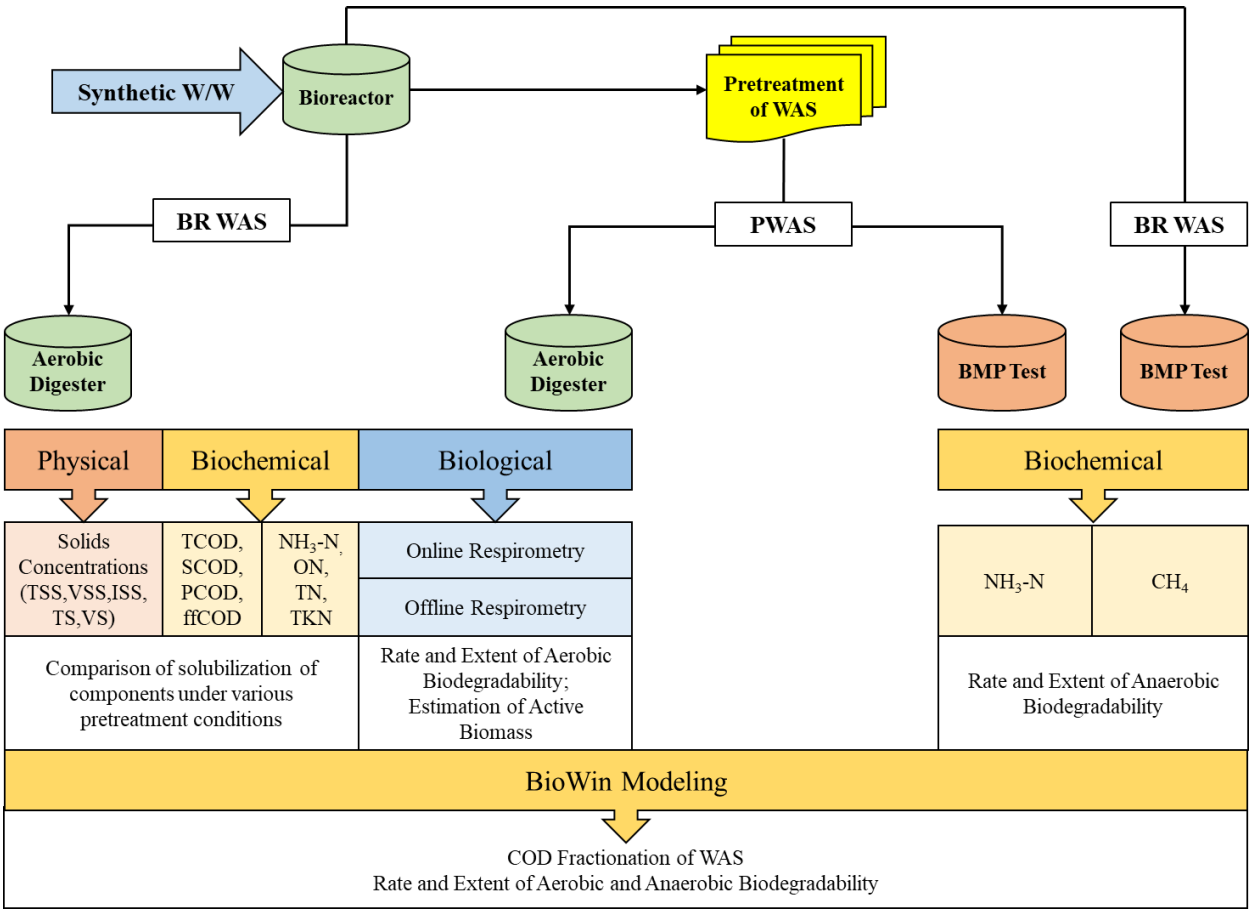


Figure 3.1 Overall Framework for Characterization of Impacts of Pretreatment on WAS

From Figure 3.1 it can be seen that a synthetic wastewater was fed to a bench-scale bioreactor (BR) to generate a waste activated sludge (BR WAS). The approach was employed so that the BR WAS that was generated was simpler in composition than authentic WAS. Hence the COD fractions that the BR WAS was composed of could be characterized to estimate aerobic and anaerobic biodegradability prior to pretreatment. The BR WAS was then pretreated at various thermal hydrolysis conditions shown in Table 3.1 using a Parr® Model 4563 Mini Pressure Reactor shown in Figure 3.2.

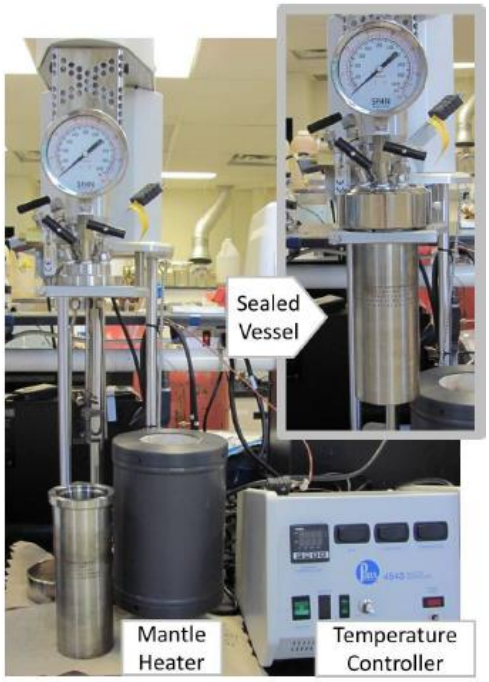


Figure 3.2 Parr® 4563 Mini Pressure Reactor for Thermal Pretreatment (Staples-Burger, 2012)

The pretreated WAS (PWAS) was generated to facilitate characterization of the impacts of thermal pretreatment on COD fractions. Physical and biochemical measurements of the BR WAS and PWAS were conducted to assess the extent to which COD fractions were solubilized by pretreatment. Table 3.2 shows all the measurements of COD, suspended solids and nitrogen species collected by methods outlined by Staples-Burger (2012). For both BR WAS and PWAS, the concentrations of total COD (TCOD) and soluble COD (SCOD) were measured. There were a total of four (4) samples collected for each measurement of TCOD and SCOD for both process streams. The particulate COD (PCOD) concentration were calculated by subtracting SCOD from TCOD. All COD data are summarized in Appendix A.

Solids data were collected for both process streams to assess whether organics were preferentially solubilized over inorganic compounds. Both total solids (TS) and total suspended solids (TSS) were characterized. For total solid measurements, the entire sample (BR WAS or PWAS) was used. Comparatively, for TSS samples, the samples were filtered through a filter with 1.5 µm pore sizes. These samples were ignited at 550°C for 45 minutes. The mass remaining on the filter represented inorganic solids (IS and ISS) and the mass burned off was the volatile solids (VS and VSS). As can be seen from Table 3.2, two samples were prepared for each measurement. Appendix A shows all the collected samples and the concentrations of various suspended solids and solids calculated.

Table 3.2 Physical and Biochemical Measurements of Various Streams

Stream	Experimental Test	Measurements	No. of Measurements
BR WAS (125°C-10, 125°C-30, 125°C-50, 150°C-10, 150°C-30, 150°C-50, 175°C-10, 175°C-30, 175°C-50)	COD	TCOD	4
		SCOD	4
		PCOD*	4
	SS	TSS	2
		VSS*	2
		ISS*	2
		TS	2
		VS*	2
PWAS (125°C-10, 125°C-30, 125°C-50, 150°C-10, 150°C-30, 150°C-50, 175°C-10, 175°C-30, 175°C-50)	COD	TCOD	4
		SCOD	4
		PCOD*	4
	SS	TSS	2
		VSS*	2
		ISS*	2
		TS	2
		VS*	2
	Nitrogen Species	Ammonia	2
		TKN	2
		sTKN	2
		ON*	2

*calculated by difference from measured data

Measurements of ammonia, Total Kjeldahl Nitrogen (TKN) and soluble TKN were conducted in duplicate for PWAS only and data describing the nitrogen species for BR WAS were not available. Using these measurements, the concentrations of organic nitrogen (ON) were calculated by subtracting the ammonia concentration from the TKN concentration for a given sample. All calculated concentrations can be found in Appendix A.

Online respirometry testing was conducted using the aerobic digester when it was fed with either BR WAS or with the various PWAS streams. Figure 3.3 shows the Jenco© model LD-900-5-DO Industrial Line DO Probe used to measure the dissolved oxygen (DO) concentration in the reactor. The probe and the aerobic digester were connected to a Jenco© model 6309-PDT Advanced Multi-Parameter Analyzer that was programmed to switch the aerators on and off according to the DO concentration in the aerobic digesters.

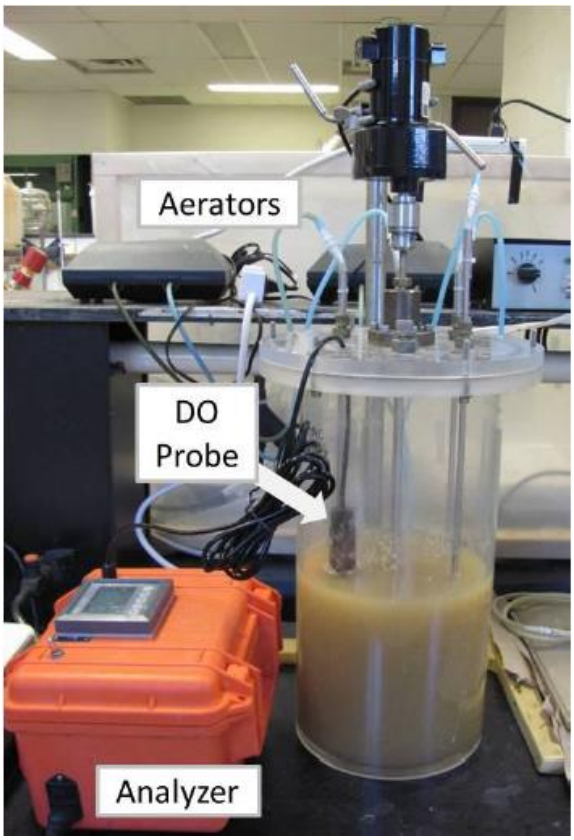


Figure 3.3 DO Probe and Analyzer Connected to Aerators in the Aerobic Digester (Staples-Burger, 2012)

The continuous DO data was used to generate oxygen uptake rate (OUR) and cumulative oxygen uptake curves for the aerobic digester over a react period. Table 3.3 shows the streams that were analyzed by online respirometry and the number of reaction periods which were characterized.

Table 3.3 Summary of Online Respirometry Tests Completed

Stream	No. of Reaction Periods Measured
BR WAS	1
125°C-10	3
125°C-30	3
125°C-50	3
150°C-10	3
150°C-30	3
150°C-50	3
175°C-10	3
175°C-30	3
175°C-50	3

Ideally, there would have been one BR WAS test associated with each PWAS test to allow for direct comparison between the input and output of the pretreatment. However, only a single online respirometry results was available for the BR WAS. With the exception of BR WAS, online respirometry was conducted over three react periods. Each react period consisted of feeding the substrate (BR WAS or PWAS) to the aerobic digester, subsequent consumption of substrate and endogenous respiration of biomass. All OUR curves derived from online respirometry conducted with the aerobic digesters can be found in Appendix B.

Offline respirometry was conducted using a Challenge Technology© AER-208 Respirometer (Figure 3.4). BR WAS, filtered BR WAS and AD WAS streams were analyzed by offline respirometry as described in Figure 3.5. Offline respirometry of PWAS was conducted in a similar manner to that shown in Figure 3.5, however the aerobic digester was acclimatized to PWAS as shown in Figure 3.6. The oxygen uptake rate (OUR) curves derived from these tests were used to determine the extent of aerobic biodegradability and the concentration of active biomass in the BR WAS and PWAS.

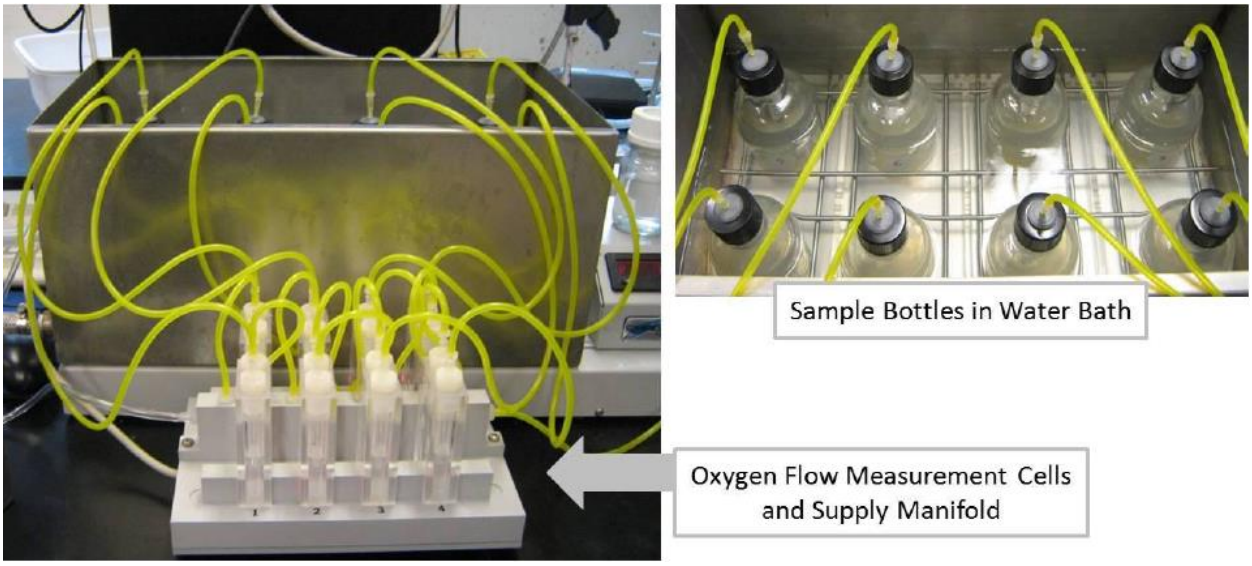


Figure 3.4 Challenge Technology AER-208 Respirometer (Staples-Burger, 2012)

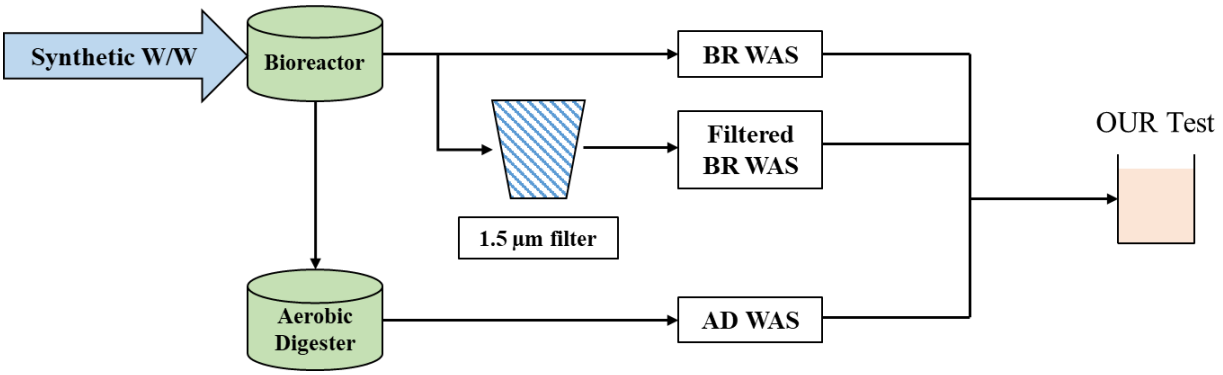


Figure 3.5 Offline Respirometry Process Flow Diagram for BR WAS

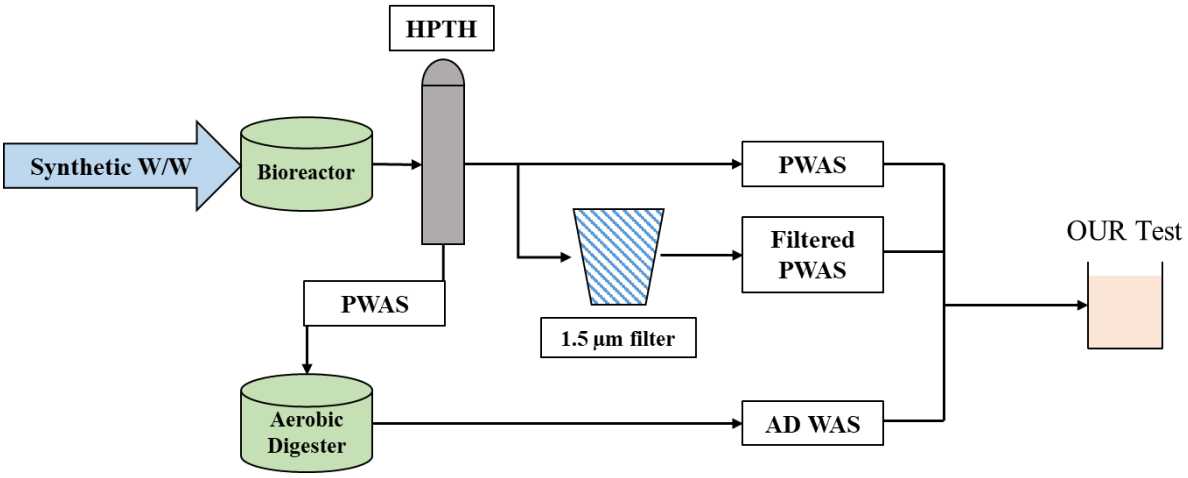


Figure 3.6 Offline Respirometry Process Flow Diagram for PWAS

Table 3.4 shows the process streams for which offline respirometry testing was conducted. For each process stream, there were four different combinations of contents assessed in the batch tests. Each combination was measured in duplicates. However, not all tests yielded measurable responses. For example, most of the batch tests with AD WAS alone showed little or no response. Similar to online respirometry, only a single offline respirometry test on BR WAS was available. The OUR curves generated from the offline respirometry tests can be found in Appendix C.

Table 3.4 Offline Respirometry Data for All Process Streams

Process Stream	Contents of Batch Respirometry	No. of Samples
BR WAS	BR WAS (150 mL) + Water (50 mL)	2
	AD WAS (50 mL) + Water (150 mL)	2
	BR WAS (150 mL) + AD WAS (50 mL)	2
	Filtered BR WAS (150 mL) + AD WAS (50 mL)	2
PWAS (125°C-10, 125°C-30, 125°C-50, 150°C-10, 150°C-30, 150°C-50, 175°C-10, 175°C-30, 175°C-50)	PWAS (150 mL) + Water (50 mL)	2
	AD WAS (50 mL) + Water (150 mL)	2
	PWAS (150 mL) + AD WAS (50 mL)	2
	Filtered PWAS (150 mL) + AD WAS (50 mL)	2

BR WAS and PWAS samples were also evaluated in biochemical methane potential (BMP) tests to determine the rate and extent of anaerobic biodegradability of the WAS before and after pretreatment. For this portion of the project, three pretreatment conditions – 125°C-10, 150°C-10, 175°C-10 – were excluded. It was deemed sufficient to conduct BMP tests for WAS pretreated for 30 and 50 minutes to determine the impact of pretreatment duration on anaerobic biodegradability. Table 3.5 shows the pretreatment conditions studied in the anaerobic digestion phase of this project.

Table 3.5 List of All Pretreatment Conditions Employed for Anaerobic Digestion

Pretreatment Condition No.	Pretreatment Temperature (°C)	Pretreatment Duration (min)
125°C-30	125	30
125°C-50		50
150°C-30	150	30
150°C-50		50
175°C-30	175	30
175°C-50		50

Table 3.6 summarizes the process streams on which BMP tests were conducted. Gas phase BMP tests were conducted to measure biogas and methane generation from the sludge samples, while ammonia tests characterized the ammonia release during digestion. Table 3.7 summarizes the duration of the gas and ammonia tests and the sampling schedule that was employed. Every test was conducted in duplicate to

assess reproducibility. A total of 36 samples were analyzed by the BMP tests. In the gas phase tests the volume of generated gas was measured regularly over the digestion period of approximately 50 days and composition was analyzed by gas chromatography. Before the start of BMP tests, initial measurements of TCOD were conducted for each process stream mentioned in Table 3.6. Table 3.8 shows all the measurements of COD conducted for BMP tests.

Table 3.6 Summary of BMP Tests Conducted

Process Stream	No. of Samples
BMP (Gas)	
Inoculum for 30 min PWAS	2
Inoculum for 50 min PWAS	2
BR WAS	2
125C-30 PWAS with Inoculum	2
150C-30 PWAS with Inoculum	2
175C-30 PWAS with Inoculum	2
125C-50 PWAS with Inoculum	2
150C-50 PWAS with Inoculum	2
175C-50 PWAS with Inoculum	2
BMP (Ammonia)	
Inoculum for 30 min PWAS	2
Inoculum for 50 min PWAS	2
BR WAS	2
125C-30 PWAS with Inoculum	2
150C-30 PWAS with Inoculum	2
175C-30 PWAS with Inoculum	2
125C-50 PWAS with Inoculum	2
150C-50 PWAS with Inoculum	2
175C-50 PWAS with Inoculum	2

Table 3.7 Duration and Sampling Intervals for BMP Tests

Type of BMP Test	Duration of Test	Sampling Intervals
Ammonia	50 Days	Day 0, 2, 5, 10, 15, 20, 35, 50
GAS (30 minute PWAS, Inoculum for 30 min PWAS, BR WAS)	46 Days	Day 0, 1, 3, 4, 6, 8, 10, 14, 19, 28, 35, 46
GAS (50 minute PWAS, Inoculum for 50 min PWAS)	50 Days	Day 0, 1, 2, 3, 4, 5, 6, 7, 8, 10, 12, 14, 18, 23, 32, 39, 50

Table 3.8 Summary of Initial TCOD Measurements for BMP Tests

Process Stream	No. of TCOD Measurements
BR WAS	2
Inoculum for 30 Minute PWAS	4
Inoculum for 50 Minute PWAS	6
125C-30	4
150C-30	4
175C-30	4
125C-50	4
150C-50	4
175C-50	4

The biogas and gas composition data were used to calculate the volumes of methane, carbon dioxide and nitrogen gas and are summarized in Appendix D. The concentrations of ammonia obtained from the BMP tests throughout anaerobic digestion were also tabulated and are summarized in Appendix D.

3.2 Analysis and Modeling Approach

The main objectives of this project were to analyze the COD fractionation of WAS before and after pretreatment, and to determine and compare the impacts of pretreatment on aerobic and anaerobic digestion. This section describes the approach that was used to meet these objectives.

3.2.1. COD Fractionation of BR WAS

The process streams of importance in this study were the BR WAS and PWAS. The goal was to analyze the impacts of thermal pretreatment on the properties of BR WAS. Table 3.9 outlines the data employed, tools used for analysis and the final parameter/values estimated for COD fractionation of BR WAS.

Table 3.9 Overview of Data and Methods – COD Fractionation of BR WAS

Data Employed	Description
Offline Respirometry	Oxygen Uptake Rate Curve of BR WAS only
Equations/Models/Computations Employed	**Description**
Biowin Integrated Model 5.0	Wastewater System Simulator
$OUR = (1-f)b_h Z_{bh,BR} e^{-b_h t(\frac{1}{24})}$	Estimation of Active Biomass from OUR driven by endogenous decay ((2.6))
$Z_{e,BR} = f b_h Z_{bh,BR} SRT_{BR}$	Estimation of Endogenous Products Concentration ((4.5))
Parameter Estimated	**Description**
$Z_{bh,BR}$	Active Biomass Concentration in BR WAS
$Z_{e,BR}$	Endogenous Products Concentration in BR WAS

As shown in Table 3.9, the COD of the BR WAS was fractionated in terms of the active biomass and endogenous product components. BioWin® was initially used to simulate the start-up of the bioreactor and to demonstrate that the major COD components of BR WAS would be active biomass and endogenous products. Further, characterizing the WAS prior to pretreatment facilitated comparison with the composition of the PWAS. The active biomass concentration ($Z_{bh,BR}$) was estimated by a nonlinear regression of (2.6) to the offline respirometry of BR WAS only. The endogenous product concentration ($Z_{e,BR}$) was then calculated on the basis of the rate of endogenous respiration and the remaining cell debris (Melcer, 2004).

3.2.2. Aerobic Biodegradability of WAS and PWAS

The aerobic biodegradability of the BR WAS and PWAS was determined from offline and online respirometry data to assess whether pretreatment changed the extent to which WAS could be aerobically biodegraded. The methods used to determine the aerobically biodegradable fraction of the COD were similar for both sources of respirometric data. Table 3.10 outlines the data and methods employed to determine the aerobic biodegradability of the BR WAS and all nine PWAS samples outlined in Table 3.1.

Table 3.10 Overview of Data and Methods – Aerobic Biodegradability of BR WAS and PWAS

Data Employed	**Description**
COD	Total COD of BR WAS and PWAS
Offline Respirometry	OUR Curve of BR WAS only, OUR Curve of PWAS + AD WAS
Online Respirometry	OUR Curve of BR WAS and PWAS
Equations/Models/Computations Employed	**Description**
$\sum OU_T = \sum OU_S + \sum OU_E$	Total, Substrate and Endogenous Respiration Cumulative Oxygen Uptake ((4.3))
$OUR = (1-f)b_h Z_{bh0} e^{-b_h t(\frac{1}{24})}$	Estimation of OUR due to endogenous respiration ((2.6))
Parameter Estimated	**Description**
$\sum OU_S$/TCOD	Aerobically Biodegradable fraction of Sample

The online OUR responses were assumed to be due to consumption of substrate (BR WAS or PWAS) and subsequent endogenous decay. The area under the entire OUR curve was estimated to determine the total cumulative oxygen uptake ($\sum OU_T$) for a test and represented the sum of the substrate ($\sum OU_S$) and endogenous respiration ($\sum OU_E$) cumulative oxygen uptakes. The value of $\sum OU_E$ was estimated by nonlinear regression of (2.6) to the tail end of the OUR curves. The value of $\sum OU_S$ was determined as the difference between the $\sum OU_T$ and $\sum OU_E$ values. The aerobic biodegradability was estimated by dividing the $\sum OU_S$ value by the TCOD concentration of the sample added to the respirometry test. Similarly, the

OUR curves generated from offline respirometry were used to determine the oxygen uptake due to substrate alone. The estimates of aerobic biodegradability from online and offline respirometry were combined to conclude whether pretreatment altered the biodegradable fraction of BR WAS.

3.2.3. COD Fractionation of PWAS

The COD fractionation of the PWAS samples (Table 3.1) was determined using the data and methods outlined in Table 3.11. This fractionation was then compared with the BR WAS composition to assess how the different levels of pretreatment altered the fractionation.

Table 3.11 Overview of Data and Methods – COD Fractionation of PWAS

Data Employed	**Description**
COD	Total, soluble, and particulate COD of PWAS
Offline Respirometry	Oxygen Uptake Rate Curve of PWAS + AD WAS
Online Respirometry	Oxygen Uptake Rate Curve of PWAS
Equations/Models/Computations Employed	**Description**
$Z_{bh,PWAS} = \frac{e^{y-intercept}}{\frac{1-Y_h}{Y_h} \times slope \times b_h}$	Estimation of active biomass from OUR during growth and decay periods ((2.5))
BioWin Integrated Model 5.0	Wastewater system simulator
Parameter Estimated	**Description**
$Z_{bh,PWAS}$	Active Biomass Concentration in PWAS
S_{bsc}	Readily Biodegradable COD Concentration
X_{sp}	Slowly Biodegradable COD Concentration

To assess whether pretreatment inactivated the biomass, the active biomass concentration was estimated by transforming the exponentially increasing portion of the PWAS OUR curves derived from offline respirometry. The natural log of the OUR values were initially calculated and plotted against time. Excel™ was then used to fit a linear equation to each data set and the resulting slope and y-intercept were employed in (2.5) to estimate the active biomass concentration.

The BioWin® process simulator was used to estimate the concentrations of readily and slowly biodegradable COD for each PWAS sample. In this approach, the endogenous products concentration in the PWAS was assumed to be the same as that estimated in the BR WAS. Analysis of COD concentrations showed that the TCOD was conserved after pretreatment. Kianmehr (2010) suggested that the inactivation of biomass by pretreatment was indicative of its conversion to biodegradable forms. Once it was verified that pretreatment inactivated most of the active biomass, it was assumed that it was converted to either S_{bsc} or X_{sp}.

A process flowsheet was developed in BioWin® to represent the offline respirometry tests. In the flowsheets, PWAS and AD WAS, were directed to a variable volume reactor, representing batch respirometry bottles. The AD WAS input had been created in a separate BioWin® process flowsheet where the AD received PWAS under steady-state conditions. The PWAS input was characterized using measured TCOD concentrations and calculated endogenous decay fractions from Section 3.2.1. The values of S_{bsc} and X_{sp} of the PWAS were then adjusted until the predicted and measured OUR responses predicted in the offline respirometry model matched the measured OUR response as indicated by minimizing the sum of squared differences.

3.2.4. Anaerobic Biodegradability of WAS and PWAS

The anaerobic biodegradability of BR WAS and PWAS were assessed to determine whether pretreatment changed the rate and extent to which WAS could be anaerobically biodegraded. Table 3.12 outlines the data and methods employed to determine the anaerobic biodegradability of the BR WAS and PWAS samples outlined in Table 3.5.

Table 3.12 Overview of Data and Methods - Anaerobic Biodegradability of BR WAS and PWAS

Data Employed	**Description**
Biochemical Methane Potential Test	Methane Generation and Ammonia Concentrations observed during Anaerobic Digestion
Equations/Models/Computations Employed	**Description**
$B = P \cdot \left(1 - exp\left(\frac{-R_m(t-\lambda)}{P}\right)\right)$	Reaction Curve – Estimation of methane production as a function ultimate methane production (P) and maximum methane production rate (R_m) ((2.8))
BioWin Integrated Model 5.0	Wastewater system simulator
Parameter Estimated	**Description**
P	Maximum Methane Production (mL/gCOD)
R_m	Maximum Methane Production Rate (mL/gCOD d)
$f_{Ze,biodegradable}$	Fraction of Endogenous products available for biodegradation

The rate and extent of anaerobic biodegradability were initially characterized by fitting the Reaction Curve to the initial slopes of the methane production curves and the ultimate methane yield from the BMP test data respectively. The Reaction Curve included parameters for maximum methane production rate and maximum methane produced which represented the rate and extent of anaerobic biodegradability respectively. It was assumed that changes in these parameters through pretreatment indicated that the anaerobic biodegradability changed due to pretreatment.

The BioWin® simulator was also fit to the BMP test results to obtain additional characterization of the anaerobic biodegradability of the WAS. Initially, the COD fractions estimated from the aerobic digestion analysis were used to model the BMP tests. If the model could not predict the measured methane production, the endogenous products decay rate was adjusted until the ultimate methane yield predicted by BioWin matched the BMP data. This approach effectively modified the biodegradable fraction of WAS as compared to the aerobic approach.

4. Results

4.1 Start-up of Reactors

BioWin® was used to simulate the start-up of the bioreactors (BR) and to confirm that the major COD components of the BR WAS was comprised of ordinary heterotrophic biomass (Z_{bh}) and endogenous products (Z_e). Additionally, the time for the BR to reach steady-state was estimated in order to generate a stable source of WAS for subsequent modeling.

In the lab, the BR was initially seeded with sludge from the Waterloo WWTP and fed with synthetic wastewater on a daily basis to generate BR WAS. The BR was operated as a sequencing batch reactor (SBR) using BioWin 5.0®, with a solids retention time (SRT) of 5 days. The concentrations of major COD components in the seed sludge from the Waterloo WWTP were modeled and estimated by Staples-Burger (2012) and it was determined that major contributors were particulate inert COD (X_i), endogenous products (Z_e) and ordinary heterotrophic biomass (Z_{bh}). The synthetic wastewater influent parameters were calculated based on the synthetic wastewater recipe used by Staples-Burger (2012) and converted to required units for BioWin®.

Figure 4.1 illustrates operation of the BR for 20 days. It shows that the BR reached steady-state around 15 days, or 3 SRTs. The major components of COD were Z_{bh} and Z_e. All other components present in the seed sludge were washed out by the time the BR reached steady-state. The rapid growth of active biomass (Z_{bh}) was observed after feeding and as the substrate was depleted, a decline in Z_{bh} was observed. This corresponded to increases in endogenous products from decay of active biomass.

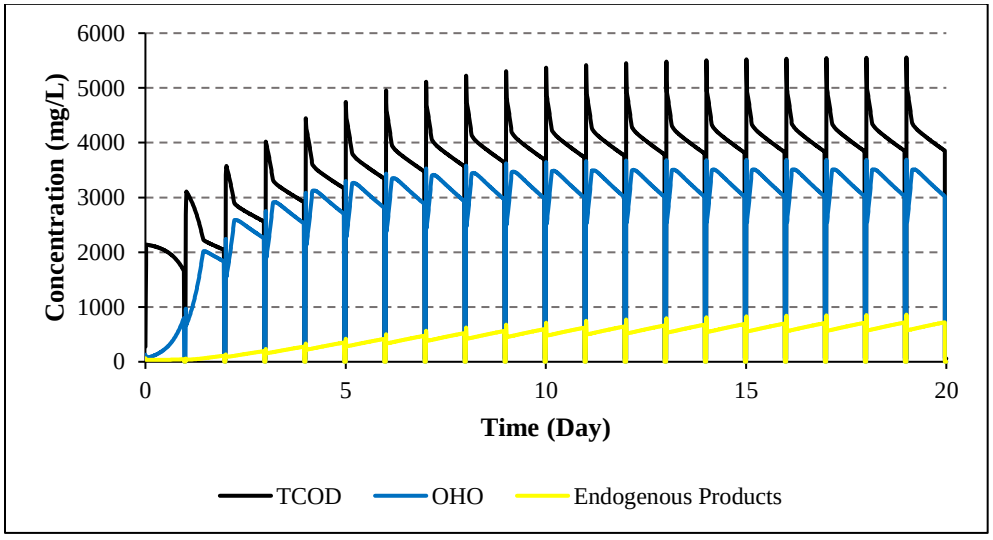


Figure 4.1 Start-up of Bioreactor and COD Components of BR WAS

Therefore, the BR reached steady-state by 15 days and was generating a steady source of WAS which was primarily composed of active biomass (Z_{bh}) and endogenous products (Z_e). This simulation agreed with a study by Ramdani et al. (2010), which concluded that reactors fed with synthetic substrate yielded WAS comprised of Z_{bh} and Z_e. The exact fractionation of the BR WAS into Z_{bh} and Z_e will be presented in Section 4.3.2.2.

4.2 Physical and Biochemical Characterization of Process Streams

4.2.1. Biological Reactor

Measurements of COD and SS were taken throughout the duration of the study in order to characterize the BR WAS and to ensure that the BR operation was stable. Figure 4.2 shows the relatively constant profile of COD and SS concentrations of BR WAS indicating that the BR was stable during this period.

The properties of the BR WAS were estimated using the data presented in Figure 4.2. The BR WAS was mostly particulate, as indicated by low concentrations of SCOD. This SCOD was assumed to consist of soluble microbial products (SMP), or S_{us}, generated in the reactor (Staples-Burger, 2012). Measurements of ffCOD were not obtained, however, Staples-Burger (2012) concluded that there was no statistical difference between ffCOD and SCOD concentrations in the BR WAS. The SCOD concentration included both soluble and colloidal COD, whereas ffCOD measurements were representative of truly soluble COD. Therefore, it was concluded that the BR WAS contained little colloidal matter. Kianmehr (2010) explained that colloidal COD was typically entrapped in extracellular polymeric substances (EPS) in WAS. On the basis of the conclusions from Staples-Burger's (2012) study, the BR WAS was assumed to not contain substantial quantities of EPS with particles in the colloidal range.

Staples-Burger (2012) calculated the average COD/VSS ratio of the BR WAS to be 1.23 ± 0.08 whereas a typical value of 1.42 is reported (Henze et al., 2008) for active heterotrophs and endogenous residue. The lower value calculated in Staples-Burger (2012) suggested the presence of stored COD in the form of glycogen or poly-hydroxy-alkanoates (PHA). In this study, the average measured COD/VSS ratio was 1.5 ± 0.16 which was slightly higher than the typical value. However, a t-test at 95% confidence level revealed that there was no statistical difference between the calculated COD/VSS ratio and the typical value and therefore, it was concluded that stored COD was not present in the BR WAS in this study. This finding validated the assumption that the BR WAS was only comprised of Z_{bh} and Z_e.

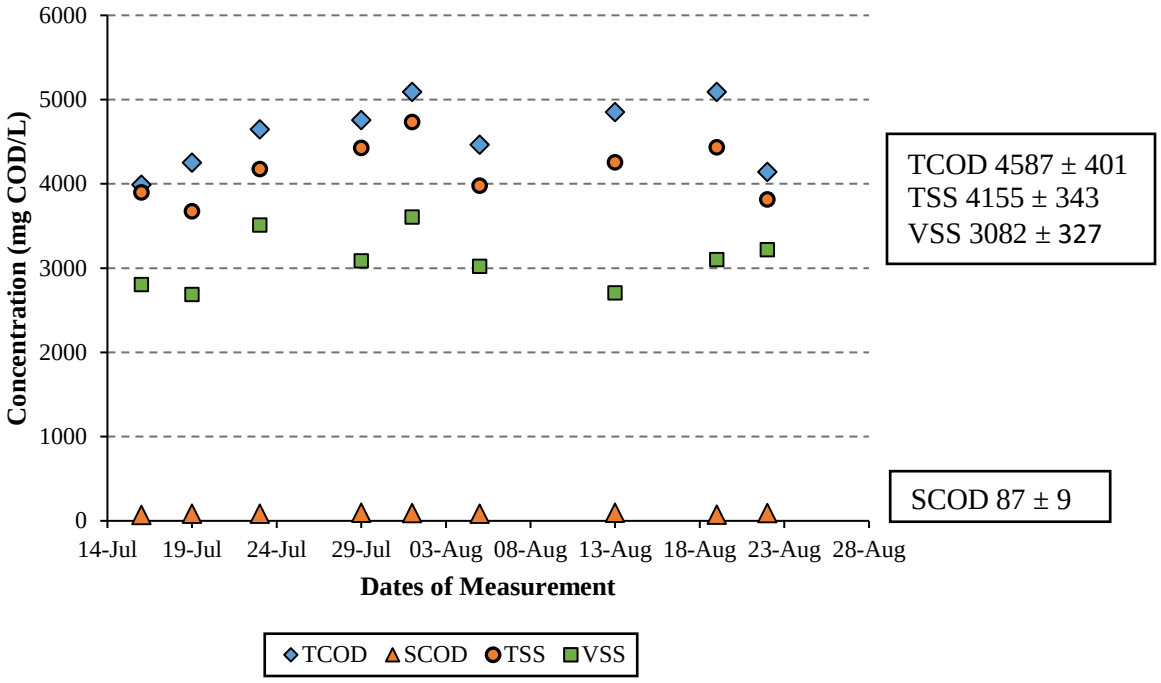


Figure 4.2 COD and SS Measurements of BR WAS

4.2.2. Effects of Pretreatment on BR WAS

The effects of HPTH pretreatment on BR WAS was evaluated in terms of physical (i.e. TSS removal, VSS destruction) and biochemical (i.e. COD and nitrogenous species solubilization) properties. There were no measurements of pH collected for this study.

Measurements of COD were collected before and after all nine pretreatment conditions. For 150°C-10, 150°C-30, 175°C-10 and 175°C-30 PWAS, the TCOD was conserved as there was no statistical difference between the TCOD concentration before and after pretreatment at the 95% confidence level. For all other pretreatment conditions, the differences were found to be statistically significant. Table 4.1 shows the differences in the TCOD concentrations before and after all pretreatment conditions. The estimates of uncertainty could not be estimated for 150°C-30 PWAS as only two measurements of TCOD were obtained. For 175°C-30 PWAS the TCOD concentrations increased after pretreatment which was unreasonable as this indicated that pretreatment generated more organics. From Table 4.1 it can be seen that the differences in TCOD were close to the typical measurement error of 10% associated with COD measurements. Viewed collectively, it was concluded that pretreatment at all levels did not significantly remove TCOD.

Table 4.1 Summary of Differences in TCOD Concentration Before and After Pretreatment

Pretreatment Condition	Difference in TCOD Before and After Pretreatment (%)
125°C-10	9.8 ± 1.3%
125°C-30	13.7 ± 1.3%
125°C-50	13.3 ± 3.1%
150°C-10	9.9 ± 9.4%
150°C-30	9.1%
150°C-50	9.4 ± 4.0%
175°C-10	7.9%
175°C-30	5.7 ± 4.2%
175°C-50	16.9 ± 3.5%

This corroborated findings from others (Bougrier et al., 2008; Braguglia et al., 2015; Graja et al., 2005; Y. Y. Li & Noike, 1992; Ramirez et al., 2009) that concluded that TCOD was conserved rather than destroyed. Bougrier et al. (2006) reported significant differences in TCOD values from raw and pretreated WAS. This was attributed to poor sampling technique and sludge being stuck to the containers during transfer. This was likely the issue for the cases that revealed a statistically significant difference between TCOD concentrations. Staples-Burger (2012) also concluded that the TCOD concentration was unchanged after pretreatment at 150°C for 30 minutes and thus no removal of organics occurred.

Prior to pretreatment, the fraction of SCOD was typically less than 1%. After pretreatment at the various temperatures and durations, COD was substantially solubilized. Figure 4.3 shows, as an example, the measured COD concentrations before and after pretreatment at 150°C for 10 minutes. The PCOD was calculated by subtracting the SCOD from the TCOD. The concentrations of the COD components as shown in Figure 4.3 were also generated for all other pretreatment conditions and are presented in Appendix E.

The SCOD and PCOD in the BR WAS and PWAS samples were compared to assess whether the changes with pretreatment were statistically significant. Using a t-test at 95% confidence level, it was concluded that the corresponding values were statistically different and hence all levels of HPTH pretreatment indicated a substantial solubilization of COD.

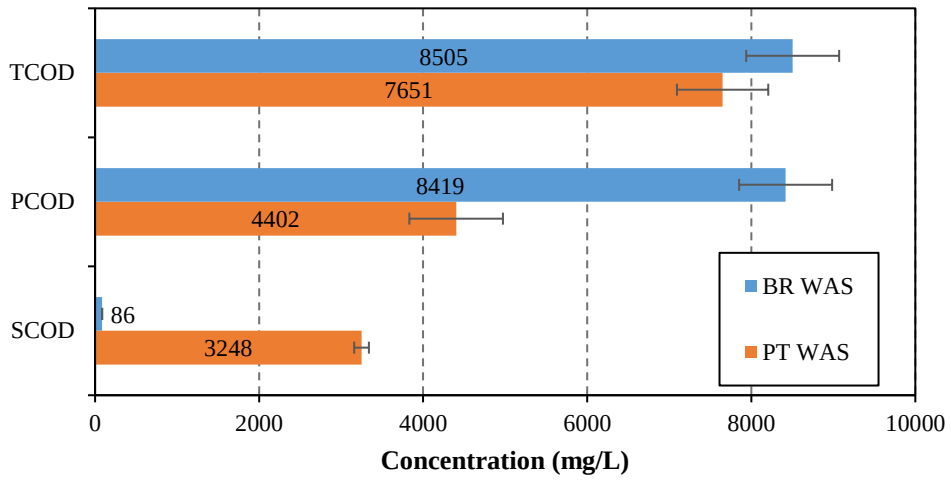


Figure 4.3 Total, Particulate and Soluble COD Concentrations Before and After Pretreatment at 150°C for 10 minutes

In order to compare the extent to which COD was solubilized across various pretreatment conditions, (2.3) and (2.4) were used. Table 4.2 summarizes the COD solubilization and COD soluble ratio for all pretreatment conditions. From Table 4.2 it can be seen that the COD solubilization ranged from 30.4 – 55.4% (31.2 to 55.9% soluble ratio). The values calculated by the two equations were similar and hence only COD solubilization was used for further analysis.

Table 4.2 Summary of COD Solubilization for all Pretreatment Conditions

Pretreatment Condition	COD Solubilization (%)	COD Soluble Ratio (%)
125°C – 10 min	30.4 ± 1.6	31.2 ± 1.5
125°C – 30 min	37.5 ± 1.6	38.3 ± 1.5
125°C – 50 min	35.6 ± 2.6	36.0 ± 2.2
150°C – 10 min	37.7 ± 1.6	36.5 ± 2.5
150°C – 30 min	39.3 ± 0.9	39.8 ± 1.9
150°C – 50 min	46.8 ± 2.7	47.2 ± 2.5
175°C – 10 min	46.3 ± 2.0	46.8 ± 1.8
175°C – 30 min	50.6 ± 1.9	51.0 ± 1.7
175°C – 50 min	55.4 ± 2.0	55.9 ± 1.9

From Table 4.2 it can be seen that the impact of pretreatment duration on solubilization was not consistent for the different temperatures. For WAS pretreated at 125°C, increasing the duration from 10 to 30 minutes substantially increased COD solubilization, however further increasing it to 50 minutes decreased the COD solubilization. Conversely, for WAS pretreated at 150°C, increasing the duration from 10 to 30 minutes had minimal impact on COD solubilization. When the duration was increased to 50 minutes, the COD

solubilization increased. Unlike pretreatment time, increasing the temperature seemed to increase the extent of COD solubilization steadily.

It was concluded in several studies (Bougrier et al., 2008; Donoso-Bravo et al., 2011; Valo et al., 2004; Wilson & Novak, 2009) that pretreatment temperature had a greater effect on COD solubilization compared to pretreatment duration. Sapkaite et al. (2017) used variance analysis to determine the significance of pretreatment temperature and duration on COD solubilization and found that both were significant. However, the importance of temperature was more significant as indicated by the higher F-value. An analysis of variance for the current set of pretreatment conditions revealed that both temperature and time were significant (Appendix F) and that temperature was more significant compared to duration. These results agreed with the findings from the literature.

In Staples-Burger's (2012) study, COD solubilization was 41 ± 5% for 150°C-30 PWAS, which was in close agreement with the results from the current study. Bougrier et al (2008) assembled COD solubilization data for WAS pretreated at various temperatures for 30 minutes from several studies. A line of best-fit was fit to the data yielded (4.1).

$$SCOD[\%] = 0.312\theta[℃] - 8.73 \quad (4.1)$$

Using (4.1), the COD solubilization at 125°C, 150°C and 175°C were 30.27%, 38.07% and 45.87% respectively. Similarly, Sapkaite et al. (2017) showed that WAS pretreated for 30 minutes at 130°C, 150°C and 180°C achieved COD solubilization of 33%, 36% and 40% respectively. The COD solubilization observed in the current study was comparable to values reported across the literature.

Suspended solids measurements were also collected before and after pretreatment. Figure 4.4 shows the suspended solids components measured for BR WAS and 150°C-10 PWAS. It can be seen that the VSS concentration substantially decreased as compared to the inorganic suspended solids (ISS) concertation. This shows that organic suspended solids were preferentially solubilized by pretreatment as compared to inorganic suspended solids. Similar conclusions were made by Staples-Burger (2012), where a significant difference was found between VSS concentrations but not for ISS concentrations. These trends in suspended solids concentrations through pretreatment were observed for all conditions that were tested (Appendix G).

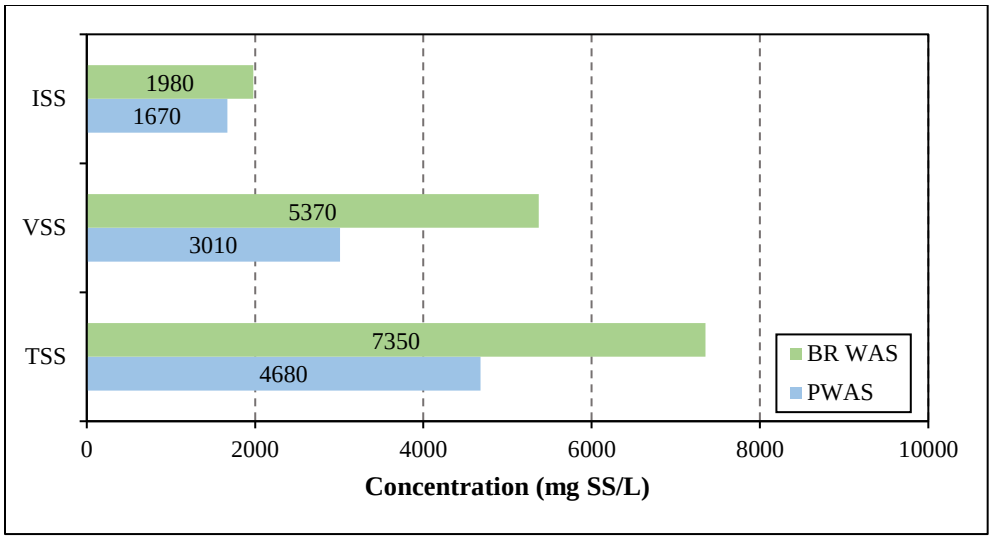


Figure 4.4 Suspended Solids Concentrations Before and After Pretreatment at 150°C for 10 minutes

TSS destruction was calculated using (2.1) to compare between studies. In the current study, the TSS decrease as calculated by (2.1) ranged from 30% to 60% as shown in Figure 4.5. The highest TSS destruction values corresponded to the 175°C-10 and 175°C-30 conditions (57% and 60% respectively). Aside from these values, the TSS destruction values ranged from 30% to 40%. Morgan-Sagasume et al. (2011) pretreated WAS used CAMBI^{TM} at 160°C for 30 minutes and found that the range of TSS destruction ranged from 20-30% while Staples-Burger (2012) reported a higher TSS destruction of 49 ± 6% for 150°C-30 PWAS. Therefore, TSS destruction in this study was consistent with the literature that has ranged from 20% to 50% although no studies have reported TSS destruction at 175°C.

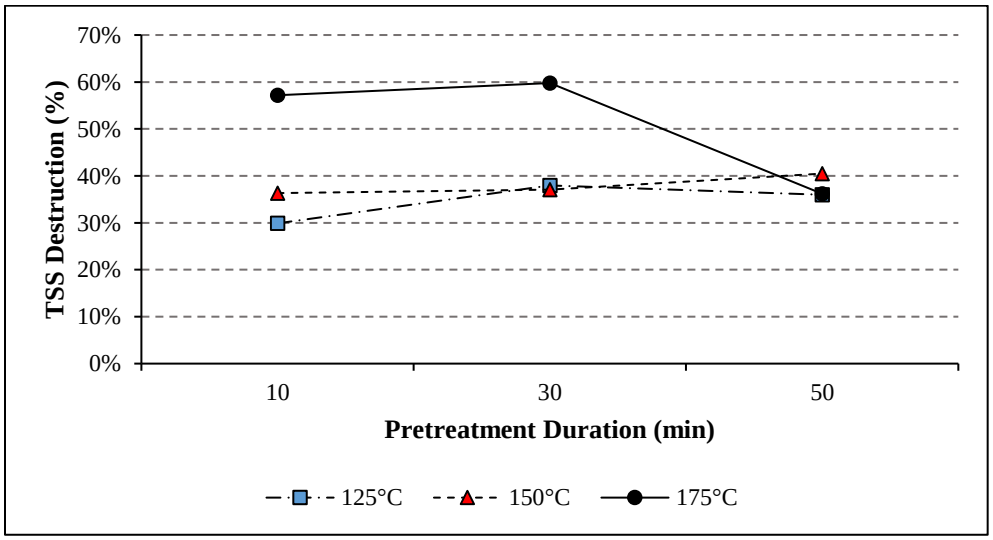


Figure 4.5 TSS Destruction due to HPTH Pretreatment

Bougrier et al (2008) calculated TSS/TS ratios before and after thermal pretreatment of five different WAS samples. For WAS pretreated at 130°C, 150°C and 170°C, the average decrease in TSS/TS ratio were 20 ± 4%, 32 ± 5%, and 44 ± 11%. Since TS concentrations were unchanged by pretreatment, the decrease in this ratio indicated that suspended solids were solubilized. In the current study, the range was comparable with values from 21 to 49%. The decreases in TSS coupled with increases in soluble matter (SCOD) in the sludge indicated that solids were solubilized rather than mineralized.

VSS solubilization was calculated using (2.2). In this study the VSS solubilization for pretreated WAS ranged from 23% to 41% as shown in Figure 4.6. Gurieff et al. (2011) and Liu et al. (2012) reported VSS solubilization of 31% and 27.5% for WAS pretreated at 165°C and 175°C respectively. Overall, the data agree with results reported in the literature and demonstrate that solids were solubilized rather than mineralized, while organic suspended solids were preferentially solubilized.

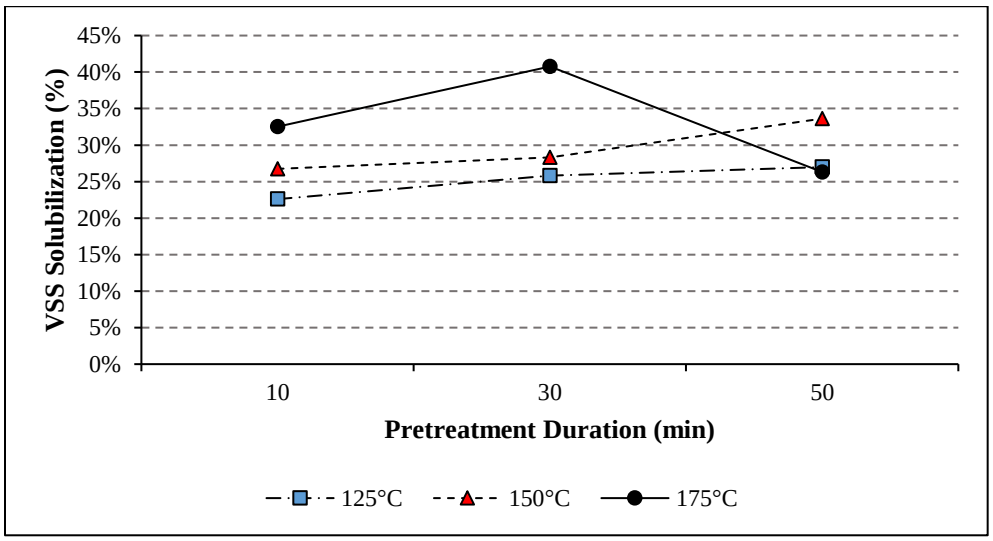


Figure 4.6 VSS Solubilization Due to HPTH Pretreatment

Several studies have shown that the TS concentration and VS/TS ratio were unchanged by pretreatment, indicating that organics were not removed/degraded by pretreatment (Braguglia et al., 2015; Morgan-Sagastume et al., 2011; Xue et al., 2015). Figure 4.7 and Figure 4.8 show the TS concentrations and VS/TS ratio before and after all pretreatment conditions. It can be seen that both TS concentration and VS/TS ratios were relatively unaffected by pretreatment at all levels. Therefore, it was concluded that organics were not removed/degraded by the pretreatment conditions employed in this study.

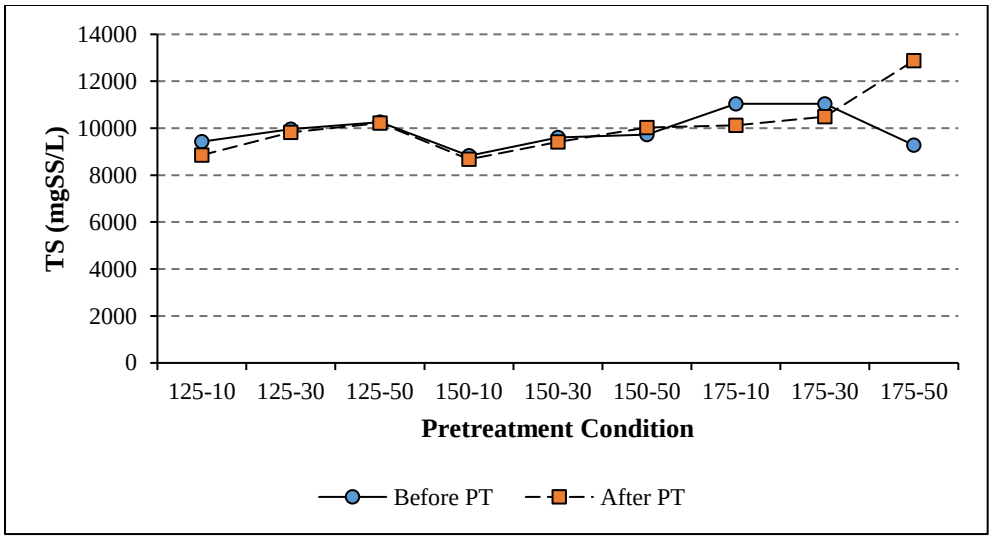


Figure 4.7 TS Concentration Before and After Pretreatment

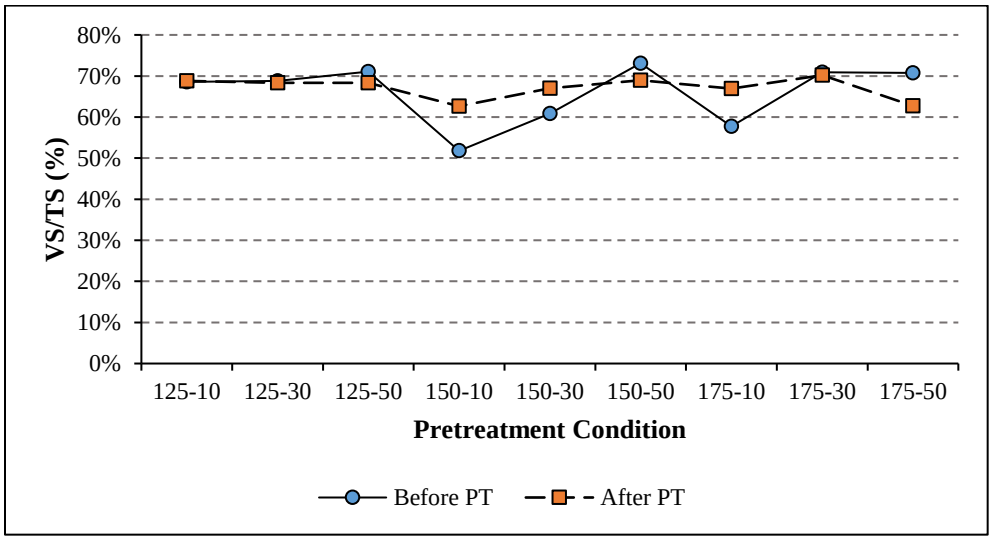


Figure 4.8 VS/TS Ratio Before and After Pretreatment

Nitrogenous species concentrations were measured in order to assess the degree to which organic nitrogen (ON) was solubilized by pretreatment. Nitrogenous species concentrations in the PWAS samples were measured, however, data on nitrogen species concentrations in the BR WAS were not available. Hence, the ON soluble ratio for the PWAS samples was calculated according to (4.2) for all of the pretreatment conditions.

$$ON\ Soluble\ Ratio\ \% = \frac{sON_{PT}}{ON_{PT}} \times 100\% \tag{4.2}$$

Figure 4.9 shows the solubilization ratios plotted for all of the pretreatment cases. The ON soluble ratio for WAS pretreated at 150°C for 30 minutes was similar to the value obtained by Staples-Burger (2012). Solubilization of ON increased with pretreatment duration and temperature. In addition, the ON solubilization results supported other responses indicating that pretreatment temperature had a greater effect compared to pretreatment duration. The increase in ON soluble ratio were 10% (125°C), 14% (150°C) and 23% (175°C) when the duration was increased from 10 to 50 minutes. Comparatively, the increase in ON soluble ratio were 36% (10 min), 52% (30 min) and 49% (50 min) when the temperature was increased from 125°C to 175°C. According to Figure 4.9, the increase in ON solubilization was substantial for WAS pretreated at 175°C. In comparison, the previously described increase in SCOD at 175°C was not as substantial. It may be possible that at very high temperatures (>175°C), proteins are more preferentially solubilized, thus yielding a higher ON solubilization ratio. Bougrier et al (2008) observed that carbohydrates were easily hydrolyzed compared to proteins for pretreatment temperatures up to 150°C but for higher temperatures, protein solubilization was higher.

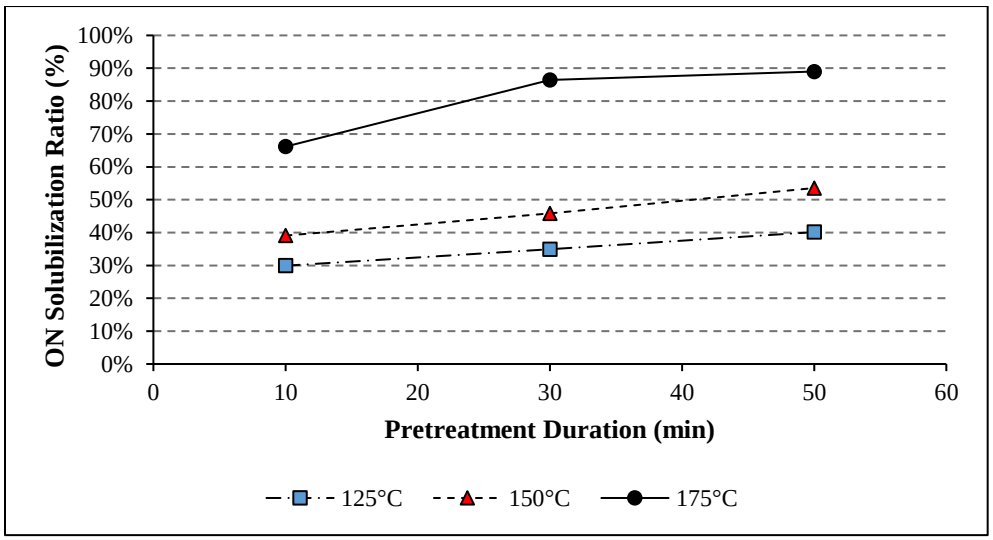


Figure 4.9 Organic Nitrogen Solubilization for all PWAS

Hence, based on COD, suspended solids and nitrogenous species solubilisation, organics were substantially solubilized over inorganics in all of the various pretreatment conditions employed in this study. Furthermore, organic matter was not significantly degraded or removed by pretreatment as indicated by the stable TS, VS/TS ratio and TCOD responses. The findings from COD and ON solubilization also substantiated results from others that pretreatment temperature was more important in solubilizing organics than pretreatment duration.

4.3 Aerobic and Anaerobic Biodegradability of Process Streams

4.3.1. Online Respirometry

Online respirometry in the aerobic digester was used to determine how pretreatment changed the biodegradable fraction of the WAS. Figure 4.10 shows online respirometry data collected for 150°C-10 PWAS as an example of a typical response. All other online respirometry data for other PWAS samples are presented in Appendix B. The online respirometry data for 175°C-50 PWAS showed a highly irregular response and thus could not be used to determine its aerobic biodegradability. A single measurement of online respirometry for BR WAS was collected for comparison with the pretreated samples. Figure 4.10 shows three reaction periods, where the initial spike in oxygen uptake rate (OUR) corresponded to when the aerobic digester was fed with PWAS. The response was decay-dominated due to a low food to microorganism (F/M) ratio. At the end of each reaction period, OUR values plateaued which implied that all of the substrates were consumed.

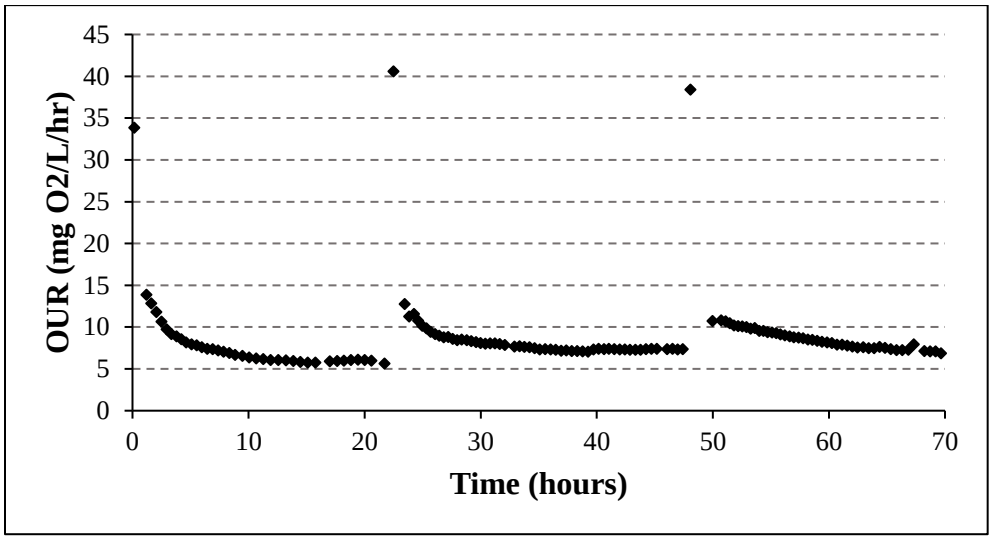


Figure 4.10 Typical OUR Curve based on Online Respirometry of WAS Pretreated at 150°C for 10 minutes

The area under each reaction period represented the total oxygen utilized, denoted by $\sum OU_T$. It was assumed that $\sum OU_T$ was the sum of two components, oxygen uptake due to substrate ($\sum OU_S$) and endogenous decay of aerobic digester biomass ($\sum OU_E$) as summarized by (4.3).

$$\sum OU_T = \sum OU_S + \sum OU_E \quad (4.3)$$

In order to determine the aerobic biodegradability of the PWAS (i.e. substrate), oxygen uptake due to substrate ($\sum OU_S$) was calculated by subtracting the oxygen utilized for endogenous decay ($\sum OU_E$) from

the total oxygen mass ($\sum OU_T$). The constant OUR values towards the end of the reaction period indicated that all of the substrates were consumed and that only endogenous decay of aerobic digester biomass was occurring at this point in the operation.

The value of $\sum OU_S$ was estimated by initially determining the active biomass concentration in the test and then calculating the oxygen uptake associated with its decay. A nonlinear regression of (2.6) to the tail end of this data was fit to determine the initial active biomass concentration in the aerobic digester. Since three reaction periods were observed, (2.6) was fit three times and the resulting active biomass concentrations were averaged. The b_h value used was 0.24 d^{-1} (Staples-Burger, 2012) because online respirometry of aerobic digester was conducted at 20°C. Then using the calculated average active biomass concentration, OUR values were recalculated based on (2.6). These OUR values corresponded to the endogenous decay of the active biomass present in the aerobic digester during online respirometry. Figure 4.11 shows the total OUR and the OUR due to endogenous decay for 150°C-10 PWAS for a single reaction period.

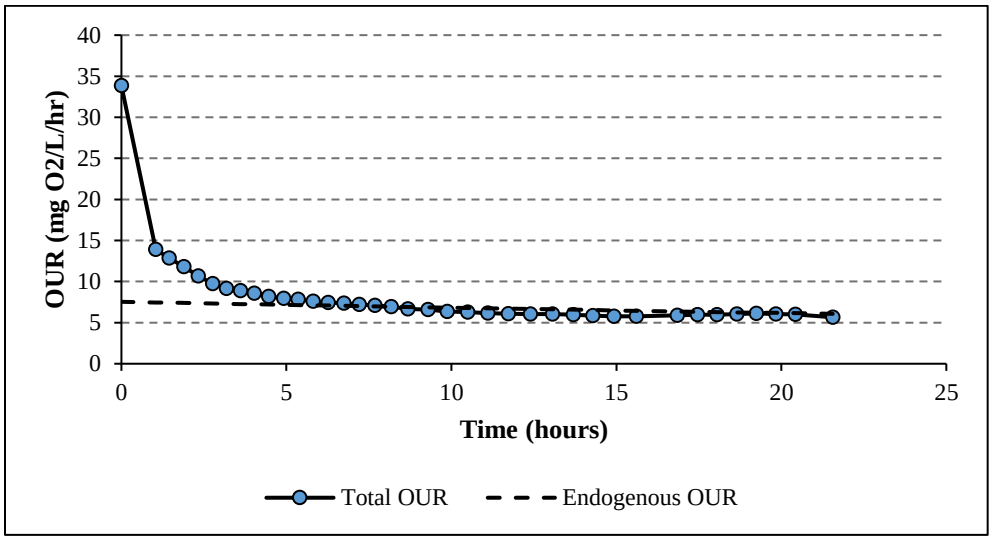


Figure 4.11 Total OUR and OUR Due to Endogenous Decay for 150°C-10 PWAS

To determine $\sum OU_S$, the area under the total OUR curve ($\sum OU_T$) was reduced by the area under the endogenous decay OUR curve ($\sum OU_E$). To evaluate the aerobic biodegradability, $\sum OU_S$ was divided by the TCOD of the PWAS added to the respirometry bottles. These calculations were performed for BR WAS and WAS pretreated under all conditions. Any differences between the $\sum OU_S$/TCOD ratio between the raw BR WAS and PWAS revealed whether pretreatment altered the aerobic biodegradability of the WAS. If the ratios were not statistically different, it indicated that aerobic biodegradability was not altered by pretreatment. Staples-Burger (2012) concluded that there was no statistical difference between the ratios for BR WAS and WAS pretreated at 150°C for 30 minutes.

Figure 4.12 shows the $\sum OU_S$/TCOD ratio for the BR WAS and all the PWAS in the current study. From Figure 4.12 it can be seen that pretreatment temperature and duration did not significantly alter the aerobic biodegradability. On average, WAS pretreated at 150°C seemed to show an increase in aerobic biodegradability as compared to WAS pretreated at 125°C and 175°C. An important note is that the online respirometry data for BR WAS was conducted after all of the pretreatment scenarios were conducted. While the BR WAS generated throughout the study was shown to be relatively stable as shown previously in Section 4.2.1, there were slight variations. Therefore, the single $\sum OU_S$/TCOD ratio calculated for BR WAS would not have been perfectly representative of the BR WAS that was pretreated at the various temperatures and durations. Furthermore, the uncertainty of the ratio for BR WAS could not be estimated since a single $\sum OU_S$/TCOD ratio was calculated. Viewed collectively, it can be seen that HPTH pretreatment did not increase the aerobic biodegradability of WAS.

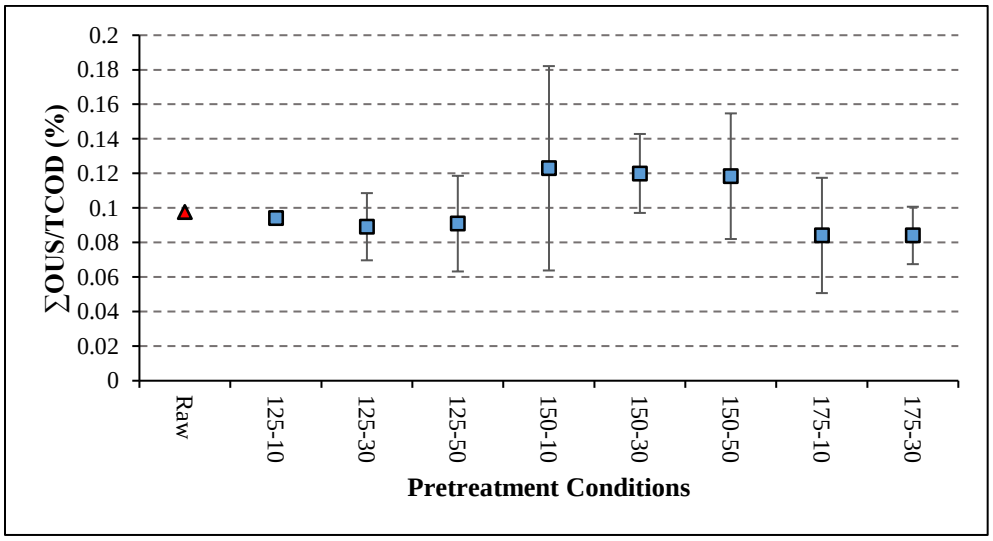


Figure 4.12 Comparison of Aerobic Biodegradability of BR WAS to PWAS Using Online Respirometry

4.3.2. Offline Respirometry

Batch respirometric tests were performed before and after pretreatment for all conditions to determine how pretreatment changed the aerobic biodegradability of WAS and to determine the active biomass concentrations in each sludge stream. For these batch tests, the F/M ratio was high enough to ensure that responses would be growth and decay driven. Two batch tests were completed for BR WAS, BR WAS inoculated with AD WAS, and filtered BR WAS to be able to estimate the aerobic biodegradability prior to pretreatment and to estimate the active biomass concentration initially present in BR WAS. The OUR responses in these tests were expected to result from decay of Z_{bh} due to the absence of any other substrates.

Figure 4.13 shows OUR responses measured for both batch tests. In the bottles containing BR WAS, the OUR decline exponentially with time as expected from decay of active biomass. The inoculated BR WAS consistently showed a higher OUR response than BR WAS as it also contained active biomass from AD WAS. There was a delayed peak around 40 hours into the batch test of inoculated BR WAS, however, the area under this peak consisted of less than 5% and was therefore considered negligible. The observed OUR responses corroborated the hypothesis that the BR WAS contained only Z_{bh} and Z_e.

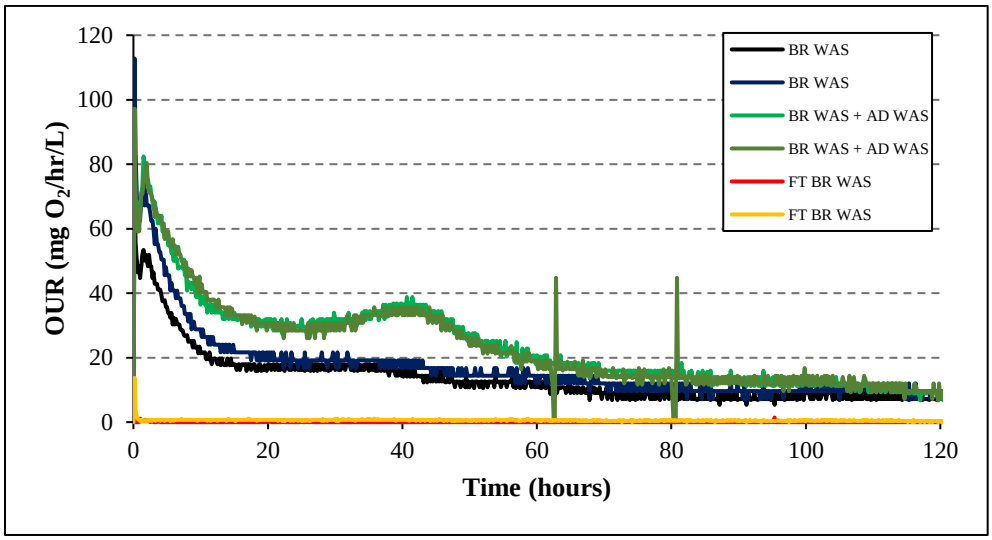


Figure 4.13 Typical OUR Curve Based on Offline Respirometry of BR WAS

After pretreatment of WAS, two batch tests for each pretreatment condition were conducted. Tests were conducted on samples containing PWAS, PWAS inoculated with AD WAS, AD WAS, and filtered PWAS inoculated with AD WAS. The bottles containing inoculated PWAS were expected to show both growth and decay as the active biomass concentration in BR WAS would be converted to readily biodegradable COD (S_{bsc}) and slowly biodegradable COD (X_{sp}) (Staples-Burger, 2012). As shown in Section 4.2.2, the various pretreatment conditions greatly increased the concentration of SCOD and since S_{us} was not generated by pretreatment, it was assumed that all SCOD resulting from pretreatment were S_{bsc}. The OUR response of AD WAS was expected to reflect endogenous respiration. For bottles containing PWAS only, no response was expected as it was hypothesized that all of the active biomass in the BR WAS would be converted to either S_{bsc} or X_{sp}. Furthermore, Donoso-Bravo et al. (2011) and Gurieff et al. (2011) concluded that biomass in thermally pretreated WAS were inactivated, resulting in sterilization of sludge.

Figure 4.14 shows two batch tests collected for 150°C-10 PWAS as an example of the offline respirometry responses. All other OUR curves for the different PWAS are presented in Appendix C. Not considering the initial OUR values of inoculated BR WAS that were likely due to remnants of synthetic rbCOD, the OUR of the inoculated PWAS samples were higher than that exhibited by the inoculated BR WAS. The increase

in OUR for inoculated PWAS was characteristic of growth on S_{bsc} and the subsequent decrease was likely due to hydrolysis of X_{sp} and endogenous decay. The batch tests revealed that there was oxygen uptake in the bottles containing only PWAS, indicating that not all biomass were inactivated by pretreatment.

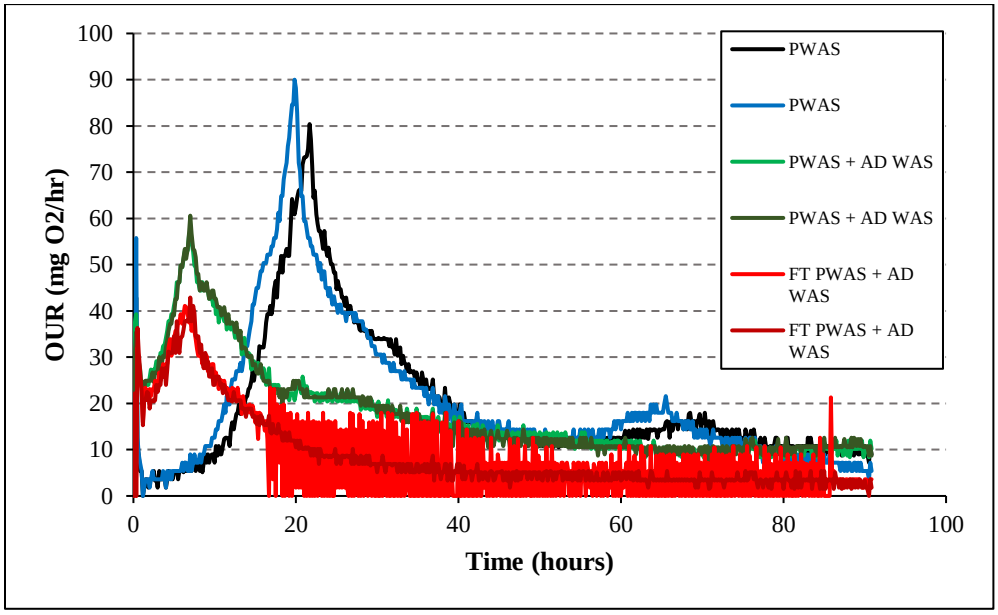


Figure 4.14 Typical OUR Curve Based on Offline Respirometry of WAS Pretreated at 150°C for 10 minutes

Out of the nine AD WAS samples (one for each pretreatment condition) used for batch respirometry, only four yielded measurable responses. The rest showed no measurable response, which was similar to what occurred in offline respirometry tests with BR WAS. The measured responses were not consistent and a distinct decay response could not be observed. This may have been due to small time steps at which OUR values were measured. The oxygen uptake may have been too small to be accurately represented at the time steps chosen (10 minutes). However, this did not explain the lack of response in some samples. Hence, the responses of AD WAS were not employed in the study.

The difference in the responses between PWAS and inoculated PWAS (Figure 4.14) indicated that the seed (AD WAS) was active. The peak in the inoculated PWAS occurred much earlier indicating that the additional active biomass in the AD WAS allowed for rapid consumption of S_{bsc}. However, the lower magnitude in the peak may suggest that there was insufficient acclimatization of PWAS to AD WAS. Guo et al. (2007) showed that acclimatization of biomass to wastewater resulted in higher OUR values during respirometry tests compared to non-acclimatized biomass fed to membrane bioreactors. Similar findings were observed in the other pretreatment conditions.

The OUR responses on filtered samples also validated some of the hypotheses made regarding the properties of BR WAS and PWAS. The filtered BR WAS response was negligible (Figure 4.13). This was attributed to the fact that the biodegradable component of BR WAS, Z_{bh}, which was capable of exerting oxygen demand was filtered out and thus no oxygen uptake was observed. Comparatively, after pretreatment, the inoculated filtered PWAS OUR curve area contributed more than 50% of the area of the inoculated PWAS OUR curve. This indicated that significant solubilization of COD of PWAS occurred which was consistent with the high levels of COD solubilisation described in Section 4.2.2.

4.3.2.1. Extent of Aerobic Biodegradability

Two methods were proposed by Staples-Burger (2012) to determine whether pretreatment changed the biodegradable fraction of WAS using batch respirometry data. Both methods relied on calculating the cumulative oxygen uptake associated with the substrate (BR WAS or PWAS) and dividing by the measured mass of TCOD (mg COD) of the substrate in the samples. The first method required the initial and final mass of TCOD in the respirometry bottle and the second method used the mass of gas phase oxygen measured by the respirometer during the test. The final mass of TCOD in the respirometry bottles were not measured in this study. Therefore, the second approach was employed to estimate whether pretreatment changed the aerobic biodegradability.

This approach was similar to the method used in online respirometry. The $\sum OU_S$ (mg O_2) was calculated for each batch respirometric test by subtracting the oxygen uptake due to endogenous respiration ($\sum OU_E$) from the total oxygen uptake in the inoculated bottle ($\sum OU_T$). However, the oxygen uptake due to endogenous respiration from batch tests were deemed to be unreliable and most showed no measurable response. Therefore, the values for $\sum OU_E$ were estimated using online respirometry as in Section 4.3.1. However, when (2.6) was used to calculate the OUR due to endogenous decay alone, the value of b_h was modified as the batch respirometry tests were conducted at 25°C. Equation (4.4) was used to obtain the rate at 25°C that was determined to be 0.28 d^{-1} in which, T was the temperature in degrees Celsius.

$$b_{h,T} = b_{h,20C}(1.029)^{T-20} \quad (4.4)$$

The biodegradability of the substrate was then evaluated by dividing the $\sum OU_S$ values by the mass of TCOD placed in the respirometry bottles. The $\sum OU_S$/TCOD ratio was calculated at various durations of the offline respirometry test as shown in Figure 4.15. With the exception of the 150°C-10 PWAS, most of the respirometry tests had been run until a distinct peak and decay and response were observed. The 150°C-10 PWAS respirometry was only conducted for 32 hours and hence only one $\sum OU_S$/TCOD was calculated. The 125°C-50 and 175°C-10 PWAS offline respirometry tests were conducted for approximately 60 hours

and hence only two $\sum OU_S/TCOD$ were calculated. When viewed collectively, it can be seen from Figure 4.15 that the aerobic biodegradability was not significantly altered by most of the pretreatment conditions. However, pretreatment at 175°C-30 and 175°C-50 seemed to have increased the aerobic biodegradability of the WAS. The OUR curves for 175°C-30 and 175°C-50 PWAS showed atypical responses as shown in Figure 4.16. The OUR curve for 125°C-50 PWAS was shown for comparison. The typical response expected was an exponential increase of OUR due to consumption of S_{bsc} and subsequent growth of biomass. Then as a result of the rate limiting hydrolysis of X_{sp}, the OUR was expected to drop suddenly and decrease steadily representing both hydrolysis and endogenous respiration. It can be seen that the OUR for WAS pretreated at 175°C did not exhibit the sharp decrease in OUR after the peak. This resulted in a larger area and corresponded to the apparent higher aerobic biodegradability for 175°C-30 and 175°C-50 PWAS. These responses exhibited by the extreme pretreatment conditions could be attributed to the formation of different substrates that have different degradation patterns.

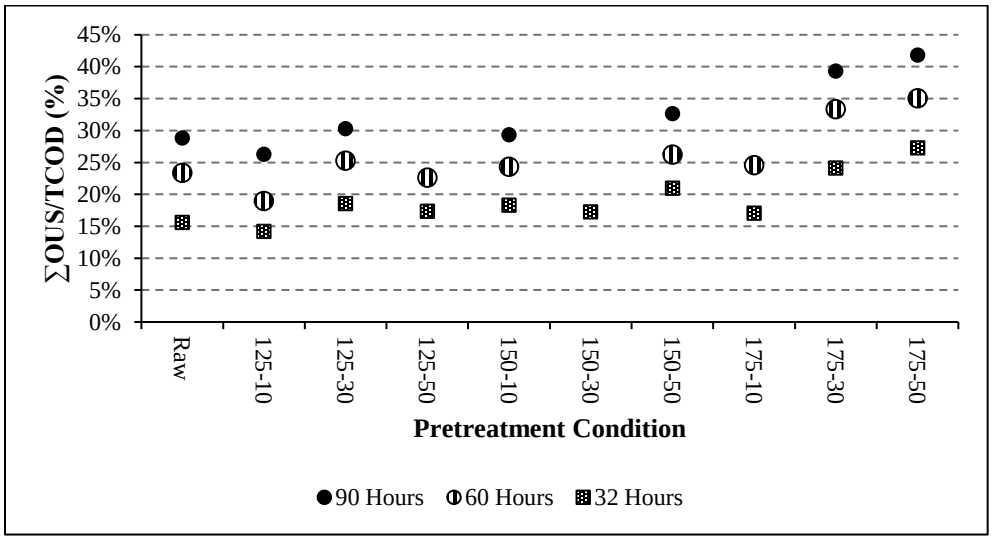


Figure 4.15 Aerobic Biodegradability of BR WAS and PWAS From Offline Respirometry

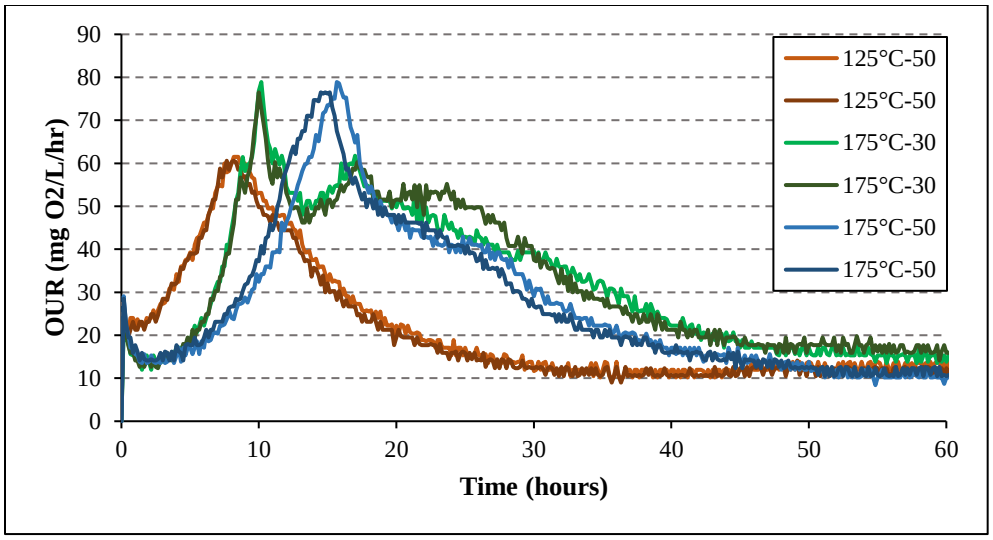


Figure 4.16 Typical versus Atypical OUR Response

In the analysis of online respirometry, it was concluded that pretreatment had no effect on aerobic biodegradability under the conditions that are most commonly employed in practice. The results of offline respirometry analysis generally agreed with the online respirometry results. The combined findings from both respirometry tests showed that the extent of aerobic biodegradability, hence the biodegradable fraction of BR WAS, was virtually unaffected by pretreatment. However, as the calculated $\sum OU_S/TCOD$ ratios showed, the aerobic biodegradability may be different for extreme pretreatment conditions and warrants additional study.

4.3.2.2. Active and Endogenous Fractions

In order to further assess how thermal pretreatment affected the WAS composition, the active and endogenous fractions of the BR WAS was initially estimated. It was hypothesized that BR WAS was comprised of active biomass and endogenous products. Since the OUR response in batch respirometry containing only BR WAS was decay driven, a nonlinear regression of (2.6) was fit to the data to estimate the concentration of active biomass in the BR WAS ($Z_{bh,BR}$). The average concentration of $Z_{bh,BR}$ was estimated to be 3773 ± 166 mg/L. The average TCOD concentration in the BR WAS was 4763 ± 176 mg/L, which meant that the average active biomass fraction was 79.2 ± 4.6%. Staples-Burger (2012) reported an average active fraction of 51 ± 4% for biomass that was generated in the same system and the lower values were attributed to the presence of storage products.

The concentration of endogenous decay products were determined by an endogenous respiration approach (Melcer, 2004) using (4.5)

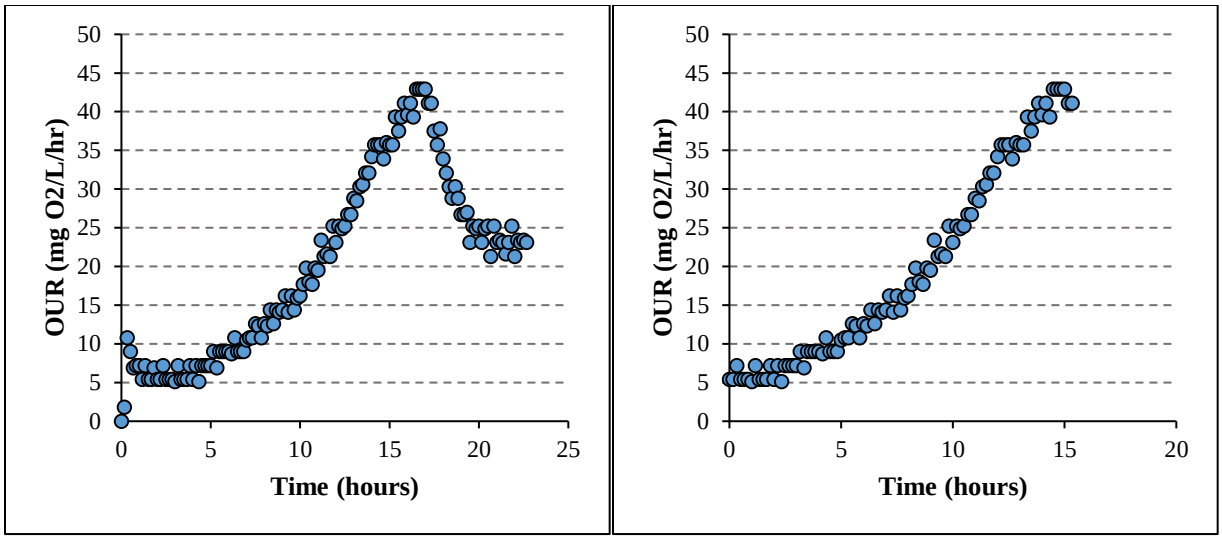
$$Z_{e,BR} = f b_h Z_{bh,BR}(SRT_{BR}) \quad (4.5)$$

in which, b_h denoted aerobic decay rate (d^{-1}), f was the endogenous fractions of organisms, $Z_{bh,BR}$ was the active biomass concentration in the bioreactor, and SRT_{BR} was the solids retention time of the bioreactor. A b_h value of 0.28 d^{-1} as determined by (4.4). The endogenous fraction of organisms, f, employed in this study was 0.2 (Staples-Burger, 2012). The average concentration of $Z_{e,BR}$ was estimated as 845 ± 37 mgCOD/L. Therefore, the average endogenous fraction was 17.7 ± 1.0% of the COD. The sum of active and endogenous COD fraction was 97.0 ± 4.7%. The remaining fraction, which consisted of S_{us}, was considered negligible and was not included as part of the BR WAS composition.

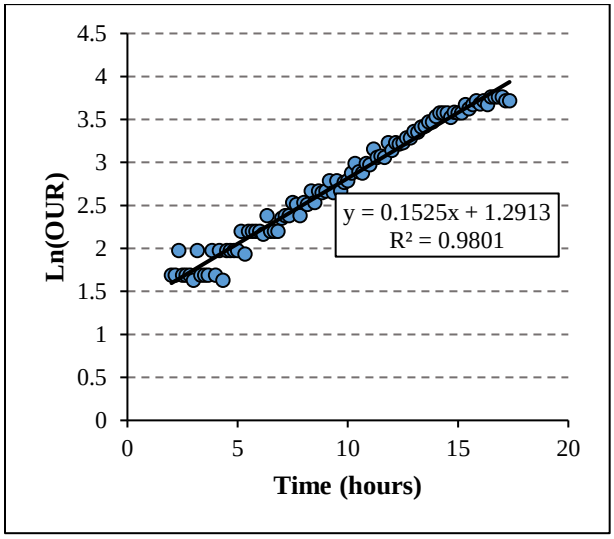
It was initially assumed that most or all of the biomass would be inactivated by pretreatment, however, OUR responses were observed in the non-inoculated respirometry tests and hence this assumption was deemed to be invalid. The OUR response for the non-inoculated PWAS tests demonstrated both growth and decay responses (Figure 4.12) and therefore a nonlinear regression of (2.6) could not be fit. Instead, the concentration of active bacteria in the PWAS was determined using (2.5) that describes exponential growth on substrate under high F/M conditions. Figure 4.17 shows the steps employed to analyze PWAS that had been pretreated at 125°C for 10 minutes. The portion of the OUR curve that exponentially increased with time was log transformed and plotted against time. A line of best fit was determined using Excel™ by performing linear regression analysis. Using the slope and y-intercept, together with typical values of b_h and Y_h in (2.5), the fractions of active biomass in the PWAS were estimated and are summarized in Table 4.3.

Table 4.3 Summary of Active Biomass Fractions in All PWAS Samples

Pretreatment Condition	Active Biomass Concentration (mg COD/L)	Fraction of TCOD
125°C – 10 min	173 ± 141	2.3 ± 1.9%
125°C – 30 min	183 ± 119	2.2 ± 1.4%
125°C – 50 min	556 ± 234	6.3 ± 2.7%
150°C – 10 min	74 ± 88	1.0 ± 1.2%
150°C – 30 min	143 ± 133	2.0 ± 1.8%
150°C – 50 min	153 ± 106	1.8 ± 1.3%
175°C – 10 min	232 ± 142	0.7 ± 0.4%
175°C – 30 min	125 ± 101	1.3 ± 1.1%
175°C – 50 min	731 ± 259	9.9 ± 3.5%



(A) (B)



(C)

Figure 4.17 Estimation of Active Biomass Concentration in PWAS (a) OUR Curve for WAS pretreated at 125°C for 10 minutes (b) Exponential Portion of OUR Curve (c) Linear Fit of Ln(OUR) versus Time

From Table 4.3 it can be seen that the fraction of active biomass in the PWAS was consistently below 5% with the exception of the 125°C-50 and 175°C-50 PWAS. The 175°C-50 results seemed unreasonable as it was not expected that the highest pretreatment duration and temperature would allow more biomass to remain viable. The 125°C-50 results also seemed unreasonable as pretreatment for 10 and 30 minutes at the same temperature inactivated more biomass. Viewed collectively, the fraction of active biomass in the

PWAS samples was low and hence it was assumed that all of the biomass was essentially inactivated for the purposes of PWAS COD fractionations.

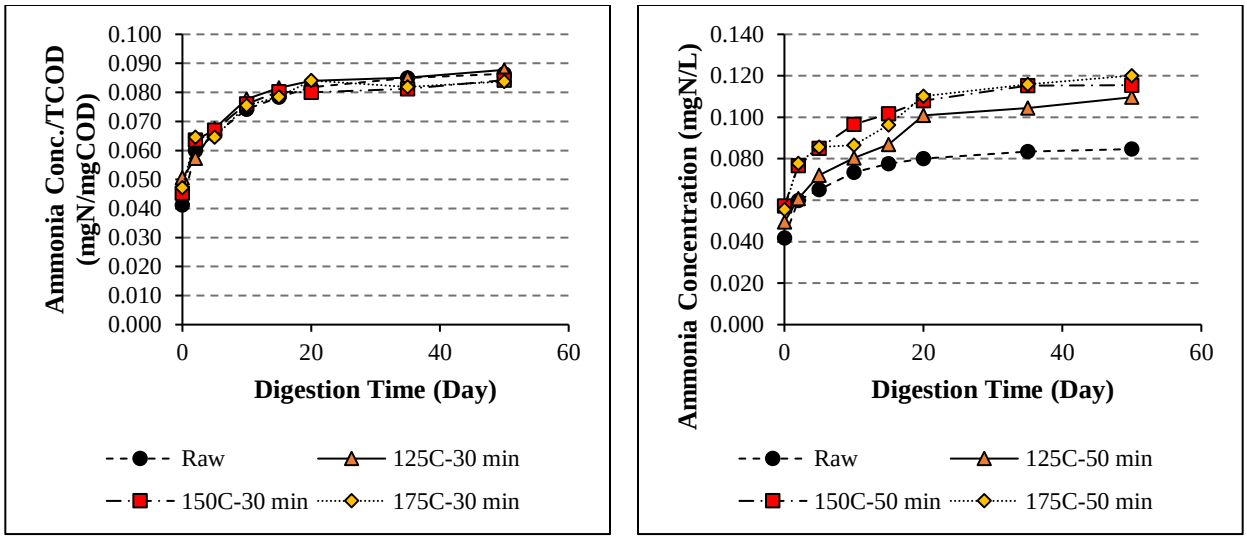
In summary, the aerobic biodegradability was found to be unchanged by pretreatment (Section 4.3.1 and Section 4.3.2) using both online and offline respirometry data. Based on these conclusions, it was concluded that the endogenous decay product fraction of the BR WAS was not converted to biodegradable COD by HPTH pretreatment. Hence, the endogenous fraction of the PWAS was assumed to be the same as BR WAS at 17.7 ± 1.0% and this value was employed in the subsequent analysis.

4.3.3. Biochemical Methane Potential Test

Biochemical methane potential (BMP) tests were employed to assess the impact of pretreatment on anaerobic biodegradability. One set of BMP tests was conducted to collect methane data and the other was used to collected ammonia generation data.

Ammonia release during anaerobic digestion is a strong indicator of the rate and extent of hydrolysis of biodegradable particulate matter. It is typically released when proteinaceous materials are broken down (Kianmehr, 2010). Figure 4.18 shows the ammonia concentration in the BMP tests for all pretreatment conditions. There were no measurements of TKN at the beginning of the tests and therefore, (2.7) could not be used to quantify the rate of ammonification. The ammonia release was normalized to the COD concentration of the PWAS samples that entered the BMP tests to allow for comparison. Conclusions regarding the rate of ammonification and hence the rate of hydrolysis of particulates, were made by comparing the plots shown in Figure 4.18.

Any changes in the initial slope of the ammonia generation indicated that the rate of ammonification was altered. The results shown below suggested that the rate of hydrolysis was unaffected by 30 minutes of pretreatment at the selected temperatures as the initial slopes of ammonia release were similar to ammonia release exhibited in BMP tests with BR WAS. The ultimate ammonia concentration in the 30 minute PWAS BMP tests were virtually unchanged when compared to BMP tests of BR WAS. Conversely, the ultimate ammonia concentration increased for WAS pretreated for 50 minutes when compared against the ammonia generation in BMP tests with BR WAS. This indicated that the extent of hydrolysis of biodegradable particulate matter increased for WAS pretreated for 50 minutes at the selected temperatures. It was difficult to determine if the rate of ammonification was increased by 50 minutes of pretreatment without quantifying it using (2.7). Therefore, any changes in the rate of ammonification due to 50 minutes of pretreatment could not be properly quantified and was inconclusive.



(A) (B)

Figure 4.18 Ammonia Concentration in BMP Test with WAS Pretreated for (A) 30 Minutes (B) 50 Minutes

In order to quantify the impacts of pretreatment on methane generation, a Reaction Curve ((2.8)) was fit to the cumulative methane production data. Matlab™ was used to fit the model using nonlinear regression methods. Figure 4.19 shows the measured cumulative methane production of all BMP tests. The methane production (mL) was normalized to the initial mass (mg COD) of PWAS that was added to the sealed serum bottle tests. Table 4.4 shows estimated parameters for the reaction curves for each PWAS test. The quality of the fit of the calibrated curves to the data was assessed by examining the R^2 value reported by Matlab™. The R^2 values ranged from 0.971 to 0.994 which indicated that the quality of the fit was adequate.

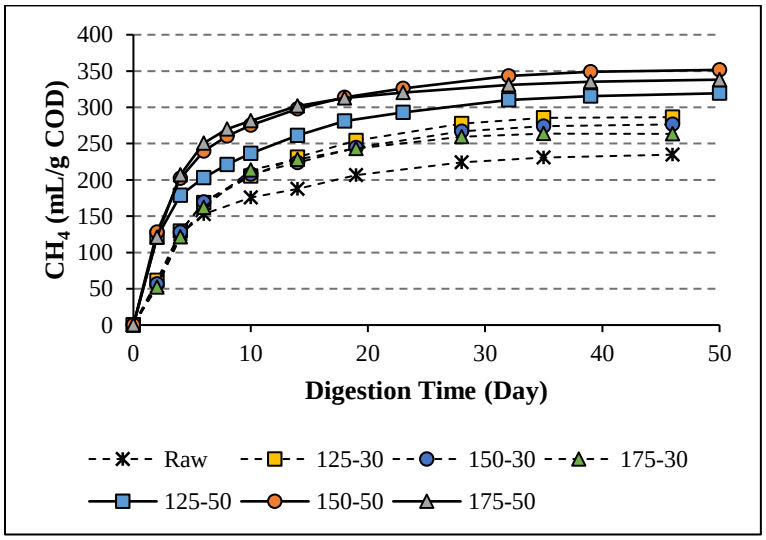


Figure 4.19 Normalized Methane Production for BR WAS and all PWAS

Table 4.4 Parameter Estimates from Reaction Curve Fitting

Pretreatment Condition	P (mL/gCOD)	R_m (mL/gCOD d)
Raw	225 ± 15	37 ± 9
125-30	283 ± 12	38 ± 5
150-30	271 ± 13	40 ± 7
175-30	263 ± 10	41 ± 5
125-50	305 ± 18	51 ± 12
150-50	336 ± 15	65 ± 11
175-50	325 ±10	74 ± 9

From Table 4.4 it can be seen that the maximum methane production (P) increased with all levels of pretreatment. The P value increased by 26%, 20% and 17% with 30 minutes of pretreatment 125°C, 150°C and 175°C respectively. For 50 minutes of pretreatment, temperatures of 125°C, 150°C and 175°C resulted in increased methane yields of 36%, 49% and 44% respectively. Sapkaite et al. (2017) conducted BMP tests on pretreated WAS for 50 days and reported the maximum methane production increased by 30%, 63% and 48% for 30 minutes of pretreatment at temperatures of 130°C, 150°C and 180°C respectively. The improvements in methane yields for 50 minutes of pretreatment at the corresponding temperatures were 45%, 48% and 55%. The differences in methane yields between the current study and those of Sapkaite et al. (2017) were likely due to the different sludge sources. Sapkaite et al. (2017) used authentic WAS sampled from a municipal WWTP. Comparatively, the current study used WAS that was generated from synthetic wastewater. Despite the differences, the improvements in methane production due to pretreatment were substantial.

By contrast, the rates of methane production were only slightly increased (3-11%) after pretreatment at the various temperatures for 30 minutes (Table 4.4). Comparatively, pretreatment at the various temperatures of pretreatment for 50 minutes appeared to substantially increase (38-100%) the rate of methane production. This was consistent with the results of Donoso-Bravo et al (2011) that indicated that pretreatment time appeared to increase the rate of biogas production. Studies reviewed by Bougrier et al. (2008) reported increases in methane production for sludge digested for periods in the range of 5-15 days. This was attributed to increases in the rate of methane yield rather than the extent of biodegradability of the pretreated WAS. Li et al. (1992) showed that the biogas yield increased by 100% for WAS pretreated at 175°C for 60 minutes digested for 5 days which was similar to the improvement in the rate of anaerobic biodegradability observed in this study for 175°C-50 PWAS. The results from this study were thus comparable with findings in the literature.

An alternate method of evaluating whether pretreatment changed the anaerobic biodegradability was to determine COD consumption through the BMP tests. This method required measures of the initial and final

COD mass in the BMP serum tests bottles. However, only the initial COD concentrations were collected in this study and hence the COD consumed was estimated from the theoretical CH_4 production per gram of COD consumed per (4.6)

$$COD\ Consumed\ (\frac{mg}{L}) = \frac{U_{CH_4}}{V_{PWAS} \cdot Y_{CH_4}} \quad (4.6)$$

in which, U_{CH4} denoted the measured ultimate methane yield (L), V_{PWAS} was the volume of pretreated sludge in serum bottles, and Y_{CH4} was the CH_4 yield per unit of COD (0.395 L/gCOD). The volume of pretreated sludge in each serum test was 0.150 L and the ultimate methane yield varied with the pretreatment conditions. The COD consumed was calculated for each condition and normalized by the TCOD concentration of PWAS in the serum bottles (Table 4.5).

Table 4.5 Summary of Digestible COD in BMP Tests

Pretreatment Condition	Digestible COD (%)	
	Sample 1	Sample 2
Raw	60	62
125°C-30	73	72
150°C-30	70	70
175°C-30	65	68
125°C-50	81	80
150°C-50	88	90
175°C-50	86	86

From Table 4.5 it can be seen that the digestible COD fraction increased with thermal pretreatment. This indicated that the biodegradable COD fraction in the PWAS was higher than that of the raw BR WAS. Consistent with the Reaction Curve results, both pretreatment temperature and duration appeared to alter the digestible COD fraction. The similar conclusions from the cumulative methane production analysis were expected as the digestible COD was based on the ultimate methane yield of the BMP tests.

Collectively, the results indicated that both pretreatment temperature and duration were important in changing the extent of anaerobic biodegradability. The results suggest that matter that was not anaerobically degradable in the BR WAS became available for the production of methane. Pretreatment time was found to be more important in increasing the rate of anaerobic biodegradability. However, improvements on the rate of hydrolysis due to HPTH were inconclusive.

4.4 Summary of COD Fractionation

Figure 4.20 summarizes the COD fractionation of raw and pretreated WAS samples that was established from direct analysis of the lab data. From the figure it can be seen that the BR WAS was composed of Z_{bh} and $Z_{e.}$ Pretreatment at various temperatures (125°C, 150°C, 175°C) and durations (10, 30, 50 minutes) then converted Z_{bh} into S_{bsc} or X_{sp}, with the fraction of Z_e unchanged by pretreatment. The figure shows only the relevant and major fractions as determined in the previous sections. Measurements of SCOD indicated that there was a small fraction of S_{us} in the BR WAS, however, this fraction was consistently less than 1% and therefore was considered negligible. The BR WAS contained 79.2 ± 4.6% active biomass and 17.7 ± 1.0% endogenous decay products. All of the active biomass was assumed to be completely inactivated by pretreatment and converted to biodegradable substrate.

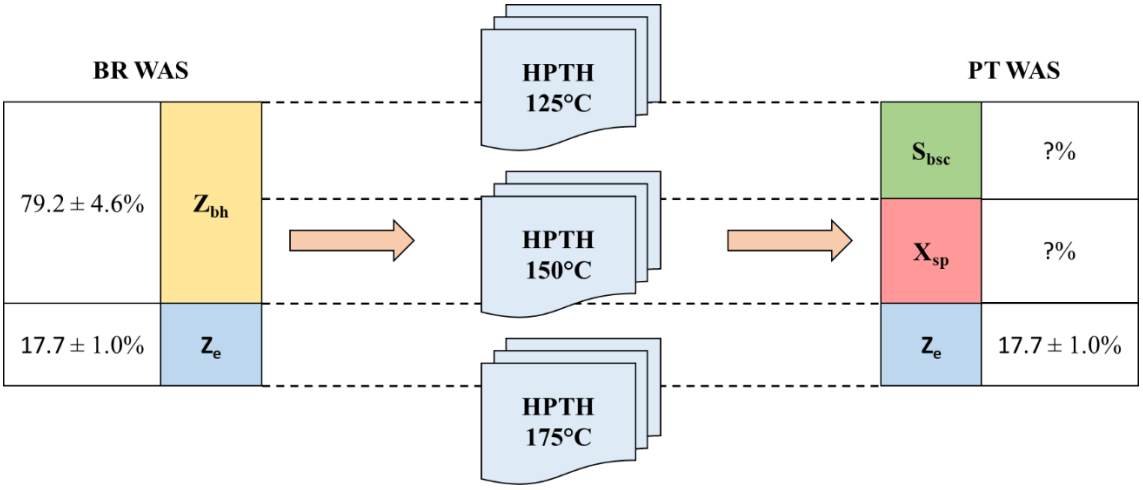


Figure 4.20 COD Fractionation of BR WAS and PWAS

The previous analysis did not provide insight into the fractions of S_{bsc} and X_{sp} that were in the samples and hence these were estimated using BioWin®. S_{bsc} and X_{sp} values were varied until the simulator predicted OUR responses for offline respirometry matched the measured responses as indicated by minimizing the sum of squares. The same PWAS COD fractionations were subsequently employed for anaerobic digestion (BMP) modeling (Section 6.0) in order to determine if biodegradability of WAS changed under different electron acceptor (aerobic versus anaerobic) conditions.

5. Modeling of Thermal Pretreatment Impacts on Aerobic Digestion of Waste-Activated Sludge

5.1 Approach

The characterization of WAS composition is typically made in terms of particle size and biodegradability as shown in Figure 5.1. The total COD (TCOD) can be divided into soluble and particulate components. Soluble COD (SCOD) can be further divided into two components, biodegradable soluble COD (bsCOD) or non-biodegradable soluble COD (nbsCOD). It was assumed that pretreatment at the selected temperatures and durations did not generate additional nbsCOD, which is referred to as S_{us}. Therefore, the concentration/fraction of nbsCOD was fixed. As a result, any soluble component generated by pretreatment was assumed to be a form of bsCOD, or readily biodegradable COD (S_{bsc}). Particulate COD (PCOD) was similarly divided into biodegradable particulate COD (bpCOD) and non-biodegradable particulate COD (nbpCOD).

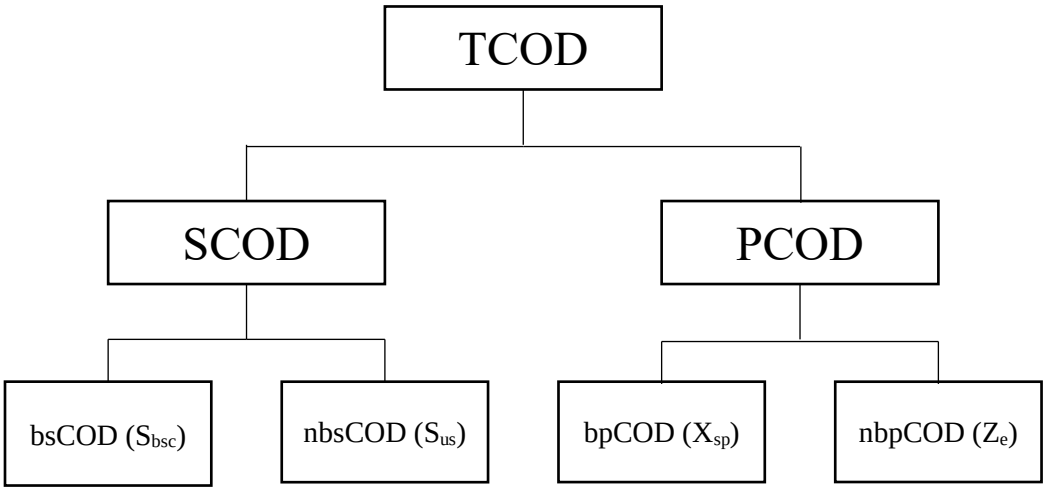


Figure 5.1 Characterization of COD based on particle size and biodegradability

In Section 4.1, it was shown that all particulate inerts (X_i) from the seed sludge were washed out from the BR. Therefore, only the endogenous decay products (Z_e) were assumed to contribute to nbpCOD in the BR WAS. Section 4.4 also concluded that these endogenous decay product concentrations remained constant through thermal pretreatment. Therefore, all PCOD less the endogenous decay products were assumed to be bpCOD, which is commonly referred to as slowly biodegradable COD (X_{sp}). A combination of OUR analysis and BioWin modeling of aerobic digestion component of this project was used to characterize the impact of thermal pretreatment on the COD fractionation of WAS.

A preliminary assessment of the WAS COD fractionation was conducted using OUR curves obtained from offline and online respirometry data (Section 4.3). The filtered samples likely contained both soluble and colloidal matter. However, it was difficult to distinguish the oxygen uptake due to consumption of truly soluble biodegradable COD and colloidal biodegradable COD. Hence, it was assumed that the OUR up to 32 hours was primarily due to truly soluble biodegradable COD (S_{bsc}) as a distinct peak and sharp decrease was observed within this time. It was not possible to distinguish whether these colloidal COD was slowly or readily biodegradable. A colloidal slowly biodegradable COD (X_{sc}) is defined in BioWin®, however, the kinetics of this fraction are the same as that of particulate slowly biodegradable COD (X_{sp}). As such, during BioWin® modeling, the colloidal components were considered to be particulate slowly biodegradable COD (X_{sp}).

BioWin® provides users with the option of selecting existing ASM models. Staples-Burger (2012) employed both the BioWin Integrated Model and ASM3 Model. The ASM3 model was previously chosen because it allowed for modeling of stored COD (X_{STO}) that was observed by Staples-Burger (2012), whereas BioWin Integrated Model did not. Since storage products were not observed in the current study, the BioWin Integrated Model was selected for modeling purposes.

A number of biokinetic parameters were assumed in order to employ the BioWin® simulator. The aerobic yield of heterotrophic organisms (Y_h), endogenous fraction of organisms (f), and aerobic decay rate (b_h) were deemed to be important parameters influencing the modeling of the aerobic digestion system (Staples-Burger, 2012). Values of Y_h, f, and b_h of 0.67, 0.20 and 0.24 d^{-1} (20°C) (Henze et al. 2008) are typically employed for activated sludge systems. These values correspond to the endogenous respiration approach, but BioWin utilizes the death-regeneration approach. The corresponding values using this approach were 0.09 and 0.53 d^{-1} at 20°C for f and b_h respectively. BioWin® was used to simulate the initial bioreactor-aerobic digester (BR-AD) system to calibrate the BioWin Integrated Model based on these three parameters. The calibration of the model was based on its ability to predict the measured particulate COD concentration of the BR WAS. Once the BioWin Integrated Model was calibrated, a thermal hydrolysis unit was used to simulate pretreatment of the BR WAS. The last step was to match the OUR responses from offline respirometry tests by varying the S_{bsc} and X_{sp} concentration of the PWAS until the squared difference between predicted and measured OUR values was minimized.

5.2 PWAS COD Fractionation from OUR Analysis

As previously discussed, it was concluded that the BR WAS was comprised of active heterotrophic biomass (Z_{bh}) and endogenous decay products (Z_e). It was determined that thermal hydrolysis converted the biomass into two fractions, readily biodegradable COD (S_{bsc}) and slowly biodegradable COD (X_{sp}). Additionally,

the endogenous fraction was assumed to be constant after pretreatment. Staples-Burger (2012) concluded that pretreatment at 150°C for 30 minutes did not generate soluble microbial products, which were characterized as non-biodegradable soluble COD (nbsCOD). Refractory compounds have been known to form at pretreatment temperatures above 175°C (Valo et al., 2004). The current study operated at temperatures within 125°C and 175°C. Therefore, all soluble components produced as a result of thermal hydrolysis were fractionated as biodegradable soluble COD (S_{bsc}) or colloidal slowly biodegradable COD (X_{sc}). Normally, soluble components are characterized as S_{bsc}. However, in this study, the filters used to retain soluble materials had pore sizes of 1.5 µm. Musser (2009) defined colloidal matter as particles that pass through filters with pore sizes of 1.5 µm but were retained on pore sizes of 0.45 µm. Therefore, the measurements of SCOD contained both truly soluble and colloidal material. Conversely, all particulate components were fractionated as particulate X_{sp}. This analysis was conducted in order to obtain preliminary estimates of the PWAS COD fractionations. The estimates of the PWAS COD fractionation were refined later using BioWin® in Section 5.4.3.

5.2.1. S_{bsc} Estimation from Respirometry Data

The soluble PWAS composition was estimated from OUR curves generated by offline respirometry tests that included filtered PWAS (FPWAS) and AD WAS samples. The area under these curves was deemed to represent the mass of oxygen utilized by uptake of the soluble and colloidal components of the pretreated substrate and endogenous decay. OUR due to endogenous respiration was estimated using online respirometry results from the aerobic digesters fed with PWAS. As described in Section 4.3.1, the tail end of the reaction cycle was attributed to endogenous respiration after all of the substrates had been consumed. Therefore, a nonlinear regression of (2.6) was fit to the tail end of each reaction period to determine the initial active biomass concentration (Z_{bh0}). Figure 5.2 shows the nonlinear regression of (2.6) to OUR responses for 125°C-30 PWAS that was typical of the other conditions.

The estimated initial active biomass concentration was then employed in (2.6) to obtain the OUR due to endogenous respiration in the offline respirometry tests. In this case, the b_h value was adjusted to account for the fact that the batch tests were operated at 25°C. The modeled endogenous respiration was then plotted with the OUR response of filtered PWAS which is shown in Figure 5.3.

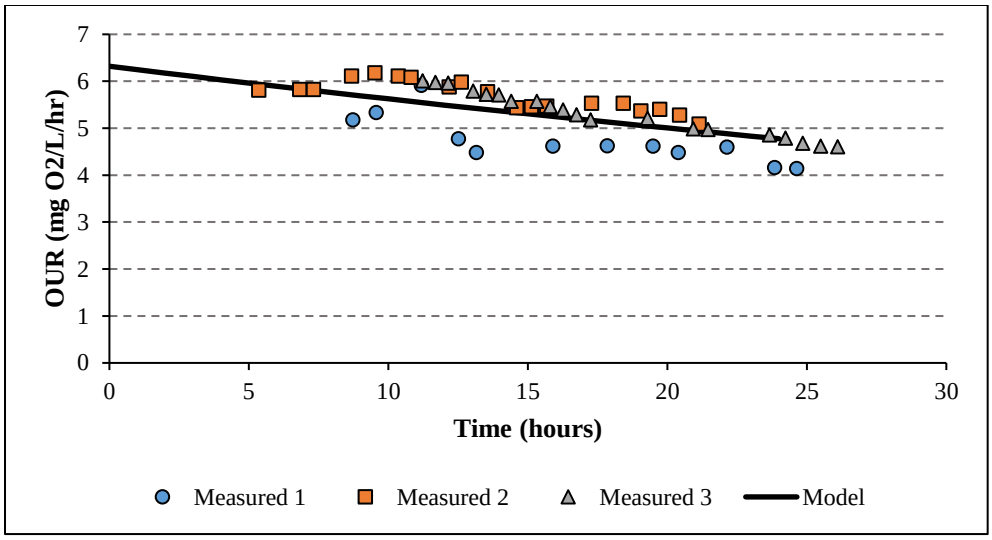


Figure 5.2 Nonlinear Regression Fit of Equation (2.6) to Online Respirometry Data

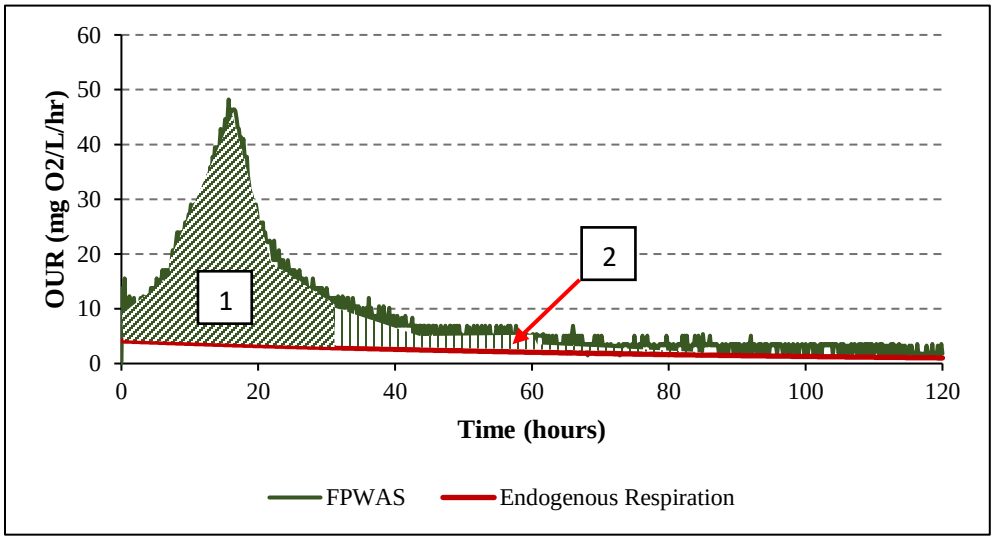


Figure 5.3 OUR Attributed to Inoculated FPWAS (125°C – 30 minutes) and endogenous respiration

The area between the OUR exerted by the inoculated FPWAS and endogenous respiration curves was attributed to the oxygen uptake by the filtered substrate (FPWAS). In the analysis, it was assumed that only the truly soluble components were readily biodegradable COD (S_{bsc}). Therefore, it was important to distinguish the area attributed to S_{bsc} and colloidal COD as the colloidal COD would respond similarly to slowly biodegradable COD (X_{sp}). In all of the OUR responses of FPWAS, there was a distinct peak and decline in OUR in the first 32 hours. This was attributed to S_{bsc} consumption and the response after the subsequent drop in OUR was assumed to result from hydrolysis of X_{sc}. Area 1 as shown in Figure 5.3 was therefore indicative of the oxygen uptake due to truly soluble substrate (S_{bsc}). Area 2 was associated with

the oxygen uptake in response to consumption of X_{sc}. The mass of oxygen consumed in the tests was adjusted to account for substrate consumed as per (5.1) to calculate S_{bsc} as a mass of COD in the tests.

$$M_{Sbsc} = \frac{M_{O_2}}{1 - Y_H} \tag{5.1}$$

in which M_{O2} denoted the mass of O_2 consumed (mg), Y_h was the heterotrophic yield (mgCOD/mgCOD), and M_{sbsc} was the mass of S_{bsc} in respirometry bottle (mg COD). M_{O2} was the area attributed to FPWAS alone for up to 32 hours. The heterotrophic yield chosen was a typical value of 0.67. Direct comparisons of M_{Sbsc} between pretreatment conditions could not be conducted as the amount of TCOD in the respirometry bottles differed slightly. Therefore, the M_{Sbsc} values were normalized with respect to the COD mass of the substrate in the respirometry bottles at the beginning of the test. This normalization was calculated using (5.2)

$$f_{Sbsc} = \frac{M_{sbsc}}{M_{TCOD}} \tag{5.2}$$

in which, M_{sbsc} denoted the mass of S_{bsc} in respirometry bottle (mg COD) and M_{TCOD} was the total COD mass in respirometry bottle (mg COD). The S_{bsc} fractions for all pretreatment conditions are summarized in Table 5.1 and from this table it can be seen that f_{Sbsc} values ranged from 13.3% to 27.1%. Generally, the fraction of S_{bsc} increased with pretreatment duration. However, the impact of temperature was not consistent as the f_{Sbsc} values sometimes decreased at increased temperatures.

Table 5.1 Summary of S_{bsc} Fractions for PWAS

Pre-treatment Condition	f_{Sbsc}
125°C – 10 minutes	0.133
125°C – 30 minutes	0.219
125°C – 50 minutes	0.189
150°C – 10 minutes	0.129
150°C – 30 minutes	0.152
150°C – 50 minutes	0.200
175°C – 10 minutes	0.169
175°C – 30 minutes	0.226
175°C – 50 minutes	0.271

The estimated f_{Sbsc} values were based on evaluating the OUR curve areas for the first 32 hours of the offline respirometry test. It is possible that for some PWAS, the rbCOD fraction was underestimated or overestimated due to the relatively arbitrary selection of the duration. An important factor not considered

in the OUR area analysis is the maximum OUR which will depend on the initial readily biodegradable COD (S_{bsc}) concentration. Therefore, BioWin® was used to improve upon these initial fractionations and these results are further discussed in Section 5.4.3.

5.2.2. X_{sp} Estimation from Respirometry Data

As previously described, the soluble COD was fractionated as S_{bsc}, while the colloidal COD was assumed to be X_{sc}. The fractions of X_{sc} (f_{xc}) were therefore calculated using (5.3)

$$f_{Xsc} = f_{scod} - f_{sbsc} \tag{5.3}$$

in which f_{scod} denoted the soluble COD fraction of PWAS and f_{Xsc} was the colloidal slowly biodegradable fraction. The values of f_{SCOD} were calculated by dividing SCOD concentration by TCOD concentration for each PWAS sample and f_{sbsc} values were calculated previously in Section 5.2.1. The fractions of calculated X_{sc} are summarized in Table 5.2.

It was assumed that non-biodegradable particulate components were not generated with pretreatment and hence particulate COD in PWAS samples was assumed to consist of Z_e and particulate slowly biodegradable COD (X_{sp}). The fraction of endogenous decay products was previously estimated in Section 4.3.2 and hence the particulate X_{sp} present in the PWAS samples was calculated using (5.4)

$$f_{Xsp} = f_{pCOD} - f_{Ze} \tag{5.4}$$

in which, f_{Xsp} denoted the fraction of particulate X_{sp}, f_{pCOD} was the particulate COD fraction of PWAS, and f_{Ze} was the endogenous decay products fraction. The particulate COD fraction of PWAS was calculated by dividing the PCOD concentration by the TCOD concentration. The total slowly biodegradable COD (X_s) was then calculated as the sum of the colloidal (X_{sc}) and particulate (X_{sp}) slowly biodegradable COD. Table 5.2 shows the fractions of the total slowly biodegradable COD (X_s) and the contributions from each colloidal and particulate slowly biodegradable COD.

Table 5.2 Fractions of Slowly Biodegradable COD (Colloidal, Particulate, Total)

Pre-treatment Condition	f_{Xsc}	f_{Xsp}	f_{Xs}
125°C – 10 minutes	0.200	0.469	0.669
125°C – 30 minutes	0.164	0.373	0.537
125°C – 50 minutes	0.156	0.401	0.557
150°C – 10 minutes	0.279	0.391	0.670
150°C – 30 minutes	0.277	0.376	0.654
150°C – 50 minutes	0.255	0.314	0.570
175°C – 10 minutes	0.217	0.384	0.600
175°C – 30 minutes	0.233	0.275	0.508
175°C – 50 minutes	0.363	0.143	0.506

From Table 5.2 it can be seen that pretreatment had varying effects on the colloidal and particulate slowly biodegradable COD fractionation of the WAS COD. It was previously assumed that the first 32 hours of OUR response was attributed to S_{bsc}. However, there was no way to determine if this was valid. As the direct examination of the OUR responses were inconclusive, BioWin® modeling was employed to account for the impact of the kinetics of biodegradation of S_{bsc} and X_{sp}.

5.3 BR-AD System Modeling

The BioWin 5.0® Integrated Model was used to simulate the bioreactor and aerobic digester (BR-AD) system as shown in Figure 5.4 to:

- Calibrate BioWin 5.0® Integrated Model on the basis of Y_h, b_h and f for subsequent modeling of the pretreated WAS and aerobic digester system (PT BR-AD)
- Confirm the fractions of active biomass (Z_{bh}) and endogenous products (Z_e) estimated in Section 4.3.2 were comparable to model results
- Determine fraction of biodegradable COD and endogenous decay products for PWAS

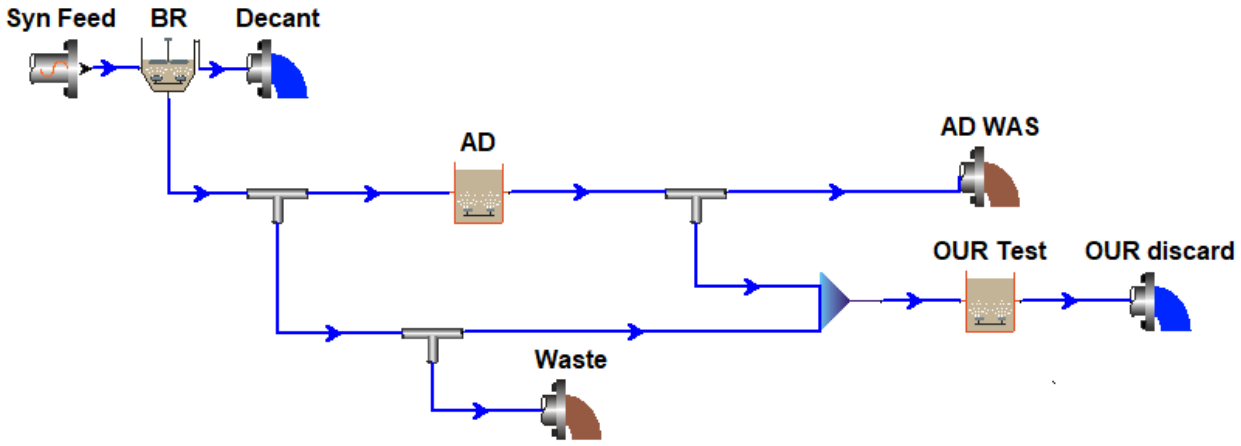


Figure 5.4 Bioreactor and Aerobic Digester System Process Flowsheet in BioWin®

A stepwise approach was used to calibrate the values of key kinetic and stoichiometric parameters such that the predicted concentrations of PCOD in the BR were found to be statistically equivalent to the average measured concentrations using t-tests at the 95% confidence level. In Section 4.2.1, it was concluded that the BR was relatively stable, however, the COD concentrations were slightly different during sampling. Hence, the process flowsheet in Figure 5.4 was calibrated nine separate times that represented the nine sampling times for each pretreatment condition.

For this study, the key kinetic parameters were b_h and f and the key stoichiometric parameter was Y_h. Typical values of f and b_h for heterotrophs of 0.20 and 0.24 d^{-1} at 20°C were employed. Since the BioWin

Integrated Model utilized the decay-regeneration approach, the f and b_h values were converted to 0.09 and 0.53 d^{-1} respectively (Staples-Burger, 2012). A typical value of Y_h in real activated sludge systems is 0.67. Therefore, the baseline for modeling BR-AD system employed f, b_h and Y_h values of 0.09, 0.53 d^{-1} and 0.67 respectively.

The baseline parameters were initially employed to determine if the measured PCOD concentrations of BR WAS could be matched by BioWin Integrated Model. However, simulations showed that the baseline parameters were unable to match the measured PCOD concentrations. Therefore, key kinetic and stoichiometric parameters were calibrated in order to improve the model predictions. Initially, Y_h was adjusted while f and b_h were held constant. For each new value of Y_h, the BR-AD system was simulated using BioWin®. The value of Y_h that simulated PCOD concentrations that were statistically equivalent to the measured values was recorded. This step was repeated by adjusting f while holding b_h and Y_h constant, as well as adjusting b_h while holding f and Y_h constant. It was noted that changing f or b_h independently did not have a significant impact on the predicted PCOD concentrations. They had to be changed beyond the normal range found in literature in order to match the concentrations. As a result, calibration was only successful in terms of Y_h and the other kinetic parameters were kept at baseline values. Table 5.3 summarizes the heterotrophic yields that were found to best describe the BR-AD configuration prior to employing each pretreatment condition. The heterotrophic yield varied from 0.67 to 0.75. The range of heterotrophic yields was relatively small, however, they reflected the fluctuations observed in the COD concentrations of BR WAS.

Table 5.3 Summary of Heterotrophic Yield for All BR-AD Systems

Phase 1 System	Y_h	Predicted BR PCOD (mg/L)	Measured BR PCOD (mg/L)
125°C – 10 min	0.67	4021	4049 ± 16
125°C – 30 min	0.73	4711	4755 ± 43
125°C – 50 min	0.75	4964	5016 ± 139
150°C – 10 min	0.68	4128	4166 ± 123
150°C – 30 min	0.66	3916	3919 ± 177
150°C – 50 min	0.72	4589	4565 ± 147
175°C – 10 min	0.73	4711	5033 ± 584
175°C – 30 min	0.75	4964	4998 ± 64
175°C – 50 min	0.70	4353	4377 ± 11

The endogenous decay products (Z_e) were predicted to be on average 18.4% of the TCOD. A t-test at 95% confidence interval revealed that there was no difference between the modeled fraction and the previously estimated fraction of 17.7 ± 1.0 %. It was concluded in earlier sections that the endogenous fraction remained unchanged by pretreatment. Therefore, in subsequent modeling of the endogenous decay product

fraction in PWAS assumed to equal 18.4%. The active biomass fraction, which was deemed to represent biodegradable COD fraction, was predicted to be on average 78.9% of the total COD and was statistically equivalent to the measured active fraction of 79.2 ± 4.6% at the 95% confidence level. It was expected that all of the active biomass would be converted to either X_{sp} or S_{bsc}. Therefore, the sum of these two fractions had to be within the predicted 78.9% in when determining the PWAS COD fractionation.

5.4 PT BR-AD System Modeling

5.4.1. Approach

The PT BR-AD system modeling was used to determine the PWAS COD fractionation. There were two major steps taken to meet this objective. The first step was to calibrate the thermal hydrolysis (TH) unit employed in BioWin to simulate HPTH pretreatment of WAS. The second step was to model the offline respirometric tests on inoculated PWAS to determine the PWAS COD fractionation by matching the measured OUR values.

The purpose of calibrating the TH unit was to characterize the PWAS that was fed to the aerobic digesters to acclimatize the biomass to the PWAS (Figure 5.5). For all the offline respirometry data collected on inoculated PWAS, the inoculum (AD WAS) was acclimatized to WAS pretreated at the same temperature for 30 minutes (Figure 5.6). Hence, the TH calibration in BioWin® was carried out using 125°C-30, 150°C-30 and 175°C-30 PWAS and details of this calibration will be discussed in Section 5.4.2. Each pretreatment condition likely modified the WAS composition differently, however, it was deemed sufficient to acclimatize the aerobic digesters with the 30 minute PWAS.

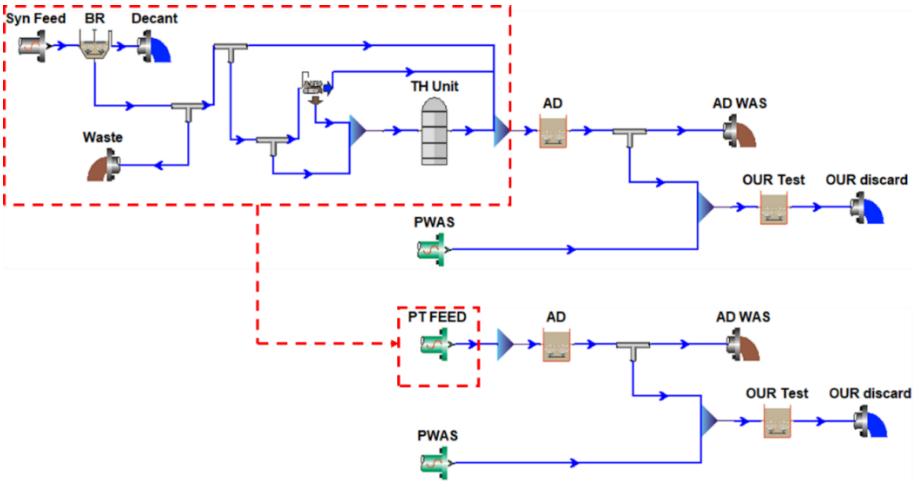


Figure 5.5 Characterization PWAS used to Acclimatize AD WAS in BioWin

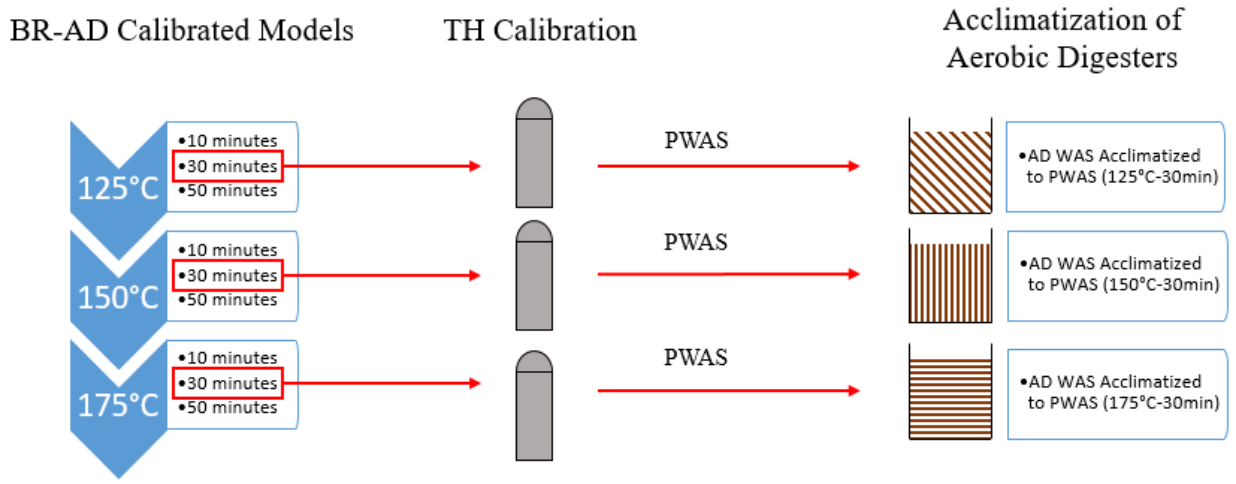


Figure 5.6 TH Calibration and Acclimatization of AD WAS

The ultimate goal of setting up the PT BR-AD system in BioWin was to model the offline respirometry tests of the PWAS (Figure 5.7). As previously mentioned, the offline respirometry tests on inoculated PWAS were conducted with PWAS and AD WAS that was acclimatized to WAS pretreated for 30 minutes. The COD fractionation of PWAS was based on changing S_{bsc} and X_{sp} concentrations to predict OUR responses exhibited by the streams shown in Figure 5.7.

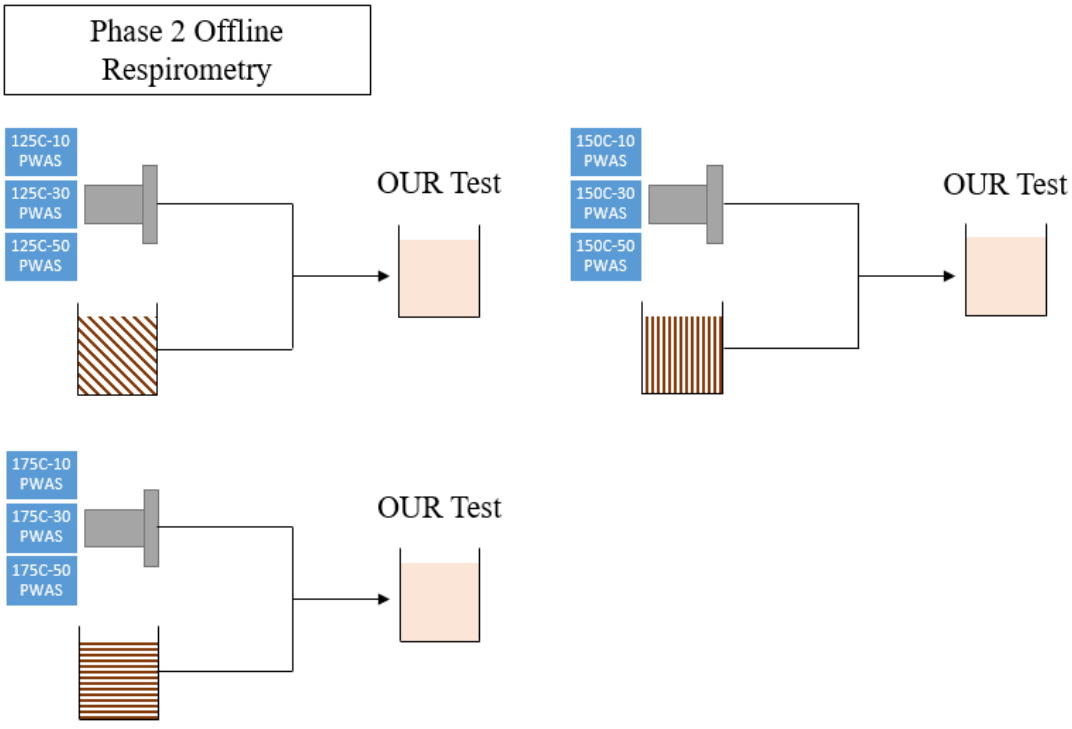


Figure 5.7 Offline Respirometry of All PWAS with Acclimatized AD WAS

5.4.2. Thermal Hydrolysis Unit Calibration

Figure 5.8 shows the process flowsheet used to calibrate the TH unit in BioWin®. The process flowsheet shown was identical to the BR-AD process flowsheet except with a dewatering unit and TH unit added to the BioWin® configuration. The dewatering unit was included as the BR WAS samples collected in the lab were gravity thickened prior to HPTH pretreatment. This process flowsheet was used to calibrate the TH unit and to characterize the PWAS fed into the aerobic digesters as previously shown in Figure 5.5.

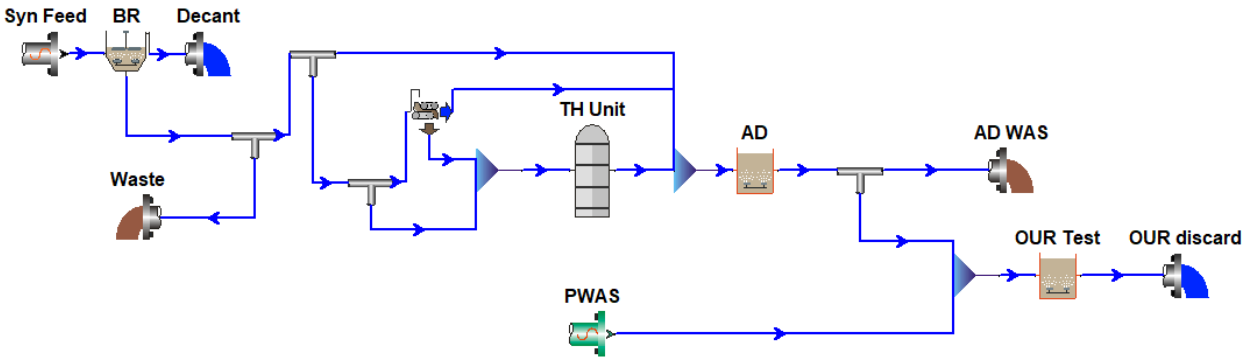


Figure 5.8 Process Flowsheet of PT BR-AD System

The thermal hydrolysis module in BioWin incorporates relationships that affect the WAS composition. Table 5.4 shows the various parameters and default values for this unit. For this study, the fraction of endogenous decay product was assumed to remain the same throughout pretreatment. Therefore, the fraction of converted biomass going to endogenous residue was set to zero. It was previously demonstrated that the biomass was inactivated by pretreatment and fully converted to biodegradable substrate. As a result, the fraction of biomass converted was kept at the default value. It was also assumed that no nbsCOD (S_{us}) were formed and thus the fraction of converted X_s going to soluble S_{us} was set to zero. The biodegradable COD of the BR WAS was assumed to be converted to either S_{bsc} or X_{sp}, therefore, the fraction of X_s converted to S_{bsc} was set to one rather than having two components which represented readily biodegradable COD. The fraction of X_s converted was the parameter that was calibrated based on matching measured COD concentrations of PWAS. The fraction of X_s converted was changed until the predicted PWAS COD concentrations (i.e. TCOD, PCOD, SCOD) coming out of the TH unit matched closely to the measured COD concentrations of PWAS samples.

Table 5.4 Thermal Hydrolysis Unit Parameters in BioWin

Hydrolysis Parameter	Default	Change
Fraction of biomass converted	1.00	-
Fraction of converted biomass going to endog. residue (remainder to X_{sp})	0.20	**0.00**
Fraction of endogenous converted	0.00	-
Fraction of converted endog. going to unbiodeg. sol. (remainder to X_{sp})	0.50	-
Fraction of unbiodegradable particulate converted (all to X_{sp})	0.00	-
Fraction of X_s converted	0.95	**?**
Fraction of converted X_s that is oxidized (remainder solubilized)	0.00	-
Fraction of converted X_s going to sol. S_{us}	0.05	**0.00**
Fraction of remaining converted X_s converted to S_{bsc} (the rest reports as S_{bsa})	0.50	**1.00**
Fraction of X_{on} hydrolyzed	0.95	-
Fraction of converted X_{on} going to N_{us}	0.05	-
Fraction of remaining converted X_{on} converted to N_{os} (the rest reports as NH_3)	1.00	-

Table 5.5 summarizes the calibrated fraction of X_s converted that was employed to characterize the 30 minute PWAS used to acclimatize the AD WAS. It can be seen that the fraction of X_s converted to S_{bsc} was equal for 125°C-30 and 150°C-30 PWAS, while it was much higher for 175°C-30 PWAS. The characterized PWAS was fed to the AD to acclimatize the AD WAS to PWAS and to provide an approximation of the concentration of active biomass (Z_{bh}) that went into the offline respirometry tests with PWAS. Therefore, the fact that not all pretreatment conditions were used to acclimatize the AD WAS was not considered to be a problem for subsequent offline respirometry test modeling.

Table 5.5 Calibrated Thermal Hydrolysis Unit Parameters

Pretreatment Condition	Fraction of X_s Converted	Predicted TCOD, SCOD	Average Measured TCOD, SCOD
125°C – 30 min	0.54	8372 mgCOD/L	8374 mgCOD/L
		3690 mgCOD/L	3713 mgCOD/L
150°C – 30 min	0.54	7256 mgCOD/L	7258 mgCOD/L
		3194 mgCOD/L	3180 mgCOD/L
175°C – 30 min	0.66	9594 mgCOD/L	9596 mgCOD/L
		5154 mgCOD/L	5194 mgCOD/L

To summarize, the initial portion of PT BR-AD modeling was done in order to:

- Calibrate the thermal hydrolysis unit in BioWin to generate PWAS that was fed to AD
- Generate AD WAS (inoculum) to be used in subsequent offline respirometry modeling
- Ensure that the AD WAS was acclimatized by WAS pretreated at various temperatures

The PWAS composition was then determined through modeling of offline respirometry tests in BioWin that is presented in the next section.

5.4.3. Calibration of PWAS Composition

Batch respirometry tests were modeled in BioWin in order to determine the fractions of S_{bsc} and X_{sp} in the PWAS samples. Figure 5.9 shows the BioWin process flowsheet used to model batch respirometry tests. The influent, "PT FEED" was characterized in the previous section and was used to simulate the AD WAS generated in the PT BR-AD flowsheet. The stream "PWAS" was employed to introduce the fractionated PWAS to the batch tests. Varying the composition of this stream allowed for estimation of the S_{bsc} and X_{sp} values for each pretreatment condition. As mentioned in Section 5.3, the sum of these two fractions represented approximately 78% of the predicted TCOD of the BR WAS.

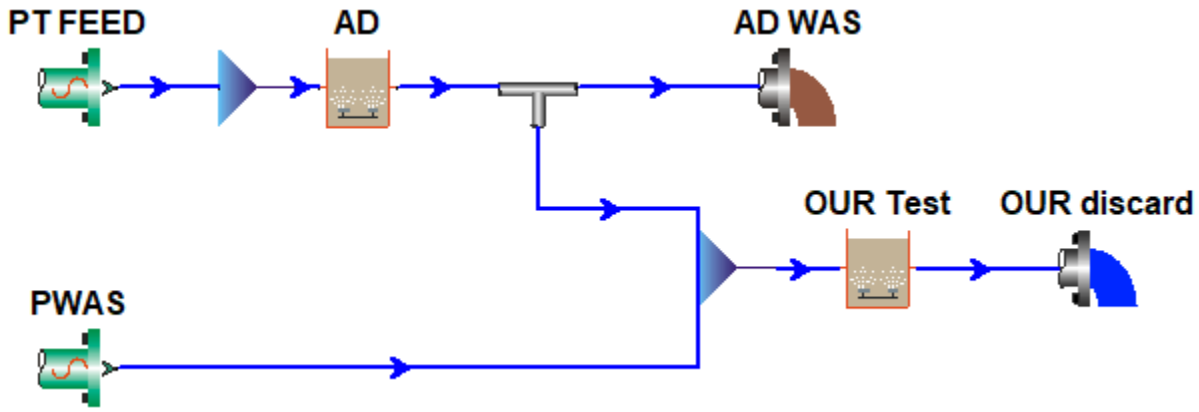


Figure 5.9 Typical BioWin Configuration of PWAS Offline Respirometry

Table 5.6 presents a typical table of values employed in the PWAS calibration process and it shows the COD components of the 125°C-10 PWAS. The concentrations of endogenous decay products (Z_e) and nonbiodegradable soluble COD (S_{us}) were determined in the BR-AD system modeling described in Section 5.3. The concentration of X_{sp} was determined by subtracting the endogenous decay products concentration from the PCOD concentration of the PWAS sample. The readily biodegradable COD (S_{bsc}) concentration was the main parameter that was changed to match the OUR curves in offline respirometry. As discussed in Section 5.2.2, the colloidal COD was assumed to be colloidal slowly biodegradable COD (X_{sc}) and was calculated using (5.3). However, in BioWin, the kinetics of the two slowly biodegradable components are not differentiated. Furthermore, the initial hypothesis was that the biodegradable fraction (Z_{bh}) of BR WAS was converted to either X_{sp} or S_{bsc}. Therefore, instead of creating a "new" fraction of COD, X_{sc} was assumed to behave as X_{sp}. Therefore, in the scenario shown in Table 5.6 below, the BioWin® X_{sp} concentration was the sum of X_{sp} and X_{sc}.

Table 5.6 Typical PWAS COD Fractionation Calibration Table

Parameter	Measured (mgCOD/L)		BioWin Integrated Model		
	Avg.	St. Dev	Parameter	Predicted (mgCOD/L)	Sum
PCOD	2663	77	X_{sp}	1909	2663
			Z_e	754	
SCOD	1410	67	S_{bsc}	953	1410
			S_{us}	52	
			X_{sc}	405	

In order to determine the COD fractionation for each PWAS, the S_{bsc} and X_{sp} concentrations were changed, while ensuring that the sum of the components were equal to the measured concentrations for PCOD and SCOD. The PWAS was then employed as an input to the simulation of the variable volume reactor, along with AD WAS in order to model and predict the oxygen uptake. The optimal COD fractionation was found by minimizing the residual sum of squares between the measured and predicted OUR values. Figure 5.10 shows the OUR exhibited by 125°C-10 PWAS with an optimized COD fractionation using least squares method. The rest of the best-fit curves for all PWAS are shown in Appendix H.

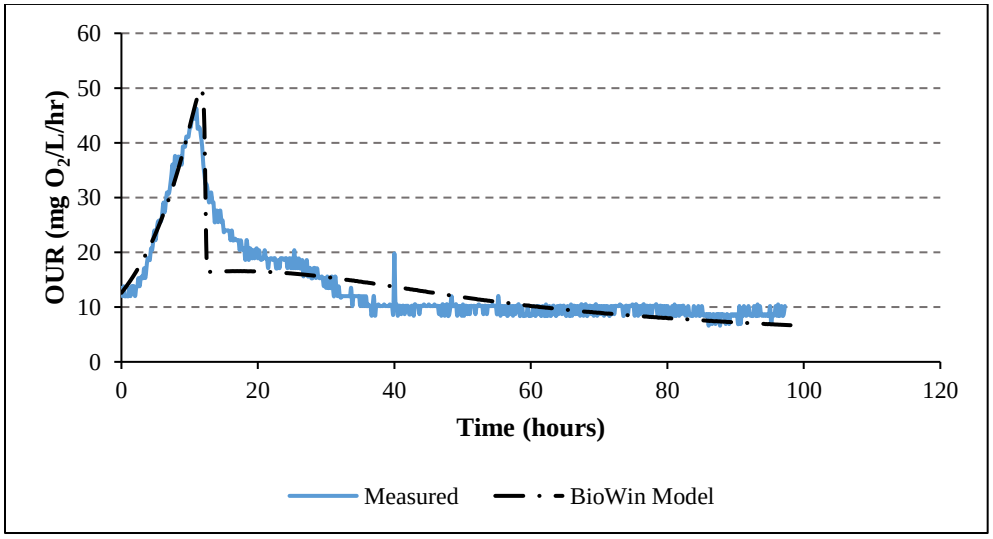


Figure 5.10 Predicted and Measured OUR of WAS Pretreated at 125°C for 10 Minutes

It can be seen from Figure 5.10 that the maximum OUR was accurately predicted by the calibrated model. The matching of the OUR response following the peak was found to be less accurate. The responses predicted by BioWin were significantly different for growth on S_{bsc} and hydrolysis of X_s, which resulted in a steep decline in OUR after the peak. In the measured response, the decline was more gradual as compared to the model prediction. This suggested that in actual sludges, the oxygen uptake for readily biodegradable and slowly biodegradable substrate cannot be clearly distinguished. Such fractionation of readily and slowly biodegradable substrate is somewhat simplistic and does not describe the gradation of values that likely

falls between the two substrate categories. However, the relatively close match between measured and predicted responses show that this type of fractionation was reasonable.

Once the optimal concentrations of S_{bsc} and X_{sp} were found for all the PWAS, they were divided by the TCOD concentration in order to normalize them for better comparison. Figure 5.11 shows the COD fractions for all PWAS as calibrated in the modeling exercise. From Figure 5.11 it can be seen that the pretreatment consistently resulted in the conversion of Z_{bh} in BR WAS to S_{bsc}. This conversion would be expected to result in an increase in the rate of aerobic biodegradability of the WAS with pretreatment.

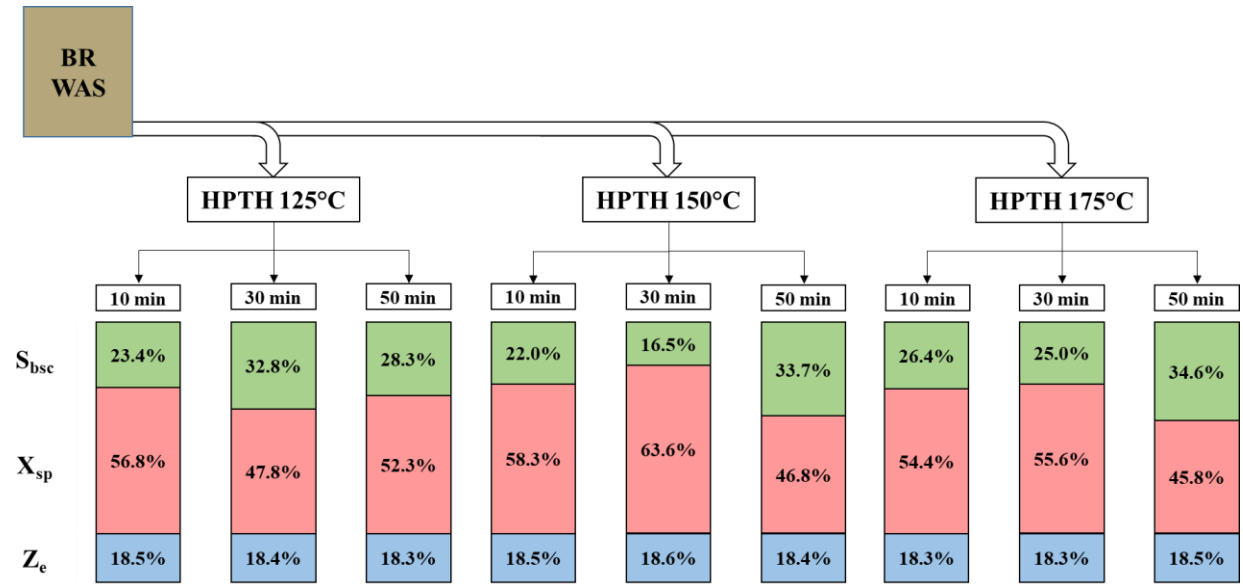


Figure 5.11 COD Fractionation of All PWAS

Unlike the COD solubilization relationships shown in Section 4.2.2, there was no consistent trend in the S_{bsc}/X_{sp} fractionation with pretreatment conditions. In Section 4.2.2, it was found that COD solubilization tended to increase with pretreatment time and temperature. However, the relationships between S_{bsc} and X_{sp} and pretreatment were more complex. For example, for WAS pretreated at 125°C, increasing the duration from 10 to 30 minutes increased the S_{bsc} fraction. Conversely, for 150°C and 175°C PWAS, increasing the duration from 10 to 30 minutes, decreased the S_{bsc} fraction. Comparing the 10 to 50 minute durations for all pretreatment temperatures, there was a consistent increase in S_{bsc}. However, the increase in S_{bsc} was not consistent when increasing the duration from 30 to 50 minutes. The effect of temperature on the fraction of S_{bsc} was similarly inconsistent. Hence, the uncertainty in the parameter (S_{bsc} and X_{sp}) estimates was considered. For some of the pretreatment conditions, solely minimizing the residual sum of squares did not indicate the overall quality of the fit. Figure 5.12 shows the "best-fit" for 175°C-30 PWAS. In this case, the BioWin Integrated Model substantially underestimated the OUR after the peak. The measured response deviated from a typical curve shape that could not be explained by the model.

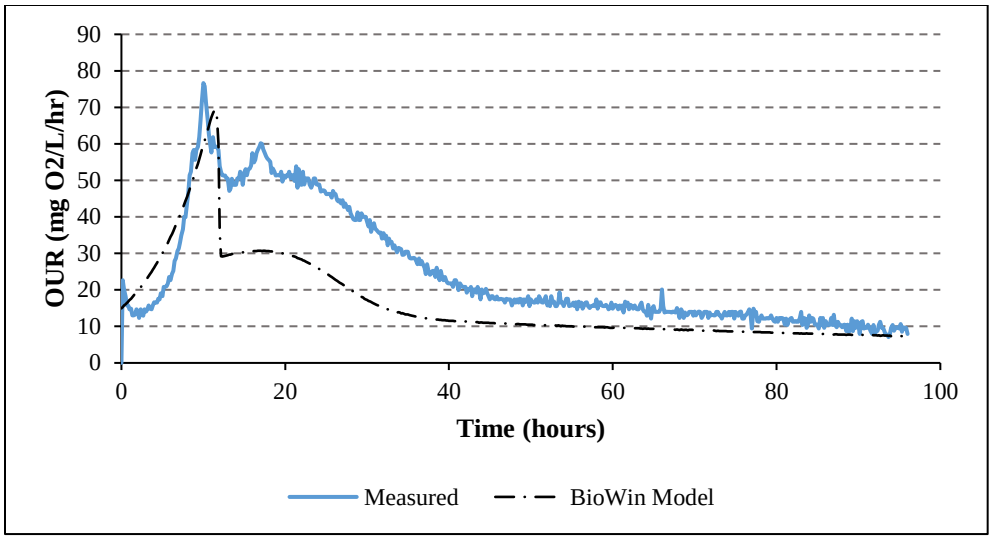


Figure 5.12 Predicted and Measured OUR of WAS Pretreated at 175°C for 30 Minutes

Motulsky & Christopoulos (2004) described a method of generating confidence intervals for estimated parameters. This method compares fits of model simulations to one set of data on the basis of the residual sum of squares. A critical sum of squares ($SS_{critical}$) which is based on the sum-of-squares (SS) on the best-fit ($SS_{best\text{-}fit}$) is calculated using (5.5)

$$SS_{critical} = SS_{best-fit}\left(F\frac{P}{N-P}+1\right) \tag{5.5}$$

in which, F denoted the critical value of F distribution for a P value of 0.05 (95% confidence) with P degrees of freedom in numerator, and N-P degrees of freedom in denominator, P was the number of parameters, and N was the number of data points. In this application, the number of parameters was two, since only S_{bsc} and X_{sp} were changed. Table 5.7 summarizes the value of $SS_{critical}$ for all PWAS tests.

Table 5.7 Summary of Critical Sum of Squares for All PWAS

Pretreatment Condition	P	N	N-P	$SS_{best\text{-}fit}$	F	$SS_{critcal}$
125°C-10	2	585	583	5920	3.0112	5951
125°C-30	2	717	715	5570	3.0083	5594
125°C-50	2	385	383	11051	3.0193	11138
150°C-10	2	539	537	12464	3.1025	12534
150°C-30	2	184	182	7541	3.0456	7667
150°C-50	2	734	732	33139	3.0080	33275
175°C-10	2	358	356	17489	3.0211	17638
175°C-30	2	576	574	81855	3.0114	82285
175°C-50	2	689	687	32104	3.0088	32244

The high $SS_{critical}$ values for some of the PWAS conditions provides an indication of the uncertainty of the parameters. The values were on average the highest for 175°C PWAS samples. These OUR curves exhibited the most atypical responses where the OUR values after the peak appeared to decline at a first-order rate.

In order to generate the 95% confidence region, one parameter was held constant (to varying degrees), while changing the other parameter until the SS was equal to $SS_{critical}$. Figure 5.13 shows the approximate 95% confidence ellipse for the 175°C-30 PWAS generated by this method. The confidence interval on the parameters was then estimated by taking the highest and lowest values of X_{sp} and S_{bsc} on the contour.

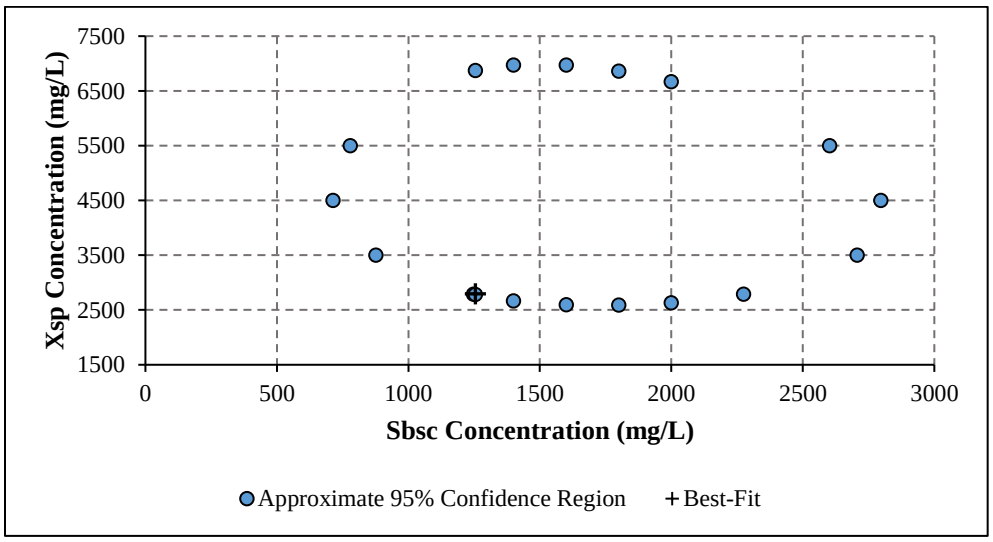


Figure 5.13 Approximate 95% Confidence Region for WAS Pretreated at 175°C for 30 Minutes

The contour was significantly asymmetrical about the best-fit. This is because the best-fit was constrained by measured COD concentrations, whereas these constraints were relaxed to determine the confidence region. For the pretreatment condition shown in Figure 5.13, the uncertainty in both S_{bsc} and X_{sp} estimation was deemed to be substantial. This reflected the relatively poor fit of the model predictions of OUR as demonstrated in Figure 5.12. The upper and lower confidence intervals of S_{bsc} and X_{sp} for all the PWAS samples are shown Figure 5.14 and Figure 5.15 respectively.

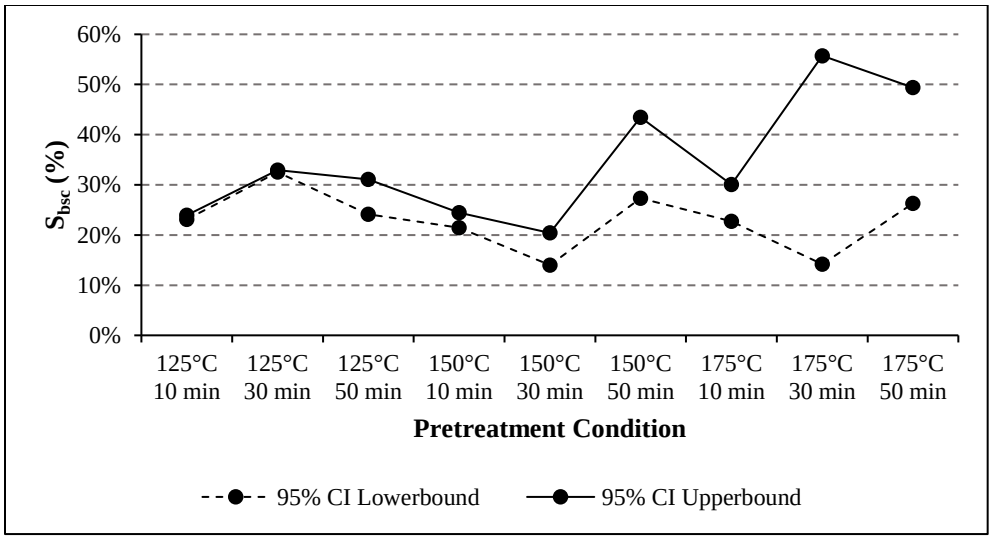


Figure 5.14 Upper and Lower Bound 95% Confidence Interval of S_{bsc}

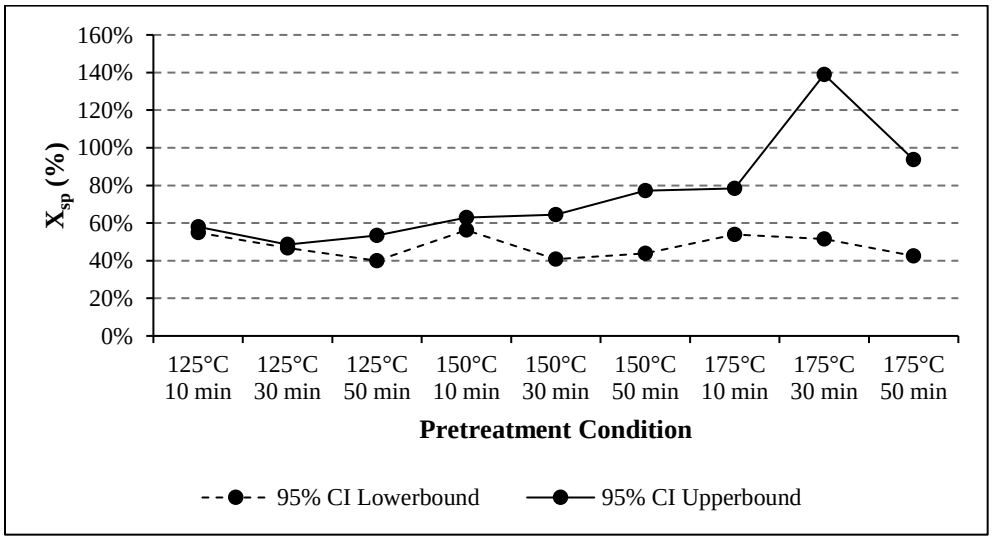


Figure 5.15 Upper and Lower Bound 95% Confidence Interval of X_{sp}

The uncertainty in the parameter estimation seemed to increase with pretreatment temperature and time and it was substantially higher for WAS pretreated at 175°C. The higher uncertainties corresponded to the increasing irregularity of the shapes of the measured OUR curves. This may suggest that as the dose (temperature-time) of pretreatment increased, the COD fractionation proposed in this study and in Staples-Burger (2012) became less applicable. As noted in Section 5.2, there were fractions of the soluble matter which was neither readily biodegradable COD (S_{bsc}) nor non-biodegradable soluble COD (S_{us}). It was suggested that this could be colloidal slowly biodegradable COD (X_{sc}). BioWin® distinguishes between colloidal and particulate slowly biodegradable COD as separate stoichiometric parameters, however, the kinetics that act upon these components are not differentiated. Combined with the findings of deteriorating

fits of COD fractionations and atypical OUR response observed in PWAS, this suggested that either the kinetics of the COD (in PWAS or AD WAS) fractions changed, or a new fraction was "introduced" by pretreatment which possessed different properties and mechanisms of reaction with active biomass.

Overall, the PT BR-AD modeling demonstrated that:

- The pretreatment conditions converted the biomass in BR WAS to S_{bsc} and X_{sp} to varying degrees.
- The degree to which COD solubilization occurred did not correspond to how much of the biodegradable COD was converted to S_{bsc}.
- The endogenous decay products fractions employed were identical to BR WAS. Furthermore, the predicted OUR responses were generally able to match the measured responses without having to alter the biodegradable fraction. Therefore, modeling of PT BR-AD also confirmed that the aerobic biodegradability did not change with pretreatment.
- The increasing uncertainty of S_{bsc} and X_{sp} estimates as pretreatment temperature and duration increased suggested that the current models cannot completely describe the effects of pretreatment on WAS behaviour. Thermal pretreatment may affect the kinetics of existing components.

6. Modeling of Thermal Pretreatment Impacts on Anaerobic Digestion of WAS

Samples of the PWAS from the PT BR-AD system were also characterized in BMP tests to determine the impacts of pretreatment on anaerobic digestion. The BioWin Integrated Model was used to model the BMP tests conducted in serum bottles to assist with data interpretations. Figure 6.1 shows the process flowsheet used in BioWin to model the BMP tests on all pretreatment conditions employed in anaerobic biodegradability testing.

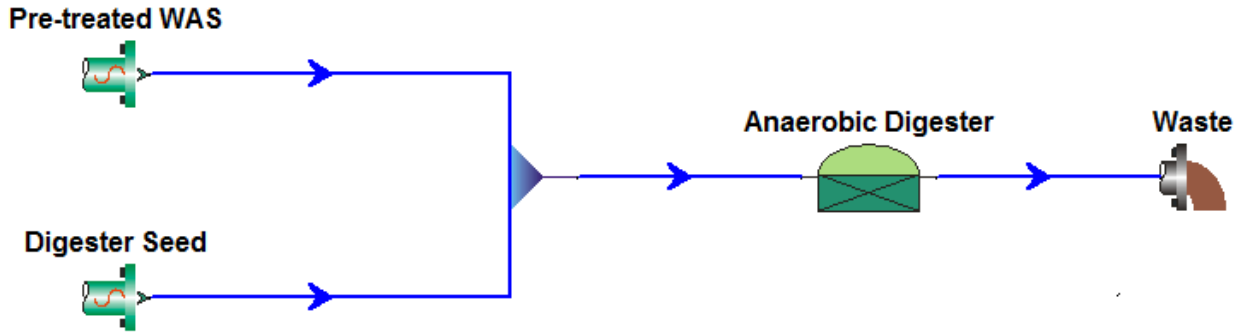


Figure 6.1 Typical BioWin Process Flowsheet for BMP Modeling

The sealed serum bottles used in the BMP tests had a total volume of 250 mL. The volumes were scaled up in BioWin® by assuming that 1 mL was equivalent to 1 m^3. Therefore, the total volume of the "Anaerobic Digester" unit was 250 m^3. Upscaling was necessary as BioWin® did not work well with very small volumes. The "Digester Seed" was seed sludge collected from Waterloo WWTP to provide a consortium of anaerobic bacteria for anaerobic digestion. The characterization of the seed is presented in Section 6.1. The other stream fed to the anaerobic digester unit was PWAS and its compositions was derived from the PT BR-AD modeling described in Section 5.4.

The purpose of BMP test modeling was to determine how pretreatment affected the anaerobic biodegradability of WAS and to determine if the COD fractionations of PWAS obtained Section 5.4 were valid under anaerobic digestion condition.

6.1 Characterization of Seed Sludge for BMP Tests

Seed sludge was collected from the primary digesters at the Waterloo WWTP. COD measurements for the digester seeds were taken on day 0 of the BMP tests. The average COD concentrations for the 30 and 50 minute seed sludges were 14216 ± 1527 mgCOD/L and 29564 ± 3618 mgCOD/L respectively. The seed was characterized in BioWin® to provide the batch anaerobic tests with a reasonable initial population of

anaerobic bacteria. EnviroSim Associates Ltd provided a working model of the Waterloo WWTP and the Region of Waterloo provided influent characteristics, flows and mixed liquor suspended solids (MLSS) profiles in the anaerobic digesters. Figure 6.2 shows the process flowsheet of the Waterloo WWTP in BioWin®.

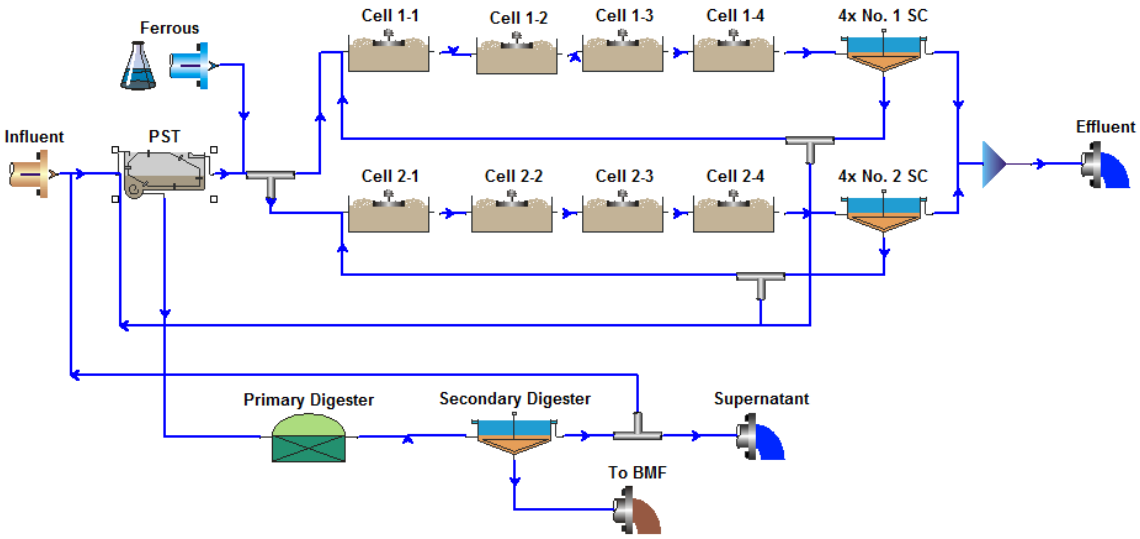


Figure 6.2 Waterloo WWTP BioWin Configuration

The average influent flow to the plant over the sampling period was 36,660 m^3 per day. The average influent characteristics are summarized in Table 6.1. The average MLSS concentrations for the aeration trains (Cell 1-1 to Cell 1-4 and Cell 2-1 to Cell 2-4) and combined WAS flow from secondary clarifiers ("SC") are summarized in Table 6.2.

Table 6.1 Average Wastewater Influent Concentrations for the Month of July – August

Influent Component	Average Concentration
Ammonia	35 mg/L
TP	10 mg/L
TKN	60 mg/L
TSS	517 mg/L
BOD_5	328 mg/L
$CBOD_5$	203 mg/L
pH	8 mg/L

Table 6.2 Average MLSS Concentrations for the Month of July - August

Parameter	Average (July 1 – Aug 7)	St Dev.
MLSS (mg/L) [Aeration Train #1]	2143	832
MLSS (mg/L) [Aeration Train #2]	2884	198
WAS Flow (m^3/d)	1499	162

In order to generate the seed compositions, data provided by the Region of Waterloo was used to calibrate the BioWin® model of the Waterloo WWTP. This was done by varying the flow splits at various junctions and process units until the predicted MLSS concentrations, WAS flow and primary digester effluent COD were statistically equivalent to the average measured values. The concentration of anaerobic bacteria for 30 and 50 minute seed sludge are summarized in Table 6.3 and Table 6.4 respectively. The 50 minute seed sludge had a higher concentration of anaerobic bacteria. This was due to the higher concentration of COD measured for this seed. A t-test at 95% confidence level showed that the difference between the 30 and 50 minute seed sludge COD was 15348 ± 3927 mgCOD/L. It should be noted that this characterization of the inoculum was not comprehensive and was primarily done to obtain approximate concentrations of anaerobic bacteria. Due to the fact that these characterizations were only approximate, adjustments were made in the subsequent modeling of BMP tests of PWAS.

The seed sludge (inoculum) was assessed to determine if the initial characterization was sufficient to proceed with subsequent BMP modeling. The characterization was assessed by determining whether the BioWin Integrated Model could predict the methane production from the seed sludge alone. Figure 6.3 shows the measured cumulative methane production from 30 and 50 minute seed sludge. There was a significant difference in methane accumulation between the two seed sludge. It may be possible that the seed sampled still contained a large amount of substrates leading to a higher methane yield.

Table 6.3 Anaerobic Bacteria Concentrations in 30 Minute Seed Sludge

State Variable	Concentration
OHO	1981
Methylotrophs	3
AOB	135
NOB	83
ANAMOX	4
PAO	3.
Propionic Acetogens	116
Methanogens (acetoclastic)	391
Methanogens (hydrogentrophic)	243

Table 6.4 Anaerobic Bacteria Concentrations in 50 Minute Seed Sludge

State Variable	Concentration
OHO	2259
Methylotrophs	4
AOB	151
NOB	93
ANAMOX	5
PAO	4
Propionic Acetogens	138
Methanogens (acetoclastic)	458
Methanogens (hydrogentrophic)	285

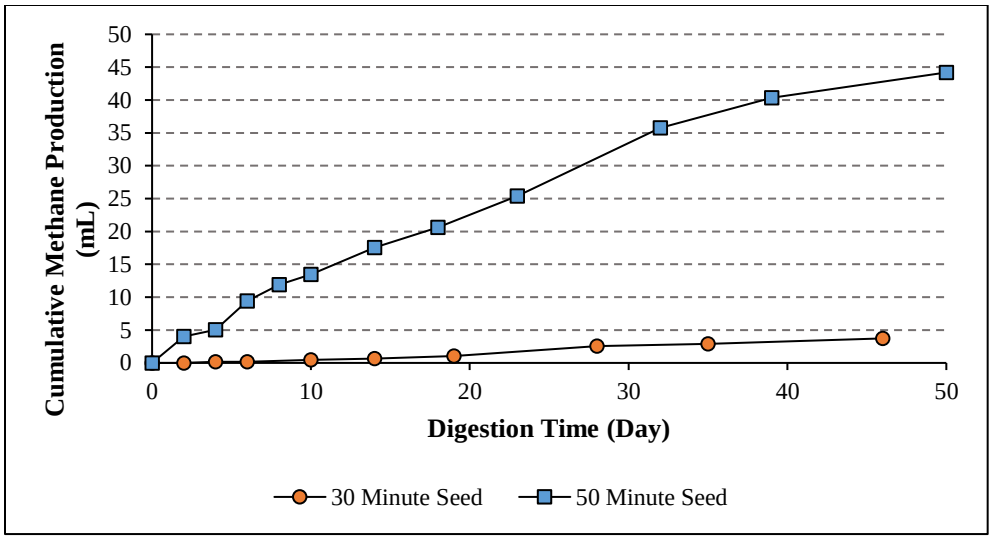


Figure 6.3 Measured Cumulative Methane Production for 30 and 50 Minute Seed Sludge

The BMP tests on inoculum alone were modeled using BioWin®. This was done by simulating the batch tests with only the seed. The measured and predicted methane accumulation is shown in Figure 6.5 and Figure 6.5 for 30 and 50 minute seed respectively. For the 30 minute seed sludge, the model slightly over-predicted the ultimate methane yield. Conversely, the model was significantly underestimated the ultimate yield for the 50 minute seed sludge. The large discrepancy between the 30 and 50 minute seed sludges may have resulted from the timing of seed sampling.

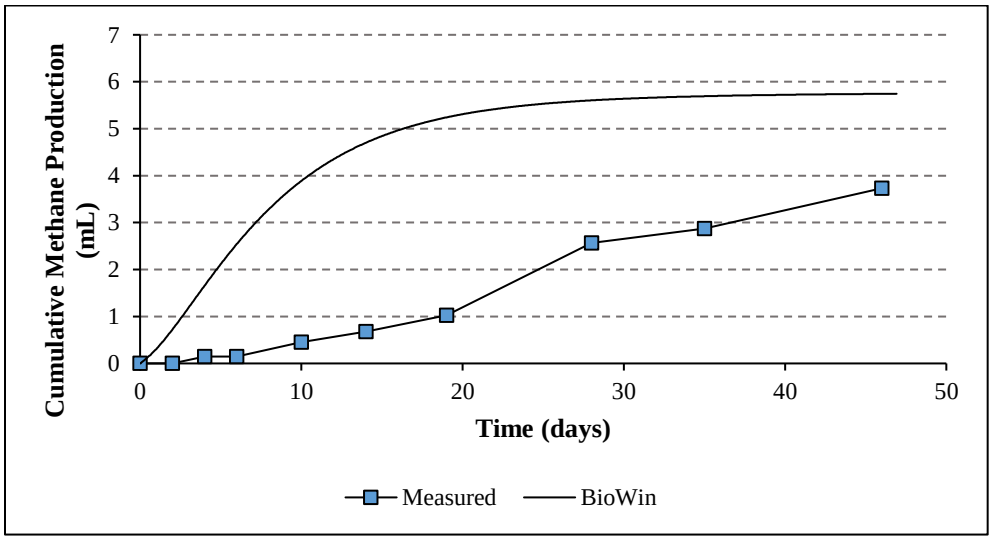


Figure 6.4 Measured and Predicted Cumulative Methane Production for 30 Minute Seed

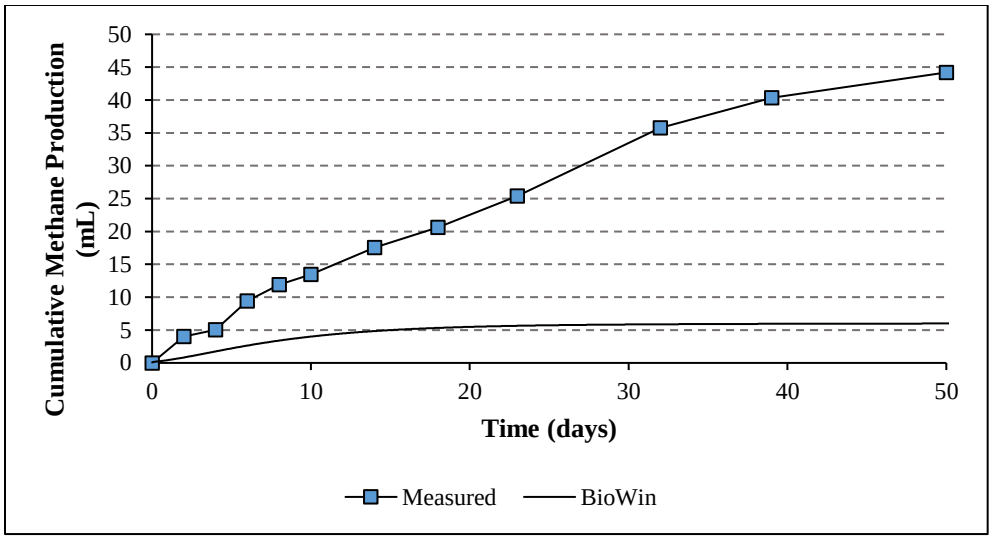


Figure 6.5 Measured and Predicted Cumulative Methane Production for 50 Minute Seed

The 30 minute seed sludge was deemed to be sufficiently characterized by the preliminary modeling as the methane yield was not substantially overestimated and since the ultimate yield was relatively low. Comparatively, the 50 minute seed sludge composition was deemed to be not reliable as there likely were substrates still in the samples collected. However, the estimation of the anaerobic bacteria concentrations were still considered to be valid. Furthermore, the contribution of the model seed sludge to methane production was minimal (less than 6 mL). Therefore, for modeling the 50 minute PWAS BMP tests, the measured methane production data used excluded the contributions from the seed sludge. This dataset was derived by calculating the methane production by substrate and seed together and then subtracting the methane production from the seed alone. The methane production due to substrate and seed, seed alone and substrate alone can be seen in Figure 6.6 for 125°C-50 PWAS.

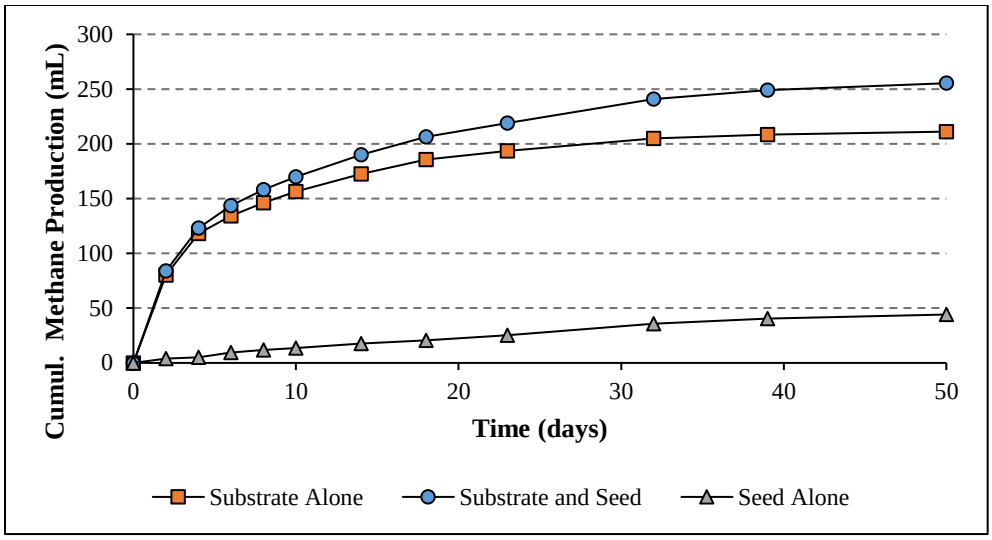


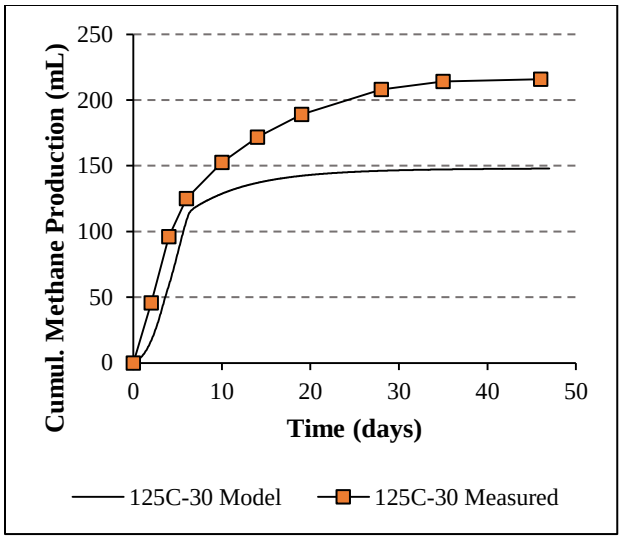
Figure 6.6 Methane Generation by 125°C-50 PWAS and 50 minute Seed Sludge

6.2 Modeling of BMP Tests

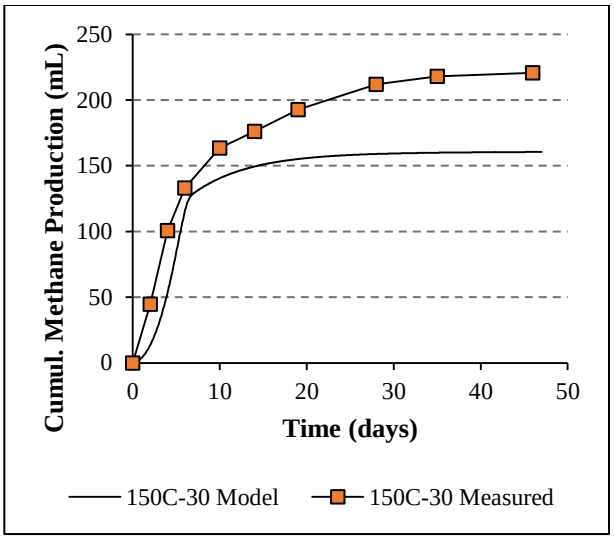
The modeling process was conducted in three sequential trials. Trial 1 used default kinetic parameters and used the PWAS as fractionated in PT BR-AD modeling as an input. In this trial, it was found that the ultimate methane yield was substantially underestimated by the model for all PWAS samples. The initial inoculum characterization was deemed to be inadequate for modeling purposes and therefore needed to be changed to improve the model fit. Trial 2 used the newly characterized seed sludge to inoculate the PWAS in the BMP modeling. The fits were improved, but still could not predict the ultimate methane yields. Therefore, Trial 3 changed the endogenous products decay rate in order to improve the model fit. The specifics of each trial are discussed in the succeeding sections. The evaluation of the quality of the model's fit was assessed by comparing the measured cumulative and daily methane production. Matching the ultimate methane yield was considered the most important factor in improving the model fit.

6.2.1. Trial 1 of BMP Modeling

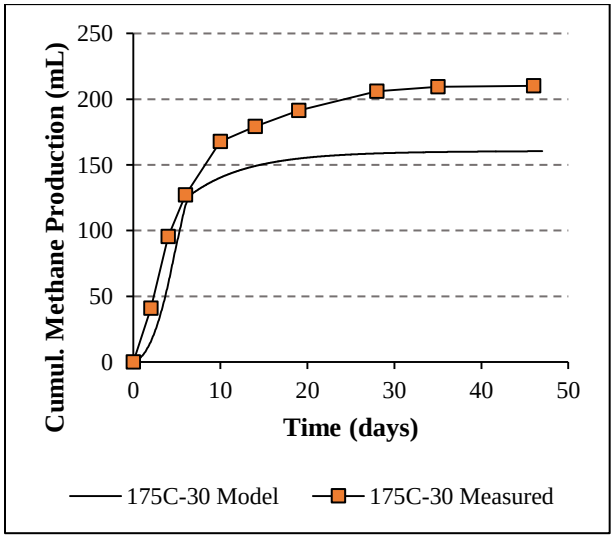
Figure 6.7 shows the observed and predicted cumulative methane production for 125°C-30, 150°C-30, and 175°C-30 PWAS samples. From this figure, it can be seen that for the first 8 days of anaerobic digestion, the model predicted the cumulative methane production reasonably well. However, beyond this point, methane production was substantially underestimated by BioWin®. Similarly, the cumulative methane production for 125°C-50, 150°C-50, 175°C-50 PWAS were also underestimated by the model (Appendix I).



(A)

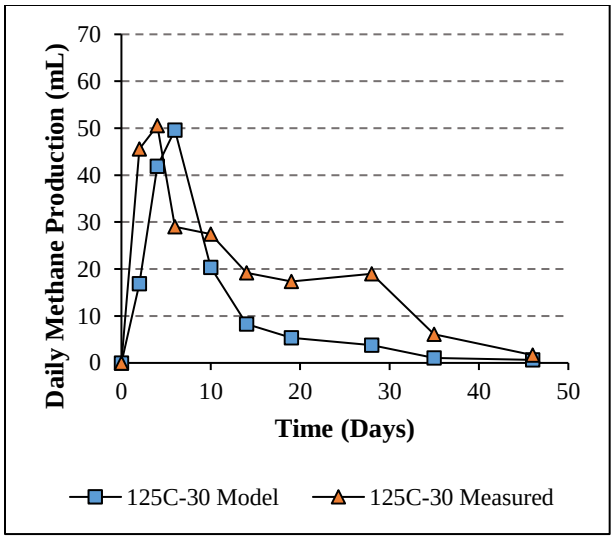


(B)

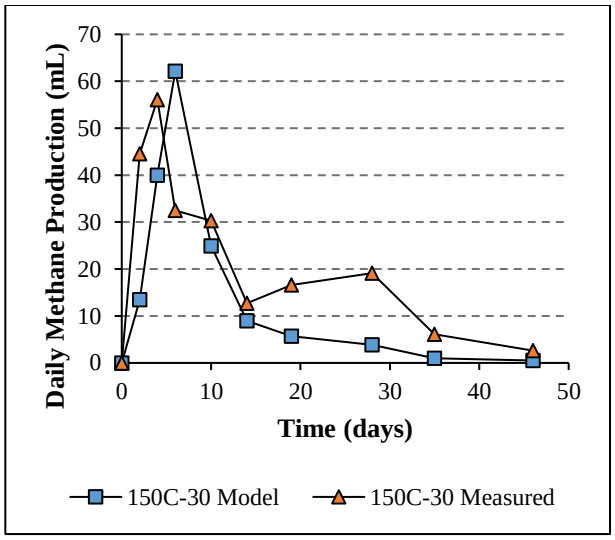


(C)

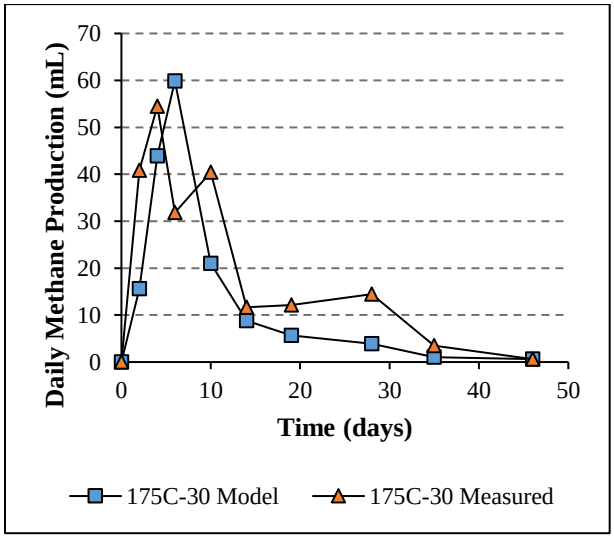
Figure 6.7 Trial 1 Predicted and Measured Cumulative Methane Production for WAS Pretreated at (A) 125°C - 30 Minutes (B) 150°C - 30 Minutes (C) 175°C - 30 Minutes



(A)



(B)



(C)

Figure 6.8 Trial 1 Daily Methane Production for WAS Pretreated at (A) 125°C – 30 Minutes (B) 150°C – 30 Minutes (C) 175°C – 30 Minutes

The predicted daily methane production was calculated as well and compared to the measured values. Figure 6.8 shows the daily methane production for WAS pretreated for 30 minutes. It can be seen from Figure 6.8 that the maximum methane production occurred on day 4 of digestion in the measured data. The model predicted this peak on day 6 of digestion. This suggested that prediction of the methane production in the BioWin® model was delayed compared to the data.

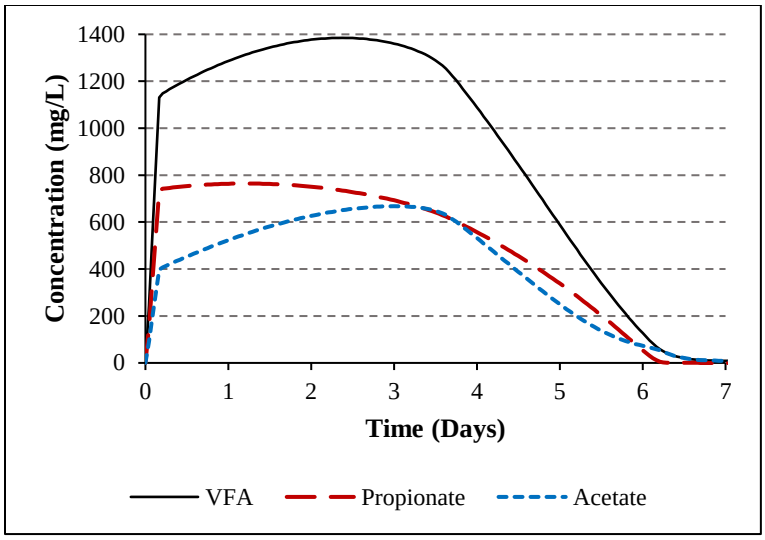


Figure 6.9 VFA Concentration Profile in BMP Tests with Initial Seed Sludge

The VFA concentration in the anaerobic digester was plotted against time for each pretreatment condition. Figure 6.9 shows a typical VFA profile in the anaerobic digester as predicted in BioWin®. Figure 6.9 shows that there was substantial VFA accumulation occurring in the simulated tests. This was largely due to the accumulation of acetate. Propionate was readily taken up by the acetogens present in the digester. Methanogens are directly responsible for converting acetate and hydrogen to methane. The accumulation of acetate suggested that the methanogen concentration in the seed was low. This likely resulted in a high F/M ratio, wherein the substrates could not be readily consumed until there were enough methanogens. The decline of acetate concentration on day 4 of digestion in Figure 6.9 indicated that at this point there were enough methanogens to readily take up acetate and convert them to methane.

These findings suggested that the initial estimation of methanogen concentration in the initial seed was likely erroneous. Hence, the methanogen concentration was increased in increments of 50 mg/L. It was found that it was necessary to increase the methanogen concentration by 300 mg/L to prevent VFA accumulation. Figure 6.10 shows the VFA profile after the additional methanogens were input to the seed sludge. From Figure 6.10, it can be seen that the acetate concentration steadily decreased with time after the addition of methanogens. Therefore, no VFA accumulation was observed. It was determined that an additional 300 mg/L of methanogen prevented any VFA accumulation for all the pretreatment conditions. Trial 2 of anaerobic digestion modeling employed the newly characterized seed sludge.

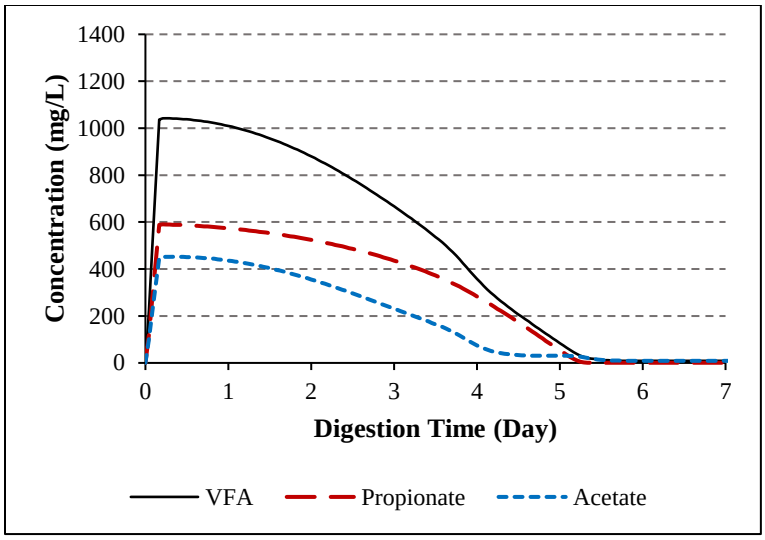


Figure 6.10 VFA Concentration Profile in BMP Tests with Changed Seed Sludge

6.2.2. Trial 2 of BMP Modeling

In Trial 2, the default BioWin® parameters were used and the same PWAS composition as described in Section 5.4 were employed. However, the methanogen concentration in the seed sludge was increased by 300 mg/L for all process flowsheets as demonstrated in the previous section. Figure 6.11 shows the measured daily methane production curve for 125°C-30 PWAS and the predicted methane production from Trial 1 and Trial 2 simulations. From Figure 6.11 it can be seen that Trial 2 modeling was able to predict the daily maximum methane production on day 4 of digestion for 125°C-30 PWAS. All other simulations for the different pretreatment conditions showed similar results. It was concluded that the change in seed sludge resulted in a better fit of the initial methane production.

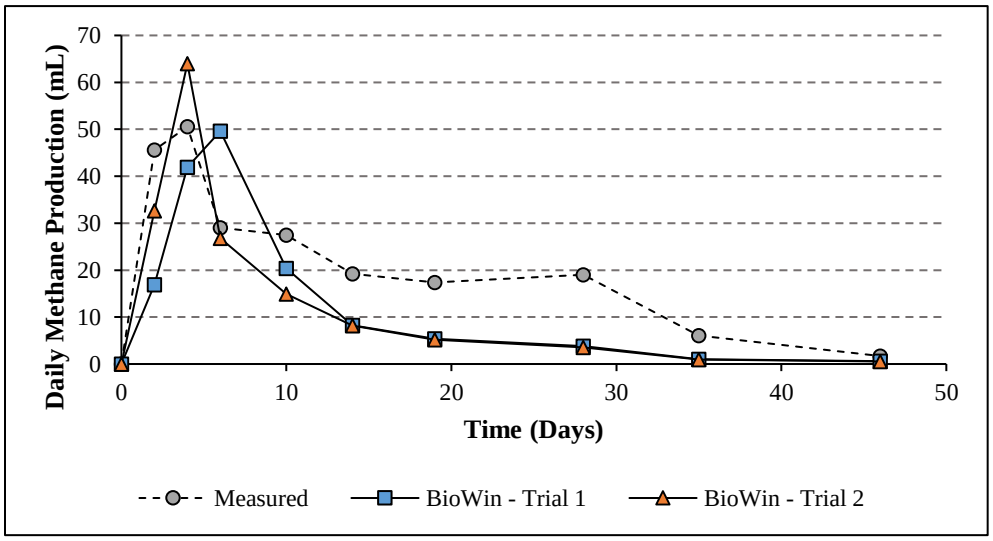


Figure 6.11 Daily Methane Production for 125°C-30 PWAS during Trial 1 and Trial 2

Figure 6.12 shows the cumulative methane production for 125°C-30 PWAS during Trial 2. It can be seen that the ultimate methane yield was still substantially underestimated. All other simulations for the different pretreatment conditions showed similar results (Appendix I).

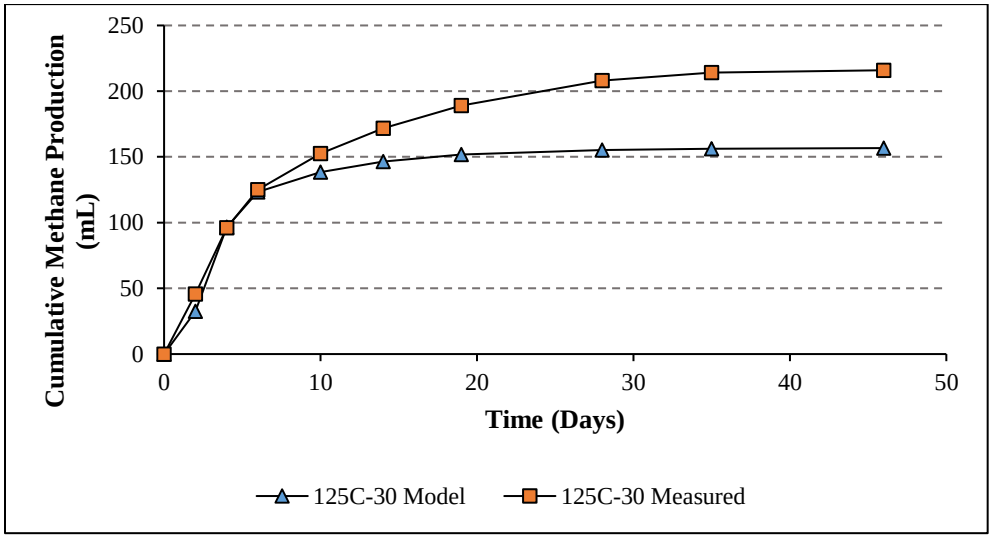


Figure 6.12 Trial 2 Predicted and Measured Cumulative Methane Production for WAS pretreated at 125°C – 30 Minutes

Jones et al. (2007) modeled methane production from a series of BMP tests to evaluate the behaviour of non-biodegradable solids under anaerobic digestion. It was found that the measured volume of biogas production from WAS exceeded the model prediction by 15%. It was suggested that the higher biogas production in the WAS was due to endogenous product (Z_e) decay. In order to verify this, it was assumed that the endogenous products decayed following a first order decay. A value of 0.0075 d^{-1} was found to improve the fit of the model to the biogas data. For the current study, it was deemed likely that the endogenous products decay rate would change with the different pretreatment conditions. In Trial 3, the endogenous products decay rate constant was adjusted until the measured and predicted ultimate methane yields were approximately equal.

6.2.3. Trial 3 of BMP Modeling

Trial 3 of BMP modeling was conducted to improve the model's prediction of the ultimate methane yield in all pretreatment conditions. Two ways of finding the optimal endogenous products decay rate were evaluated. The first method minimized the residual sum of squares between the measured and predicted cumulative methane production curves. However, this method was found to cause the ultimate methane yield to be overestimated in some cases. In the second method, the endogenous products decay rate was fit on the basis of matching the ultimate methane yield. This method ensured that the ultimate methane yield was accurately predicted. The disadvantage of this approach was that the initial methane production tended

to be underestimated. However, it was believed that the ultimate methane yield is a better indicator of the biodegradable COD. Therefore, the second method was chosen to calibrate the endogenous product decay rate.

The model fits were significantly improved by incorporating an endogenous products decay rate. Figure 6.13 shows the model's prediction of the cumulative methane production for WAS pretreated at 125°C for 30 minutes. The ultimate methane yield was predicted accurately and similar improvements in fits were observed for all PWAS (Appendix I).

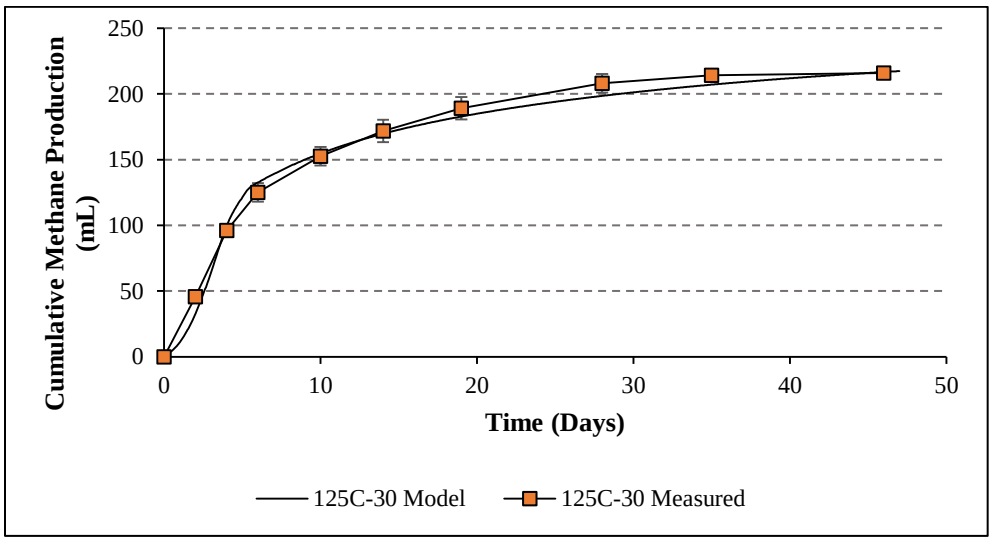


Figure 6.13 Measured and Predicted Cumulative Methane Production for WAS Pretreated at 125°C for 30 Minutes in Trial 3

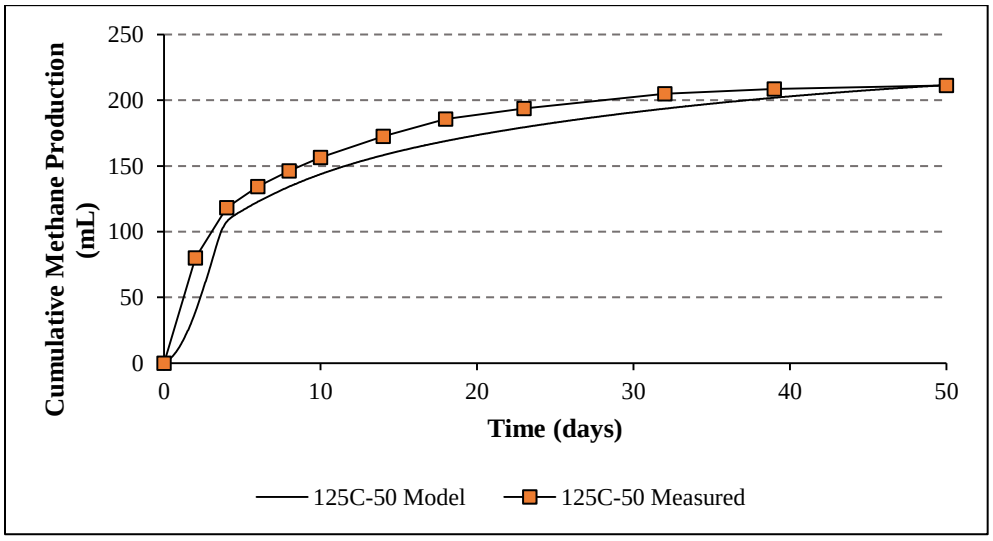


Figure 6.14 Measured and Predicted Cumulative Methane Production for WAS Pretreated at 125°C for 50 Minutes in Trial 3

Figure 6.14 shows the model prediction of methane production of WAS pretreated at 125°C for 50 minutes. For all WAS samples pretreated for 50 minutes, the initial methane production could not be accurately predicted despite the change in seed sludge characteristics (Appendix I). However, predicting the ultimate methane yield was deemed to be more important as it represented the biodegradable fraction of the COD under anaerobic digestion. The initial methane production is a complex process that involves various stages of anaerobic digestion and without other data to support further changes in seed sludge, the lack of the model's ability to match the initial methane production was not considered pivotal.

Table 6.5 Calibrated Endogenous Products Decay Rate for All PWAS

Pretreatment Condition	Endogenous Products Decay Rate (d^{-1})
125°C – 30	0.023
150°C – 30	0.017
175°C – 30	0.013
125°C – 50	0.015
150°C – 50	0.022
175°C – 50	0.019

The calibrated endogenous products decay rates for all pretreatment conditions are shown in Table 6.5. Jones et al. (2007) employed an endogenous products decay rate constant of 0.0075 d^{-1} for untreated WAS and the average endogenous products decay rate presented in Table 6.5 was 0.018 d^{-1}. When Trial 2 was repeated by employing the average endogenous products decay rate of 0.018 d^{-1}, it was found that the model fits did not significantly deteriorate as the difference in ultimate methane yields only ranged from 1.4% to 5.8%. Therefore, HPTH pretreatment increased the endogenous products decay rate constant by 58%, indicating that more non-biodegradable COD was converted to biodegradable COD by HPTH pretreatment.

From Table 6.5 it can be seen that there was no relationship between the endogenous products decay rate and pretreatment temperature and duration. However, as the values of decay rates indicated, this meant that endogenous products became available for biodegradation under anaerobic digestion. The fraction of endogenous products that became biodegradable was calculated by (6.1)

$$f_{Ze,biodegradable} = \frac{Z_{e,initial} - Z_{e,final}}{Z_{e,initial}} \quad (6.1)$$

in which, $Z_{e,initial}$ denoted the endogenous products concentration at the beginning of BMP test and $Z_{e,final}$ was the endogenous products concentration at the end of BMP test. Table 6.6 shows the calculated fraction of endogenous products that became biodegradable for all PWAS. The calculated f_{Ze} values indicated that a substantial fraction of the endogenous decay products converted to biodegradable components (X_{sp}). The

fraction of endogenous decay products that became available as substrate ranged from 29% to 52%. The average fractions of Z_e that became biodegradable was 40% and 46% for WAS pretreated for 30 and 50 minutes respectively. Comparatively, the average fractions of Z_e that became biodegradable was 45%, 45% and 38% for WAS pretreated at 125°C, 150°C and 175°C respectively. It can be concluded from these results that increasing the pretreatment duration tended to increase the amount of Z_e converted to biodegradable substrate. However, the impact of pretreatment temperature on converting Z_e was not consistent.

Table 6.6 Fraction of Endogenous Decay Products made Biodegradable under Anaerobic Digestion

Pretreatment Condition	$f_{Ze,biodegradable}$
125°C – 30 min	0.51
150°C – 30 min	0.39
175°C – 30 min	0.29
125°C – 50 min	0.40
150°C – 50 min	0.52
175°C – 50 min	0.47

Viewed collectively, the results of the anaerobic digestion trials indicated that the previously determined PWAS COD fractionation described in Section 5.4 could be employed under anaerobic digestion conditions. However, the biodegradability of the WAS changed under anaerobic digestion as illustrated in Figure 6.15. A fraction found to be non-biodegradable under aerobic digestion, Z_e, became biodegradable under anaerobic digestion. HPTH pretreatment was able to convert up to approximately 50% of the Z_e to biodegradable substrate (X_{sp}) and it was found that pretreatment duration increased the fraction of converted Z_e whereas the impact of pretreatment duration was inconsistent.

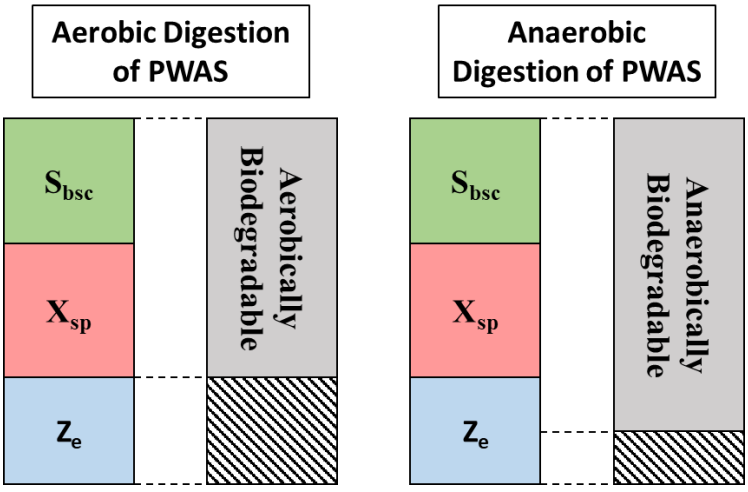


Figure 6.15 Changes in Biodegradability under Different Electron Acceptor Conditions

7. Conclusions

This study sought to characterize the COD of WAS before and after HPTH pretreatment for a wide range of pretreatment conditions and to compare the impacts of pretreatment on aerobic and anaerobic biodegradability. The WAS was fractionated using respirometric data and the BioWin Integrated Model. The same WAS COD fractionation was employed during the anaerobic digestion phase to determine whether the biodegradability of WAS changed under different electron acceptor conditions. The following summarizes the specific conclusions made in this study.

HPTH pretreatment at 125°C, 150°C, and 175°C did not significantly remove/degrade organic matter. This conclusion was based on the findings that TCOD concentrations, TS concentrations and VS/TS ratio before and after pretreatment were unchanged by HPTH pretreatment.

HPTH pretreatment at 125°C, 150°C, and 175°C substantially solubilized organics. The COD, ON and VSS solubilization ranged from 30 – 55%, 23 – 41% and 30 – 89% respectively. Both pretreatment temperature and time had a significant impact on increasing organics solubilization. These findings were consistent with prior research on HPTH pretreatment.

The BR WAS that was generated using synthetic wastewater was found to be composed of 79% active biomass (Z_{bh}) and 18% endogenous decay products (Z_e). There were no storage products generated by pretreatment. This conclusion was based on:

- The calculated COD/VSS ratio was 1.5 ± 0.16 which was close to the typical value of 1.42 for active heterotrophs and endogenous residue.
- OUR responses from offline respirometry of BR WAS showed that the OUR value declined exponentially with time. The lack of any growth suggested that storage products were no present and hence the OUR curve exhibited decay of active biomass and endogenous respiration only.
- The fractions of Z_{bh} and Z_e were estimated using the OUR responses containing BR WAS only. The fractions were verified by modeling the BR-AD system on BioWin®.

HPTH pretreatment at 125°C, 150°C, and 175°C had no impact on the extent to which WAS was aerobically biodegraded. The aerobic biodegradability was assessed by calculating $\sum OU_s$/TCOD ratios for BR WAS and all PWAS using offline respirometry and online respirometry data. The differences in the ratios between BR WAS and PWAS were not significant which indicated that the aerobic biodegradability was virtually unchanged by HPTH pretreatment.

HPTH pretreatment at 125°C, 150°C and 175°C increased the rate at which WAS could be aerobically biodegraded. The rate of aerobic biodegradability was assessed by calculating the concentration of readily

biodegradable COD (S_{bsc}). All pretreatment conditions showed that the active biomass in BR WAS was partially converted to S_{bsc}. The range of S_{bsc} fraction was 16.5 – 34.6% in this study. Furthermore, the OUR response on inoculated PWAS peaked earlier and higher than the OUR response on inoculated BR WAS, which was characteristic of growth on S_{bsc}.

HPTH pretreatment at 125°C, 150°C and 175°C increased the extent to which WAS could be anaerobically biodegraded. This conclusion was based on the increase in the maximum methane production observed which ranged from 17 – 49%.

HPTH pretreatment at 125°C, 150°C and 175°C increased the rate of anaerobic biodegradability. However, the pretreatment duration was found to be more important in changing the rate of anaerobic biodegradability. The increase in maximum methane production rate by HPTH pretreatment ranged from 3 – 11% for WAS pretreated for 30 minutes and 38 – 100% for WAS pretreated for 50 minutes for the three temperatures employed in this study.

HPTH pretreatment at 125°C, 150°C and 175°C converted the biodegradable fraction (Z_{bh}) of BR WAS into varying fractions of S_{bsc} and X_{sp}. The fractions were determined by modeling the offline respirometry tests using BioWin. The fractions of S_{bsc} and X_{sp} were altered until the predicted and measured OUR values matched as indicated by minimizing the sum of squared differences. The fraction of S_{bsc} varied from 16.5 – 34.6% and the fraction of X_{sp} varied from 45.8 – 63.6%. It was concluded that the degree of COD solubilization and the fraction of S_{bsc} had no correlation. A separate PWAS COD fractionation based on OUR analysis indicated that there may be another fraction which was colloidal that may be readily or slowly biodegradable COD.

It was determined that both pretreatment temperature and duration were important in solubilizing organic matter in the WAS. However, the impact of pretreatment temperature and duration on the WAS COD fractions were inconclusive. The increase in organics solubilization did not necessarily correspond to higher fractions of S_{bsc} in the PWAS.

The results of BioWin modeling indicated that the aerobic and anaerobic biodegradability of PWAS was different. The PWAS COD fractionation obtained through offline respirometry test modeling had a consistent fraction (18.4% of TCOD) of endogenous decay products. The same PWAS COD fractionation was employed for BMP test modeling and it was concluded that up to 50% of the endogenous decay products (Z_e) were converted to biodegradable substrate (X_{sp}). This finding was based on the endogenous products decay rate that was employed in BioWin® to match the predicted and measured ultimate methane yields.

8. Recommendations

Using methods outlined by Staples-Burger (2012) and Kianmehr (2010), the current study was successful in characterizing the impacts of HPTH pretreatment on a simplified WAS and comparing the biodegradability of the pretreated WAS under different electron acceptor conditions. It is recommended that future studies look into the following:

- Development of a COD based stoichiometric pretreatment model for the range of HPTH pretreatment conditions employed in this study. There was not enough data to fully develop a pretreatment model. An extensive characterization of the WAS before and after pretreatment will help in developing this pretreatment model which can be incorporated into wastewater simulators such as BioWin®
- Detailed investigation into the impacts of other HPTH pretreatment parameters on WAS. The influence of decompression and pre-heating time on WAS solubilization and subsequent impacts on anaerobic digestion are still not clear. If these less-studied parameters have a significant impact on WAS characteristics and improve anaerobic digestion, it will be beneficial to be able to incorporate them into a pretreatment model as previously described.
- Investigation of the kinetics of the different COD species measured. It was shown in the current study that the OUR curves started to deviate from typical shapes as the pretreatment dose (temperature-time) increased. Furthermore, in the OUR analysis, there were components that were believed to be colloidal biodegradable COD (X_{sc}). In the current study, they were assumed to behave like X_{sp}, but further study is warranted to verify this assumption. The kinetic rates of the hydrolysis process could be measured on filtered and flocculated, filtered and whole samples to compare the rates by truly soluble COD, colloidal COD, and particulate COD separately. The rates of hydrolysis derived from these tests could be used to develop or modify existing models to better predict the behaviour of pretreated substrates under aerobic or anaerobic digestion.
- Investigation of HPTH pretreatment impacts on authentic WAS generated from raw municipal wastewater. Many of the literature reviewed used authentic WAS to characterize the impacts of HPTH pretreatment on WAS solubilization. Developing pretreatment models using authentic WAS data will be of practical use as the full-scale systems currently employed pretreat real sludge derived from WWTP. This can be further extended to include studies investigating the impacts of HPTH pretreatment on other biomass fractions other than Z_{bh}, such as autotrophic bacteria which are responsible for nitrification. These other biomass are present in significant concentrations in real activated sludge systems. Additional research is required to determine if HPTH pretreatment will impact these other biomass to a similar extent.

References

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Appendix A Physical and Biochemical Data

Table A.1 COD of WAS Before and After Pretreatment at 125°C – 10 Minutes

Process Stream	COD (mg/L)		
	TCOD	SCOD	PCOD
BR WAS	8330	95	8235
	8230	90	8140
	8193	95	8098
	8380	90	8290
PWAS (125°C – 10 min)	7432	2694	4739
	7432	2656	4776
	7557	2569	4988
	7445	2419	5025

Table A.2 COD of WAS Before and After Pretreatment at 125°C – 30 Minutes

Process Stream	COD (mg/L)		
	TCOD	SCOD	PCOD
BR WAS	9826	112	9714
	9577	82	9495
	9689	112	9577
	9727	82	9644
PWAS (125°C – 30 min)	8380	3816	4564
	8280	3853	4427
	8380	3616	4764
	8455	3566	4888

Table A.3 COD of WAS Before and After Pretreatment at 125°C – 50 Minutes

Process Stream	COD (mg/L)		
	TCOD	SCOD	PCOD
BR WAS	10575	67	10507
	10126	80	10046
	10176	67	10108
	9839	80	9759
PWAS (125°C – 50 min)	8929	3479	5449
	8779	3928	4851
	8717	3566	5150
	8866	3691	5175

Table A.4 COD of WAS Before and After Pretreatment at 150°C – 10 Minutes

Process Stream	COD (mg/L)		
	TCOD	SCOD	PCOD
BR WAS	9328	85	9243
	8330	87	8243
	8031	85	7946
	8330	87	8243
PWAS (150°C – 10 min)	7881	3367	4514
	8330	3167	5163
	7208	3192	4015
	7183	3267	3916

Table A.5 COD of WAS Before and After Pretreatment at 150°C – 30 Minutes

Process Stream	COD (mg/L)		
	TCOD	SCOD	PCOD
BR WAS	7731	62	7669
	8230	80	8150
PWAS (150°C – 30 min)	7282	3142	4140
	7233	3217	4015

Table A.6 COD of WAS Before and After Pretreatment at 150°C – 50 Minutes

Process Stream	COD (mg/L)		
	TCOD	SCOD	PCOD
BR WAS	9427	100	9328
	8978	67	8911
	9577	82	9495
	9203	72	9131
PWAS (150°C – 50 min)	8230	4589	3641
	8180	4514	3666
	8529	4277	4252
	8754	4177	4576

Table A.7 COD of WAS Before and After Pretreatment at 175°C – 10 Minutes

Process Stream	COD (mg/L)		
	TCOD	SCOD	PCOD
BR WAS	9128	95	9033
	9727	100	9627
	9614	82	9532
	9577	70	9507
PWAS (175°C – 10 min)	9477	4527	4951
	10575	4564	6011
	9390	4315	5075
	11597	4389	7208

Table A.8 COD of WAS Before and After Pretreatment at 175°C – 30 Minutes

Process Stream	COD (mg/L)		
	TCOD	SCOD	PCOD
BR WAS	10325	90	10235
	10076	92	9983
	10213	92	10121
	10101	92	10008
PWAS (175°C – 10 min)	10176	5200	4976
	9278	5424	3853
	9577	5063	4514
	9353	5088	4265

Table A.9 COD of WAS Before and After Pretreatment at 175°C – 50 Minutes

Process Stream	COD (mg/L)		
	TCOD	SCOD	PCOD
BR WAS	8779	92	8687
	9278	82	9195
	9053	87	8966
	8604	100	8505
PWAS (175°C – 10 min)	7332	5050	2282
	7532	4976	2556
	7407	4963	2444
	7407	4963	2444

Table A.10 Ammonia Concentration of all PWAS

PT Temp. (°C)	PT Duration (min)	x Dilution	Raw Ammonia Data		Average	Conc. x Dilution (mgN/L)
			Meas 1	Meas. 2		
125	10	10	12.741	11.419	12.080	121
	30	10	10.584	10.539	10.562	106
	50	10	11.861	12.051	11.956	120
150	10	10	13.620	13.838	13.729	137
	30	10	13.912	14.000	13.956	140
	50	10	11.995	12.145	12.070	121
175	10	10	12.763	13.020	12.892	129
	30	10	10.443	10.485	10.464	105
	50	10	11.402	11.525	11.464	115

Table A.11 Total Kjedahl Nitrogen Concentration of all PWAS

PT Temp. (°C)	PT Duration (min)	x Dilution	Raw TKN Data		Average	Avg. Blank Values	Raw TKN - Blank	Corrected TKN (mgN/)
			Meas 1	Meas. 2				
125	10	75	4.466	3.683	4.075	-0.789	4.684	365
	30	75	3.199	3.382	3.291	-0.789	4.080	306
	50	75	4.430	4.370	4.400	-0.789	5.189	389
150	10	75	4.114	4.172	4.143	-0.769	4.911	340
	30	75	3.753	3.885	3.819	-0.769	4.587	315
	50	75	4.816	4.997	4.907	-0.769	5.675	426
175	10	75	4.423	4.390	4.407	-0.767	5.173	388
	30	75	3.938	4.024	3.981	-0.767	4.748	356
	50	75	3.723	3.908	3.816	-0.767	4.582	344

Table A.12 Soluble TKN Concentration of all PWAS

PT Temp. (°C)	PT Duration (min)	x Dilution	Raw sTKN Data		Average	Avg. Blank Values	Raw sTKN - Blank	Corrected sTKN (mgN/L)
			Meas 1	Meas. 2				
125	10	25	8.240	6.989	7.615	-0.137	7.752	194
	30	25	6.886	6.889	6.888	-0.137	7.025	176
	50	25	8.873	9.075	8.974	-0.137	9.111	228
150	10	25	13.787	13.893	13.840	-0.121	13.961	349
	30	25	14.484	14.434	14.459	-0.121	14.580	365
	50	25	11.225	11.252	11.239	-0.121	11.360	284
175	10	25	11.794	11.972	11.883	-0.130	12.013	300
	30	25	12.728	12.774	12.751	-0.130	12.881	322
	50	25	12.545	12.673	12.609	-0.130	12.739	318

Table A.13 Organic Nitrogen and Total Nitrogen Concentration of all PWAS

PT Temp. (°C)	PT Duration (min)	ON (mgN/L)	sON (mgN/L)	pON (mgN/L)	TN (mgN/L)
125	10	244	73	171	486
	30	200	70	130	412
	50	270	108	161	509
150	10	542	212	330	477
	30	491	225	226	455
	50	305	163	142	546
175	10	259	171	88	517
	30	251	217	34	461
	50	229	204	25	458

Table A.14 Solids Data for BR WAS and 125°C-10 PWAS

Sample	Vol	Weight (g)	Dry (g)	Burned (g)	TS (mg/L)	TSS (mg/L)	VS (mg/L)	VSS (mg/L)	ISS (mg/L)
TS Raw	10	1.2811	1.3785	1.3119	9740	-	6660	-	-
	10	1.2946	1.3857	1.3230	9110	-	6270	-	-
TS PT	10	1.2937	1.3820	1.3211	8830	-	6090	-	-
	10	1.3250	1.4139	1.3529	8890	-	6100	-	-
TSS	5	1.4184	1.4562	1.4244	-	7560	-	6360	1200
Raw	5	1.4176	1.4561	1.4235	-	7700	-	6520	1180
TSS PT	5	1.4097	1.4365	1.4149	-	5360	-	4320	1040
	5	1.4008	1.4275	1.4060	-	5340	-	4300	1040

Table A.15 Solids Data for BR WAS and 125°C-30 PWAS

Sample	Vol	Weight (g)	Dry (g)	Burned (g)	TS (mg/L)	TSS (mg/L)	VS (mg/L)	VSS (mg/L)	ISS (mg/L)
TS Raw	10	1.2844	1.3837	1.3319	9930	-	5180	-	-
	10	1.3302	1.4300	1.3787	9980	-	5130	-	-
TS PT	10	1.2953	1.3938	1.3290	9850	-	6480	-	-
	10	1.3278	1.4258	1.3675	9800	-	5830	-	-
TSS	5	1.4165	1.4588	1.4319	-	8460	-	5380	3080
Raw	5	1.4305	1.4733	1.4461	-	8560	-	5440	3120
TSS PT	5	1.4148	1.4412	1.4270	-	5280	-	2840	2440
	5	1.3961	1.4225	1.4083	-	5280	-	2480	2440

Table A.16 Solids Data for BR WAS and 125°C-50 PWAS

Sample	Vol	Weight (g)	Dry (g)	Burned (g)	TS (mg/L)	TSS (mg/L)	VS (mg/L)	VSS (mg/L)	ISS (mg/L)
TS Raw	10	1.2927	1.3952	1.3359	10250	-	5930	-	-
	10	1.2891	1.3919	1.3327	10280	-	5920	-	-
TS PT	10	1.2910	1.3937	1.3229	10270	-	7080	-	-
	10	1.3144	1.4162	1.3501	10180	-	6610	-	-
TSS	5	1.4034	1.4476	1.4175	-	8840	-	6020	2820
Raw	5	1.4022	1.4467	1.4148	-	8900	-	6380	2520
TSS PT	5	1.3995	1.4281	1.4111	-	5720	-	3400	2320
	5	1.4110	1.4390	1.4217	-	5600	-	3460	2140

Table A.17 Solids Data for BR WAS and 150°C-10 PWAS

Sample	Vol	Weight (g)	Dry (g)	Burned (g)	TS (mg/L)	TSS (mg/L)	VS (mg/L)	VSS (mg/L)	ISS (mg/L)
TS Raw	10	1.2998	1.3886	1.3277	8880	-	6090	-	-
	10	1.3112	1.3989	1.3383	8770	-	6060	-	-
TS PT	10	1.2879	1.3757	1.3153	8780	-	6040	-	-
	10	1.2972	1.3829	1.3248	8570	-	5810	-	-
TSS	5	1.4044	1.4413	1.4139	-	7380	-	5480	1900
Raw	5	1.4181	1.4547	1.4284	-	7320	-	5260	2060
TSS PT	5	1.4433	1.4661	1.4514	-	4560	-	2940	1620
	5	1.4291	1.4531	1.4377	-	4800	-	3080	1720

Table A.18 Solids Data for BR WAS and 150°C-30 PWAS

Sample	Vol	Weight (g)	Dry (g)	Burned (g)	TS (mg/L)	TSS (mg/L)	VS (mg/L)	VSS (mg/L)	ISS (mg/L)
TS Raw	10	1.3334	1.429	1.3684	9560	-	6060	-	-
	10	1.3275	1.4241	1.3677	9660	-	5640	-	-
TS PT	10	1.3325	1.4274	1.3631	9490	-	6430	-	-
	10	1.3227	1.4161	1.3542	9340	-	6190	-	-
TSS	5	1.4165	1.4558	1.4281	-	7860	-	5540	2320
Raw	5	1.4308	1.4695	1.4411	-	7740	-	5680	2060
TSS PT	5	1.4279	1.4525	1.4380	-	4920	-	2900	2020
	5	1.4200	1.4445	1.4301	-	4900	-	2880	2020

Table A.19 Solids Data for BR WAS and 150°C-50 PWAS

Sample	Vol	Weight (g)	Dry (g)	Burned (g)	TS (mg/L)	TSS (mg/L)	VS (mg/L)	VSS (mg/L)	ISS (mg/L)
TS Raw	10	1.3145	1.4117	1.3433	9720	-	6840	-	-
	10	1.3346	1.4319	1.3624	9730	-	6950	-	-
TS PT	10	1.3082	1.4079	1.3380	9970	-	6990	-	-
	10	1.3303	1.4312	1.3603	10090	-	7090	-	-
TSS	5	1.4340	1.4739	1.4400	-	7980	-	6780	1200
Raw	5	1.4333	1.4769	1.4406	-	8720	-	7260	1460
TSS PT	5	1.4206	1.4443	1.4263	-	4740	-	3600	1140
	5	1.4329	1.4589	1.4394	-	5200	-	3900	1300

Table A.19 Solids Data for BR WAS and 175°C-10 PWAS

Sample	Vol	Weight (g)	Dry (g)	Burned (g)	TS (mg/L)	TSS (mg/L)	VS (mg/L)	VSS (mg/L)	ISS (mg/L)
TS Raw	10	1.3245	1.4358	1.3563	11130	-	7950	-	-
	10	1.3150	1.4254	1.3480	10950	-	7740	-	-
TS PT	10	1.3165	1.4068	1.3451	9030	-	6170	-	-
	10	1.3216	1.4338	1.3571	11220	-	7670	-	-
TSS	5	1.4351	1.4788	1.4480	-	8740	-	6160	2580
Raw	5	1.4250	1.4698	1.4389	-	8960	-	6180	2780
TSS PT	5	1.4340	1.4515	1.4394	-	3500	-	2420	1080
	5	1.4266	1.4470	1.4333	-	4080	-	2740	1340

Table A.19 Solids Data for BR WAS and 175°C-30 PWAS

Sample	Vol	Weight (g)	Dry (g)	Burned (g)	TS (mg/L)	TSS (mg/L)	VS (mg/L)	VSS (mg/L)	ISS (mg/L)
TS Raw	10	1.3087	1.4183	1.3382	10960	-	8010	-	-
	10	1.3095	1.4207	1.3394	11120	-	8130	-	-
TS PT	10	1.3063	1.4131	1.3399	10680	-	7320	-	-
	10	1.3077	1.4107	1.3393	10300	-	7140	-	-
TSS	5	1.4198	1.4668	1.4307	-	9400	-	7220	2180
Raw	5	1.4218	1.4695	1.4335	-	9540	-	7200	2340
TSS PT	5	1.4294	1.4500	1.4353	-	4120	-	2940	1180
	5	1.4118	1.4293	1.4169	-	3500	-	2480	1020

Table A.20 Solids Data for BR WAS and 175°C-50 PWAS

Sample	Vol	Weight (g)	Dry (g)	Burned (g)	TS (mg/L)	TSS (mg/L)	VS (mg/L)	VSS (mg/L)	ISS (mg/L)
TS Raw	10	1.3061	1.3988	1.3336	9270	-	6520	-	-
	10	1.3290	1.4218	1.3558	9280	-	6600	-	-
TS PT	10	1.3119	1.4343	1.3535	12240	-	8080	-	-
	10	1.3193	1.4544	1.3704	13510	-	8400	-	-
TSS	5	1.4323	1.4724	1.4416	-	8020	-	6160	1860
Raw	5	1.4229	1.4624	1.4328	-	7900	-	5920	1980
TSS PT	5	1.4332	1.4768	1.4479	-	8720	-	5780	2940
	5	1.4236	1.4490	1.4316	-	5080	-	3480	1600

Appendix B Online Respirometry Data

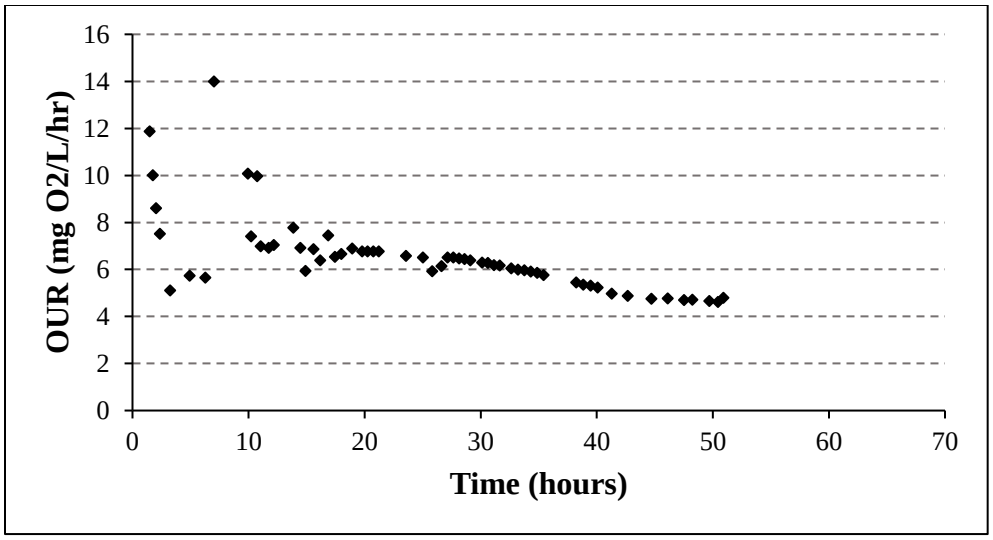

Figure B.1 Online Respirometry Data for BR WAS

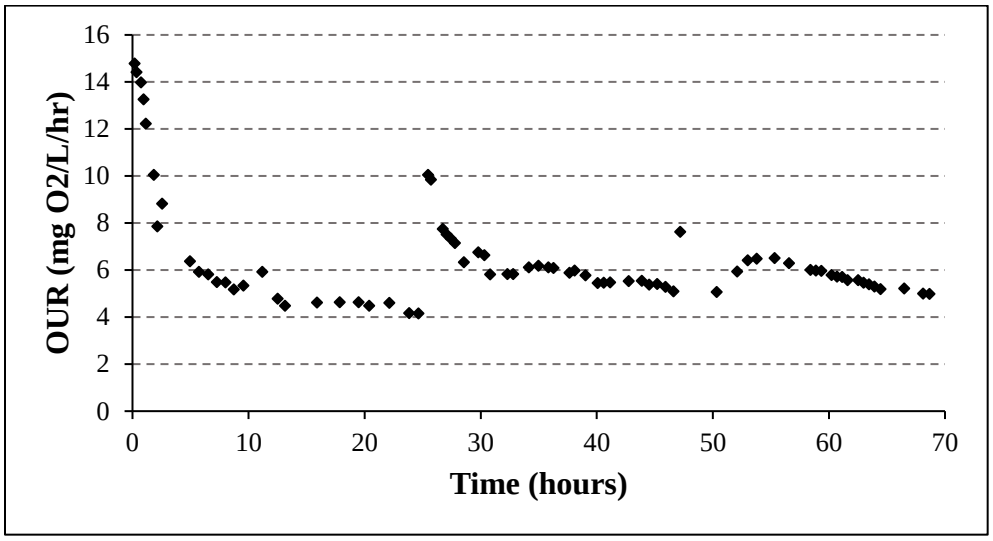

Figure B.2 Online Respirometry Data for 125°C-10 Minute PWAS

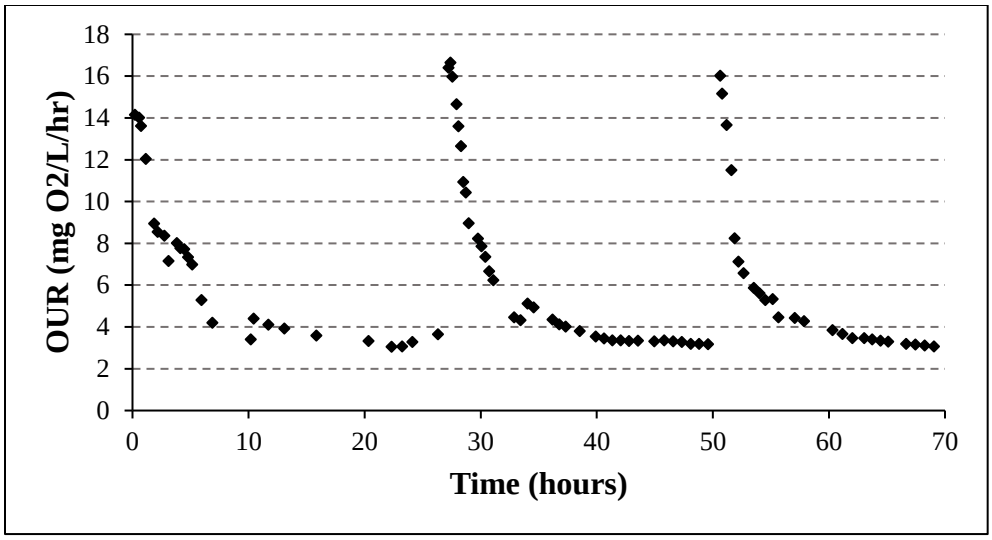

Figure B.3 Online Respirometry Data for 125°C-30 Minute PWAS

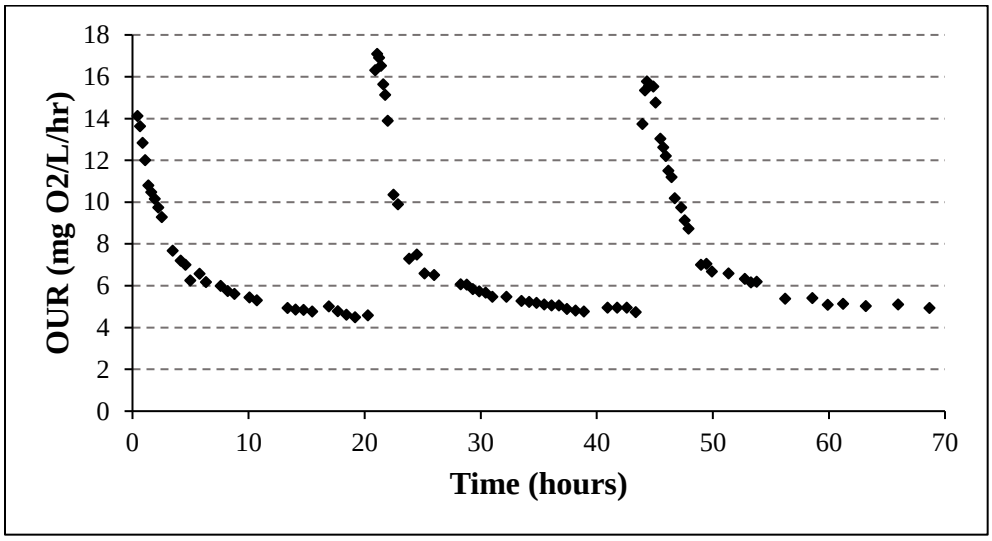

Figure B.4 Online Respirometry Data for 125°C-50 Minute PWAS

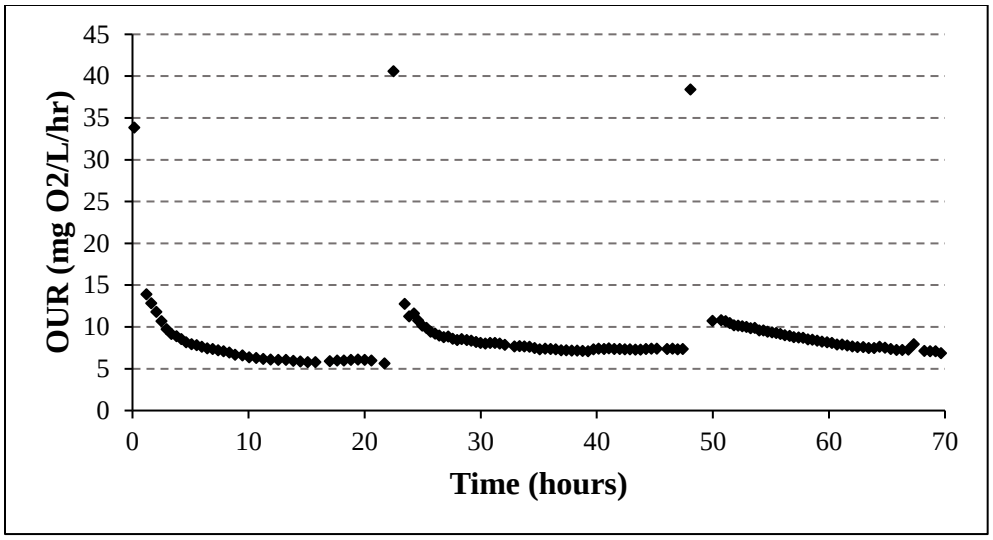

Figure B.5 Online Respirometry Data for 150°C-10 Minute PWAS

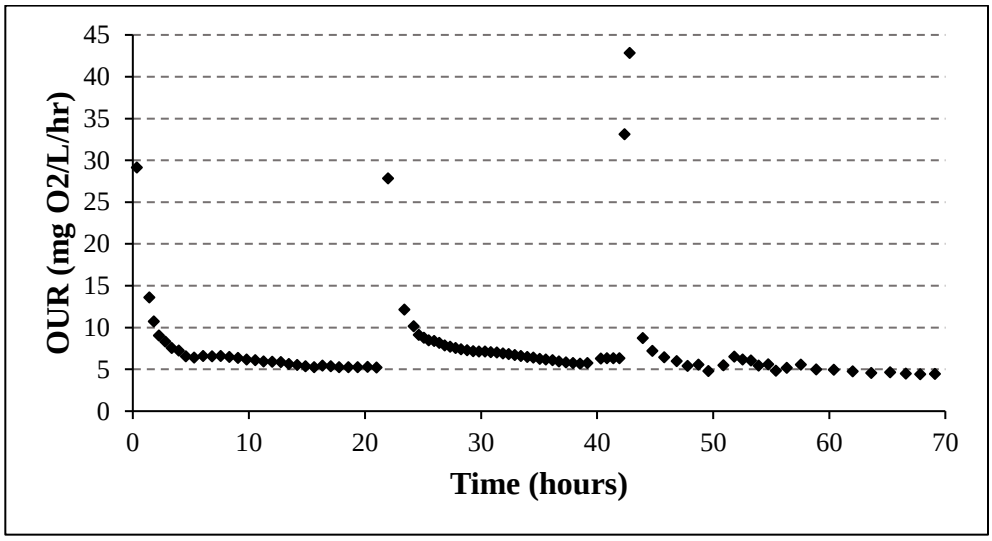

Figure B.6 Online Respirometry Data for 150°C-30 Minute PWAS

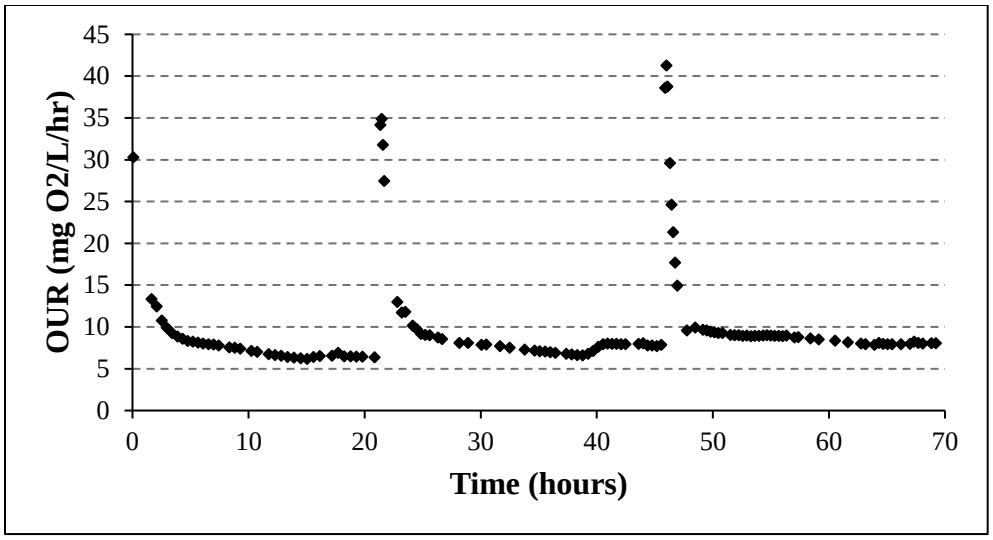

Figure B.7 Online Respirometry Data for 150°C-50 Minute PWAS

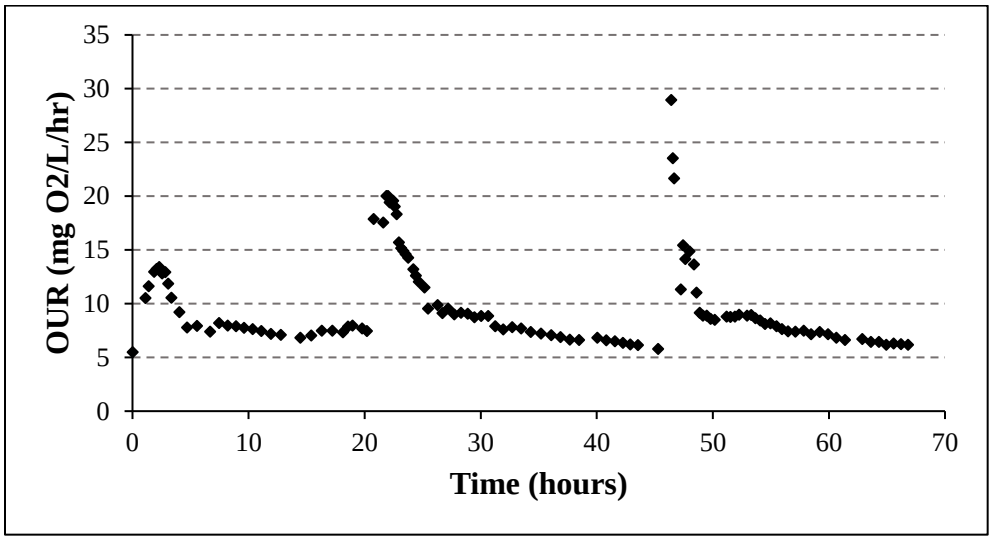

Figure B.8 Online Respirometry Data for 175°C-10 Minute PWAS

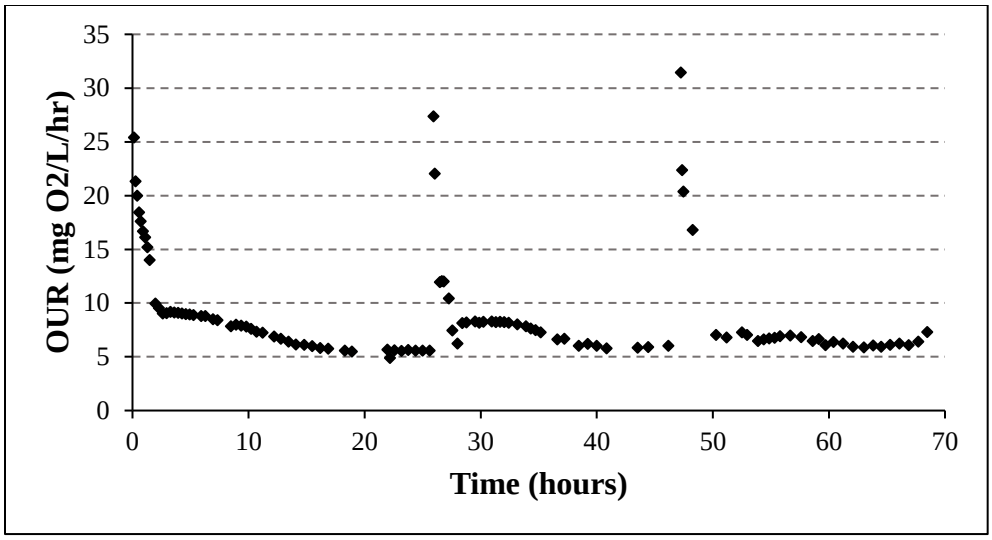

Figure B.9 Online Respirometry Data for 175°C-30 Minute PWAS

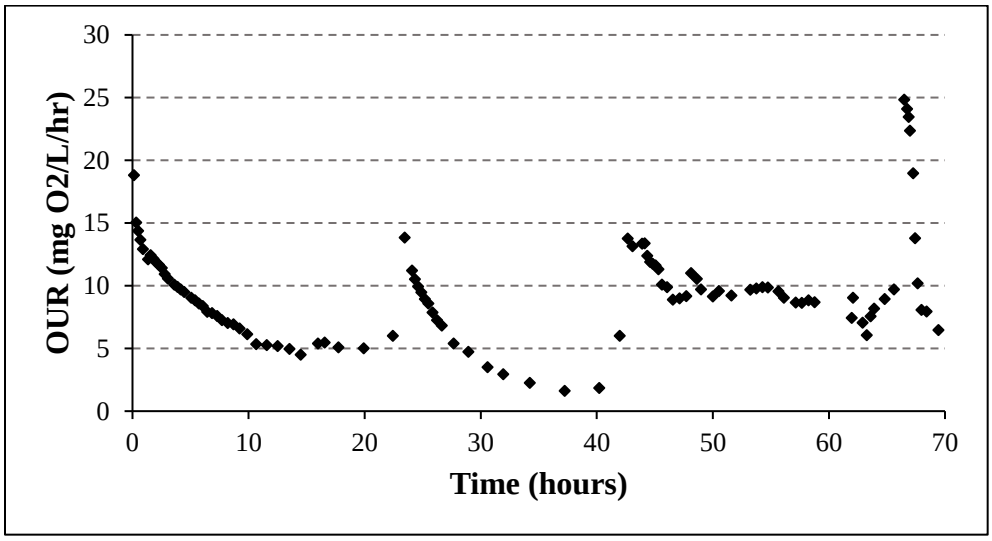

Figure B.10 Online Respirometry Data for 175°C-50 Minute PWAS

Appendix C Offline Respirometry Data

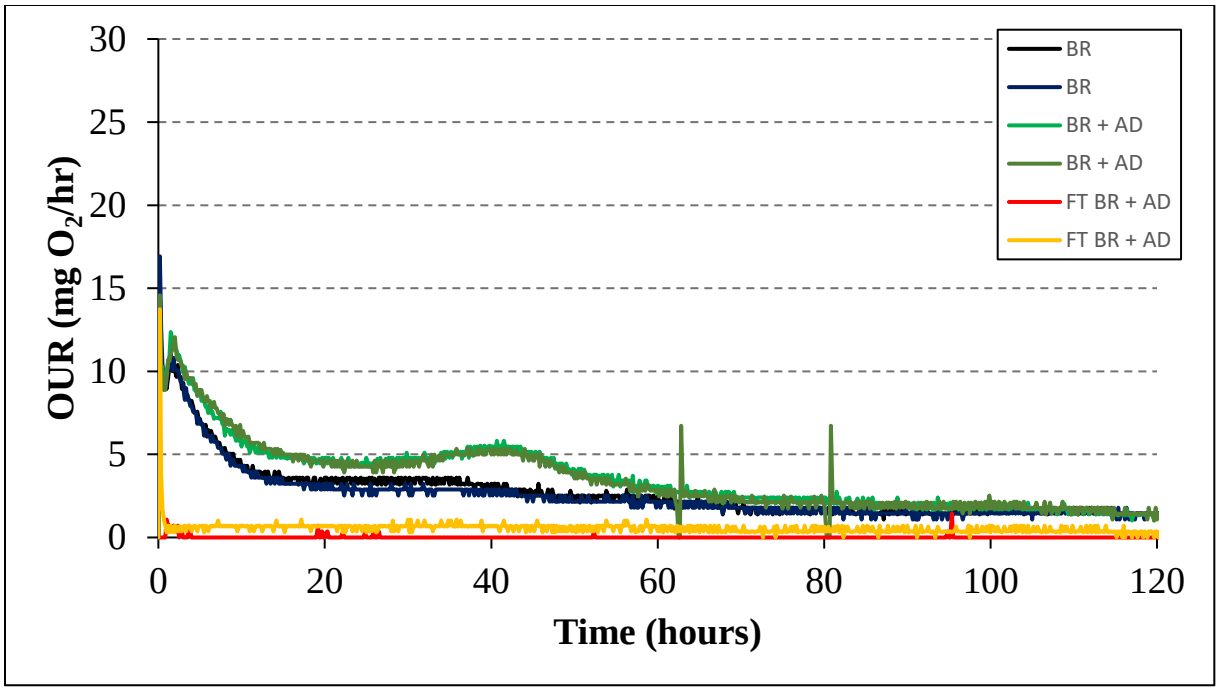

Figure B.1 Offline Respirometry Data for BR WAS

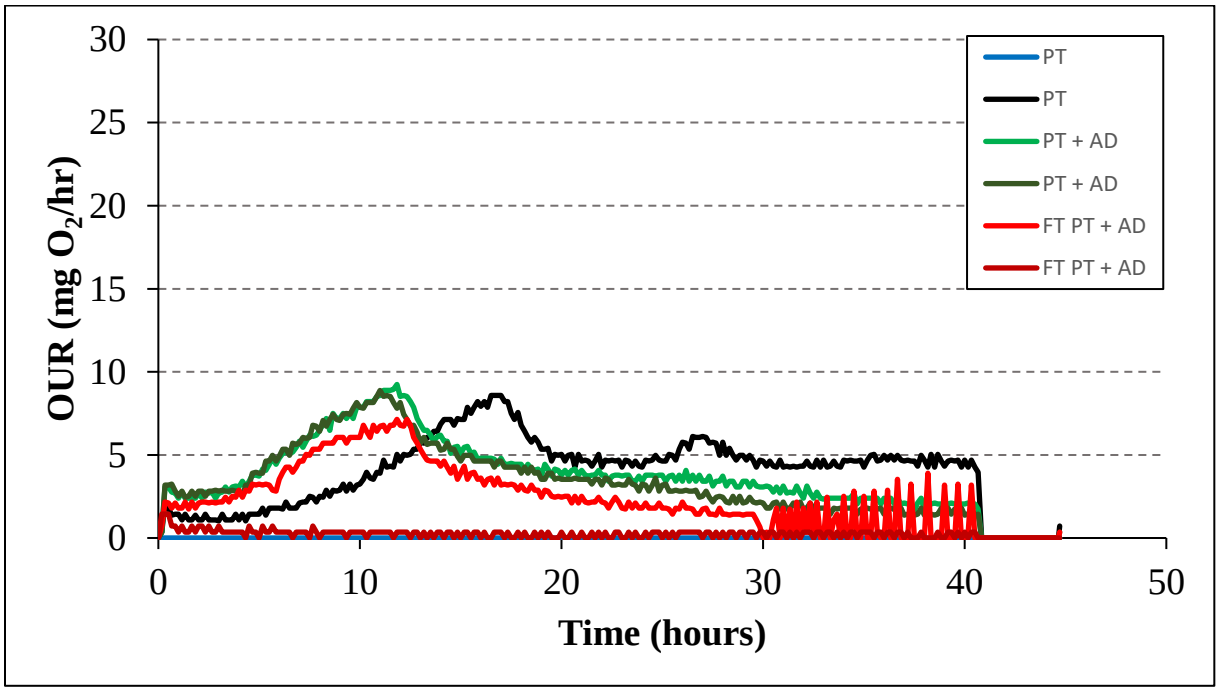

Figure B.2 OUR Curve based on Offline Respirometry Data for 125°C-10 Minute PWAS

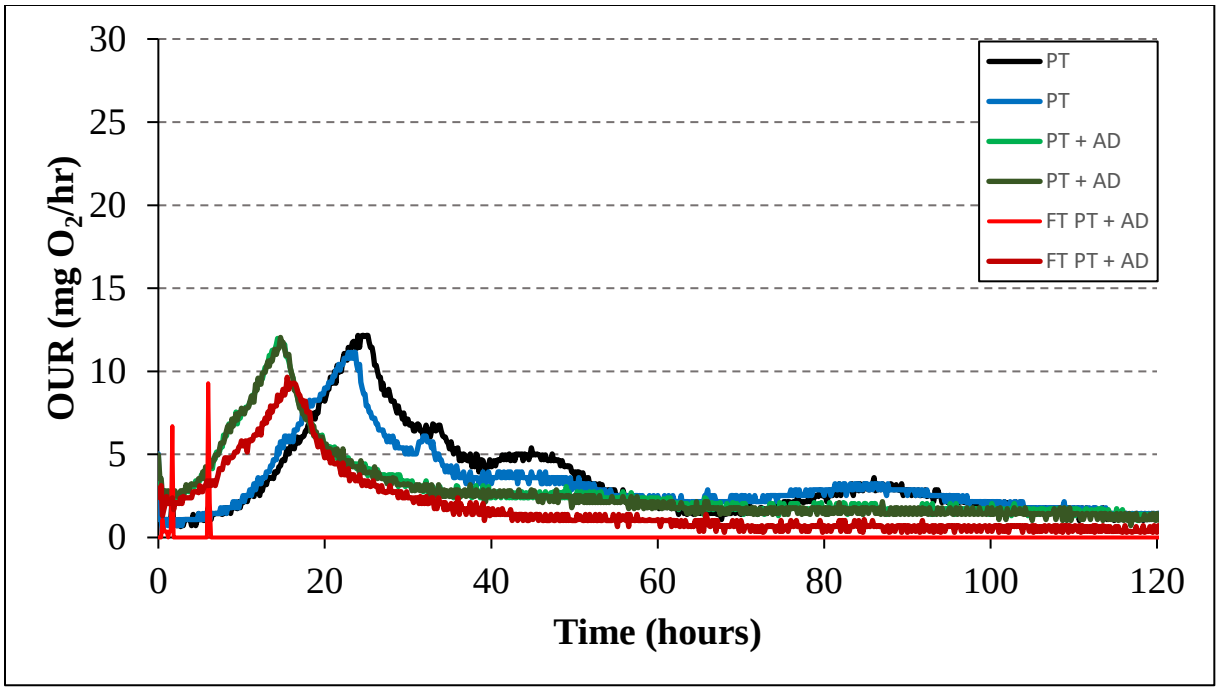

Figure B.3 OUR Curve based on Offline Respirometry Data for 125°C-30 Minute PWAS

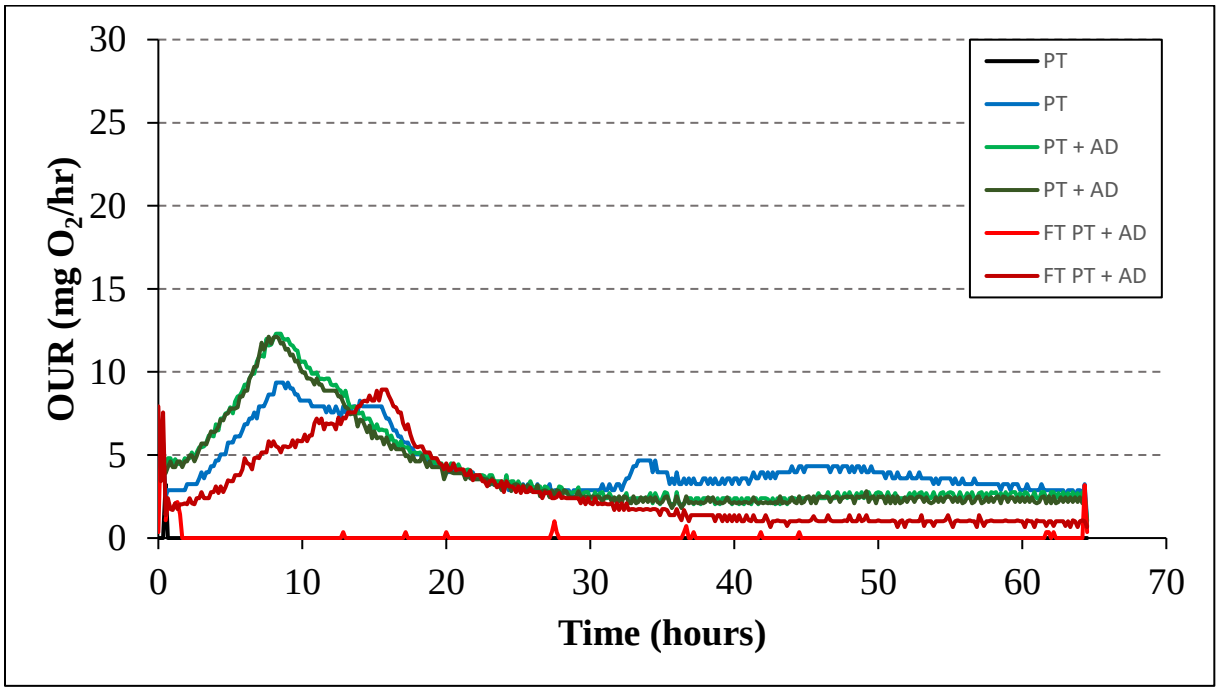

Figure B.4 OUR Curve based on Offline Respirometry Data for 125°C-50 Minute PWAS

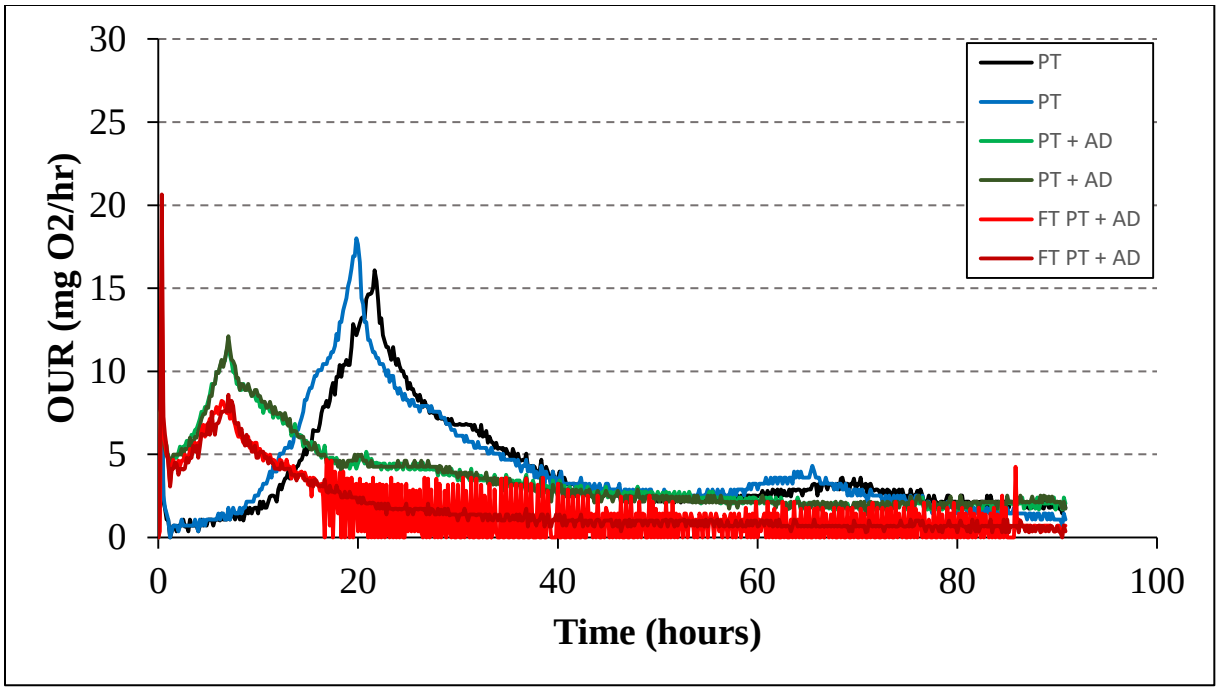

Figure B.5 OUR Curve based on Offline Respirometry Data for 150°C-10 Minute PWAS

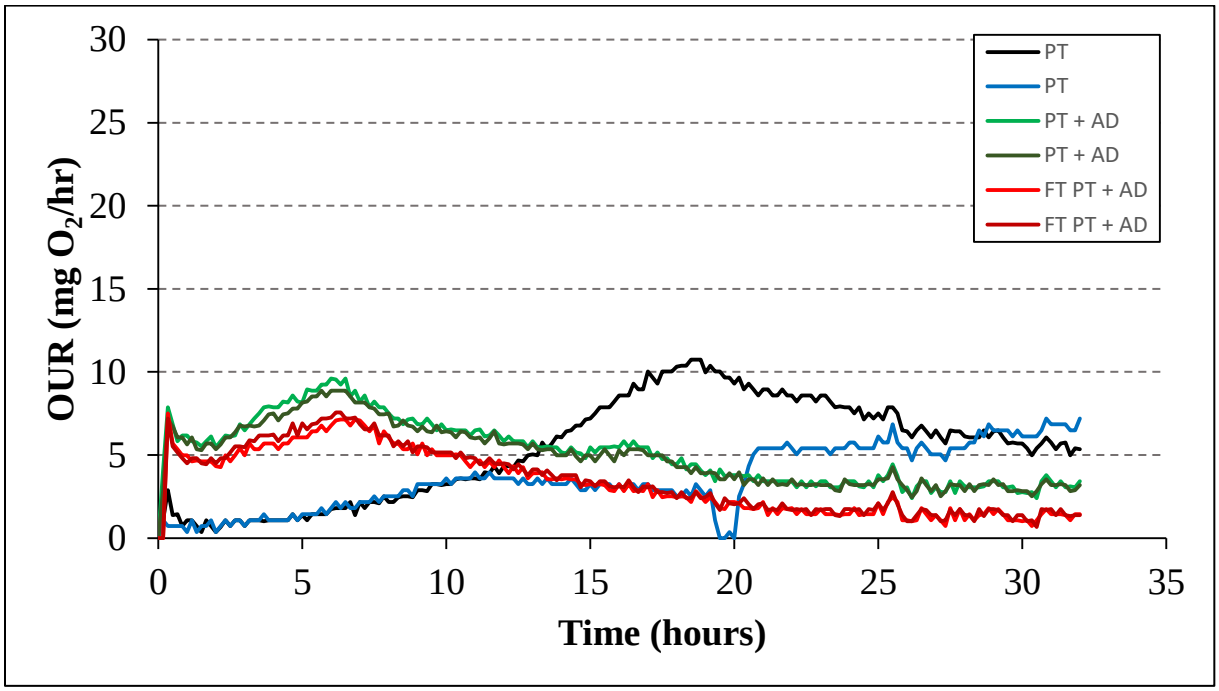

Figure B.6 OUR Curve based on Offline Respirometry Data for 150°C-30 Minute PWAS

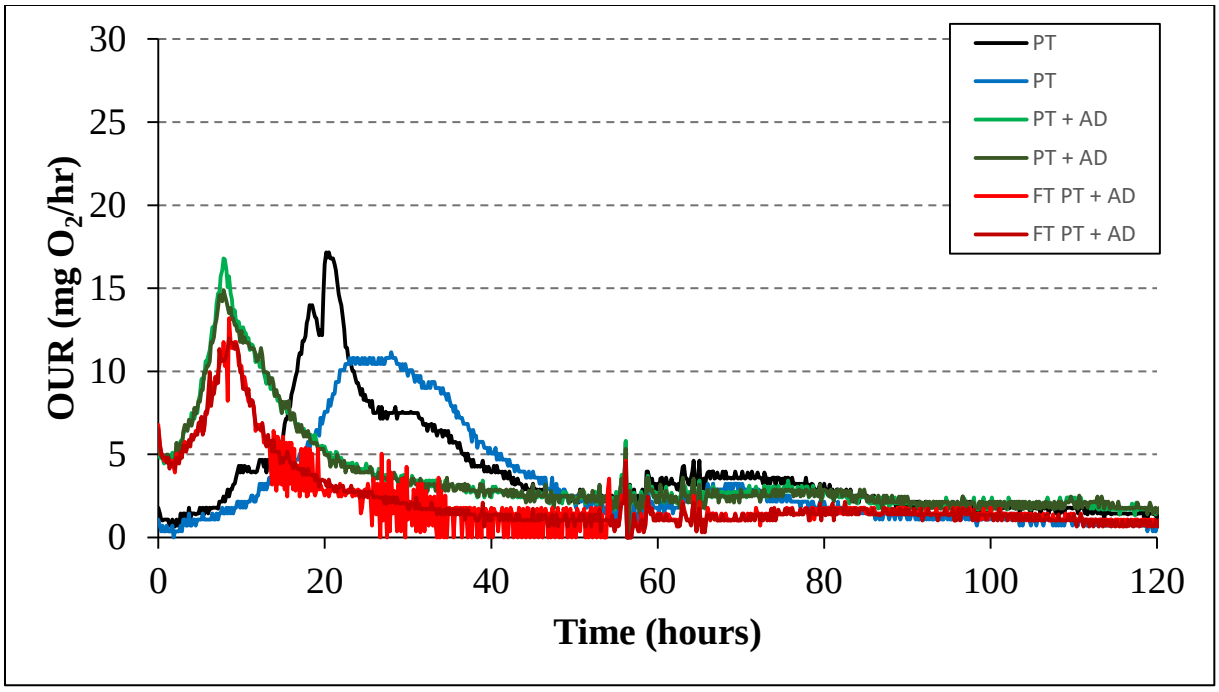

Figure B.7 OUR Curve based on Offline Respirometry Data for 150°C-50 Minute PWAS

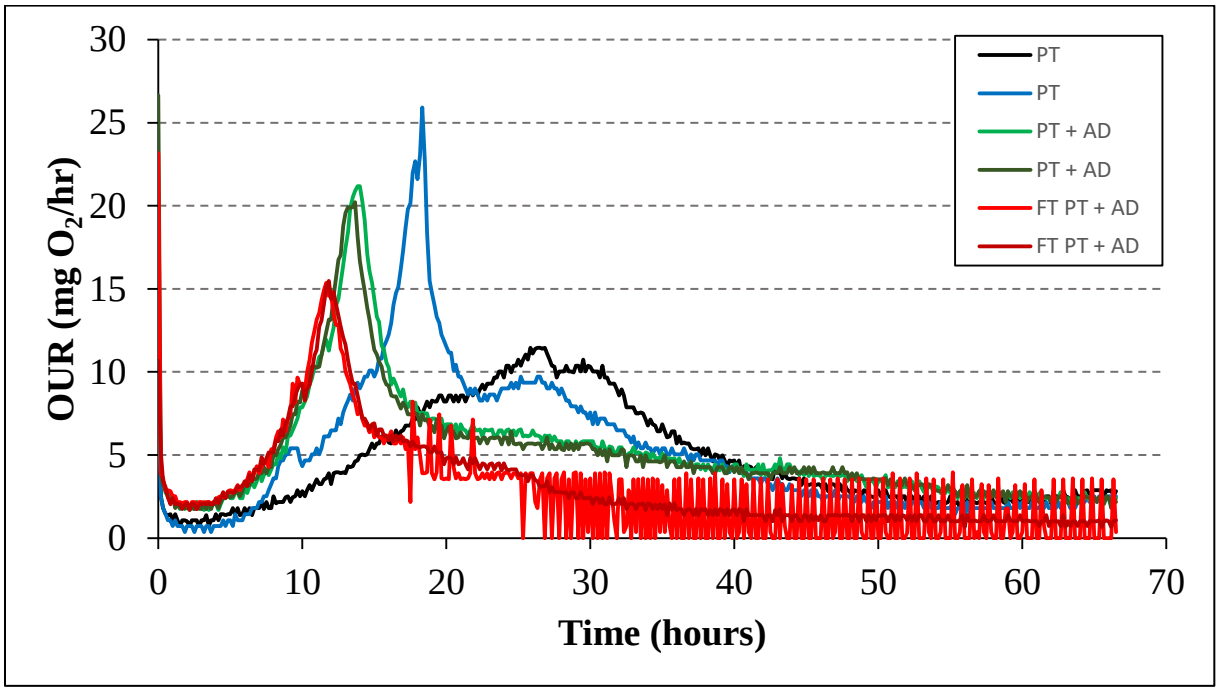

Figure B.8 OUR Curve based on Offline Respirometry Data for 175°C-10 Minute PWAS

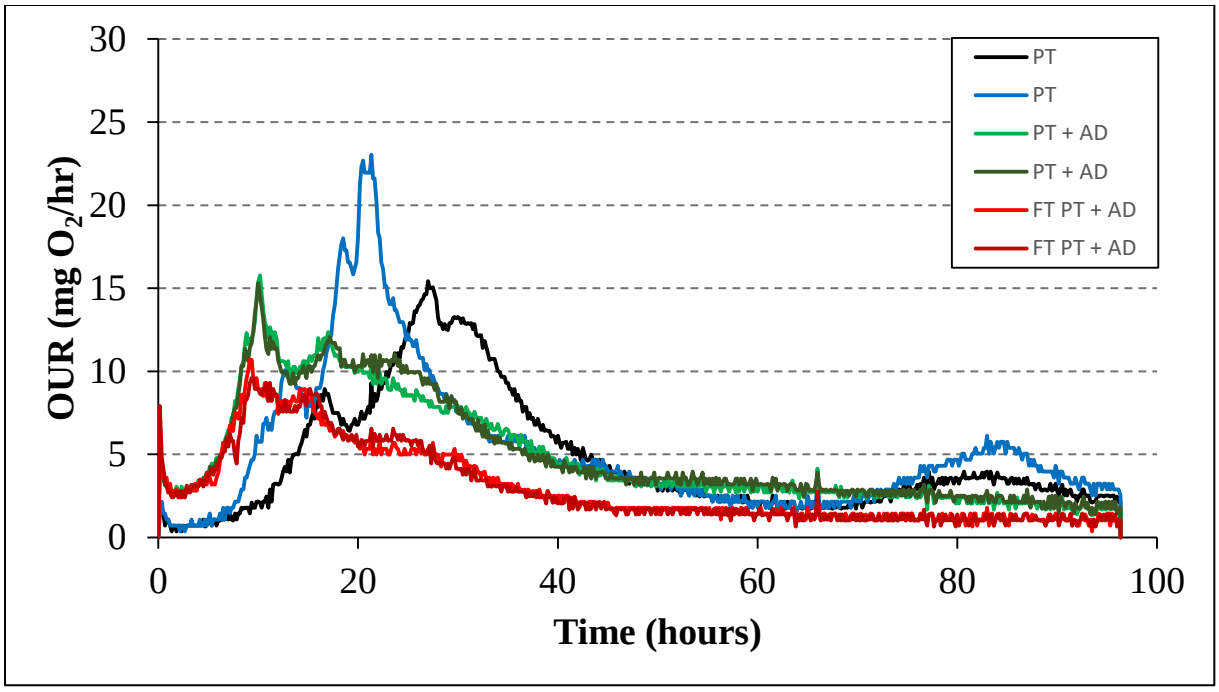

Figure B.9 OUR Curve based on Offline Respirometry Data for 175°C-30 Minute PWAS

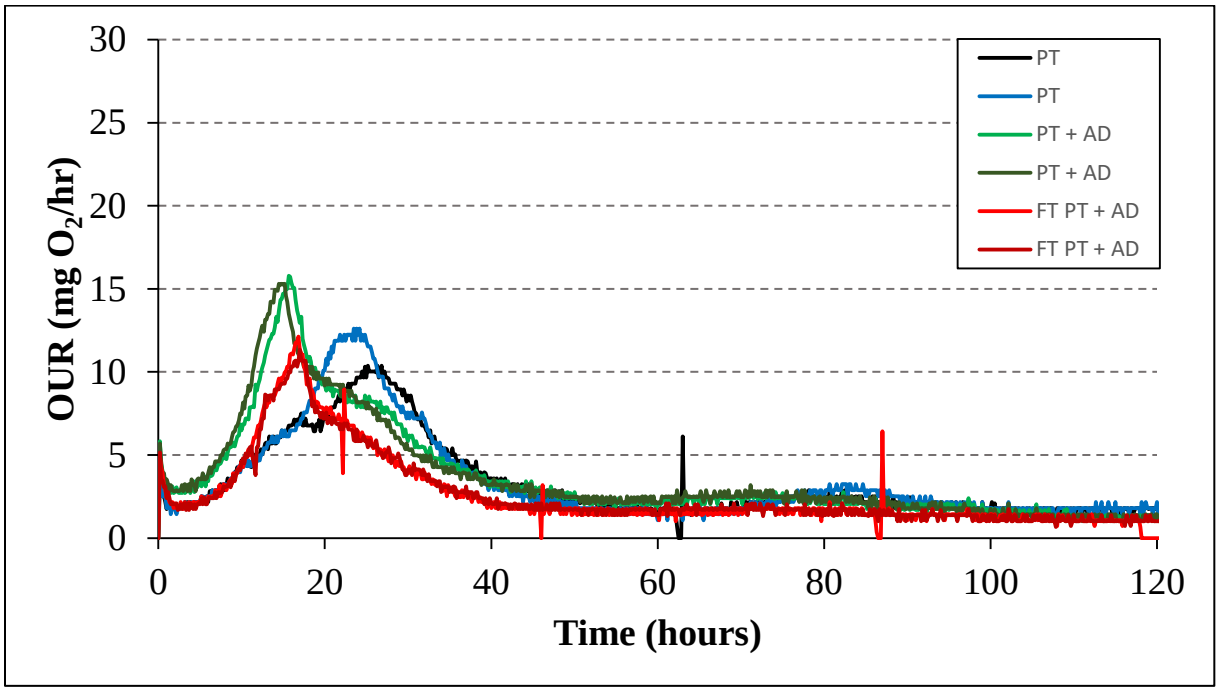

Figure B.10 OUR Curve based on Offline Respirometry Data for 175°C-50 Minute PWAS

Appendix D BMP Data

Table D.1 Ammonia Released during BMP Tests on BR WAS and 30 Minute PWAS

Sample	Day	xDilution	Conc. xDilution	Corrected Ammonia Conc.	TCOD (mgCOD/L)	Ammonia Conc./TCOD
RAW	0	25	199	210	5095	0.041
	2	25	278	305		0.060
	5	25	302	3333		0.065
	10	25	340	378		0.074
	15	25	359	399		0.078
	20	25	372	416		0.082
	35	25	388	433		0.085
	50	25	395	440		0.086
125°C – 30 min	0	25	232	250	4938	0.051
	2	25	260	283		0.057
	5	25	302	334		0.068
	10	25	345	384		0.078
	15	25	362	403		0.082
	20	25	371	415		0.084
	35	25	377	420		0.085
	50	25	389	433		0.088
150°C – 30 min	0	25	222	237	5230	0.045
	2	25	301	333		0.064
	5	25	316	350		0.067
	10	25	356	397		0.076
	15	25	376	420		0.080
	20	25	374	418		0.080
	35	25	382	425		0.081
	50	25	395	440		0.084
175°C – 30 min	0	25	230	247	5222	0.047
	2	25	305	337		0.065
	5	25	305	337		0.065
	10	25	354	394		0.075
	15	25	368	410		0.078
	20	25	391	439		0.084
	35	25	384	428		0.082
	50	25	393	437		0.084
30 Minute Seed	0	25	145			
	2	25	142			
	5	25	145			
	10	25	150			
	15	25	157			
	20	25	151			
	35	25	164			
	50	25	169			

Table D.2 Ammonia Released during BMP Tests on BR WAS and 50 Minute PWAS

Sample	Day	xDilution	Conc. xDilution	Corrected Ammonia Conc.	TCOD (mgCOD/L)	Ammonia Conc./TCOD
RAW	0	25	199	213	5095	0.042
	2	25	278	305		0.060
	5	25	302	331		0.065
	10	25	340	374		0.073
	15	25	359	395		0.078
	20	25	372	408		0.080
	35	25	388	425		0.083
	50	25	395	431		0.085
125°C – 30 min	0	25	204	218	4408	0.049
	2	25	248	268		0.061
	5	25	290	317		0.072
	10	25	324	355		0.080
	15	25	348	383		0.087
	20	25	403	445		0.101
	35	25	418	460		0.104
	50	25	438	483		0.110
150°C – 30 min	0	25	217	235	4100	0.057
	2	25	286	314		0.077
	5	25	316	349		0.085
	10	25	358	396		0.097
	15	25	377	417		0.102
	20	25	401	442		0.108
	35	25	428	473		0.115
	50	25	430	473		0.115
175°C – 30 min	0	25	210	226	4075	0.056
	2	25	288	317		0.078
	5	25	317	349		0.086
	10	25	322	353		0.087
	15	25	357	392		0.096
	20	25	406	449		0.110
	35	25	427	472		0.116
	50	25	443	489		0.120
30 Minute Seed	0	25	130			
	2	25	145			
	5	25	154			
	10	25	169			
	15	25	177			
	20	25	193			
	35	25	204			
	50	25	213			

Table D.3 BMP Gas Phase Data for 30 Minute Seed Sludge

Sample	Day	Gas Produced (mL)	Cumul. Gas Production (mL)	CH_4 Fraction	CO_2 Fraction	N_2 Fraction
30 Minute Seed Sample 1	0	0	0	0%	0%	0%
	1	14	14			
	2	4	18	0%	2%	98%
	3	0	18			
	4	3	21	10%	2%	88%
	6	0	21	12%	2%	86%
	8	1	22			
	10	2	24	13%	3%	84%
	14	1	25	15%	3%	82%
	19	2.5	27.5	18%	4%	78%
	28	8	35.5	19%	5%	76%
	35	1.5	37	21%	5%	74%
	46	4	41	23%	23%	72%
30 Minute Seed Sample 2	0	0	0	0%	0%	0%
	1	13	13			
	2	4	17	0%	2%	98%
	3	2	19			
	4	2	21	0%	2%	98%
	6	0	21	12%	3%	85%
	8	0	21			
	10	1.5	22.5	14%	3%	83%
	14	2	24.5	15%	4%	81%
	19	1.5	26	16%	4%	80%
	28	8	34	19%	5%	76%
	35	1.5	35.5	20%	5%	75%
	46	3.5	39	23%	5%	72%

Table D.4 BMP Gas Phase Data for 50 Minute Seed Sludge

Sample	Day	Gas Produced (mL)	Cumul. Gas Production (mL)	CH_4 Fraction	CO_2 Fraction	N_2 Fraction
50 Minute Seed Sample 1	0	0	0	0%	0%	0%
	1	12	12			
	2	12	24	18%	3%	79%
	3	4	28			
	4	1	29	21%	4%	75%
	5	8.5	37.5			
	6	8	45.5	27%	6%	67%
	7	3.5	49			
	8	4	53	29%	7%	64%
	10	6	59	31%	8%	61%
	12	5.5	64.5			
	14	6	70.5	37%	9%	54%
	18	8	78.5	39%	9%	52%
	23	12	90.5	42%	12%	46%
	32	24	114.5	46%	14%	40%
	39	9.5	124	48%	15%	37%
	50	8	132	50%	15%	35%
50 Minute Seed Sample 2	0	0	0	0%	0%	0%
	1	13	13			
	2	11	24	15%	3%	81%
	3	5	29			
	4	0	29	20%	4%	76%
	5	8.5	37.5			
	6	8.5	46	25%	6%	69%
	7	5	51			
	8	5.5	56.5	26%	6%	67%
	10	4.5	61	29%	7%	64%
	12	5	66			
	14	7	73	33%	8%	59%
	18	8.5	81.5	36%	10%	54%
	23	11.5	93	39%	11%	50%
	32	23	116	42%	13%	45%
	39	10.5	126.5	44%	14%	41%
	50	8	134.5	47%	14%	39%

Table D.5 BMP Gas Phase Data for BR WAS

Sample	Day	Gas Produced (mL)	Cumul. Gas Production (mL)	CH_4 Fraction	CO_2 Fraction	N_2 Fraction
Raw A	0	0	0	0%	0%	0%
	1	12	12			
	2	12	24	18%	3%	79%
	3	4	28			
	4	1	29	21%	4%	75%
	6	8.5	37.5			
	8	8	45.5	27%	6%	67%
	10	3.5	49			
	14	4	53	29%	7%	64%
	19	6	59	31%	8%	61%
	28	5.5	64.5			
	35	6	70.5	37%	9%	54%
	46	8	78.5	39%	9%	52%
Raw B	0	0	0	0%	0%	0%
	1	32	32			
	2	99	131	38%	24%	38%
	3	75	206			
	4	52	258	55%	28%	17%
	6	42	300	57%	29%	13%
	8	22	322			
	10	13.5	335.5	58%	30%	12%
	14	19	354.5	59%	30%	11%
	19	28	382.5	61%	32%	7%
	28	28	410.5	60%	32%	8%
	35	11	412.5	59%	32%	9%
	46	6	427.5	60%	32%	9%

Table D.6 BMP Gas Phase Data for 125°C-30 PWAS

Sample	Day	Gas Produced (mL)	Cumul. Gas Production (mL)	CH_4 Fraction	CO_2 Fraction	N_2 Fraction
125°C – 30 min A	0	0	0	0%	0%	0%
	1	63	63			
	2	63	126	35%	22%	43%
	3	50	176			
	4	47	223	52%	24%	24%
	6	50	273	56%	25%	18%
	8	26	299			
	10	21	320	60%	27%	14%
	14	38	358	61%	28%	12%
	19	28	286	62%	29%	9%
	28	31	417	61%	31%	8%
	35	10	427	61%	30%	9%
	46	2.5	429.5	61%	30%	9%
125°C – 30 min B	0	0	0	0%	0%	0%
	1	65	65			
	2	67	132	36%	22%	42%
	3	54	186			
	4	47	233	50%	25%	24%
	6	52	285	57%	25%	17%
	8	26	311			
	10	19	330	60%	27%	14%
	14	25	355	61%	27%	12%
	19	28	383	62%	29%	9%
	28	31	414	62%	30%	8%
	35	10	424	61%	30%	9%
	46	3	427	61%	29%	9%

Table D.7 BMP Gas Phase Data for 150°C-30 PWAS

Sample	Day	Gas Produced (mL)	Cumul. Gas Production (mL)	CH_4 Fraction	CO_2 Fraction	N_2 Fraction
150°C – 30 min A	0	0	0	0%	0%	0%
	1	72	72			
	2	62	134	33%	24%	42%
	3	54	188			
	4	53	241	53%	25%	22%
	6	54	295	59%	25%	16%
	8	33	328			
	10	17	345	61%	27%	12%
	14	21	366	60%	28%	12%
	19	28	394	62%	28%	10%
	28	32	426	61%	29%	9%
	35	10	436	61%	30%	9%
	46	4.5	440.5	62%	29%	10%
150°C – 30 min B	0	0	0	0%	0%	0%
	1	69	69			
	2	64	133	34%	24%	43%
	3	52	185			
	4	54	239	52%	25%	23%
	6	57	296	58%	26%	16%
	8	33	329			
	10	18	347	59%	27%	14%
	14	22	369	59%	30%	12%
	19	26	395	61%	29%	10%
	28	31	426	60%	30%	10%
	35	10	436	60%	29%	10%
	46	4	440	61%	29%	9%

Table D.8 BMP Gas Phase Data for 175°C-30 PWAS

Sample	Day	Gas Produced (mL)	Cumul. Gas Production (mL)	CH_4 Fraction	CO_2 Fraction	N_2 Fraction
175°C – 30 min A	0	0	0	0%	0%	0%
	1	70	70			
	2	55	125	31%	27%	42%
	3	47	172			
	4	57	229	51%	26%	23%
	6	55	284	57%	26%	17%
	8	40	324			
	10	25	349	62%	26%	12%
	14	20	369	61%	26%	13%
	19	20	389	63%	29%	9%
	28	23	412	61%	30%	9%
	35	5.5	417.5	61%	29%	10%
	46	1	418.5	61%	29%	10%
175°C – 30 min B	0	0	0	0%	0%	0%
	1	78	78			
	2	59	137	31%	26%	42%
	3	49	186			
	4	58	244	52%	26%	22%
	6	56	300	58%	26%	16%
	8	43	343			
	10	22.5	365.5	62%	27%	12%
	14	18	383.5	61%	28%	10%
	19	19	402.5	62%	28%	9%
	28	24	426.5	62%	29%	9%
	35	6	432.5	61%	29%	10%
	46	1	433.5	61%	29%	10%

Table D.9 BMP Gas Phase Data for 125°C-50 PWAS

Sample	Day	Gas Produced (mL)	Cumul. Gas Production (mL)	CH_4 Fraction	CO_2 Fraction	N_2 Fraction
125°C – 50 min A	0	0	0	0%	0%	0%
	1	72	72			
	2	114	186	46%	23%	31%
	3	46	232			
	4	28	260	52%	25%	22%
	5	16	276			
	6	19	295	55%	27%	17%
	7	13	308			
	8	14	322	57%	28%	15%
	10	24	346	57%	29%	15%
	12	20	366			
	14	17	383	61%	30%	10%
	18	29	412	60%	29%	11%
	23	19	431	62%	30%	8%
	32	33	464	61%	31%	8%
	39	13	477	61%	31%	8%
	50	10.5	487.5	61%	30%	8%
125°C – 50 min B	0	0	0	0%	0%	0%
	1	68	68			
	2	116	184	45%	22%	33%
	3	47	231			
	4	28	259	52%	26%	22%
	5	17	276			
	6	22	298	55%	27%	18%
	7	13	311			
	8	11	322	56%	28%	16%
	10	18	340	55%	28%	17%
	12	15	355			
	14	15.5	370.5	60%	28%	12%
	18	25	395.5	60%	29%	11%
	23	22	417.5	62%	30%	8%
	32	38	455.5	62%	31%	8%
	39	14	469.5	60%	31%	9%
	50	10.5	480	61%	30%	8%

Table D.10 BMP Gas Phase Data for 150°C-50 PWAS

Sample	Day	Gas Produced (mL)	Cumul. Gas Production (mL)	CH_4 Fraction	CO_2 Fraction	N_2 Fraction
150°C – 50 min A	0	0	0	0%	0%	0%
	1	73	73			
	2	104	177	47%	24%	29%
	3	53	230			
	4	31	261	55%	26%	18%
	5	23	284			
	6	24	308	58%	27%	15%
	7	12	320			
	8	13	333	60%	27%	13%
	10	18	351	59%	28%	13%
	12	16	367			
	14	13.5	380.5	61%	29%	10%
	18	20	400.5	59%	28%	13%
	23	19	419.5	63%	30%	8%
	32	33	452.5	62%	30%	8%
	39	12.5	465	61%	30%	9%
	50	9	474	62%	30%	8%
150°C – 50 min B	0	0	0	0%	0%	0%
	1	69	69			
	2	113	182	45%	23%	32%
	3	54	236			
	4	32	268	54%	25%	21%
	5	25	293			
	6	23	316	57%	27%	16%
	7	13.5	329.5			
	8	13.5	343	58%	27%	15%
	10	19	362	58%	26%	14%
	12	15.5	377.5			
	14	13.5	391	61%	28%	12%
	18	23	414	59%	29%	12%
	23	21	435	62%	30%	8%
	32	35	470	61%	30%	9%
	39	13.5	483.5	61%	30%	9%
	50	9	492.5	62%	30%	8%

Table D.11 BMP Gas Phase Data for 175°C-50 PWAS

Sample	Day	Gas Produced (mL)	Cumul. Gas Production (mL)	CH_4 Fraction	CO_2 Fraction	N_2 Fraction
175°C – 50 min A	0	0	0	0%	0%	0%
	1	71	71			
	2	110	181	44%	24%	33%
	3	63	244			
	4	36	280	55%	25%	20%
	5	24	304			
	6	27	331	59%	27%	14%
	7	11.5	342.5			
	8	12	354.5	59%	28%	13%
	10	14	368.5	60%	29%	11%
	12	14	382.5			
	14	13	395.5	62%	29%	9%
	18	17	412.5	60%	28%	12%
	23	15	427.5	62%	30%	8%
	32	27	454.5	62%	31%	7%
	39	12	466.5	61%	32%	7%
	50	9	475.5	62%	30%	7%
175°C – 50 min B	0	0	0	0%	0%	0%
	1	63	63			
	2	112	175	44%	24%	33%
	3	61	236			
	4	35	271	54%	25%	21%
	5	25	296			
	6	29.5	325.5	59%	27%	14%
	7	14	339.5			
	8	11	350.5	59%	28%	13%
	10	14.5	365	59%	29%	11%
	12	13	378			
	14	14	392	61%	29%	10%
	18	16	408	59%	29%	12%
	23	15	423	62%	30%	8%
	32	27	450	62%	31%	7%
	39	12	462	62%	31%	8%
	50	9	471	62%	30%	8%

Appendix E COD Concentrations Before and After Pretreatment

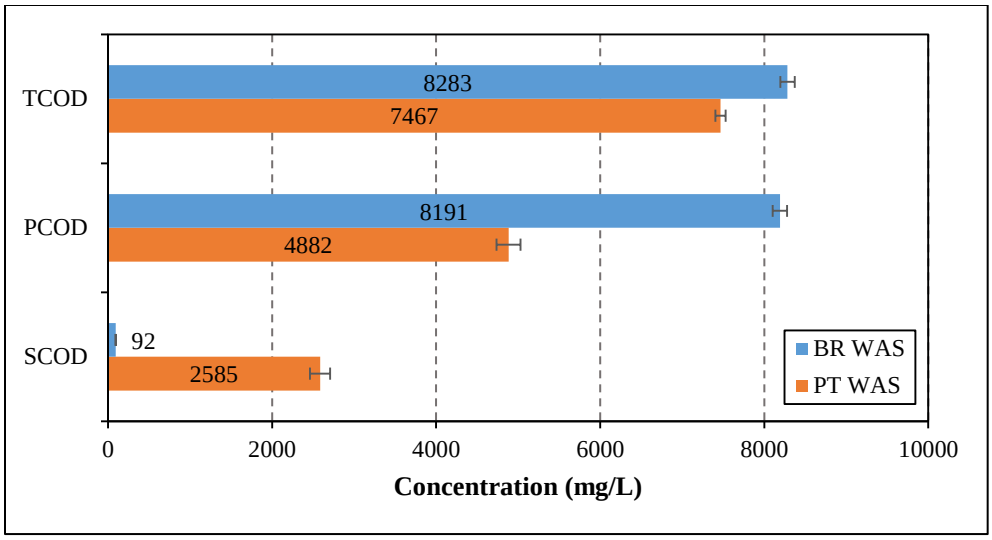

Figure E.1 Total, Particulate and Soluble COD Concentrations Before and After Pretreatment at 125°C for 10 minutes

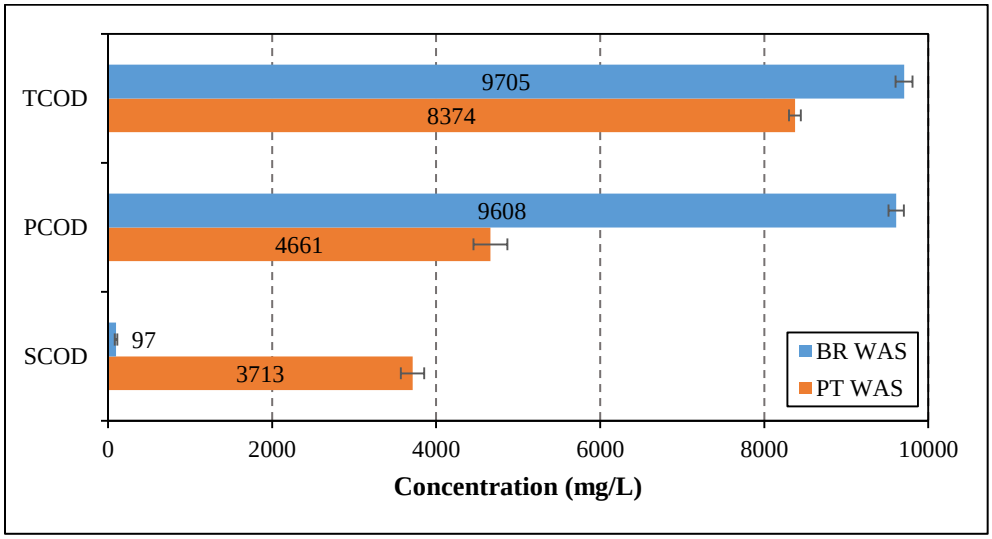

Figure E.2 Total, Particulate and Soluble COD Concentrations Before and After Pretreatment at 125°C for 30 minutes

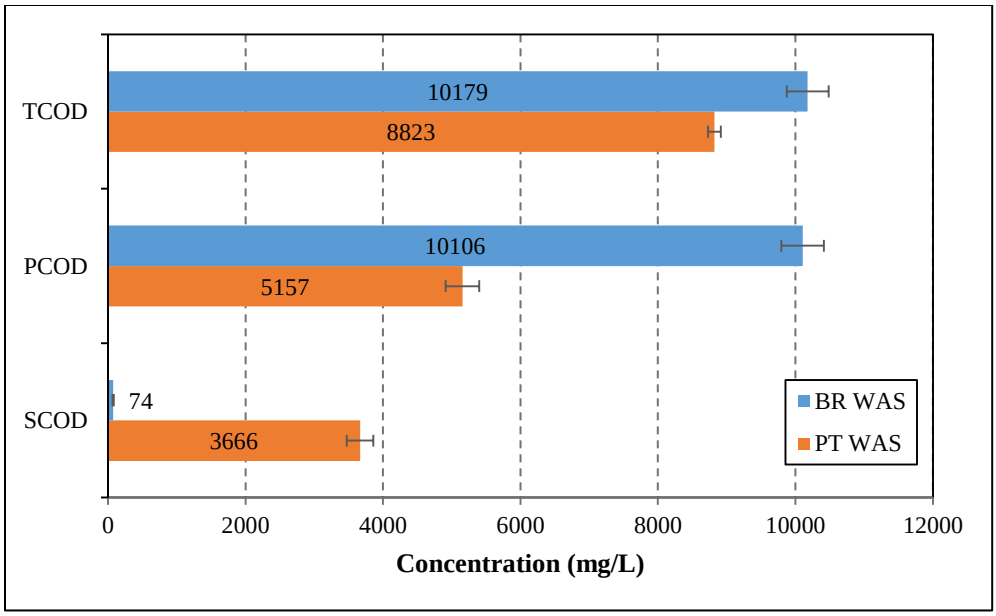

Figure E.3 Total, Particulate and Soluble COD Concentrations Before and After Pretreatment at 125°C for 50 minutes

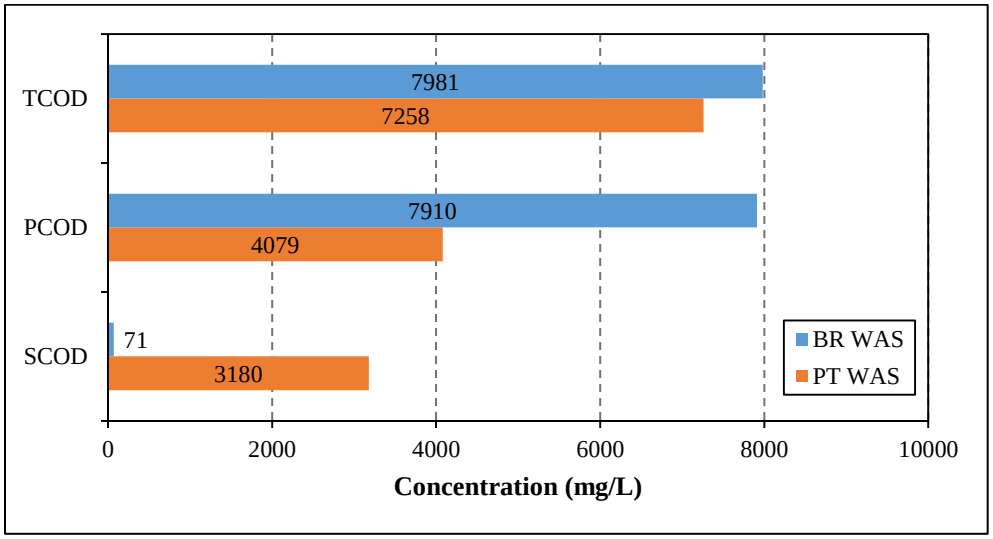

Figure E.4 Total, Particulate and Soluble COD Concentrations Before and After Pretreatment at 150°C for 30 minutes

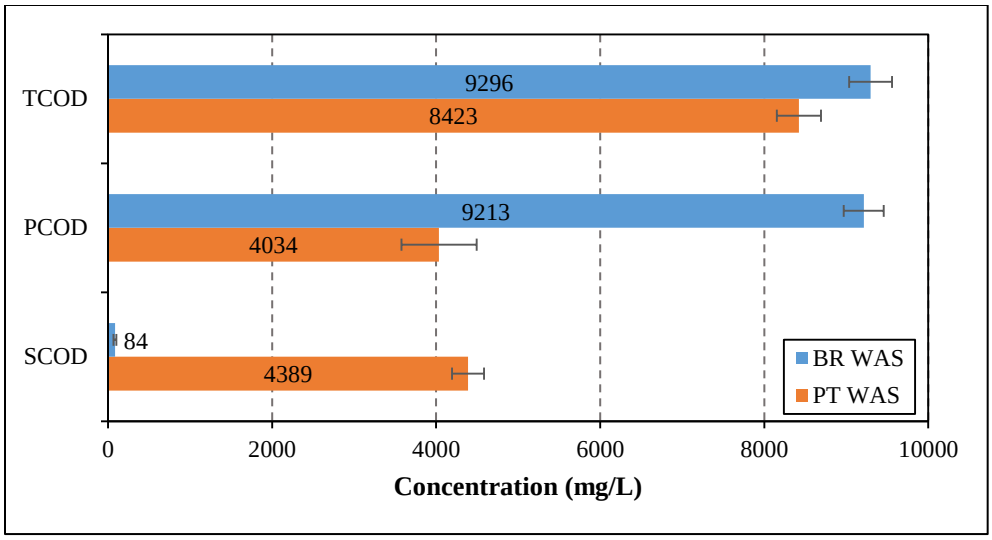

Figure E.5 Total, Particulate and Soluble COD Concentrations Before and After Pretreatment at 150°C for 50 minutes

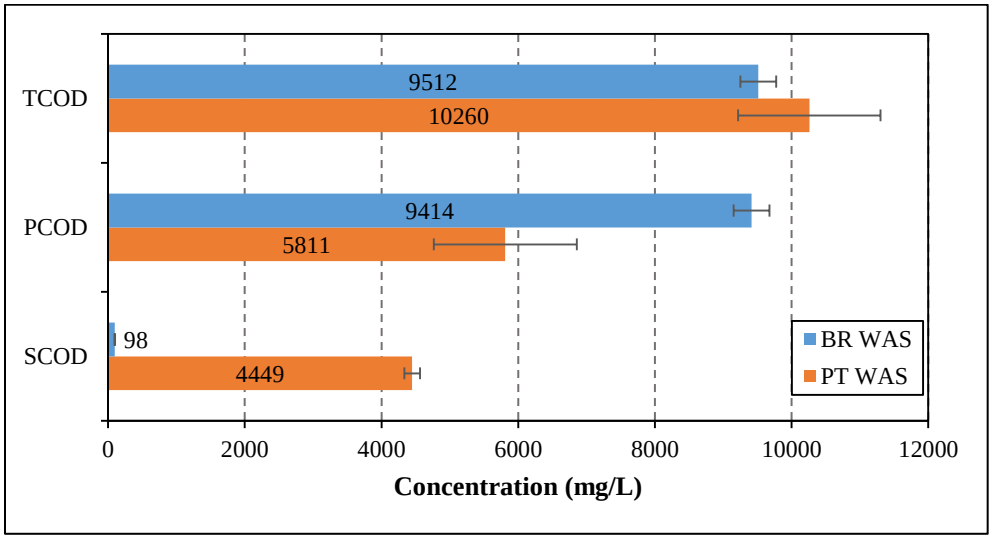

Figure E.6 Total, Particulate and Soluble COD Concentrations Before and After Pretreatment at 175°C for 10 minutes

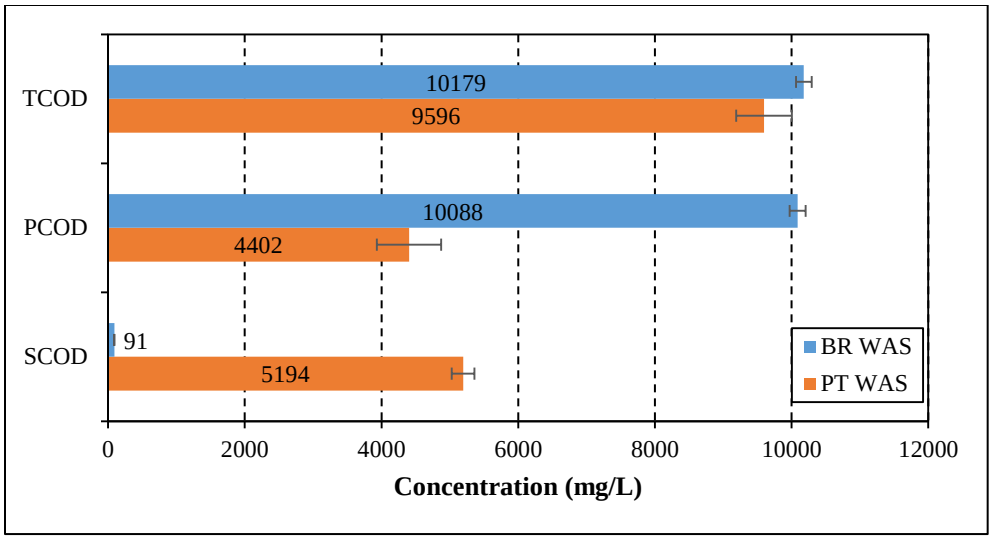

Figure E.7 Total, Particulate and Soluble COD Concentrations Before and After Pretreatment at 175°C for 30 minutes

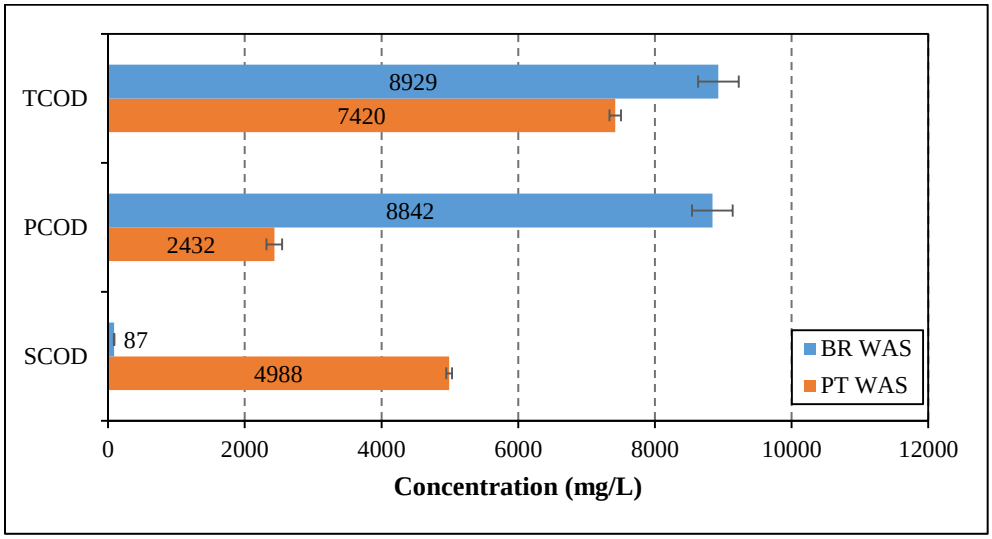

Figure E.8 Total, Particulate and Soluble COD Concentrations Before and After Pretreatment at 175°C for 50 minutes

Appendix F ANOVA Table

Table F.1 ANOVA Table for COD Solubilization After Pretreatment

Source of Variation	Sum of Squares	DF	Mean Square	F_o	F_{crit}
A: Temperature	0.15971	2	0.07986	209.66	3.35
B: Time	0.03681	2	0.01841	48.32	3.35
AB	0.00990	4	0.00247	6.50	2.73
Error	0.01028	27	0.00038		
Total	0.21671	35			

Appendix G Solids Concentrations Before and After Pretreatment

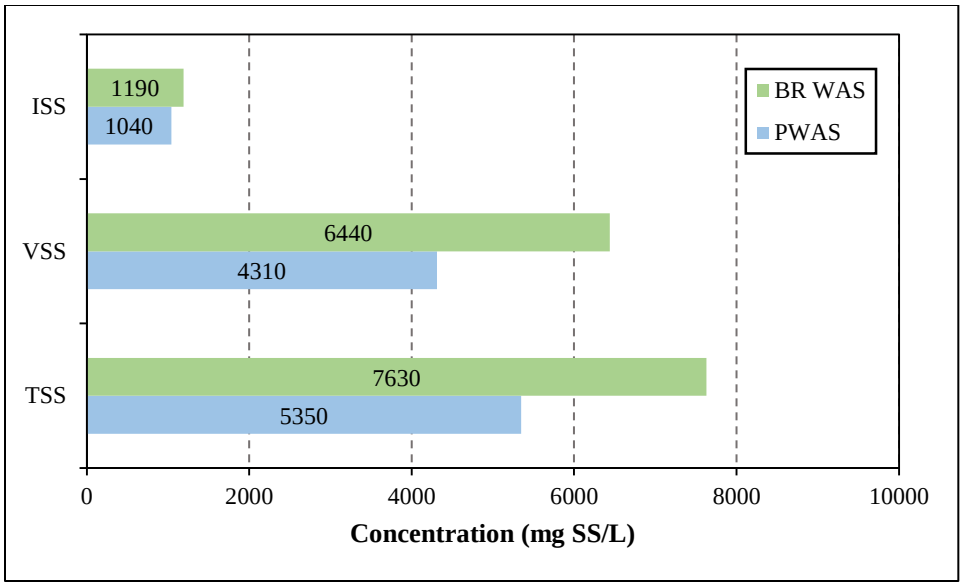

Figure G.1 Suspended Solids Concentrations Before and After Pretreatment at 125°C for 10 minutes

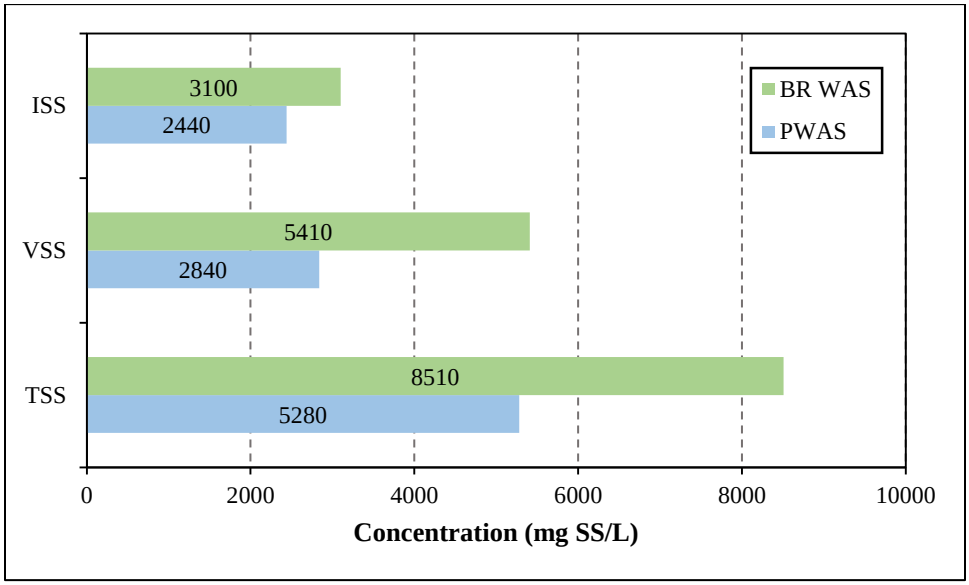

Figure G.2 Suspended Solids Concentrations Before and After Pretreatment at 125°C for 30 minutes

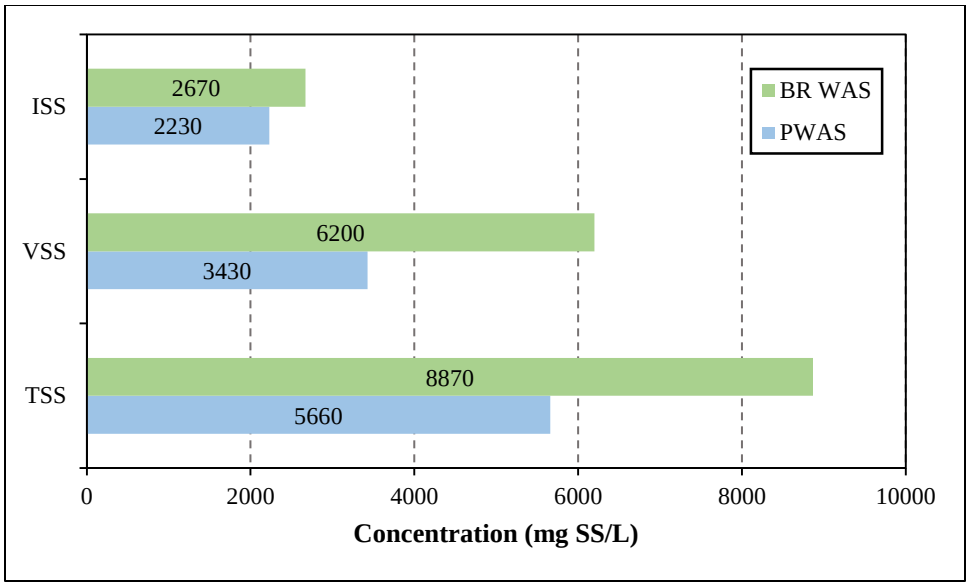

Figure G.3 Suspended Solids Concentrations Before and After Pretreatment at 125°C for 50 minutes

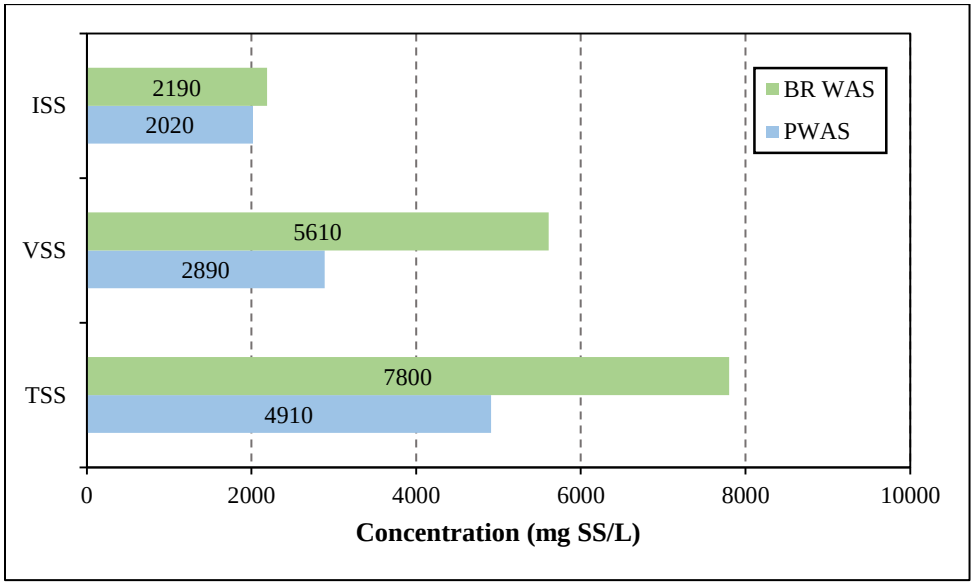

Figure G.4 Suspended Solids Concentrations Before and After Pretreatment at 150°C for 30 minutes

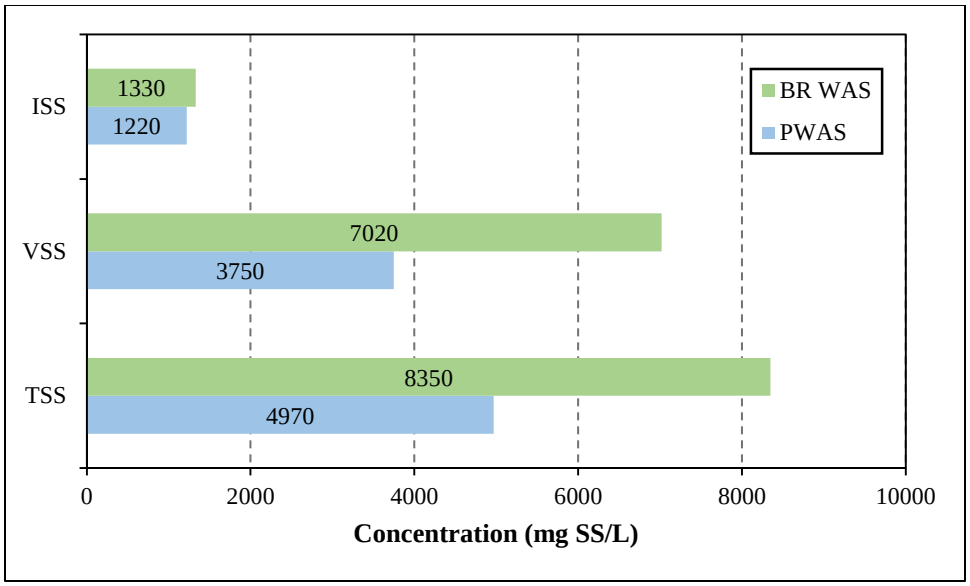

Figure G.5 Suspended Solids Concentrations Before and After Pretreatment at 150°C for 50 minutes

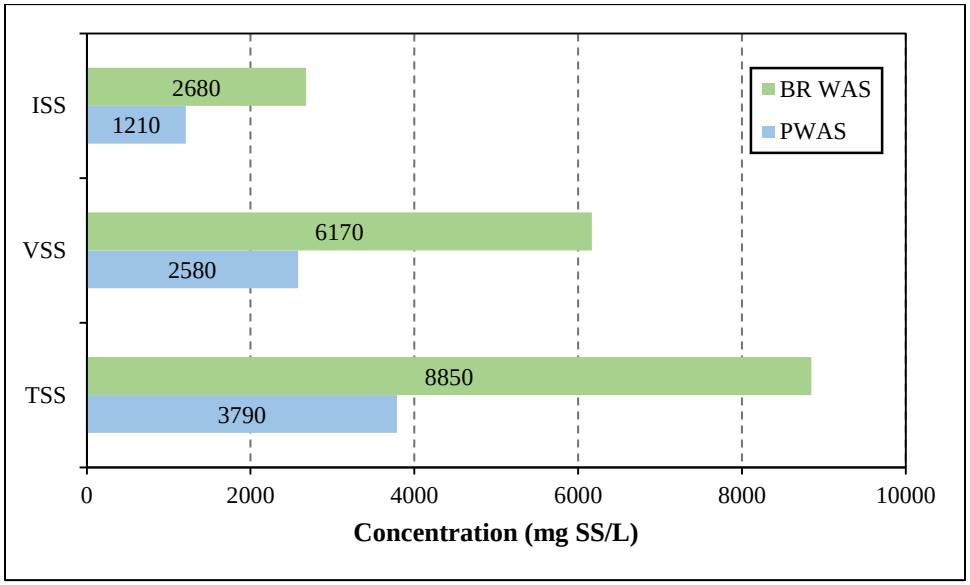

Figure G.6 Suspended Solids Concentrations Before and After Pretreatment at 175°C for 10 minutes

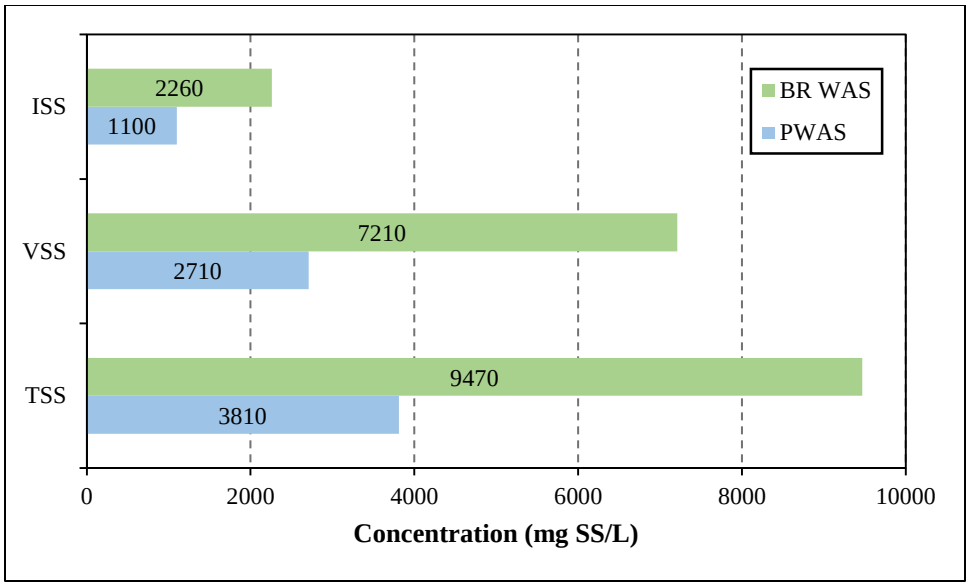

Figure G.7 Suspended Solids Concentrations Before and After Pretreatment at 175°C for 30 minutes

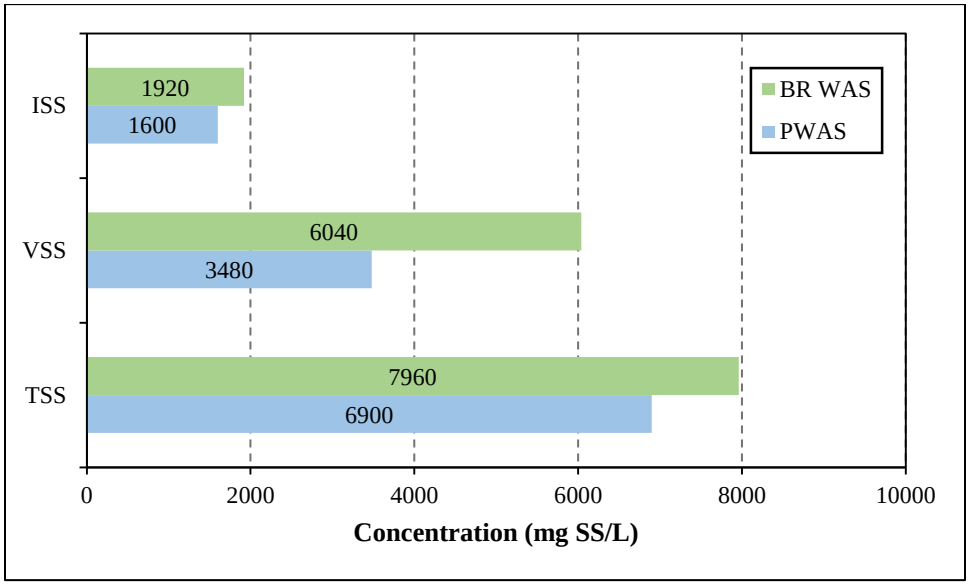

Figure G.8 Suspended Solids Concentrations Before and After Pretreatment at 175°C for 50 minutes

Appendix H Best-Fit of PWAS COD Fractionation

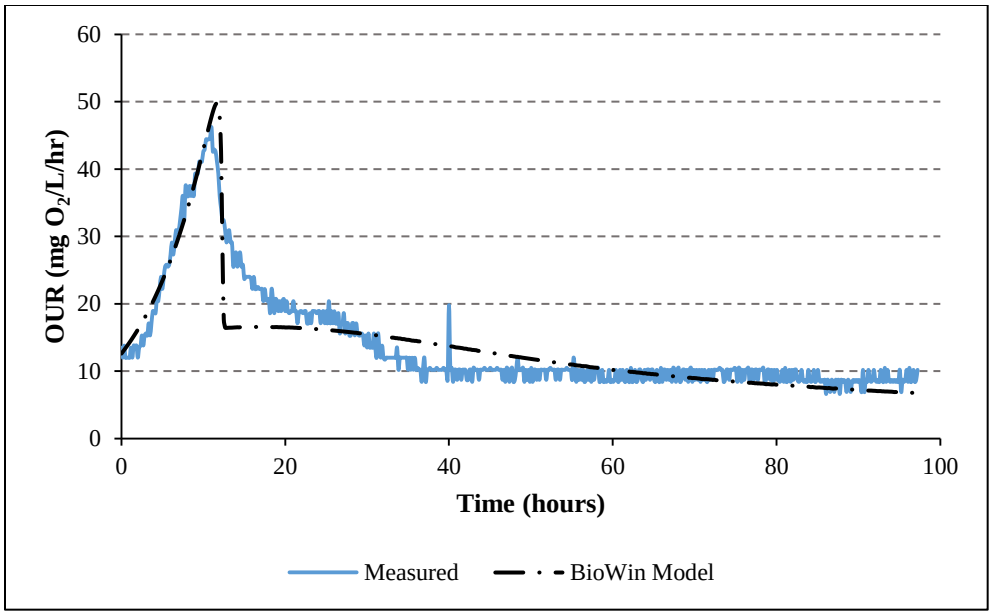

Figure H.1 Predicted and Measured OUR for WAS Pretreated at 125°C for 10 Minutes (Best-fit)

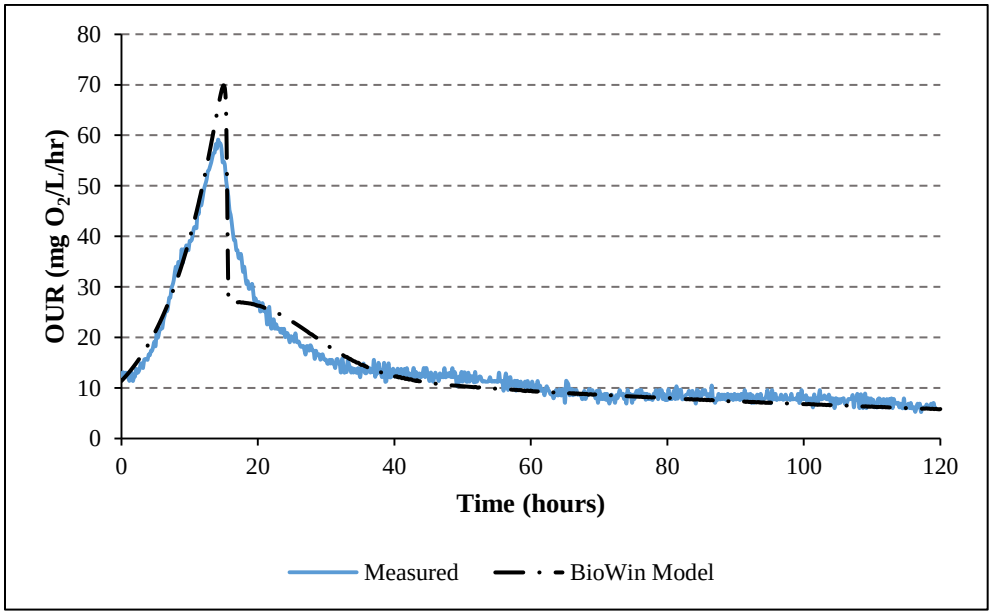

Figure H.2 Predicted and Measured OUR for WAS Pretreated at 125°C for 30 Minutes (Best-fit)

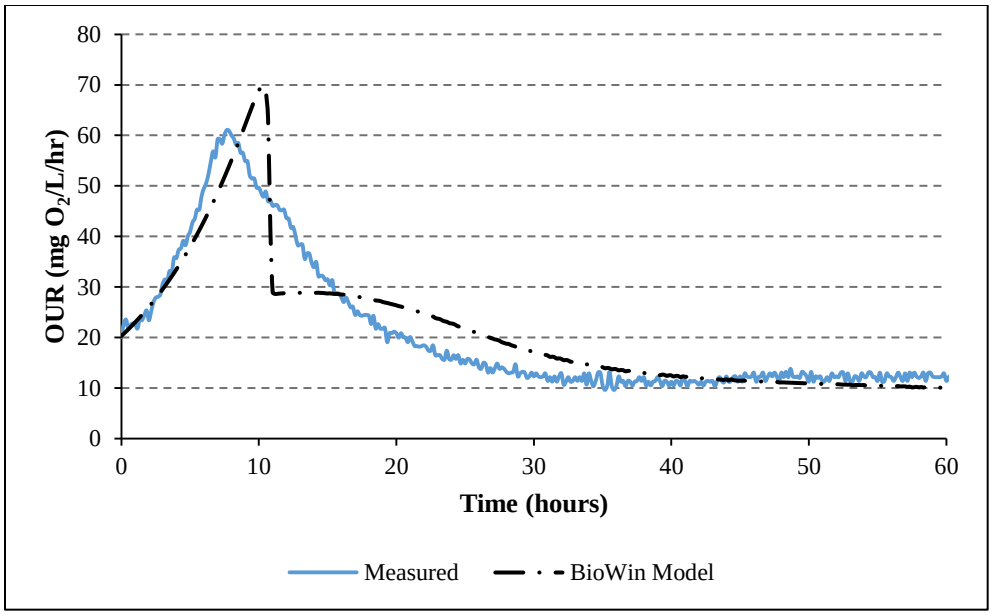

Figure H.3 Predicted and Measured OUR for WAS Pretreated at 125°C for 50 Minutes (Best-fit)

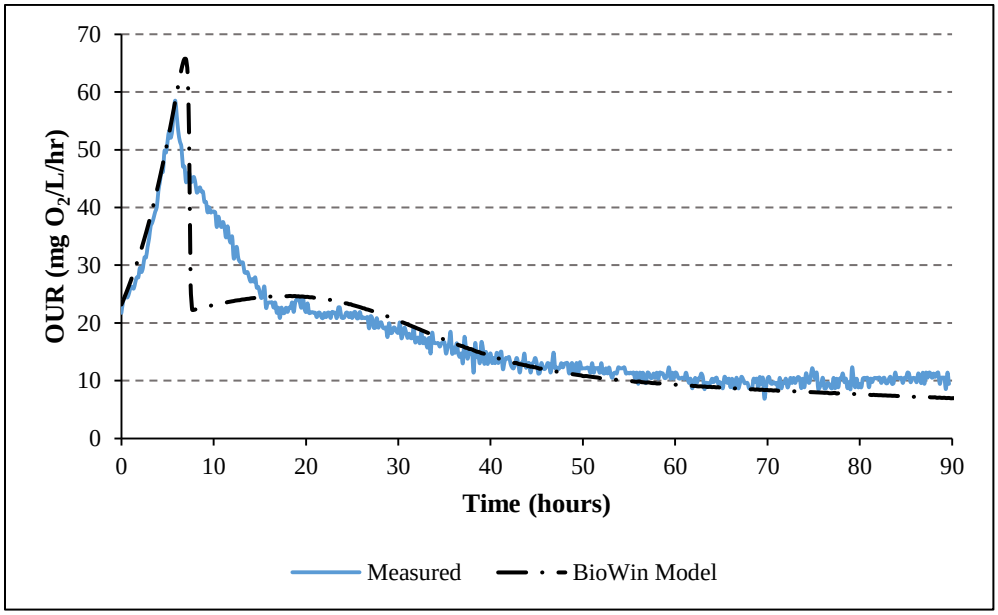

Figure H.4 Predicted and Measured OUR for WAS Pretreated at 150°C for 10 Minutes (Best-fit)

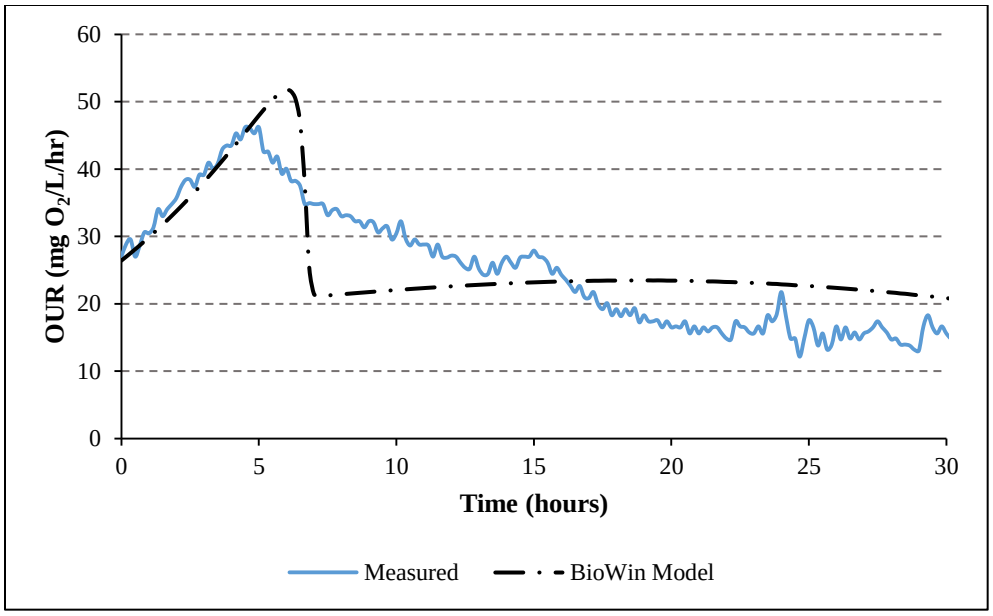

Figure H.5 Predicted and Measured OUR for WAS Pretreated at 150°C for 30 Minutes (Best-fit)

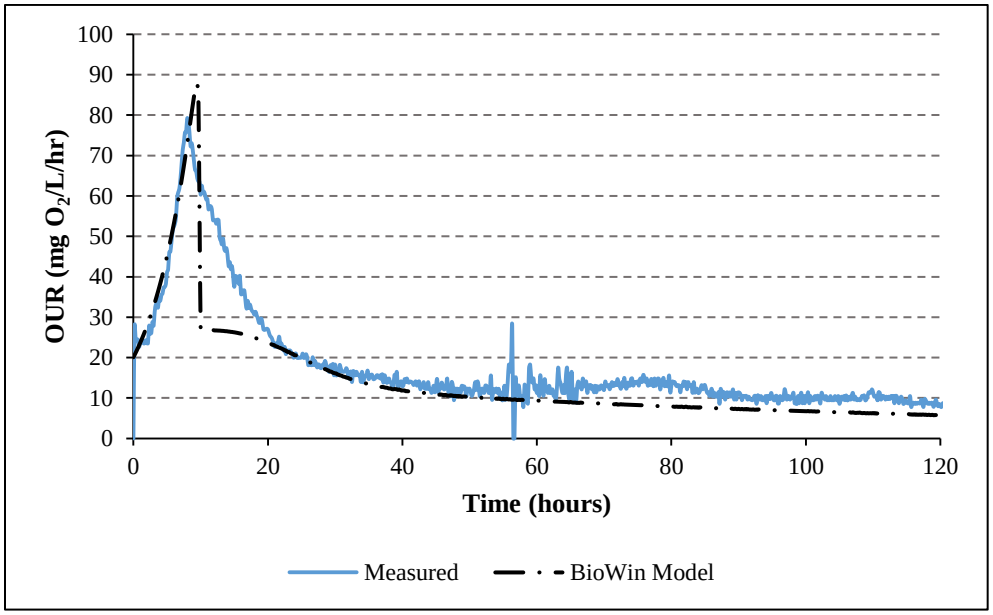

Figure H.6 Predicted and Measured OUR for WAS Pretreated at 150°C for 50 Minutes (Best-fit)

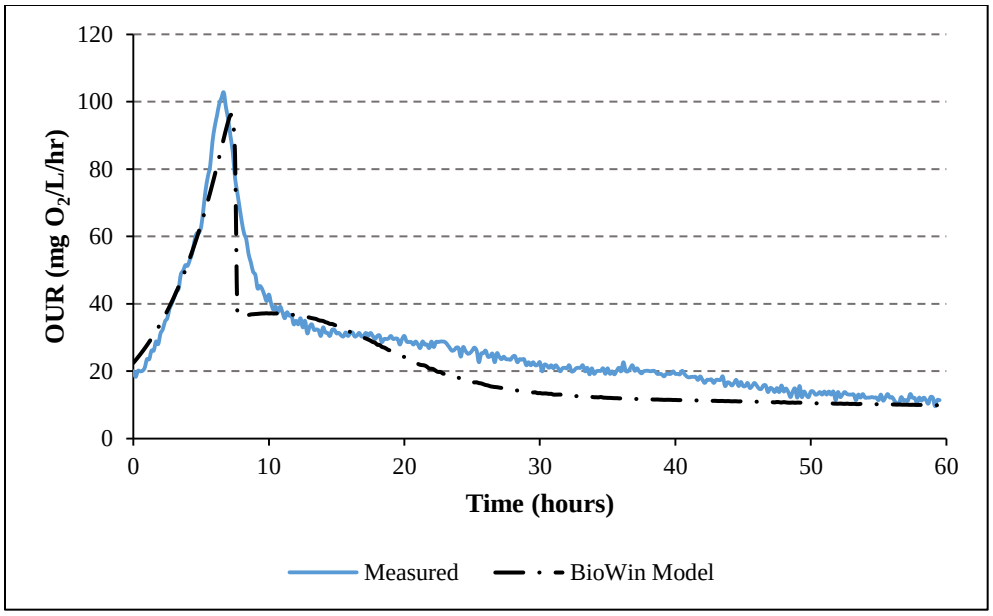

Figure H.7 Predicted and Measured OUR for WAS Pretreated at 175°C for 10 Minutes (Best-fit)

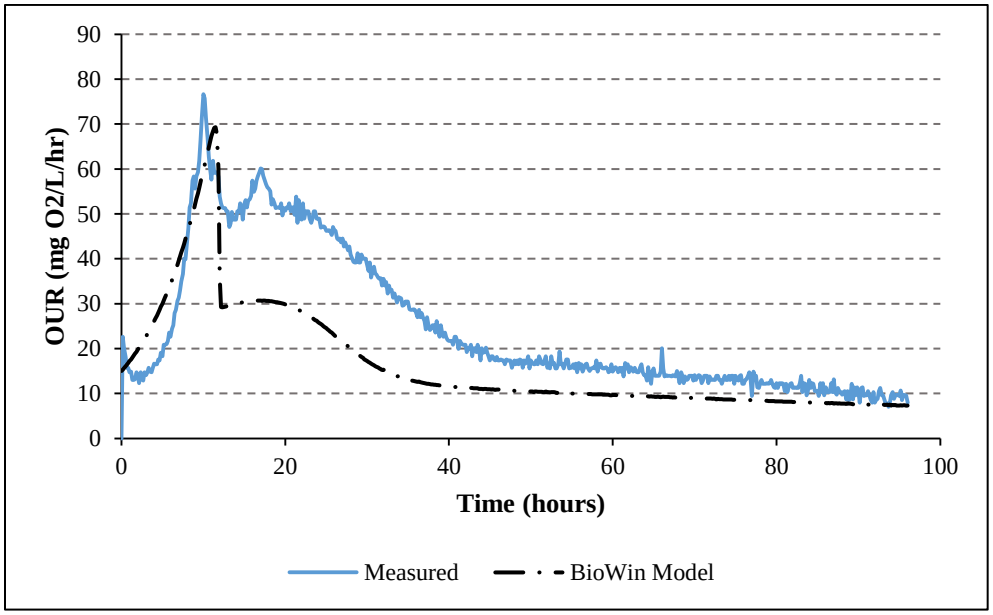

Figure H.8 Predicted and Measured OUR for WAS Pretreated at 175°C for 30 Minutes (Best-fit)

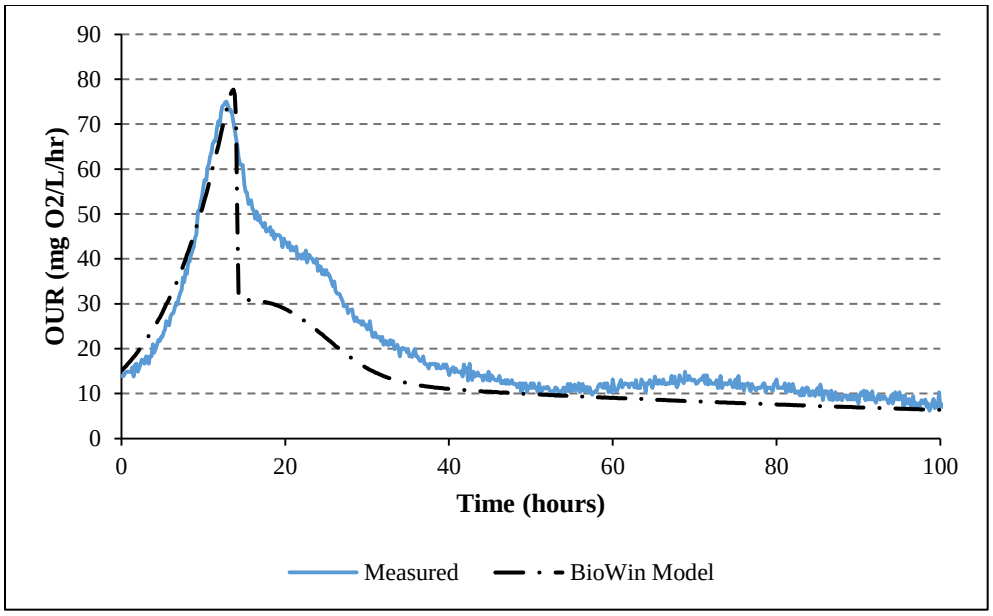

Figure H.9 Predicted and Measured OUR for WAS Pretreated at 175°C for 50 Minutes (Best-fit)

Appendix I Cumulative/Daily Methane Production Curves

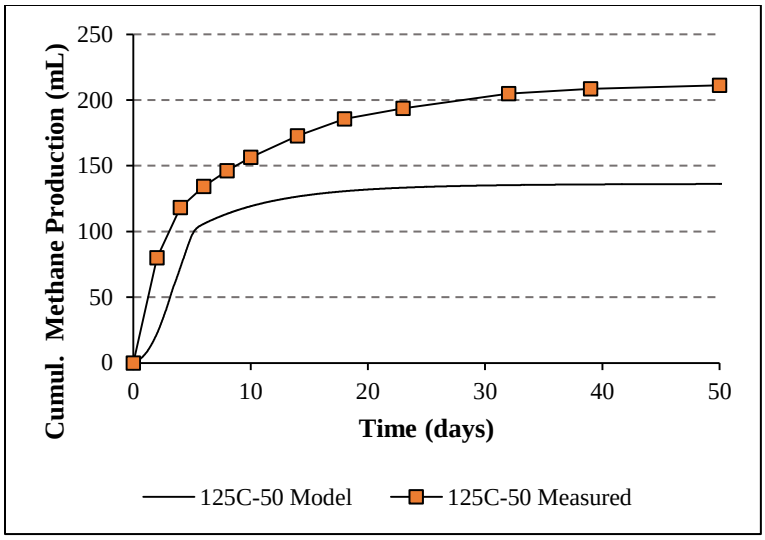

Figure I.1 Trial 1 Predicted and Measured Cumulative Methane Production for WAS Pretreated at 125°C – 50 Minutes

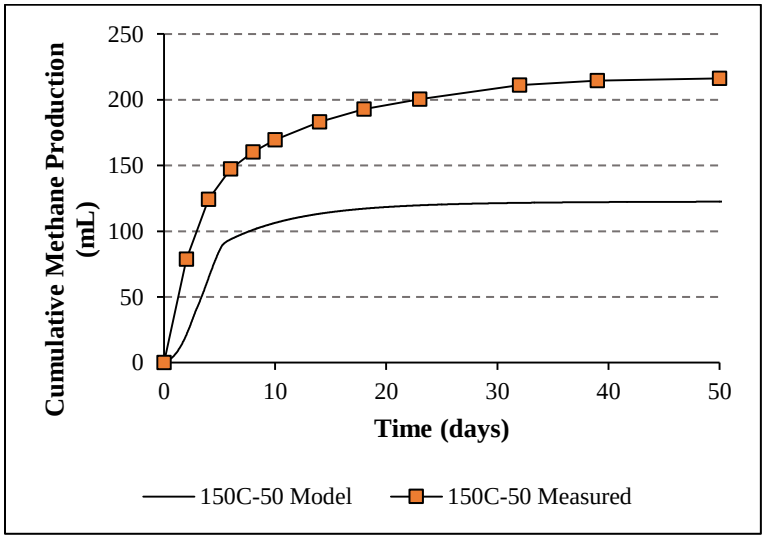

Figure I.2 Trial 1 Predicted and Measured Cumulative Methane Production for WAS Pretreated at 150°C – 50 Minutes

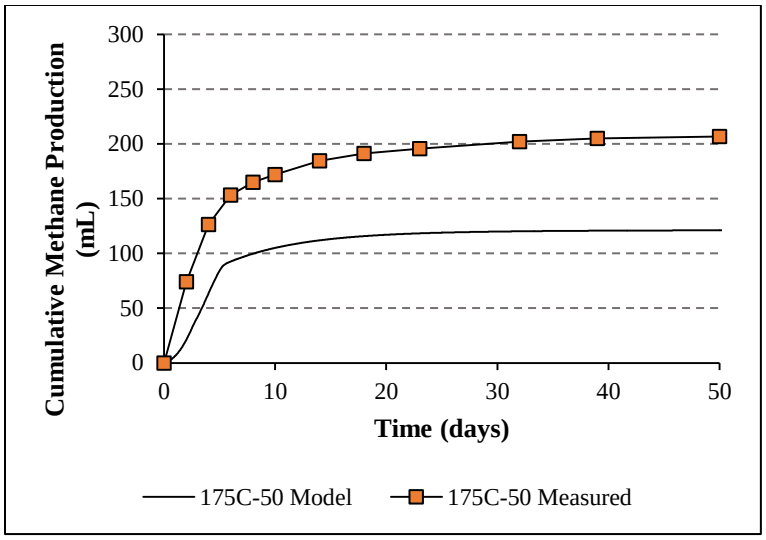

Figure I.3 Trial 1 Predicted and Measured Cumulative Methane Production for WAS Pretreated at 175°C – 50 Minutes

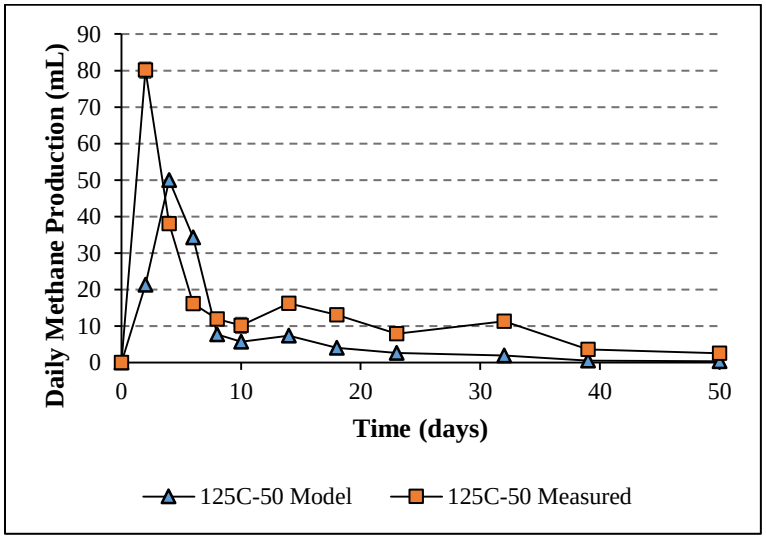

Figure I.4 Trial 1 Predicted and Measured Daily Methane Production for WAS Pretreated at 125°C – 50 Minutes

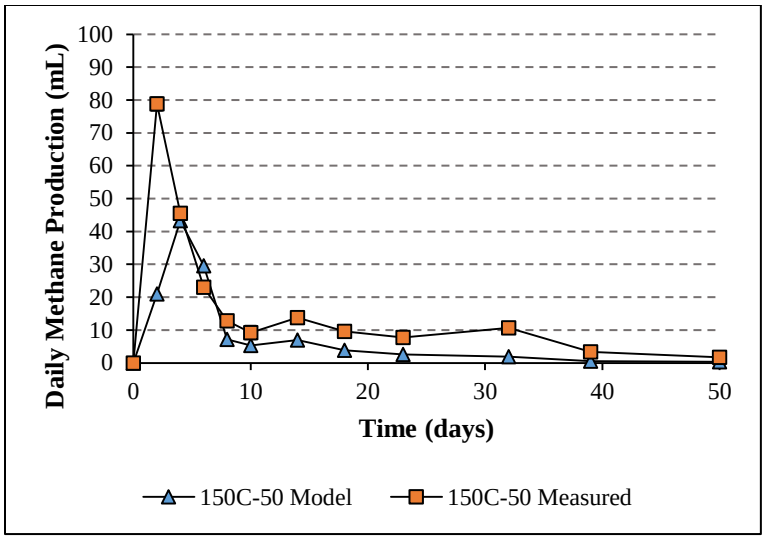

Figure I.5 Trial 1 Predicted and Measured Daily Methane Production for WAS Pretreated at 150°C – 50 Minutes

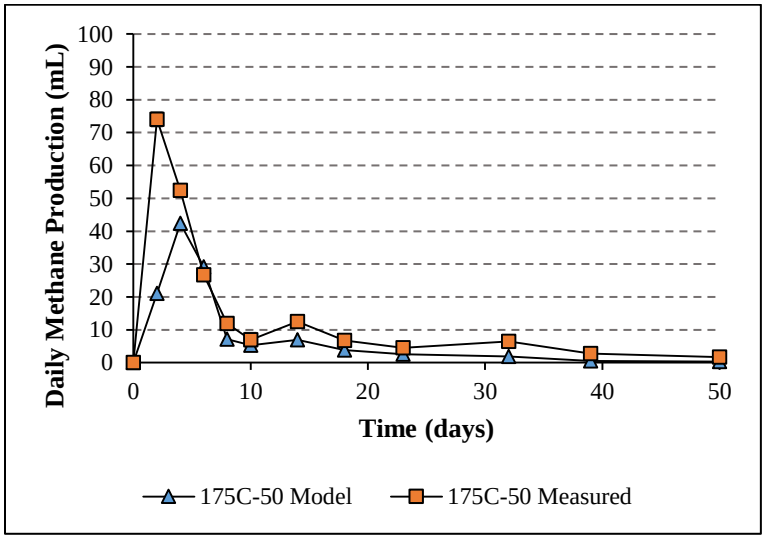

Figure I.6 Trial 1 Predicted and Measured Daily Methane Production for WAS Pretreated at 175°C – 50 Minutes

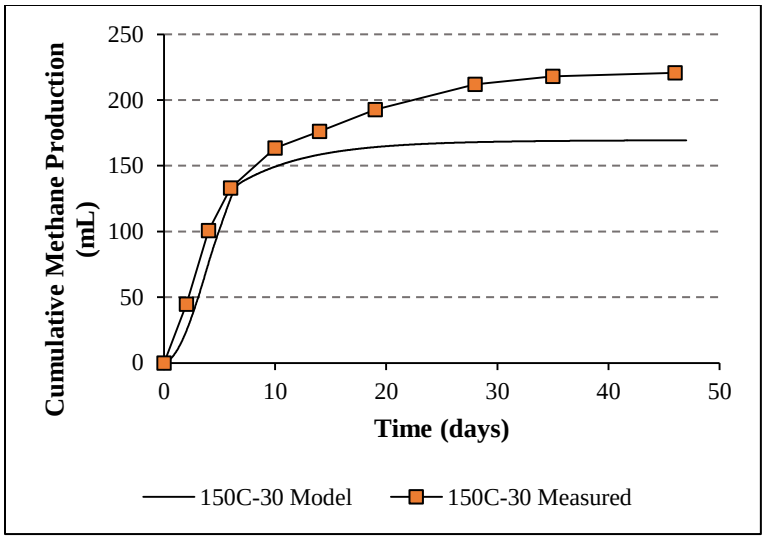

Figure I.7 Trial 2 Predicted and Measured Cumulative Methane Production for WAS Pretreated at 150°C – 30 Minutes

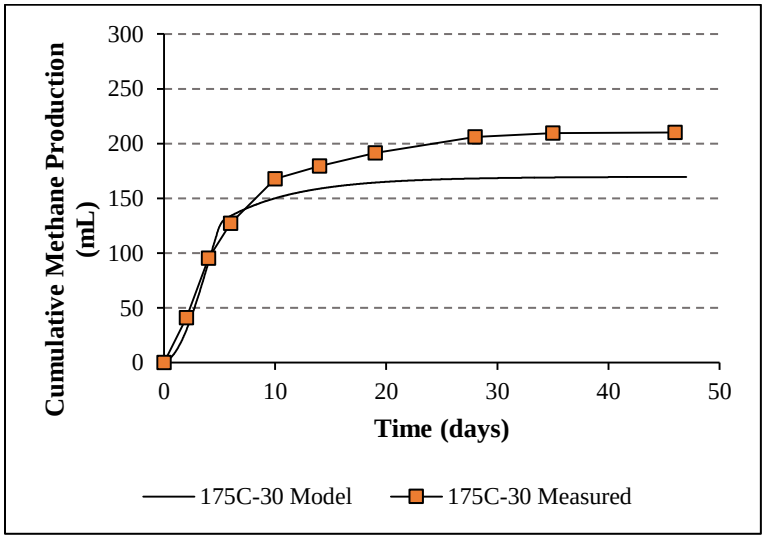

Figure I.8 Trial 2 Predicted and Measured Cumulative Methane Production for WAS Pretreated at 175°C – 30 Minutes

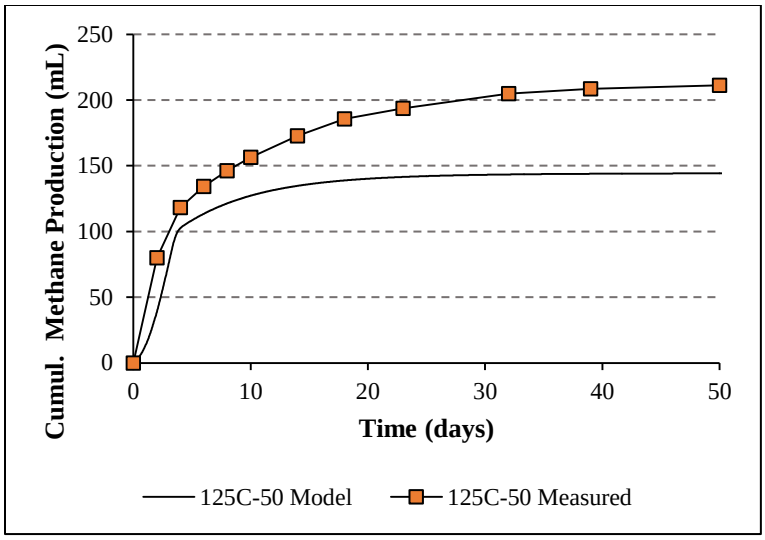

Figure I.9 Trial 2 Predicted and Measured Cumulative Methane Production for WAS Pretreated at 125°C – 50 Minutes

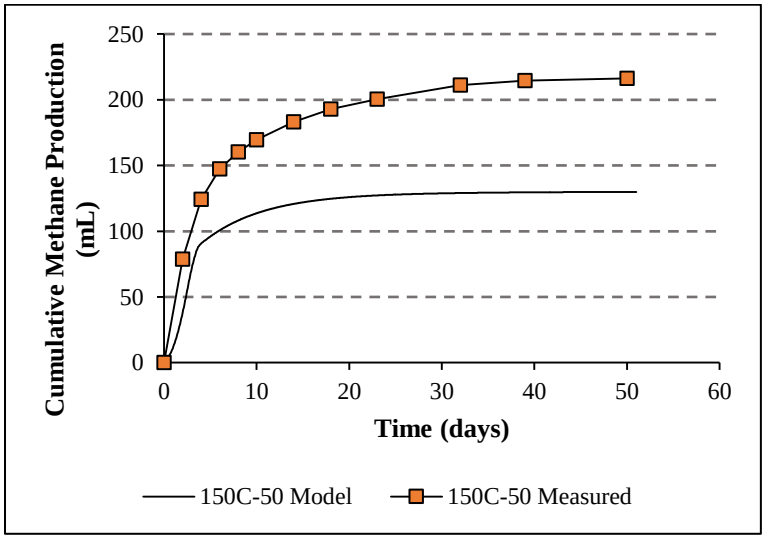

Figure I.10 Trial 2 Predicted and Measured Cumulative Methane Production for WAS Pretreated at 150°C – 50 Minutes

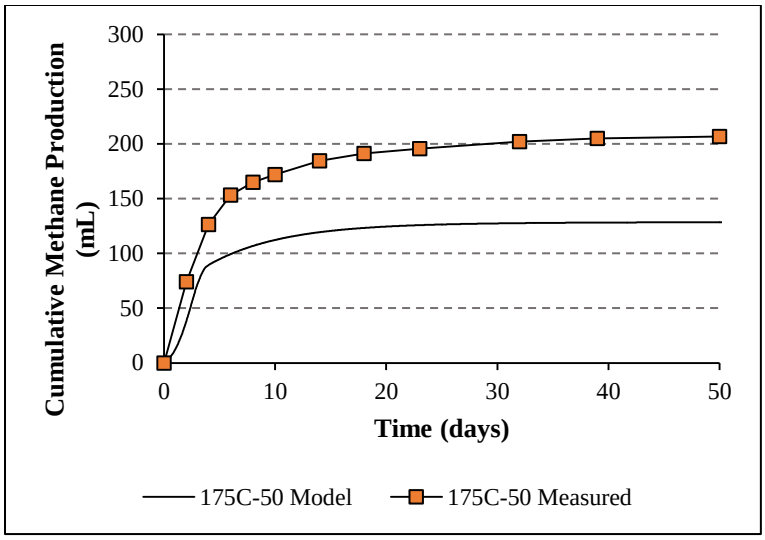

Figure I.11 Trial 2 Predicted and Measured Cumulative Methane Production for WAS Pretreated at 175°C – 50 Minutes

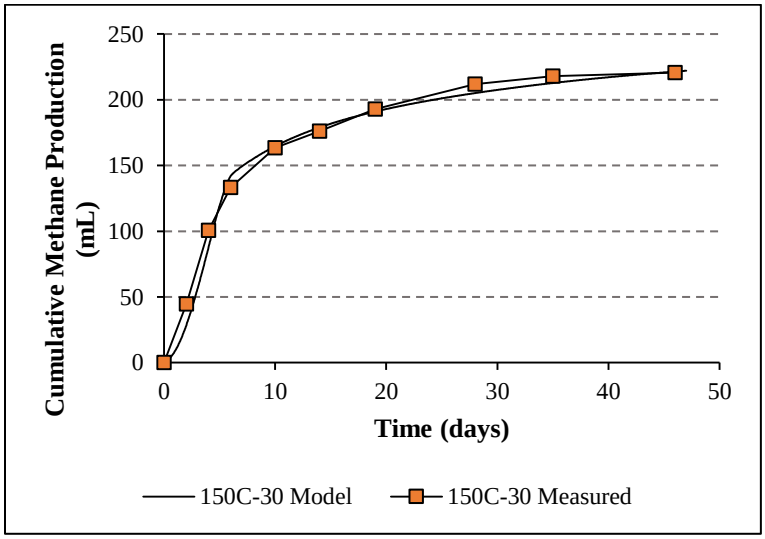

Figure I.12 Trial 3 Predicted and Measured Cumulative Methane Production for WAS Pretreated at 150°C – 30 Minutes

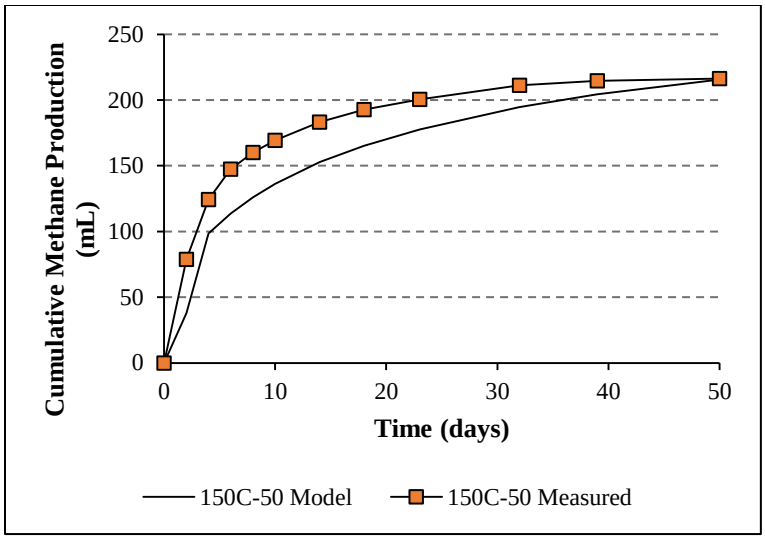

Figure I.13 Trial 3 Predicted and Measured Cumulative Methane Production for WAS Pretreated at 150°C – 50 Minutes

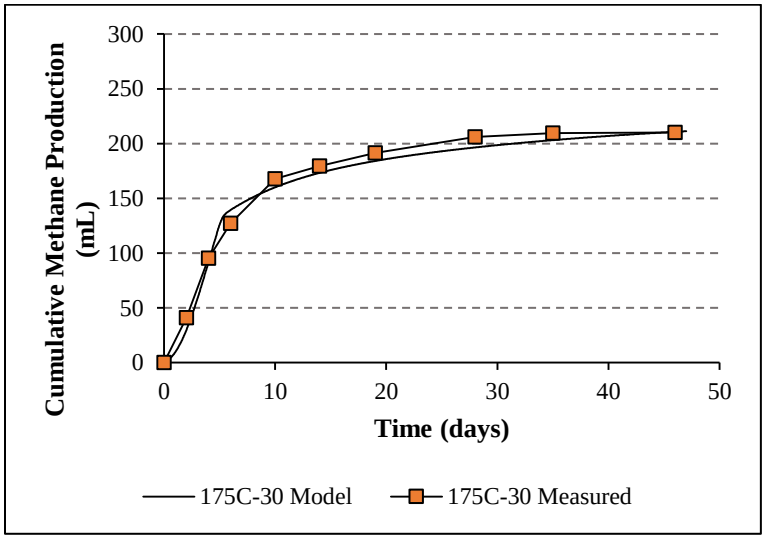

Figure I.14 Trial 3 Predicted and Measured Cumulative Methane Production for WAS Pretreated at 175°C – 30 Minutes

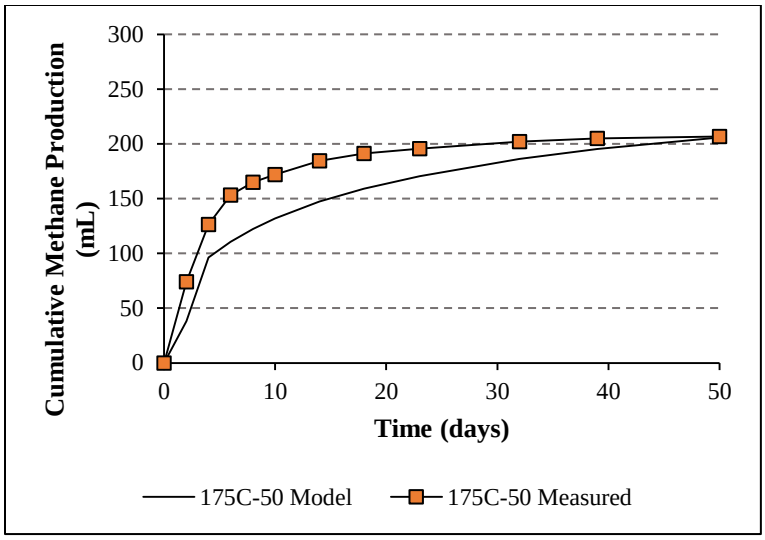

Figure I.15 Trial 3 Predicted and Measured Cumulative Methane Production for WAS Pretreated at 175°C – 50 Minutes