Mauritius Research Council

Effects of Ultrasound Irradiation on Anaerobic Digestion of Solid Wastes

Final Report

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Mauritius Research Council

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FINAL REPORT

"Effects of Ultrasound Irradiation on Anaerobic Digestion of Solid Wastes"

Submitted to the

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By

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APPENDIX D
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MAURITIUS RESEARCH COUNCIL
FINAL REPORT

PART I- PROJECT IDENTIFICATION INFORMATION

1. Type the name of the MRC Scheme under which grant is made
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2. Award Dates (MM/YYYY) From: April 2011 To: September 2012
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3. Organisation and Address
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   Effects of Ultrasound Irradiation on Anaerobic Digestion of Solid Wastes

Mauritius Research Council

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The summary (about 200 words) must be self-contained and intelligible to a scientifically or technically literate reader. Without restating the project title, it should begin with a topic sentence stating the project's major thesis. The summary should include, if pertinent to the project being described, the following items:

- The primary objectives and scope of the project
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PART II - SUMMARY OF COMPLETED PROJECT

The effects of ultrasound (UtS) pre-treatment (i.e. irradiation using ultrasound waves - sonication) have been studied on the anaerobic digestion (AD) of vegetable wastes (VW) using biochemical methane potential (BMPs) assays. The main feature of this research work has been to assess the changes in cumulative biogas production resulting from AD of the pre-treated and untreated samples of VW for different sonication times (10, 40 and 60 minutes) and ultrasonic specific energy applied in the assays. Volatile solids, total solids, volatile fatty acids, chemical oxygen demand, soluble chemical oxygen demand and pH were monitored using standard methods (APHA, 1998). For all assays, the operating parameters were the same except that no pretreatment was applied to the wastes in the control assays. Results indicated a significant increase in the soluble organics content for sonicated samples. Best results in terms of biogas production and organic matter solubilization were obtained with a sonication specific energy at 4940 KJ/kgTS (optimum level) and for a sonication time of 40 minutes. Above 4940 KJ/kgTS, sonication did not enhance solubilisation of organic matter in the assasys. Cumulative biogas production increased in the following order: UtS-40mins (3020 mL) > UtS-10mins (2030 mL) > UtS-60mins (1285 mL) > untreated sample (700 mL). The overall inference of this work is an enhancement in the methanogenic reaction rate and biogas yield with sonication used as a pretreatment. The projected biogas production and energy generation were also calculated with an input of 40 tons of VW per day. It has been estimated that sonication for 40 minutes would bring the most revenue (MUR 7,276,150) from the sale of electricity to the national grid when compared to scenarios with other sonication conditions.

PART III - TECHNICAL INFORMATION

1.1 Background

Solid waste generation is a major problem both for developed and developing countries in terms of managing and disposing huge amount of wastes. Waste generation is increasing every year and this increase is attributed to an increase in population, more economic development and improving lifestyle. Waste generation in the United States of America (US), for instance, was 243 million tons in 2009. In Europe, it has been estimated by the Organisation for Economic Corporation and Development (OECD) that the amount of wastes generated would increase by 45% in 2020 as compared to 1995 (European Commission, 2011). As for Mauritius, a small island with a population of 1.25 million, the amount of wastes generated in 2010 was 414,543 tons (CSO, 2011).

1.2 Solid Wastes in Mauritius

In Mauritius, solid wastes are classified into the following broad fractions: municipal solid wastes (MSW) (~70%), industrial non-hazardous wastes (~15%), construction and demolition wastes (~11%), health care wastes (0.2%), hazardous wastes (5%) and sludge (0.08%) (Mohee *et al.*, 2010). In Mauritius, MSW contributes the highest proportion of the solid wastes going to the Mare Chicose Sanitary Landfill and is in the order of 60-70% (Mohee *et al.*, 2010). MSW, in itself, can be further subdivided into food wastes, yard wastes, textiles, paper, metals, glass, plastics and others as illustrated in Figure 1.1.

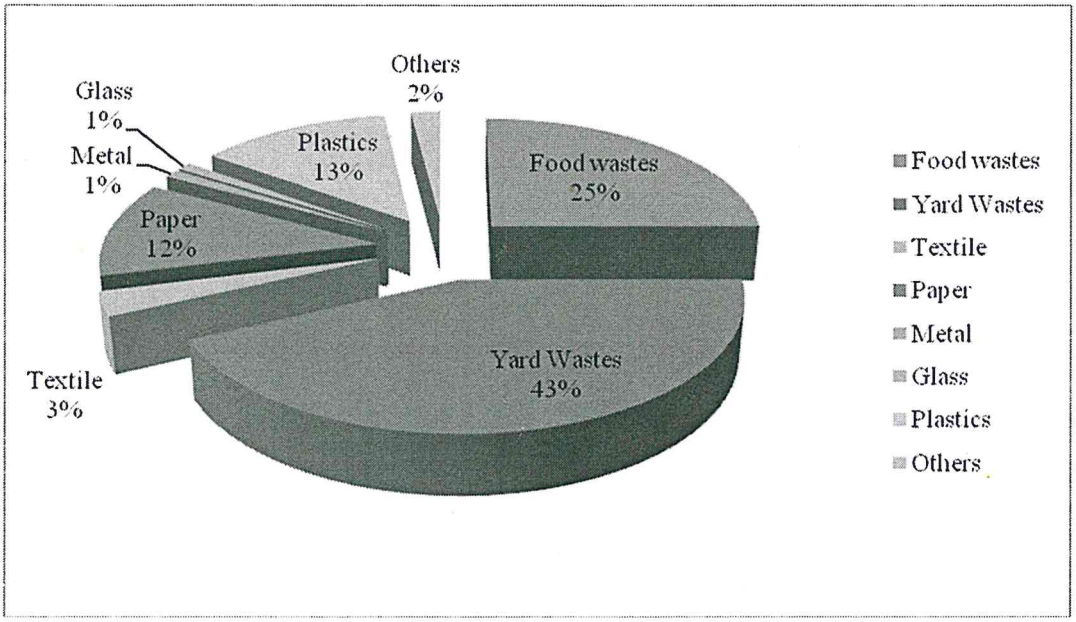

Figure 1.1: Composition of MSW in Mauritius (Source: Surroop, 2010)

From Figure 1.1, it is observed that the organic fraction of MSW (OFMSW) in Mauritius is 80% (paper, yard and food wastes combined) and the amount of recyclable materials is 27% (metals, glass, plastics and paper combined).

1.3 Problem Statement

The amount of solid wastes (~414,600 tons) generated in 2010 in Mauritius is expected to increase to 510,000 tons by 2034 (Mohee *et al.*, 2010). This increase is presently attributed mainly to the forcasted increase in population of about 0.4% since 2009 (CSO, 2010b). Another factor contributing to the increase in solid wastes generation is rapid economic development. With rapid economic development, applicable to developing countries like Mauritius, there is improving lifestyle whereby people tend to consume more goods and generate more wastes. This increase in waste generation represents a major burden on the sole landfill in Mauritius at Mare Chicose. The Mare Chicose Sanitary Landfill started operation in 1997 and was originally receiving about 6,800 tons of wastes (Mohee and Bhurtun, 2002) but is now receiving more than 400,000 tons of wastes annually. This has caused the landfill at Mare Chicose to reach full capacity and since there are no other suitable sites for the construction of a new landfill in

Mauritius (Mohee *et al.,* 2010), there is a major problem of disposal and/or treatment of ~400,000 tons of wastes annually.

Since waste generation cannot be restrained and the amount of waste generated will keep on increasing, there is a need to provide a solution to this waste problem. The various options that exist for solid waste management are landfilling and landfill gas use, recycling, thermal treatment such as mass or fuel burn and incineration without energy recovery and biological treatment such as composting and anaerobic digestion (Figure 1.2).

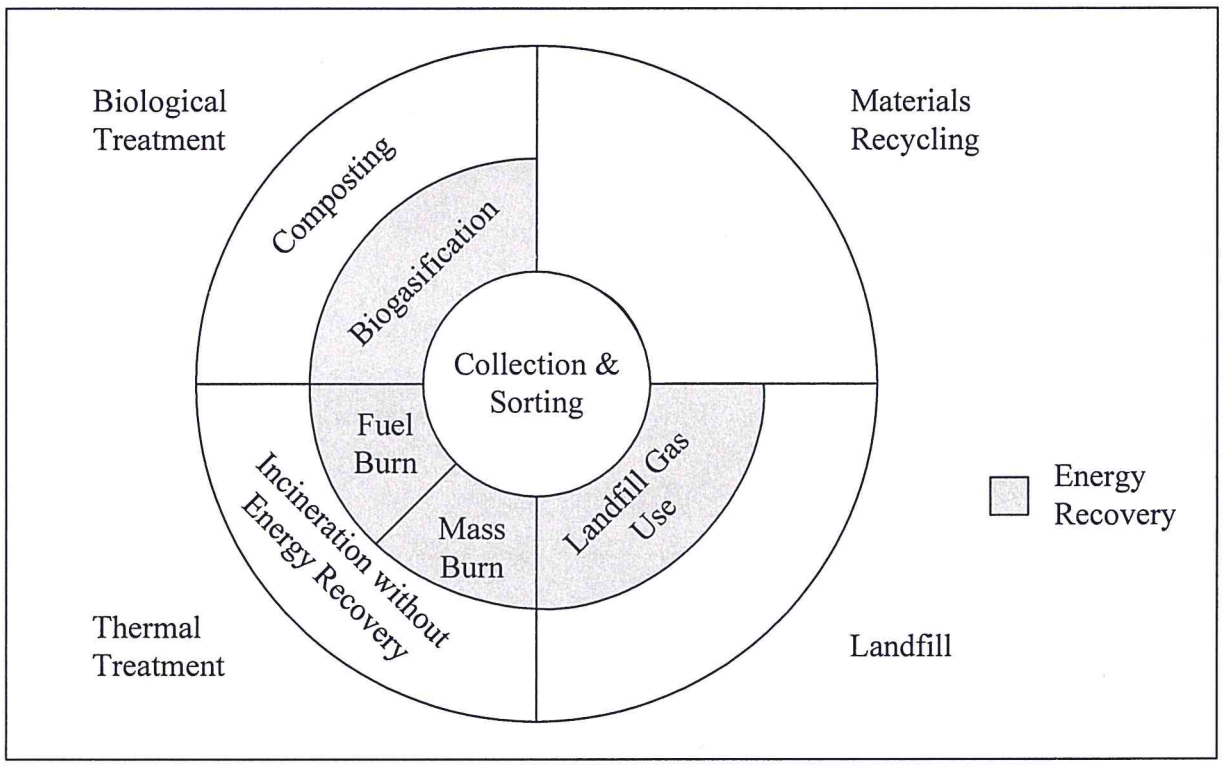

Figure 1.2: Elements of Integrated Waste management

(Adapted from: McDougall et al., 2001)

Landfilling, though being one of the options for waste management, is not an option for Mauritius. The current landfill at Mare Chicose is already saturated and the possibility of constructing another landfill on the island is limited and not a sustainable decision considering the scarcity of appropriate land for landfill construction in Mauritius. As for recycling, it is

applicable for the recyclable fraction of MSW whereby used materials such as paper, glass, plastics and metals can be recycled. Considering thermal treatment options, these are suitable for reducing the amount of wastes generated and they also produce energy and electricity. However, thermal treatment options also cause environmental emissions in the process. There was a proposed project of a Waste to Energy (WTE) plant of capacity 300,000 tons (Mohee *Et al.*, 2010) to incinerate wastes generated in Mauritius and produce electricity. However, due to considerable resistance by environmental groups on the island, this project could not be realized. As for composting, it is a viable treatment option for waste management in Mauritius since the organic fraction of MSW (OFSWM) is quite high in the order of 80% (Surroop, 2010). The waste management system in Mauritius actually may boast a composting plant at La Chaumière of capacity exceeding 100,000 tons (Mohee *et al.*, 2010) whereby solid wastes are received and are converted into saleable compost for the Mauritian market. However, even if 100,000 tons of wastes are directed from the landfill to the composting plant, around 300,000 tons of wastes remain untreated, and untapped as a resource.

1.4 Rationale of the Study

A potential solution to the aforementioned problem is Anaerobic Digestion (AD). Anaerobic Digestion has been observed to be reliable for the reduction in the volume of wastes as well as the production of biogas which can be used for the production of energy and electricity (Chen *et al.*, 2008; Ward *et al.*, 2008; Nguyen *et al.*, 2007). The application of AD to the Mauritian context is suitable since besides providing a solution to the increasing waste generation problem, AD would also produce biogas which fits in well under the Maurice-Ile-Durable (MID) Concept, and the shift towards renewable energies (or bioenergy). The recent scientific interest in bioenergy can be traced through three main stages (Plieninger *et al.*, 2006). The first stage of discussion started with the 1973 oil crisis and the publication of the Club of Rome's report on 'The Limits to Growth'. Along with Rachel Carlson's 'Silent Spring', the Limits to Growth report was an iconic marker of the environmental movement's emergence and a precursor to the concept of sustainable development. The second stage of interest in bioenergy began in the

1980s in Europe as a result of agricultural overproduction and the need to diversify farm income. Triggered by increasing concern over climate change, a third stage started at the end of the 1980s, and continues to this day.

The composition of wastes in Mauritius is such that the organic fraction is 80% (Surroop, 2010). Hence, this makes AD a most plausible option for waste management in the island. In Mauritius, vegetables wastes (VW) can be obtained from markets, supermarkets, commercial areas, hotels and household premises. These wastes fraction represent almost 25% of the gross food wastes generated (Surroop, 2010). For this study, cabbages, carrots, potatoes and beetroots were used representatively. The average wastes quantities of the latter four vegetables (in a wasted form) account to a total of almost 1160 tonnes as reported by CSO (2010). Therefore, annually around 1100 tonnes of wastes could be potentially used as feedstock for anaerobic digestion.

Anaerobic Digestion and Pretreatment - Anaerobic Digestion can be defined as the breakdown and stabilisation of organic materials by microbial organisms in the absence of oxygen to produce methane, carbon dioxide and a stable, innocuous sludge that can be used as soil conditioner or fertiliser (Fantozzi and Buratti, 2009; Appels *et al.*, 2008; Chen *et al.*, 2008; Ward *et al.*, 2008). However, stand-alone AD processes have a long retention time due to the inherently slow hydrolysis step. It also requires large reactor volume, has low degradation efficiency while the biogas production is not optimised. All these effects are attributed to an inaccessibility of the polymers to the microorganisms for degradation (Hendriks and Zeeman, 2009; Taherzadeh and Karimi, 2008). In view to increase the bioavailablity of the readily degradable organic fractions, various techniques have been employed to solve the aforementioned problems so as to enhance AD. These can be broadly classified into physical, physicochemical, chemical and biological techniques. All these technologies help to disrupt cells structure, increase solubilisation, anaerobic digestion and biogas production (Ward *et al.*, 2008).

Quite recently, Appels *et al.* (2008) discussed that ultrasound (UtS) irradiation is, without any doubt, the most powerful method to disrupt sludge cells and this is the reason for its investigation in this research study. The application of UtS irradiation as pre-treatment to the substrate prior to AD helps to further degrade the complex molecules in the substrate, accelerates the slow process of hydrolysis and enhances anaerobic digestion and biogas production (Xie *et al.*, 2009; Bougrier *et al.*, 2008; Ward *et al.*, 2008; Chu *et al.*, 2001). Bearing in mind the gradual promosie of sonication in AD processes, it is projected that the results of this proposed research shall constitute a comprehensive and novel contribution to the knowledge in the field. Also, depending on the quality and variability of the results, it is inherently felt that pilot–scale UtS irradiation schemes may then be designed for solid wastes pretreatment prior to treatment by anaerobic digestion. The table below shows the use of different substrates and their corresponding amount of biogas obtained.

Table 1.1: Biogas production yields reported in past studies

Substrates	**Amount of Biogas and/or Methane**	**Reference**
Flocculated Activated Biosolids	316 g CH_4/Kg DS * 280 g CH_4/Kg DS**	Chu *et al.* (2002)
Waste Activated Sludge	2400 mL of biogas* 700 mL of biogas **	Simonetti *et a*l. (2010)
Sludge	220 mL of biogas* 150 mLof biogas **	Erden *et al.* (2009)
Waste Activated Sludge	334 mL CH_4/ COD_{added} 325 mL CH_4/ COD_{added} 221 mL CH_4/ COD_{added}	Bougrier *et al.* (2006)

*Sonicated Sample **Untreated sample

Digestate - Upon exhaustion of the wastes, digestate is obtained which is the by-product of methane and heat production in a biogas plant, coming from organic wastes. Depending on the biogas technology, the digestate is composed of solid phase and liquid phase (fugate) which is distinguished based on their dry matter (DM) content. Digestate containing less than 15% DM content is referred as liquid digestate, while the solid digestate contains more than 15% DM. Solid digestate can be used similar to the composts or could be composted with other organic residues and can be more economically transported over grater distances than the liquid material (Møller *et al.*, 2000). For this study, characterization of the digestate was done in order to investigate whether any treatment prior to land application is required or the digestate can be used directly. All the more, the quality of a digestate depends on the digestion process applied and the composition of ingestates. Digestate is a very complex material, and therefore it has effects on the physical, chemical and biological properties of the soil, depending on the soil types. The recycled organic wastes are suitable for contribution to maintain the soil nutrient levels and soil fertility (Tambone *et al.*, 2007). Comparing to other organic materials, the amendment properties rank sequentially as compost digestate > digested sludge >> ingestate, on the basis of organic matter (OM) degradability (Tambone *et al.*, 2010).

1.5 Types of Anaerobic Digestion Processes

Anaerobic digestion processes can be classified based on the temperature, the solid concentration employed and the number of stages used as illustrated in Figure 1.3.

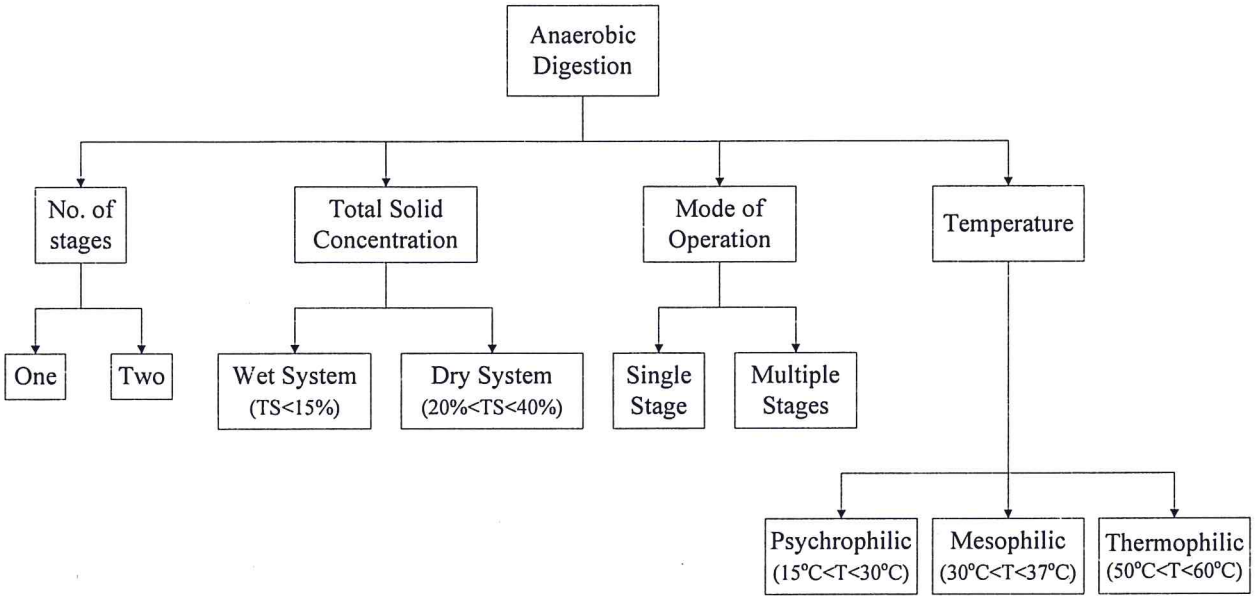

Figure 1.3: Types of Anaerobic Digestion (Source: Nguyen, 2008)

Since single stage batch anaerobic digestion is being employed in study and the effects of temperature are discussed later, the solid concentration is immediately discussed here. Based on solid concentration, there are principally three types of anaerobic digestion: Low solids anaerobic digestion, semi-solids (medium solids) anaerobic digestion and high solids anaerobic digestion (Nguyen, 2008; Tchobanoglous *et al.*, 1993). In low solids anaerobic digestion, the organic fraction is fermented at a solid concentration of 4-8%, in semi-solid anaerobic digestion, the degradation is performed at 7-15% while in high solids anaerobic digestion, the degradation process occurs at a solid concentration of 20% or higher (Nguyen, 2008; Tchobanoglous *et al.*, 1993). Low and medium solids anaerobic digestions constitute the wet systems while high solids anaerobic digestion represents the dry system. Both the 3 types of AD consist of the same steps of operation as listed below:

1. Preparation of the substrate such as sorting and size reduction.
2. Addition of moisture content to reach desired solid concentration (mostly for low solids AD).
3. Adjustment of pH, temperature, alkalinity and C:N ratio.

4. Seeding with an appropriate inoculum.
5. Capture, storage and measurement of biogas produced.
6. Dewatering of digested sludge.

The advantage of high solid anaerobic digestion is that less water needs to be added as compared to low solids anaerobic digestion. Additionally, more biogas is produced per unit volume of the reactor size with high solids anaerobic digestion. However, high solids anaerobic digestion is more difficult to monitor and the parameters are more vulnerable to changes. To reach a compromise, semi solids anaerobic digestion has been used in this study at a solid concentration of 7-15%.

1.6 Sample Collection, Treatment and Characterization

The type of substrate used is important because it determines the rate of anaerobic digestion and it can also inhibit the process completely (Deublein and Steinhauser, 2008). Some substrates with complex structure tend to take more time to degrade while other substrates can take only a few days to degrade completely. Additionally, depending on the nature and composition of the substrate used, intermediate digestion products such as fatty acids or ammonia can inhibit the digestion process (Deublein and Steinhauser, 2008).

The substrates used for this research study were mixed vegetable wastes/residues. Vegetable wastes have been chosen as they form part of a large portion of OFMSW which contributes about 80% of municipal solid wastes generated in Mauritius (Surroop, 2010). Ward *et al.* (2008) indicated that vegetable wastes tend to degrade easily and this can inhibit the AD process due to the premature acidification of the digester contents which are produced as a result of a relatively 'rapid' rate of hydrolysis moving to the acidogenesis phase.

Vegetable wastes used - Vegetable wastes (VW) were collected from the market of Vacoas, Mauritius. The inoculum was obtained from mature vegetable wastes and cow dung lab-scale anaerobic digesters (over 6 months old). The fractions in the VW used were cabbages, carrots,

beetroots and potatoes. All the substrates to be fed were first chopped to a quasi uniform size mechanically using a shredder and grinder after a manual coarse size reduction using knives. Size reduction was done to increase surface area. The VW and inoculum used were characterized (in triplicates) in terms of total solids (TS), volatile solids (VS), pH, volatile fatty acids (VFA's), alkalinity and chemical oxygen demand (COD) according to procedures APHA (1998).

Table 1.2: Characteristics of vegetable wastes and inoculum

	Vegetable Wastes	Inoculum
Total Solids (%)	11.98±1.42	3.88±0.78
Volatile Solids (%)	93.93±2.36	69.29±3.45
pH	7.88±0.21	7.85±0.19
Alkalinity (meq/L)	253±12	8.3±0.5
Volatile Fatty Acids (meq/L)	179.4±9.1	10±0.8
Chemical Oxygen Demand (mg/L)	33846±458	3759±102

1.7 Design and of Set-up of Biochemical Methane Potential (BMP) assays

Biochemical methane potential (BMP) assays serve as a very good and reliable method to evaluate the performance of AD processes (Angelidaki *et al.*, 2009). In this regard, anaerobic digesters and finally BMP assays were designed and set-up (Figure 1.4). These were 2-L plastic bottles with thick rubber septum. The rubber septums were drilled with 2 holes in each of them so as to pass the tubings. The plastic bottles were protected from light by placing the bottles in black plastic bags and these were sealed. Light is not lethal to methanogens but does inhibit the methanogenic process. Hence, AD should be performed in complete darkness (Deublein and Steinhauser, 2008). The tubing from the digester was connected to a flask which contained 0.05 mol/L H_2SO_4 so that biogas was collected and measured. From the flask, the tubing was then connected to an inverted cylinder whereby the volume of biogas would be determined by the downward displacement of acidified water as shown Figure 1.4.

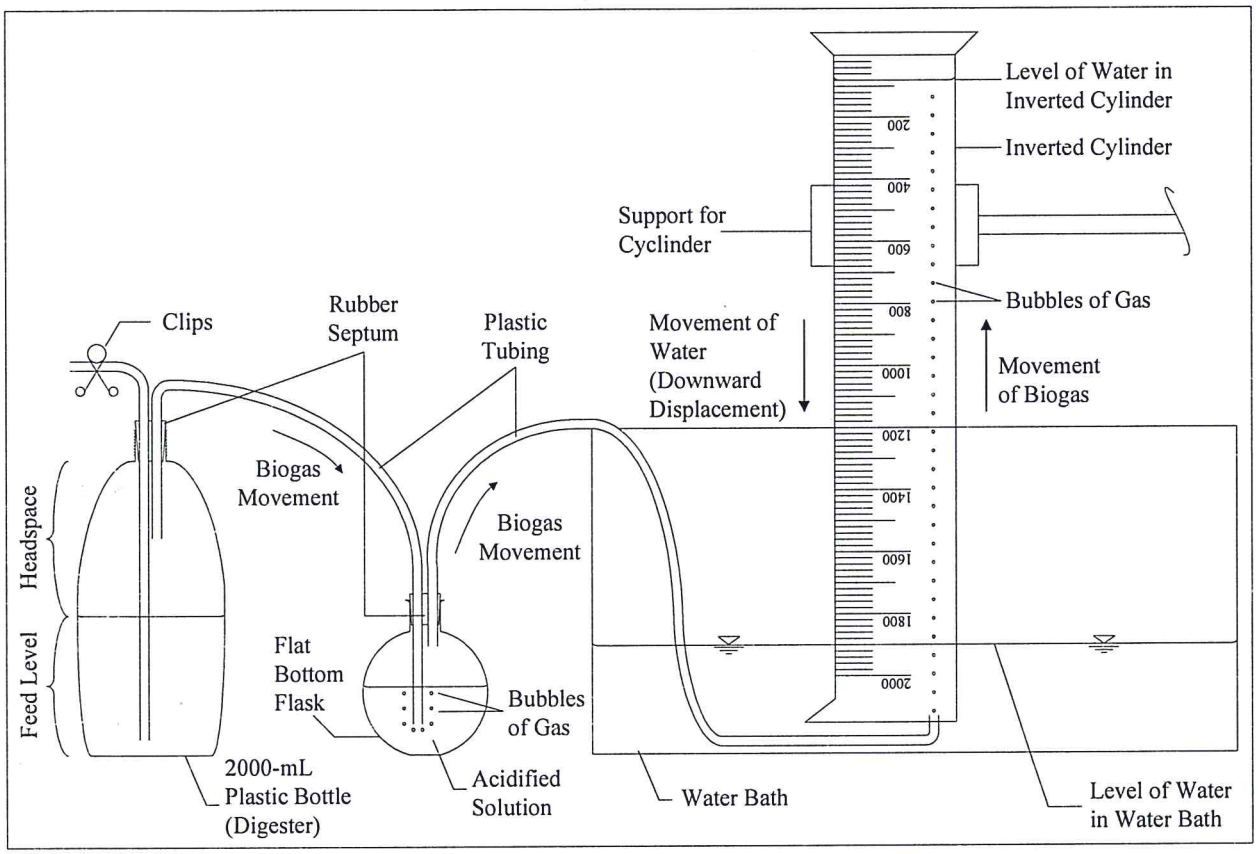

Figure 1.4: Biogas measurement by downward displacement of water

After mechanical pre-treatment of the vegetable wastes and characterisation of the substrate and the inoculum, 400±5 grams of vegetable wastes comprising of potatoes, carrots, cabbage and beetroot (mass ratio 1:1:1:1) were weighed accurately and the required amount of water was added to achieve a final moisture content of 95±0.9%. This substrate was then inoculated with microorganisms at an Food:Microorganism ratio of 4:1 (F:M on volume basis). The pH was then adjusted to near 7.2. 500 mL of the inoculated substrate was then placed in the anaerobic digester and the rubber septum was tightly inserted and sealed with silicone to prevent any leakage/loss of gas. The anaerobic digester was then purged with nitrogen (N_2) gas to render it completely anaerobic. The tubing from the digester was connected to a flask which contained 0.05 mol/L H_2SO_4 so that biogas was collected and measured. From the flask, the tubing was

then connected to an inverted cylinder whereby the volume of biogas was determined by the downward displacement of acidified water as shown in Figure 1.4. The anaerobic digestion process was allowed to run for a period of 24 days (Plate 1.1). All BMPs were run in duplicate, with one dedicated for biogas collection and the other for sampling of slurry for analytical tests.

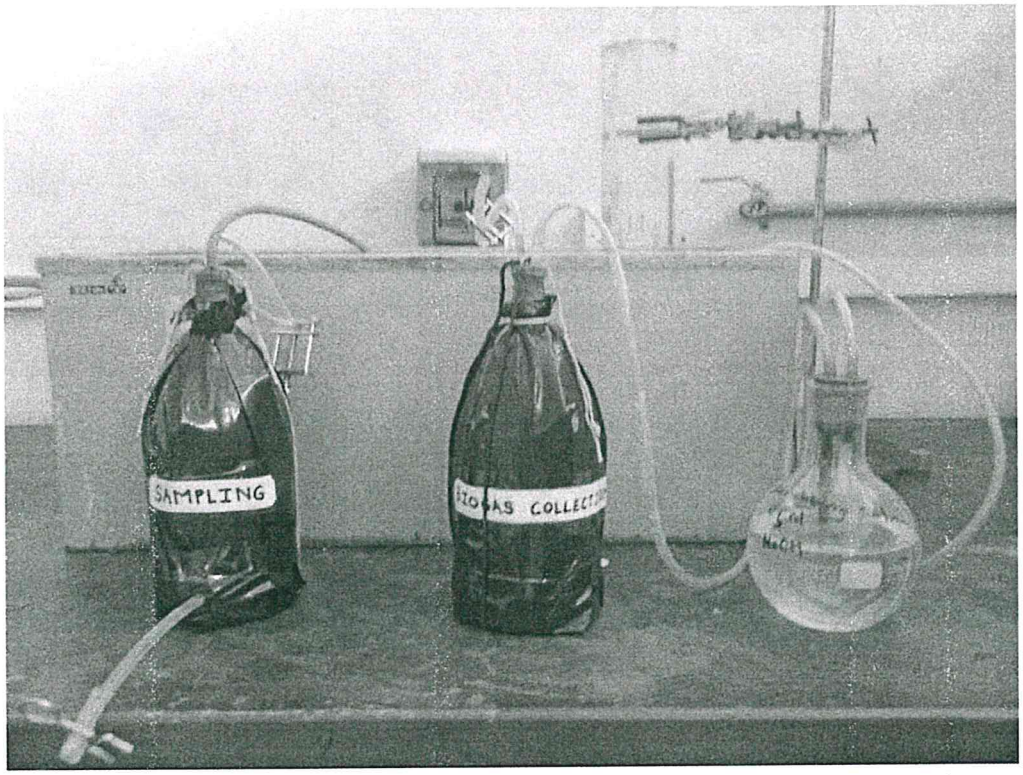

Plate 1.1: Experimental Set-up of BMP assay

1.8 Ultrasound Irradiation

The ultrasonic processor or sonicator comes with an ultrasonic generator, a convertor cable, an ultrasonic convertor, the ultrasonic horns/probes and a sound enclosure as illustrated in Plates 1.2 - 1.4. The ultrasonic electronic generator transforms AC line power to a 20 KHz signal that drives a piezoelectric converter/transducer. This electrical signal is converted by the transducer to a mechanical vibration due to the characteristics of the internal piezoelectric crystals. The vibration is amplified and transmitted down the length of the horn/probe where the tip longitudinally expands and contracts. The distance the tip travels is dependent on the

amplitude selected by the user through the touch screen pad (Plate 1.6). As the amplitude setting is increased, the sonication intensity increases within the test sample.

In liquid, the rapid vibration of the tip causes cavitation, the formation and violent collapse of microscopic bubbles as explained previously. The collapse of thousand of cavitations bubbles releases tremendous energy in the cavitation field. The erosion and shock effect of the collapse of the cavitation bubble is the primary mechanism of fluid processing. The probe tip diameter dictates the amount of sample that can be effectively processed. Smaller tip diameters (microtip probes) deliver high intensity sonication but the energy is focussed within a small, concentrated area. Larger tip diameters can process larger volumes but offer lower intensity. The choices of a generator and horns/probes are matched to the volume, viscosity and other parameters of the particular application. Horns are available for both direct and indirect sonication. The sound enclosure provides personal protection from the noise generated by ultrasonics. The enclosure reduces sound levels by approximately 25% when compared to sonication done in an open setting.

Plate 1.2: Ultrasonic Processor (Qsonica Q500)

Plate 1.3: Ultrasonicator (Qsonica Q500)

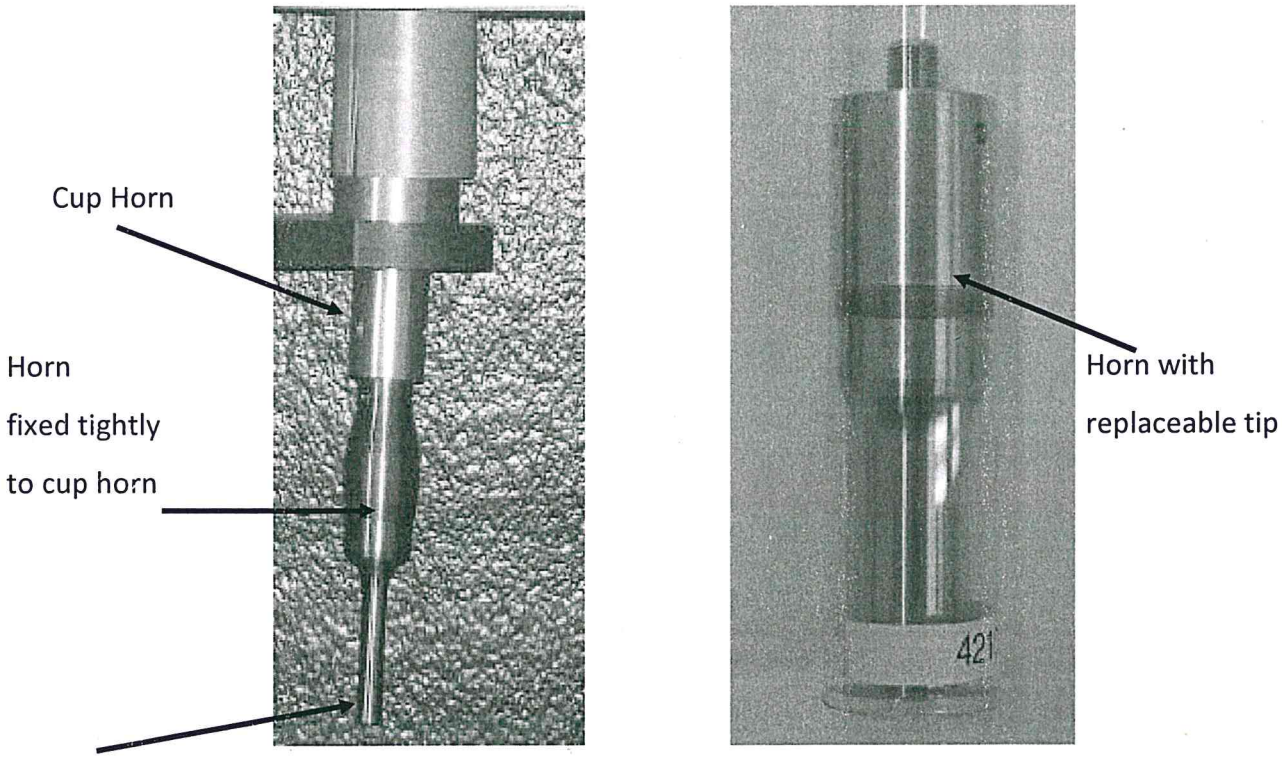

Plate 1.4: Tip and Horn of Ultrasonicator

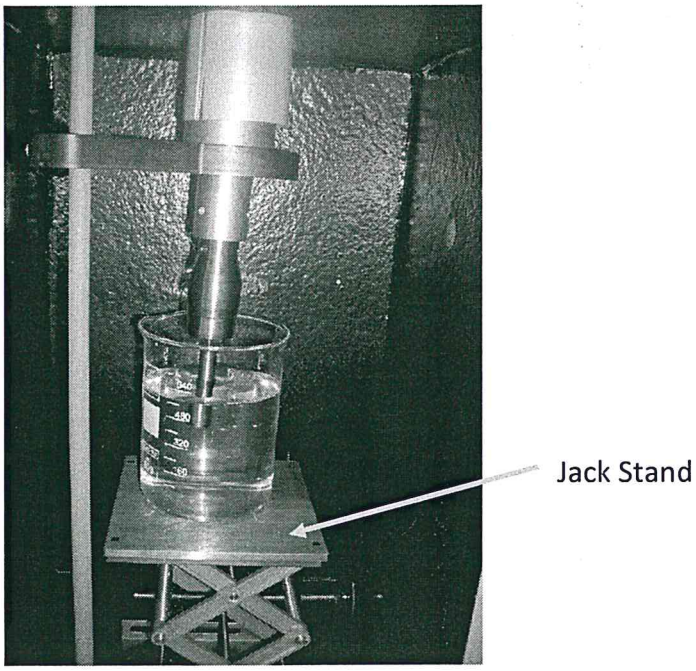

Plate 1.5 : Irradiating Sample with *Ultrasonicator (Qsonica Q500)*

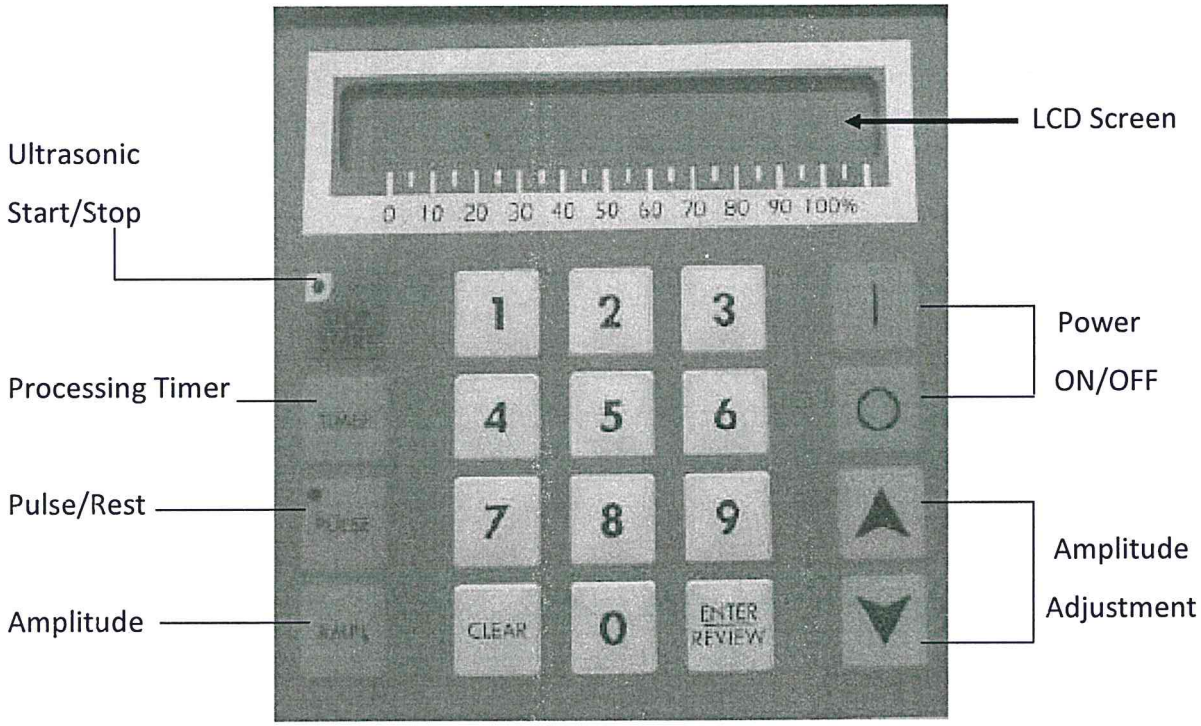

Plate1.6: Operating features in Ultrasonic Processor

The sonication times used were 0 (control), 10, 40 and 60 minutes. Depending on the sonication times, the specific energies used were calculated as expressed in Equation. 1.1:

$$Specific\ Energy = \frac{Power}{Total\ Solids \times Volume} \qquad \text{(Eqn. 1.1)}$$

where:

Specific Energy (KWh/Kg TS) = Energy absorbed by the sample

Power (KW) = Power being supplied by the sonicator

Total Solids (kg/L) = Solids remaining after heated in oven

Volume (L) = Amount of sample used for sonication

After sonication, the ultrasonicated substrate was allowed to cool to room temperature and was inoculated with microorganisms at an F:M ratio of 4:1 (volume ratio). This substrate was then placed in the anaerobic digester and the remaining procedures were similar to those for the control set-up whereby the anaerobic digestion process was allowed to run for a period of 24 days.

Table 1.3: BMPs assays Pre-treatment time and Conditions

Sample	Sonication time (mins)	Mass of Substrate Used (g)	Mass of Inoculums (g)	F:M ratio	Specific Energy (kW/kg TS)
Control	No sonication	400	100	4:1	0
UtS-10	10	400	100	4:1	1280
UtS-40	40	400	100	4:1	4940
UtS-60	60	400	100	4:1	7323

1.9 Findings and key discussions

1.9.1 Chemical Oxygen Demand & Soluble Chemical Oxygen Demand

The SCOD variations with respect to specific energy is shown in Figure 1.5 below

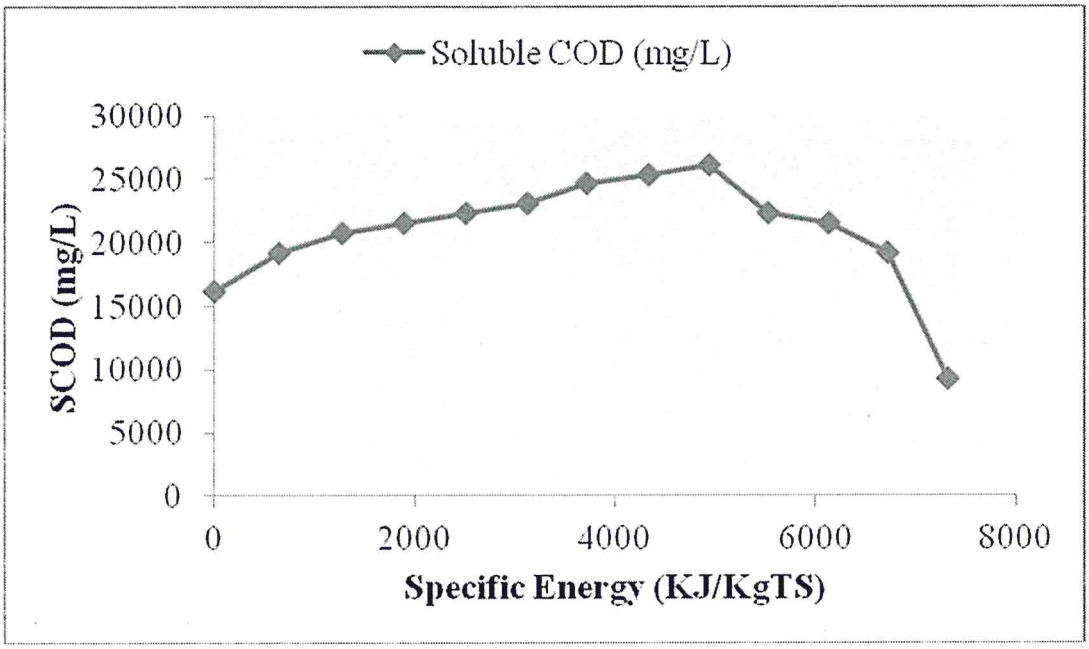

Fig. 1.5 Soluble COD variation with Specific Energy

Solubilisation gives an indication of the amount of biogas produced. From Fig. 1.5, SCOD is seen to increase with increasing SE. This means that a considerable fraction of the released COD was transformed into biodegradable organic components. The maximum SCOD was obtained for a specific energy of 4940 KJ/Kg TS and sonication time of 40 min. Upto 4940 KJ/Kg TS, hydroxyl radicals attack the organic substances and destroyed the microorganism's cell walls in the biomass and oxidise them to dissolved organic substances, which are released to the liquid phase and increase the SCOD.Hence, greater biodegradability is expected from a reaction time of 40 min and SE 4940 KJ/Kg TS. For specific energies above 4940 KJ/Kg TS, SCOD decreased. Similar evaluation was reported by Erden *et al.,* 2009. Decreasing solubilisation may be explained by strong oxidation effects of radicals (Erden *et al.,* 2009). For higher specific supplied energies, solubilisation were lower which may be due to cell death of the VW cells' walls. According to the study of Erden *et al.,* 2009, it was seen that high ultrasonic energies

promote oxidation by radicals leading to mineralization preceding solubilization of sludge. This holds true for this study also. During sonication, there is the production of heat within the sample hindering the formation of bubbles which is important for cavitation, as a result of this, at higher sonication time, the SCOD was decreased. From research of Erden *et al.*, 2009, temperature was one of the factor which caused the SCOD of the sludge to decrease when sonication time was increased. This study follows the same trend, i.e when the sonication time was increased (above 40 min corresponding to SE 4940 KJ/Kg TS), the temperature kept on increasing resulting in SCOD reduction. The COD and SCOD variations during the AD process are shown in Figure 1.6 and Figure 1.7.

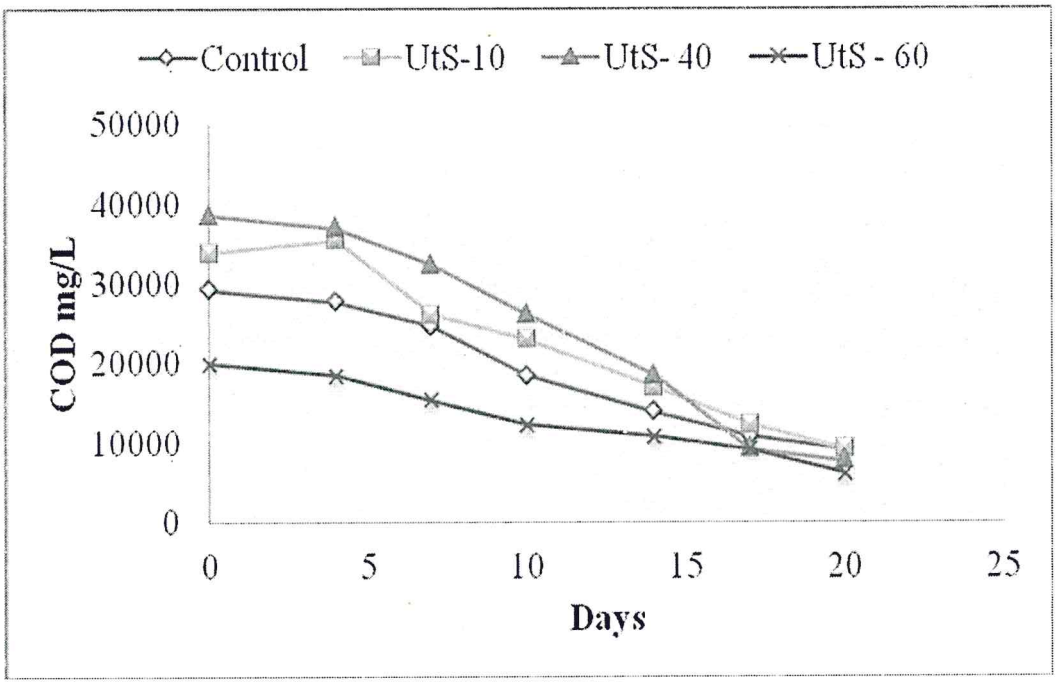

Fig. 1.6 COD variation during AD

Chemical Oxygen Demand is an indication of the amount of organic matter present in a particular system. When there is high organic matter, the oxygen demand is high and the COD gets a high value. From Figure 1.6, it is noticed that there is a decreasing trend during the anaerobic digestion processes in all 4 BMP assays indicating that the process of degradation took place in all experiments. This decrease could be accounted by the removal of organic matter in the systems through AD process (Rubia *et al.*, 2006) through the several AD process phases.

Initially, the BMP assays were high in COD illustrating that they were heavily loaded with organic matter (Sarkar *et al.*, 2006). The reason for this could be that the VW used for this research were fresh organics, so there has been no degradation initiated yet. From Figure 1.6, it can be equally observed that the initial COD for the control, UtS- 10, UtS- 40 and UtS- 60 assays were 29230.8mg/L, 33846.2mg/L, 38461.1mg/L and 20000 mg/L, respectively. The % decrease in the COD for the control, UtS-10 and UtS-40 were 73.68%, 86.37%, 80.0% and 76.92%, respectively. Higher COD removal was obtained for the sonicated samples as sonication would have most plausibly caused the disruption of microbial cells thereby increasing the surface area for biodegradation. This ultimately led to the removal of COD being improved (Aldin *et al.*, 2010; Tiehm *et al.*, 2001).

The samples sonicated for 10 and 40 minutes showed greater disintegration than the control implying that sonication had improved biodegradability. However, this observation did not coincide for the sample sonicated for 60 minutes because the corresponding reduction in COD was less than those recorded for the BMPs pretreated at the other two sonication times (UtS-10 and UtS-40). A possible explanation for this could be that above 40 minutes (which presently stands out as the 'optimum sonication time') of cavitation, the cell wall of the VW was disrupted in such a way that some of the organic matter within the VW itself was not being released due to oxidation of radicals (Erden *et al.*, 2009).

The degradation of COD and SCOD occurred due to methanogenic activities whereby the methanogens degraded and converted the solubilised organic matter into CH_4 and CO_2 (Appels *et al.*, 2008). However, not all the COD could be degraded by the methanogens as indicated by the 73.68%, 86.37%, 80.0% and 76.92% COD reduction. COD is classified into soluble and particulate COD (Paztor *et al.*, 2009). During AD, only SCOD is easily degraded by the microorganisms. The variation of SCOD for this study is shown in Figure 1.7.

As for particulate COD which consists of inert COD, slowly biodegradable COD, these are hard to degrade unless adequately solubilised during hydrolysis.

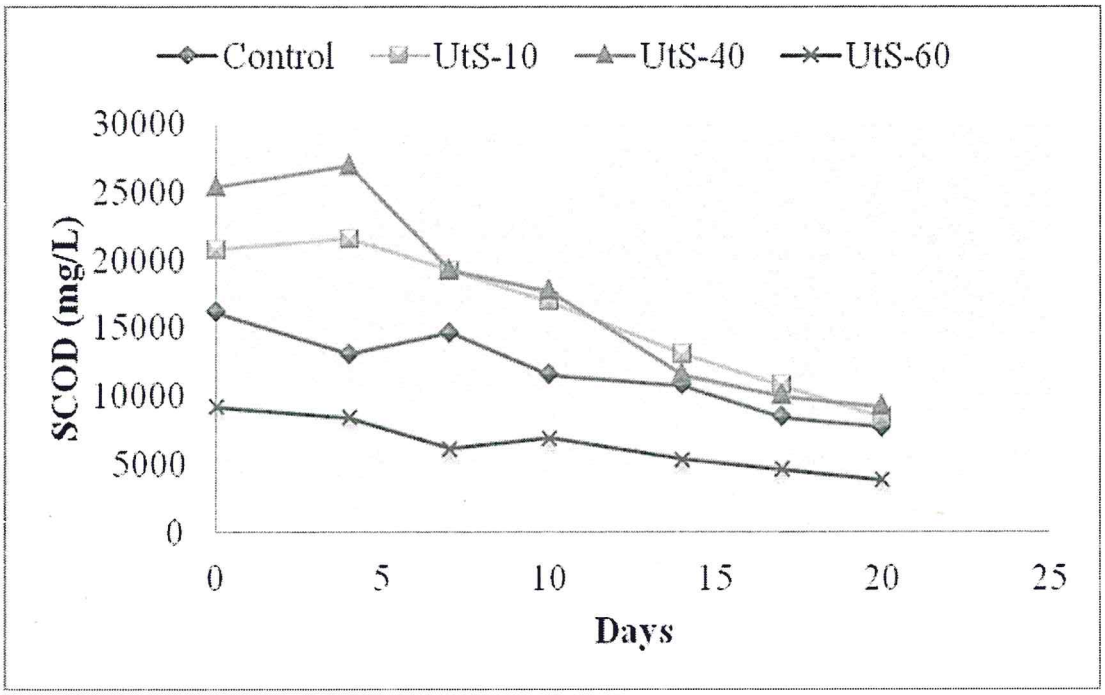

Fig. 1.7 SCOD variation during AD

The initial SCOD concentration in the samples were 16153.85 mg/L, 20769.23 mg/L, 25384.62 mg/L and 9230.77 mg/L for the non-preatreated, Uts-10, UtS-40 and Uts-60, respectively. Destruction of the floc structure and disruption of cells results in the release of organic sludge components into the liquid phase (Erden *et al.*, 2010; Gupta *et al.*, 2006). Thus, characteristics of the assays supernatant were also affected by the ultrasonic pre-treatment. The percent decreases in SCOD for the control, UtS-10, UtS-40 and UtS-60 were 52.38%, 59.26%, 63.63% and 58.33%, respectively. It may therefore be observed that SCOD removal was higher in the sonicated samples (Uts-10, UtS-40 and Uts-60) than for the control. This would be most seemingly because following sonication, cell lysis becomes more pronounced. Hence, more solubilised organic compounds ended in the filtrate of the slurry (Gupta *et al.*, 2006; Elliot and Mahmood, 2007). However, UtS-60 had a lower decrease in SCOD than those recorded from the UtS-10 and UtS-40 BMP assays. Possible reasons might be that lysate activity was no more being enhanced due to a decrease in cavitation (Erden *et al.*, 2009) or simply the microbial cells

were disrupted until little amount of organic matter was left. Lysate activity has been found to be closely connected to the increment of soluble COD in total COD (Dohányos *et al.*, 2004). It is observed from Figure 1.7 that SCOD initially increased on the 4th day of the experiment for the sonicated samples (UtS-10 & UtS-40) and that of the control was increased on the 7th day, which may be explained by the fact that the corresponding assay CODs were being solubilised and hydrolysed much faster for the pretreated samples than in the control, supporting that ultrasonic pre-treatment enhances biochemical activity of the hydrolytic phase in AD (Salsabil *et al.*, 2009).

On the 4th day, the SCOD concentrations of the UtS-10 and UtS-40 assays gradually increased to reach 21538.5 mg/L and 26923.1 mg/L respectively. This could be possibly due to the hydrolysis of the accumulative particulate matter (Jiang *et al.*, 2007; Mao *et al.*, 2007) . The increased SCOD in these pretreated VW samples reflected the release of more lignocellulosic components (Cheng *et al.*, 2010). For the non-pretreated one and the UtS-60 assay, a slight increase was noted on the 7th and 10th day, respectively. This meant that the hydrolysis phase was occurring at that point of time.

The UtS-60 assays took longer to reach the rate limiting hydrolysis stage, and this being as a result of cavitation being onset and the cell walls of the VW being destroyed to an extent which no more remained favourable for anaerobic digestion (i.e. there might have been the formation and/or release of other materials which could have proven to be inhibitory (Chen *et al.*, 2008).

For the control, the hydrolysis stage was observed three days after the corresponding hydrolysis phase onset for the UtS-10 & UtS-40 assays. The latter observation supported that adequate sonication could, on the other hand, assist in enhancing breakdown of cell membranes for a desired favourable process chemistry of the AD process (Bhaskaracharya *et al.*, 2009).

1.9.2 Total Solids and Volatile Solids

The total solids variation during the AD process is illustrated in Figure 1.8.

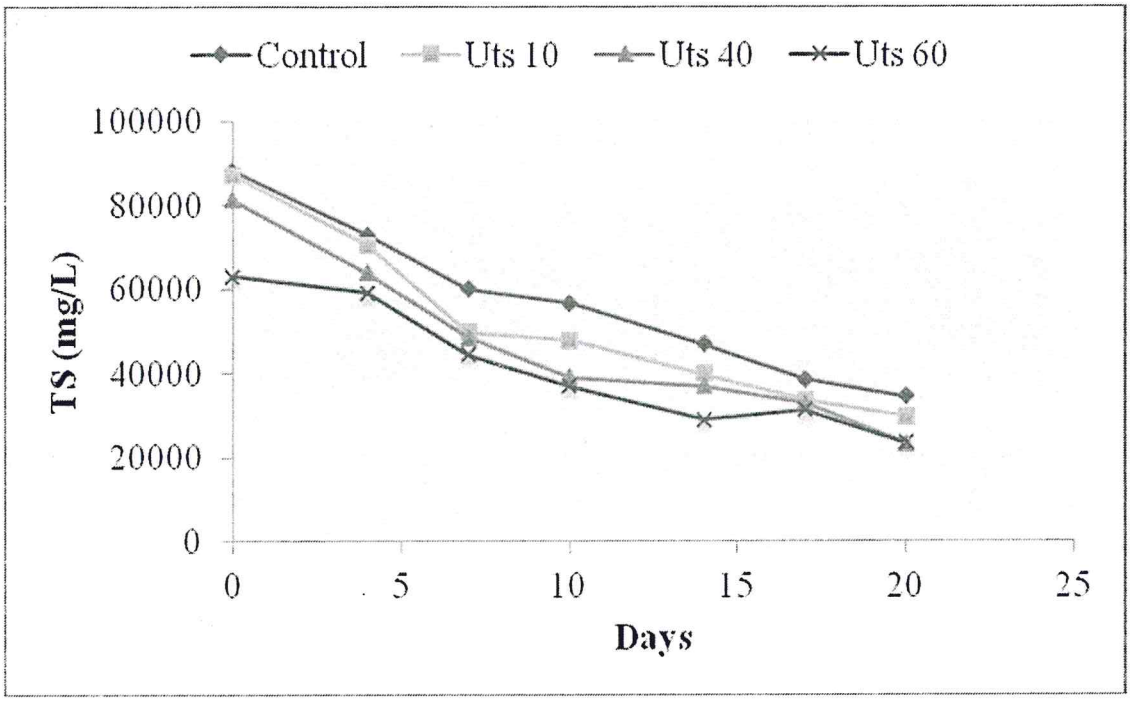

Fig. 1.8 TS variation during AD

Total solids are used to determine the loading rate of anaerobic digester and give useful clues as to when maintenance is needed. The volatile (volatile solids – VS) content gives an indication of the amount of organic material in the waste. High volatile content in biological process is desirable because it guarantees the material stock as an energy resource and sustains microbial growth. Total solids are normally classified as fixed solids (ash) and volatile solids but only the volatile solids will be converted during the acidogenesis and methanogenesis stages during AD process (Tchobanoglous *et al.*, 1993. For this study, a decrease in TS was noted in all the samples (Figure 1.8). The percentage decrease in TS for the control, UtS-10, UtS-40 and UtS-60 assays were 60.86%, 65.86%, 71.24% and 62.67%, respectively. It can be observed that samples sonicated showed greater removal of TS and VS (Figure 1.8 & 1.9) than in the control. This observation may be attributed to the effects of ultrasonic radiation causing higher solubilisation of the TS and VS (Erden *et al.*, 2010).

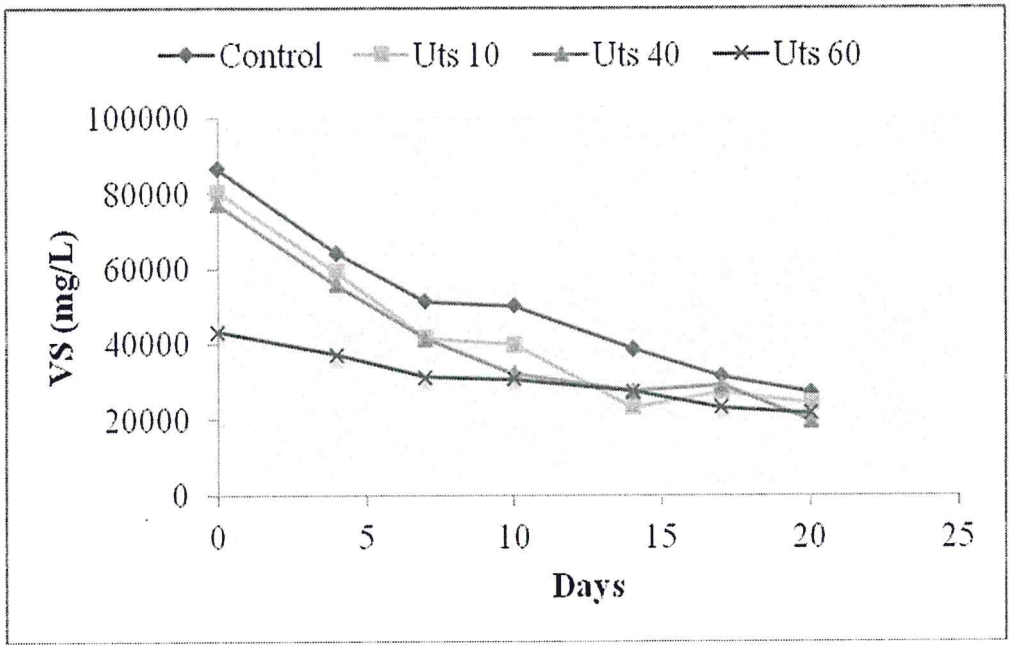

Fig. 1.9 VS variation during AD

Volatile solids reduction is an important parameter for measuring biodegradation of raw material, which directly indicates the metabolic status of some of the most delicate microbial groups in the anaerobic system (Elango *et al.*, 2007). The decrease of VS in the samples was 68.59%, 69.69%, 74.40% and 49.77% for the control, UtS-10, UtS-40 and UtS-60 assays, respectively. It is noticed that the sample pretreated for 60 minutes showed lower TS and VS reductions than the corresponding decreases recorded from the control. This could be explained as follows: at higher sonication time, there is volatilisation of part of the solids. This kind of volatilisation has been reported by Erden *et al.* (2009). During the AD process, the volatile solids fractions were eventually converted into the major constituent species (methane and carbon dioxide) of biogas leading to a corresponding decrease of TS. Moreover, from Figure 1.8 and Figure 1.9, it may be observed that there was no complete destruction of TS and VS. This tallied with the fact that the substrates in the assays comprised biodegradable volatile solids (BVS) and refractory volatile solids (RVS) (Kanhaniyan, 1995), of which only the BVS was degraded to some extent.

1.9.3 pH, VFA and Alkalinity

The variations in pH, volatile fatty acids (VFA) and alkalinity during the AD process are illustrated in Figure 1.10 to Figure 1.12.

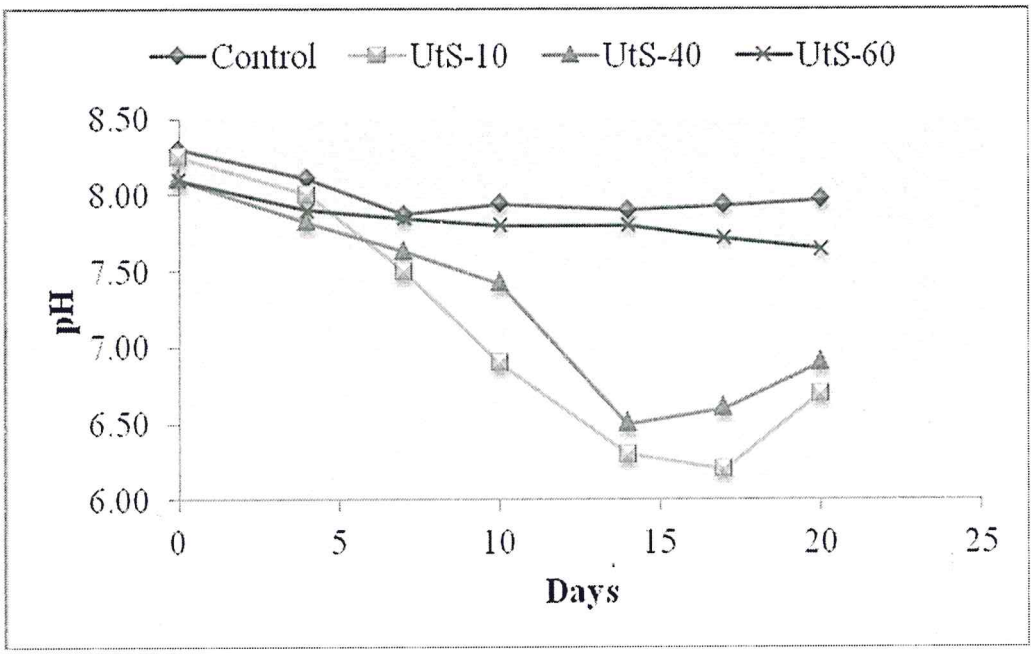

Fig. 1.10 pH variation during AD

The pH value in a digester is a very important parameter which implies the process stability. A general decrease in pH has been observed for all assays. The initial pH were 8.30, 8.25, 8.1 for the control, UtS-10, UtS-40 and UtS-60, respectively, which then decreased to reach a value of 7.97, 6.70, 6.90 and 7.65, respectively. According to Regional Information Service Centre for South East Asia on Appropriate Technology (RISE-AT 1998), the optimum pH value for AD lies in the range of 5.5 – 8.5. Hence there was no need for pH adjustment for the digesters as they were within the range as stated by RISE-AT (1998). Decreasing pH may be explained by acidic compound formation due to floc disintegration (Erden *et al.,* 2009; Rani *et al.,* 2012).

pH for the UtS-60 assay and the control were comparable but that of the UtS-10 and UtS-40 assays showed considerable decrease. However, all the samples had a decreasing trend in the pH, this being due to the formation of organic acids (H^+ ions) by acetogenic bacteria (Appels *et al.*, 2008). The rate of VFA formation was high enough and this led to an accumulation of VFA in the assays and a decrease in pH (Bougrier *et al.*, 2008). pH for the UtS-10 and UtS-40 assays were in the range 6.8 to 7.4 as from the 10^{th} day which was favourable for the activity of methanogens thus leading to biogas production (Sharma *et al.*, 1999).

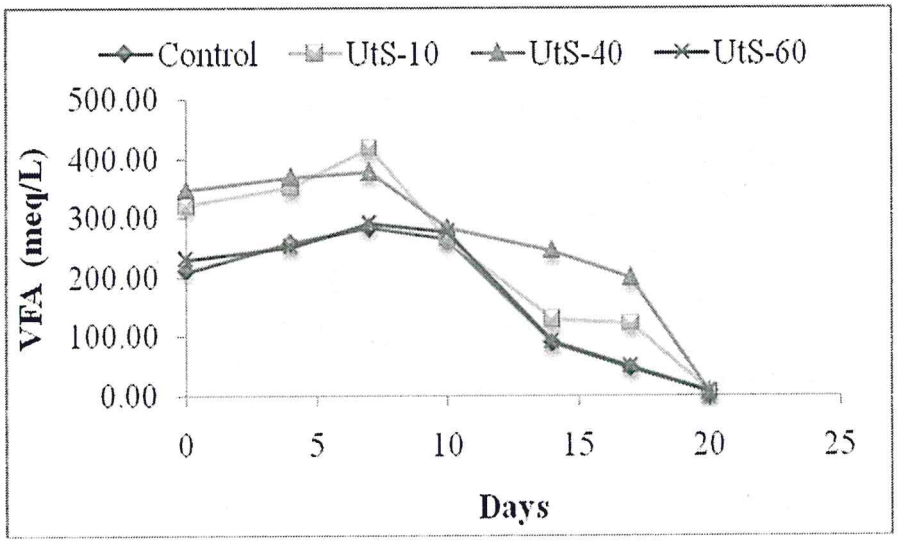

Fig. 1.11 VFA variation during AD

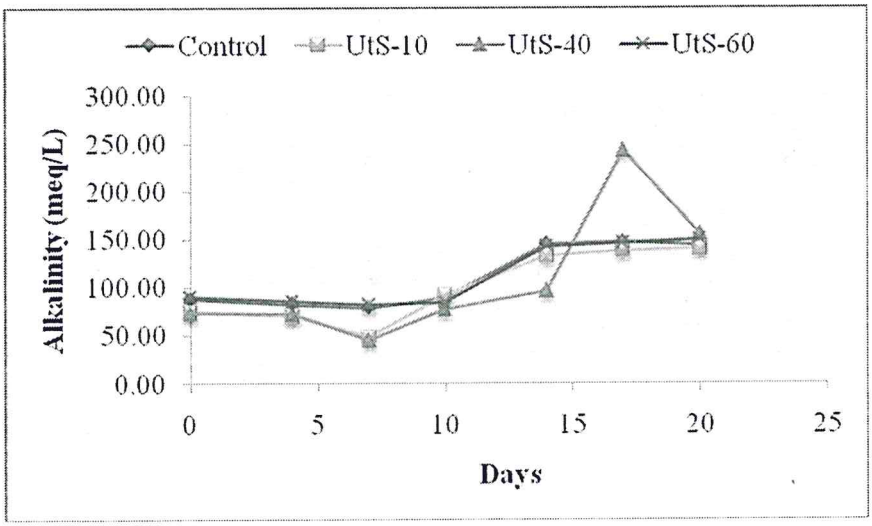

Fig. 1.12 Alkalinity variation during AD

Around the 7th day, the VFA level was high and at its peak in all the digesters, this being due to the rapid acidification of the VW hydrolysis products in the acidogenesis and acetogenesis phase of the AD process (Dogan *et al.,* 2009). During the first seven days, the acidogenesis and acetogenesis were dominant over the methanogenesis reactions. After the 7th day, the VFA started to decrease as the methanogenesis phase started to get on stream. During this phase, the methanogens convert the acetic acid and H_2 to CH_4 and CO_2 (Fantozzi and Buratti 2009; Deublein and Steinhauser, 2008). During the first seven days of the study, when the VFA was increasing, the alkalinity was decreasing. This decrease was due to the formation of CO_2 which then escaped in the biogas produced (Santos *et al.,* 2012). The decrease in the VFA concentration for the control, UtS-10, UtS-40 and UtS-60 assays were 97.03%, 98.03%, 98.70% and 97.40%, respectively. It was noted that the highest VFA reduction among all the sonicated samples was for the UtS-40 assay, followed by UtS-10 and finally UtS-60 assays.

1.94 Cumulative Biogas Production

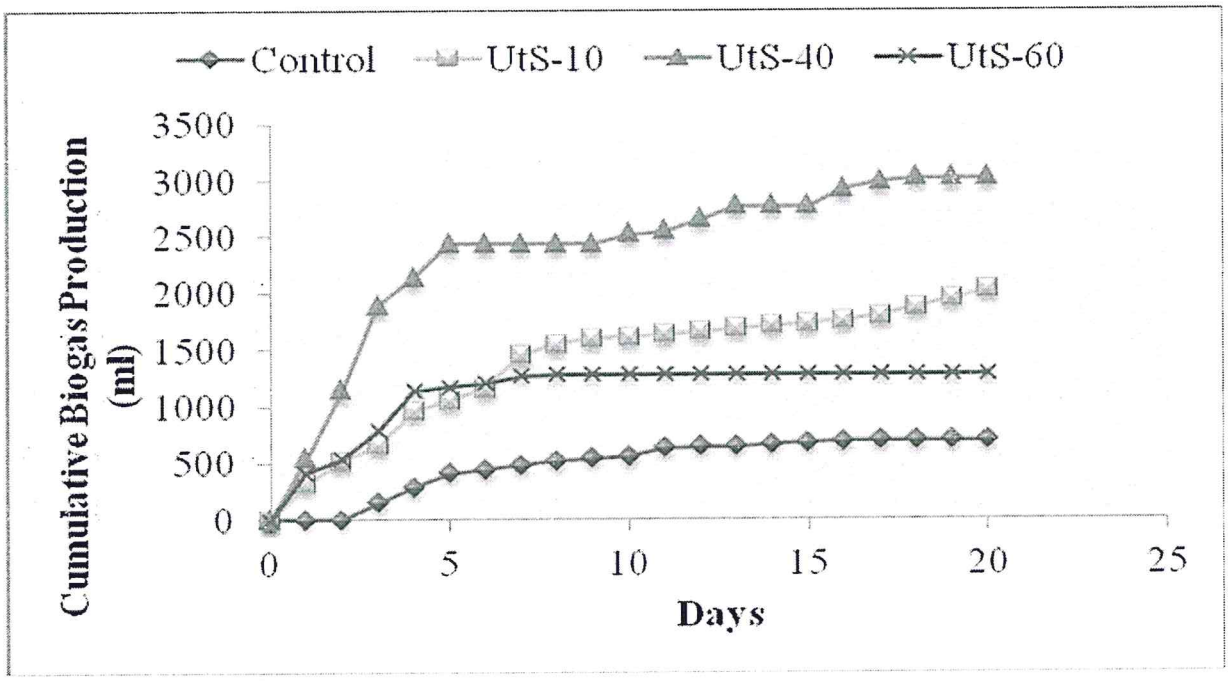

Fig. 1.13 Cumulative biogas prodcution during AD in the assays

After 18 days, all samples were almost totally degraded since no more biogas was being produced (Figure 1.13). It is noticed that both the untreated and the sonicated substrates were effective in producing biogas. From Figure 1.13, it is observed that ultrasonic irradiation pre-treatment resulted in a biogas production higher than for the control. Compared to the untreated sample, there was no lag phase for the pre-treated ones. There was quasi immediate biogas production – within 5 to 7 hours of sealing the digesters and mounting the BMP assays. This could be explained on basis of the chemical barriers overcome for the hydrolysis step following sonication (Apul and Sanin, 2010). During the first 3 days of the AD of the control, the inoculum used was getting acclimatised to the new environment and the substrates were being hydrolysed. During this period, the methanogens did not have any specific species to metabolise and convert into biogas. This was the most plausible reason for the delay in biogas production. In contrast, the cumulative biogas yield increased in the following order: UtS-40 > UtS-10 > UtS-60 > untreated sample. This clearly showed that sonication had had a positive effect on the overall process chemistry of the anaerobic digestion of the several organic fractions and molecules produced during the solubilisation of the VW organic matter.

In terms of solubilisation, the samples which were sonicated showed better results as well as higher biogas production. This may be hypothesised to be due to more successful disruption of particles resulting in more organic matter being available for anaerobic digestion (Erden *et al.*, 2010). Also, a larger reduction in volatile solids was noticed for the sonicated samples which explains the production as well as the enhancement of biogas in the pre-treated BMPs assays as shown below in Table 1.4. By day 20, The cumulative biogas production of the digester stabilised at the final value. Biogas production was observed to stop. Reters *et al.* (2003) reported that the remaining readily biodegradable material is probably entrapped within cells by cell walls that contain cellulose and are thus not accessible to microbial degradation until the cellulose is degraded. Parawira *et al.* (2004) suggested that more easily degradable compounds were digested before degradation of complex material taking place after that period.

Table 1.4: Cumulative Biogas Production (mL) from assays tested in this study

Day	Control	UtS-10	UtS-40	UtS-60
1	0	0	540	0
2	0	320	1140	420
3	0	520	1890	540
4	150	660	2140	790
5	290	960	2440	1140
6	415	1060	2440	1175
7	445	1160	2440	1210
8	485	1460	2440	1275
9	525	1550	2440	1285
10	540	1605	2520	1285
11	565	1615	2550	1285
12	635	1635	2650	1285
13	645	1665	2770	1285
14	650	1690	2770	1285
15	665	1715	2770	1285
16	680	1760	2920	1285
17	690	1800	2985	1285
18	700	1875	3020	1285
19	700	1950	3020	1285
20	700	2030	3020	1285

1.10 Characterisation of digestate

Table 1.5: Physical, chemical and biological properties of digestate

Parameter	Control	UtS-10	UtS-40	UtS-60
pH	7.97	6.70	6.90	7.65
COD (mg/L)	7692	4615	7692	4615
TS (mg/L)	34500	29750	23350	23500
VS (mg/L)	27200	24320	19760	21700
	Stability CO_2.C (mg)/organic matter(g)/day			
Day 1	42	39.6	21.6	36
Day 2	28.8	24.9	24.0	27.5
Day 3	18.5	21.6	14.4	22.5
Day 4	15.6	9.6	6.0	8.4
Nitrogen N (% Dry basis)	0.784	1.624	0.224	1.4
Phosphorus P (% Dry basis)	0.007	0.0007	0.0005	0.0007
Potassium K (% Dry basis)	0.0005	0.001	0.001	0.001
E-coli (CFUs per mL or g of sample)	$2.0x\ 10^3$	1.9×10^3	$9.0X\ 10^2$	$1.6\ X\ 10^3$
Total Coliform (Number of CFUs per mL) (Using MPN* Technique)	1.2	0.9	0.5	0.9

*Most Probable Number

Table 1.6: Typical Nutrient Value of Compost

Nutrient	Dry Weight
Nitrogen**	> 0.8%
Potassium*	0.5 % to 1 %
Phosphorus*	0.8 % to 1 %

Table 1.7: Respiration Rating Index

Respiration Rate (mg CO_2.C/g organic carbon/day)	Rating
< 2	Very stable
2 – 5	Stable
5 – 10	Moderately stable
10 – 20	Unstable
> 20	Extremely Unstable

Table 1.8: Pathogen Standard for Compost

Pathogen	Limit
Escherichia Coli (E-coli) **	≤ 1000 CFU/ g
Salmonella, 25 g fresh mass **	Absent in 25 g

*** Source: Composting Factsheet 382.500-15, 1996**

**** Source: Mauritius Standard 2010**

Comparing the parameters tested for the digestates with that of the standard for compost from Table 1.6 – 1.8, it is clearly seen that the digestates did not comply with the requirements of the standards. From Table 1.5, pH values of control and UtS-40 were near neutral. The nitrogen contents recorded from the control and UtS-40 assays were below the acceptable limit. From the respiration test, it was seen that all digestates showed the largest release of CO_2 during the first day of incubation due to the mineralisation of the most easily-degradable organic fraction of digestate. Mineralisation then decreased to reach values which showed moderate stability of

all the sonicated samples on the 4th day. The digestate of the untreated sample, however, was not stable on the fourth day. Total coliform was high in all the digestates. E-coli levels were also very high in all the digesters except for the UtS-40 assays with less than 1000 CFUs per mL.

1.11 Electricity generation from vegetable wastes

For this study, the amount of energy obtained from an input of 40 tons of wastes as a representative basis was calculated. The amount of energy which can be potentially produced is 741,378.5 KWh which may then be saleable to the national grid. The revenue obtained for this amount of electricity sale would potentially amount to MUR 4,077,582. The quantities of biogas produced in laboratory set-ups as well as expected the biogas formation and electricity generation on a projected large scale are tabulated below.

Table 1.9: Biogas, electricity and potential revenues from Up Scaling of BMPs Assays

Sample	Biogas obtained during practical (L)	# Biogas which could be obtained annually (m^3)	# Methane which could be obtained annually (m^3)	# Electricity sold to the Grid annually (MW)	# Revenue (MUR) Obtained from Electricity
Control	0.70	50.80	30.48	307.66	1,692,128
UtS-10	2.03	147.33	88.40	892.21	4,907,171
UtS-40	3.02	218.45	131.07	1,322.94	7,276,150
UtS-60	1.30	91.44	91.44	553.78	3,045,830

#: *Expected Results when BMPs Assays will be projected to large scale*

The payback period for setting an industry processing 40 tons of food wastes per day on a theoretical basis will be of the tune of 6.81 to 7 years. The cost of all equipments was obtained from a design project at University Of Mauritius for the year 2010. The cost was then worked out for the year 2012 using the following equation:

$$Present\ Cost = Original\ Cost\left(\frac{Index\ value\ at\ present\ time}{Index\ value\ at\ time\ original\ cost\ was\ obtained}\right) \quad \text{(Eqn. 1.2)}$$

Below is an abstract of the preliminary cost analysis which was performed for setting up the AD industry.

Table 1.10: Cost factors in preliminary cost analysis of a potential biogas system using ultrasound pretreatment

	MUR
Equipment Cost	28,781,419
Total Direct Cost	98,576,360
Total Capital Investment	174,602,573
Total Fixed Charges	19,590,409
Total Direct Production Costs	59,706,223
Depreciable fixed capital investment	148,412,187
Depreciation per year	14,841,219
Total General Expenses	34,850,674
Revenue from Electricity	4,077,582
Revenue from Compost	122,980,484
Total Revenue from electricity and compost	127,058,066
Net Annual Profit	6,940,138

From the above table, it is seen that the Net Annual profit is expected to the tune of 6,940,138 MUR. Using the equation below, the payback period was calculated.

$$Payback\ period = \frac{Depreciable\ fixed\ capital\ investment}{Average\ profit\ per\ year + Average\ depreciation\ per\ year} \quad \text{(Eqn. 1.3)}$$

1.12 Conclusions

Pollution continues to grow around the world. Governments and industries are constantly on the lookout for technologies that will allow for more efficient and cost-effective waste treatment. Mauritius is also trending in the same path as the other countries in order to alleviate its problem. One technology that can successfully treat the organic fraction of wastes is anaerobic digestion (AD). When used in a fully-engineered system, AD not only provides pollution prevention, but also allows for energy, compost and nutrient recovery. Thus, AD can convert a disposal problem into a profit centre.

This work has shown that ultrasonic pre-treatment (i.e. sonication with low frequency ultrasound waves) is an effective method for the enhancement of biogas production. Disintegration increased with increasing specific energy. A specific energy of 4940 KJ/Kg TS corresponding to a sonication time of 40 minutes is efficient for cell lysis of the VW. Disintegration at 4940 KJ/Kg TS causes floc/cell disruption leading to soluble organic matter in the supernatant layers. Beyond this value of specific energy of sonication and reaction time, it was seen that the effect of ultrasonic irradiation did not promote further release of soluble organic material in the slurry due to a decrease in the amount of SCOD. As specific energy increased, temperature was equally increased. This increase in temperature lead to a decrease in cavitation resulting in a decrease in the disruptive capacity which could have otherwise led to more pronounced solubilisation or organic matter.

From the results obtained presently, it is concluded that pre-treatment of substrates using the low frequency sonication method was effective in the suppression of the low kinetics of the rate determining hydrolysis step. The results obtained from the biochemical methane potential (BMP) assays unanimously suggest that sonication leads to an increase in the anaerobic biodegradability of VW. From the analysis made, it can be concluded that the digestates obtained from this study could not be applied to agricultural land. The E-coli present in the

digestates can pose risks to the plant. Further treatment need to be done to meet the standard of the MS 2010 and those obtained from Compost Factsheet.

Ultrasound irradiation as a pre-treatment has shown its effectiveness in the production of biogas in this study. For upscaling, 40 tons / day of VW was used as basis for input and the expected amount of biogas, methane, electricity and revenue from the selling of the energy were calculated based on the measurements of biogas obtained from lab-scale during this study. Calculations for upscaling process showed that fermentation of sonicated VW will potentially bring more revenue as compared to untreated VW since the amount of biogas obtained is much more from sonicated wastes. Comparing the pre-treated samples, wastes sonicated for 40 minutes have shown best results in terms of biogas production and electricity generation on large scale. In this scenario of pretreatment, MUR 7,276,150 may be obtained from the sale of electricity to the national grid. If there is any potential to implement an AD plant on a national level with planned sonication systems, then the wastes used should be pre-treated using ultrasonic irradiation for a period of 40 minutes in order to get the maximum amount of energy.

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Samples calculations for Amount of Methane which could be obtained per year (L) and Amount of Revenue (MUR) Obtained from Electricity

From 500 g of Wastes input, 700 ml of Biogas is obtained for a HRT of 20 days (Experimental work).

0.000551156 tons of VW gives 0.7 Litre of biogas

From 40 tons of wastes input,

$$\frac{0.7}{0.000551156} \; x \; 40 \; = 50802.31 \; L \; of \; biogas \; is \; obtained$$

From Conversion,

1 kg = 1.0 litre

Therefore, 50802.31 kg of biogas is obtained from 40 tons of VW

Biogas consists essentially of 60 % methane and 40 % carbon dioxide (Ferrer et al., 2011).

Hence, 30481.39 Kg of Methane is obtained and 20320.93 Kg of Carbon Dioxide from 40 tons of wastes per day

The amount of methane obtained is 30481.39 kg from 40 tons of VW for HRT of 20 days (Batch Studies)

Per day the amount of methane obtained is 1524.07 Kg

Calorific Value of Methane is 783 KJ/mol (estimated from Schley et al., 2010) Mr of methane = 16

From 16 kg of methane, 783 KJ is obtained

1524.07 kg of methane will therefore gives 74584 KJ of energy

However, the diesel engine has an efficiency of 40 %, hence 29833.66 KJ of energy is obtained

$$Energy - Power \; x \; Time$$

29833.66 = Power x 24

Power = 1243.07 KWh is obtained for one day

According to Ostrem (2004), 25% of the energy produced is used on site and 75% is sold to the local power grid.

Thus, 932.30 KWh is obtained per day to be sold to the grid

Plant will be operational for 330 days, therefore a total of 307659.6 KW will be sold to the grid annually at a rate of 5.50 MUR per KWh.

Revenue obtained from selling to the grid is MUR 1,692, 128

Sample	Amount of Biogas obtained during practical (L)	Amount of biogas which could be obtained for whole year (L)	Amount of Methane which could be obtained per year (L)	Amount of Electricity sold to the Grid annually (KW)	Amount of Revenue (MUR) Obtained from Electricity
Control	0.70	50,802.3	30,481	307,659.6	1,692,128
UtS-10	2.03	147,326.7	88,396	892,212.9	4,907,171
UtS-40	3.02	218,449.9	131,070	1,322,936	7,276,150
UtS-60	1.30	91,444.14	91,444	553,787.3	3,045,830

Note: * The price is not available as CEB is not currently purchasing electricity. No data about the purchasing price is available. Therefore, an average price/unit is used. The value is provisional.

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