Effect of Alkaline Pretreatment on Anaerobic Digestion of Organic Fraction of Municipal Solid Waste

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Abstract

The rapid accumulation of municipal solid waste is a significant environmental concern in our rapidly growing world. Due to its low cost, high energy recovery and limited environmental impact anaerobic digestion (AD) is a promising solution for stabilizing the organic fraction of municipal solid waste (OFMSW). Hydrolysis is often the rate-limiting step during AD of wastes with high solid content; this step can be accelerated by pretreatment of waste prior to AD.

This thesis presents the results of alkaline pretreatment of OFMSW using NaOH and KOH. Four different pH levels 10, 11, 12 and 13 at two temperatures 23±1°C and 80±1°C were examined to study the effects of the pretreatment on (i) enhancing the solubility of the organic fraction of the waste, and (ii) enhancing the AD process and the biogas production. The effects on solubility were investigated by measuring changes in the soluble COD (SCOD) concentrations of pretreated wastes and the enhanced AD was investigated by measuring volatile solids (VS) destruction, total COD (TCOD) and SCOD removal in addition to biogas and methane production using biochemical methane potential (BMP) assay and semi-continuous laboratory reactor experiments. Pretreatment at pH 13 at 80±1°C demonstrated the maximum solubility for both NaOH and KOH pretreated samples; however the BMP analysis demonstrated that pretreatment at pH 12 at 23±1°C showed the greatest biogas yield relative to the removed VS for both chemicals. Thus pretreatment at pH 12 at 23±1°C using NaOH and KOH were examined using semi-continuous reactors at three different HRTs: 10, 15 and 20 days. Pretreatment demonstrated a significant improvement in the AD performance at SRTs of 10 and 15 days.

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List of Abbreviations

AD	Anaerobic Digestion
C:N	Carbon to Nitrogen Ratio
COD	Chemical Oxygen Demand
CSTR	Continuous Stirred Tank Reactor
eCO_2	Carbone Dioxide Equivalent
EPA	United States Environmental Protection Agency
EU	Europe Union
F/M	Food to Microorganism Ratio
GHG	Green House Gases
HPR	Herbal-Extraction Process Residue
HRT	Hydraulic Retention Time
MAP	Microwave-Assisted Alkaline Pretreatment
MB	Bead Mill
M-OFMSW	Model Organic Fraction of Municipal Solid Waste
MPS	Mean Particle Size
MSW	Municipal Solid Waste
Mt	Megatonne
MW	Microwave
MWIN	Municipal Waste Integration Network
MWP	Microwave-Assisted Water Pretreatment
OFMSW	Organic Fraction of Municipal Solid Waste
OLR	Organic Loading Rate
POME	Palm Oil Mill Effluent
PPS	Pulp and Paper Sludge

RCA	Recycling Council of Alberta
ROPEC	Robert O. Pickard Environmental Center
SCOD	Soluble Chemical Oxygen Demand
SRT	Solid Retention Time
SS	Suspended Solids
SSKW	Source Separated Kitchen Waste
SSO	Source Separated Organics
TCOD	Total Chemical Oxygen Demand
TS	Total Solids
THMB	Thermally Hydrolyzed Municipal Bio-waste
TVFAs	Total Volatile Fatty Acids
U.S	United States
VFA	Volatile Fatty Acid
VS	Volatile Solids
WAS	Waste Activated Sludge
WWTP	Waste Water Treatment Plant

CHAPTER 1: INTRODUCTION

1.1 Background

Developed and developing countries are facing serious challenges in managing their rapidly increase in waste generation. This increase is linked directly to both population and economic growth throughout the world, municipal solid waste (MSW) represents approximately 25-35% of the total generated waste. Thirty-four million tonnes of solid waste was generated in Canada in 2008, with approximately 32% of the waste being organic from sources such as food waste, leaf and yard wastes (Statistics Canada, 2010). The disposal of this large quantity of waste is an urgent economic and environmental issue with growing populations and lower availabilities of land for disposal. Inadequate disposal of waste can cause serious environmental problems such as soil, groundwater and surface water contamination due to the direct waste contact or leachate; air pollution due to uncontrolled greenhouse gase (GHG) emissions from anaerobic decomposition or burning of the waste, and spreading of diseases by different vectors such as birds and insects (Visvanathan and Glawe, 2006).

Anaerobic digestion (AD) is often considered an environmentally and economically advantageous option for the treatment of the organic fraction of municipal solid waste (OFMSW). Low level energy consumption, methane gas production, waste stabilization and waste volume reduction as well as the small footprint required for AD facilities compared to other waste treatment technologies are some advantages of AD (Torres et al., 2008; Marin et al., 2010). Although AD of solid waste is a promising resolution, the digestion of the OFMSW has demonstrated low biodegradation rates due to the complexity of the organic material (Sawayama et al., 1997).

AD can be generalized as being comprised of four distinct biochemical stages; hydrolysis, acidogenesis, acetogenesis and methanogenesis (Mata-Alvarez, 2003). For wastes with complex organics and high solids content the hydrolysis of the complex organic matter to soluble

particles is often the rate-limiting step (Torres et al., 2008; Chulhwan et al., 2005). Therefore, pretreatment of complex organic waste with high solids content prior to anaerobic digestion is beneficial in increasing the global rate of AD. Pretreatment processes are often designed to increase the solubilization of organic waste and improve the efficiency of the anaerobic decomposition of the waste by breaking down complex polymeric organics into simpler molecules (Penaud et al., 1999). Many pretreatment methods have been studied, such as mechanical pretreatment (Muller et al., 1998; Hartmann et al., 2000), ultrasound pre-treatment (Chu et al., 2002), thermal hydrolysis (Sawayama et al., 1997), microwave pre-treatment (Eskicioglu et al., 2007; Dogan and Sanin, 2009; Marin et al., 2010), and chemical pre-treatment (Torres et al., 2008; Zheng et al., 2009).

Chemical pretreatment of waste prior to AD with alkaline pretreatment has been extensively studied, results from various alkaline compounds demonstrate that NaOH and KOH are the optimum reagents for chemical pretreatment (Valo et al., 2004; Li et al., 2008; Dogan and Sanin, 2009). Although various studies have investigated the effect of chemical pretreatment of organic waste prior to AD, limited knowledge currently exist about the effect of chemical pretreatment of OFMSW prior to AD (Mata-Alvarez, 2003).

1.2 Research Objectives

The main objective of this research is to investigate the effects of alkaline pretreatment on solubilization and anaerobic digestion performance of OFMSW. These specific objectives are as follows:

- Determine the effect of alkaline pretreatment on the solubilization of OFMSW using NaOH and KOH alkaline reagents;
- assess the effects of alkaline NaOH and KOH pretreatment of OFMSW on biogas production and anaerobic digestion performance through biochemical methane potential (BMP) assays;

- evaluate biogas production and anaerobic digestion performance of OFMSW pretreated waste using semi-continuous flow reactors under the optimum conditions observed through the BMP assays;
- evaluate the cost benefits of using AD and alkaline pretreated AD to divert OFMSW from landfills in Ottawa.

1.3 Thesis Layout

Chapter 2 of this work presents a literature review which provides an overview of the world waste generation, disposal and management; this chapter also discusses AD and pretreatment in combination with AD as alternative technologies to divert OFMSW from landfills. Chapter 3 describes the materials and analytical methods used to perform the experimental work of this study. Chapter 4 presents the results and discussion of the solubilization, BMP assays and semi-continuous reactors experiments in addition to a cost estimation of an AD facility in Ottawa, Canada. Finally, conclusions and recommendations for future work are presented in Chapter 5.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

The Industrial Revolution of the 19th century that occurred in many parts of the world caused a huge industrial expansion, a great increase in the scale and complexity of the economy, and a substantial increase in the quantities of wastes produced. The nature of the wastes have changed as well; waste now contains a complex mix of materials such as plastics, metals, hazardous materials and much more (Statistics Canada, 2008; EC, 2010).

Waste is simply defined as materials unwanted by the producer; waste can be solid, liquid or gaseous, and hazardous or non-hazardous. Waste is classified by source (residential, commercial, institutional, and industrial) or by composition (organic, paper, glass, metal, plastic, etc.).

Waste is an important issue that now affects every species in the world. As the global population continues to increase the waste production also continues to grow. However, the growth in waste production is increasing at an even faster rate than the population due to increasing consumption rates and shorter product life-spans (Xudong, 2008). Since every waste material has inherently different physical and chemical properties, each waste material has a different impact on the environment. Innovative waste management policies are hence crucial to reducing the impact of these wastes on human health and the environment (Statistics Canada, 2008; EC, 2010).

2.2 Municipal Solid Waste (MSW)

2.2.1 MSW

Municipal solid waste (MSW) includes waste generated from residential, commercial, industrial and institutional activities. MSW (more commonly known as trash or garbage) consists of items that we use in our daily life and inevitably throw away when there is no more need for them.

These items are ultimately collected and managed by municipalities. MSW constitutes about 25-35% of the total waste generated in high income countries (World Bank, 1999) .Table 2.1 shows sources and types of MSW (EC, 2010).

MSW is especially important because of its composition, its distribution among many generators and its direct link to consumption patterns (Blumenthal, 2011).

Table 2.1: Sources and types of solid wastes (World Bank, 1999).

Source	Typical waste generator	Types of solid waste
Residential	Single and multifamily dwellings	Food wastes, paper, cardboard, plastics, textiles, leather, yard wastes, wood, glass, metals, ashes, special wastes (e.g., bulky items, consumer electronics, white goods, batteries, oil, tires), and household hazardous wastes
Industrial	Light and heavy manufacturing, fabrication, construction sites, power and chemical plants	Housekeeping wastes, packaging, food wastes, construction and fabrication, construction sites, demolition materials, hazardous wastes, ashes, special wastes
Commercial	Stores, hotels, restaurants, markets, office buildings, etc.	Paper, cardboard, plastics, wood, food wastes, glass, metals, special wastes, hazardous wastes
Institutional	Schools, hospitals, prisons, government centers	Same as commercial

2.2.2 MSW Production

In Canada the total MSW generated has been steadily increasing since the 1980s, which is related to the continuous trend towards urbanization, and a shift in the types and patterns of consumption, household revenue, and lifestyles of Canadians (OECD, 2008). The amount of municipal waste generated per capita in Canada has also been steadily increasing since 1980.

Between 1990 and 2005, Canadians increased their municipal waste per capita by 24% reaching about 791 kg per capita of municipal waste each year.

In 2009, Americans produced about 243 million tons of MSW, or around 712 kg of waste per capita per year (EPA, 2011). The handling and disposal of MSW is a growing concern in the U.S as the volume of waste generated continues to increase. Figure 2.1 shows clearly this increasing trend for the past 50 years.

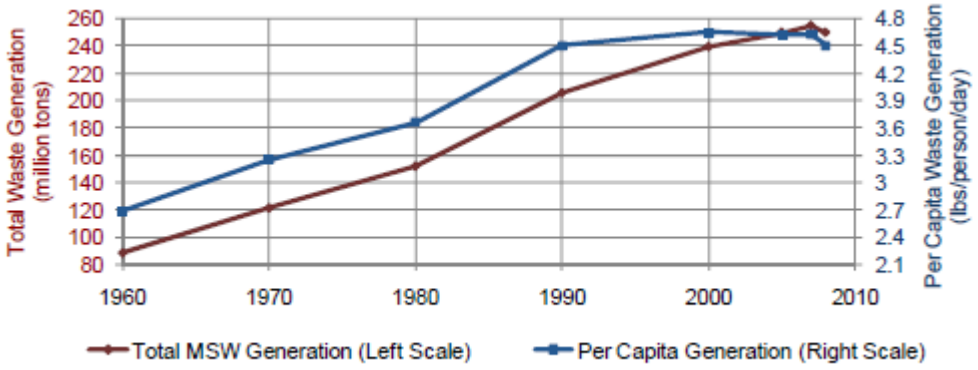

Figure 2.1: U.S annual MSW generation, 1960 -2009 (EPA, 2011).

The countries forming the Europe Union (EU) produce up to 3 billion tonnes of waste every year. On average each of the 500 million people in EU throws away about half a tonne of household garbage every year. This huge amount of wastes has a detrimental impact on the local environment due to the release of pollutions and the production of greenhouse gas emissions which contribute directly to climate change (EC, 2010).

In other parts of the world the uncontrolled and unmonitored urbanization of the developing countries in Asia are creating potentially serious waste disposal problems. Urban areas of Asia produce about 760,000 tonnes of MSW per day; by 2025 this figure will increase up to at least 1.8 million tonnes of MSW per day (World Bank, 1999; Visvanathan and Trankler, 2005).

According to the Organization for Economic Co-operation and Development (OECD, 2008) report that compares the MSW generation of the 17 member countries, Canada ranked in the last place with a daily per capita production of municipal waste almost twice as much as the year's best performer, Japan (Figure 2.2).

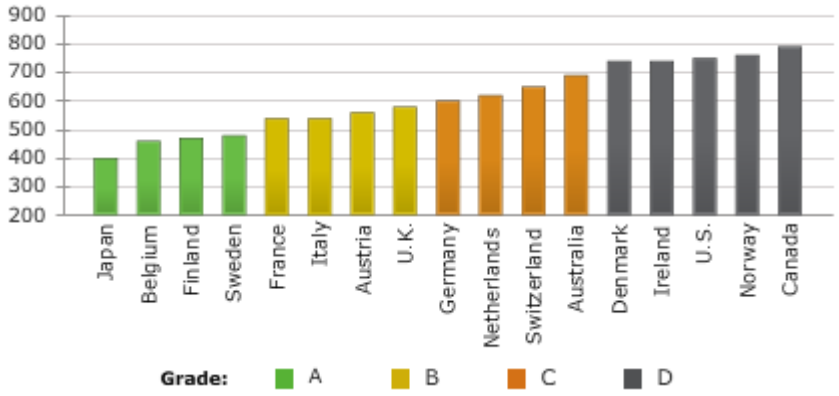

Figure 2.2: World municipal waste generation 2005, or most recent (Kilograms per capita) (OECD, 2008).

2.2.3 MSW Composition

Waste composition is the main factor that influences the emissions from solid waste treatment facilities as different wastes contain various amounts of degradable organic carbon and fossil carbon.

The composition of waste is a guide to the most effective way to deal with the waste. For example, the composition allows the engineer to estimate the amount of biodegradable organic carbon that can be composted or bio-treated, and the amount of recyclable materials that can be diverted from the landfills. Figures 2.3 and 2.4 show the 2005 Canadian and American waste composition (EPA, 2011).

Geographical location, population's standard of living, energy source and weather play a significant role in municipal waste composition. Thus, MSW compositions vary between city to city in the same country and it also varies by day of the week, season and year in the same city (OECD, 2008; IPCC, 2006).

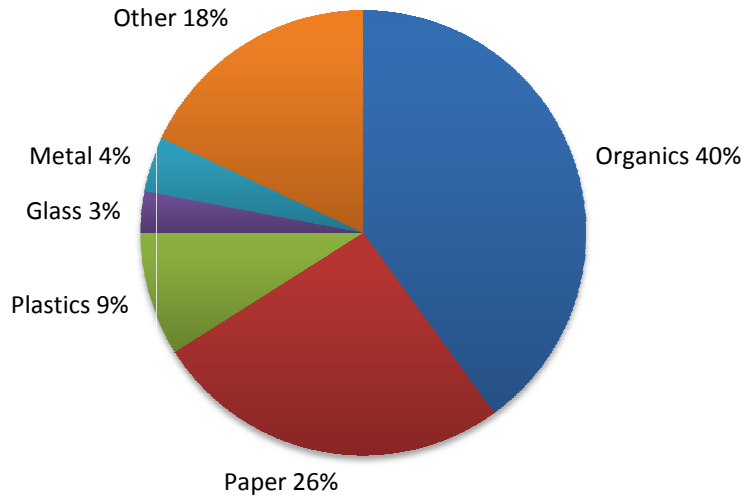

Figure 2.3: Composition of MSW by weight, 2005 (Statistics Canada, 2008).

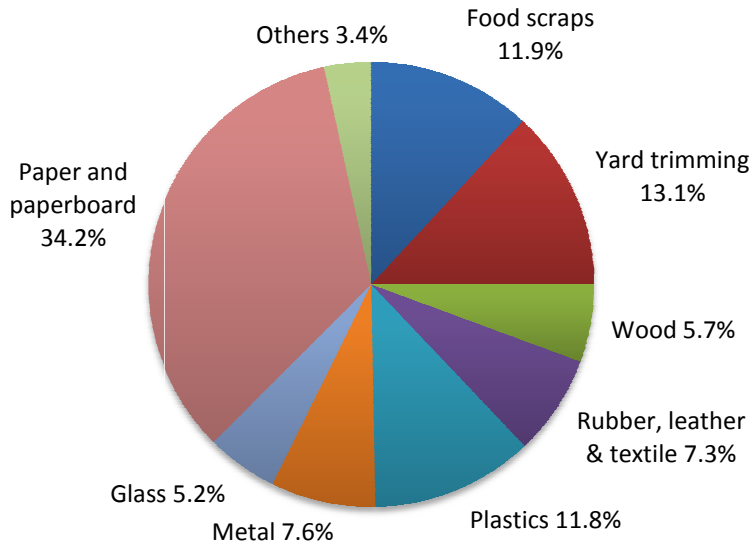

Figure 2.4: Total MSW generation in USA, 2005 (EPA, 2005).

As a general trend, in low and middle income countries biodegradable organic matter represents a high percentage of the total MSW produced, ranging from 40 to 85 percent of the

total MSW. As countries develop and become more urbanized, the waste composition changes, the presence of papers, paper packaging, plastics, multi material packing items and consumer products increase significantly in the waste (World Bank, 1999). An example of this is presented in Figure 2.5 below; this figure shows the average urban waste compositions for low, middle, and high income Asian countries (World Bank, 1999).

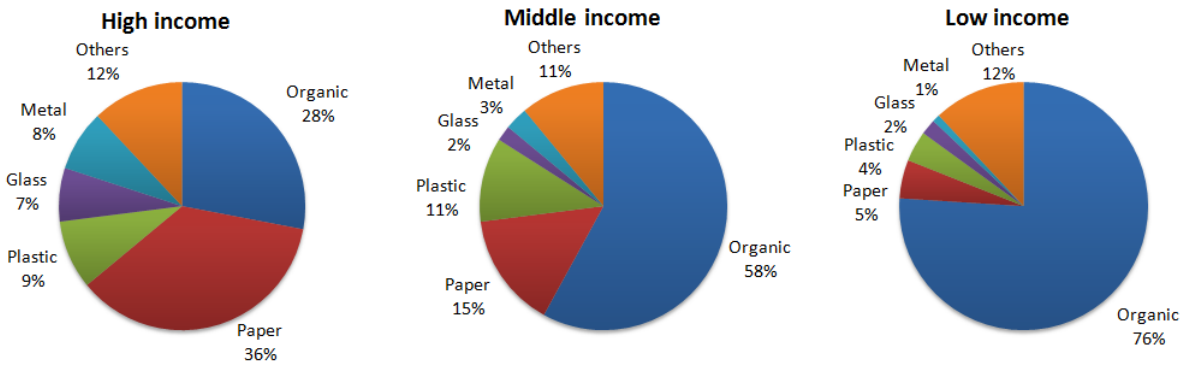

Figure 2.5: Waste composition of low, middle, and high income countries in Asia (World Bank, 1999).

2.2.4 OFMSW

Organic waste, also known as bio-waste, is the organic fraction of the municipal solid waste. This waste includes garden, kitchen and food waste. Organic waste makes up the largest component of residential waste in Canada; equalling about 40% of the total MSW generated. In 2002 Canadian households generated more than 12 million tonnes of residential solid waste with only 2.5 million tonnes being diverted through recycling, reuse, or composting. The remaining 9.5 million tonnes of generated waste was disposed into landfills or incinerated (Statistics Canada, 2008).

Organic waste accounts for about one third of the total MSW, which is approximately 88 million tonnes across Europe every year with 40% of organic waste in EU going into landfills (EU, 2010). In 2009 the U.S. generated 34 million tonnes of waste just from food (food waste is about 14% of the total municipal solid stream), less than 3% of this huge amount of food waste was recovered or recycled and the remaining 33 million tonnes was landfilled (EPA, 2011).

2.3 Municipal Solid Waste Management and Methods of Disposal

Managing the rapidly increasing waste generated across the world is a serious challenge that current Governments face. It is becoming critical that countries have waste management policies that aim to reduce the environmental and health impact of these wastes (EC, 2010). Conventional MSW disposal and treatment strategies include landfilling, incineration, recycling, composting and anaerobic digestion. Landfilling, composting and anaerobic digestion are discussed in the following sections of this chapter. Landfilling is one of the oldest waste treatment methods, but still highly used for MSW disposal all around the world. Composting and anaerobic digestion are alternative methods used to divert MSW from landfills.

2.3.1 Landfilling

Landfilling is the disposal of waste on or in the earth's surface and it is one of the oldest forms of waste disposal and treatment. Although this method is not a preferred option as Landfilling waste has many serious adverse impacts on health and environment, this method is still the most common way to dispose of the waste in many countries, including Canada, U.S, China and some European countries (Statistics Canada, 2008).

The decomposition process of biodegradable waste in landfills produces a mixture of gases which are composed primarily of methane (CH_4). Methane is a powerful green house gas which is 21 times more potent than carbon dioxide (CO_2) in terms of its effect on global warming (Environment Canada, 2010; EC, 2010). Another output of the decomposition process in landfills is the leachate that may contain different contaminants like heavy metals (Pb, Ni, Cu, Hg), dissolved organic matter (alcohols, acids, aldehydes, etc.), and inorganic compounds (common cations and anions such as sulphate, chloride and ammonia). Leachate can contaminate soil, surface and ground water (EC, 2010). However modern landfills are very different from old-style landfills; liners are used in new sanitary landfills to prevent leachate from moving into groundwater, also they include collection and treatment systems for leachate and gas emissions (Statistics Canada, 2008).

Canada sends the majority of its municipal solid waste to landfills, with only a small percentage incinerated. In 2000, Canada's landfills accepted 23 million tonnes of waste which is about 95% of the total amount of waste disposed that year (the remaining 5% was incinerated) (Statistics Canada, 2008). In 2008, the total waste generated was 34 million tonnes which was handled by the waste management industry; 26 million tonnes was disposed of in landfills or incinerated (Statistics Canada, 2008).

Canadian landfills are responsible for 20% of the national methane emissions. Canadian landfills generate about 27 Megatonne (Mt) of carbon dioxide equivalents (eCO_2) annually, with approximately 20 Mt eCO_2 being emitted into the atmosphere and the remaining 7 Mt eCO_2 being captured and combusted. Restricting the release of 7 Mt eCO_2 is equivalent to removing approximately 5.5 million cars off the road (Environment Canada, 2010).

The high reliance on landfills in Canada is most probably because of the high availability of land (OECD, 2008). As 30% of landfills in Canada were expected to be full by 2010 (Statistics Canada, 2008), municipalities are facing an urgent challenge to find viable locations for waste disposal. Although there is ample space to create landfill sites many residents refuse to have landfills close to their communities. For example when Toronto's Keele Valley landfill reached the full capacity in 1990s the municipality proposed shipping Toronto's municipal waste to Kirkland Lake ,Ontario, by rail (about 590 kilometers) but the 9,000 residents of the Kirkland Lake refused accepting Toronto's municipal waste to be dumped in an abandoned mine in their community. The community ended up preventing this dumping of waste in their communities and since 2003 Toronto's municipal waste has been exported to a landfill in Michigan, U.S (OECD, 2008).

Currently, in the United States, 54.3% of the municipal solid waste is disposed of in 1,831 landfills across the country. While the total number of landfills has been decreased steadily in the U.S., the total capacity has increased (EPA, 2011; CSS, 2008)

In some of the European Union (EU) countries landfilling is still the most common form of MSW disposal. For example Bulgaria landfills 100% of its waste. But this is not the case for all EU countries where many EU countries are successful in diverting their waste from landfills.

Between 1995 and 2009 the amount of MSW landfilled in the EU was reduced from 141.3 to 95.7 million tonnes, which is equal to an approximate annual decline of 2.7%. Figure 2.6 shows the decline in amount of waste landfilled per capita for this period (1995-2009) in EU.

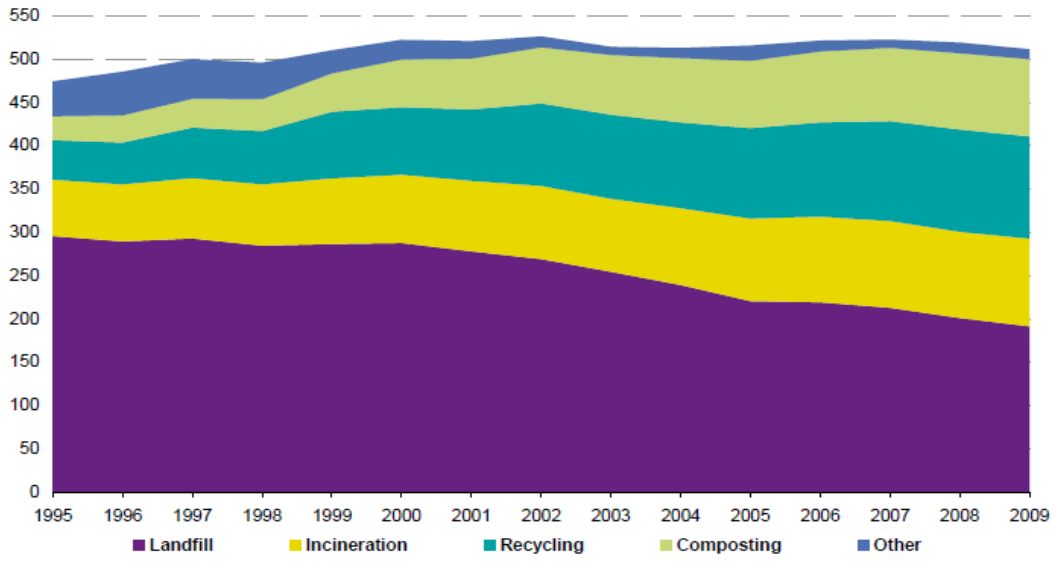

Figure 2.6: Municipal waste treatment, EU, (kg per capita) (Blumenthal, 2011).

This reduction of MSW landfilled in EU is the dedicated resolve of the EU to minimize the negative effect of waste while maximizing the benefits of good waste. EU countries used many material recovery strategies to divert waste from landfilling. For example in Sweden, Denmark and Germany, there has been a ban on landfilling municipal waste before treating it using anaerobic digestion (AD) or incineration. The adoption of this strategy has resulted in a drop in the landfilled municipal waste per capita in Sweden from 64 kg/capita in 2003 to 7 kg/capita in 2009. In the Netherlands the direct disposal of mixed municipal waste was banned in 2003 resulting in only 4 kg per capita MSW being directly landfilled in 2009 (EC, 2010; Blumenthal, 2011).

As a result of the increasing concern for the environment, communities around the world now realize that in order to safely handle the current and future MSW with minimum inverse impact

to health and environment, existing waste management systems need to be improved. Thus innovative ways to reduce generated solid waste while increasing the amount of waste diverted from landfills by using waste as a resource of energy and good materials are urgently needed.

This need has resulted in communities turning to organic management programs that reduce their reliance on conventional residential treatment disposal technologies (landfilling and incineration). Re-using, recycling, composting and anaerobic digestion are examples of popular waste diversion methods, with the last two methods being preferred for the organic fraction of municipal solid waste (OFMSW) (Statistics Canada, 2008; MWIN, 2006).

Composting and AD offer a biological route to divert the organic waste from landfills, however it should be noted that composting is energy consuming process while AD is an energy producing process. Further details regarding composting and AD are discussed in the following sections.

2.3.2 Composting

Composting is the aerobic process where the microorganisms decompose organic matter under controlled conditions to produce a biologically stable end product. MSW composting breaks down the degradable portion of the waste like plants, animal tissues and food waste. The final result is a significant reduction (up to 50%) in the organic mass. During the composting process microorganisms oxidize organic matter using oxygen as an electron acceptor and produce mainly carbon dioxide and water vapor while releasing heat (Ipek et al., 2002). A generalized mass balance for microbial composting is shown in Figure 2.7.

Figure 2.7: Mass balance of composting process (MWIN, 2006).

2.3.2.1 Composting biology

The organisms responsible for the composting process include the following six groups listed according to their abundance: bacteria, actinomycetes, fungi, protozoa, worms, and larvae (Techobanoglous, 2002). Although actinomycetes are bacteria, they are named separately because of their special role in the curing stage of the composting stage.

2.3.2.2 Composting phases

The composting process can be divided in three main stages:

Lag phase

This phase starts as soon as composting conditions are established and can be considered as the period of adaptation of the microbes to the waste environment.

Microbes start to proliferate feeding on sugars, starches, simple celluloses, and amino acids which are available in the raw waste. The result is the release of nutrients from the degraded waste. In this stage the temperature begins to rise in the mass of waste because of the accelerating activity of the microorganisms. This stage may last for several days (Techobanoglous, 2002).

Active phase

This phase is also called the high rate composting phase. The transition from lag phase to active phase can be noted by an exponential increase in microbial counts numbers and a related intensification of microbial activity. This stage mainly involves the development of bio-oxidation reactions; the available organic matter is used as an energy and carbon source by the microorganisms. The activity remains at peak levels until an available nutrients or easily decomposed materials are no longer available. During this period the temperature increases continuously and may reach 70°C or higher. The duration of this stage varies depending on the environmental and operation conditions; it may last for five or six days or as long as two to five weeks (Techobanoglous, 2002).

Curing phase

This phase involves the production of macromolecular humus-like substances and the formation of mature compost. In this phase the easily decomposable materials have decreased significantly and the portion of materials that are more resistant to biodegradation rises. Thus, this phase is characterized by a steady decline in microbial proliferation.

The temperature also continuously declines in this phase until it reaches ambient temperature, this may take a few weeks to as long as a year or two depending on the type of waste and the environmental and operational conditions (Moustakas et al., 2007). A typical composting process flow diagram is shown in Figure 2.8 below.

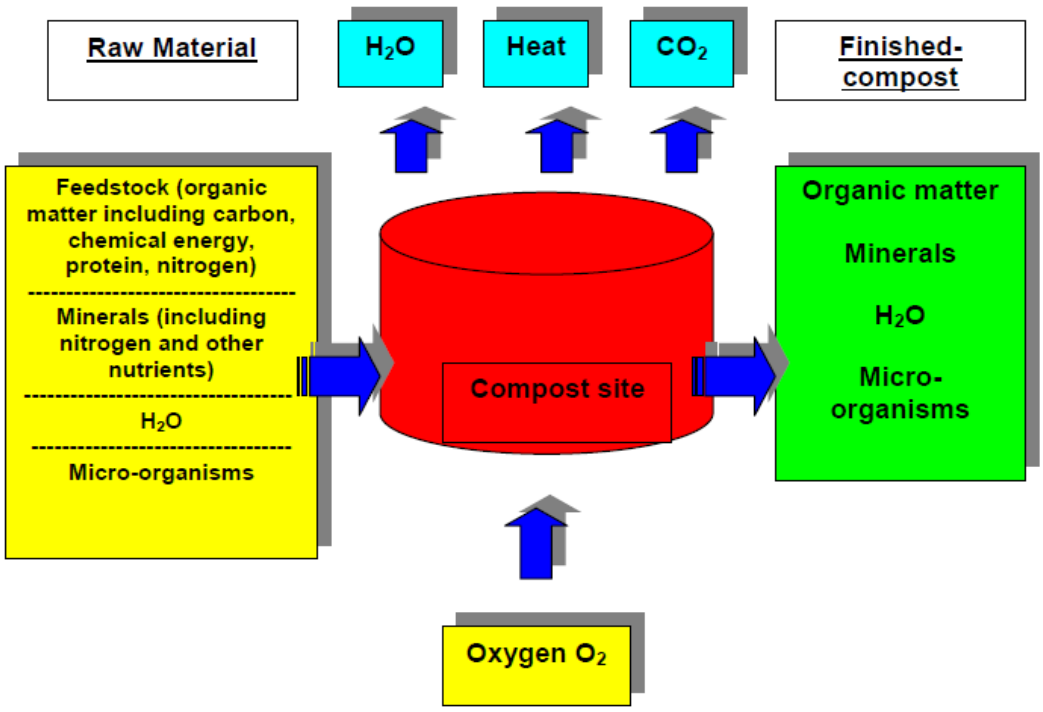

Figure 2.8: Composting process flow chart (Kumar, 2011).

2.3.2.3 Composting systems

The composting systems can be classified in two main categories the "windrow "and the "in-vessel" composting systems.

Windrow composting system

Windrow composting is the most common method used for rapid composting of organic wastes. Generally in this type of composting the mixed materials are placing in long narrow piles. Windrows are typically 10 to 12 feet deep, 3to 12 feet wide, and up to hundreds of feet long. The cross section of the windrows is usually trapezoidal or triangular. Regarding the aeration of the system, windrows may be "turned windrow" type or "forced air windrow or static pile" type, or a combination of the two (Moustakas et al., 2007). Figure 2.9 below shows a schematic diagram of aerated static pile composting.

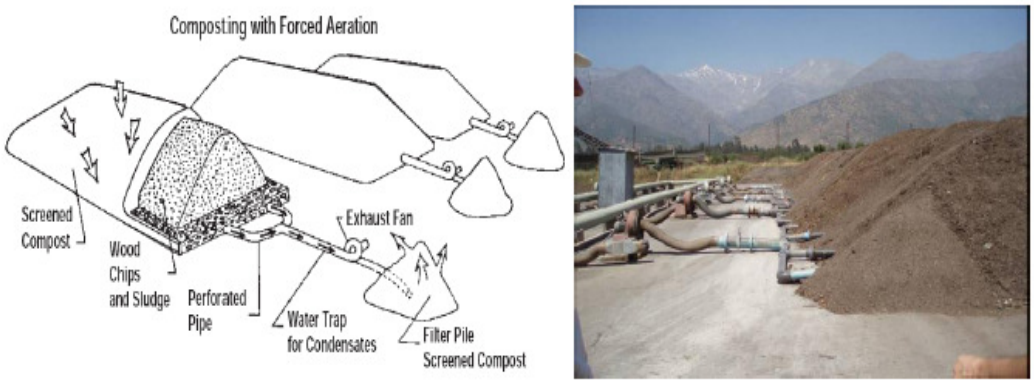

Figure 2.9: Schematic diagram of aerated static pile composting (Techobanoglous, 2002).

In-vessel systems

In-vessel composting refers to the composting process within a container, building or vessel. These composting systems help the operators to have closer control over the process in comparison with the other composting methods. Also in-vessel systems help to minimize odors problem and reduce process time by providing beneficial environmental conditions with respect to oxygen availability concentration, temperature, and moisture. In–vessel systems, also called bioreactors, use forced aeration and mechanical turning to speed up the composting process. However, because in-vessel systems have high capital, operating, and maintenance costs (ranging from $40 to $150 per wet ton of waste), these systems are not often used to

compost yard waste; they are usually used to compost sludge, mixed solid waste, and other hard-to-manage materials (Moustakas et al., 2007).

2.3.2.4 Composting in Canada

Canadian gardeners in general are familiar with backyard composting. Larger scale centralized composting facilities has become more common since the early 1990s in Canada, where these facilities are used by households as well as commercial establishments. Also some businesses and other organizations in the industrial, commercial and institutional sectors increasingly use on-site composting facilities (Statistics Canada, 2008).

Across Canada many municipalities encourage the public to divert the organic waste to composting facilities using policies and incentives. For example, some municipalities such as Hamilton and Quebec City collect residential yard waste as part of their composting programs. In other regions municipalities encourage residents to compost organic waste at home, by offering manuals, instructions and workshops on building compost bins. Also there are many local governments that offer subsidized compost bins as well (Statistics Canada, 2008).

From 2000 to 2004, a 70% increase was observed in centralized composting facilities. In 2002, Canada had 351 centralized facilities that compost organic waste, compared with 255 in 2000. Furthermore, by 2004 each Canadian sent about 51 kg of organic waste for composting (Statistics Canada, 2008).

2.3.2.5 Composting health issues

In large scale composting facilities (especially during shredding, turning or screening operations) airborne bacteria, fungi and other microorganisms have been measured in high concentrations. Although these concentrations quickly drop to background levels within a short distance, concerns has been voiced over potential health problems that may be caused by the exposure to these compost microorganisms. Studies of compost workers show a low serious negative health effects (Swan et al., 2002). Also pathogenic bacteria that may be present in compost, especially compost that contains animal manures or biosolids, are normally destroyed by the heat generated during the composting process (Statistics Canada, 2008).

2.3.3 Anaerobic Digestion

A second common method of diverting organic waste from landfills is to send the waste to AD systems. Historically, the potential for energy recovery, rather than the environmental benefits, has resulted in an increased interest in AD technology (Griffin et al., 1998). Methane gas produced by AD can be used to replace other sources of power such as fossil fuels. From a greenhouse gas point of view anaerobic digestion restricts the release of greenhouse gases and is thus advantageous as compared to composting. Anaerobic digestion is also an attractive MSW treatment technology because it reduces the volume of MSW, stabilizes the MSW, produces a residual that can be used for soil conditioning, and has a smaller footprint than composting systems (EC, 2010).

2.3.3.1 Anaerobic digestion definition

AD is defined as the biological decomposition of organic materials by anaerobic microorganisms (Figure 2.10). During this process the anaerobic microorganisms metabolize organic materials to more stabilized forms while producing a high energy gas mixture (biogas) that consists mainly of methane (CH_4) and carbon dioxide (CO_2) (Wastesum, 2009).

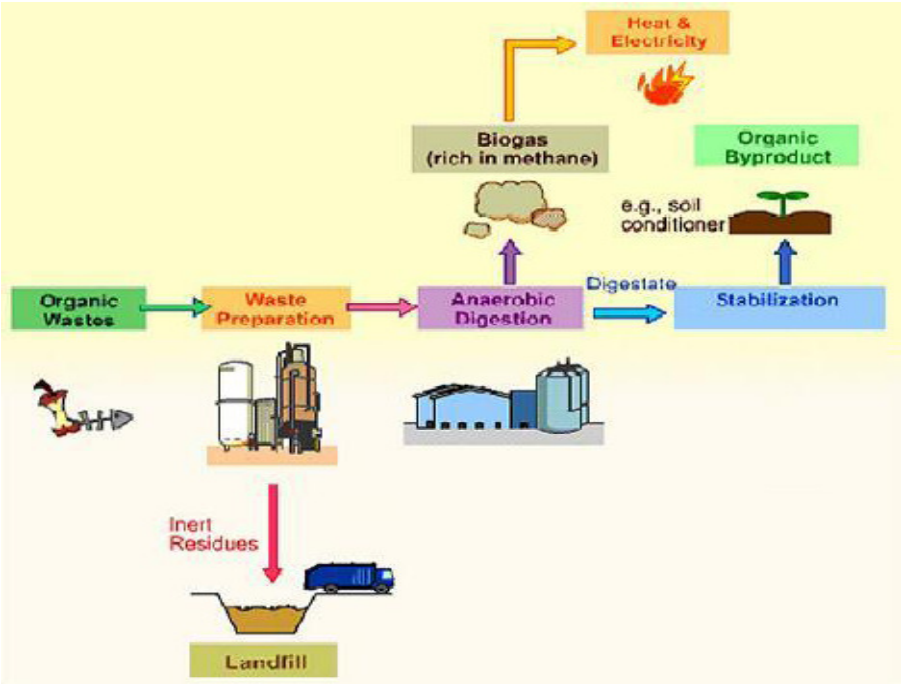

Figure 2.10: Anaerobic digestion flow chart (Wastesum, 2009).

2.3.3.2 History of anaerobic digestion

Historical evidence indicates that the AD process is one of the oldest technologies used by human. During the 10^{th} century BC biogas was used for heating bath water in Assyria (Verma, 2002). However the industrialization of AD started in 1859 with the first digestion plant being constructed in Bombay, India. By 1895, AD was used in England where biogas was recovered from a sewage treatment facility and used to fuel street lamps in Exeter, England (Verma, 2002; EPA, 2008). Prior to 1920, most of the AD took place in anaerobic ponds, but as the understanding of AD process improved over time new equipment and improved operational techniques led to the development of heated, mixed, closed tank systems.

India, China and Southeast Asia responded to the energy crisis of 1973 by expanding their AD activities. Most of the AD systems were small digesters using human, animal and kitchen wastes. In recent years, due to growing environmental pressures and the high energy prices, Europe is expanding its AD market (Verma, 2002).

Current AD facilities in Europe generally have had a good record in treating a wide range of waste streams such as farm, industrial, and municipal wastes. There are more than 600 farm-based simple digesters, more than 30 large centralized digesters, and more than 30 large centralized digesters currently under construction in Europe (Verma, 2002).

2.3.3.3 Anaerobic digestion biology

The anaerobic digestion of organic matter requires the concerted action of a consortium of microorganisms (bacteria, archaea and fungi). These bacteria work in the absence of oxygen, converting organic matter to intermediate molecules such as sugar, hydrogen and acetic acid which are subsequently converted to biogas. The resulting biogas in most systems consists of 60%–70% methane and 30%–40% carbon dioxide, with trace components of ammonia (NH_3) as well as hydrogen sulphide (H_2S). The AD process has four key biological and chemical stages; hydrolysis, acidogenesis, acetogenesis and methanogenesis, as shown in Figure 2.11 (Mata-Alvarez, 2003; Moustakas et al., 2007).

Hydrolysis (liquefaction)

This is the first stage of the AD process, where the hydrolytic microorganisms produce hydrolytic enzymes that decompose the complex (long-chain) organic polymers such as

proteins, polysaccharides and lipids to monomeric soluble compounds. These soluble products are small enough to allow their transport across the cell membranes of the acidogenic bacteria (Mata-Alvarez, 2003). Hydrolysis is often the rate-limiting step in the AD processes for waste containing lipids and/or high organic content (e.g., food waste, sludge, animal manure) (Griffin et al., 1998; Mata-Alvarez, 2003; Chou et al., 2010). The simplified hydrolysis/ liquefaction reactions are as follows:

Lipids → Fatty Acids

Polysaccharides → Monosaccharides

Protein → Amino Acids

Nucleic Acids → Purines & Pyrimidines (Verma, 2002).

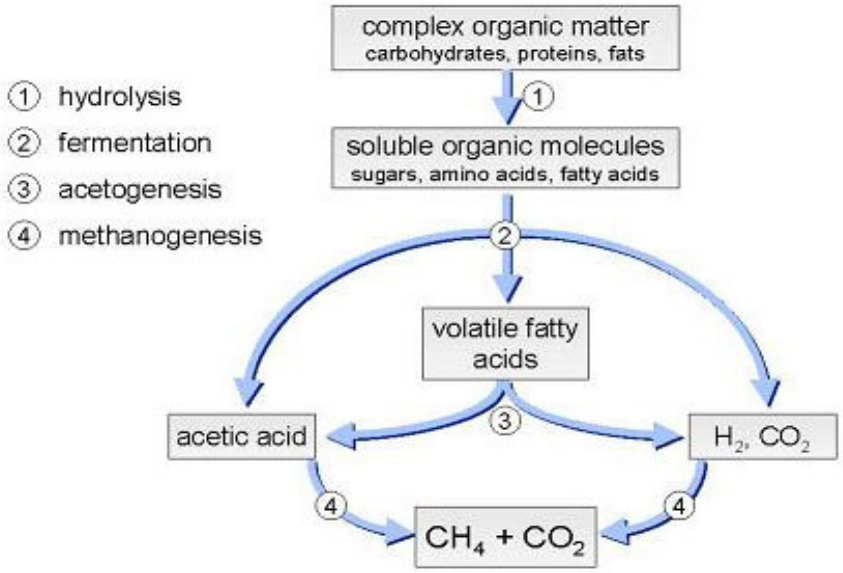

Figure 2.11: The stages of AD process (EPA, 2011).

Acidogenesis (fermentation)

This is the second stage in the AD process. In this stage the acidogenic bacteria break down the products produced during hydrolysis. The products produced during this stage are volatile fatty

acids, ammonia, carbon dioxide and hydrogen sulfide as well as other by-products (Griffin et al., 1998; Verma, 2002).

Acetogenesis

During this stage of AD simple molecules that have been produced from the previous stage (e.g. acetate (CH_3COO^-)) are further degraded by acetogenic bacteria. The result of this stage is the production of mainly acetic acid (CH_3COOH) along with carbon dioxide and hydrogen (Moustskas et al., 2007).

Methanogenesis

This is the final stage of AD process; in this stage methanogenic microorganisms (also called methane producers) convert the intermediate products of the previous stages into methane, carbon dioxide and water. Methanogenic archaea produce methane in two ways: first by using acetic acid molecules to generate carbon dioxide and methane and second by the reduction of carbon dioxide with hydrogen to form methane and water. Usually the methane production via carbon dioxide reduction is higher than the methane production via acetic reaction, however in anaerobic digesters the limited quantity of hydrogen results in the acetate reaction being the primary producer of methane in this stage (Techobanoglous, 2002; Verma, 2002). The methanogenesis reactions can be expressed as:

$$\underset{\text{(Acetic acid)}}{CH_3COOH} \rightarrow \underset{\text{(Methane)}}{CH_4} + \underset{\text{(Carbon dioxide)}}{CO_2}$$

$$\underset{\text{(Ethanol)}}{2C_2H_5OH} + CO_2 \rightarrow CH_4 + 2CH_3COOH$$

$$CO_2 + \underset{\text{(Hydrogen)}}{4H_2} \rightarrow CH_4 + \underset{\text{(Water)}}{2H_2O}$$

The remaining non-digestable organic material and the dead bacteria form the digestate that is removed from the digesters and dewatered (Moustakas et al., 2007). The liquid stream from

the dewatering process is often filtered and circulated back to the digester. The dewatered solid is then commonly cured aerobically to form compos with the final product being screened to remove any undesirable materials before being used on land or sold as soil (Griffin et al., 1998; Moustakas et al., 2007).

2.3.3.3 Environmental conditions and variables controlling the AD process

AD is very sensitive to changes in environmental conditions. Therefore to operate an AD reactor successfully it is necessary to maintain the reactor conditions such that the microorganisms remain active. Usually the effect of environmental factors on AD process is evaluated by the methane yield of the process. Brief descriptions of the most important environmental factors follow below.

Temperature

Anaerobic digestion processes, like other biological processes, depend strongly on temperature. To provide optimum digestion conditions for the production of methane there are mainly two temperature ranges of operation:

- Mesophilic: 30-40°C, usually 35°C.
- Thermophilic: 50-65°C, usually 55°C (Mata-Alvarez, 2003).

Generally, anaerobic digestion processes are more sensitive to temperature than aerobic process. Anaerobic digesters operating under thermophilic conditions usually are more efficient in terms of retention time, loading rate and gas production. However thermophilic AD systems can become more readily imbalanced and are therefore more difficult to operate. For example, the thermophilic digestion of highly biodegradable waste can cause acidogenesis to over produce more acids that in turn negatively impact methanogenesis and ultimately reduce the efficiency of the overall digestion (Mata-Alvarez, 2003). Also thermophilic conditions require an input of heat which makes this process more problematic than mesophilic digestion. However with respect to sterilization of the waste, the higher temperatures of the thermophilic digestion increase the effectiveness of eliminating pathogens, viruses and seeds (Verma, 2002).

pH level

During AD, the optimum pH level depends on the anaerobic fermentation stage. During the acidification process the acidogenic microorganisms prefer a pH between 5.5 and 6.5, while during the methanogenesis process methanogenic microorganisms prefer a pH between 6 and 8.

When both cultures coexist in the same bioreactor (e.g. one stage process) methanogenesis is considered to be the most sensitive step, and so it is necessary to maintain the pH of the reactor near 7.0 (Griffin et al., 1998; Moustakas et al., 2007). Acetogenesis can cause the accumulation of a large amount of organic acids that will lower the pH in a one stage reactor and as mentioned above this will inhibit the methanogenic microorganisms. The pH of the reactor can be buffered by adding bicarbonate alkalinity (Verma, 2002; Mata-Alvarez, 2003). Alkalinity is defined as the ability of the system to neutralise acids and thus resist the changes in pH.

Carbon to nitrogen ratio (C:N)

C:N ratio represents the relation between the amount of carbon and nitrogen available in the organic materials. For anaerobic digesters the optimum C:N ratio is between 20 and 30. High C:N ratios may result in the complete consumption of nitrogen by methanogens that results in lower consumption of carbon and lower gas production. On the other hand if the C:N ratio is low ammonia may accumulate in the system, pH values to rise potentially exceeding 8.5, and inhibit methanogenic activity (Verma, 2002).

Organic loading rate

The organic loading rate (OLR) is defined as the quantity of substrate introduced into the reactor volume for a given time. The substrate can be defined by means of different measured parameters, as total solids (TS), volatile solids (VS) or chemical oxygen demand (COD). For organic waste usually volatile solids is used to express the OLR as kg of volatile solids (VS) per cubic meter of reactor volume per unit time (Mata-Alvarez, 2003). OLR is a measure of the biological conversion capacity of the AD system. OLR can be considered as one of the main controlling parameters in AD continuous systems. Overloading the reactors by feeding the

system above its sustainable OLR results in the accumulation of inhibition substances in the digester slurry (e.g. volatile fatty acids) and lower biogas yields are observed.

Solid retention time

The average solid retention time (SRT) in the reactor is the ratio between the content of the solids in the reactor and the solids flow rate extracted from the reactor. SRT is one of the most important factors that control the conversion of solids to gas (Mata-Alvarez, 2003).

In a conventional completely mixed, or plug flow digester, the hydraulic retention time (HRT) equals the solid retention time (SRT). However, in a variety of retained biomass reactors the SRT exceeds the HRT. As a result, the retained biomass digesters can be much smaller while achieving the same solids conversion to gas.

The volatile solids conversion to gas is a function of SRT. At low SRT values there is not sufficient time available for the microbes to grow and replace the microorganisms lost in the effluent. In this case the rate of microorganisms loss exceeds the rate of its growth and “wash-out" occurs. The SRT at which “wash-out” occurs is termed the "critical SRT". When the quantity of biomass extracted from the reactor is equal to the biomass produced in the reactor, the reactor is operating under steady-state SRT conditions (Mata-Alvarez et al., 2000; Mata-Alvarez, 2003).

Nutrients and trace metals

Availability of appropriate concentrations of nutrients and trace elements (micronutrients) is essential for biological waste processing. Nutrients (e.g. phosphorus and nitrogen) and trace metals (e.g. Fe, Ni, Mg, Ca, Se) are essential for the metabolic activities of existing microbial cells to proceed. Therefore, the presence of nutrients and trace metals provide the needed physicochemical conditions for the optimum microbial activities. If there is a deficiency in one or more of the nutrients the waste degradability will be severely affected (Moustakas et al., 2007). OFMSW usually contains high enough quantities of nutrients and micronutrients for microorganisms activities not to be limited (Mata-Alvarez, 2003).

Toxicity and Inhibition

There are many substances that at given concentrations are inhibitory or toxic for anaerobic microorganisms, especially methanogenic microorganisms. The problem of inhibitory or toxic substances is far from simple, since some toxic substances are stimulants at low concentrations for the anaerobic digestion process. Table 2.2 below lists the concentrations (mg/L) for inhibition and toxicity of heavy metals for anaerobic digestion.

VFAs, free ammonia and hydrogen sulphur are the most frequent inhibitory and/or toxic substances. For OFMSW anaerobic digestion inhibition or toxicity problems is usually due to excess of VFAs. Other toxic compounds are rare especially if source separation of waste is carried out (Mata-Alvarez, 2003).

Table 2.2: Inhibition and toxicity of anaerobic digestion by heavy metals (BALKWASTE, 2010).

Heavy Metal	Inhibition (mg/L)	Toxicity (mg/L)
Copper (Cu)	40-250	170-300
Cadmium (Cd)	-	20-600
Zinc (Zn)	150-400	250-600
Nickel (Ni)	10-300	30-1000
Lead (Pb)	300-340	340
Chromium III (Cr)	120-300	200-500
Chromium VI (Cr)	100-110	200-420

2.3.3.4 Advantages and disadvantages of anaerobic digestion process

AD has advantages as well as disadvantages compared to other waste management strategies. Table 2.3 summarizes some of these advantages and disadvantages.

Table 2.3: Advantages and disadvantages of AD as a waste management alternative (Verma, 2002; Crolla et al., 2004).

Advantages	Disadvantages
▪ AD contributes to reducing greenhouse gas emissions (a well managed AD system aims to maximise methane production, but at the same time restrict the release of any gases to atmosphere) ▪ Energy generated through AD helps reduce the demand for fossil fuels. AD systems can be energy independent by using the collected methane to supply heat and electricity for the operation of the unit. ▪ AD reduces the risk of soil and water pollution. ▪ AD process converts the waste into potentially saleable products: biogas, soil conditioner and liquid fertilizer ▪ AD treatment can reduce up to 80% of odour problems that are common to other treatment methods ▪ AD reduces pathogens levels and destroys weed seeds in the final products ▪ AD units have a small foot print as compared to other technologies	▪ AD has significant capital, operation and maintenance costs. As with all waste management systems AD projects require traffic movement, this problem greatly influence costs and emissions. (AD plant location should be chosen carefully to have minimum distance between production of waste, the storage tank and the digester) ▪ AD present risk to human health because of the pathogenic content of the feedstock (an appropriate plant design and feedstock handling procedures can minimize this problem) ▪ AD units are associated with some risk of fire and explosions in AD plant (to avoid these risks natural gas collecting system installation is required) ▪ A large scale AD plants may have some visual impact (a possible solution for this is by partially sinking the digester into the ground to reduce visual impact that will help for easier load, or by landscaping)

2.3.4 Pretreatment to Enhance AD

The degradation of particulate substrate (e.g. solid waste) into soluble substrates, known as hydrolysis is the rate-limiting step during anaerobic digestion (Eastman et al., 1981; Izumi et al., 2010). Mechanical disintegration of solid waste reduces the particle size of waste, thus improving the AD performance by increasing the specific surface of substrate available to the microorganisms. Another way to enhance AD performance is by pretreating the waste to break the polymer chains into soluble components (monomers), this will improve the hydrolysis of the organic matter, accelerate the AD process, increase the biogas production, as well as reduce the digestion time and the amount of final residuals (Sawayama et al., 1996; Mata-Alvarez, 2003).

Mechanical, thermal, microwave, chemical and their combinations are the main pretreatment methods used to enhance the AD process of organic materials.

2.3.4.1 Mechanical pretreatment

Mechanical disintegration has been widely studied as a method of pretreatment to increase solubilization and enhance the anaerobic digestion of sludge and organic materials. There are several size reduction processes currently used, such as simple grinders, stirred ball mills, high pressure homogenisers, shear-gap homogenizers and ultrasonic pressure (Verma, 2002).

The particle size of the solid waste has an important effect on the biogas production during the anaerobic digestion process. Sharma et al. (1988) reported the effect of influent particle size on the anaerobic digestion of agricultural and forest residues. In this study the raw material was ground using a portable grinder to produce 5 different particle sizes (0.088, 0.4, 1.0, 6.0 and 30 mm) while measuring the maximum quantity of biogas produced using the 0.088 and 0.4 mm particles. The size reduction of the waste particles was shown to increase the available surface area for the microorganisms during the anaerobic digestion process and thus results in increased degradation yields and an accelerated digestion process (Mata-Alvarez, 2003).

Comminution as a method of size particles reduction, and the effect of applying it on organic materials prior to anaerobic digestion process was investigated by Palmowski and Muller (1999). This study used four different substrates, applied different methods to reduce the

particle size of samples and then reported the improvement in gas production from the anaerobic digestion process. Table 2.4 below summarizes the results and shows the positive effects of reducing particle sizes on AD processes. Size reduction was shown to be most effective for substrates that are difficult to biodegrade; such as sun flower seeds, maple leaves and hey stems.

Table 2.4: Effect of comminution of different organic materials on their anaerobic biodegradability (Muller et al., 1998; Mata-Alvarez, 2003).

Substrate	**State of the samples**	**Type of comminution applied**	**Improvement in biogas production**	**Reduction of technical digestion time***
Mixture of potatoes, apples and carrots	2.2 cm pieces	Rubbed with a grater	-	50 %
Meat	2.2 cm pieces	Ground with a kitchen machine by cutting stress	2 %	23 %
Sunflower seeds	5 mm pieces	Ground with a kitchen machine by cutting stress	19 %	45 %
Maple leaves	2.2 cm pieces	Ground with a flour mill by shear stress	14.4 %	59 %
Hay stems	1.5 cm pieces in water suspended	Ground in a stirred ball mill with water	18 %	52 %

* Technical digestion time: time to reach 80% of the maximal biogas production.

Izumi et al. (2010) studied the effect of particle size reduction on anaerobic digestion of food waste, by running a batch anaerobic digestion test for 16 days. The food waste was ground to reduce the particle size using a house hold disposer and then using a bead mill (BM). Six levels of pretreatment were applied to the waste by changing the total number of revolutions of the BM between 300 and 40,000 revolution and by varying the operation time and number of revolutions per minute. The mean particle size (MPS) was in the range of 0.391–0.843 mm after the pretreatment. The methane production rate was shown to increase with decreasing the

MPS until a maximum improvement for each sample was reached. The high methane production observed with smaller MPS substrates was suggested to be because of the increase in the surface area of the substrate available for the microorganisms during the anaerobic digestion process. However a methane production rate decrease was observed for sample pretreated at the highest number of revolutions (40,000 revolutions) despite this being the maximum degree of pretreatment. The postulated explanation was that organic overloading occurred due to excessive size reduction.

2.3.4.2 Thermal pretreatment

Thermal pretreatment (high temperature pretreatment) is a physical method that differentiates liquid organic material from solid organic material and also loosens the cell structure of the remaining solid particles (Mata-Alvarez et al., 2000).

The use of thermal treatment was often applied after AD process to improve dewaterability. This arrangement had many disadvantages such as the generation of odours and the production of liquor that is high in organics. This liquor may increase the COD loading to the secondary facilities by up to 30% (Haug, 1978).

The work of Haug (1978) pioneered today's research on thermal pretreatment. Haug proposed the use of thermal treatment prior to AD in order to overcome the problems previously faced with thermal treatment after AD. Also the residual heat in the sludge after the thermal pretreatment can be beneficial for mesophilic or thermophilic digestion and save heating energy.

Haug studied the effect of thermal pretreatment on the biodegradability and dewaterability of primary sludge, waste activated sludge (WAS) and a 1:1 by weight mixture of these two types of sludge. The results showed that thermal pre treatment of primary sludge at 175°C had no significant effect on either the total biogas production or methane production, and in contrast the same thermal pretreatment of activated sludge resulted in a 60% increase in the methane yield compared to untreated sludge.

Thermal pretreatment improved AD by increasing the rate of hydrolysis, which leads to a greater extent of solubilization of COD. As the pressure and temperature of thermal hydrolysis

increases the organic waste become short-chain fragments that are better suited for biological digestion by micro-organisms (Wang et al. 2010). The effect of different thermal pretreatment temperatures was also evaluated by Stuckey and McCarty (1984).

Stuckey and McCarty investigated the effect of thermal pretreatment on anaerobic digestibility and toxicity of WAS from a WWTP with a solids concentration of 4.3% TS. The thermal pretreatment of WAS was evaluated at a temperature range from 150 to 275°C with 25°C intervals. The positive effect of thermal pretreatment on the solubilization of WAS was found to be maximum at 175°C. At this temperature the maximum WAS biodegradability occurred as well for both mesophilic (35°C) and thermophilic (55°C) conditions. The increase in biodegradability of WAS with increasing pretreatment temperature up to 175°C was thought to be attributable to the improvement in accessibility of biologically active sites after pretreatment. In the contrast when pretreatment temperatures were higher than 200°C the WAS biodegradability decreased and this was explained most likely because of the formation of toxic compounds to anaerobic digestion.

J.Wang et al. (2006) evaluated the effect of thermal pretreatment of food waste on anaerobic digestion in a hybrid anaerobic solid-liquid (HASL) system. The laboratory scale HASL system was developed in order to be used in industrial-scale operations to minimize the amount of food waste for disposal in Singapore, the HASL system included acidogenic and methanogenic cylindrical reactors.

The batch experiments were carried out simultaneously in three identical HASL systems operated in a constant temperature room at 35 ± 1°C for 2 weeks. The food wastes used in the study were typical wastes generated daily from a university canteen. Wastes were shredded into particles of 6.0 mm average size. Thermal pretreatment of food waste at 70°C for 2 hours (experiment E1) and at 150°C for 1 hour (experiment E2) improved the hydrolytic and acidogenic processes in the acidogenic reactor as well as the methanogenesis process in the methanogenic reactor. The results of the study showed that the average rate of COD production increased by 1.4% and 5.5% in experiments E1 and E2 in comparison with the control. The maximum rate of methane production was 4.2 dm^3/day for the control, 5.5 and 7.1

dm^3/day for experiments E1 and E2 respectively. Also the application of thermal pretreatment on food waste prior to anaerobic digestion halved the time required to produce the same quantity of methane compared with the control. The most effective pretreatment was the conditions used for experiment E2, using 150°C heat for 1h.

In 2010 W.Wang et al. evaluated the effect of thermal pretreatment on organic solids, and how it improves the hydrolysis of municipal biowaste (MB). The MB used in the study contained food waste (FW), fruit-vegetable waste (FVW), and dewatered sewage sludge (DSS). The thermal pretreatment was conducted at 175°C for 60 min.

The volatile dissolved solids to volatile solids (VDS/VS) ratio was used to evaluate the solubilization and hydrolyzation of MB. The VDS/VS before thermal hydrolysis of FW, FVW and diluted DSS were 51%, 44% and 4% respectively, this ratio increased after thermal hydrolysis to 62%, 58% and 50% respectively. These results gave a clear indication that a large part of organic solids were dissolved during the course of thermal hydrolysis.

Meanwhile, the hydrolysis of VS had a positive effect on the biodegradability of MB. To evaluate this effect BMP tests were carried out for MB (a mixture of FW, FVW and diluted DSS) and thermally hydrolyzed municipal bio-waste (THMB). Cumulative methane production of THMB was 13.6% higher than MB. The maximum methane production rate for MB and THMB was 38 mL /gVS day and 75 mL /gVS day. Wang study concluded that the thermal hydrolysis pretreatment clearly alleviated the problem of hydrolysis of solid organics as a rate limiting step. The large part of organic compounds that dissolved contributed to a high digestion rate and the methane production was subsequently improved by the molecular structure destruction of the solid organics.

2.3.4.3 Microwave pretreatment

Microwaves emit an electromagnetic spectrum that ranges between millimeter waves (0.01 m) and radio waves (1 m). Microwave (MW) irradiation is characterized by frequencies between 30 and 0.3 GHz. In a microwave oven, the waves generated are tuned to frequencies that can be absorbed by the polar materials. The polar material simply absorbs the energy and gets warmer (Hong et al. 2004). Usually samples with high moisture content (such as food) are good

candidates for MW irradiation. However, not all materials can be heated rapidly by microwaves. In general materials may be classified into three groups, i.e. conductors, insulators and absorbers, as illustrated in Figure 2.12 below.

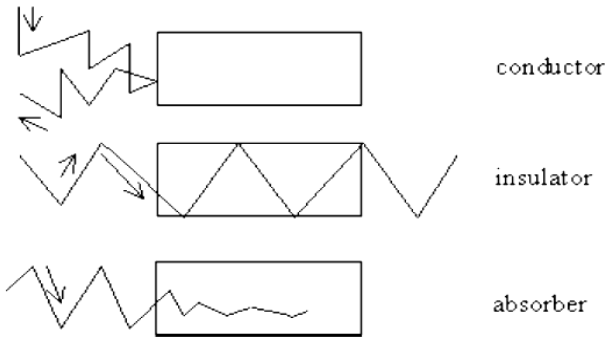

Fig 2.12: Microwave absorption characteristics for conductors, insulator and absorber (Jones et al., 2002).

The use of microwave irradiation has risen over the last 20 years. The main applications of microwave heating today include food processing, wood drying, organic decomposition, medical waste sterilization, killing of pathogens in food, animal manures, and soil (Jones et al., 2002).

There are many studies that investigated the effect of MW on solubilization and anaerobic digestion of sludge, kitchen waste, and OFMSW (Hong et al., 2004; Marin et al., 2010, Shahriari et al., 2011).

Marin et al. 2010 investigated the effect of high temperature and pressure microwave (MV) as a pretreatment to enhance anaerobic biodegradability and methane production from a model kitchen waste (KW). The heating rates used were 7.8, 3.9 and 1.9 °C/min, the final pretreatment temperature was 175°C with 1 min holding time. The results of the study proved the positive effect of microwave irradiation in solubilization of particulate chemical oxygen demand (COD) resulting in higher soluble COD, protein and sugar concentrations in the supernatant phase (<0.45 lm) and in the whole fraction of pretreated KW compared to controls (not pretreated KW), the highest level of solubilization was achieved at a heating rate of 1.9°C/min.

A BMP assay at 33°C was run to examine the anaerobic biodegradability of the supernatant and the whole fraction of pretreated KW and compare the results with the control (not pretreated).The results indicated an increase in anaerobic biodegradability between 5% and 16% for the supernatant fraction relative to controls. For the whole fraction, anaerobic biodegradability was improved by 9% at a heating rate of 7.8 °C/min.

The same authors (Marin et al., 2011) investigated the effect of high temperature and pressure MW pretreatment of source-separated kitchen waste (SSKW). The temperature used for the pretreatment was 175°C with 1 min holding time, and 7.9°C/min heating rate. Equation 2.1 was used for solubilization assessment.

$$\% \, Solubilization = \frac{SCOD_f - SCOD_i}{TCOD} \times 100\% \qquad 2.1$$

Where:

SCOD = the soluble chemical oxygen demand (f: final; i: initial; mg/g_{sample})

TCOD = the total chemical oxygen demand (mg/g_{sample}).

The pretreatment under the previous conditions enhanced the solubilization of chemical oxygen demand (COD) of the SSKW by 43% in comparison with control.

Anaerobic biodegradability of MW pretreated SSKW samples was determined by biochemical methane potential assay (BMP) at 33°C temperature, cumulative biogas production from MW pretreated samples was 11% more than it from control. Furthermore, methane yield for MW pretreated SSKW was 289 L CH_4 / g VS_{added} , this is about 9% higher than methane yield for control which was 265 L CH_4 / g VS_{added}. The improvement in biogas production in the case of pretreated SSKW compared to control, suggested that MW pretreatment successfully improved the hydrolysis of complex organic components. Inoculum had not been previously exposed to the MW irradiated SSKW, but the absence of a lag phase in the BMP experiment suggested that there was no potential toxicity effects of the pretreated sample exist other than those

associated with system overloading. That means that there is no need for a long inoculum acclimation period when considering start up and running semi-continuous digesters for the anaerobic treatment of the MW irradiated SSKW.

Shahriari et al., 2011 studied the enhancement effect of high temperature and pressure microwave (MW) pretreatment of the organic fraction of municipal solid waste (OFMSW) on solubilization prior to anaerobic digestion (AD). During the study three temperatures were tested 175°C, 154°C and 115°C, at three MW intensities based on temperature ramp times(20, 40 and 60 minutes).Also two water contents were evaluated 20% and 30%. The results of solubilization showed that the highest increase in solubilization occurred under the conditions (175°C and 30% water content), the MW pretreatment under these conditions resulted in having soluble COD of 1.61, 1.62 and 1.58 times higher than the control for MW intensity ramp times of 20, 40 and 60 minutes, respectively.

2.3.4.4 Chemical and microwave pretreatment

Cheng and Liu, 2009 investigated microwave-assisted alkaline (NaOH) pretreatment (MAP) applied to herbal-extraction process residue (HPR) to determine the enhancement effect of this pretreatment method on solubilization and biogas production. In this study raw herbal-extraction residue HPR was dried at room temperature in air, and then milled to 60-mesh powder before use. Three methods of pretreatment were used; first, alkaline pretreatment was used to treat 10 g of HPR that was boiled in 100 ml NaOH solution with alkali loading 0.08 g NaOH/g HPR for 15 min; second pretreatment using microwave-assisted alkaline pretreatment (MAP), a 10 g of the grounded HPR was mixed with 100 mL of NaOH solutions with different alkali loadings (0.02-0.16 g NaOH/g HPR) and then the mixtures were irradiated with microwaves at 700 W for a given time; third microwave-assisted water pretreatment (MWP) was applied where 10 g of ground HPR was mixed with 100 ml distilled water, then the mixture was irradiated with microwaves at 700 W for 15 min.

Solubilization results showed that MAP resulted in more weight loss of HPR than the other two pretreatments. The weight loss of HPR correlated with solubilization of their components (such as cellulose, hemicellulose, lignin, etc.) in the aqueous solution. As a result, higher soluble COD

concentrations were observed in solutions pretreated with MAP than in those pretreated with MWP or alkaline pretreatment.

To study the effect of the different pretreatments on biogas production, HPR samples subjected to different pretreatment methods were used in anaerobic digestion assay. For all three pretreatment HPR samples a significant improvement in cumulative methane production was observed compared to untreated HPR. The HPR pretreated with microwave irradiation combined with NaOH solution (MAP) had the highest cumulative biogas production of 1286 mL obtained after 20 days of digestion.

Pretreatment increased the amount of soluble compounds released from lignocellulosic HPR, which are easily utilized by anaerobic bacteria for biogas fermentation. As the microwave irradiation time and the alkali concentration increased, the HPR weight loss increased as well due to the increase in solubilization of HPR compounds.

2.3.4.5 Chemical and thermo-chemical pretreatment

Chemical pretreatment using various acid and alkaline reagents has been widely used to enhance the anaerobic digestion of organic materials (Penaud et al., 1999; Torres et al., 2008; Lin et al., 2009). Alkaline pretreatment has been more extensively studied than acid pretreatment with respect to the anaerobic digestion process since anaerobic bioconversions require a slightly alkaline pH (Mata-Alvarez, 2003).

Alkaline pretreatment has been used to solubilize various substrates such as lignocellulosic materials (corn stover, switchgrass, woodchips, etc.), WAS and the OFMSW (Lin et al., 2009; Chou et al., 2010). These studies have been predominantly based on the addition of sodium hydroxide.

Ray et al. (1990) studied low-level alkaline solubilization of waste activated sludge to enhance the AD process. The study found that adding 20 meq NaOH /L to the WAS (1% total solids) for 24 hours at room temperature improved volatile solids removal by 25-35%, COD removal by 30-75%, and gas production by 29-115% for AD. The biogas yields with respect to the volatile solids and COD removal for pretreated sludge at 7.5 day retention time were similar to those obtained for sludge with no pretreatment at 20 days retention time. Also for all runs, the

reactors fed with pretreated sludge had a higher percentage of methane in the produced biogas.

Lin et al. (2009) used alkali pretreatment on pulp and paper sludge (PPS) to enhance its solubilization and anaerobic digestion. 0.3%, 0.6% and 1.2% sodium hydroxide solutions were used to pretreat PPS. Alkali pretreatment of the PPS samples hydrolyzed the organic matter in the PPS samples resulting in an increase in the concentration of soluble chemical oxygen demand (SCOD) from 1664.0 mg/L to a maximum value of 20472.7 mg/L for samples pretreated with 1.2% NaOH solution. The effects of chemical pretreatment represent an order of magnitude increase in COD solubilization. In general as the concentration of the added treatment reagent sodium hydroxide increased solubilization of the samples COD. During the pretreatment experiments the alkalinity of pretreated samples was 2.5-19.6 times higher than alkalinity of control sample. The study showed that pretreatment helped to increase samples alkalinity which affords higher buffer capacity avoiding any drop in pH during the AD process.

The second part of the Lin et al. (2009) study was the evaluation of alkali pretreatment on the AD of PPS using lab-scale single stage digesters at 37°C. The results of the study showed that the methane yield increased in bioreactors fed with pretreated PPS. As concentrations of sodium hydroxide were increased the methane yield also increased. The fractional increase of methane yield in bioreactos B, C and D increased by 0.3%, 0.6% and 1.2%, respectively, as the concentration of sodium hydroxide used for pretreatment increased from 54% to 83% and finally to 88%.

Different alkali reagents have been used in different studies for alkali pretreatment (Penaud et al., 1999; Torres et al., 2008). A study by Torres et al. (2008) used lime ($Ca(OH)_2$) to pretreat OFMSW in order to enhance the COD solubilization and biogas production during the AD process. The pretreatment was performed in a batch, 1L reactor at room temperature. Two independent variables were considered, the concentration of lime (40-100 meq $Ca(OH)_2$/L) and the time of solubilization (1 and 6hrs). The effectiveness of pretreatment was evaluated by the degree of solubilization, which was calculated using equation 2.1 mentioned before.

The optimal solubilization of COD observed occurred when 62 meq $Ca(OH)_2$/L was added for 6.0 hours. Under these conditions 11.5% of the COD was solubilized. This study also operated two 1L stirred reactors as batch reactors fed with 40, 60, 80 and 100 mL. One of the reactors was loaded with waste that was pretreated with 62.0 meq $Ca(OH)_2$/L for 6.0 hrs, the other reactor was loaded with un-pretreated waste. The highest methane yield was observed for the pretreated waste and it was 0.15 m^3 CH_4/kg volatile solids (VS), which was a 172% increase of methane production compared to the un-pretreated reactor.

Regardless of the nature of the substrate applied to chemical pretreatment, the major variables affecting the pretreatment process appear to be solids concentration, treatment time, nature of alkaline agents and alkali concentrations (Penaud et al., 1999; Torres et al. 2008; Lin et al., 2009). The later variable was studied by Zhu et al. (2010) who used different NaOH loadings (1%, 2.5%, 5.0% and 7.5% w/w) to apply alkali room temperature pretreatment to corn stover in order to enhance the biogas production. The pretreatment showed an increase in lignin degradation from 9.1% to 46.2% when NaOH concentration increased from 1.0% to 7.5%. Following pretreatment corn stover samples were digested using 2L reactors operated at 37°C for 40 days. NaOH addition of 1% and 2.5% did not show any significant improvement on the biogas yield, however at high NaOH (5.0% NaOH) additions a cumulative biogas yield of 372.4 L /kg VS that was 37.0% higher than that of the un-pretreated samples was observed after 40 days of digestion.

Corn stover pretreated with 7.5% NaOH caused failure of the methane production during the anaerobic digestion process. The high load of NaOH used in this case caused fast production of VFAs during the hydrolysis and acidogenesis stages, which led to an overly acidic environment (pH 6.0) that inhibited the methanogens.

Chou et al. (2010) investigated the effects of temperature, NaOH concentration and reaction time on solubilization of palm oil mill effluent (POME). A total of 36 experiments were carried out at 30, 40, 50 and 60°C, with NaOH concentrations ranging from 0 to 16 g/L. The reaction time ranged from 24 to 72 hrs. The study showed that NaOH pretreatment resulted in similar COD solubilization as compared to high temperature pretreatment. NaOH additions

demonstrated increased COD solubilization between 50.7% and 83.9% compared to un-pretreated POME samples. This led Chou to conclude that the thermal alkaline pretreatment broke down the complex particulate structures in POME and released the extracellular and intracellular biopolymers such as proteins, carbohydrates, and lipids into the soluble phase.

The maximum COD solubilization of 82.6% was obtained at 32.5°C with the addition of 8.8 g/L of NaOH and over a 41.2 hrs reaction time. A statistical analysis demonstrated that temperature, NaOH concentration and reaction time all had an individual significant effect on the solubilization of POME.

Penaud et al. (1999) evaluated the influence of sodium hydroxide addition during the thermo-chemical pretreatment of a microbial biomass on COD solubilization and anaerobic biodegradability. The study evaluated the influence of the dose of NaOH added at ambient temperature on the pretreatment process; various quantities of NaOH was added to 600 ml of substrate to reach concentrations ranging from 0 to 26.1 g NaOH /L. The results of this work showed that COD solubilization and total solids reduction increased as the dose of NaOH increased, where a maximum value of 63% COD solubilization and 33% total solids elimination was reached when 4.6 g of NaOH/L was added. When the dose of NaOH was increased from 4.6 g NaOH/L up to 26.1 g NaOH/L, a slower COD solubilization increase was observed.

The influence of NaOH addition with heating at 140°C for 30 min was studied by Penaud et al. (1999). The same concentrations of NaOH were added as in the previously described experiment; however the samples were now heated for 30 min in mechanically stirred autoclaves to reach 140°C. The addition up to 4.6 g NaOH/L increased the pH from 4 to 10 while increasing COD solubilization from 37 to 80%. Furthermore, when the dose of NaOH added was increased above 4.6g of NaOH/L, the pH increased from 10 to 12 and the COD solubilization increased again, but in this case at a slower rate. From this work it is observed that heating in addition to alkaline pretreatment amplifies COD solubilization: 26.1 g of NaOH/L increased COD solubilization by 75.4% at ambient temperatures and 85.1% at 140°C.

Penaud et al. (1999) also investigated the effects of alkaline pretreatment on the microbial biomass. The study investigated the influence of four alkali agents NaOH, KOH, $Mg(OH)_2$ and

$Ca(OH)_2$ at a pH of 12 and at ambient temperatures and 140°C. The results show that at both temperatures the monobasic agents (NaOH and KOH) led to higher solubilization percentages than dibasic agents ($Mg(OH)_2$ and $Ca(OH)_2$). The authors postulated that the reason is that the dibasic agents only partially dissociated. . At ambient temperatures the maximum solubilization reached was 60.4% when NaOH was added; on the other hand maximum solubilization reached 83.7% for KOH pretreated samples at 140°C.

CHAPTER 3: MATERIALS AND METHODS

3.1 Materials

3.1.1 M-OFMSW

Organic waste, such as kitchen and restaurant waste, varies from day-to-day in composition (Neves et al., 2008). A model organic fraction of municipal solid waste (M-OFMSW) was used in this study in order to maintain a homogeneous waste composition. The M-OFMSW includes components from the major food groups that are representative of food used in Canadian kitchens and was derived based on the Canadian Food Guide (Health Canada, 2009). The components of the M-OFMSW used in this study are shown in Table 3.1. The model waste was prepared the day before the experiments were performed. The waste was mixed in a food processor to generate a particle size range between 1-5 mm and the resulting mixture was stored in a zipper-lock storage bags at 4°C. The waste was allowed to reach room temperature prior to testing.

Table 3.1: Model-OFMSW composition.

Composition	Percentage (%w/w)
Cooked rice	18
Cooked pasta	18
White cabbage	11
Carrot	11
Banana	11
Apple	11
Cooked ground beef	10
Dog food (wet)	10
Total	100

The prepared M-OFMSW had a total solids concentration of 18.2% ± 0.3 (w/w). This solids concentration is high relative to the findings of Torres et al. (2008) who recommended that samples of OFMSW have 8% total solids concentrations. Water was added to the waste mixture in order to make it easier to mix during the alkaline pretreatment and when sampling for analysis. Adding enough water was requirement to enable the pretreatment chemicals to be

uniformly mixed in the sample. This process is supported by Zheng. M. et al. (2009) who studied alkali pretreatment of corn stover using NaOH, and found that applying wet state pretreatment (moisture content 80-90%) helped reduce the amount of chemicals used for the pretreatment by enabling chemical distribution within the sample. To achieve 8% total solids in our model waste samples 55% (w/w) water was added and mixed into the samples.

3.1.2 Anaerobic Inoculum

Anaerobic inoculum used in this study was obtained from the Robert O. Pickard Environmental Center (ROPEC) sewage treatment plant in Ottawa, ON. The mesophilic anaerobic inoculum was maintained in a 5-L side-armed volumetric flask reactor, which was initially filled with 3L of WAS obtained from ROPEC. The flask was placed on a shaker rotating at 90 rpm at 35°C. The SRT of the inoculums reactor was set at 24 days by the daily withdrawing of 125 mL of digested sludge and adding a 125 mL of 1:1:3 (by volume) mixture of M-OFMSW, water and sludge from ROPEC. Gas production was measured daily using a wet-tip meter to assess the activity; steady state conditions of the inoculums reactor were verified by stable daily gas production, which occurred after about 6 weeks. Total COD, TS, PH and VFAs and gas composition were measured occasionally.

3.1.3 Alkaline Reagents

A literature search revealed that the three most commonly used pretreatment alkaline reagents of M-OFMSW were NaOH, KOH and $Ca(OH)_2$. Preliminary experiments using these three chemicals to pretreat the model waste used in this study showed that $Ca(OH)_2$ was not suitable as it did not improve COD solubilization. The final decision was to use NaOH and KOH as alkaline reagents. Past research work showed that these two chemicals demonstrated the best overall efficiency in solubilzation of various wastes, as well as enhancing anaerobic digestion performance (Valo et al., 2004; Li et al., 2008; Dogan and Sanin, 2009; Zheng et al., 2009).

3.2 Experimental Plan

The experimental work for this study was divided into four main stages as shown in Figure 3.1. The first stage was the preparation of model waste, choosing the suitable amount of water to be added, and characterizing the waste samples. The second stage included alkaline pretreatment of the waste samples under two different temperatures 23±1°C and at 80±1°C, using four different pH levels (10, 11, 12 and 13). Two alkaline reagents were tested: NaOH and KOH. Stage three included two BMP assays; the first BMP assay investigated NaOH pretreated samples and the second BMP assay investigated KOH pretreated samples; the results of this identified the optimum pretreatment conditions for both pretreatment chemicals. Finally the fourth stage was the anaerobic digestion of the pretreated samples using semi-continuous reactors.

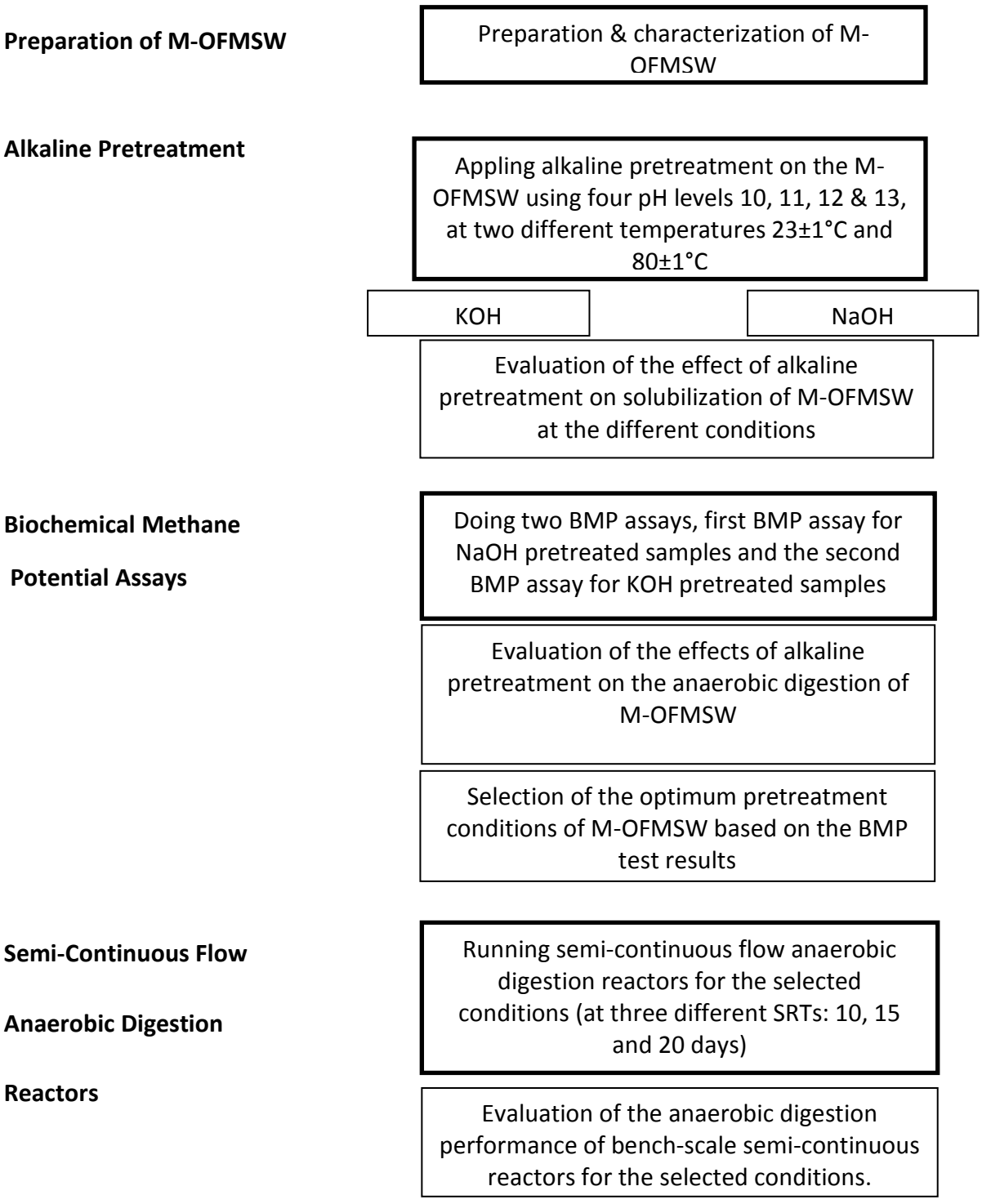

Figure 3.1: Experimental approaches for the study.

3.2.1 Alkaline Pretreatment

For the alkaline pretreatment of samples two alkaline reagents were used NaOH and KOH, each alkaline reagent was examined at four pH levels 10, 11, 12 and 13, and two different temperatures 23±1°C and 80±1°C.

In the case of NaOH the effect of mixing time was examined at 1 hr and 6 hrs mixing time. The results showed no significant effect of mixing for more than one hour, hence 1 hr was set as the mixing time for pretreatment at 23±1°C and as the holding time in case of pretreatment at 80±1°C.

Pretreatment of the model waste was performed by adding 220g of distilled water to 180 g of waste in a 1L Kimax® beaker followed by the addition of the alkaline base to the mixture. For NaOH pre-treated samples, 5N NaOH solution was added until the desired pH level was reached. A control 55:45 by volume distilled water to waste was run for each of the experiments. The controls and pre-treated samples were mixed using an electrical stirrer machine (Phipps & Bird Stirrer, Model 7790-400, USA) for 1hr with a rotation speed of 80 rpm at 23±1°C (Figure 3.2). The heated samples were covered with aluminum foil, and placed in an oven until the temperature of the samples reached 80±1°C. The samples were maintained at 80±1°C 1hr. After the holding time, the samples were left on the counter to cool down and reach room temperature prior to analysis. Soluble chemical oxygen demand (SCOD) was measured after centrifuging the samples for 90 min at 10000 rpm and filtering each sample through a 0.45 µm pore size filter. The increase or decrease in the solubility of waste was evaluated using equation 3.1 in which the SCOD of the pre-treated samples were compared to SCOD measurements for the control sample.

$$\% \text{ Solubilization} = \frac{SCOD_{Sample}}{SCOD_{Control}} \times 100\% \qquad 3.1$$

Where :

$SCOD_{Sample}$ is the soluble chemical oxygen demand for pre-treated sample (mg/g_{sample})
$SCOD_{Control}$ is the soluble oxygen demand for control sample (with no pre-treatment).

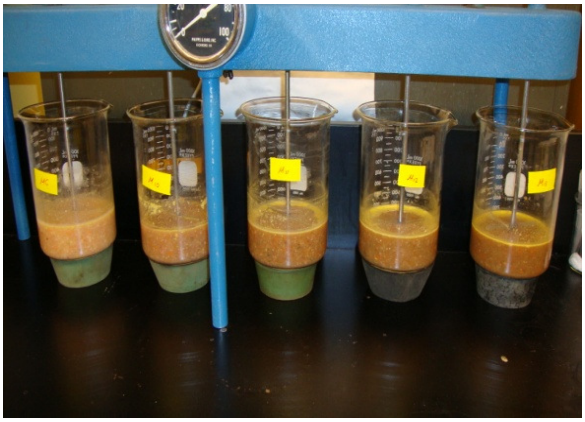

Figure 3.2: Stirrer used to mix the pretreated samples.

3.2.2 BMP Assays

The effects of pre-treatment at different temperatures and pH levels on biodegradability of model waste were tested using two batch mesophilic biochemical methane potential (BMP) assays according to Owen et al. (1978). In the first BMP test the control sample and NaOH pretreated samples were studied at four pH levels and at two temperatures 23±1°C and 80±1°C. The second BMP test investigated the control and KOH pre-treated samples. All samples used in the BMP test were diluted to a volatile concentration of 6.0±0.2 g VS/L, 130 ml of diluted sample and 20 ml of Inoculum were placed in each of the 250 ml serum bottles, shown in Figure 3.3. A buffering capacity of 4000 mg/L alkalinity as $CaCO_3$ added to each bottle using equal amounts of $NaHCO_3$ and $KHCO_3$ bottle to neutralize the acids produced during digestion. The final preparatory step was to purge the bottles with N_2 gas for 2 minutes to remove oxygen gas from the headspace of the bottles and maintain anaerobic conditions. All batch reactors were prepared in duplicate. Finally after sealing with butyl rubber stoppers and screw caps, bottles were kept in a temperature controlled incubator shaker (New Brunswick Scientific Co. Inc., NB, Canada) at 35±1^{o}C with a motion of 90 rpm. Biogas production was measured regularly using a gas manometer. pH values, total fatty acids (VFAs), and biogas composition were monitored weekly. Samples used in the BMP test were characterized prior to digestion and after the digestion was completed. The anaerobic digestion performance during the BMP test was

evaluated based on the biogas production, the percentage of methane in the biogas, the volatile solids destruction and COD removals achieved during digestion.

Figure 3.3: BMP bottles.

3.2.3 Semi-Continuous Flow Anaerobic Digestion Reactors

The optimum pretreatment case from BMP1 and BMP2 were chosen for the semi-continuous flow reactors. The selected samples were those pretreated with NaOH and KOH at pH 12 at 23±1°C. A control sample was again operated in parallel to the pretreated samples. Side-armed 1-L Erlenmeyer volumetric flasks were used as semi-continuous flow reactors (Figure 3.4). The side-arm was used for feeding the reactor by attaching a 10-cm piece of tubing to the side arm of each reactor; the tubing was closed at the end with a Castaloy screw compressor clamp to prevent gas from leaking. The flasks upper openings were sealed tightly with two-hole rubber stoppers, after choosing the rubber stoppers with proper size to close tightly the flask opening two holes were made in the stoppers, holes were made slightly smaller than the diameter of the tube used to ensure that no gas leakage will occur from these ports. One of these ports used to withdraw the effluent samples from the reactor while the smaller port supported the gas tubing. A 5-cm piece of hard plastic tube was inserted in each port with rubber tubing attached to the end of the effluent tube; this tubing was tightly closed with a Castaloy screw compressor clamp. The tube in the smaller port was connected with tubing to a 2-L tedlar bag

for the collection of biogas. The working volume in the reactors was 800 ml, 300 ml of sample and 500 ml of inoculum mixture were added to each reactor. The inoculum mixture contained (2:3 V/V) of acclimated inoculum from ROPEC and granular inoculum which was used previously in anaerobic baffled reactors (Kennedy and Barriault 2005). A mixture with equal amounts of $KHCO_3$ and $NaHCO_3$ was added to each reactor to ensure an alkalinity concentration of 4000 mg/L alkalinity as $CaCO_3$. All the reactors had an initial pH value between 7.4 and 7.7. The reactors were purged for about 3-4 minutes with nitrogen gas before finally sealed with the stoppers and adding a layer of silicone all around the connecting areas between the glass with stopper, stopper with tubes and tubes with tubing to ensure gas-tightness of the reactors. All reactors were kept at 35±1°C in a (New Brunswick Scientific Co. Inc., NB, Canada) incubator which was set at a 90 rpm rotational speed.

Three SRTs 20, 15 and 10 days (SRT was equal to HRT) were examined (Mata-Alvarez, 2003). To maintain the desired SRT a constant volume effluent sample was withdrawn and the same volume of feed was added daily for each reactor. The effluent was extracted using a 50 ml syringe that was adapted to fit tightly into the sampling tubing. After connecting the syringe to the sampling tubing the screw compressor clamp was opened, then the desired volume of effluent/ feed was withdrawn/ added. Finally the compressor clamp was closed tightly before removing the syringe. The feed samples for reactors were prepared every week or two and kept in the refrigerator; samples were brought to room temperature before the feeding process. Reactors were considered reaching a steady state when stabilization of the daily biogas production occurred (biogas production fluctuate within a 10% range).

The biogas production was measured daily using a manometer and gas composition was measured every two weeks. Effluent TCOD, SCOD, pH, TS, VS, alkalinity and ammonia were determined once weekly for the reactor effluent.

Figure 3.4: Semi-continuous flow reactors.

3.3 Analytical Methods

3.3.1 Alkalinity

Standard Method 2320B was used to measure alkalinity. The test was performed on the supernatant of the samples which was obtained by first centrifuging the samples in a Thermo-scientific centrifuge machine (Sorvall Legend™, T+/RT+ Thermo Scientific, Germany) for 60 to 90 minutes depending on the samples viscosity at 10,000 rpm. The liquid was subsequently filtered through 0.45 µm pore size filters (GN-6 Matricel®, Pall Corporation). Known volumes of filtered samples (supernatant) were placed in Erlyenmeyer flasks and 0.1 N sulphuric acid was titrated into the sample. A magnetic stirring rod and a Thermix® stirrer model 120MR, set at speed 4 was used to mix the samples. The amount of acid needed to reach a pH value of 8.3 and 4.6 was recorded. pH was monitored using a Fisher Accumet® Model 925 pH meter (Fisher Sci., Ottawa, ON). The pH electrode was thoroughly rinsed with distilled water and dried with Kimwipes® task wipers between each sample.

Alkalinity as mg CaCO3/L was calculated using equation 3.2.

$$Alkalinity\ ,mg\ CaCO_3/L = \frac{A \times N \times 50{,}000}{(mL)\ Sample\ titrated} \qquad 3.2$$

Where:

A = mL of standard acid used for titration

N = normality of standard acid.

3.3.2 Ammonia

Ammonia ($NH_{3(aq)}$ and $NH_4^+{}_{(aq)}$) was determined according to Standard method 4500D. Samples were centrifuged in a Thermo-scientific centrifuge machine (Sorvall Legend™, T+/RT+ Thermo Scientific, Germany) with a relative centrifugal force of 11,292 for 60 to 90 minutes depending on the sample viscosity. After the centrifuging step the liquid portion was extracted from the centrifugal tubes and filtered through a 0.45 µm pore size filters (GN-6 Matricel®, Pall Corporation). An Orion ammonia electrode (model 95-12) and a Fisher Accumet® model 750pH/ion meter (Fisher Sci.) were used for ammonia measurements. Calibration curves were prepared each time the probe was used to ensure accuracy of the measurements.

Filtered samples were placed in Erlyenmeyer flasks and 1mL of 10N NaOH solution was added to raise the pH higher than 11. A magnetic stirring rod was placed in the flask, the samples were stirred using a Thermix® stirrer model 120MR, set at speed 4. The electrode was thoroughly rinsed with distilled water and dried with Kimwipes® task wipers between each sample. The electrode was immersed in a 10 mg NH_3-N/L solution between measurements.

3.3.3 pH

The pH was measured using a glass electrode in combination with a Fisher Accumet® Model XL25 dual channel pH/ion meter. Before taking the pH measurements samples stored in the refrigerator were brought to room temperature. Samples from semi-continuous reactors were an exception to this practice, where pH measurements were determined immediately after taking the sample from the reactor to minimize contact of sample with air; thus the pH was measured at samples temperature of 35±2°C. Between measurements electrode was rinsed with distilled water, dried with Kimwipes® task wipers and immersed in a pH 7 buffer solution.

3.3.4 Total and Volatile Solids

Standard Method 2540G was used to analyze total and volatile solids. The porcelain evaporating dishes used were prepared first by washing, rinsing with tap water, soaking in 10%

(v/v) sulphuric acid over night and then rinsing with distilled water before placing in a Thermolyne muffle furnace model F62730 at 550°C for 1hr. The evaporating dishes were allowed to cool down for 30 minutes in a Precision mechanical convection oven model 23 maintained at 105°C, and subsequently cooled to room temperature for 1 hr in a desiccator.

The prepared dish was weighted on a Mettler Toledo Classic Plus Model AB204 analytical balance and the weight was recorded (B) and a well mixed sample was placed in the dish and the weight of sample and the dish was recorded (C). This procedure was repeated until the samples finished. The samples were dried over night in the Precision mechanical convection oven at 105°C, then the dishes were subsequently transferred to a desiccator for about 1hr to cool down before weighting then on the analytical balance (A). The dishes then were placed in the muffle furnace at 550°C for 1hr. After ignited the samples dishes were transferred to the Precision mechanical convection oven at 105°C for 30 minutes to partially cooling down then transferred to a desiccator for 1hr to completely cool down reaching room temperature before weighting the dishes on the analytical balance (D).

The percentage of total solids and volatile solids in samples were calculated using equations 3.3 and 3.4.

$$\textit{\% Total Solids (TS)} = \frac{(A-B)}{(C-B)} \times 100\% \qquad 3.3$$

$$\textit{\% Volatile Solids (VS)} = \frac{(A-D)}{(A-B)} \times 100\% \qquad 3.4$$

Where:

A = weight of dried residue + dish

B = weight of dish

C = weight of wet sample + dish

D = weight of residue + dish after ignition.

3.3.5 Total and Soluble Chemical Oxygen Demand (TCOD and SCOD)

The closed reflux, colorimetric Standard Method 5250D was used to measure the total and soluble COD. Total COD was measured from unfiltered samples and soluble COD was measured

from filtered samples. The filtered samples were prepared by following the same steps previously described in alkalinity section. The digestion solution and sulphuric acid reagents required for COD determination were prepared according to Standard Methods. The calibration curve was prepared by diluting a COD stock solution containing 850 mg/L of potassium hydroxide phthalate (COD of 1,000 mg/L) to the following standards: 0, 100, 200, 300, 400, 500, 600 and 700 mg/L as COD. Standards were prepared in duplicates with the exception of the 0 and 500 mg/L standards which were prepared in triplicate. Kimax culture tubes (25 x 150mm) with Teflon-lined screw caps were used: these tubes were washed with soap solution then soaked in a 10% sulphuric acid solution and left overnight and subsequently the tubes were washed again with water, then rinsed twice with distilled water before use.

TCOD and SCOD samples appropriately diluted and a 10 mL of diluted solution was pipetted into the Kimax tubes followed by the addition of 6ml of digestion solution and 14 ml of sulphuric acid reagent using calibrated dispensers with fixed volume attached on the top of each bottle. After adding the reagents to the COD tubes they were capped and mixed with a Fisher vortex Genie 2^{TM} , then the tubes were placed in a Precision mechanical convection oven set at 150°C for three hours, cooled in the fumehood for an hour covered with a box to protect them from light. The tubes were then left in a closed cabinet overnight and the day after the absorbance of the digested solutions in the tubes was measured using a Coleman Perkin–Elmer Spectrophotometer model 295, at a light absorbance wavelength of 600 nm. The surface of the tubes were cleaned with distilled water and dried with Kimwipes® task wipers before using the spectrophotometer to avoid any disturbance of the reading. The absorbance readings for the tubes were interpolated using the calibration curve to finally get the COD concentration for the samples.

3.3.6 Biogas Production

Batch experiments

Water displacement method using a U-tube manometer was used to measure the production of biogas in the batch bottles. A BD 21G1½ needle connected to one side of the U-tube manometer was inserted in the rubber stopper of the batch bottles. A valve was opened to allow the biogas to flow into the manometer and displace water until the gas in the bottles

pressure reached atmospheric pressure. The change in water level in the manometer was recorded.

Semi-continuous reactors

Biogas produced in the semi-continuous flow reactors was collected in 2L-Tedlar bags (Chromatographic Specialties Inc., ON, Canada). Daily biogas production was measured using a Cole Palmer easy-load pump model 75553-02 with a Masterflex speed controller to pump the contents of the tedlar bags into a customized U-tube manometer. The biogas volume was calculated by multiplying the height of water column displaced by the biogas and the cross-sectional area of the manometer tube.

3.3.7 Biogas Composition

Biogas samples for composition analyses were taken by inserting the tip of BD 21G1½ needle which was attached to a 1 ml syringe through the stopper of the batch bottle. Representative samples were collected by withdrawing biogas once or twice into the bottle before taking the final 1-ml biogas sample. Half of the sample was wasted in the air before the rest 0.5 ml sample was injected manually into the injection port of the gas chromotograph (GC). Samples of the semi continuous reactors were taken by inserting the tip of the needle into the septum ports on the tedlar bags that collected the produced biogas from the reactor. The biogas composition was determined using a Hewlett Packard 5710A gas chromotograph, the GC was equipped with a 3380A model integrator and a 5705A thermal conductivity detector that used helium as the carrier gas. National Instruments^{TM} Lab VIEW version 6.0 was used to identify and read the GC output and determine the biogas composition as percentage of nitrogen, methane and carbon dioxide.

3.3.8 Volatile Fatty Acids

Analysis of volatile fatty acids (VFAs) was accomplished using an Agilent 6890 Series Gas Chromatograph (GC) equipped with a flame ionization detector, an injection port with a temperature of 250°C, and an Agilent 7683 Series auto-sampler. Helium was the carrier gas running at a flow rate of 1.7 ml/min.

An internal standard solution was prepared to contain a concentration of 2000 mg/L for isobutyric acid, and a VFA standard solution with a concentration of 2000 mg/L for each of the three acids: acetic, butyric and propionic acid. The GC calibration was done using a vial containing 0.5 ml of the internal standard and 0.5 ml of the VFA standard. The calibration step was repeated until 2000 ± 50 mg/L of each acid was measured. The VFA analysis was performed on filtered samples, which were prepared by putting 1ml of the sample in 1.5 ml Eppendorf centrifuge tubes and then centrifuging the samples for 20 minutes using a Brinkmann Eppendorf centrifuge model 5415 machine set at 14,000 rpm. Centrifuged samples were filtered using an Acrodisc® LC 13 mm diameter 0.2 µm PVDF membrane syringe filter. Equal amounts of filtered samples and internal standard solution were dispensed into the vials, and vials were covered with parafilm layer, mixed for few seconds on a Fisher vortex Genie 2^{TM}, and then placed in the auto-sampling GC tray to be analyzed for the concentration of acetic, propionic and butyric acids in mg/L.

3.3.9 Sample Preservation

The least stable parameters were measured prior to the more stable parameters. In most cases the experimental analyses of all the parameters were done within 24-48 hrs of sampling. However when the analyses of the samples required additional time, the samples were preserved as described in Table 3.2. After each use, all bottles and caps used for storing samples were washed with soap water then rinsed with distilled water.

Table 3.2: Sample preservation

Analyses	Type of sample	Preservation	Bottle Type for storage samples	Maximum storage time
pH	Whole sample	Refrigerated, 4°C	Plastic or glass	7 Days
Alkalinity	Filtered sample (0.45µm)	Refrigerated, 4°C	Plastic or glass	14 Days
Ammonia	Filtered sample (0.45µm)	Adding concentrated H_2SO_4 to get pH < 2 Refrigerated, 4°C	Plastic or glass	14 Days
VFAs	Filtered sample (0.2µm)	Adding the 0.5 ml Internal standard solution Frozen	Glass vials	14 Days

TS/VS	Whole sample	Refrigerated, 4°C	Plastic or glass	7 Days
TCOD	Whole sample	Adding concentrated H_2SO_4 to get pH < 2 Refrigerated, 4°C	Glass	7 Days
SCOD	Filtered sample (0.45µm)	Adding concentrated H_2SO_4 to get pH < 2 Refrigerated, 4°C	Glass	7 Days

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Effect of Alkaline Pretreatment on M-OFMSW Solubilization

To study the effect of alkaline pretreatment on M-OFMSW solubibilization, two alkaline reagents NaOH and KOH were used to apply pretreatment on the model waste samples and different doses of NaOH and KOH were used to reach pH 10, 11, 12 and 13. These pretreatment conditions were applied at 23±1°C and 80±1°C. Total and soluble chemical oxygen demand (TCOD and SCOD), total and volatile solids (TS and VS), pH, ammonia (NH_3-N and NH_4^+-N) and total volatile fatty acids (TVFAs) were monitored throughout the study. The effects of the alkaline reagent used, pH, and temperature on the pretreatment of organic waste samples are shown in Tables 4.1 to 4.4. The arithmetic mean and standard deviation of replicate measurements are listed, except for TVFAs the values in the tables are based on duplicate measurements.

The improvement in solubilization, which is represented as the ratio between SCOD values of the pretreated sample and the control are presented in Figures 4.1 and 4.2. The SCOD ratio ($SCOD_{Sample}/SCOD_{Control}$) gives a direct indication regarding the increase in the solubilization of the samples where an SCOD ratio greater than 1.0 that demonstrating the SCOD for the sample increased with pretreatment. Solubilization is important as increasing the soluble organic matter content of samples will theoretically increase the easily biodegradable content of the waste and thus will lead to an improved performance of the anaerobic digestion (AD) process (Haug, 1978; Li and Noike, 1992).

Table 4.1: Organic waste characterization for NaOH pretreated samples at 23±1°C.

	Sample				
Parameter	**Control**	**pH 10**	**pH 11**	**pH 12**	**pH 13**
$pH_{initial}$	5.5± 0.0	10.0±0.0	11.0±0.0	12.0±0.0	13.0±0.0
pH_{final}	5.4±0.0	9.7±0.0	10.6±0.0	11.8±0.0	13.0±0.0
TCOD(mg/g)	115.6±0.6	117.5±0.6	117.6±1.5	118.0±1.0	120.1±0.4
SCOD(mg/g)	41.3±0.3	45.8±1.3	47.0±1.2	50.1±1.6	47.7±2.1
TS(% w/w)	9.0±0.1	9.0±0.0	9.0±0.0	8.7±0.0	8.4±0.1
VS(%w/w)	8.6±0.0	8.6±0.0	8.6±0.0	7.9±0.1	7.4±0.1
[a]VS/TS(%)	96.1±0.5	95.4±0.4	95.4±0.2	91.4±0.0	88.3±1.4
[b]TVFA(mg/Kg)[b]	27±8	61±12	295±22	588±25	882±23
NH_3-N(mg/L)	113.7±2.0	148.9±0.5	145.0±3.0	484.1±20.1	Not detected

[a] Data: arithmetic mean ± combined error for TS and VS values. [b] Summation of acetic, propionic and butyric acids.

Table 4.2: Organic waste characterization for NaOH pretreated samples at 80±1°C.

	Sample				
Parameter	**Control**	**pH 10**	**pH 11**	**pH 12**	**pH 13**
$pH_{initial}$	5.8±0.1	10.0±0.0	11.0±0.0	12.0±0.0	13.0±0.0
pH_{final}	5.1±0.0	9.3±0.2	10.2±0.1	11.8±0.0	12.5±0.7
TCOD(mg/g)	113.8±0.4	115.5±2.4	116.9±1.4	118.8±1.2	119.8±1.3
SCOD(mg/g)	43.9±0.4	51.6±0.5	53.9±2.3	58.5±1.0	77.8±2.6
TS(% w/w)	9.1±0.0	8.9±0.0	8.8±0.0	8.5±0.0	8.3±0.0
VS(%w/w)	8.8±0.1	8.6±0.4	8.5±0.1	7.8±0.1	7.0±0.2
[a]VS/TS(%)	96.7±0.3	96.9±0.4	96.2±0.3	91.9±0.7	83.5±1.4
[b]TVFA(mg/Kg)	27±8	100±10	---	614±19	1127± 31
NH_3-N(mg/L)	113.7±2.0	130.9±9.1	136.1±3.0	443.1±12.3	Not detected

[a] Data: arithmetic mean ± combined error for TS and VS values. [b] Summation of acetic, propionic and butyric acids.

Table 4.3: Organic waste characterization for KOH pretreated samples at 23±1°C.

	Sample				
Parameter	**Control**	**pH 10**	**pH 11**	**pH 12**	**pH 13**
$pH_{initial}$	5.7±0.1	10.0±0.0	11.0±0.0	12.0±0.0	13.0±0.0
pH_{final}	5.6±0.0	9.4±0.2	10.5±0.0	11.8±0.1	13.0±0.1
TCOD(mg/g)	119.0±0.8	117.3±1.2	117.3±0.8	116.0±0.6	115.3±1.6
SCOD(mg/g)	45.5±1.1	47.2±0.6	49.7±0.0	54.1±0.1	73.1±1.5
TS(% w/w)	8.5±0.1	8.4±0.0	8.3±0.0	8.1±0.1	7.7±0.1
VS(%w/w)	8.2±0.0	8.0±0.0	7.8±0.1	7.1±0.1	6.7±0.1
[a]VS/TS(%)	96.1±0.6	95.3±0.3	94.1±0.7	87.8±1.4	86.5±1.1
[b]TVFA(mg/Kg)	13±4	86±6	196±8	423±15	905±11
NH_3-N(mg/L)	122.0±2.1	148.6±5.2	152.6±2.1	443.1±12.3	Not detected

[a] Data: arithmetic mean ± combined error for TS and VS values. [b] Summation of acetic, propionic and butyric acids.

Table 4.4: Organic waste characterization for KOH pretreated samples at 80±1°C.

	Sample				
Parameter	**Control**	**pH 10**	**pH 11**	**pH 12**	**pH 13**
$pH_{initial}$	5.6±0.0	10.0±0.0	11.0±0.0	12.0±0.0	13.0±0.0
pH_{final}	5.3±0.0	9.1±0.1	10.2±0.0	11.7±0.0	12.5±0.1
TCOD(mg/g)	118.1±1.7	117.3±0.5	116.5±0.8	116.1±0.1	114.9±1.6
SCOD(mg/g)	44.9±0.6	45.2±0.3	48.2±0.2	53.9±0.8	72.7±0.1
TS(% w/w)	8.2±0.0	8.0±0.0	7.9±0.0	7.7±0.1	7.6±0.0
VS(%w/w)	7.9±0.0	7.6±0.0	7.5±0.0	7.1±0.1	6.5±0.1
[a]VS/TS(%)	96.0±0.6	96.1±0.3	95.7±0.3	92.5±1.4	85.0±1.2
[b]TVFA(mg/Kg)	13±4	119±9	305±21	680±18	1209±42
NH_3-N(mg/L)	122.0±2.1	141.3±2.5	140.9±6.8	386.9±16.1	Not detected

[a] Data: arithmetic mean ± combined error for TS and VS values. [b] Summation of acetic, propionic and butyric acids.

Figure 4.1 shows the effects of NaOH pretreatment on COD solubilization, where the data represents the arithmetic mean and error bars represent the 95% confidence intervals of replicate measurements. From Figure 4.1 we see that alkaline pretreatment using NaOH at 23±1°C caused a significant increase in the SCOD of pretreated samples; for example at pH 10 and 11 the SCOD of pretreated samples were 10.8±0.2 and 11.4±1.4% higher than the SCOD of the control. A maximum SCOD increase was reached at pH 12 with 21.1±1.8% more SCOD than the control. These results show a significant increase in SCOD with increased pH. It should be noted that when the pH was further increased to 13 the SCOD improvement was 11.5±0.9 % which is less than the increase that was observed at pH 12 and not significantly different from the increase observed at pH 12.

Combining NaOH with heat (80±1°C) increased the SCOD for pretreated samples as compared to the pretreated samples at the same pH at 23±1°C. The SCOD ratio ranged from 1.17±0.0 at pH 10 to a maximum of 1.77±0.03 at pH 13. A significant increase in solubilization is observed up to a pH of 13 is in agreement with the results of previous studies on organic waste that reported a significant increase in solubilization when the severity of pretreatment condition increased (Sawayama et al., 1997; Dogan and Sanin., 2009; Marin et al., 2010).

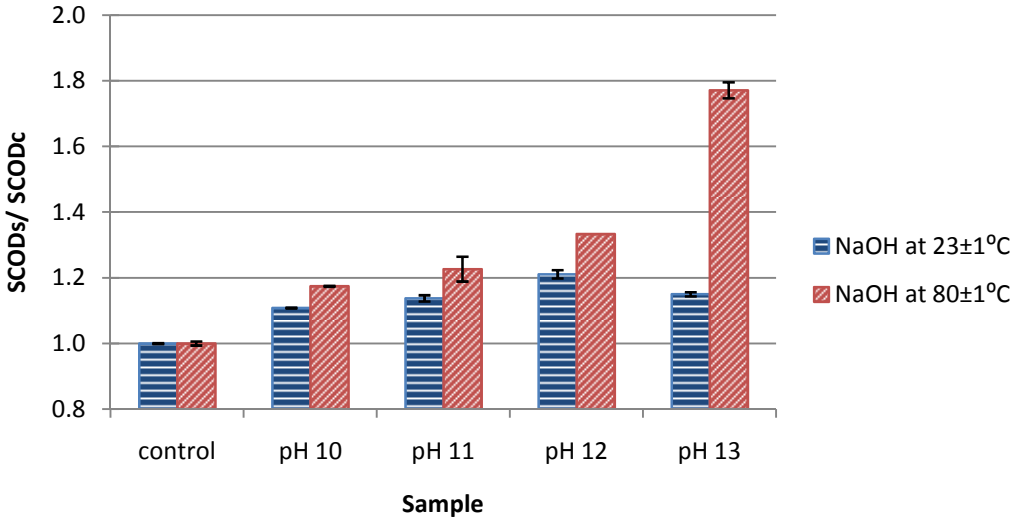

Figure 4.1: Effect of NaOH pretreatment on COD solubilization.

Figure 4.2 shows the SCOD ratio for KOH pretreatment, where the data represents the arithmetic mean and error bars represent the 95% confidence intervals of replicate measurements. The comparison between Figure 4.2 and Figure 4.1 shows that the COD solubilization of KOH pretreatment was less than the NaOH pretreatment for all samples except for pretreatment at pH 13 at 23±1°C. Penaud., (1999) observed similar results when the effect of NaOH and KOH pre-treatment on solubilization of a microbial biomass was studied. Penaud results showed that the use of NaOH at pH 12 yields higher solubility than the use of KOH at the same pH level. However, this study demonstrates that the KOH pretreated samples at pH of 13 and 23±1°C had significantly higher SCOD solubilization than the sample pretreated with NaOH under these conditions.

At 23±1°C pretreatment with KOH at pH 10 resulted in a SCOD ratio of 1.04±0.01, as pH level increased above 10 the SCOD ratio increased reaching a maximum value of 1.61±0.03 at pH 13. Thus a significant difference in COD solubilization was observed at different pH values for KOH pretreatment. It is noteworthy that KOH pretreatment at 80±1°C did not have any significant effect on SCOD concentrations when comparing with samples pretreated under the same pH condition at 23±1°C.

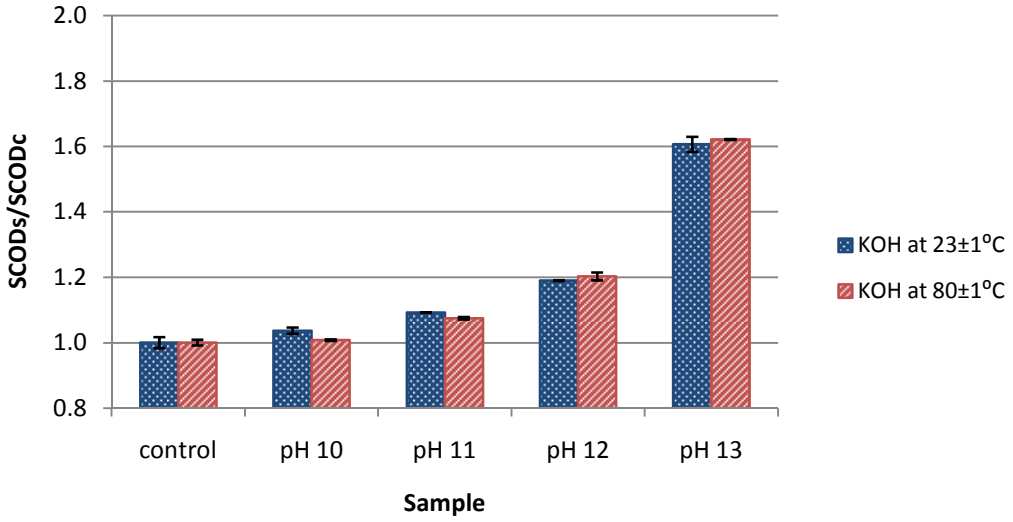

Figure 4.2: Effect of KOH pretreatment on COD solubilization.

In addition to the effect of alkaline pretreatment on COD solubilization of M-OFMSW, alkaline pretreatment also demonstrated a notable swelling effect on the pretreated sample. Torres et al., (2008) noted that an increase in the surface area of organic waste particles occurred after alkaline pretreatment, which enhanced the accessibility of waste particles to enzymatic attack by microorganisms leading to enhance the AD process performance.

TS and VS measurements of the control sample and the different pretreated samples were calculated using equations 4.1 and 4.2. Figure 4.3 and 4.4 present the TS% and VS% values for NaOH and KOH pretreatment respectively. The figures show the arithmetic mean and the error bars represent the 95% confidence intervals of duplicate measurements.

$$\textit{\% Final Total Solids (TS)} = \frac{(A-B-Y(C-B))}{(C-B-Y(C-B))} \times 100\% \quad 4.1$$

$$\textit{\% Final Volatile Solids (VS)} = \frac{(A-D)}{(A-B-Y(C-B))} \times 100\% \quad 4.2$$

Where:

A = weight of dried residue + dish

B = weight of dish

C = weight of wet sample + dish

D = weight of residue + dish after ignition

X = gram of alkali reagent added to 400 g of sample for pretreatment

Y = X/400 = gram of alkali reagent added per gram of sample.

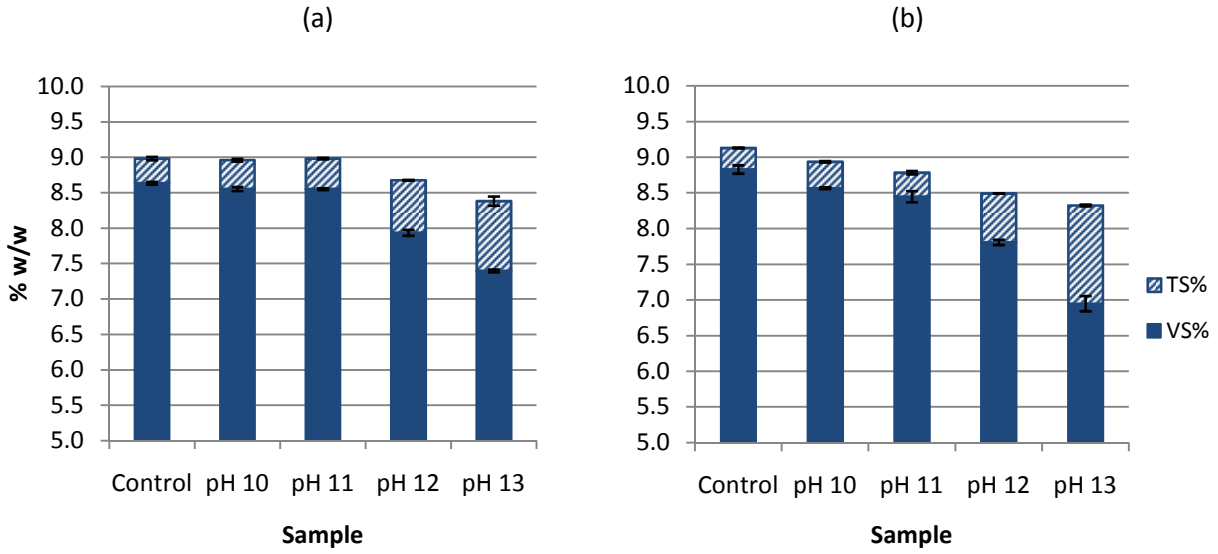

Figure 4.3: TS and VS % (w/w) for NaOH pretreatment at (a) 23±1°C, and (b) 80±1°C.

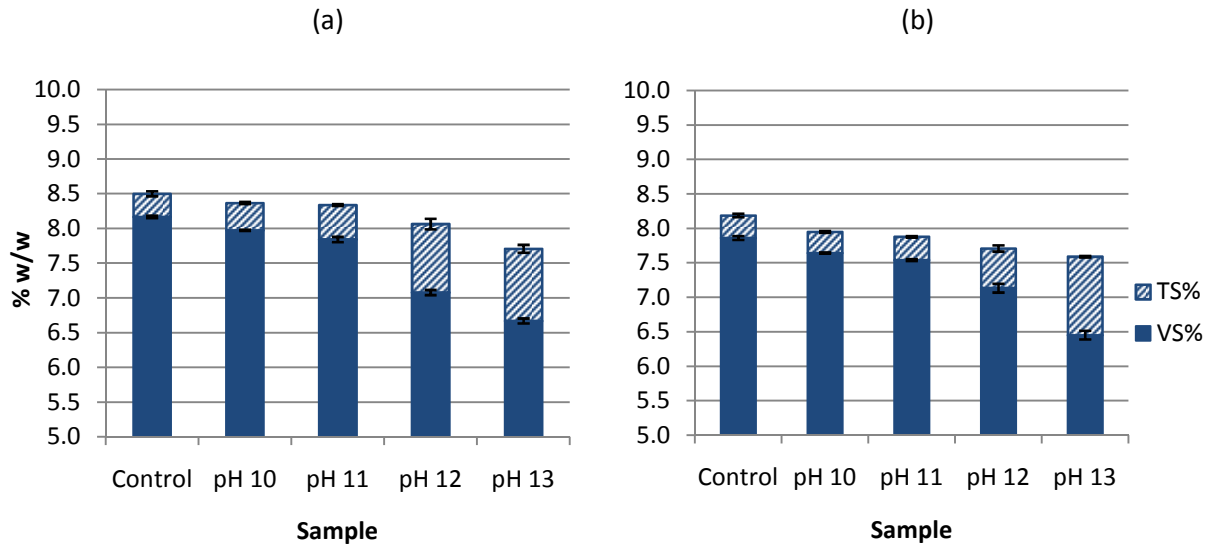

Figure 4.4: TS and VS % (w/w) for KOH pretreatment at (a) 23±1°C, and (b) 80±1°C.

TS measurements in Figure 4.3 show a significant decrease due to pretreatment with the reduction in VS being more notable. The maximum VS reduction (Equation 4.3) for NaOH pretreated samples is reported as 21.3±1.9 % for samples pretreated at pH 13 at 80±1°C.

$$\%VS\ Reduction = \left(\frac{VS\ control - VS\ sample}{VS\ control}\right) x\ 100\% \quad (4.3)$$

Where:

$VS_{control}$ = VS of control

VS_{sample} = VS of pretreated sample.

On the other hand for KOH pretreatmet the samples pretreated at 23±1°C with pH 13 showed a maximum VS reduction of 18.34±1.46%. These results show that alkaline pretreatment at increasing pH levels result in significant decrease in the TS and VS of the samples. With respect to TS, the change in TS cannot be explained mechanistically in this study however a similar decrease in TS was observed by other studies (Cheng and Liu, 2009; Marin et al., 2010; Shahriari et al., 2011). The decrease in VS may occur due to the chemical reactions that took place during the alkaline pretreatment and the change that happen to the waste characteristics.

The pH values were measured twice during each solubilization study, once at the beginning of the experiment ($pH_{initial}$) and again at the end (pH_{final}). It can be observed from the pH values reported in Tables 4.1 to 4.4 for samples pretreated with NaOH and KOH respectively, that a gradual drop in pH values was reported for all samples with the different pretreatment conditions, which can be attributed to the neutralization effect of the acidic products during the pretreatment process (Torres et al., 2008). Such a pH drop is not uncommon to occur after applying extreme pretreatment conditions. Similar results of previous studies were observed after applying lime alkaline pretreatment on OFMSW (Torres et al., 2008).

TVFA values are presented in Figure 4.5. The data represents the arithmetic mean of duplicate measurements. VFAs measurements include acetic, butyric, and propionic acid concentrations. As expected TVFAs increased due to pretreatment, and it can be observed from Figure 4.5 that at pH value of 12 and 13 the pretreatment caused a dramatic significant increase in TVFAs concentrations compared to the lower pH levels. Moreover combining pretreatment with a temperature of 80±1°C caused a further significant increase in TVFAs at a pH 13 for both NaOH

and KOH pretreated samples. At a pH value of 12 the KOH pretreated samples also demonstrated a significant increase in TVFAs while all other pH values for NaOH and KOH demonstrated that no significant increase in TVFAs are observed by increasing the temperature to 80°C.

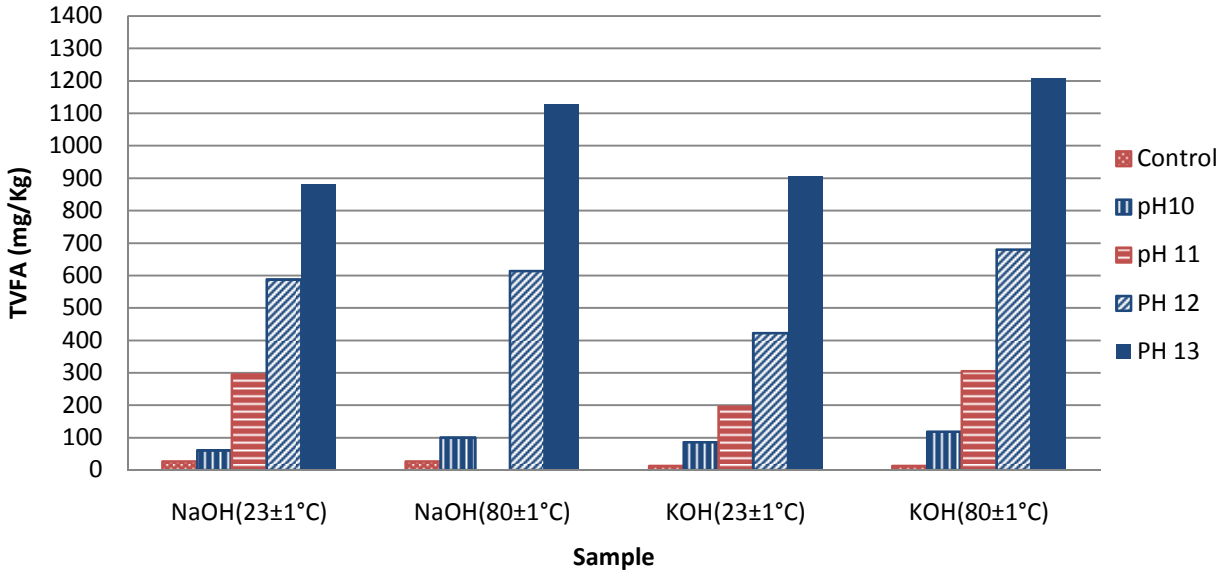

Figure 4.5: TVFAs concentrations for pretreated samples.

4.2 BMP Assays

The effects of pre-treatment at different temperatures and pH levels on the anaerobic digestion of M-OFMSW was tested according to the Owen et al. (1978) batch mesophilic BMP assay. The experimental phase tested NaOH and KOH pretreated samples.

4.2.1 NaOH- BMP Assay

NaOH pretreated samples and a control sample were examined in duplicate. Acclimated inoculum was used to eliminate lag-phase or inhibition at early stages of the test. The characteristics of the acclimated inoculum used for the BMP assay are presented in Table 4.5;

arithmetic mean and standard deviation of duplicate measurements (between parentheses) are given.

Table 4.5: Acclimated inoculum characterization.

Parameter	
pH	7.7 (0.1)
TS (g/kg)	24.4 (0.0)
VS (g/kg)	15.7 (0.0)
TCOD (g/kg)	20.1 (0.1)
SCOD (g/kg)	19.0 (1.1)
NH_3-N (mg/L)	1086 (72)

4.2.1.1 Biogas production during NaOH-BMP test

Cumulative biogas values used in the figures and calculations below are the net biogas production from BMP batch bottles; that is the quantity of produced biogas in the bottle minus the average volume of biogas produced in the inoculum bottles. Inoculum bottles contained 50.0±0.2 mL of inoculum, these bottles had an average biogas production of 68.9±4.9 mL over the time period of the BMP assay. All other BMP batch bottles contained only 20 g of inoculum which contributes to approximately 27.5±2.0 mL of biogas produced in these bottles.

Cumulative biogas volumes of samples pretreated with NaOH at 23±1 °C are shown in Figure 4.6. Figure 4.7 shows cumulative biogas volumes of samples pretreated with NaOH at 80±1°C. Data in the figures are arithmetic means for duplicate reactors.

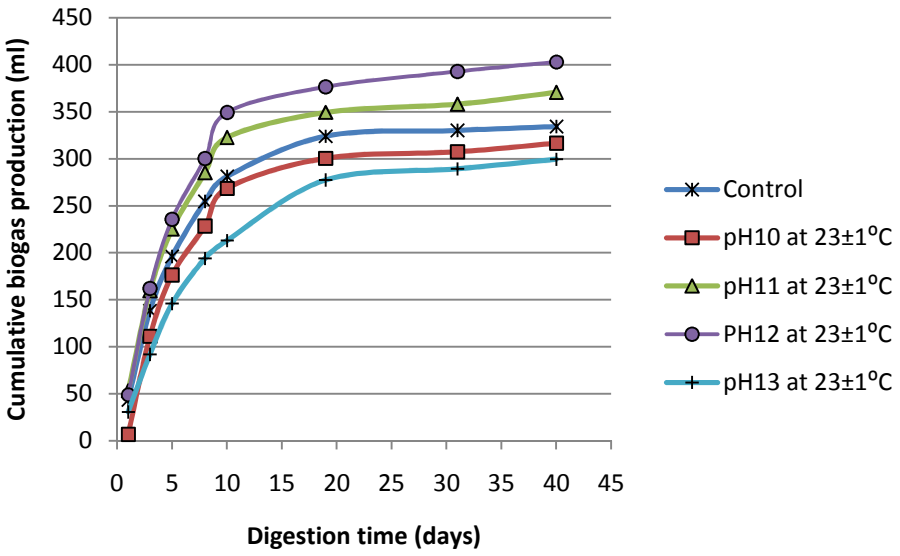

Figure 4.6: Cumulative biogas production for samples pretreated with NaOH at 23±1°C.

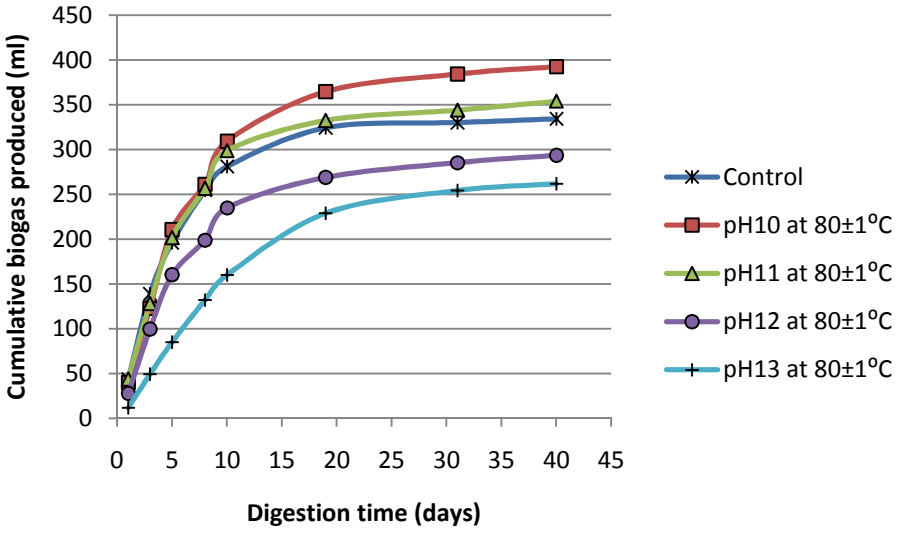

Figure 4.7: Cumulative biogas production for samples pretreated with NaOH at 80±1°C.

Figures 4.6 and 4.7 show that a negligible lag-phase is observed at the beginning of the BMP assay, hence the inoculum is assumed to have been adequately acclimatized prior to the BMP assay. Figure 4.8 shows the relative (to control) biogas production for samples pretreated with NaOH at 23±1°C. Figures 4.6 and 4.8 show that during the BMP assay samples pretreated at pH

11 and 12 had significantly higher biogas production rates than the non-pretreated control samples. Samples pretreated at pH 12 had the highest biogas production which at the end of the testing phase which was 20.6±0.7% greater than the control. Samples pretreated at pH 10 and 13 continually demonstrated lower biogas production rates compared to control throughout the entire test period. Samples pretreated at pH 13 at 23±1°C produced a significant lower cumulative biogas volume of 299.5±3.2 mL which is 10.4±0.3 % lower than the cumulative biogas produced by control.

Figure 4.9 shows the relative cumulative biogas production for samples pretreated using NaOH at 80±1°C. The samples pretreated at pH 10 and 11 initially demonstrated slightly lower (not significant) biogas production rates than the control, but after about four days the samples pretreated at pH 10 showed an increase in the biogas production rate relative to the non-pretreated control. Samples pretreated at pH 10 demonstrated a high biogas production rate during the BMP assay as compared to other samples and after 40 days showed 17.4±0.6% more cumulative biogas production than the control; this is a significant difference. On the other hand samples pretreated at pH 12 and 13 showed a low biogas production rate during the BMP assay, with samples pretreated at pH 13 showing a significant difference in cumulative biogas production compared to control. Specifically, samples pretreated at pH 13 produced 21.7±0.6% less cumulative biogas than the control. The observed low biogas production during the BMP assay for samples pretreated at pH 13 at both temperatures (23 and 80±1°C) might be due to the formation of refractory compounds that are hard to digest. Shahriari et al. (2011) observed that the pretreated model organic waste samples at high microwave temperature (175°C) changed to a dark brown color, this change in samples color was suggested to happen due to the formation of melanoidins compounds (brown nitrogen copolymers) at high temperatures. These melanoidins compounds are difficult for the microorganisms to digest. In the current study samples pretreated at high pH levels as pH 13 displayed a dark brown color, and the color being even darker in the case of samples pretreated at pH 13 combined with heat (80±1°C). These qualitative visual observations may be indicative of the formation of refractory material and subsequently may contribute to the low biogas production for samples pretreated at pH

13. Figures A.1 and A.2 in Appendix (A) show the described change in OFMSW samples color after the pretreatment.

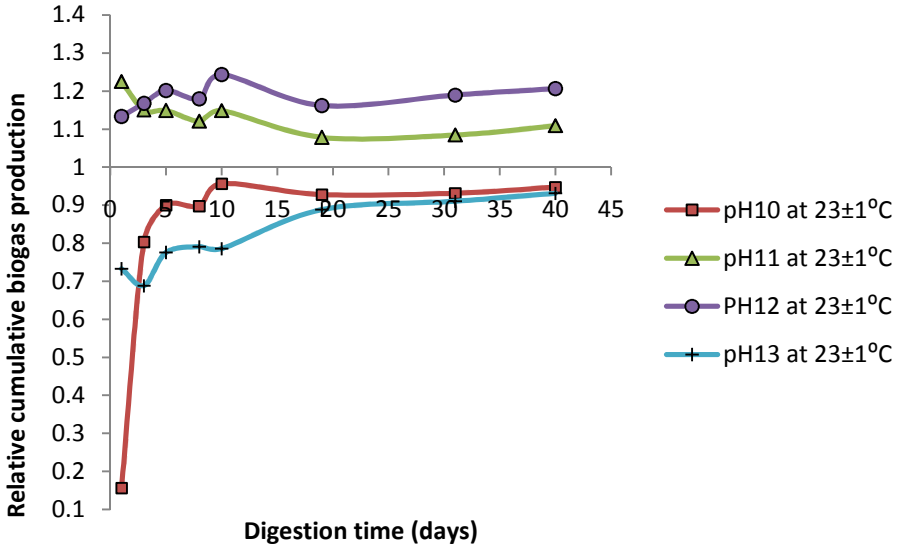

Figure 4.8: Relative cumulative biogas production for samples pretreated with NaOH at 23±1°C.

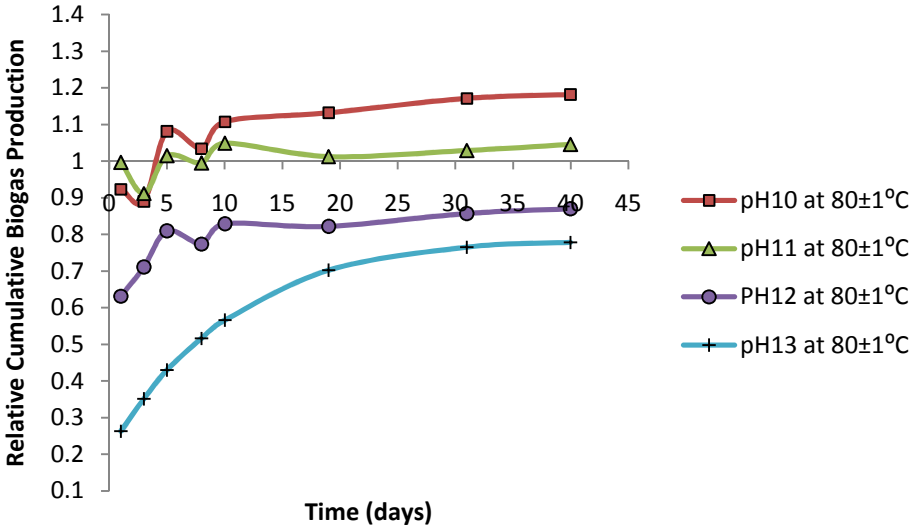

Figure 4.9: Relative cumulative biogas production for samples pretreated with NaOH at 80±1°C.

Figures 4.10 and 4.11 show the cumulative methane gas production during the BMP assay for samples pretreated at 23±1°C and 80±1°C, respectively. The data points represent the arithmetic mean for duplicate reactors. As it is observed from these figures the trends of methane gas production for the pretreated samples are very similar to the trends of biogas production. Biogas composition for samples was measured three times during the BMP assay, the average methane fraction of the biogas ranged from 51.4±1.2 to 58.2±0.1%.

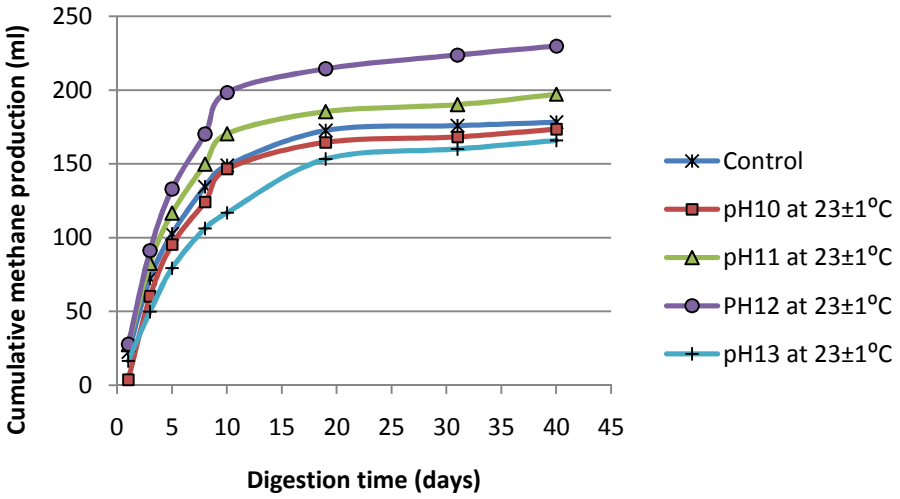

Figure 4.10: Cumulative methane production for samples pretreated with NaOH at 23±1°C.

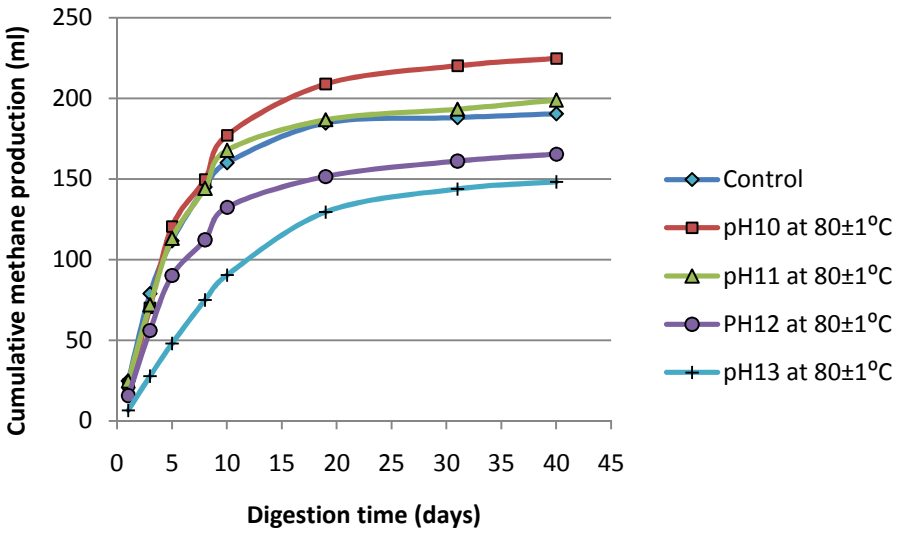

Figure 4.11: Cumulative methane production for samples pretreated with NaOH at 80±1°C.

Figure 4.12 and 4.13 demonstrate the percentage of improvement or inhibition in biogas and methane production for the pretreated samples relative to the non-pretreated control. As observed from the NaOH-BMP assay results the NaOH pretreatment did not have a significant effect on biogas or methane production at low pH levels at 23±1°C. The significant improvement in biogas and methane production is observed at pH 11 with a 10.9±0.5% improvement in cumulative biogas production compared to control (Figure 4.12). At a pH of 12 the maximum improvement in biogas production reached 20.6±0.7% compared to the control; this significant improvement in cumulative biogas production indicates that organic materials were more readily available for consumption and larger quantities of organic material were available for consumption by the microorganisms after the pretreatment. When samples where pretreated at high temperature (80±1°C), the samples with lower pH levels showed significantly higher biogas production during the BMP assay. For example, samples pretreated at pH 10 at 80±1°C demonstrated a 17.4±0.6% increase in cumulative biogas production as compared to the control (Figure 4.13). Pretreatment at pH 12 at 80±1°C showed a significant reduction in the cumulative biogas production during the BMP assay. Despite the high COD solubilization that occurred at pH 13 (Figure 4.1 and 4.2), this high pH level led to a significant inhibition in the biogas production during the NaOH-BMP assay for both temperatures at 23±1°C and 80±1°C.

The inhibition was most notable and significant in the case of high temperature pretreatment (at 80±1°C). The cumulative biogas production at the end of the NaOH-BMP assay for samples pretreated at pH 13 at 80±1°C was 21.7±0.6 % less than the control. Again this significant decrease in biogas production may be attributed to the formation of inhibitory compounds that are hard to degrade or that may be exerting a toxic effect on the methanogenic microorganisms.

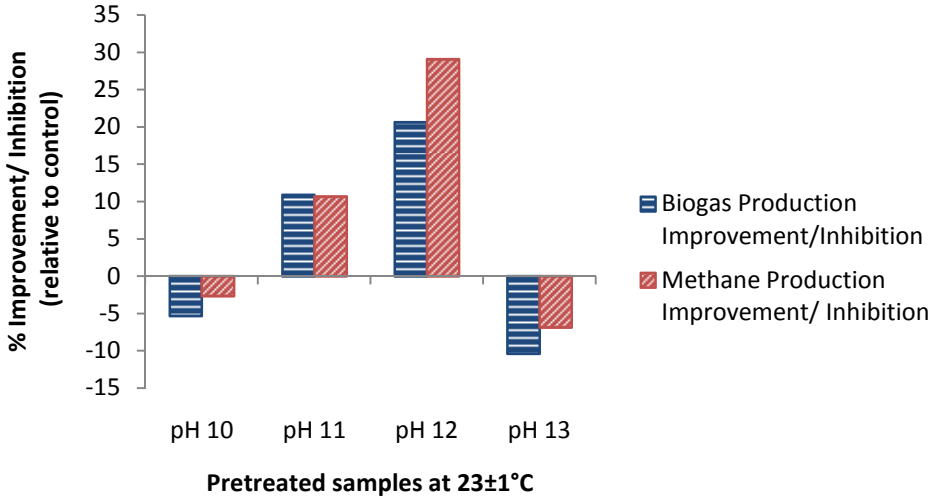

Figure 4.12: Biogas and methane production improvement/ inhibition compared to control, at 23±1 °C.

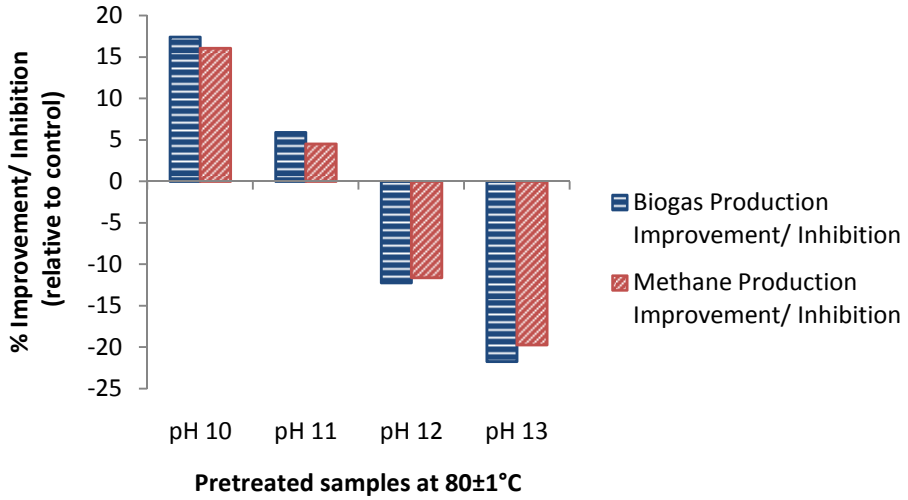

Figure 4.13: Biogas and methane production improvement/ inhibition compared to control, at 80±1 °C.

4.2.1.2 VS removal during the BMP assay for NaOH pretreated samples

Figure 4.14 shows the arithmetic mean of VS concentrations for duplicate samples used in the NaOH-BMP assay, the final values represent the arithmetic mean of VS concentrations for duplicate batch reactors. This figure indicates the VS destruction that occurred during the BMP assay and it gives an indication of how much organic matter was converted to methane during the BMP assay. It is evident from the Figure 4.14 that the initial concentrations of VS for all samples were 6.1±0.1 (g/kg).

In general the VS removal ranged from 65.8 to 77.5% with the lowest VS removal occurring for samples pretreated at pH 13 at both temperatures 23±1°C and 80±1°C. The highest VS removals occurred in samples pretreated at pH 11 and 12 at 23±1°C which both showed significant difference in VS destruction compared to control.

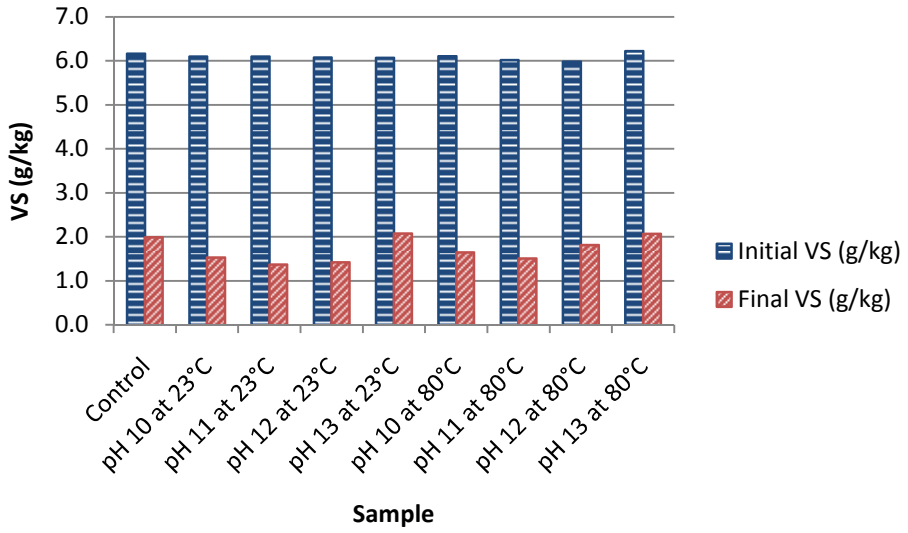

Figure 4.14: Initial and final VS concentrations for the NAOH-BMP assay.

Calculated VS removal and methane gas yields are shown in Table 4.6. The data in the table represents the arithmetic mean of duplicates, and the associated standard deviation or combined error.

From Table 4.6 we see that the highest methane yield relative to the removed VS is observed for samples pretreated at pH 12 at 23±1°C, which is significantly higher than the control by 15.8±0.7%. Also samples pretreated at pH 10 at 80±1°C demonstrated significantly higher methane yields relative to the removed VS as compared to the control by 8.6±0.7%. On the other hand samples pretreated at the highest pH level (pH 13) in combination with heat (80±1°C) had the lowest methane yield relative to the removed VS; the yield was 19.2±1.3% less than the control which is a significant difference. In general the yields relative to the removed VS ranged from 236 to 338 mL/g.

Table 4.6: VS removal and methane yields for samples during the NaOH-BMP assay.

Sample	Methane produced (ml)	VS removal (%)	Methane yield (mL CH_4/g VS_{added})	Methane yield (mL CH_4/g $VS_{removed}$)
Control	178.1±4.7	67.7±1.2	179.7±5.2	291.9±9.1
pH 10 at 23±1°C	173.4±9.6	74.9±3.9	194.6±10.8	259.8±19.9
pH 11 at 23±1°C	197.1±4.3	77.5±0.7	221.4±4.8	285.6±6.7
pH 12 at 23±1°C	229.8±6.1	76.6±0.9	258.9±7.2	338.0±9.6
pH 13 at 23±1°C	156.8±1.8	65.8±2.0	176.8±2.1	268.6±8.8
pH 10 at 80±1°C	206.7±5.0	73.0±5.3	231.6±5.6	317.1±24.1
pH 11 at 80±1°C	186.1±4.2	74.8±1.9	211.6±5.6	282.7±8.8
pH 12 at 80±1°C	157.4±0.8	69.7±1.0	180.2±1.6	258.7±3.4
pH 13 at 80±1°C	143.0±2.4	66.7±4.0	157.3±4.4	236.0±13.9

4.2.1.3 TCOD and SCOD removal during the NaOH- BMP assay

Table 4.7 below shows the results of TCOD and SCOD removal and the methane yield for the NaOH pretreatment BMP experiments. The arithmetic mean of duplicates and the associated combined errors are presented.

Table 4.7 demonstrates that the TCOD removal ranged from 42.0±0.9% for samples pretreated at pH 13 at 23±1°C to 58.1±1.3% for samples pretreated at pH 12 at 23±1°C. No significant improvement of TCOD removal is observed for the NaOH pretreated samples over the control. The highest TCOD removal is seen for samples pretreated at pH 12 at 23±1°C, which is 2.4% greater than the TCOD removal for control. In contrast samples pretreated at pH 13 had a

significantly lower TCOD removal compared to control. Samples pretreated at pH 13 at 23±1°C and 80±1°C had 10.3 % and 25.7% less TCOD removal than control, respectively. The TCOD removals for pretreated samples at both temperatures 23±1°C and 80±1°C are significantly lower than the control and the other pretreated samples.

Table 4.7: TCOD and SCOD removal and methane yields for samples during the NaOH-BMP assay.

Sample	TCOD removal (%)	SCOD removal (%)	Methane yield (mL CH_4/g $TCOD_{removed}$)
Control	56.7±0.8	93.2±1.1	245.1±7.3
pH 10 at 23±1°C	57.1±0.2	94.7±0.4	239.6±13.3
pH 11 at 23±1°C	56.7±1.8	94.8±0.6	285.4±10.8
pH 12 at 23±1°C	58.1±1.3	96.9±0.4	302.6±10.5
pH 13 at 23±1°C	50.9±1.0	89.4±1.1	217.9±5.0
pH 10 at 80±1°C	56.0±2.0	95.3±1.0	301.3±12.7
pH 11 at 80±1°C	55.6±0.6	95.0±0.8	272.8±6.8
pH 12 at 80±1°C	53.4±0.9	94.0±0.2	222.2±3.9
pH 13 at 80±1°C	42.0±0.9	88.1±1.3	212.8±5.8

The methane yield relative to the removed TCOD ranged from 212.8±5.8 to 302.6±10.5 mL/g, with the highest yield observed for samples pretreated at pH 12 at 23±1°C followed by samples pretreated at pH 10 at 80±1°C. The methane yield relative to the removed TCOD values in general were significantly less than the theoretical expected value of 350 mL of methane related to gram of TCOD removed (Penaud et al., 1999; Speece, 1996), but still within the range reported in literature as 100 to 350 mL of methane related to gram of TCOD removed (Droste, 1997).

From the SCOD results shown in Table 4.7 we observe that the SCOD removal results follow the same approximate trend as the TCOD removal results with the maximum SCOD removal occurring for pretreated samples at pH 12 at 23±1°C. The minimum SCOD removal was again observed for samples pretreated at pH 13 at 80±1°C. The results for pH 13 pretreated samples suggest that the soluble organic materials that were released during the pretreatment of these samples may be difficult to degrade.

4.2.1.4 Ammonia during the NaOH-BMP assay

During the anaerobic digestion process ammonia released in the system is due to the digestion of organic materials; however ammonia at high concentrations inhibits methanogens microorganisms. Kayhanian (1999) states that for the digestion of OFMSW ammonia concentrations of 1200 mg/L have an inhibitory effect on the anaerobic digestion process in the system. In the current study ammonia was measured at the beginning and the end of the NaOH-BMP assay, the results are represented in Figure 4.15. Ammonia concentration values are the arithmetic mean for duplicates.

As we see in Figure 4.15, ammonia concentrations increased significantly during digestion, but remained below the toxic threshold levels for anaerobic digestion systems throughout the experiments.

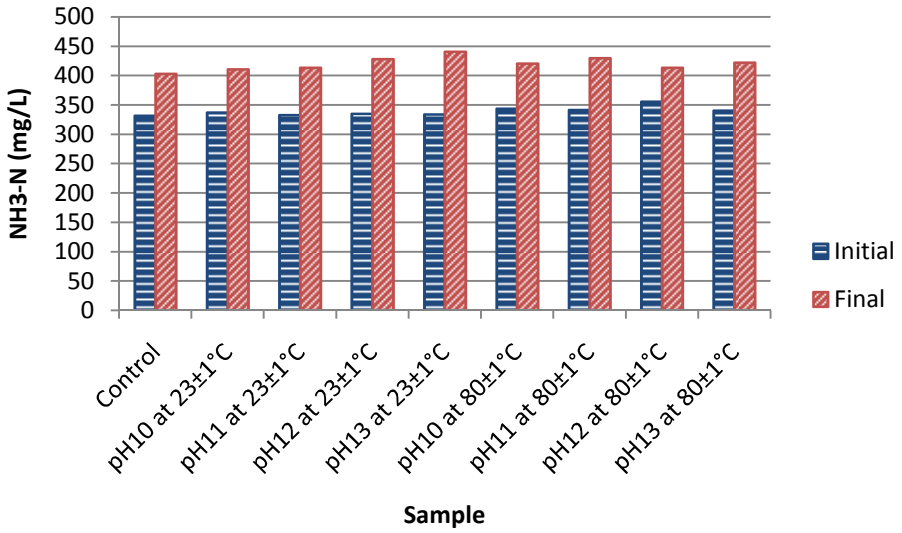

Figure 4.15: Initial and final ammonia concentrations for the NaOH-BMP assay.

4.2.1.5 TVFAs during the NaOH-BMP assay

Total volatile fatty acid (TFVA) concentrations were measured four times during the digestion period for the NaOH BMP assay. Figure 4.16 shows the TVFAs during the BMP assay at 23±1°C,

and Figure 4.17 represents the TVFAs for the pretreated samples at 80±1°C. Data are arithmetic mean of duplicates. The shape of the curves representing TVFAs concentration for the different samples is a result of the limited four data points.

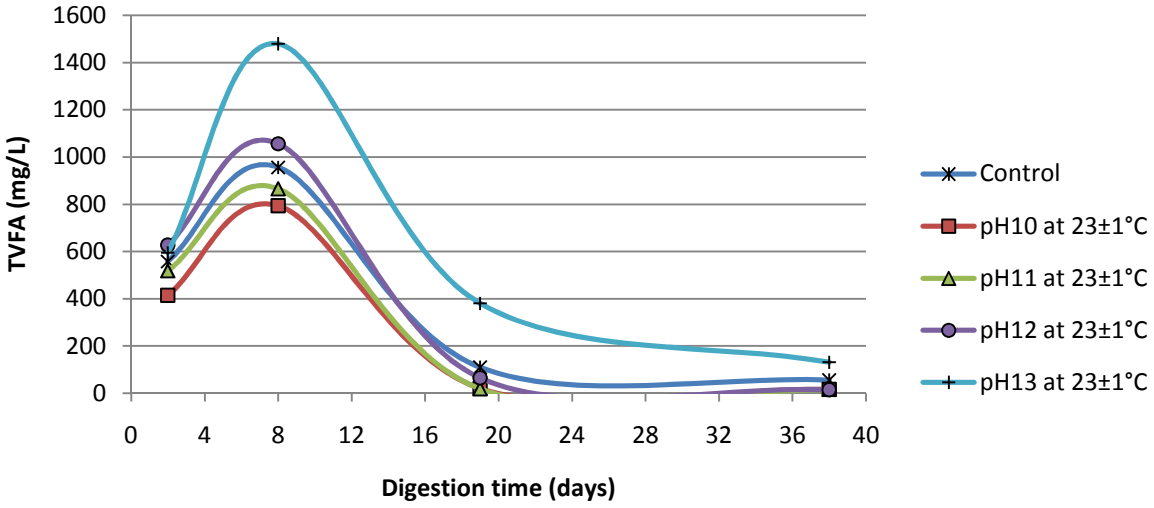

Figure 4.16: TVFAs NaOH pretreated samples at 23±1°C during the NaOH-BMP assay.

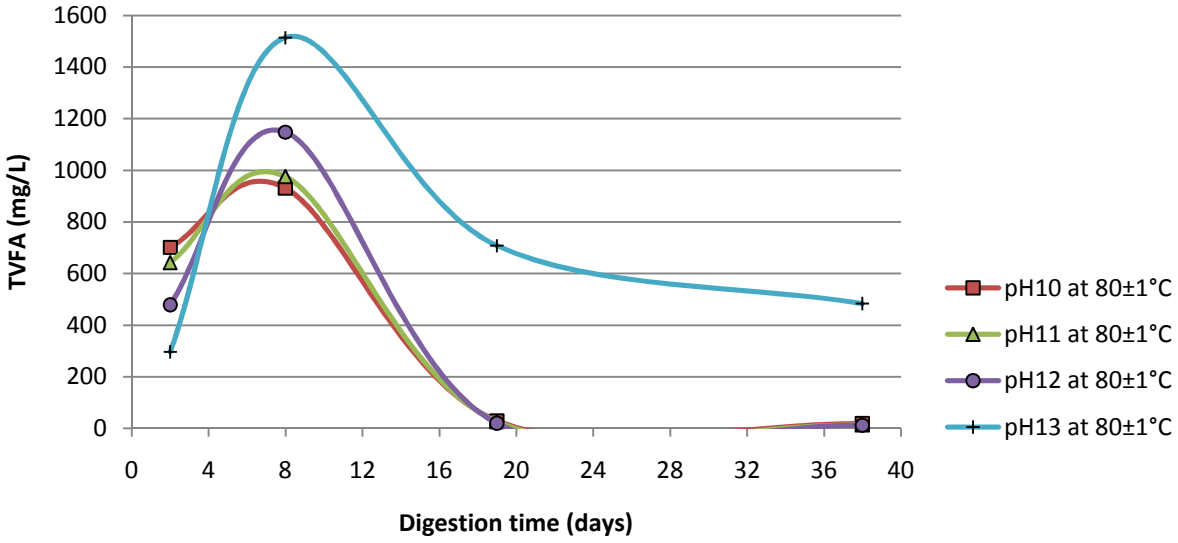

Figure 4.17: TVFAs for NaOH pretreated samples at 80±1°C during the NaOH-BMP assay.

The maximum TVFAs accumulations in all samples were observed during the beginning of the second week of digestion; subsequently the TVFAs decreased dramatically and approached zero by the end of the third week of digestion, except for the samples at pH 13 which remained at higher TVFA concentrations until the end of the BMP assay. The high accumulation of TVFAs for the pH13 samples might contribute to the low biogas production during the test as high TVFA concentrations can cause inhibition of biogas production in AD systems (Mata-Alvarez, 2002).

4.2.2 KOH-BMP Assay

In this BMP assay KOH pretreated samples are investigated in duplicate.

4.2.2.1 Biogas production during the KOH- BMP assay

The cumulative biogas volumes produced by the KOH pretreated samples at 23±1°C and at 80±1°C are demonstrated in Figure 4.18 and 4.19. The data are the arithmetic mean for duplicate reactors.

Figures 4.18 and 4.19 show that a lag phase is once again not observed during the BMP assay at 23±1°C and 80±1°C. This might be as mentioned before in the NaOH-BMP discussion due to the proper acclimation of inoculum to this type of waste prior to the BMP assay. As shown in Figure 4.18, the highest biogas production for samples pretreated at 23±1°C was observed for samples pretreated at pH 12. These samples produced 31.6±0.8% more cumulative biogas than control and this maximum improvement is significantly higher than the maximum improvement that was observed during the NaOH-BMP assay.

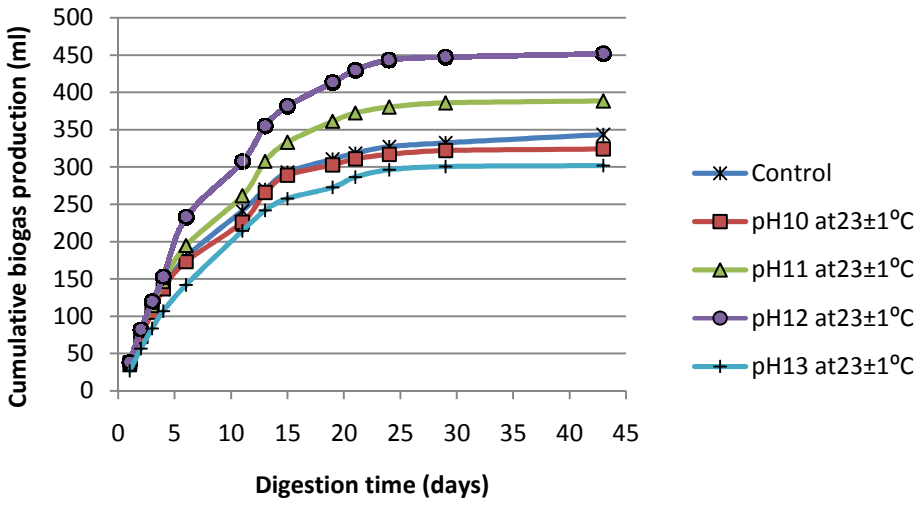

Figure 4.18: Cumulative biogas production for samples pretreated with KOH at 23±1°C.

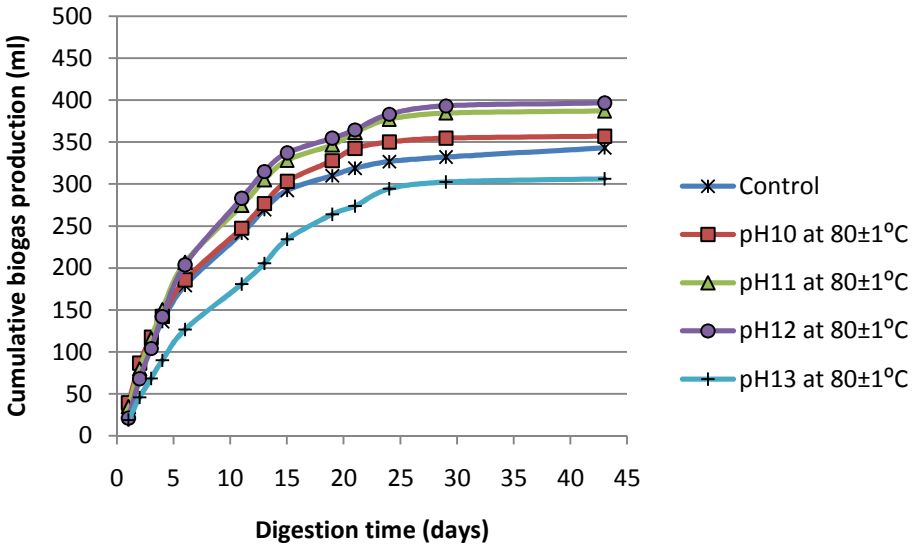

Figure 4.19: Cumulative biogas production for samples pretreated with KOH at 80±1°C.

Figure 4.20 and 4.21 represent the cumulative biogas production, relative to the control, for samples pretreated at 23±1°C and 80±1°C, respectively. Figure 4.20 represents the relative biogas production for samples pretreated at 23±1°C. At the beginning of the BMP assay, samples pretreated at pH 10 and 12 demonstrated similar biogas production rates with the pH

12 pretreated samples showing the highest biogas production after 40 days. Samples pretreated at pH 11 showed slightly lower biogas production rate compared to the non-pretreated control at the start of the experiments but started to demonstrate a significantly higher biogas production than control after about 2 days. The exception were the samples pretreated at pH 13 which started the assay with a low biogas production and continued the same trend throughout the experiment and after 40 days produced 12.1±0.3% less cumulative biogas production than the control.

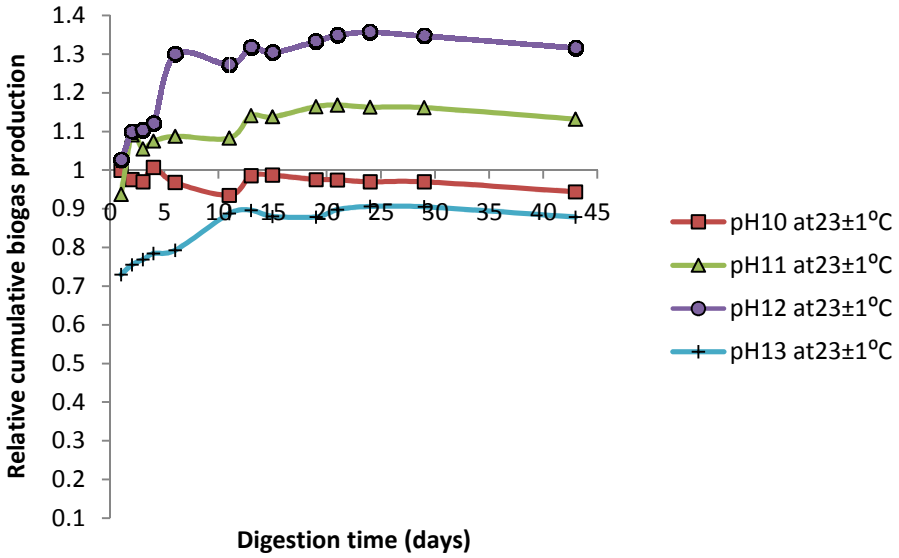

Figure 4.20: Relative cumulative biogas production for samples pretreated with KOH at 23±1°C.

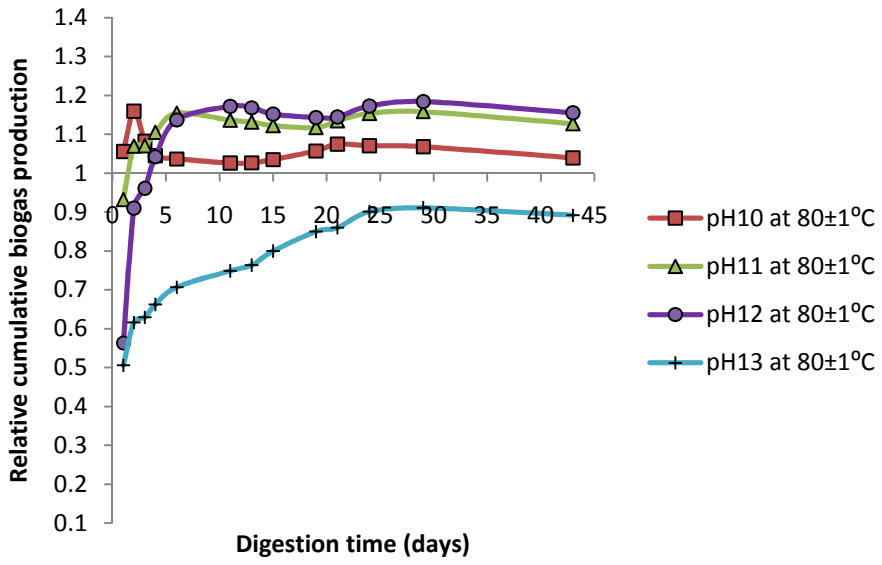

Figure 4.21: Relative cumulative biogas production for samples pretreated with KOH at 80±1°C.

As shown in Figure 4.12 for samples pretreated at 80±1°C, all samples started with significantly lower biogas production relative to control except the samples pretreated at pH 10. Three days after the beginning of the BMP assay all the samples reached a significantly higher biogas production than the control except the samples pretreated at pH 13. At the end of the BMP assay the samples pretreated at pH 12 had the highest cumulative biogas production, which was 15.5±0.5 % greater than the control. Samples pretreated at pH 13 were the only samples that demonstrated significantly less cumulative biogas production than the control. Again the low biogas production during the KOH-BMP assay for samples pretreated using KOH at pH 13 at both temperatures of 23±1°C and 80±1°C might be due to the formation of refractory compounds that are difficult to digest. However the inhibition in cumulative biogas production caused by KOH pretreatment at the highest pH level of 13 was not as severe as NaOH pretreated samples at pH 13.

Methane composition for samples was measured three times during this BMP assay, the methane fraction of the biogas ranged from 52.2±0.4 to 57.1±0.1%. Figures 4.22 and 4.23 represent the cumulative methane gas production during the BMP assay for samples pretreated at 23±1°C and 80±1°C, respectively. The data are arithmetic means for duplicate reactors. These

figures clearly show that the trends of methane gas production for the pretreated samples are similar to the trends of biogas production.

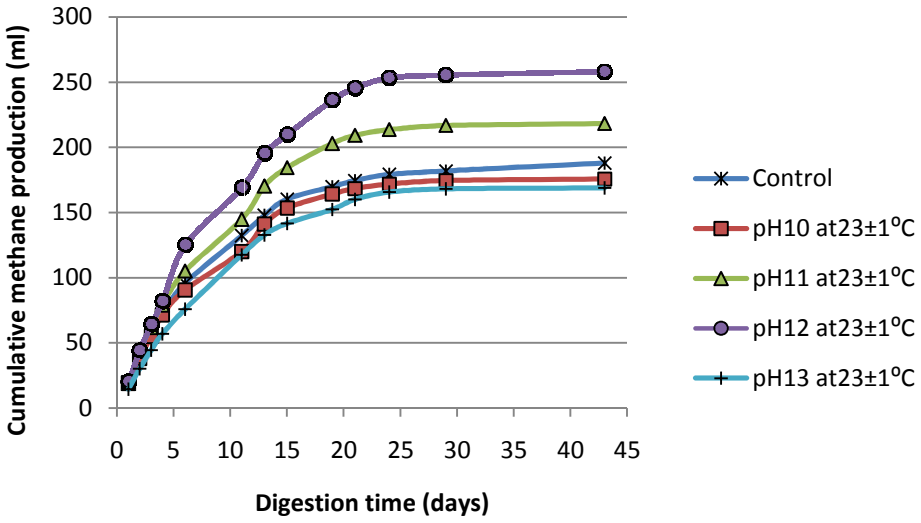

Figure 4.22: Cumulative methane production for samples pretreated with KOH at 23±1°C.

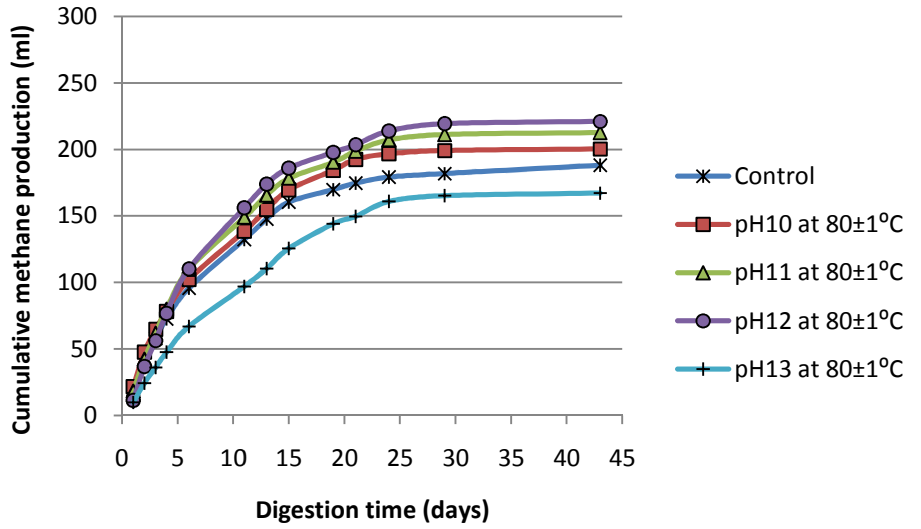

Figure 4.23: Cumulative methane production for samples pretreated with KOH at 80±1°C.

Using KOH for alkali pretreatment of OFMSW at certain pH values had a positive effect on the biogas production during the BMP assay. The improvement or inhibition in cumulative biogas production and cumulative methane production compared to the control are represented in Figures 4.24 and 4.25 for samples pretreated at 23±1°C and 80±1°C, respectively. The maximum cumulative biogas improvement was 31.6±0.8% at pH 12 at 23±1°C, which is significantly greater and in fact about 1.5 times greater than the maximum improvement in the cumulative biogas production observed for NaOH pretreated samples at 23±1°C. On the other hand samples pretreated with KOH at pH 13 at 23±1°C had a significantly lowest cumulative biogas production than the non pretreated control; 12.1±0.3% less than the control.

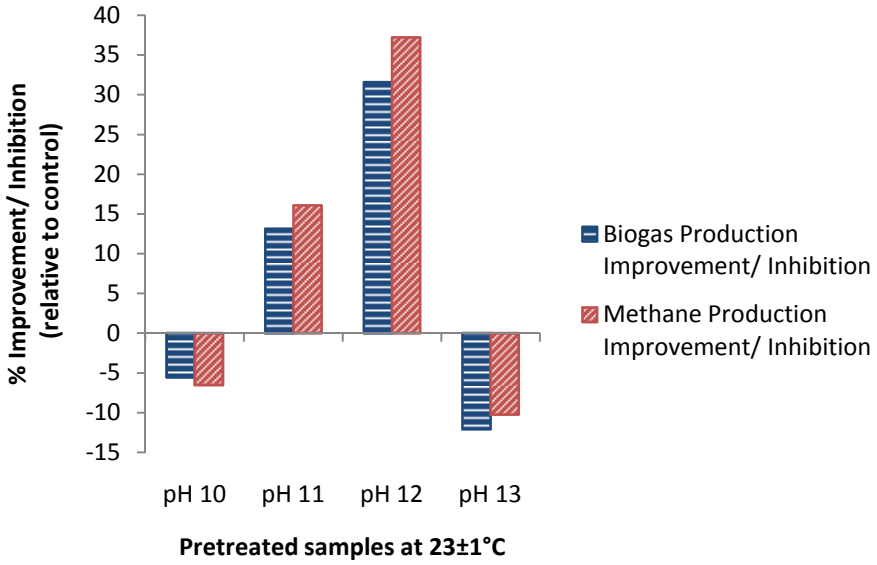

Figure 4.24: Biogas and methane production improvement/ Inhibition compared to control, at 23±1°C.

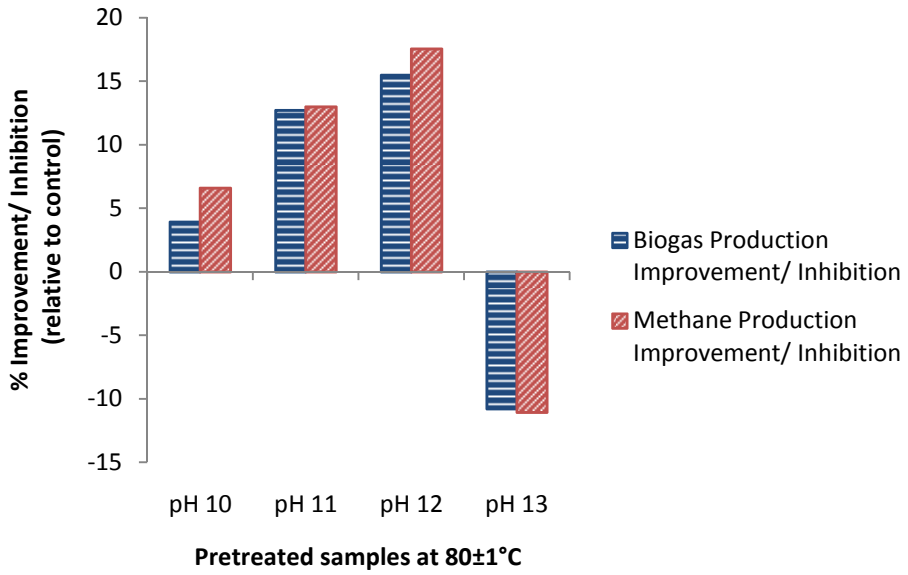

Figure 4.25: Biogas and methane production improvement/ Inhibition compared to control, at 80±1°C.

4.2.2.2 VS removal during the KOH- BMP assay and methane yield

Figure 4.26 shows the initial and final VS concentrations for KOH pretreated samples. The initial concentrations of VS are approximately similar for all the samples with the average initial VS concentration being 6.0±0.2 (g/kg). The initial values in the figure represent arithmetic mean of VS concentrations for duplicate measurements for the samples used in the BMP assay, the final values represent arithmetic mean of duplicate batch reactors.

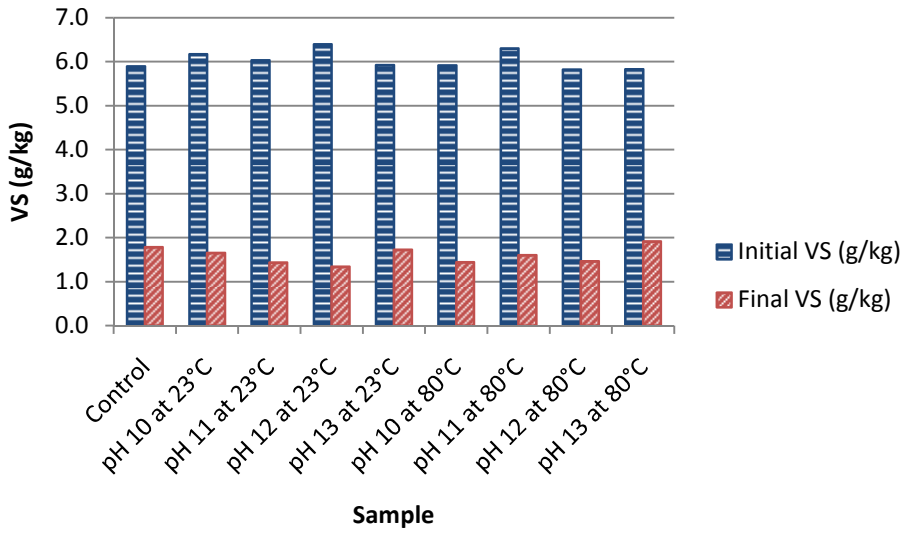

Figure 4.26: Initial and final VS concentrations for the KOH-BMP assay.

The observed VS removal ranged from 69.8±2.4% for the control to 79.0±2.1% in the case of samples pretreated at pH 12 at 23±1°C. Samples pretreated at pH 13 at 23±1°C and 80±1°C had slightly higher but not significant VS removal compared to the control.

Table 4.8 shows the VS removal and the methane gas yield related to the removed VS. The data represents the arithmetic mean of duplicates, and the standard deviation or combined error. As we see from the table the methane yield related to the removed VS was higher for all samples compared to the NaOH BMP yields. These results suggest that KOH is a more efficient than NaOH for the alkaline pretreatment of OFMSW prior to anaerobic digestion.

Table 4.8: VS removal and methane yield for all samples during the KOH-BMP assay

Sample	Methane produced (ml)	VS removal (%)	Methane yield (mL CH_4/g VS_{added})	Methane yield (mL CH_4/g $VS_{removed}$)
Control	188.1±7.5	69.8±2.4	218.5±9.9	313.2±15.3[c]
pH 10 at 23±1°C	175.8±2.2	73.3±1.2	195.2±3.0	266.5±7.6
pH 11 at 23±1°C	218.3±1.6	76.3±0.9	247.9±3.1	325.0±3.6
pH 12 at 23±1°C	258.0±4.7	79.0±2.1	276.5±7.5	349.9±11.1
pH 13 at 23±1°C	168.8±4.0	70.9±3.0	195.4±7.0	275.7±14.1
pH 10 at 80±1°C	200.4±6.6	75.7±0.8	232.3±7.2	307.1±14.6
pH 11 at 80±1°C	212.5±2.4	74.6±2.8	231.1±6.6	309.6±16.5
pH 12 at 80±1°C	221.1±10.5	74.9±0.6	260.4±11.6	347.8±3.4
pH 13 at 80±1°C	167.3±5.8	67.2±0.8	196.7±6.5	292.7±13.9

4.2.2.3 TCOD and SCOD removal during the KOH-BMP assay

The TCOD and SCOD results of the KOH pretreated samples are shown in Table 4.9, where the data in the table are arithmetic means of duplicates and the associated combined error. The TCOD removal ranged from 50.8±1% to 59.9±0.3%, and SCOD removal ranged from 91.9±1.1% to 97.8±0.1%. The highest TCOD and SCOD removal were for samples pretreated at pH 12 at 23±1°C. Samples pretreated at pH 13 at 23±1°C and 80±1°C had the lowest TCOD and SCOD removal. The maximum methane yield related to removed TCOD was for samples pretreated at pH 12 at 80±1°C and it was 277.3 mL/g; followed by samples pretreated at pH 11 at 23±1°C with 276.5 mL/g. Methane yield values for the control and pretreated samples in this BMP assay also were significantly less than the theoretical expected value of 350 mL/g, but still within the range reported in literature review as 100 to 350 mL/g.

Table 4.9: TCOD and SCOD removal and methane yield for all samples during the KOH-BMP assay.

Sample	TCOD removal (%)	SCOD removal (%)	Methane yield (mL CH_4/g $TCOD_{removed}$)
Control	55.8±0.7	96.0±0.6	259.4±20.8
pH 10 at 23±1°C	56.5±0.7	97.0±0.3	223.6±18.8
pH 11 at 23±1°C	56.7±0.1	96.5±0.9	276.5±3.5
pH 12 at 23±1°C	59.9±0.3	97.8±0.1	269.3±10.4
pH 13 at 23±1°C	51.1±0.4	92.2±1.1	212.8±12.1
pH 10 at 80±1°C	55.7±0.5	96.0±0.5	264.1±19.1
pH 11 at 80±1°C	57.5±0.4	97.2±0.5	253.1±12.7
pH 12 at 80±1°C	56.0±0.3	95.8±0.3	277.3±15.7
pH 13 at 80±1°C	50.8±0.2	91.9±1.1	213.6±8.7

4.2.2.4 Ammonia during the KOH-BMP assay

Ammonia was measured at the beginning and the end of the KOH-BMP assay, the results are represented in Figure 4.27. Ammonia concentration values are the arithmetic means for duplicate samples. The final ammonia concentrations measured at the end of the BMP assay for pretreated samples were significantly higher than the initial ammonia concentrations, but ammonia concentrations in the batch bottles were much lower than the toxic levels for anaerobic digestion systems.

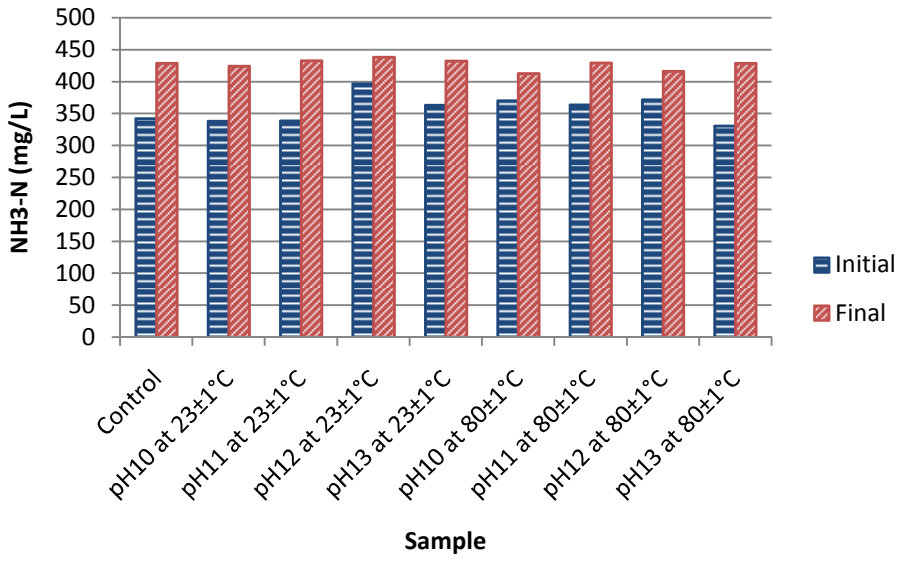

Figure 4.27: Initial and final ammonia concentrations for the KOH-BMP assay.

4.2.2.5 TVFAs during the KOH-BMP assay

Total volatile fatty acids (TFVAs) concentrations for all the batch bottles of the KOH-BMP assay were measured four times during the digestion period. Figure 4.28 shows the TVFA concentrations during this BMP assay for pretreated samples at 23±1°C, and Figure 4.29 represents the TVFA concentrations for the pretreated samples at 80±1°C. Data in the figures are the arithmetic means for duplicates. The maximum TVFA accumulations occurred during the second week of digestion followed by a decreased in TVFA concentrations approaching zero by the end of the third week of digestion. The pretreated samples at pH 13 at 23±1°C and 80±1°C the TVFAs concentrations were in general higher than TVFAs concentrations of control and other pretreated samples and continued at the same trend until approaching the zero at the end of the BMP assay.

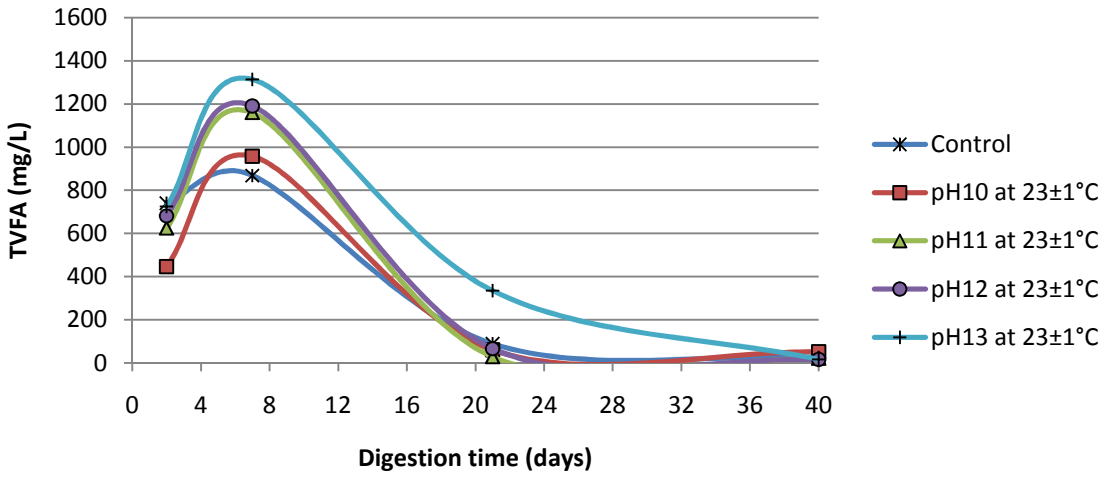

Figure 4.28: TVFAs for control and pretreated samples at 23±1°C during the KOH-BMP assay.

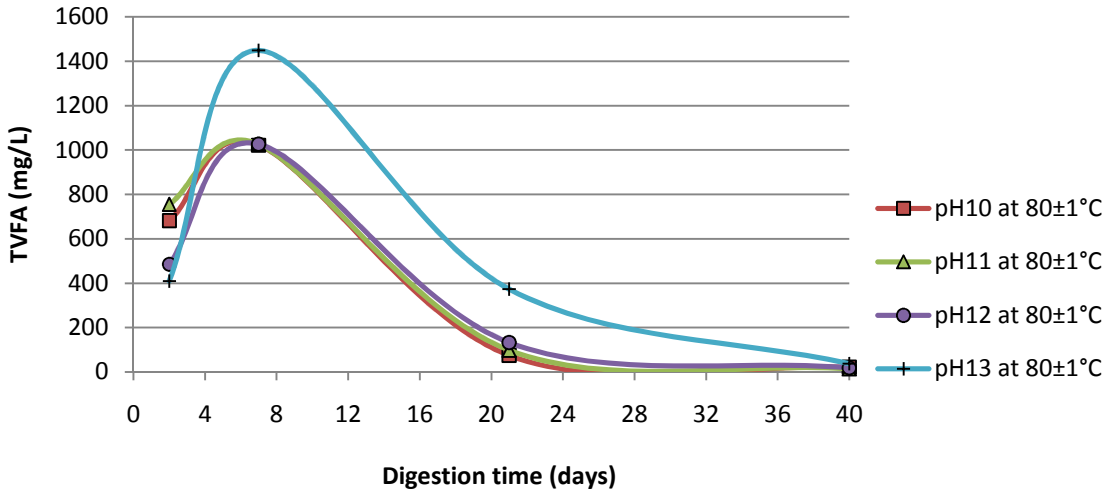

Figure 4.29: TVFAs for control and pretreated samples at 80±1°C during the second BMP assay.

4.3 Semi-Continuous Anaerobic Reactors

A total of nine mesophilic reactors were operated in this experimental phase, each with a 0.8-L working volume. The reactors were divided into three sets with each set operating at a different solid retention times (SRT) of 10, 15 and 20 days. Every set included three reactors with the first acting as a control, the second being fed with samples pretreated with NaOH at

pH12 at 23±1°C, and the last reactor being fed with samples pretreated with KOH at pH 12 at 23±1°C (Figure 4.30).

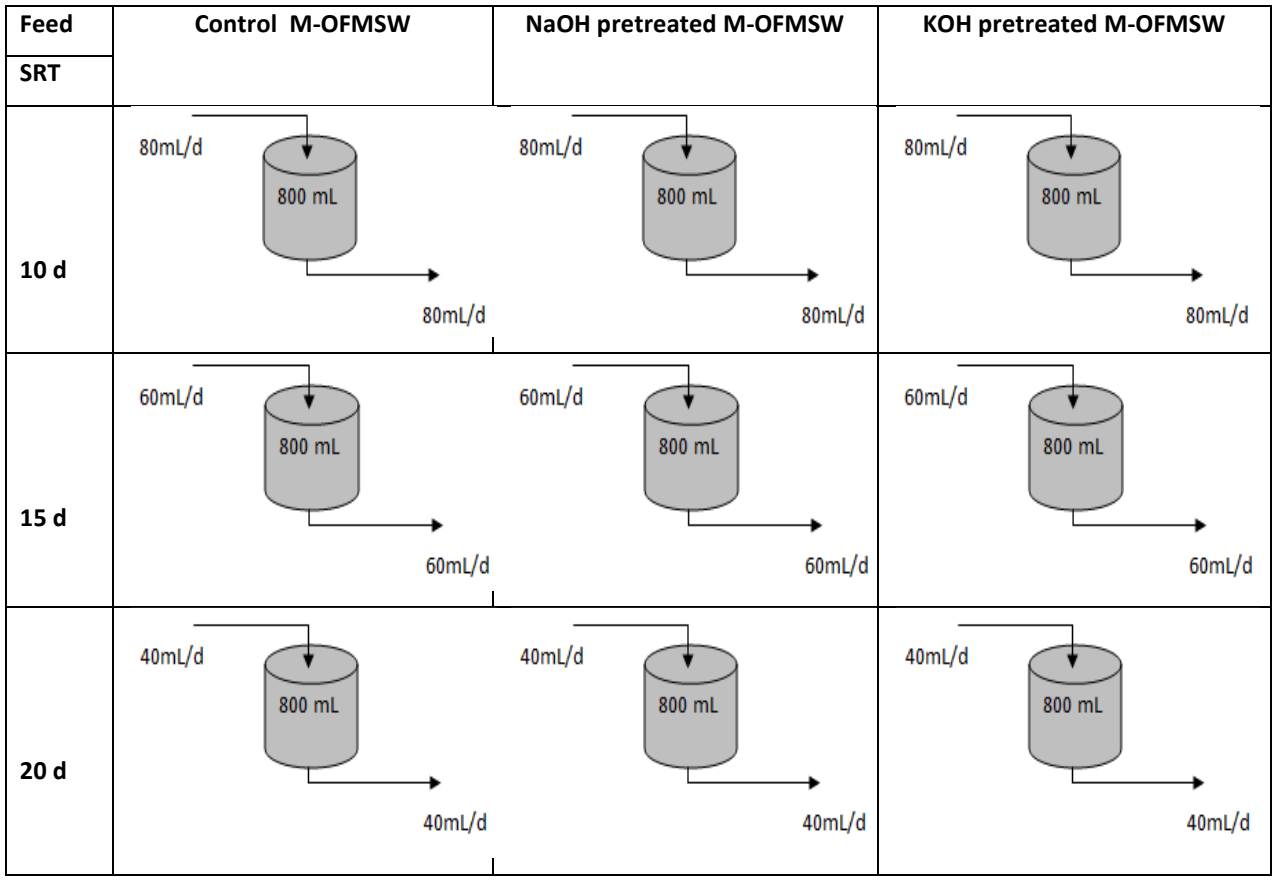

Figure 4.30: Schematic of semi-continuous reactor experimental set-up.

The NaOH-BMP assay results shown in Chapter 4.2.1 demonstrate that samples pretreated using NaOH at pH 12 at 23±1°C had the best anaerobic digestion performance and thus its performance was chosen for semi-continuous investigation. These samples showed a 20.6±0.7% greater cumulative biogas production than the control and the highest TCOD and SCOD removal of 58.1±1.3% and 96.9±0.4%, respectively. Furthermore, these samples demonstrated a 76.6±0.9% VS removal and the highest methane yield of 338±9.6 mL of methane relative to gram of VS removed.

The KOH-BMP assays results for samples pretreated using KOH shown in Chapter 4.2.2 demonstrate that samples pretreated at pH12 at 23±1°C are the optimum pretreatment condition when using KOH and thus these conditions were chosen for semi-continuous investigation. Samples pretreated at pH 12 at 23±1°C using KOH had a 31.6±0.8% greater cumulative biogas production than the control, and these samples showed the highest VS, TCOD and SCOD removals of 79.0±2.1%, 59.9±0.3, and 97.8±0.1, respectively. Furthermore these samples had the highest methane yield of 349.9±11.1 mL of methane relative to gram of VS removed.

4.3.1 Biogas Production of Semi-Continuous Reactors

The daily biogas productions of the different semi-continuous reactors are shown in Figures 4.31, 4.32 and 4.33 for SRT 10, 15 and 20 days, respectively. The reactors were considered to achieve steady-state when the daily biogas fluctuation was less than 10%. Reactors operated at the various SRTs of 10, 15 and 20 days needed on average approximately two times their SRTs to achieve steady state conditions. In general it was observed that the reactors fed with pretreated waste required shorter times to achieve steady state as compared to the control. For example, in case of the semi-continuous reactors operated at an SRT of 20 days, the control reactor needed 50 days to achieve steady state conditions, whereas 40 and 36 days were required for the reactors fed with NaOH and KOH pretreated waste to achieve steady state conditions, respectively.

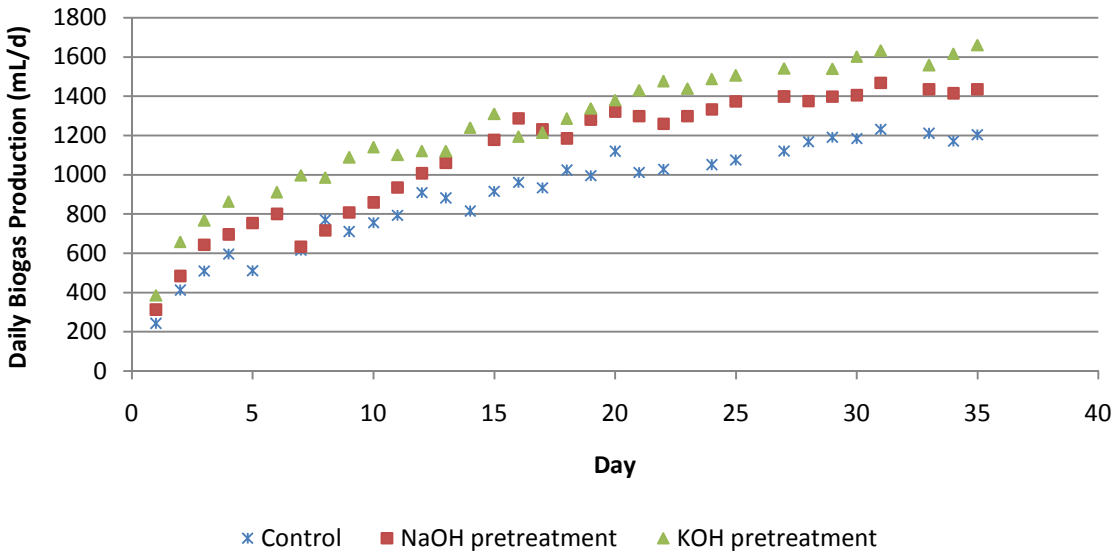

Figure 4.31: Daily biogas production during the semi-continuous digestion at 10 days SRT.

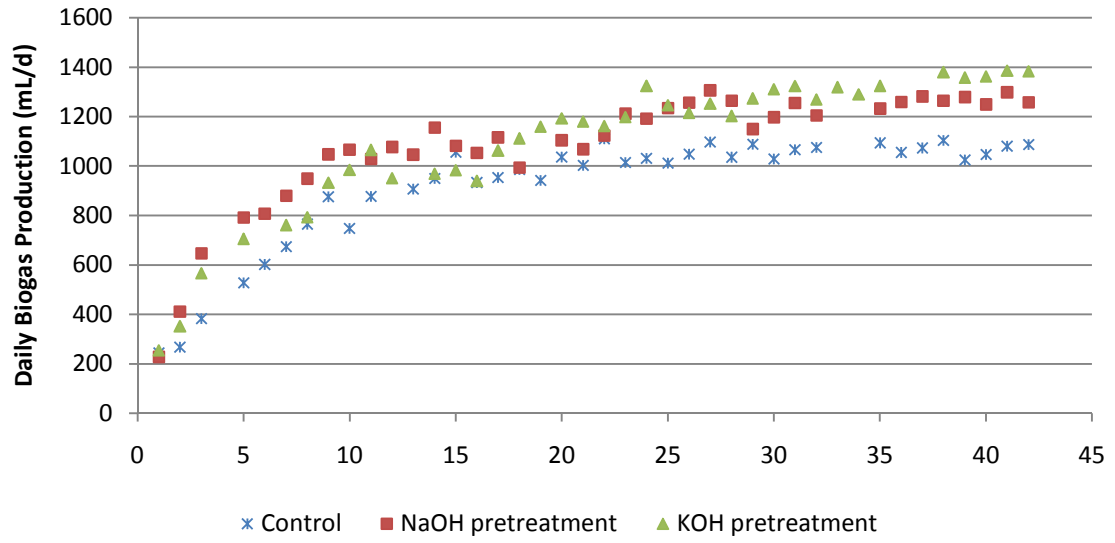

Figure 4.32: Daily biogas production during the semi-continuous digestion at 15 days SRT.

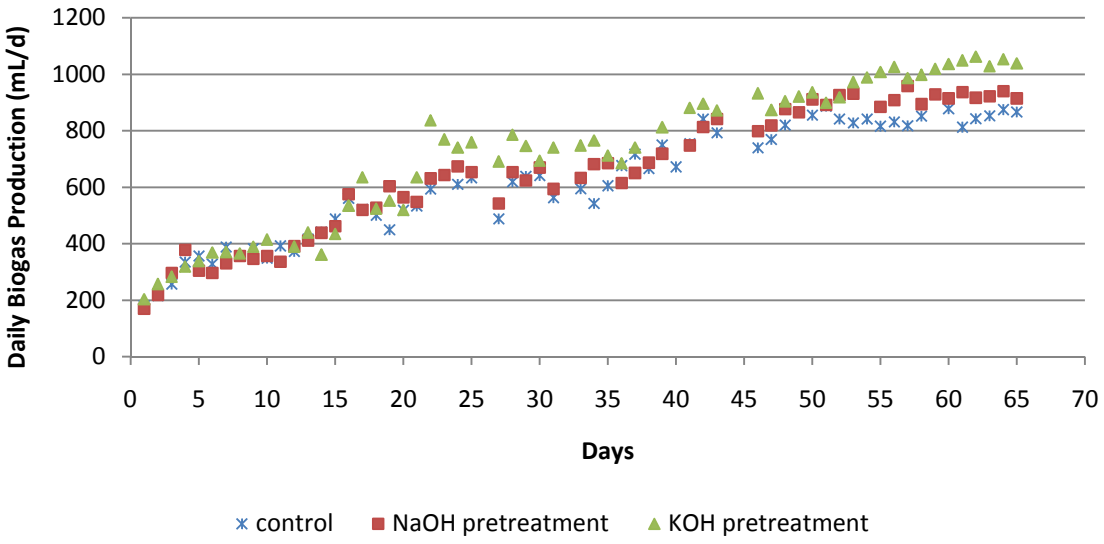

Figure 4.33: Daily biogas production during the semi-continuous digestion at 20 days SRT.

The steady state daily biogas and methane production are shown in Figure 4.34. Data in the figure are arithmetic means over the steady state conditions and the error bars show the 95% confidence intervals. The average daily biogas production for the control reactors were 1138±77, 1058±30 and 836±36 mL/d at SRT 10, 15 and 20 days, respectively. Reactors fed with NaOH pretreated samples had 1345±79, 1229±60 and 864±85 mL/d average daily biogas production at SRT of 10, 15 and 20 days, respectively. Whereas reactors fed with KOH pretreated samples had the highest average daily biogas production at the three different SRTs, with the average daily biogas production being 1481±128, 1305±59 and 922±111 mL/d at SRT 10, 15 and 20days. As we observe from these results the daily biogas production increased as the SRT decreased for reactors fed with the same sample with the increase at all SRTs being significant. The observed increase in gas production at lower SRTs may also be attributed to the higher loading rates at lower SRTs, which is analyzed below in the results normalized per VS and TCOD loading. Also from Figure 4.34 we observed a statistically significant positive effect of pretreating the waste on the daily biogas production at SRTs of 10 and 15 days for both NaOH and KOH pretreatment. NaOH pretreatment caused an increase of 18.2, 16.2 and 3.3% on the average daily biogas production compared to the control for SRT 10, 15 and 20 days, respectively. KOH pretreatment resulted in a 30.1, 23.2 and 10.3% higher average daily biogas

production compared to the control at SRT of 10, 15 and 20 days, respectively. Compared to the control the increase in biogas production caused by both NaOH and KOH pretreatment are statistically significant at SRT 10 and 15 days, but are not statistically significant at SRT of 20 days. The results show that KOH is more efficient than NaOH for the alkaline pretreatment prior to AD.

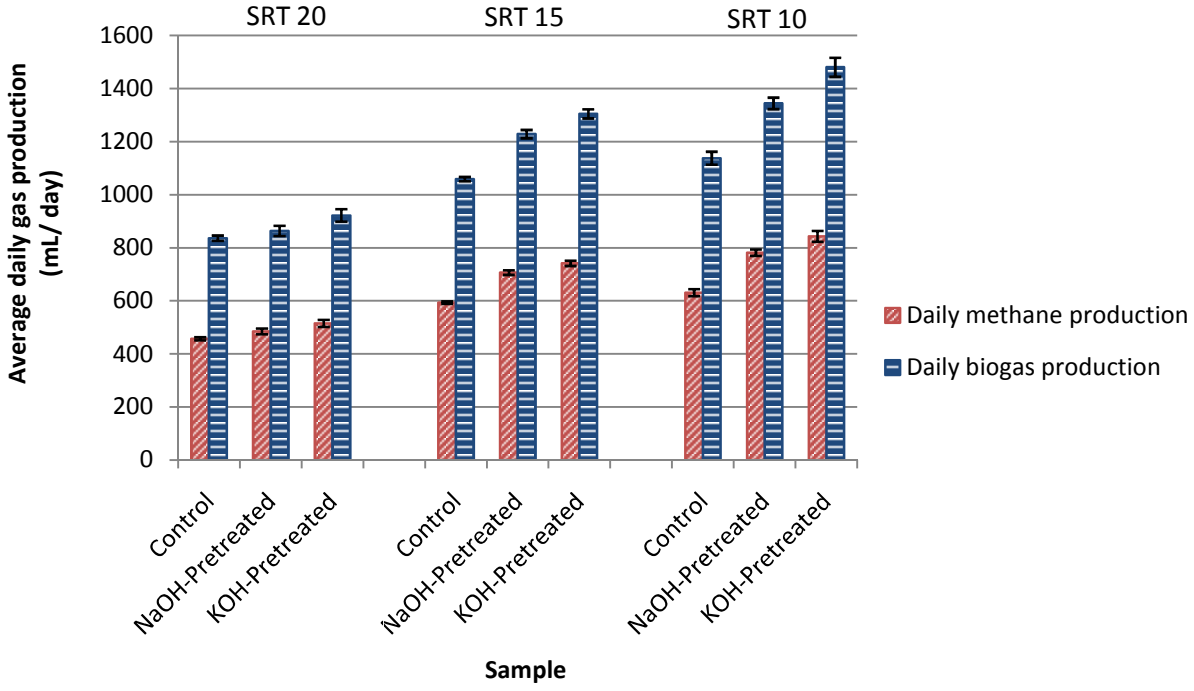

Figure 4.34: Average daily biogas/ methane production for the semi-continuous reactors.

Figures 4.35 and 4.36 show the biogas yields and methane yields relative to the VS and TCOD added to the reactors at 10, 15 and 20 day SRTs. The data are arithmetic means of the daily measurements during the steady state period, and error bars show the 95% confidence intervals. Both figures demonstrate that at higher SRTs greater biogas and methane yields are observed; where a significant statistical difference exists between the biogas and methane produced at SRTs of 20 and 10 days and again between SRTs of 15 and 10 days. From this observation we can conclude that organic loading rate (OLR) is in fact masking the effect of SRT shown in Figure 4.34.

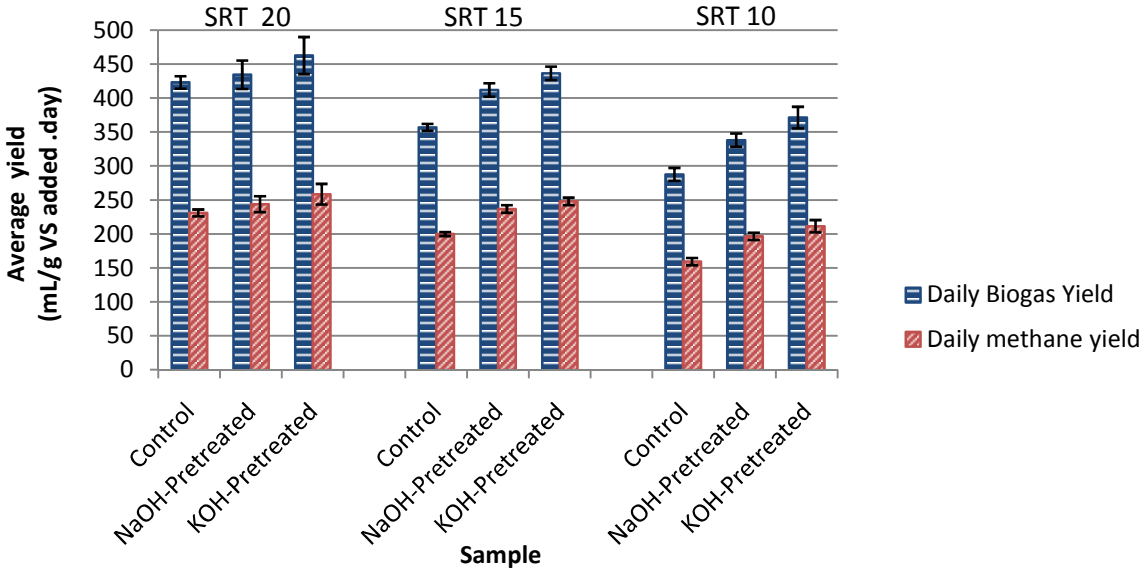

Figure 4.35: Biogas and methane yields per gram of VS added.

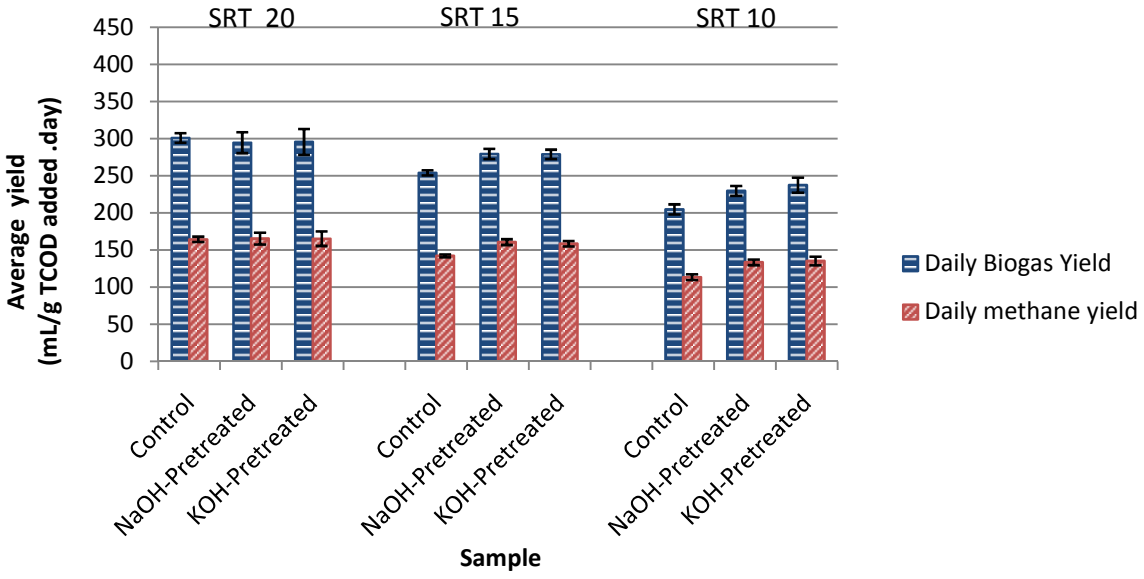

Figure 4.36: Biogas and methane yields per gram of TCOD added.

Biogas composition was measured several times during the semi-continuous reactor experiment; no statistically significant effect of SRT on the steady state biogas composition was

observed for all three SRTs, however the biogas produced from reactors fed with pretreated samples demonstrated a slightly higher methane percentage as compared to the control. In general the percentage of methane ranged from 54.6±0.81 to 58.2±0.13% for all reactors, which is very close to methane percentage obtained from the BMP assays results.

4.3.2 VS, TCOD and SCOD Removal and Methane Yields for Semi-Continuous Reactors

Table 4.10 summarizes the organic loading rates, along with VS, TCOD and SCOD removal rates, as well as daily volumetric biogas and methane production. The data in the table are arithmetic means followed by the associated standard deviation.

The percentage VS destructions during the semi-continuous experiments are shown in Figure 4.38. The data are arithmetic means of four VS measurements during the steady state period, and the error bars show the 95% confidence intervals. The VS destructions at SRT 20 days are similar and in fact the differences between the control and the samples pretreated with NaOH or KOH are not statistically significantly different from each other. The VS destruction at SRT 20 days ranged from 79.1±1.7 for NaOH pretreated samples to 77.2±1.4% for KOH pretreated samples. When the SRT decreased to 15 days VS destruction decreased as well. A highest VS destruction at SRT 15 was observed for KOH pretreated waste (75.8±1.4%), followed by the NaOH pretreated waste (74.9±1.9%) and finally the control (69.3±0.6%). At this SRT of 15 days NaOH and KOH pretreatment demonstrates a statistically significant higher VS destruction than the control. A further statistically significant decrease in VS destruction occurred when the SRT was decreased to 10 days. VS destruction ranged from a maximum of 60.3±1.1% for KOH pretreated samples to a minimum of 52.6±0.3% for the control.

Table 4.10: Summary of semi-continuous reactor measurements.

Sample	Control			NaOH			KOH		
	Solids retention time SRT (days)								
Organic loading rate	**10**	**15**	**20**	**10**	**15**	**20**	**10**	**15**	**20**
g VS/ L.d	4.9±0.0	3.7±0.0	2.5±0.0	5.0±0.0	3.7±0.0	2.5±0.0	5.0±0.0	3.7±0.0	2.5±0.0
g TCOD/ L.d	7.0±0.0	5.2±0.0	3.5±0.0	7.3±0.1	5.5±0.0	3.7±0.0	7.8±0.1	5.8±0.1	3.9±0.0
g SCOD/ L.d	2.7±0.0	2.0±0.0	1.3±0.0	3.4±0.1	2.6±0.0	1.7±0.0	3.4±0.1	2.6±0.0	1.7±0.0
Influent VS (g/ kg)	49.7±0.1	49.1±0.2	49.5±0.1	49.9±0.1	49.5±0.2	49.7±0.0	50.1±0.0	49.9±0.2	49.4±0.1
Effluent VS (g /kg)	23.5±0.2	15.1±0.1	10.7±0.2	21.2±0.5	12.4±0.3	10.4±0.2	19.9±0.4	12.2±0.2	11.3±0.2
VS removal (%)	52.6±0.3	69.3±0.6	78.3±1.2	57.5±1.3	74.9±1.9	79.1±1.7	60.3±1.1	75.8±1.4	77.2±1.4
Influent TCOD (g/ kg)	69.1±0.3	70.6±0.3	68.8±0.4	73.2±0.1	74.0±0.3	72.7±0.5	77.3±0.3	78.1±0.6	78.6±0.2
Effluent TCOD (g /kg)	33.9±0.5	27.5±0.3	21.4±0.4	34.7±0.4	26.7±0.8	22.3±0.6	34.8±0.7	27.2±1.5	23.0±0.3
TCOD removal (%)	50.9±0.8	61.0±0.7	68.9±1.5	52.6±0.6	63.9±1.9	69.4±1.9	54.9±1.2	65.2±3.7	70.7±0.9
Influent SCOD (g/ kg)	26.6±0.3	26.8±0.1	26.4±0.2	34.0±0.3	34.6±0.3	33.7±0.1	34.4±0.3	34.6±0.2	34.0±0.2
Effluent SCOD (g /kg)	8.5±0.3	4.3±0.2	1.3±0.0	8.7±0.1	4.3±0.0	2.1±0.1	7.7±0.3	4.0±0.1	1.9±0.1
SCOD removal (%)	68.0±2.2	83.9±3.5	95.2±1.5	74.3±1.3	87.7±1.0	93.8±2.7	77.6±2.9	88.4±2.9	94.4±3.5
CH_4 (%)	55.9	56.0	54.6	56.8	57.5	56.1	57.0	58.2	55.9
Biogas production (mL/d)	1138±77	1059±30	836±37	1345±79	1229±60	864±85	1481±128	1305±23	922±111
CH_4 production (mL/ d)	631±43	593±17	457±20	782±45	707±34	485±48	843±73	742±34	515±62

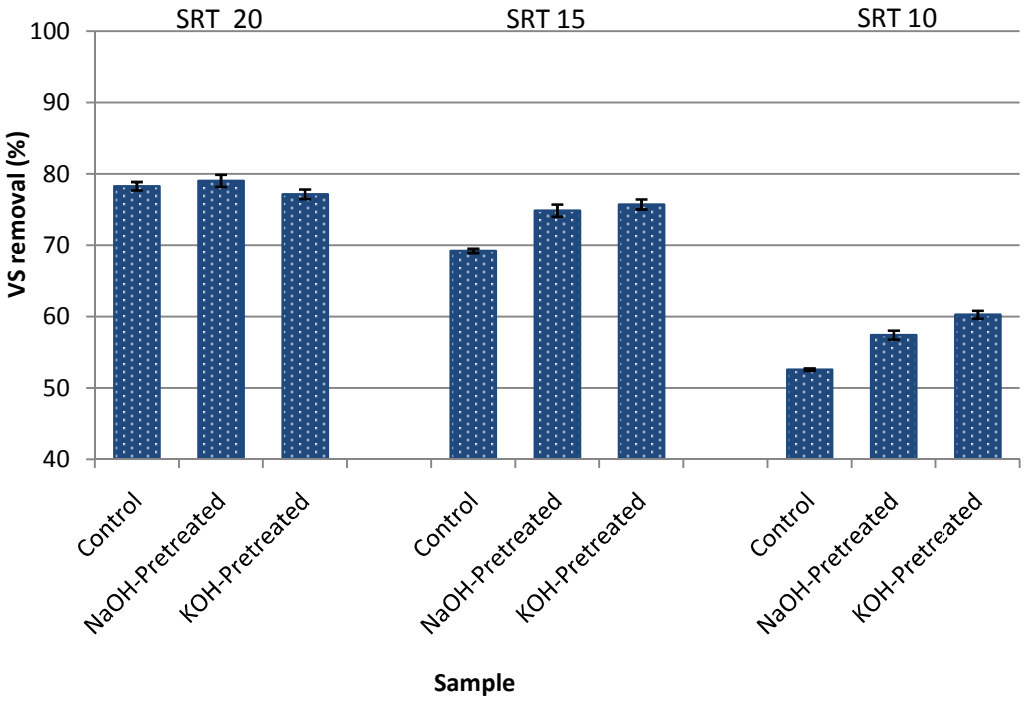

Figure 4.37: VS removal for the semi-continuous reactors.

From Figure 4.37 we see that alkaline pretreatment using NaOH and KOH had a statistically significant greater VS destruction at SRT 15 and 10 days, and the effect of KOH pretreatment was more potential in VS reduction than NaOH. At SRT 20 days the three samples; control, NaOH and KOH had a very similar VS removal % which ranged from 77.2±1.4% to 79.1±1.7. These high and similar VS removal values for the different samples might suggest that SRT of 20 days is sufficient time to biodegrade the M-OFMSW without pretreatment.

Figure 4.38 shows the biogas yields and methane yields relative to the VS removed for the reactors at 10, 15 and 20 day SRTs. The data are arithmetic means of the daily measurements during the steady state period, and error bars show the 95% confidence intervals. At all three SRTs KOH pretreated samples showed statistically significant higher biogas yields while methane yields were again highest of KOH pretreated samples but only statistically significantly

higher than NaOH samples at SRT of 20 days. The biogas and methane yields for the same pretreatment showed small or statistically insignificant changes at various SRTs. However KOH pretreated samples had a statistically significant higher biogas and methane yields compared to the other samples at all SRTs.

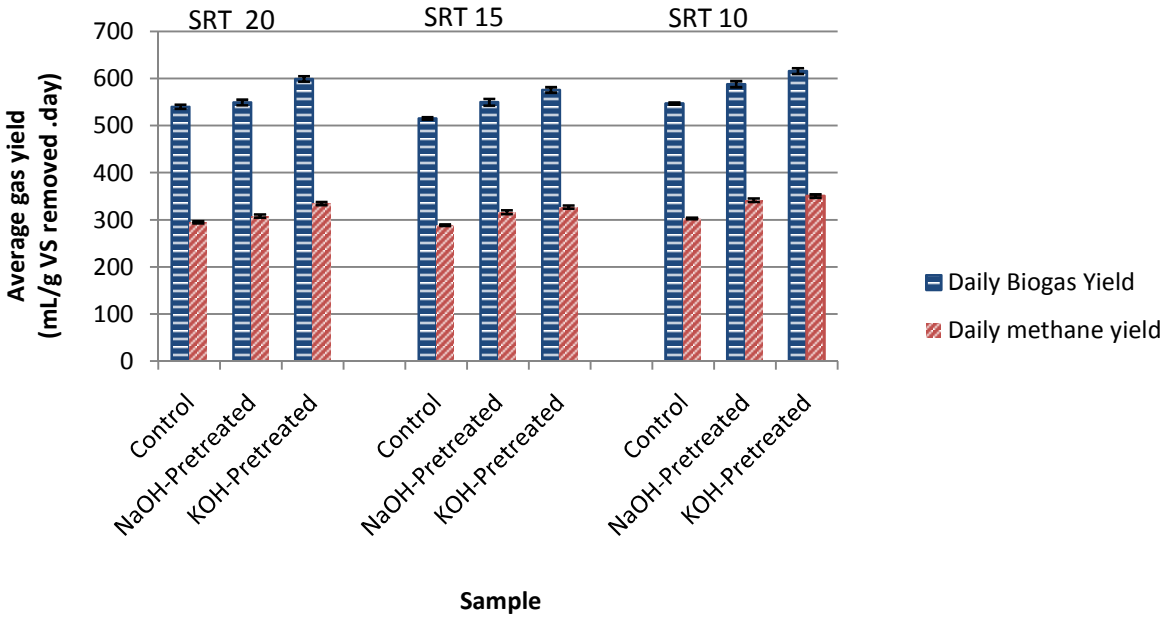

Figure 4.38: Biogas and methane yields per gram of VS removed.

Figure 4.39 shows the TCOD and SCOD removals during the semi-continuous digestion. The data are arithmetic means of four TCOD and SCOD measurements during the steady state period, and the error bars show the 95% confidence intervals.

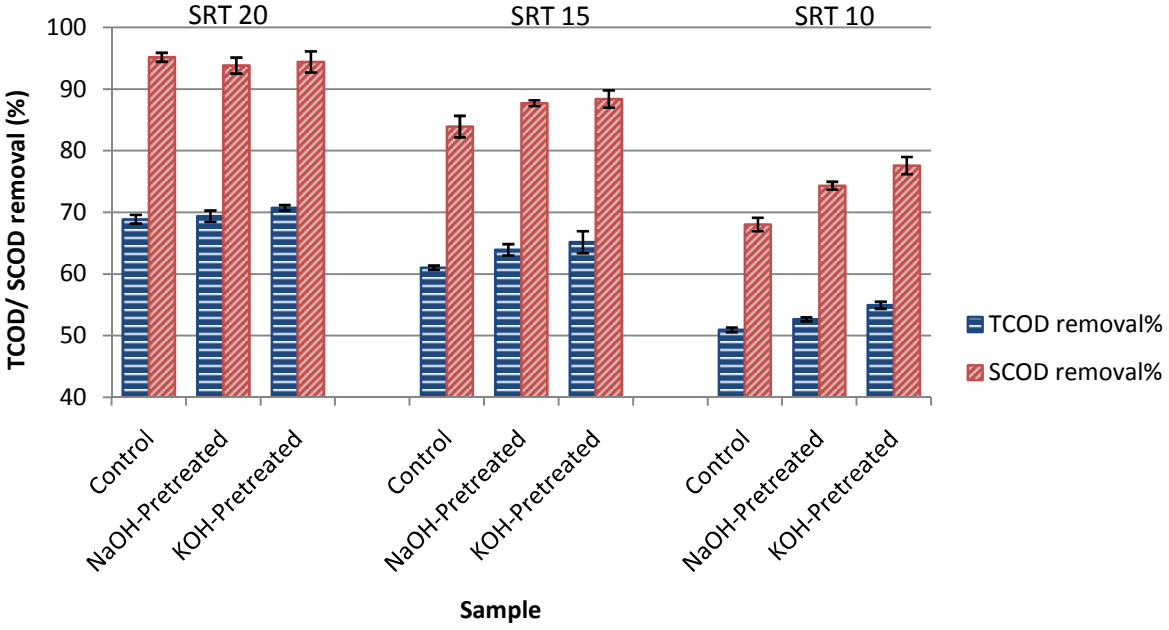

Figure 4.39: TCOD and SCOD removals for the semi-continuous reactors.

Figure 4.39 above shows that TCOD and SCOD removals follow the same trend as VS destruction. The removal efficiency shows a statistically significant decrease with decreasing SRT values for all the samples. An explanation for this is that as SRT decreases the organic loading rate (g VS/ reactor.day) increases and so there is more organic material to be degraded in shorter time, hence a lower observable removal efficiency. Again as observed before in VS removal at SRT 20 days showed no statistical difference for TCOD and SCOD removal where the TCOD removal at an SRT of 20 days ranged from 68.9±0.7% to 70.7±0.4%, and SCOD removal ranged from 93.8±1.3% to 95.2±0.7%. At SRT 20 days NaOH pretreated samples had the highest TCOD removal, and control had the highest SCOD removal. However at SRT 15 and 10 days KOH pretreated samples had the highest TCOD and SCOD removals.

Figure 4.40 represents biogas and methane yields relative to the TCOD removed for the different samples at 10, 15 and 20 day SRTs. The data are the arithmetic means, and the error bars show the 95% confidence intervals. At SRT 20 days control had the highest biogas yield of 436.8±9.2 mL/g biogas relative to gram of TCOD removed.

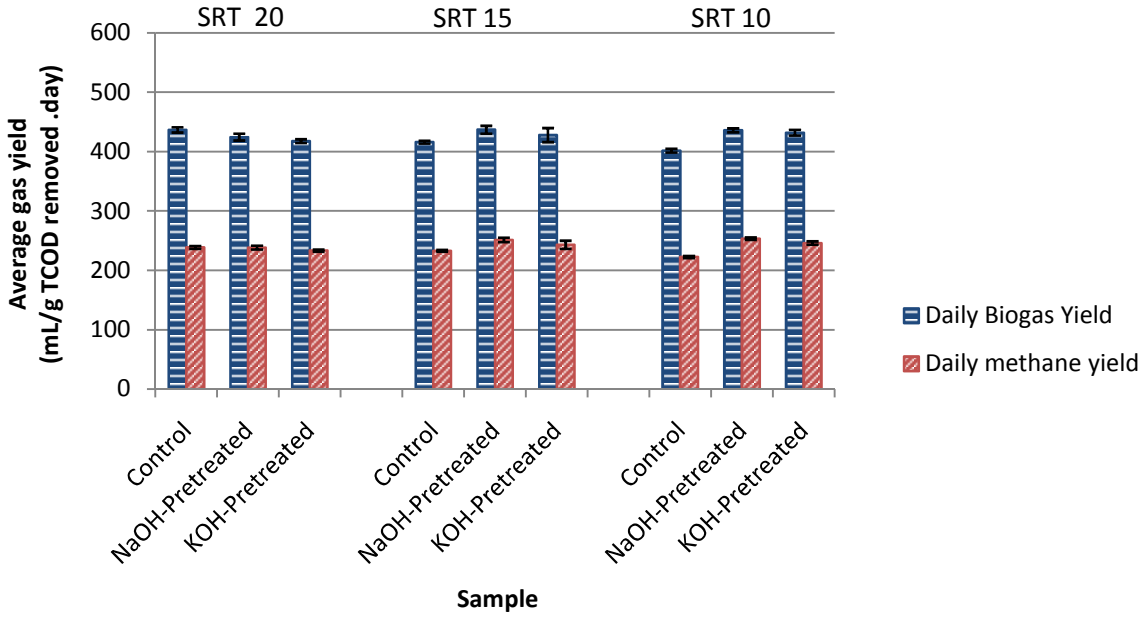

Figure 4.40: Biogas and methane yields per gram of TCOD removed.

NaOH and KOH pretreated samples showed a slight increase (not statistically significant) in biogas and methane yields relative to gram of TCOD removed at SRT of 10 and 15 days. In contrast, the control reactors showed a statistically significant decrease in biogas and methane yields as the SRT decreased. In general methane yields ranged from 222.7±3.5 to 253.5±3.8 mL of methane relative to gram of TCOD removed, these values are lower than the methane yield obtained from the BMP assays for the same samples (Tables 4.7 and 4.9). Moreover, these values are significantly lower than the theoretical expected value of 350 mL of methane related to gram of TCOD removed (Penaud et al., 1999), but still remain within the range reported in literature as 100 to 350 mL of methane related to gram of TCOD removed (Droste, 1996).

4.3.3 pH, Alkalinity, Ammonia, and TVFAs for the Semi-Continuous Reactors

pH, alkalinity, ammonia, and TVFA measurements for the semi-continuous reactors are presented in Table 4.11. Alkalinity, ammonia and TVFAs concentrations (mg/L) represented in the table are the arithmetic mean of four measurements for the reactors effluent during the

steady state operation, and the associated standard deviation. pH values are the arithmetic mean of daily pH measurements.

Table 4.11: Steady state pH, ammonia, TVFA and alkalinity for the semi-continuous reactors.

Sample	Control			NaOH			KOH		
	Solids retention time (days)								
	20	15	10	20	15	10	20	15	10
pH	7.5±0.1	7.4±0.1	7.6±0.1	7.6±0.1	7.5±0.1	7.6±0.1	7.5±0.0	7.6±0.0	7.6±0.1
Ammonia(mg/L)	696±64	727±133	789±0.3	733±114	786±120	849±89	817±25	834±48	872±80
TVFA(mg/L)	833±66	770±110	826±198	1467±165	1507±178	1518±179	2124±335	2225±309	2461±621
Alkalinity(mg/L)	4000±236	5083±118	6250±118	4300±141	5167±236	5600±283	5083±118	6833±236	7083±118
TVFA/Alkalinity	0.20	0.15	0.13	0.34	0.29	0.27	0.42	0.33	0.35

Bicarbonate alkalinity was added to the reactors weekly or when any reactor had a pH drop to less than 7.4 in order to maintain an adequate buffering capacity in the reactors. The continuous buffer adjustments helped maintain the reactors pH values within a range of 7.3-7.7 which is a suitable range for anaerobic digestion (Mata-Alvarez, 2003). In general during the study reactors fed by pretreated samples had statistically significantly higher alkalinity concentrations than control reactors, and had more stable pH values hence the addition of bicarbonate alkalinity for these reactors was less frequently needed. Total alkalinity is the sum of three major constituents: bicarbonate (HCO_3^-), carbonate (CO_3^{-2}) and hydroxide (OH^-). Thus adding pretreated samples with NaOH or KOH to the reactor increased the hydroxide ions concentration in the pretreated samples which lead to an increase in the total alkalinity of these reactors.

Table 4.11 shows that TVFA concentrations for all samples are higher at lower SRTs, but not statistically significant different. This increase in TVFAs is generally due to the increase in the organic loading rate with lower SRT (Mata-Alvarez, 2003). Also the accumulation of TVFAs in reactors fed with pretreated samples was statistically significantly higher than the control

reactors at all SRTs. It should be noted that the high buffering capacity of the pretreated reactors prevented any drop in the pH. In all TVFA measurements acetic acid was the dominant fraction, making up to 62-80% of the TVFAs.

The TVFAs per alkalinity ratio is a common tool used to monitor the stability of the anaerobic process. When this ratio is between 0.3 and 0.4 the system is considered to be operating under stable conditions. When this ratio is above 0.4 this indicates that stressed conditions have been initiated and can be indicative of an upset in the stability of the system (Mata-Alvarez, 2002; Warith et al. 2005). From Table 4.11 we see that this ratio was low for all reactors at SRT 15 and 20 days and increased slightly to a range from 0.33 to 0.42 at SRT 10 as the organic loading rate increased. The TVFAs per alkalinity ratio for all reactors indicate that all reactors were stable during the operation period.

Ammonia concentrations are represented as well in Table 4.11. Ammonia concentrations increase with lower SRTs. At an SRT of 10 days the maximum ammonia concentrations ranged from 817±25 to 872±80 mg/L, these maximum ammonia concentrations are less than 1200 mg/L which is considered to have inhibitory effect on anaerobic digestion (Kayhanian, 1999).

In summary the control along with the NaOH and KOH pretreated samples were operated successfully at three different SRTs. At SRT 20 days the three reactors showed a very close with no statistically significant difference in VS, TCOD and SCOD removals, and samples pretreated with KOH had the highest biogas production of 10.3% greater than the control. At an SRT of 15 days the removal efficiency decreased for all samples and KOH pretreated samples had the greatest removal efficiency compared to the control and NaOH pretreated samples. Also at SRT 15 days KOH pretreated samples had the highest biogas production which was 23.2% times the biogas production of control at the same SRT. At the lowest SRT of 10 days KOH pretreated samples had 30.1% more biogas production than control and the highest VS, TCOD and SCOD removal. The results of the semi-continuous reactors demonstrate that KOH is more efficient than NaOH for the alkaline pretreatment prior to AD (Penaud et al., 1999; Valo et al., 2004).

4.4 Cost Estimations of Using AD Technology for Municipal Organic Waste in Ottawa, Canada

The potential for energy production and the small footprint of AD facilities are the main reasons for the increased interest in AD technology in recent years. Biogas produced from anaerobic digesters generates heat and electricity which can be used to recuperate the heat and electrical requirements of the AD facility itself; furthermore these facilities in some instances may produce electricity that exceeds the power requirements of the plant and thus they can become a source of electricity to local electrical grids. It is currently difficult to estimate the energy that will be produced from a new full-scale anaerobic digestion facility. Moreover, very limited information is available on the capital or operational costs associated with AD facilities. Thus, employing available information from existing full scale anaerobic digestion facilities is currently the most accurate method of performing projected economic analysis of a future AD plant.

According to BALKWASTE (2010) one should consider the following criteria when estimating the cost of an AD system:

- Predevelopment costs (e.g. siting and permitting, environmental impact assessment, hydrological investigations, etc.);
- construction costs (e.g. infrastructure costs like access roads, piping, utility structures, etc., and equipment costs such as tanks, machinery, electronics, etc.); and
- operating costs (e.g. maintenance fees, labour, materials, training, supervision, etc.)

It should be noted that the AD process generates biogas, which requires explosion proof buildings and gas handling equipment as well as high skill level operators (special training with gas handling and explosive situations). These specific requirements and the associated costs restrict AD facilities from being a practical alternative for small communities. However AD can be a potential economically competitive technology for large communities that produce enough waste to recover the capital and operational costs of the treatment facility (BALKWASTE, 2010).

In 2006 an evaluation of various types of organics management and residual treatment/disposal options for different sized community (population of 20,000, 80,000, 200,000 and 800,000) was performed under the guidance of the Municipal Waste Integration Network (MWIN) and Recycling Council of Alberta/Canada (RCA). The indicators used to evaluate the different methods included to following factors: environmental, social, economic, energy and greenhouse gases effects. The costs were calculated based on information available from operating AD plants in Europe and the Canadian Dufferin Organics Processing Facility in Toronto (MWIN, 2006). The criteria used to evaluate AD installation in Ottawa, Canada and the results for AD evaluation are presented in Appendix C. Table C.1 shown in Appendix C shows the estimated costs of AD facilities to process source separated organics (SSO) for different size communities. From Table C.1 we can see that the estimated costs for AD treatment range from $257 per input tonne for small communities (population of 20,000), to $68 per input tonne for larger communities (population of 800,000). It is clear from this cost differential that AD is a significantly more beneficial alternative for larger communities. These findings were used in this study to project experimental results of this work to the city of Ottawa, Canada. Ottawa is a large community with a current population that exceeds one million people and it is a city that has recently evaluated its kitchen waste disposal options.

The cost estimations for implementing an AD treatment facility to treat SSO in Ottawa and the cost benefit of pretreatment of the waste using NaOH and KOH at pH12 is herein explored based on the experimental findings of this work. The cost benefit analysis of the proposed AD facility is based upon a 20 year projected growth in the city. The projected population of Ottawa was estimated based on the 2008 population with the 2032 population being predicted based on an annual growth rate of 1.2% (City Ottawa, 2011). Thus the population of Ottawa that was registered as 1,011,800 residents in 2011 is estimated to be 1,136,000 in 2031.

Ottawa generated 1,040,000 tonnes of waste in 2006, which is equivalent to 1194 kg/capita/year. Residential waste is about 31-32% of the total waste, thus in 2006 every resident in Ottawa generated on average 356 kg of residential waste with a total of 310,000 tonnes of residential waste being generated in the city in 2006 (City Ottawa, 2011). In 2011

Ottawa delivered 53,420 tonnes of organic waste to the Orgaworld composting plant, which represents just above 43.1% of the total organic waste generated in the city in 2011. Assuming that with time the average organic waste diversion efficiency will increase to 60%, in 2031 it is estimated that Ottawa will divert 96,787 tonnes to AD. A summary of the population and waste generation for Ottawa 2011/2031 are shown in Table 4.12.

Table 4.12: Ottawa population and waste generation in 2011 and 2031.

Year	2011	2031
Population	1,011,800	1,136,000
Residential waste (tonne)	360,201	404,416
Organic waste (tonne)	144,080	161,766
Diverted organic waste (tonne)	53,420	97,060

Chemicals costs

Table 4.13 summarizes the predicted quantities of NaOH and KOH required for pretreatment of the organic waste at pH 12 prior to AD. The values shown in the table are based on yields generated from the experimental work of this study.

Table4.13: Chemical amounts and prices.

Alkaline reagent	NaOH		KOH	
Best price (US$/tonne)	220		300	
Amount of reagent required (tonne/tonne of waste)	0.004		0.0075	
Year	**2011**	**2031**	**2011**	**2031**
Total amount required for pretreatment (tonne/year)	475	863	890	1617
Total cost (US$/year)	104,000	190,000	267,000	485,000

Capital, operating and maintenance costs along with net facility costs, defined as the gross annual cost minus the annual electricity revenues were extrapolated for an AD installation set to operate in Ottawa. This extrapolation is based upon the results of the MWIN and RCA studies shown in Table C.1 and the extrapolation is shown in Figures C.2.1, C.2.2 and C.2.4 in Appendix C. The final cost per tonne and the electricity generated is also extrapolated based on the same method and are shown in Figures C.2.3 and C.2.5 in the same Appendix.

4.4.1 Capital Cost of AD facility

The estimated cost of the proposed AD facility is listed in Table 4.14 for various sized communities and for Ottawa. As we see from the results presented in Table 4.14 an AD facility installation that meets the treatment needs of Ottawa will require a capital cost of $38 million CDN. Because Ottawa is a large community, the cost per input tonne of organic waste is $63 in 2011, which will decrease to $61 in 2031 as the population increases. These prices are very competitive compared to the prices of landfilling and composting in the city. Ottawa is currently charged $96 a tonne for dumping of household-type garbage at the Trail Road landfill (City Ottawa, 2011). Also more recently Ottawa signed a 20-years contract with Orgaworld composting plant to compost 80,000 tonnes/year at a cost of $93/tonne. In 2010 Ottawa sent 53,420 tonnes for composting (Ottawa citizen, 2011), which sets the current price per tonne at $139/tonne. In addition to the AD benefits of land saving, generating green energy, controlling greenhouse gas (GHG) emissions, and eliminating odor problems, the cost of treating one tonne of organic waste is $30 less than composting and $33 less than landfilling. This difference in cost/tonne can be applied over an 18 years period to entirely offset the capital cost of the AD facility. The preliminary results for facility capital cost offset is based on the estimated methane production from SSO without pretreatment.

Table 4.14: Estimated costs of AD facilities for different size communities and for Ottawa 2011-2031.

	Population	Capital cost	Total O&M cost	Electricity revenues	Net facility cost	Cost per input tonne
		($)	($/year)	($/year)	($/year)	($)
	20,000	3,000,000	239,000	14,000	515,000	257
	80,000	7,000,000	578,000	53,000	1,170,000	156
	200,000	12,000,000	1,085,000	130,000	2,060,000	111
	800,000	32,000,000	3,815,000	700,000	6,134,000	68
Ottawa 2011	1,011,800	35,000,000	4,620,000	805,000	7,178,000	63
Ottawa 2031	1,136,000	38,000,000	5,184,000	910,000	8,053,000	61

4.4.2 Methane Yield per Tonne of Waste

Table 4.15 shows the calculated methane yields per tonne of mixed waste, where $waste_{(mix)}$ is used to indicate a 45:55 waste to water mixture. The 45:55 waste to water ratio is used as it was deemed optimal during the experimental work of this study. Hence during the costs analysis the estimated amount of waste to be collected was converted to the equivalent $waste_{(mix)}$.

Table 4.15: Calculated methane yield and improvement in methane yield from the experimental work.

Sample	SRT (day)	Daily Feed of $waste_{(mix)}$ (g)	Daily CH_4 Production (ml/d)	CH_4/tonne of $waste_{(mix)}$ (m^3/tonne)	Improvement in CH_4 yield (%)
Control	10	45.8	631	13.8	-
	15	34.4	593	17.2	-
	20	22.9	457	20.0	-
NaOH pretreated samples	10	49.2	782	15.9	15.2
	15	36.9	707	19.2	11.6
	20	24.6	485	19.7	-
KOH pretreated samples	10	52.4	843	16.1	16.4
	15	39.3	742	18.9	9.9
	20	26.2	515	19.7	-

As shown in Table 4.15, NaOH and KOH pretreatment improved the methane yield at SRTs of 10 and 15 days. An SRT of 15 days was chosen for the AD because the reactors operated at this SRT demonstrated a high biogas production and high organic removals.

Table 4.17 summarizes the net revenue of an AD facility operating at an SRT of 15 days; the net revenue is based upon electrical revenue and chemical costs used for alkali pretreatment. It is noted again that the predicted quantity of waste produced by the city of Ottawa was adjusted to yield mixed waste value for the generation of the values shown in Table 4.16.

Table 4.16: Calculated net revenue ($/year) for the three waste options.

Sample	year	Electrical revenue($/year)	Chemical costs($/year)	Net revenue ($/year)
No pretreatment	2011	805,000	-	805,000
	2031	910,000	-	910,000
NaOH	2011	898,000	104,000	794,000
pretreatment	2031	1,016,000	190,000	826,000
KOH	2011	885,000	267,000	618,000
pretreatment	2031	1,000,000	485,000	515,000

From the calculated net revenues ($/year) presented in Table 4.16 we see that treating organic waste without pretreatment is the most economical option for AD plant operations through 2011 to 2031. The second most profitable option is NaOH pretreatment, where projection show that this option becomes more economically favorable than the no pretreatment option for the 2011 capacity when the NaOH price is less than $200/tonne. However for the 2031 capacity, the NaOH pretreatment option becomes economically favorable only if the NaOH price is less than $123/tonne which is a 44% reduction in the predicted market price of NaOH. KOH pretreatment option is the least economical for both the 2011 and 2031 capacities due to high market prices of KOH and the large quantity of KOH required for pretreatment.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

The effects of alkaline pretreatment on solubilization and anaerobic digestion of organic fraction of municipal solid waste (OFMSW) were investigated during this research. The main conclusions of this work are:

- Alkaline pretreatment using NaOH and KOH has shown the ability to enhance COD solubilization of OFMSW. The maximum solubilization of the organic waste was observed at pH 13 for both chemicals at 23±1°C and again at 80±1°C;
- despite the high COD solubilization that occurred at pH 13 for both alkali reagents, this high pH level inhibited biogas production during the NaOH and KOH BMP assays. It is inferred from visual observation of the treated waste that this inhibition occurred due to the formation of complex compounds of low biodegradability;
- KOH pretreated samples outperformed NaOH pretreated samples with respect to cumulative biogas production measured during the BMP assay. Thus KOH pretreatment of OFMSW yields a more efficient biogas production;
- the BMP assays results showed that alkaline pretreatment at pH 12 and 23±1°C was the optimum pretreatment condition for both chemicals NaOH and KOH;
- semi-continuous AD laboratory reactors fed with OFMSW operating at 10 and 15 days SRT demonstrated that pretreatment with NaOH and KOH results in a statistically significant increase in VS, TCOD and SCOD removal rates and a statistically significant increase in biogas production as compared to non-pretreated samples;
- semi-continuous laboratory reactors performing AD of OFMSW of pretreated and non-pretreated samples demonstrated a statistically significant increase in biogas production as the SRT decreased and the loading rate increased. At an SRT of 20 days the alkaline pretreatment did not show any statistically significant improvement in the AD performance of OFMSW, which is inferred to be due to sufficient contact time for

degradation of the OFMSW without the added benefit of applying pretreatment prior to AD;

- AD is an economically competitive technology to treat the OFMSW in the city of Ottawa, Canada. Preliminary cost estimations for implementing an AD facility to treat source separated organic waste (SSO) in Ottawa showed that the proposed facility can entirely offset its capital cost over a period of 18 years. AD of organic waste with no pretreatment was found to be the most economical option; although findings show that a 20 to 44% reduction on the current market price of NaOH makes NaOH pretreatment the most economically favourable option. The high market prices of KOH resulted in AD in combination with KOH being the least economically favourable option.

5.2 Recommendations

The following recommendations are suggested in order to improve the comprehensive picture of the potential for alkaline pretreatment prior to anaerobic digestion of OFMSW:

- Examine the alkaline pretreatment effects on a more representative organic waste or on real SSO instead of using the current model organic waste;
- investigate the potential of thermophilic AD of alkaline pretreated organic waste;
- study the performance of AD of alkaline pretreated organic waste using fixed film reactors;
- investigate the performance of dual stage AD of alkaline pretreated organic waste;
- investigate the effect of combining the alkali pretreatment with other pretreatment methods like microwave (MW), ultrasound, heat > 100°C;
- study the potential of co-digestion of alkaline pretreated organic waste with wastewater treatment residuals or animal manures; and
- perform a more comprehensive study to determine the economical, environmental, and social effects of having AD facility to treat the SSO in Ottawa.

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APPENDIX A: Images of Pretreated Samples

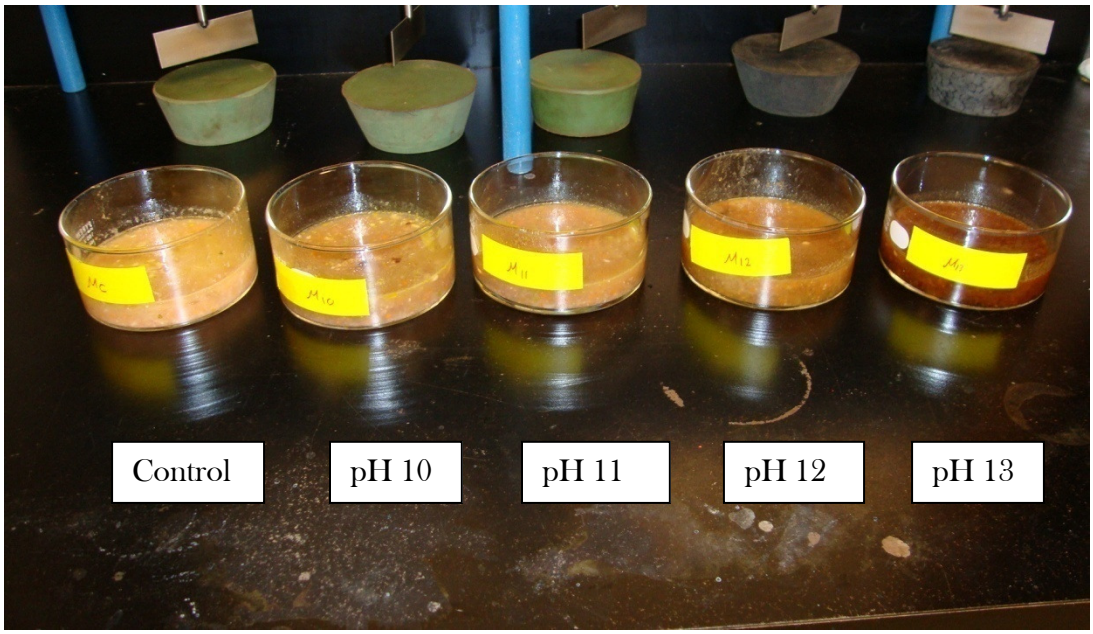

Figure A.1: Samples after NaOH pretreatment at 23±1°C.

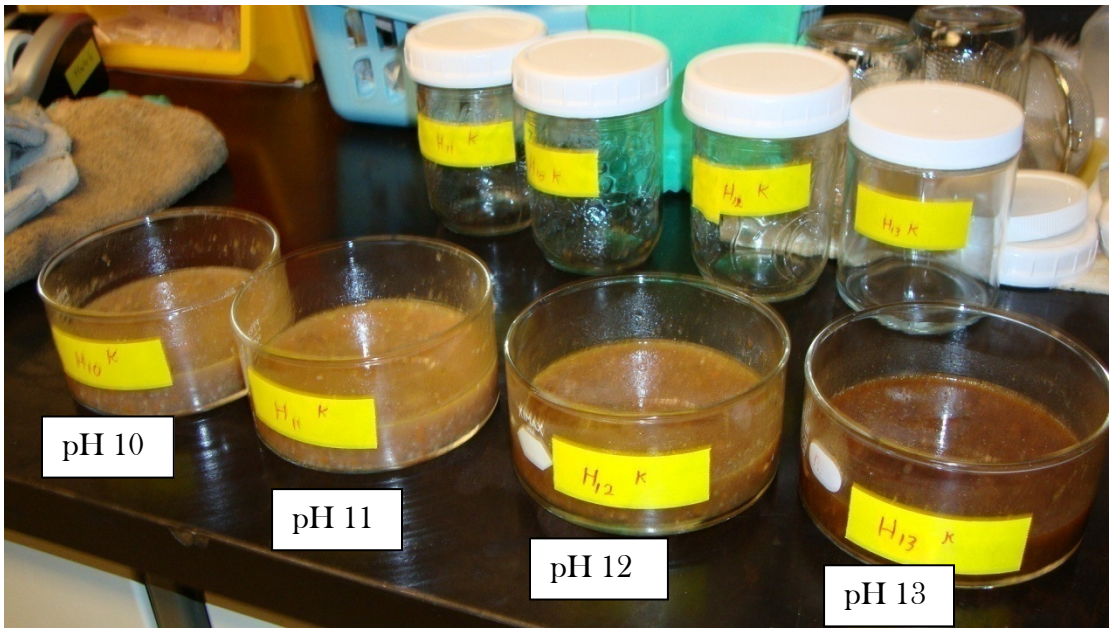

Figure A.2: Samples after KOH pretreatment at 80±1°C.

APPENDIX B: Combined Error Calculations

If a variable **Z** depends on (one or) two variables (**A** and **B**) which have **independent** errors (ΔA and ΔB) then the rule for calculating the error in **Z** is tabulated in following table for various different simple relationships.

Table B.1: Rules for error calculations.

Relation between Z and (A,B)	Relation between errors ΔZ and (ΔA , ΔB)
Z = A + B	$(\Delta Z)^2 = (\Delta A)^2 + (\Delta B)^2$
Z = A - B	$(\Delta Z)^2 = (\Delta A)^2 + (\Delta B)^2$
Z = AB	$\left(\frac{\Delta Z}{Z}\right)^2 = \left(\frac{\Delta A}{A}\right)^2 + \left(\frac{\Delta B}{B}\right)^2$
Z = A/B	$\left(\frac{\Delta Z}{Z}\right)^2 = \left(\frac{\Delta A}{A}\right)^2 + \left(\frac{\Delta B}{B}\right)^2$
$Z = A^n$	$\frac{\Delta Z}{Z} = n\frac{\Delta A}{A}$
Z = ln A	$\Delta Z = \frac{\Delta A}{A}$
$Z = e^A$	$\frac{\Delta Z}{Z} = \Delta A$

APPENDIX C: Cost Analysis

C.1 Assumptions and results of MWIN &RCA study

The results of Municipal Waste Integration Network (MWIN) and Recycling Council of Alberta (RCA) study, (2006) are presented in Table C1 below. The following assumptions were used for the AD costs calculations:

- Biogas production of 110 m^3/tonne for SSO
- Composting of digestate at $25/tonne
- No revenue from heat sales
- Revenue of 6 cents/kWh for green, renewable power
- Disposal of residue at $30/tonne.

Table C.1: Estimated Costs of AD facilities to process source separated organics (SSO)(MWIN, 2006).

	Population 20,000	Population 80,000	Population 200,000	Population 800,000
Annual Input Quantity to Facility (tonnes)	2,000 tpy	7,500 tpy	18,500 tpy	100,000 tpy
Capital Cost ($)	**$3,000,000**	**$7,000,000**	**$12,000,000**	**$32,000,000**
Capital Financing ($/year)				
Annual Capital Charge ($/year)	$291,000/y	$643,000/y	$1,100,000/y	$3,020,000/y
Operating and Maintenance (O&M) Costs ($/year)				
O&M Costs ($/year)	205,000	450,000	770,000	2,115,000
Off Site Curing and Residue Disposal ($30/t)	34,000	128,000	315,000	1,700,000
Total O&M Cost ($/year)	$239,000	$578,000	$1,085,000	$3,815,000
Gross Annual Cost ($/year)	**530,000**	**1,200,000**	**2,200,000**	**7,300,000**
Electricity Revenues (6 cent/kwhr)	14,000	53,000	130,000	700,000
Heat Revenues (assume zero)	0	0	0	0
Net Facility Costs ($/year)	515,000	1,170,000	2,060,000	6,134,000
Cost per Input Tonne ($/year)	**$257**	**$156**	**$111**	**$68**

C.2 Cost estimations of using AD facility in Ottawa, Canada

Capital cost:

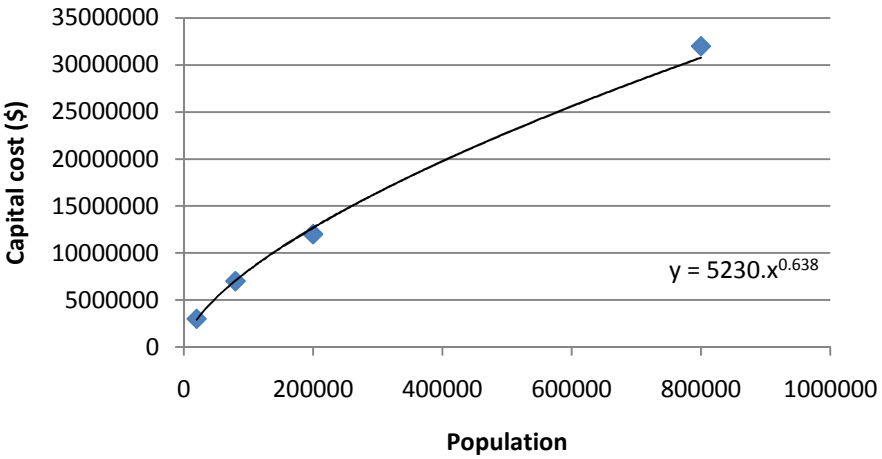

Figure C.2.1: Data used to extrapolate the capital cost.

Total operation and maintenance (O&M) cost:

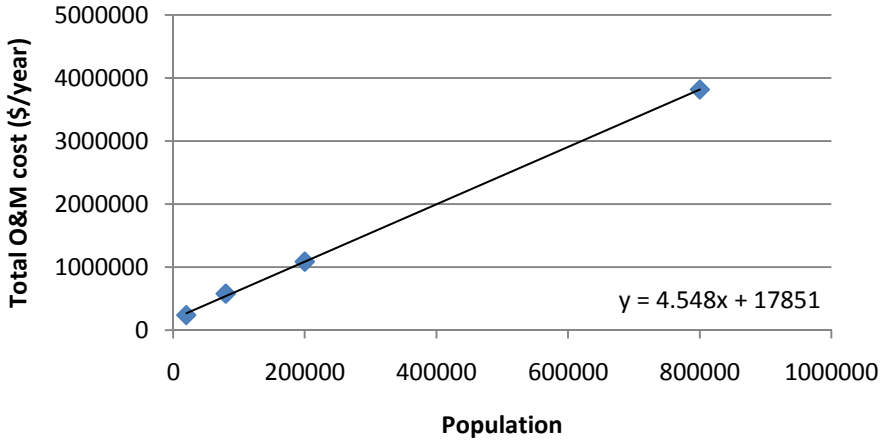

Figure C.2.2: Data used to extrapolate the total O&M cost.

Electricity revenue:

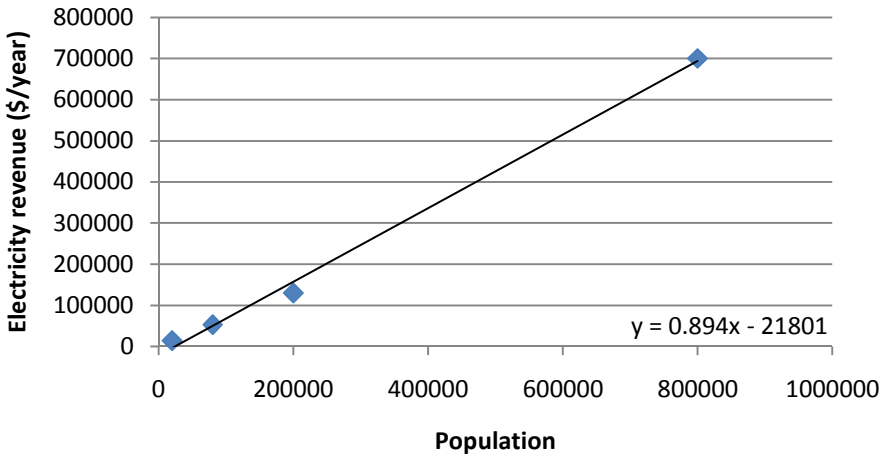

Figure C.2.3: Data used to extrapolate the electricity revenue.

Net facility cost:

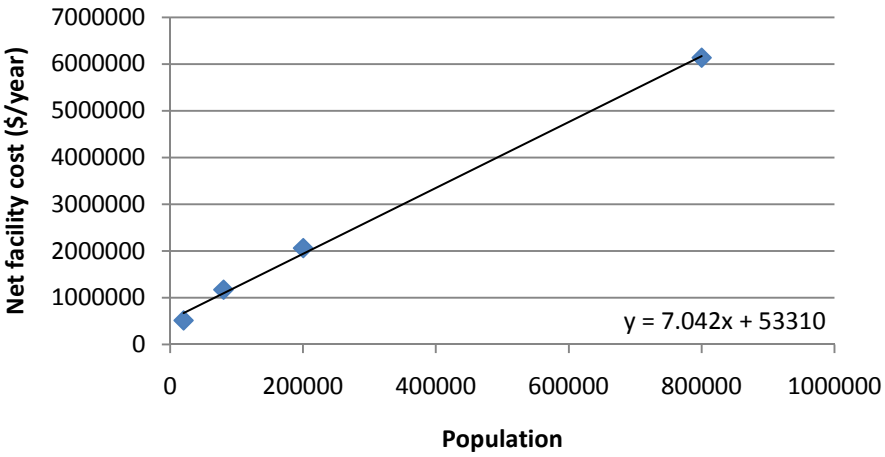

Figure C.2.4: Data used to extrapolate the net facility cost.

Cost per tonne:

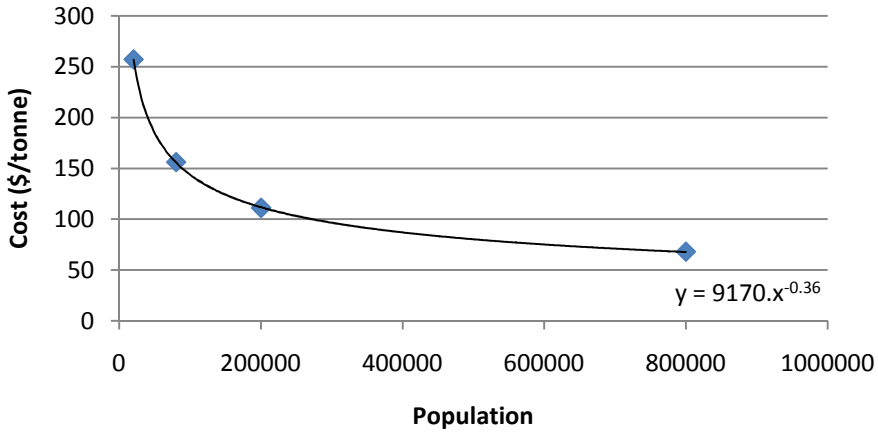

Figure C.2.5: Data used to extrapolate the capital cost.

C.3 Calculation of savings from using AD instead of composting or landfilling for treating SSO in Ottawa, Canada

Saving over composting ($)							
year	Year order	saving	Total saving	Saving in 2011*		Saving in 2031	
2011	1	1602600	1602600	1602600		3105920	
2012	2	1674187	3276786.7	Increase in saving every year =			71586.6667
2013	3	1745773	5022560.1				
2014	4	1817360	6839920.2	* Composting price = $93/ tonne constant for 20 years			
2015	5	1888947	8728867	(Ottawa-Orgaworld composting contract)			
2016	6	1960534	10689400.5	AD price in 2011 = $63/ tonne			
2017	7	2032120	12721520.7	AD price in 2031 = $61/ tonne			
2018	8	2103707	14825227.6				
2019	9	2175294	17000521.2				
2020	10	2246880	19247401.5				
2021	11	2318467	21565868.5				
2022	12	2390054	23955922.2				
2023	13	2461640	26417562.6				
2024	14	2533227	28950789.7				
2025	15	2604814	31555603.5				
2026	16	2676401	34232004				
2027	17	2747987	36979991.2				
2028	18	2819574	39799565.1	After 18 years total saving = capital cost of the AD palnt			
2029	19	2891161	42690725.7	designed for 2031 capacity.			
2030	20	2962747	45653473				
2031	21	3034334	48687807				

C.4 Calculation of net revenue from AD facility in Ottawa, Canada using different NaOH prices

At SRT 15 days							
		Electrical revenue	Chemical amoun	Chemical cos	Discount	Chemicals costs	Net revenue
		($/year)	(tonne/year)	($/tonne)	(%)	($/year)	($/year)
2011	Control	805000	-				
2031		910000	-				
2011	NaOH	898000	475	220		104500	793500
2031		1016000	863	220		189860	826140
For 2011				198	10	94050	803950
898000-805000 =		93000		198	10	170874	845126
93000/475 =		195.7894737					
For 2011 capacity NaOH pretreatment become more				187	15	88825	809175
economic than control when NaOH price is < 200 $/tonr				187	15	161381	854619
For 2031				176	20	83600	814400
1016000-910000 =		106000		176	20	151888	864112
106000/863 =		122.8273465					
For 2031 capacity NaOH pretreatment become more				154	30	73150	824850
economic than control when NaOH price is < 123 $/tonr				154	30	132902	883098
				132	40	62700	835300
				132	40	113916	902084
				110	50	52250	845750
				110	50	94930	921070