PRODUCTION OF METHANE FROM PALM OIL MILL EFFLUENT BY USING ULTRASONICATED MEMBRANE ANAEROBIC SYSTEM (UMAS)

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BORANG PENGESAHAN STATUS TESIS

JUDUL : PRODUCTION OF METHANE FROM PALM OIL MILL EFFLUENT (POME) BY USING ULTRASONICATED MEMBRANE ANAEROBIC SYSTEM

SESI PENGAJIAN : 2011/2012

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PRODUCTION OF METHANE FROM PALM OIL MILL EFFLUENT BY USING ULTRASONICATED MEMBRANE ANAEROBIC SYSTEM (UMAS)

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Thesis submitted in partial fulfillment of the requirements

for the award of the degree of

Bachelor of Chemical Engineering (Gas Technology)

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Special Dedication to my supervisor, my family members,
my friends, my fellow colleague and all faculty members
for all your care, support and believe in me.

ACKNOWLEDGEMENTS

I would like to thank God for providing all the needs to accomplish this research proposal. I would like to express my sincere appreciation to my potential supervisor, Dr Abdurahman H.Nour his valuable suggestions, comments, patience and trust during this work.

Great appreciation goes to my friends whom have been helping each other and sharing their opinion. I am grateful to the librarian of University Malaysia Pahang for guiding use to look for information. My heartfelt gratitude also goes to University Malaysia Pahang for providing us chances and also all the facilities.

Last but not least, I also would like to express my greatest gratitude to my parents, Mr. Yap Chee Siong and Madam Fong Yoke Chun for their unconditional love, patience, understanding and support throughout the study.

ABSTRACT

The direct discharge of the Palm Oil Mill Effluent (POME) wastewater causes serious environmental pollution due to its high chemical oxygen demand (COD), total suspended solids (TSS) and biological oxygen demand (BOD). The conventional ways for POME wastewater treatment have both economical and environmental disadvantages. In this study, the potential of ultrasonic-assisted membrane anaerobic system (UMAS) was evaluated as alternative and cost effective method for treating POME wastewater to avoid fouling. Throughout the experiment, the removal efficiency of COD was 95% with HRT of 6 days. The BOD removal efficiency was 74% while TSS removal rate was from 91 to 99.5%.The methane gas production efficiency was 82.14%.The UMAS treatment efficiency was greatly improved by UMAS introduction. The membrane fouling and polarization at the membrane surface was significantly reduced.

Key words: UMAS, Anaerobic,POME,COD,membrane,Ultrasonic

ABSTRAK

Pelepasan air pemprosesan kelapa sawit (POME) tanpa rawatan akan menyebabkan pencermaran kerana ia mengandungi keperluan oksigen kimia (COD), keperluan oksigen biologi (BOD) dan jumlah pejal (TSS) yang tinggi. Rawatan konventional bukan sahaja memerlukan kos yang tinggi juga menyebabkan pencermaran. Dalam kajian ini, potensi kaedah rawatan dengan system membran anaerobik berultrasonik (UMAS) dikaji supaya dijadikan pilihan alternatif dan kaedah kos efektif untuk rawatan air pepmprosesan kelapa sawit dan menggelakkan masalah fouling. Sepanjang kajian ini, didapati bahawa kadar penurunan keperlun oksigen kimia adalah 95% pada hari ke-6.Kadar penurunan keperluan oksigen biologi pula didapati sebanyak 74% manakala kadar penurunan jumlah pejal(TSS) mencatatkan rekod 91% hingga 99.8%.Bacaan tertinggi gas metana yang dihasilkan semasa kajian adalah sebanyak 82.14%.Kecekapan system rawatan UMAS ditingkat dengan ultrasonic yang dipasang. Masalah fouling membrane dan polarisasi didapati berkurangan.

Kata kunci: UMAS,Anaerobik,POME, COD, membran,Ultrasonik

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LIST OF SYMBOLS

<	less than
=	equal
%	Percentage
˚C	Degree Celsius
P	Pressure
T	Temperature

LIST OF ABBREVIATIONS

BOD	Biological Oxygen Demand
CDM	Certified emission reduction
CER	Clean development mechanism
CO_2	Carbon dioxide
COD	Chemical Oxygen Demand
CUF	Crossflow Ultrafiltration
Da	Dalton
GHG	Green House Gases
GFTS	Green Technology Financing Scheme
HRT	Hydraulic Retention Time
IR	Infrared
NaOH	Sodium hydroxide
MAS	Membrane Anaerobic system
MLSS	Mixed liquor suspended solid
MPOB	Malaysian Palm Oil Board
MWCO	Molecular cut off
OLR	Organic Loading Rate
POME	Palm Oil Mill Effluent
PVC	Polyvinyl chloride
RO	Reverse Osmosis
SRT	Solid Retention Time
SS	Suspended Solid
TPAD	Temperature phase anaerobic digester
TSS	Total Suspended Solid
UF	Ultrafiltration

UMAS	Ultrasonicated Membrane Anaerobic System
US	Ultrasonic
VFA	Volatile fatty acid
VSS	Volatile Suspended Solid
VS	Volatile Solid
W/W	Weight to weight

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

With the increasing awareness on the environmental issues and the rising of oil price, all governments across the world are forced to looking for alternative energy, the same phenomenon happen in Malaysia as well. The Renewable energy has been recognized as the country's fifth fuel under the 8th and 9th Malaysian Plans. Nowadays, the government claimed to commit to adopting Renewable Energy and Green Technology. The government launched the Green Technology Financing Scheme (GTFS) on 26 Jan 2010 to encourage the effort of looking for alternative energy. The government will play its role, covering two per cent of the loan's interest rate and providing a guarantee of 60 per cent on the financing. The remaining 40 per cent will be covered by banks.

In the 21st century, renewable energy and sustainable energy as well as green technology would be the core of economic growth for all countries. This reflects that Malaysian is in high demand of expertise in Renewable and sustainable energy, hence the project of producing methane gas from palm oil Mill effluent is a high potential project. In addition, Malaysia is the world’s primary palm oil producer. It ranked as the

second largest export revenue earner with a total combined value of RM4.5 billion in December 2009. Malaysian palm oil production is expected to reach 18 million tonnes in 2010.Hence, the amount of effluents that produce is escalating, and the waste resources would never be the limitation.

In the process of palm oil milling, Palm Oil Mill Effluent (POME) is produced as a result of sterilization of fresh oil palm fruit bunches, clarification of palm oil and effluent from hydro cyclone operations. POME is a viscous brown liquid which with fine suspended solid and possess high value of COD and BOD. Hence, it is a high strength organic polluter. The discharge of effluent from palm oil mill have been regulated by the Environment Quality (Prescribed Premises) (Crude Palm Oil) Order, 1997 and the Environmental Quality (Prescribe Premises) (Crude Palm Oil) Regulations, 1997 which promulgated under the Environmental Quality Act,1974. In order to reach the requirement of standard discharge limit, waste water treatments can never to be dismissed. It incurs high non-profitable cost in an industry to resolve this problem either the waste water have to be reduced or the treatment have to be enhanced in cost effective way. Instead of the conventional ponding system, the membrane anaerobic system (MAS) will be proposed to be utilized. The system consists of two technology which is anaerobic digestion and membrane separation technology.

The anaerobic digestion is the degradation of complex organic matters under the absence of oxygen. In the process, POME is degraded into methane, carbon dioxide and water. , there is a sequence of reactions involved; hydrolysis, acidogenesis (including acetogenesis) and methanogenesis. Hydrolysis is where complex molecules (i.e., carbohydrates, lipids, proteins) are converted into sugar, amino acid and etc. In the step of acidogenesis, acidogenic bacteria will break down these sugar, fatty acids and amino acids into organic acids which mainly consist of acetic acid (from acetogenesis) together with hydrogen and carbon dioxide. Hydrogen and carbon dioxide will be utilized by hydrogenotropic methanogens while acetic acid and carbon dioxide will be utilized by acetoclastic methanogens to give methane as a final product. Hence, it enables the concept of waste to energy.

With the addition of application of membrane filtration in the system, the efficient of wastewater treatment is elevated that is capable of retaining biomass concentration within the reactor and produce high quality effluent. It is proven to be an effective way in separating biomass solids from digester suspensions and recycle them to the digester.

However, in this membrane anaerobic system has to be monitored properly as the processes rely solely on the micro-organism to break down the pollutants. The micro-organism is very sensitive to changes in the environment thus great care have to be taken to maintain a conducive environment for the micro organism. Besides, there will be problem arises in the membrane system due to the characteristic of POME as it is a high suspended solids effluent. The membrane will be suffered from fouling and degradation during use. Thus, the objective of this study is to investigate optimum condition of the anaerobic digestion system as well as method to overcome the membrane fouling problem.

1.2 PROBLEM STATEMENTS

POME is a high strength wastewater. The direct discharge of Palm Mill Oil Effluent will cause severe environment pollution. Coming to the context of water and air pollution, POME is one of the agricultural wastes to blame on. Greenhouse gasses emitted from Palm Oil Mill Effluent anaerobic treatment pond such as methane and carbon dioxide exerted greenhouse effect to the earth. The capturing of methane gas will save the environment. Besides, the treatment of POME often incurs high non-profitable cost in an industry that reduces the company profit. In addition, the cost of fossil fuel increases with the increasing demand and the depleting resource making it even valuable. The concept of transforming waste to energy makes waste treatment seem more appealing and cost-effective.

1.3 OBJECTIVES OF THE STUDY

The research aims to solve the problem statements by accomplishing the following specific objectives:

a) To enhance the production of methane gas by providing a best condition.

b) To enhance the treatability of POME by Membrane anaerobic system.

c) To made an overall evaluation on Membrane Anaerobic System in treating POME.

1.4 SCOPE OF RESEARCH

In order to execute the objectives, a 150 L bioreactor system with ultrasonic will be designed in order to optimize the production of methane and overcome membrane fouling problem. The parameters such as pH and temperature are controlled and maintain in optimum operating condition. The production of methane gas in varying retention time is investigated. The system performances were evaluated with parameter such as Chemical Oxygen Demand, Biological Oxygen Demand, Total Suspended Solid, and Volatile Suspended Solid for the raw material, material in the reactor and the treated permeate to observe the efficiency of the system.

1.6 RATIONALE AND SIGNIFICANT

The study can contribute by providing an alternative renewable energy that can be apply in the industry in return overcome the dependency on fossil fuel which is incurs high cost. Besides, it can protect the environment by reducing the emission of green house gasses to the environment such as methane gas and carbon dioxide. Meanwhile, reducing cost for POME treatment. It is also a good opportunity to attract foreign investor.

CHAPTER 2

LITERATURE REVIEW

2.1 PALM OIL MILL EFFLUENT (POME)

POME is generated as a result of sterilization of fresh palm oil fruit bunches, clarification of palm oil and effluent from hydro cyclone operation. (Borja et al, 1996) POME is a high strength agro-industrial polluter due to high value of COD and BOD.POME is in a form of highly viscous dark brown colloidal with fine suspended solid. POME colloidal suspension of 95-96% water, 0.6-0.7% oil and 4.5% total solids (Ma, 1993). The characteristic of POME are shown in Table 2.1. In 1980, Malaysian mills discharged 6 million tonnes of effluent which contain equivalent BOD as load generated by population of 7.3 million. However it's highly amendable by anaerobic digestion.

Table 2.1: Characteristic of untreated POME

Parameter	Concentration
pH	4.7
Temperarture	80-90
BOD 3-day, 30˚C	25,000
COD	50,000
Total soilids	40,500

Suspended solids	18,000
Total volatile Solids	34,000
Ammoniacal-Nitrogen	35
Total Nitrogen	750

*All parameter in mg/l except pH and temperature (˚C)

Source: (A.L Ahmad, 2003)

2.2 KYOTO PROTOCOL AND GOVERNMENT POLICY

In 1997, the Kyoto Protocol was adopted, calling for stronger action in reducing Green House Gases or GHG emission in the post 2000. Under the protocol, developed countries have a legally binding commitment to reduce their collective emissions of six greenhouse gases by at least 5% based on the 1990 levels by the period 2008 to 2012. The Protocol also establishes an emission trading regime including clean development mechanism (CDM) to facilitate countries to fulfill their commitments. CDM allows developed nations to achieve part of their reduction obligations by buying emission reductions from projects that reduce greenhouse gas emissions in developing countries period. On 12th March 1999, Malaysia signed the Kyoto Protocol and ratified it on 4th September 2002. With the ratification of the Kyoto Protocol by the Malaysian Government, this implies that Malaysians can benefit from investments in the GHG emissions reductions. (Lim, C.H. et al, 2006)

The utilization of methane gas from Palm Oil Mill Effluent (POME) for electricity generation can be used to obtain certified emission reduction (CER) and to be credited by clean development mechanism (CDM). (Poh P.E et al, 2009) The project will also contribute positively to Malaysian Government sustainable development effort to supply Renewable Energy to the nation for electricity generation under Five-Fuel Policy. Five-Fuel Policy was introduced in 2001 under the 8th Malaysia Plan to augment the National Energy Policy was introduced in 1979. The aim was to guide the country's energy mix towards five fuels namely oil, gas, coal, hydro and renewable energy. Due to the unfulfilled target, the effort is continued the Fifth-Fuel Policy to be

continued into the 9th Malaysia Plan from 2006 to 2010. (Kementerian Tenaga, Air Dan Komunikasi, 2005)

2.3 METHANE GAS FOR ELECTRICITY GENERATION

The generation of electricity from methane is possible, in all cases the steps that must be gone through are twofold, chemical energy to mechanical energy, and then from mechanical energy to electrical energy. For these conversion processes to be achieved, suitable engine is needed, and in principle there are two types of engine which have been used for biogas digester electricity generation that is gas engine and steam turbine.

According to the Malaysia Palm Oil Board (MPOB), 0.65 m3 POME is generated from every processed ton of Fresh Fruit Bunch. Based on a study of the potential for electricity generation from POME that have done by MPOB, if there was 38,870,000 m^3 of POME produced for every 59,800,000 tons of Fresh Fruit Bunches process annually. The annual energy content of the generated methane gas can be calculated to 7.07E+09 kWh. Based on a conversion efficiency of 38 percent (gas engine), the potential annual electrical power generation would be 2.69E+09 kWh. Thus, Palm Oil Mill Effluent has a huge potential for power generation (N.A Ludin et al, 2006).

2.4 POME TREATMENT

2.4.1 Ponding System/Lagoon system/Open Digester tank

Ponding system is the most common system employed in Malaysia which counted for 85% of the total treatment plant in Malaysia. In a ponding system it is basically divided into de-oiling pond tank, acidification ponds, anaerobic ponds and facultative pond or aerobic ponds. The discharge after the facultative or aerobic require further reduce of BOD to comply with the discharge standards. The typical size of the

ponding system is equivalent to half a soccer field which is able to sustain the processing capacity of 54 tons per hour. This method is favored due to it can achieve reasonable degree of treatment with low construction and operating cost and is easily maintained as the technology employed is relatively unsophisticated. However, a large land space is required. Direct emission of gasses generated in the treatment process will impose green house effect to the environment. Besides, the effectiveness in meeting the stringent standard is unsatisfactory. (Poh P.E et al, 2009)

Open digester tank are used for POME treatment when limited land area is available for ponding system. Apart from that, in the investigation by Yacobs et al (2006), he proved that anaerobic system emitted higher amount of methane compare to the open digester tank with an average methane composition of 54.4% compare to open digester tank. (Poh P.E et al, 2009)

2.4.2 Anaerobic Digestion

A biochemical process by which organic matter is decomposed by bacteria in the absence of oxygen, producing methane and other by products. It's much depends on the bacterial consortia for degradation process, thus a longer time is require. The condition is also required to be always in the optimum condition for the bacterial to survive, as the bacterial are sensitive. However, anaerobic digestion is widely used to treat waste as it require low energy, high organic removal rate, low sludge production and production of methane as valuable by product. (Poh, P.E. et al, 2009)

The degrading process of POME consists of four stages that is hydrolysis and acidogenesis, fermentation, acetogenesis, methanogenesis (Poh, P.E et al,2009). In the first stage of hydrolysis, the polymeric organic materials are hydrolysed to its constituent such as glucose, fatty acids and amino acids by hydrolytic bacteria. The hydrolysis process is of significant importance in high organic waste and may become rate limiting. Solubilisation involves hydrolysis process where the complex organic matter is hydrolysed into soluble monomers. Fats are hydrolysed into fatty acids or

glycerol; proteins are hydrolysed into amino acids or peptides while carbohydrates are hydrolysed into monosaccharides and disaccharides.

In fermentation stage, the hydrolysed products are converted to volatile fatty acids, alcohols, aldehydes, ketones, ammonia, carbon dioxide, water and hydrogen by the acid-forming bacteria. The organic acids formed are acetic acid, propionic acid, butyric acid and valeric acid. Volatile fatty acids with more than four-carbon chain could not be used directly by methanogens (Wang et al., 1999).

The following stage is acedogenesis, where organic acids are further oxidised to acetic acid and hydrogen and carbon dioxide which are used in the subsequent process. Acetogenesis also includes acetate production from hydrogen and carbon dioxide by acetogens and homoacetogens.The transition of the substrate causes the pH of the system to drop which beneficial to acidogenic and acetagenic.(K.M Ostrem et al,2004)

Finally the reaction come across the the stage of methanogenesis. One is conversion of acetate to carbon dioxide and methane by acetotrophic organisms and another is reduction of carbon dioxide with hydrogen by hydrogenotrophic organisms. (Ling,L.Y, 2007).

Typical reaction of anaerobic digestion:

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH+CO_2 \quad [1]$$

$$C_2H_5OH+CO_2 \longrightarrow CH_4+ 2CHOOH \quad [2]$$

$$CH_3COOH \longrightarrow CH_4 + CO_2 \quad [3]$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \quad [4]$$

The advantages of adopting anaerobic system are low energy requirement as no aeration needed. Methane is produced as a valuable end product and generates sludge that could be used for land application. There are several anaerobic treatment method that have been widely used such as Anaerobic filtration, fluidized bed reactor, up-flow

anaerobic sludge blanket reactor (UASB), Up flow anaerobic sludge fixed-film reactor (UASFF), continuos stirred tank reactor and Anaerobic contact process. Although these high rate or hybrid reactors are successfully shortened the retention time and efficiency (as shown in table) but all these biological treatment systems need proper maintenance and monitoring as the processes solely rely on micro-organisms to degrade the pollutants. How to ensure the stability of the system deserves most urgent concern. (Y.J Zhang et al, 2007) .The summary of comparisons of all other method are shown in table 2.2.

Table 2.2: Comparisons of various treatment methods on POME treatment

Performance of various anaerobic treatment methods on POME treatment

	OLR (kg COD/m^3day)	Hydraulic retention time (days)	Methane composition (%)	COD removal efficiency (%)	Reference
Anaerobic pond	1.4	40	54.4	97.8	Yacob et al. (2006a)
Anaerobic digester	2.16	20	36	80.7	Yacob et al. (2005)
Anaerobic filtration	4.5	15	63	94	Borja and Banks (1994b)
Fluidized bed	40.0	0.25	N/A	78	Borja and Banks (1995b)
UASB	10.63	4	54.2	98.4	Borja and Banks (1994c)
UASFF	11.58	3	71.9	97	Najafpour et al. (2006)
CSTR	3.33	18	62.5	80	Tong and Jaafar (2006)
Anaerobic contact process[a]	3.44	4.7	63	93.3	Ibrahim et al. (1984)

N/A: data unavailable.
[a] In terms of BOD.

Source: (Poh P.E et al, 2009)

2.4.3 Membrane Separation Technology

Membrane Separation technology is always employed in waste treatment as it's able to produce consistent and good water quality after treatment plants as well as it's able to disinfect the treated water. There have been inspiring performances by using membrane separation technology. For instances, A.L Ahmad et al (2003) have shown that the combination of UF & RO is able to achieve COD removal of 98.8%,BOD removal of 99.4%, Turbidity of 100% and pH 7 as a result. Another group of researcher have incorporated Hollow fiber membrane in their three phase decanter system to give

89.9% COD removal, 99.4% of TSS elimination, 97.9% Turbidity reduction and 92.9% for color removal (S.S Raja et al, 2005).However, short membrane life, membrane fouling and expensive cost are major constraint of this technique. In order to prolong the membrane life span and produce crystal clear effluent as well as methane as the end product, the integration of anaerobic system and membrane separation technology in a bio reactor is investigated by some researchers.

2.4.4 Membrane Anaerobic System

The idea of integration of the anaerobic digestion system and membrane separation technology is to enable the biomass to be retained in the reactor which improves methane gas emission as well as producing constant high quality effluent. According to Y.J Zhang et al in 2007 she has incorporating Expanded Granulated Sludge Blanket (EGSB) with UF & RO. As a result, COD Removal of 93%, biogas conversion rate of 43% is achieved. As we compared the result to the previous table, the biogas generation appears to improve drastically. In the later years, H.N Abdurahman et al (2011) have shown another more inspiring result by his Membrane Anaerobic System which a design of anaerobic bioreactor equipped with UF module membrane where COD Removal efficiency 96.6%-98.4% and biogas conversion rate up to 73% as a final result.

However, although the membrane fouling problem may relief compared to the case without anaerobic digestion as pretreatment but the membrane fouling problems still an issues and the idea of back flushing membrane which require an operation break is not feasible to the industrial application. Hence, as a solution application of ultrasonic technology in solving the membrane fouling problem is going to be investigated in this research work.

2.5 METHANOGENS

Methanogen are specialized group of Archae that utilized a limited number of substrates, principally acetate, carbon dioxide and hydrogen for methane production or methanogenesis. These substrate resulted from the degradation from more complex substrate. Methane-forming bacteria have many shapes (bacillus, coccus, and spirillum), sizes (0.1 to 15μm), and growth patterns (individual cells, filamentous chains, cubes, and sarcina). Methane-forming bacteria are oxygen-sensitive anaerobes and are found in habitats that are rich in degradable organic compounds. In these habitats oxygen is rapidly removed by bacterial degradation of the organic compounds.

Methane-forming bacteria are active within the pH range of 6.8 to 7.2. Methane forming bacteria are sensitive to pH values <6.8 and >7.2. With decreasing pH, methane-forming bacteria become less active, while fermentative bacteria remain active and continue to produce fatty acids. These acids destroy alkalinity and depress pH resulting in inhibition of methane-forming bacteria. Also, with decreasing pH, increases in the quantities of hydrogen sulphide (H2S) and hydrogen cyanide (HCN) occur. These two inorganic compounds are highly toxic to methane-forming bacteria. With increasing pH, an increase in the quantity of ammonia (NH3) occurs. Ammonia also is toxic to methane-forming bacteria. Therefore, anaerobic digesters should be operated at a near neutral pH value and should be monitored as needed to ensure an acceptable pH value and alkalinity residual.

Sufficient alkalinity is necessary for proper pH control. Alkalinity serves as a buffer that prevents rapid change in pH. Enzymatic activity of methane-forming bacteria is adversely affected by pH values <6.8 and >7.2. Adequate alkalinity in an anaerobic digester can be maintained by providing an acceptable volatile acid-to alkalinity ratio. The range of acceptable volatile acid-to-alkalinity ratios is 0.1 to 0.2.

Because methane-forming bacteria reproduce very slowly (generation times of 3–30 days) and produce very few offspring (sludge) from the degradation of substrates (approximately 0.02 pounds of sludge per pound of substrate degraded), methane-

forming bacteria require smaller quantities of most nutrients. However, there are a few nutrients that are required by methane-forming bacteria in quantities two to five times greater than most other bacteria. These nutrients are cobalt, iron, nickel, and sulphur.

Methanogenesis occurs through three basic biochemical reactions that are mediated by three different groups of methane-forming bacteria (acteoclastic methanogens, hydrotrophic methanogens, and methyltrophic methanogens). Acetoclastic methanogens produce methane by "splitting' acetate as shown in reaction equation 5. Hydrogenotrophic methanogens produce methane by combining hydrogen and carbon dioxide [6] while methyltrophic methanogens produce methane by removing methyl (−CH3) groups from simple substrates. In anaerobic digesters, acetoclastic methane-forming bacteria produce most of the methane, while hydrotrophic methane-forming bacteria produce approximately 30% of all methane. Methyltrophic methane-forming bacteria produce a relatively small quantity of methane in anaerobic digesters.

$$CH_3COOH \text{----------} > CH_4 + CO_2 \quad [5]$$

$$CO_2 + 4H_2 \text{----------} > CH_4 + 2H_20 \quad [6]$$

(Michael H. Geradi, 2006)

2.6 ANAEROBIC DIGESTION OPERATION

2.6.1 pH

pH is the crucial factor that determine whether the Membrane anaerobic system is working. The microbial community in anaerobic digester is sensitive to pH change. The pH affects the process in 2 ways that are affecting the enzymatic activity by changing their proteic structure which may occur drastically as a result of changes in the pH and affecting the toxicity of a number of compounds indirectly eg sulphide toxicity. The optimum pH for methane producing microorganism to achieve optimum growth range between 6.6 and 7.4 (V.S Marcos et al,2005). Methane producing bacteria require a neutral to slightly alkaline environment (pH 6.8 to 8.5) in order to produce methane

(D.A Burke et al, 2001). Acid forming bacteria grow much faster than methane forming bacteria. If acid-producing bacteria grow too fast, they may produce more acid than the methane forming bacteria can consume. Excess acid builds up in the system. The pH drops, and the system may become unbalanced, inhibiting the activity of methane forming bacteria. Methane production may stop entirely.

Besides, the methanogenesis is strongly affected by pH and will be inhibited by the acid condition. The optimum pH for the methanogenesis stage is pH between 7.2-8.2 .If the pH fall below the pH of 6, anaerobic degradation rate will decrease and the lipids are not degraded (Ling,L.Y., 2007).The Acetic and butyric acids are favourable substrate for methanogens which form under neutral and acidic condition.

In addition, sudden pH change (pH shock) can adversely affect the process, and recover depend on series of factors, related to the type of damage caused to the microorganism (either permanent or temporary). The buffer capacity used must be understood to avoid changes in pH (V.S Marcos et al, 2005).

2.6.2 Mechanical Mixing

Mixing will provides good contact between substrate and microbes ensure the temperature is uniform, reduce resistance to mass transfer, minimized build up of inhibitory intermediate and stabilizes environment conditions (N.H Abdurahman et al, 2010). The same theory is proposed by Leslie Grady et al (1999) as well where mixing able to bring bacteria consortia into contact with food. The agitation of the mixing will also reduce the particle size which promotes the release of biogas from mixing (Karim et al, 2005).

The bioreactor with stirrer have been applied by a mill under Keck Seng (Malaysia) Berhad in Masai Johor since 1980s.The palm oil mill successfully achieved 83% COD removal and production of 62.5% methane production (Poh P.E et al, 2009). In the research of Kim.M et al (2002), Mesophilic non-mixed reactor failed earlier than the continuously stirred reactors even though it showed much better performance than

the continuously fed reactors prior to reactor failure when organic loading rate added up until reactor failure. (Kim.M et al, 2002).Besides, mechanical mixing is also exhibit a positive results in producing methane gas in the research of Choorit W. et al where a Mesophilic continuous stirred tank reactor is being used. Another inspiring example is research done by Ugoji (1997), the experiments display a result of COD removal in between 93.6 to 97.7% (Poh P.E, 2009). However, the complete mixed system is more sensitive to temperature changes (Kim M.et al, 2002).

In the animal waste research of Karim et al (2005) suggested that mixing improved the performance of digesters treating waste with higher concentration while slurry recirculation showed better results compared to impeller and biogas recirculation mixing mode. Mixing also improved gas production as compared to unmixed digesters. (Poh P.E, 2009) Boe K. et al have adopted intermittent mixing in the research of biogas production from manure rather than vigorous mixing (Boe K. et al, 2009). Research of Kaparaju et al. (2008) is also agreed with the theory of intermittent mixing advantageous over vigorous mixing. However, mixing during start up is not beneficial as the digester pH will be lowered resulting in performance instability as well as leading to a prolonged start-up period.(Poh P.E, 2009).However there are no systematic research on mixing in treatment of POME.

2.6.3 Organic Loading Rate

Organic Loading rate is a measure of the anaerobic digestion biological conversion capacity. Various studies have proven that Organic Loading Rate (OLR) will reduce COD removal efficiency. However, it give a positive impact on the gas production where increase of with OLR until a stage when methanogens could not work quick enough to convert acetic acid to methane which in return increased the hydrogen partial pressure concomitantly decreased the methane yield. (N.H Abdurahman et al, 2010), (H.Patel et al,2002).

2.6.4 Temperature

The temperature range for anaerobic digestion can be categorised into Psychrophilic (<25˚C), Mesophilic (25 to 40˚C) and thermophilic (<45˚C).Methane production have been documented in various range of temperature, but the most productive in either mesophilic conditions, at 30-35˚C or in the thermophilic range at 50-55˚C.Once the maximum specific growth rate of microbial population rises as the temperature increase. However, maintaining a uniform temperature in the reactor maybe more important, once the anaerobic process is considered very sensitive to abrupt temperature changes, which may cause unbalance between the two largest microbial population and consequently result in process failure (the usual limit is about 2 ˚C per day) (V.S Marcos et al, 2005).

In mesophilic temperature condition methane forming micro-organism range belong to the genera *Mathanobacterium, Methanobrevibacter* and *Methanospirillum*, which are hydrogen-using micro-organism and to the genera Methanosarcina and Methnosaeta which are organism that use acetate to form methane. The temperature affects the biological enzymatic reaction rate and influencing substrate diffusion rate. (V.S Marcos et al, 2005).There are several research successfully produce methane in Mesophilic temperature such as K.M Ostrem et al proved that for the mesophilic digester to operate to the optimum, the temperature have to be maintained at 30-35˚C(K.M. Ostrem et al,2004). Besides, N.H Abdurahman et al conducted their experiment in the Mesophilic temperature range and shown positive result in the production of methane (N.H Abdurahman, 2010). In the research of Zhang Y.J et al has once again shown that Mesophilic temperature range favour the production of methane (Zhang Y.J et al, 2007).

As mentioned before, methane production is productive in thermophilic condition as well. However, for a thermophilic digester the start up period is much longer than mesophilic digester to allow mesophilic sludge to acclimatize with the substrate as well as temperature swift (Poh P.E et al, 2010). There are several attempts to overcome this problem such as by introducing seed sludge for cultivation of mixed culture but it takes a longer time and even more expertise (eg. Molecular biology to

identify the microbes in mixed cultured) to get the digester works well. (Poh P.E et al, 2010) Hence, the operational experience in this temperature range not been satisfactory and still many pending question such as whether resulting benefits overcome disadvantage, including additional energy required which increase operational cost, the poor quality supernatant and instability of the process. Besides, the external effects of the temperature on bacterial cell are important. For example, the degree of dissociation of several compound depend strongly on temperature such as specific case of ammonia. The thermodynamic of several reactions are also affected such as the dependence of the hydrogen pressure in anaerobic digesters where fermentation occurs in appropriate manner (V.S Marcos et al, 2005). B.K. Ahring et al (1995) shown that the perturbation of temperature impose the greatest effect on the final product of the such as methane production. Methane production almost ceased after the increase of temperature and had not resumed even 10 days later indicating the importance of a stable temperature of the process.

In the later year, the temperature phase anaerobic digester (TPAD) is developed in with combination of mesophilic and thermophilic condition, the two stage digester show improvement in performance. More than 20 full scaled TPAD systems have been set up in United State for wastewater treatment (S.Sung, 2003). Despite of the advantages of the system, some researchers would go for other options as there are disadvantages in separating the acidogenic and methanogenic reaction which in turn disrupt the synthrophic relationship between bacteria and methanogens in addition of the complicated control process (Boe K et al, 2009).

As a result, Mesophilic digester would be chosen as the digester in this experiment to produce methane in a steady performance with the minimum constraint.

2.6.5 Hydraulic Retention time

Hydraulic Retention Time (HRT) is the number of days the materials stays in the tank. The Hydraulic Retention Time equals the volume of the tank divided by the daily flow (HRT=V/Q). The hydraulic retention time is important since it establishes the

quantity of time available for bacterial growth especially for the growth of hydrolytic acidogenic bacteria and subsequent conversion of the organic material to gas (D.ABurke., 2001) The HRT is closely related to the OLR and substrate concentration, thus a good balance have to be achieve for good digester operation. (N.H Abdurahman, 2010).

2.6.6 Solid Retention time

The Solids Retention Time (SRT) is the average time the activated-sludge solids are in the system. The SRT is an important design and operating parameter for the activated-sludge process and is usually expressed in days. (Lenntech, 2010) Although the calculation of the solids retention time is often improperly stated, it is the quantity of solids maintained in the digester divided by the quantity of solids wasted each day as shown in equation below:

$$SRT = \frac{(V)(Cd)}{(Qw)(Cw)} \qquad [7]$$

V = Digester Volume

Cd = Solid Concentration in the digester

Cw = Solid Concentration in the waste

Qw = Volume wasted each day

In a conventional completely mixed, or plug flow digester, the HRT equals the SRT. However, in a variety of retained biomass reactors the SRT exceeds the HRT. (D.A Burke, 2001) As a result, the retained biomass digesters can be much smaller while achieving the same solids conversion to gas. At a low SRT sufficient time is not available for the bacteria to grow and replace the bacteria lost in the effluent. If the rate

of bacterial loss exceeds the rate of bacteria growth, "wash-out" occurs. The SRT at which “wash-out” begins to occur is the "critical SRT". (M. Clara et al, 2004).

2.6.7 Volatile Fatty Acid

Volatile Fatty acid had been use as the process balance indicator. Change in VFA level were shown to be a good parameter, under unstable operation, intermediate such as volatile acid and alcohol accumulates at different rate depending on the substrate and type of perturbation causing instability. The volatile fatty acid accumulation reflects a kinetics uncoupling between acid producers and consumers and is typical for stress situations. (B.K Ahring et al, 1995) Review back to the fermentation stage the acidogenic bacteria convert the less soluble organic compounds to organic acids such as acetic acid, propionic acid and butyric acid which known as volatile fatty acids, alcohol and other intermediates. (Husnul Azan T. et al, 2006) Hence, accumulation of VFA indicates that the further digestion into methanogenic stage is affected. Besides, the imbalance can be reflected by pH, volatile solid reduction and gas composition. However, these are often too slow for the optimal detection of sudden changes. The VFA concentration results in pH drop in turn causing toxicity to the system. pH changes are small in highly buffered systems as often seen in reactor with high ammonia loads even when the process is severely stressed. Hill et al (1987) suggested that acetate concentration higher than 13mM have been suggested to indicate imbalance. Hill (1982) proposed that the propionate/acetate ratio should be used as a process indicator and a stable process should be below 1.4. In the later year on 1988, Hill and Holmberg showed that isobutyrate or isovalerate below 0.06 indicate stable process however different system have their own normal level VFA. (B.K Ahring et al,1995) Several studies shown that high concentration of VFA have no effect on the biogas process.

2.7 MEMBRANE TECHNOLOGY

Advance treatment process such as membrane separation shows accelerated market growth result by the stringent environmental legislation and water scarcity around the world. Application of membrane technology which commonly employed in waste water treatment can contribute to developing an efficient waste water treatment process to produce high quality effluent and retain the biomass concentration within the reactor at the same time.

In general there are 5 types of membrane filtration process that are conventional filtration, microfiltration, ultra filtration, nanofiltration and reverse osmosis. The selection type of membrane process depends on the particles size that requires separation. Table 2.3 shows the filtration processes with their properties and applications. On the other hand, table 2.4 shows the apparent dimension of some particles.

Table 2.3: Filtration process with their properties and applications

Filtration Process	Pore size	Seperation capability	Pressure (bar)	Application examples
NF	1-10nm	Mw200-20,000	5-25	Purification of sugar and salts,water treatment
UF	5-100nm	Mw of 10K-500k	0.5-5	Pharmaceutical industry, waste water treatment
MF	50nm-5µm	Bacteria and colloids	0.5-3	Prefiltration in water treatment, sterile filtratio

(Source: Ramakrishna et al, 2011)

Table 2.4: Apparent Dimensions of various Particles

Particle	**Dimension (μm)**
Yeast's, Fungi	1-10
Bacteria	0.3-10
Viruses	0.03-0.3
Protein ($10^4 - 10^6$ molwt)	0.002-0.1
Enzymes	0.002-0.005
Antibiotics , Polypeptides	0.0006-0.0012
Sugars	0.0008-0.001
Water	0.0002

Source : (N.H Abdurahman et al, 2011)

Membrane characteristics are relied on the geometry, flow direction, the surface characteristics (normally denoted by pore size) and materials which determining its properties such as the surface charges, hydrophobicity and porosity.

Pore size is the main physical properties determine its application for various feed solution characteristic. Ultra filtration membrane manufacturer frequently characterize their membranes using the "cut off" concept rather than pore size. The nominal molecular cut off weight defined as the lower limit of a solute molecular weight for which rejection is 95%-98%. As the molecular weight reduce the mean pore diameter for most UF is decreased. Hence, MWCO is a rough indication of the membrane ability to remove a given compound despite of other factor. (Norman N.Li, 2008) .

Besides, the materials of the membrane have great influence on performance. Synthetic polymer can be dividing into two classes that is hydrophobic and hydrophilic. Polysulfone ans polyethersulfone is hydrophilic and use for UF process. Hydrophobic membranes such as polytetraflouroethylene, polyvinylidene fluoride, polyethene are

commonly used for MF. The fouling potential for the hydrophobic membrane is highly due to the high binding affinity of the proteins and humic substances.

Besides, the surface charges implies different fouling tendency. Generally, membrane materials carry a negative charge because natural organic matter is negative charge at neutral pH due to phenolic and carboxylic functional groups. A negative charge of membrane therefore prevent deposition of foulant by charge repel.

2.7.1 Hollow fiber membrane

The hollow fiber configuration is the most common configuration for MF and UF membrane. The hollow fibers are 05-1.0mm (less than 5mm) in diameter and several thousand of hollow fibers are packed in a module. The most important merits is that no extensive pretreatment needed as the membrane can be backwashed. The excellent mass-transfer properties conferred by the hollow fibre configuration soon led to numerous commercial applications in various field. The hollow fibre membranes have two major advantages over flat sheet membranes. One is that hollow fibres have much larger ratio of membrane area to unit volume, and hence higher productivity per unit volume of membrane module. Another is that they are self-supporting which can be back-flashed for liquid separation. (Cheresources, 2010).

Hollow fibre membrane can be operated in two different flow modes which are shell side feed and bore side feed. The bore side feed has its advantages over shell side feed including minimal pressure drop inside the fibers. The diameter is usually larger than those of the fine fibres used in shell side feed system, it is important to ensure all fibres have identical fibres diameters and permeance to ensure module performance. Feed pressure is usually limited below 150 psig.

UF system are operate in two possible filtration modes which is cross flow configuration in which the feed water is pumped tangential to the membrane while the water that does not permeate is recirculation as concentrate and combine with feed. In

dead end or direct filtration all the feed water passes through the membrane. Therefore recovery is 100% and small fraction is used periodically for back wash. Although dead end filtration require lower energy but the cross flow filtration suit the system better where recirculation of retentate is encouraging.

2.8 MEMBRANE FOULING

A major obstacle for the application of Hollow fibre membrane in MAS is the rapid decline of the permeation flux as a result of membrane fouling (Cheresources, 2010). Fouling refers to blockage of membranes pores during filtration caused by the combination of sieving and adsorption particulates onto membrane surface and within the membrane pore. This blockage of the pores causes a flux decline over time when all other parameter kept constant. The predominant fouling mechanisms observed with ultrafiltration and micro filtration membranes are classified into three categories: the build-up of a cake layer on the membrane surface, blocking of membrane pores, and adsorption of fouling material on the membrane surface or in the pore walls (M.O.Laminen, 2004). To establish strategies for fouling control, understanding of the fouling mechanisms is indispensable. Sludge characteristics are significant parameters that affect membrane fouling in MAS.

Fouling can be broadly classified into backwashable and irreversible. Backwash able can be removed either by backwashing or chemical cleaning while the irreversible type neither of the method can recover the original flux.

Fouling can also be classified according to type of the fouling materials. Four categories of the membrane fouling are generally reognised. They are:

a) Inorganic fouling
b) Particle /colloidal fouling
c) Microbial fouling
d) Organic fouling

In organic fouling is caused by the deposition of inorganic materials such as metal hydroxides. Precipitates form when the concentration of such materials over its saturation concentration. This type of fouling usually appears to be a problem for reverse osmosis and NF.

Particulates/ Colloidal fouling are due to algae, bacteria and some natural organic matter fall into the size range of particles and colloids. However they are different from other inert particles and colloids such as silt and clays. In most cases colloid and particles do not foul the membrane because it is largely reversible by hydraulic cleaning. Cross flow filtration can be used to control colloid fouling. (Norman N.Li, 2008)

Microbial Fouling is a result f formation of a biofilms on the membrane surfaces. Such films grow and release biopolymers as a result of microbial activity. Bacteria attached on the membrane and started to multiply and produce extracellular polymeric substances to form a viscous, slimy and hydrated gel. Severity of microbial fouling is greatly related to the characteristic of the feed.

Organic Fouling is an issue with lot of conflicting opinion, some researcher agree that proteins, amino acid sugars, polysaccharides and polyoxyaromatics as strong foulant while some partially agree showed organic colloidal fraction caused the most significant fouling. Some conclude that humic acid later fulvic acid. There is no definite answer, so further research on this subject is required. (Norman N.Li, 2008)

Membrane Fouling are sometimes related to the sludge settling problems where Sludge filamentous bulking and sludge deflocculating are the most common problems result in a deterioration of effluent quality. (F. Meng et al, 2007)

Deflocculation refers to a dysfunction of the activated sludge process characterized by the formation of a very small sludge floc, or the absence of floc formation. Deflocculation can be the result of operating conditions and environmental stresses such as shift in temperature, toxic compounds, metals, dissolved oxygen concentration, pH, substrate loading, and nutrient characteristics. (F. Meng et al., 2007)

Sludge bulking is a term used to describe the excessive growth of filamentous bacteria in activated sludge system, it is a condition in which sludge settling rates decrease and the thickening characteristics of settled sludge are poor. The existence of a small quantity of filamentous bacteria in sludge suspension can benefit the formation of strong flocs, which can be defined as normal sludge flocs. (F.Meng et al, 2007)

2.9 Methods reduce membrane fouling

Fouling rate can be slackened through different strategies as chemical cleaning or turbulent aeration.

2.9.1 Hydraulic Cleaning technique

One of the most helpful methods for fouling remediation is certainly represented by the sub-critical flux operation. (G. Andreottola et al, 2006)

From the Finding of Alves and Pinho and Schafer et al. on this phenomenon, it was have been proven that the cross flow velocity directly affecting the fouling rate where at higher cross flow velocity, the high shear tangential exerted to the membrane surface allowed the sweeping away of the deposited particles; therefore, the fouling layer on the surface of the membrane reduced. (A.L Ahmad et al, 2004) As a consequence, higher organic matter could pass through the membrane and percentage rejection become lower. (H.Mourad and M.Martine, 2002) also observed this in their study on the relationship between permeate flux and cross flow velocity. They tested for the highest cross flow velocity, and 88% of the mass carried by convection to the membrane surface was swept away by the tangential flow. The high shear tangential to the membrane surface swept deposited particles away (A.L Ahmad et al, 2004).

2.9.2 Backwashing/Chemical washing

For the conventional method, the UF were treated by chemical cleaning. The membranes were first circulated with clean water to flush out POME remaining in membranes, and then circulated with chemical solution mixed by 1% (*W*/*W*) NaOH and 0.6% (*W*/*W*) NaClO for 25 min. Finally, the membranes were rinsed again with clean water until a neutral pH was achieved.

Backwashing experiences degradation of flux between backwashes and requires a break in operation to be performed and problems incurred when chemical costs, waste disposal, and significant capital investments for equipment are needed.

2.9.3 Ultrasonic technology

Another remedy that is proven to be effective is by ultrasonic cleaning. Ultrasound is a sound wave travelling through a medium at a frequency above 18 kHz. Removal of particles on fouling surface can be accomplished with the right frequency, power intensities and duration. In comparison with other current membrane cleaning technologies include hydraulic, chemical, and mechanical methods, ultrasonic appear to be a better choice as common hydraulic cleaning technique.

2.9.3.1 Mechanism

In a liquid medium, ultrasound creates oscillating regions of high and low pressure. Cavitation bubbles are formed when the pressure amplitude exceeds the tensile strength of liquid during the rarefaction of sound waves. The cavitation bubble collapses during the compression cycle of sound waves. Localized hotspots are formed in aqueous solution reaching average bubble temperature of 4200K, peak core temperatures of 1700K and pressure of 500 atm at the bubble core. Acoustic streaming, micro streaming, micro streamers, micro jets and shock waves are generated as a result of ultrasound (D. Chen et al, 2006).

The high temperature and pressure resulting from cavitation collapse dissociate water into hydrogen atom and hydrogen radicals. More importantly with respect to membrane cleaning, cavitation collapse also produces a number of phenomena that results in high velocity fluid movement (M.O Laminen et al, 2004).

Several different mechanisms may lead to particles release from a particles-fouled surface as a result of ultrasound includes acoustic streaming. Acoustic streaming defined as the absorption of acoustic energy resulting in fluid flow. Acoustic streaming does not require the collapse of cavitation bubbles. This mechanism causes bulk water movement toward and away from the membrane cake layer that may scour the particle away. It is found to be an aid to cleaning the membranes but is likely not an important detachment mechanism. Acoustic streaming may remove detached particles from the vicinity of the membrane surface (M.O Laminen et al, 2004).

Micro streaming is another mechanism which is time independent circulation of fluid occurring in the vicinity of bubbles set to motion by oscillating sound pressure. Oscillation of bubble cause rapid fluctuation in the magnitude and direction of the fluid movement and as a result significant shear forces occur. Micro streaming result in a dynamic velocity profile that will exert drag forces on the particles leading to removal. Micro streaming works in conjunction with other mechanism such as micro streamer to clean membrane surface (M.O Laminen et al, 2004).

Micro streamer is a mechanism where cavitation bubble form at nucleation sites within the liquid and are subsequently translated to a mutual location are called micro streamer. The bubbles travel in ribbon like structure along tortuous paths at velocities approximately an order of magnitude faster than the average velocity of the fluid. The antinodes located on the fouled surface may result in bubbles scouring away particles. It is likely to be the major mechanism for detaching particles from the membrane (M.O Laminen et al, 2004).

Micro jets are formed when a cavitation bubble collapse in the presence of an asymmetry. During collapse, the bubble wall accelerates more than one side opposite to a solid surface, resulting in the formation of strong jet of water estimated velocity of

100-200m/s. Micro jet although present, appear in isolated site and do not greatly removed particles from membrane surface (M.O Laminen et al, 2004).

2.9.3.2 Factor influencing effectiveness

Ultrasound aids cleaning may be affected by a number of factors, such as orientation and position of the ultrasonic field, ultrasonic power intensity and frequency, membrane material, membrane housing, operating pressure, and fouling material.

2.9.3.2.1 Power intensity and frequency

M. cai et al (2010) found that the performances of permeate flux were significantly enhanced by Ultrasonic frequencies of low frequency which is 28kHz and 45kHz but no obvious enhancement was observed for the Ultrasonic frequency at 100kHz.The resistances at the frequency of 28 and 45 kHz were decrease significantly resulting in an increase of permeate flux while at frequency of 100kHz the resistance were similar to that without Ultrasonic. The solution concentration may be decrease by acoustic stream and bubble cavitation effect (M. Cai et al,2010).

The same trend of result reported by M.O Lamminen et al (2004), increasing cleaned flux ratio with decreasing of frequency was found. This can be explained although there are more collapse but the collapse tend to be less violently producing lower temperature and pressure this suggested that violence of collapse at lower frequencies is more important than increased number of weaker collapse.

In the research of M.O Lamminen et al (2004), suggest that increasing power intensity result in greater cleaning of the membranes. Increase of power intensity to the system increases the number of cavitation bubbles formed and increase the size of the cavitating zone due to higher pressure amplitude of the sound wave with increased power intensity. The hydrodynamic turbulence induced increased with power intensity resulting from the implosion of bubbles that are collapse and increase absorption of acoustic energy by the medium. Complete recovery occurred on the increasing shorter time scale as frequency decreased or power intensity increased.

2.9.3.2.2 Particle concentration, hydrophobicity and size

Increasing the particle concentration may result in increase of attenuation of acoustic energy, enhanced nucleation of cavitation bubbles and increased viscosity of the solution. The effect of particle concentration is that particles induce additional cavitation bubbles within the solution in the zone of the cavitation close to ultrasonic probe. Particles act as nuclei within the liquid from which bubble can grow. Cavitation bubbles attenuate sound waves due to both scattering and absorption and thus impede the propagation of the sound waves, especially at its resonance size. The scattering and absorption results in a decrease of sound wave intensity compared to that in the absence of bubbles. Thus, the sound wave intensity decrease more rapidly with distance from source at high particle concentration compare to those with low particle concentration. The ability of the ultrasound to remove particles from the membrane surface as measure by lift force of particles is reduced (D.Chen et al,2006).

The sound wave intensity in the presence of hydrophilic silica particles was significantly higher than that for hydrophobic silica particles. This trend verify that sound waves intensity decreased more rapidly due to bubble shielding caused by hydrophobic particles inducing more cavitation bubbles near source than hydrophilic particles. The turbulence generated is less effective as the distance between the cavitation bubbles and the membrane surface is larger (D.Chen et al,2006).

On the other hand, the particle size influence the efficiency in the way of larger particles would be more effectively removed by ultrasonic turbulence due to greater drag and lift forces. However, particle size did not significantly affect sound wave intensity. (D.Chen et al, 2006).

2.9.3.2.3 Distance

When the membrane is outside the cavitations' region, the main mechanism of microjets, microstreaming, shock waves, microstreamers and acoustic streaming may directly contributed to the cleaning action of the ultrasound. However when the membrane is outside the cavitation region, the main mechanism of ultrasonic cleaning is

acoustic streaming and ultrasonically generated turbulence. A major difference between the fluid movement within or outside the cavitation region is the energy density, which is extremely high within the cavitation region

At closer distance between the ultrasonic probe and membrane surface, more ultrasonic energy and ultrasonically generated turbulence is focused on the membrane surface and therefore better permeate recovery was obtained. (D.Chen et al, 2006)..

2.9.3.2.4 Filtration Pressure

Permeate flux improvement decrease with increasing of filtration pressure. Higher filtration pressure cause higher drags force on the particle at the membrane surface. The permeate drag force is proportional to permeate velocity through the membrane. Thus, increase pressure because stronger permeation drags force lead to greater membrane fouling.

Another theory behind the filtration pressure is the increase of the compressive forces driving cavitation bubbles formed. The increased compressive force results in the increase of the velocity of the bubble wall during implosion. Consistent with an expected increase in violence of cavitation collapse. In addition, fewer bubbles present in solution at higher pressure may limit bubble shielding, in which bubbles attenuate sound waves due to both scattering and absorption also improved cleaning. Thus, stronger acoustic stream and ultrasonic generated turbulence form in return created higher velocity gradient produced more shearing stress cleaning membrane surface.

However, the increase of drag force is more significant compare to the turbulence increase (D. Chen et al, 2006).

2.9.3.2.5 Continuos/ pulse Operation

The permeate flux improvement decrease as the pulse interval increased. The loss of permeate flux improvement with increasing pulse interval was likely due to

periodic losses in Ultrasonicated generated turbulence and subsequent deposition of particles. However, pulsing affect bubble dynamics. During sonication, some bubbles grow by rectified diffusion to size greater than the resonance size are ineffective at producing cavitation effects and cause scattering and absorption of ultrasonic waves. Therefore, in continuous ultrasound, some bubbles are ineffective and wasted. (D.Chen et al, 2006) Pulse ultrasound did not result in damage of membrane but slightly less effective than continuous ultrasound. (M.O Lamminen et al, 2006).

2.9.3.3 Membrane integrity

Membrane damage was found when membrane located just within the ultrasonic cavitation region. Literature suggests microjets and .or shock waves are likely responsible for the surface damage of membrane. The velocity of microjets can be greater than 100m/s and the pressure amplitude of shock wave can be as high as 1GPa. (D.Chen et al, 2006). (M.O Laminen et al,2006) reported at higher applied power susceptible to cause membrane damage when operate at continuos mode.

CHAPTER 3

MATERIALS AND METHODS

3.1 INTRODUCTION

This research carried out in UMP laboratory using UMAS laboratory scale. UMAS system is integrated with the anaerobic digestion technique, membrane technology and ultrasonic technology at the same time. The raw materials (POME) have gone through a fermentation process in where complex organic matters were degraded and production of methane gas takes places. Then this process would be further enhanced by a membrane UF module which allowed the removal of suspended solid by ultrafiltration to give a good quality effluent. The biomass that retained by the membrane recycled back to reactor while the remaining permeate was discharged. The ultrasonic that equipped with the membrane UF module housing played its part in preventing membrane fouling. The micro organism were left in the bioreactor for the first few days to acclimatized with the bioreactor environment until the system is establish where the micro organism would self generate and retained the sufficient amount of microbial in the system. The experiment carried out in mesophilic condition the performance in these conditions was investigated by evaluating pH, VSS, TSS, COD and BOD.

3.2. EXPERIMENTAL SETUP

The schematic diagram of pilot plant POME was shown in Figure 3.1 and 3.2 laboratory digester of Ultrasonicated Membrane Anaerobic System (UMAS) with an effective 50L volume was used to treat the raw POME. The UMAS consists of cross flow ultrafiltration CUF membrane apparatus, a centrifugal pump and an anaerobic reactor. The reactor was made up of PVC with inner 15cm and a total height 100cm.The reactor was covered with aluminum foil, which prevented direct sunlight.

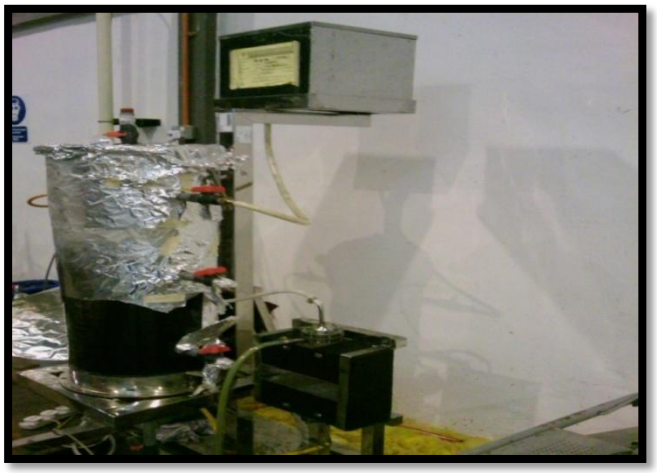

Figure 3.1: experimental setup

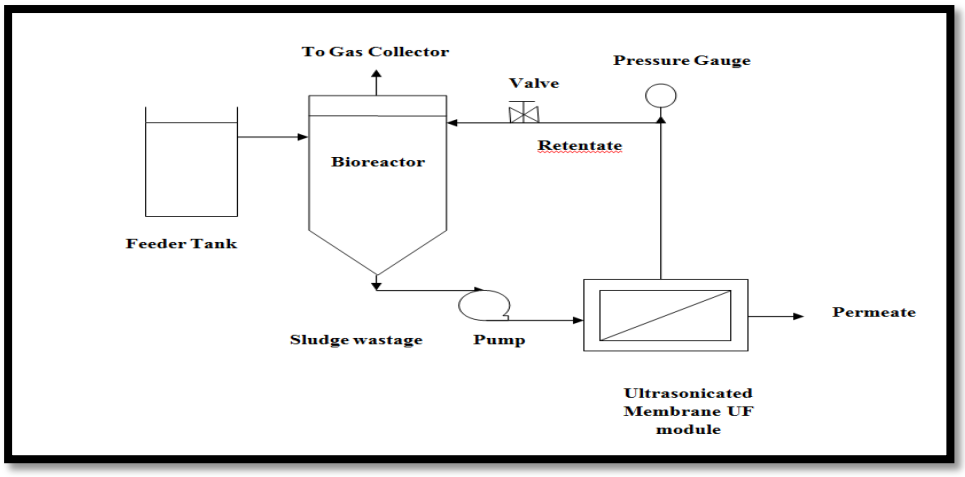

Figure 3.2: Schematic diagram of experimental set up

3.2.1 Hollow fiber membrane

The UF membrane module has molecular cut off (MWCO) of 200,000 and the tube diameter of 1.25cm and average pore size of 0.1μm.The length of each tube was 30cm.The total effective area of the membrane is $0.024m^2$. The maximum operating pressure on membrane was 55 bars at 70˚C or 70 bar 20˚C and it could be used in pH range from 2 to 12.The operating pressure was maintained at 1.5-2 bar by manipulating the gate valve at the retentate line after the CUF unit.Figure 3.3 shows the hollow fiber membrane used.

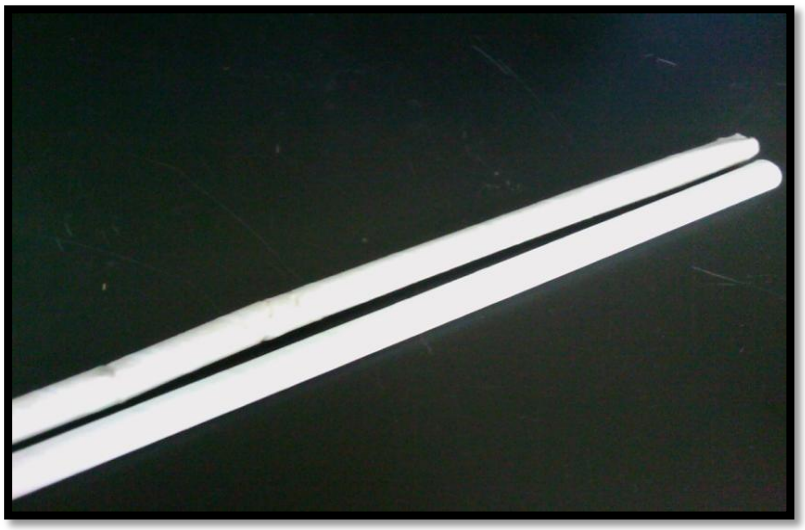

Figure 3.3: Hollow Fiber Ultrafiltration membrane

3.2.2 ULTRASONIC SYSTEM

The ultrasonic frequency was 25 kHz, with 6 units of permanent transducers and bonded to the two sided of the tank chamber and connected to one unit of 250 watts 25kHz Crest's Genesis Generator.

3.3 RAW MATERIAL - POME

POME samples were collected from Palm Oil Mill at FELDA Lepar Hilir and preserved in PVC containers at a temperature lower than 4℃ and higher than the freezing point to prevent the wastewater from undergoing biodegradation caused by microbial action. Before the experiment started, the raw POME is screened to remove unwanted suspended materials. Figure 3.4 shows the anaerobic pond of raw POME.

Figure 3.4 : Sampling anaerobic pond of raw POME

3.4 BACTERIA CULTURE

Firstly, the nutrient broth was prepared by dissolve 28g of broth with readily ratio of nutrient in 1L of water in a Scott bottle. The bottle was inverted for a few times. Then it was sent into autoclave for sterilization together with all of the apparatus that would be used at a temperature of 150˚C.The bottles are made sure to be close loosely to prevent pressure build up in the bottle. After that, the nutrient broth is taken out to left cool in room temperature or in water bath. While waiting for the nutrient broth to cool off, dilution of the sample POME can be done by adding distilled water to 100ml in a test tube containing 10mL of POME sample. Then from the previous test tube we transfer 10mL to another new test tube and add distilled water until 100mL.This step

repeated for 10 times to ensure the density of the sample is low enough to enable the bacteria detection under spectrometer. Then the diluted POME sample would be charge into the nutrient broth in Scott bottle. The Scott bottle will now ready to be incubated in a shaker incubator for a day. After that it will be tested by spectrometer to ensure there are enough bacteria otherwise it will be left for longer time until the density of bacteria is satisfying.10 set of this medium culture will be prepared which accounted for 10% of the reactor volume.

3.5 REACTOR OPERATION

The Raw POME that is collected from site is charge to the digester from feeder tank and it is left in the tank for 3days the micro-organism acclimates with the reactor, the process will be speeded up by cultured micro-organism in prior. Some of the POME from feeder tank is collect and test for the parameters such as pH, COD, BOD, TSS and VSS to obtain initial characteristic of the POME. In this experiment, the pH is controlled in the range of 6.8 to 7 while the optimum pressure is set to be 1.5 to 2.0 bar and the temperature was maintained within 25˚C to 37˚C. After acclimation period, the micro-organism community was stable then some of the POME in the feeder tank was collected to test and the reactor was left to operate (pump is switch on) for 5 hours, in this period the POME from the digester was pressurized into the UF membrane. After 5 hours, the permeate (filtrate) from the reactor are collected and tested for various parameters. The POME in the digester that has gone through biological degradation was also collected for the COD and BOD test. The gas that produced was collected by the designated syringe. The experiment was conducted for every of the subsequent days until the 7^{th} day or steady result obtained.

3.6 ANALYTICAL METHOD

3.6.1 Methane gas measurement

The biogas measured by using 20L displacement bottle. The gas method used to perform this analysis is J-tube analyzer as shown by Figure 3.5 and 3.6, the method

assume that gas that produced only two gasses that is methane and carbon dioxide then the sodium hydroxide solution (NaOH) is added to the composition. The remaining volume is methane gas. The device consists of a glass tube connected by a flexible hose to a syringe. Initially, the device was filled hose to a syringe. Initially, the device was filled with 0.5M NaOH solution, the glass tube was inserted to the gas line, where a column of biogas is drawn into the glass tube until a certain mark and the end of the glass tube then immersed in water. By manipulating the syringe many times, the NaOH solution was absorbing the carbon dioxide CO_2, as evidence from reduction in the length of the biogas column and then measures the biogas column again (N.H Abdurahman, 2010). This method has been proven to collect methane gas efficiently in the research done by N.H Abdurahman et al. This method is employed as it is economical and simple to operate. In comparison to others device such as wet test meter and gas chromatography which is used by Zhang Y.J et al incurred high cost and complex procedures (Zhang Y.J et al, 2007).

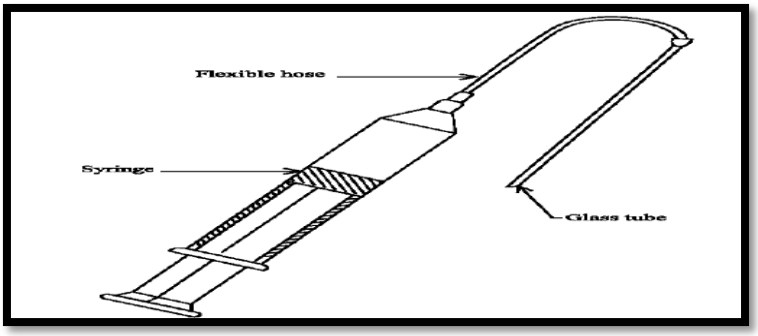

Figure 3.5 : Schematic Diagram of J-tube

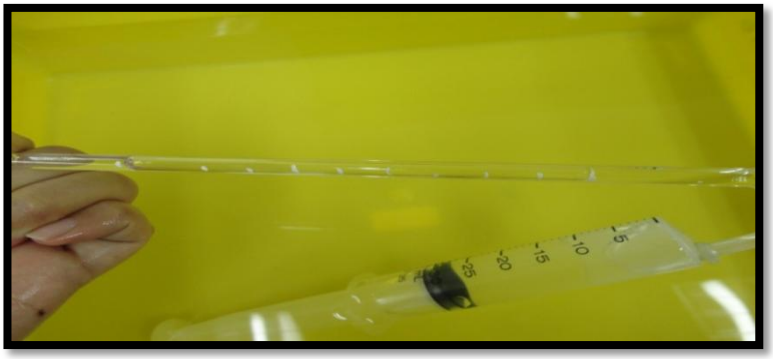

Figure 3.6: J-tube methane gas composition measurement

3.6.2 Chemical Oxygen Demand

The chemical oxygen demand (COD) was measured using Spectrophotometer HACH DR/2400 @ DR/2800(Figure 3.7) and COD Digester Reactor. A sample of 2 ml was placed in a vial with the oxidizing acid solution that was then held at 150 ℃ for 2 h. After cooling, the sample was then analysed in the HACH spectrophotometer. The colour of the samples varied from orange to dark green, indicating COD strength in the range of 0-15,000 mg/L.

Figure 3.7: HACH Spectrophotometer

3.6.3 Biological Oxygen Demand

The biological oxygen demand (BOD) of wastewater was measured using a Dissolved oxygen meter. 10mL sample was added into a 500 mL beaker and dilution water is added up to 300 mL into the same beaker. The pH value of the samples was adjusted to 6.5 to 7.5 by adding acid or alkali. The Dissolved oxygen in the sample was measured prior to putting it into incubator for five days. Figure 3.8 showed the DO meter used. The BOD which in turn can be calculated by formula below;

$$BOD_5, mg/L = (D_1 – D_2) / P$$

Where;

D_1 = DO value in initial sample

D_2 = DO value in final sample

P = Decimal volumetric fraction of sample used

Or;

BOD_5, mg/L = (D_1 – D_2) x Dilution factor

Dilution factor = Bottle volume (300mL) / Sample volume

Figure 3.8: DO meter

3.6.4 Total suspended solid

The total suspended solid (TSS) was measured to identify the amount of inorganic or organic particles or immiscible liquid that suspended in the sample. Firstly, the glass fibre filter disk was dried in the oven at 103˚C to 105˚C for 1 hour, and then it would be put in desiccators and weighed. The filtering apparatus will be assembled as shown in Figure 3.9 and filtration process will be started by begin suction. The filter was wetted with a small volume of distilled water to seat it.50ml of the sample pipette onto the centre of filter disk in a Buchner flask by using gentle suction. Filter was washed by 3 successive 10ml volumes of distilled water and 3 min suction is continued to completion. The filter was transfered to aluminum weighing dish/crucible dish as a support. The filter was dried at least one hour at 103˚C to 105˚C for 1 hour in an oven,

cool in desiccators to balance temperature and weigh. The cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained.

Figure 3.9: Filtering apparatus

3.6.5 Volatile suspended solid

In order to measure the volatile suspended solid, the residues from end samples from TSS test was continued to dried and firing in furnace with a temperature of 550˚C for 30 minutes. The organic fraction or volatile substances was converted to carbon dioxide, water, vapor and other gasses and escaped. The remaining materials will represent the inorganic or fixed residue. Figure 3.10 show a muffle furnace.

Figure 3.10: Muffle Furnace

3.7 MEMBRANE CLEANING

For the conventional method, the UF were treated by chemical cleaning. The membranes were first circulated with clean water to flush out POME remaining in membranes, and then circulated with chemical solution mixed by 1% (*W*/*W*) NaOH and 0.6% (*W*/*W*) NaClO for 25 min. Finally, the membranes were rinsed again with clean water until a neutral pH was achieved. The efficiency of the cleaning procedure was checked by comparing the clean water filtration flux to the initial flux. The second method used was to soak the membrane in 0.1 M NaOH for a day (24hours) rigorous brushing with water. In both methods membrane was taken out from membrane housing. However, this method has its limitation where a plant has to be shut down for the cleaning process or 2 membranes are installed and being used alternatively but this would incur more cost in a long run. Besides, constantly back flushing will degrade the membrane and hence shorten its life span. In order to overcome this problem, an ultrasonic is equipped on membrane housing where the ultrasonic send sound wave constantly to the membrane to detach the foulant.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

This chapter presents results obtained from experiment conducted according to the methodology in chapter 3. In order to achieve the objective of enhancing methane gas emission and treatability of POME the operational parameters such as pH and temperature was controlled strictly. The UMAS efficiency was evaluated for the parameters COD, BOD, VSS, TSS and Methane gas composition. These parameters were measured every day before and after membrane treatment for 5 hours. The raw data Table and the details calculations are enclosed in the appendix.

4.2 TOTAL SUSPENDED SOLID AND VOLATILE SUSPENDED SOLID

Figures 4.1 and 4.2 showed the Total suspended solid and volatile suspended solid profile of the bioreactor throughout the experiment respectively. The results show that, the TSS content was increased from 9950mg/L in the first day to 19940 mg/L in day 5^{th}.This corresponded to organic matter that are not accumulated in reactor at early stage were hydrolyze and fermented into soluble form. (A.P.V Rajaletchumy ,2010).

Apart from that, it has also indicated that the mass of microbial cell that has developed in the system increased. However, not all the solid participates in the conversion of the organic substrate as there is inorganic fraction that does not play an active role in biological treatment. Therefore, this may be represented by VSS more accurately as not all the solid mass participates in the conversion of the organic fraction. The VSS results supported the TSS result whereby the VSS showing the same trend that the VSS increased from 2380 mg/L to 15290 mg/L on the 5^{th} day. E.Sanchez et al, (2005) has also relied on VSS for the microorganism concentration estimation. However, VSS provided only estimation as the increase in volatile solids concentration may attribute by accumulation of compound such as fats, oil, and insoluble polysaccharide. (Michael H Gerardi, 2006).

VSS fraction increased drastically from day 4 to day 5 which indicated that the long solid retention time as a result of UMAS which able to facilitate the decomposition of suspended solid. The same experience reported by N.H Abdurahman, (2010). On the other hand showing the microbial acclimatized well to the bioreactor environment.

TSS and VSS reduction always serve as an indicator on performance of anaerobic digestion. In this study, results showed that the UMAS was able to remove TSS efficiently in permeate which recorded the removal rate of 98 to 99.8% of removal rate. This may attribute by the hollow fiber membrane which able to retained biomass back into the reactor while giving permeates with minute amount of suspended solid created and also prolong the solid retention time which promoted anaerobic digestion. The color of the treated POME was significantly different after passing through the UF membrane which turned light yellow as compared to the unfiltered POME which was dark brown to black.

Toward the end of the experiment which starting from the 7th day onwards, the microbial degradation of total suspended solid has came to the bottleneck where the total suspended solid reduction started to slow down where 3590mg/L of total

suspended solid remained in the system used up 5 days to reduce to 1580mg/L. The relative slow degradation possibly due to the fraction of the solid are relative complex molecules that are not directly used by a bacteria or poorly biodegradable which required longer time to convert it into soluble matter. There is also a trend of VSS fraction reduction from 77% to 70% which corresponds to inorganic matter accumulation. This explanation is consistent with the conclusion of (Y.J Zhang et al, 2007).

The SS removal efficiency of present work was higher as compared to 81.43% reported by SS Raja et al (2005) who employed treatment by hollow fibre polyethersulphone membrane with 100000 MWCO and decanter system as pretreatment. It was largely contributed by the biological treatment that been integrated in the system. In comparison to the MAS systems without ultrasonic conducted by A.P.V Rajaletchumy (2010), the maximum TSS removal rate was found to be 53.8% which was lower than the 99.8% on the same day. The effect may be indirectly or directly, where the membrane efficiency increased directly by the ultrasonic, while the growth of microbial community contribute to TSS destruction has promoted by the higher solid retention time indirectly.

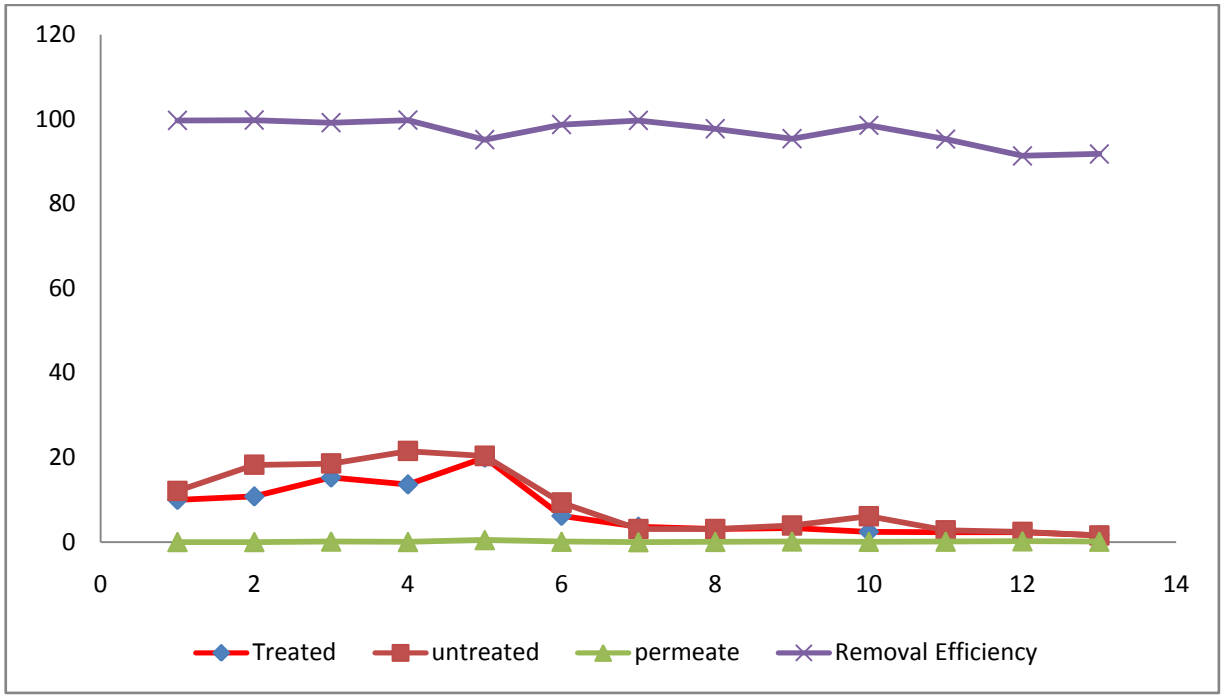

Figure 4.1: Total suspended solid

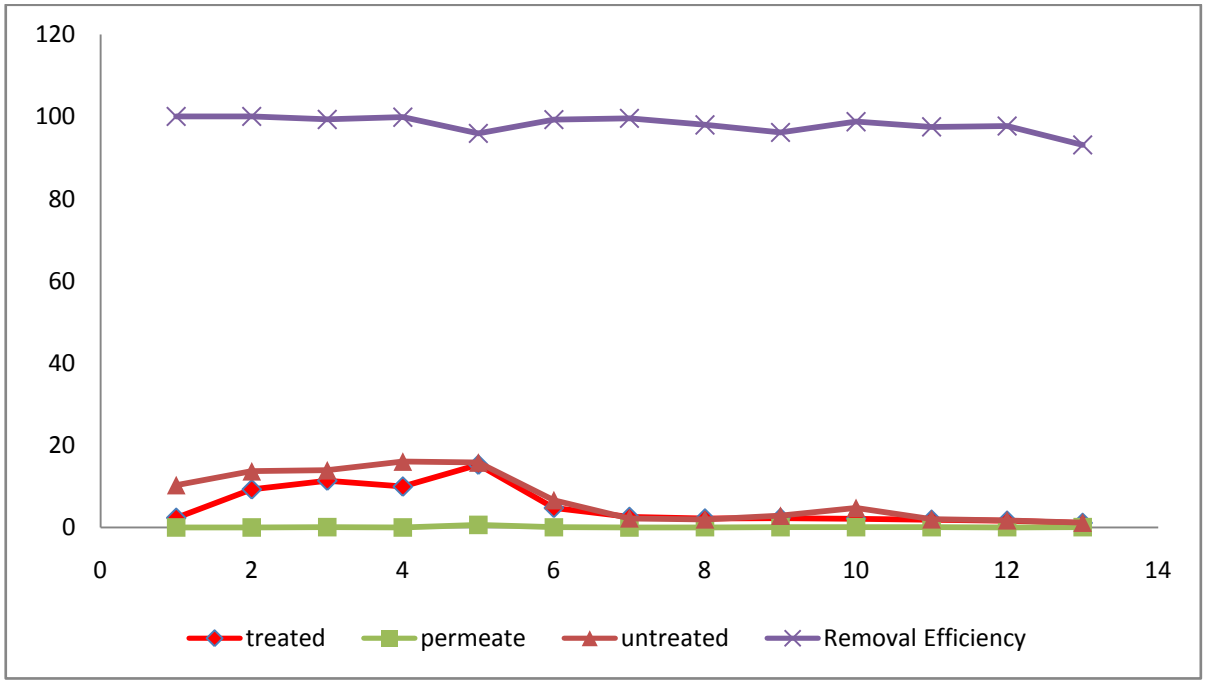

Figure 4.2: Volatile Suspended Solid

4.3 CHEMICAL OXYGEN DEMAND AND BIOLOGICAL OXYGEN DEMAND

The organic matter can be classified into soluble fraction and a particulate fraction. Hence, COD and BOD served as the variables representing the soluble fraction of substrate concentration. Figure 4.3 and 4.5 illustrates COD and BOD profile respectively. In the beginning of the experiment, the COD increased from 20650mg/L to 25700mg/L while BOD increase from 861mg/L to 1647.5 mg/L indicating that assimilation of complex organic compound into simple soluble compound. Somehow, COD obtained greater values compared to BOD because COD measure biodegradable and non biodegradable organic compound while the later did not. The fluctuation occurs where some of the BOD and COD values of the 2nd day in the system were even greater than influent are due to the recycle of solid in the system making high particulate organic matter represented by the microbial population. This conclusion was supported by literature of (V.S Marcos et al, 2005).

The results shown the COD removal rate of the reactor increased from 89.1% to 95% which was highest on the 6th day as shown in Figure 4.4 and Figure 4.6. On the other hand, BOD parameter recording the same trend by increasing from 38.5% removal rate on the first day to the peak of 74.3% removal rate. This was due to the active utilization of the substrate by the microbial population for their growth as well as for methane generation. It can be observe that the VSS which serve as microbial population indictor develop to maximum on the 5th day giving 15300mg/L, the relationship between SS concentration and COD removal rate could be found whereby increase in SS in the system could improve COD removal. It is consistent with Poh P.E et al (2010) finding which the COD removal efficiency increases when the MLSS increase. Besides, methane composition of 81.5% of biogas achieved. Hence, there was also a strong linear correlation between COD and methane gas production observe. The same observation reported by M.F Basri (2010) where biogas and methane production increase by COD removal.

On the 9th day, it can be observed on the BOD and COD removal rate have dropped below 57 % and 81% respectively. The slowdown in the digestion rate correspond to the fraction of biodegradable compound in soluble fraction were removed rapidly as low energy yield obtained from volatile acids by methane forming bacteria, as the amount of substrate utilization per unit of methane forming organism is high. Therefore, speed up the utilization of biodegradable substrate leaving the complex or non biodegradable fraction of substrate in the reactor. The low digestion rate may also associate with the reduction of microbial population as the growth restricted by the exhaustion of nutrient or substrate in the reactor. At this stage the total removal of COD achieved approximately 80% compared to the Influent feed at the beginning as there was no additional substrate added in as organic loading rate was not a parameter for this study, therefore substrate may served as the limiting factors. The similar experience was found in the research of (Poh P.E et al, 2010), suggested that additional substrate must be added into system when substrate reduction up to 80% to prevent substrate to becoming limiting factor.

Ultra filtration membrane has play it part in increase the COD efficiency whereby the organic of molecular weight higher than 200kDa are susceptible to being absorbed into membrane hole (A.P.V Rajaletchumy,2010), leading to the high COD removal rate up to 95% and 73.2% of BOD removal.

As compared to the highest COD removal rate of 70% in the previous research done by (A.P.V Rajaletchumy, 2010) UMAS able to reach removal rate of 92.4% in the same period of time. The performance difference may be contributed by the Ultrasonic equipped with the membrane which manage to emit ultrasonic irradiation in return creating turbulence flow which would triggered the removal of fouling particles from membrane surface in return retained the biomass in the system resulting in higher SRT for microbial degradation.

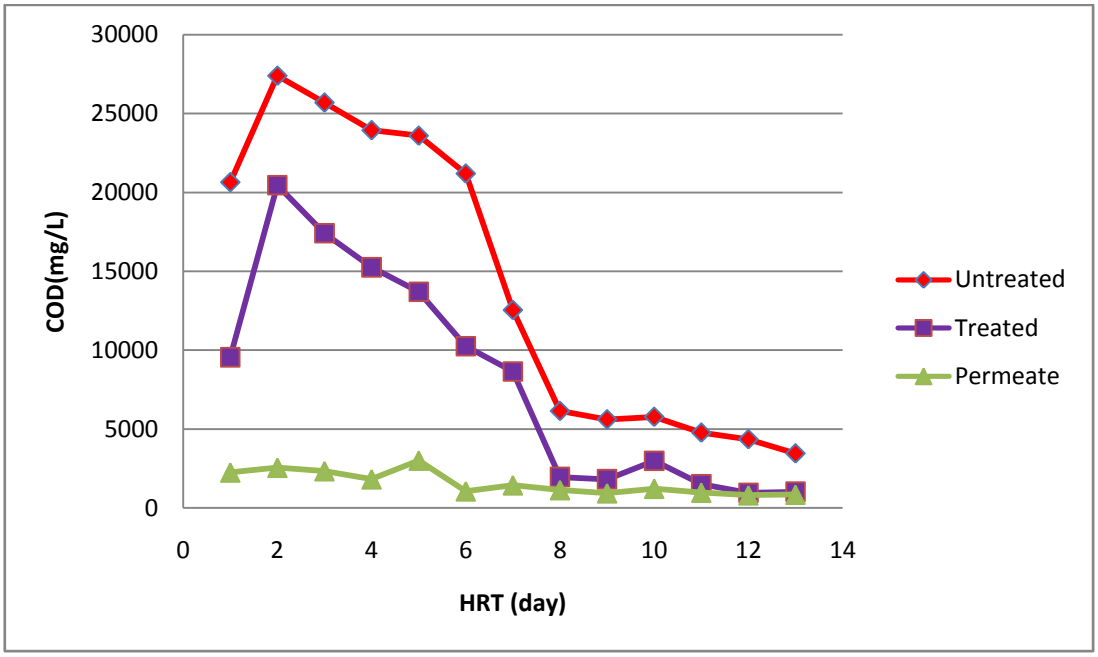

Figure 4.3: Chemical Oxygen Demand

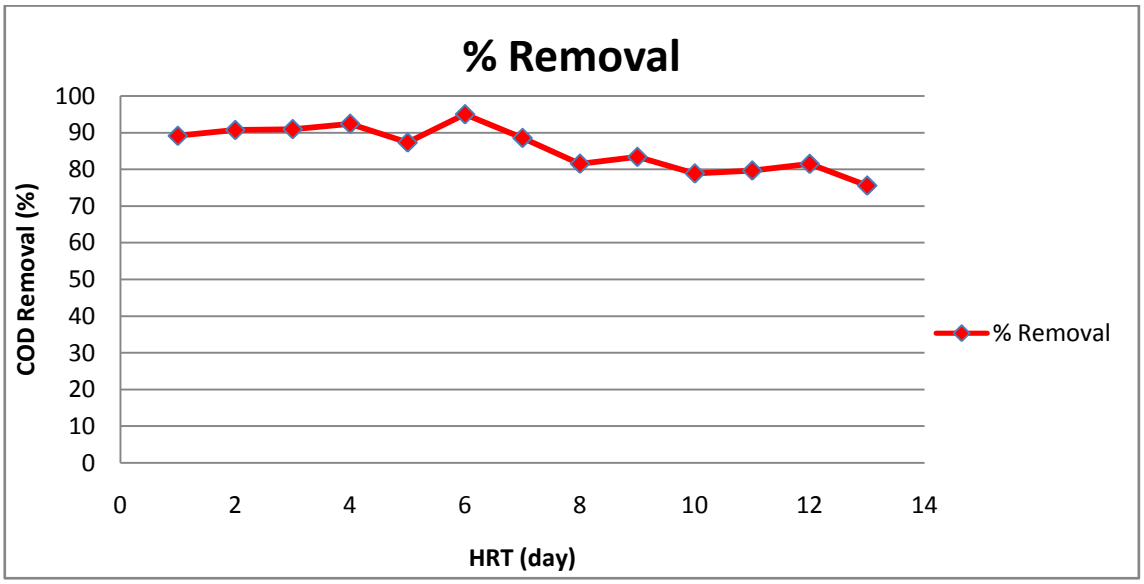

Figure 4.4: COD Removal Efficiency

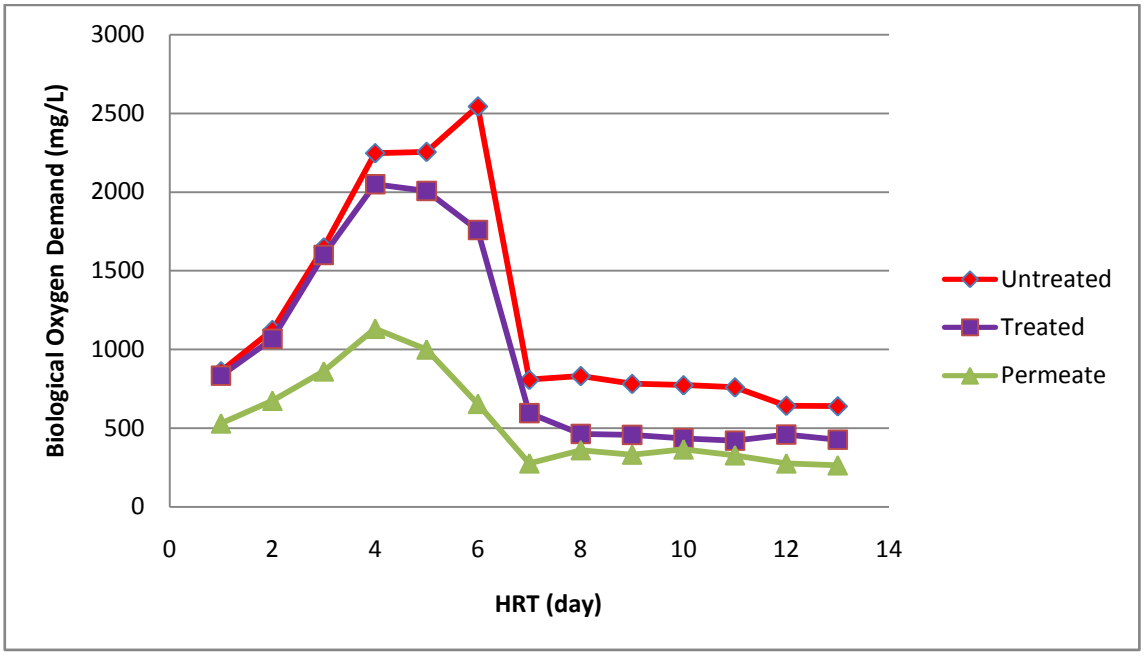

Figure 4.5: Biological Oxygen Demand

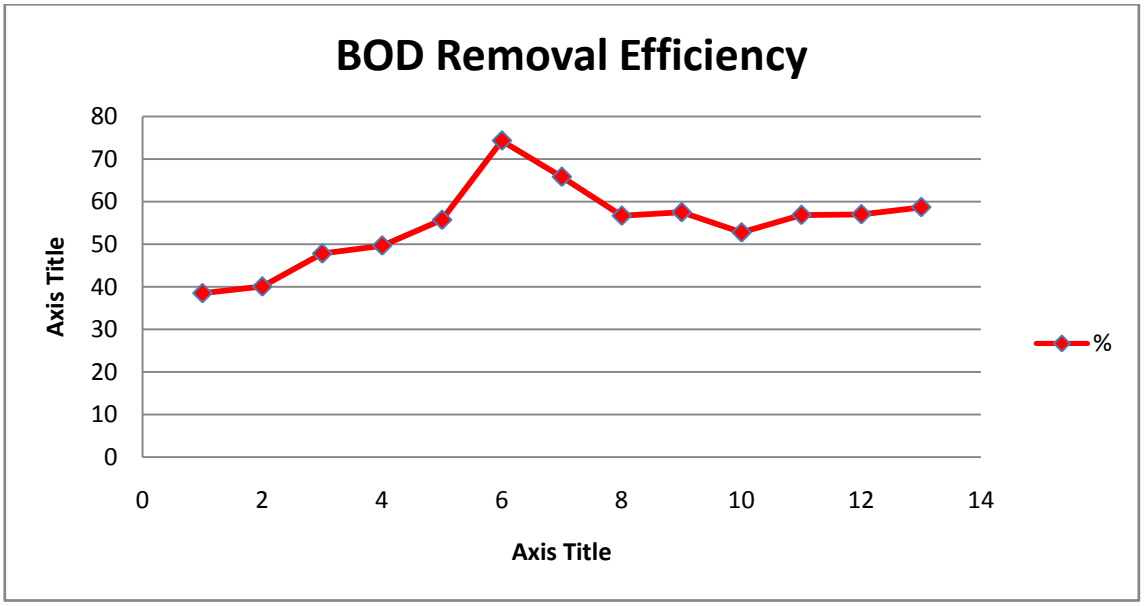

Figure 4.6: Biological Oxygen Demand Removal Efficiency

4.4 METHANE GAS COMPOSITION

Figure 4.7 illustrated the biogas composition profile throughout the experiment. The biogas composition is important parameter to evaluate the system balance whereby it reveals the ratio between acid former and methanogens. In this study, it can be found that the methane concentration is in a low level which is only 28% on the first day of operation. The biogas composition is relate closely to the microbial population mass, VSS results displaying the same trend where the microbial development started from 2300mg/L to 15290mg/L. From this point of view, the microbe in the system was acclimatizing to the reactor environment and started to develop in the system. However, the low concentration of the methane can be related to the oxygen contamination during the charging of inoculums into the system on that day which in return dilutes the gas and inhibiting the growth of methanogens. The similar problem encountered by (M.F Basri et al, 2010) during loading of material into the bioreactor. The low percentage may also contributed by the high substrate concentration in the beginning making the reaction favorable to acidogenesis in turn produced higher percentage of CO2 compared to methane which can also be observe from the pH drop of 0.3 from 7.16 to 6.86.it was once again assuring that there was active assimilation of particulate organic matter. Similarly, the result of COD and BOD are also reflected the same things.

The system regain stable gradually achieving more than 70% on the 4^{th} day and maintained composition of 78-82.14% started from 6^{th} to 11^{th} day and decreased slightly to 76-77.7%. This was due to the increase of the SRT which was favorable for methanogenic bacteria and to obtain better adapting biofilm. (E.Sanchez et al, 2004) The same conclusion made by M.A de la Rubia et al (2006) that more COD being used to generated methane when SRT increase due to the microbial population becoming adapted to new operational condition. It is notable that biogas composition increased with the total COD and BOD removal. For instance, the BOD and COD removal rate on the 6th day recorded the highest removal giving us the methane composition of 81.2% on the same day. Despite of the reduction in COD and BOD removal rate on the subsequent day, the biogas composition was only affected on the 11^{th} day. As discussed

earlier, there was only low energy yield obtained from volatile acids by methane forming bacteria so the amount of substrate utilization per unit of methane forming organism is high hence the COD utilization is rapid. On the 12^{th} and $13^{th\ day}$ the decomposition rate of complex organic compounds not as rapid as the methane conversion rate hence hydrolysis stage became rate limiting factor. M.F Basri et al (2005) had also found that a considerable portion of COD was not being degraded in the digester due to it complex nature of plant cell walls which are difficult to hydrolyze microbiologically. The explanation has found to be consistent with literature review of (Michael H. Gerardi, 2003).

In this study, the highest methane composition was found to be 82.14% .The high percentage is contributed by the membrane system that able to separate the hydraulic retention time and solid retention time by recirculation of biomass. The prolonged solid retention time of the UMAS has allowed for the decomposition of the suspended solid and subsequent conversion to methane.(N.H Abdurahman et al,2010) Besides, sludge recirculation create modest mixing which enhanced the digestion process by distributing bacteria, substrate, and nutrients throughout the digester as well as equalizing temperature. The metabolic activities of acetate forming bacteria and methane forming bacteria require that they be in close spatial contact. (Michael H.Gerardi, 2003)

The highest methane composition of 82.14% was found to be higher than the conventional method which recorded 54.4% and 36% for the anaerobic pond and open digesting tank (Poh P.E et al,2009). The result was comparable to that achieved by G.D Najafpour et al (2006) which reported the range of 62-82% for both of the system and present system were superior in term of biomass retention.

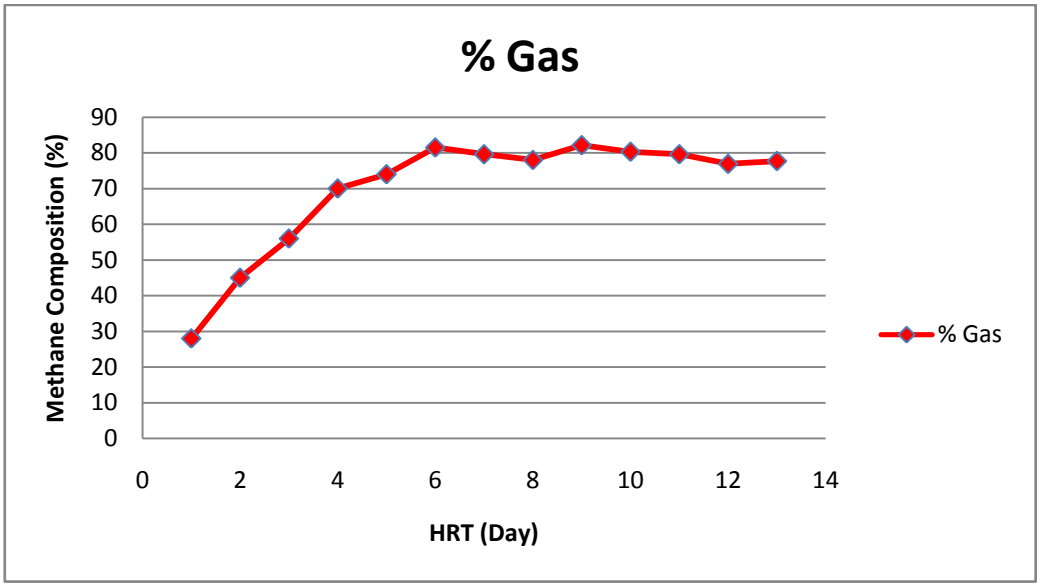

Figure 4.7: Methane Gas Composition

4.5 pH

The performance of an anaerobic digester was highly dependent on the pH as the enzymatic activity of the microbial community was very sensitive to pH changes. Besides, it would also affect the toxicity of a number of compounds such as sulfide indirectly. Generally, the methane producing microorganism has optimum growth in pH range within 6.6-7.4 although the stability may be achieved in a wider range within 6-8. Hence, the pH of the anaerobic digester was maintained within the range. Before starting the experiment the raw POME was poised to pH 7.2 to prevent the pH drop out from the optimum range result from production of volatile acid in the system causing. As expected at the beginning stage of the experiment, pH was dropped from 7.16 from the first day to 6.82 on the 4th day. The system regains more alkalinity on the subsequent day and stabilized this indicating that the volatile acid was converted into methane in the system. The pH were maintained in the ranged of 6.9 to 7.4 until the 11th day. According to finding of Poh P.E et al (2010), pH rise in the system indicate the methanogens have adapted to the environment. The pH increased again reached up to 7.8 which correspond to the fast utilization of CO_2 in the system and also the methane

formation rate exceeding the hydrolysis rates which delay the further formation of volatile acid.

4.6 ULTRASONIC SYSTEM

In this study, the effectiveness of the Ultrasonic can be seen from the permeability yield, permeate quality and the pressure drop of the system. The permeability yield improvement can be seen from the permeate volume collected in the experiment which is direct proportional to the membrane flux. The flux of the membrane throughout the experiment have calculated by measuring the quantity of permeate collected in 5 hour period and divided by the effective membrane area for filtration with is $0.048m^2$ for four membrane (T.Y Wu et al.,2007). It was found that the flux reduction accounted for 37.7% in 8 days operation compare with the flux in the beginning of the experiment. The similar study has been done by P.Sui et al (2008) using different approach by measuring the filtration resistance. It was found that the total filtration resistance was only 30% of that without ultrasonic after 28 days of operation which shown better performance. However, the performance difference can be explained as properties of wastewater used was vary, synthetic wastewater was used in P.Sui et al (2008) was lower strength wastewater compare to POME with high suspended solid and organic content. In the mean time, the pressure drop of the system is not significant throughout the experiment.

There are some improvements of result in TSS and COD removal parameter as compared with the experimental result done on the system without ultrasonic by (A.P.V Rajaletchumy, 2010). It was found that the highest COD removal and TSS removal achieve by A.P.V Rajaletchumy (2010) were 70% and 53.8% respectively. In comparison with the current result the COD removal reached up to 92.4% and TSS removal of 99.8% on the same HRT 4 day. The performance may attributed by Ultrasonic equipped with the membrane which manage to emit ultrasonic irradiation in return creating turbulence flow which would triggered the removal of fouling particles

from membrane surface in return retained the biomass in the system resulting in higher SRT for microbial degradation. The same explanation can be applied when comes to comparison with the methane content obtained by N.H Abdurahman et al (2010) which is 76.3% as compare with 82% found in present work. Hence, it could be found that the permeate improvement relied more significantly on the microbial digestion compare to physical separation result from reduction of fouling problems. It is reported by L.Wang et al (2008) that the membrane fouling did not affect the water quality as foulant does not change and destroy the properties of membrane. Some researcher even found that membrane fouling layer increased the resistance for organic matter to pass through in return causing lower concentration of COD and BOD in the permeate.(A.L Ahmad et al,2005) (T.Y Wu et al,2007). Although fouling was able to increase COD and BOD removal efficiency, somehow fouling still an unfavorable condition as it reduce membrane permeability incurs higher cost for high membrane surface area and capital cost in replacing membrane.

There are also no damage found on the membrane and also no negative effects that on the bacterial activity which is not consistent with the finding of P.sui et al (2008) which found that ultrasonic irradiation has slight negative effect on bacterial activity. Besides, the operating frequency of 25 kHz and an adjustable power output of 250W are found to be effectively reduced the fouling layer on the polysulphone membrane used.

4.7 PROBLEM FOUND DURING EXPERIMENT

Problem arose on the 5^{th} day where leakage of treated POME found to happen in the fitting joint of membrane and housing. The leakage is probably results by the degradation of membrane after a period of time of frequent chemical cleaning where the membranes are found soften and hard to fitted in the housing when the pressure exerted on the membrane the membrane fallout from the housing causing a gap where leaking happen. The contaminated permeate are found to have higher suspended solid. The colors of permeate is darker than usual. Hence, the experiment is stopped and replace

with new membrane. Figure 4.8 and Figure 4.9 shown membrane housing and degraded membrane.

Figure 4.8: Membrane housing

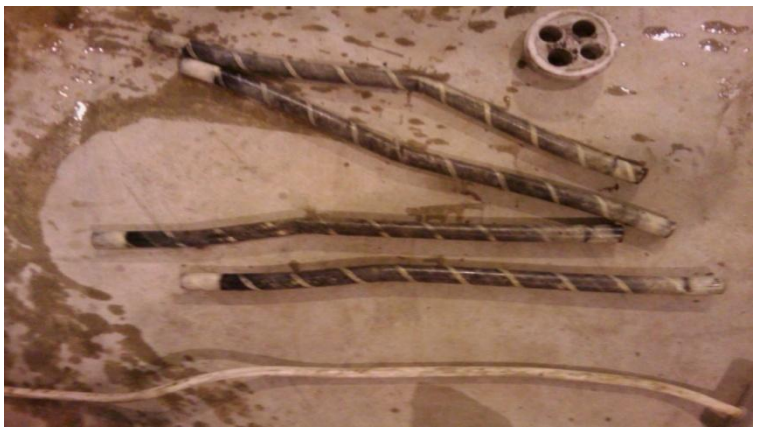

Figure 4.9: Degraded Membrane pull out from housing.

CHAPTER 5

CONCLUSIONS & RECOMMENDATIONS

5.1 CONCLUSION

UMAS was found to be an effective system in treating POME and producing methane gas effectively in a short period. From this study, the COD removal rate found to be in the range of 75.5% to 95%. The performance of the system has also implied in the BOD removal rate which fall within 38.5% to 74.3%. Another added value of the system was the high methane composition that was produced where recorded highest methane composition of 82.14%. This showed that the system has overcome the problems of slow anaerobic grow rate which appear to be a disadvantage in the conventional POME treating method. The system has successfully separated the hydraulic retention time and solid retention time by equipping membrane in the system whereby the filtrate was discharged and the sludge was recycled back into the system. In this way, the solid free effluent can be reducing in the mean time COD removal rate can be greatly improved. Besides, due to the high solid retention time and the recycling of the slow growing bacteria the microbial mass in the system can be maintained in considerable amount.

In additional, the Ultrasonic attached to the membrane has solved one of the most critical problems during the membrane anaerobic system which was membrane fouling. Membrane fouling has reduced the membrane flux so reduce the membrane efficiency and shortened the life of membrane therefore increase the capital cost. The turbulence that created by the ultrasonic during operation has removed particles that blocking the pore efficiently. As a result, the quality of the effluent was elevated with lower COD as well as the higher biomass retention efficiency.

From the parameter that were evaluated, the UMAS was good alternative in treating high strength wastewater .The objective of this study was attained where the efficiency of the reactor has been increased by using ultrasonic as compared with the previous results by higher COD removal rate improvement by 32% as well as 71% higher TSS removal rate.

5.2 RECOMMENDATION

(i) Study on the effect of the frequency intensities of ultrasonic on the efficiency of foulant removal.

(ii) Equipped the system with mixing induced more even distribution of substrate and microbe as well as equalizing temperature.

(iii) Conduct the experiment under thermophilic condition as higher temperature may increase the microbial activity hence increasing the methane production rate.

(iv) Install gas analyzer for more accurate reading and purging system to prevent oxygen contamination.

(v) Volatile fatty acid as a parameter indicating process stability as parameter such as pH, volatile solid destruction and gas composition often too slow for optimal detection of sudden changes.

REFERENCES

A.L Ahmad, S. Ismail and S. Bhatia, 2003.Water recycling from palm oil mill effluent (POME) using membrane technology.*Desalination*,**157**:87-95.Elsevier..

A.L. Ahmad, S. Ismail and S. Bhatia, 2004. Membrane treatment for palm oil mill effluent: Effect of transmembrane pressure and crossflow velocity.*Desalination* **179** (2005) 245-225. Elsevier.

A.L Ahmad, S. Ismail and S. Bhatia, 2005. Ultrafiltration behaviour in the treatment of agro-industry effluent: Pilot scale studies.*Chemical Engineering Science* **60**.5385-5394.Elsevier.

A.M.B Alves and M.N Pinho,2000.Ultrafiltration for colour removal of tannery dyeing wastewater.*Desalination*,**130**(2000)147-154.

A.P.V. Rajaletchumy,2010. "Evaluation of Palm Oil Mill Effluent (POME) By Membrane Anaerobic System (MAS)" Thesis, University Malaysia Pahang.

Boe K., I. Angelidaki, 2009.Serial CSTR digester configuration for improving biogas production from manure. *Water Res* **43** (1) (2009):166-72.

Borja, R., Banks, C.J., S ánchez, E., 1996a. Anaerobic treatment of palm oil mill effluent in a two-stage up-flow anaerobic sludge blanket (UASB) reactor. *Journal of Biotechnology* **45**.

Borja, R. Banks, C.J,1994b.Treatment of palm oil mill effluent by upflow anaerobic filtration.Journal of *Chemical Technology and Biotechnology* **99**, 222-226.

Borja, R. Banks, C.J,1994c.Anaerobic digestion of palm oil mill effluent using an up-flow anaerobic sludge blanket anaerobic.*Biomass and Bioenergyenergy* **61**,103-109.

Borja,R.Banks, C.J,1995.Comparison of an anaerobic filter and anaerobic fludized bed reactor treating ice-cream wastewater to organic, hydraulic, temperature and pH shocks.*Journal of Biotechnology* **39**, 251-259.

B.K Ahring, M.Sandberg, I Angelidaki,1995. Volatile Fatty Acid as indicators of process imbalance in anaerobic digestors. *Appl Microbial Biotech* (1995) **43**: 559-565.Spinger-Verlag.

Cheresources.com, 2010. Hollow Fibre Membrane, Retrieved March 15, 2010 from http://www.cheresources.com/hmembranes.shtml

Choorit. W., Wisarnwan.P., 2007.Effect of temperature on the anaerobic digestion of palm oil mill effluent. *Electronic journal of biotechnology* **10**,376-385.

D. A. Burke, 2001. Options for Recovering Beneficial Products From Dairy Manure, Environmental Energy Company.

D.Chen, L.K Weavers and H.W Walker,2006. Ultrasonic control of ceramic membranes fouling: Effect of particles characteristics. *Water Research* **40** (2004) 840-850.

D. Chen, L.K Weavers and H.W Walker, 2006. Ultrasonic Control of ceramic membrane fouling by particles: Effect of ultrasonic factors.*Ultrasonic Sonochemistry* **13** (2006) 379-387.

E.Sanchez, R. Borja, L. Travieso, A.Martin and M.F Colmenarejo, 2005.Effect of influent substrate concentration and hydraulic rentention time on the performance of down-flow anaerobic fixed bed reactors treating piggery wastewater in tropical climate.*Process Biochemistry*,**40** (2005) 817-829.Elsevier.

F. Meng and F. Yang , 2007. Fouling mechanisms of deflocculated sludge, normal sludge, and bulking sludge in membrane bioreactor. *Journal of membrane science* (2007) **305**:1-2,Pages:48-56.

G. Andreottola and G. Guglielmi,2006. Critical flux determination in two MBRs for municipal wastewater treatment.

G.D Najafpour,A.A.L. Zinatizadeh, A.R Mohamed, M.Hasnain Isa, and H.Nasrollahzadeh,2006.High rate anaerobic digestion of palm oil mill effluent in an upflow anaerobic sludge-fixed film bioreactor.*Process chemistry* **41** (2006)370-379.

H. Patel and D. Madamwar, 2002.Effects of temperatures and organic loading rates on biomethanation of acidic petrochemical wastewater using an anaerobic upflow fixed-film reactor. *Biosurce Technology* Vol **82**,Issue 1,Elsevier.

Hill DT, Cobb SA,and Bolte JP, 1987.Using volatile fatty acid relationships to predict anaerobic digester failure.*Trans ASAE* **30**:496-501

Hill DT,1982.A comprehensive dynamic model for animal waste methanogenesis.*Trans ASAE* **25**:1374-1380.

H.Mourad and M.P Martine,2002.Analysis of deposit behaviour in crossflow microfiltration by means of thickness measurement.*Chem.Eng.J.*,**86**(3)(2002),251-257.

Husnul Azan T, Faridah A.H.A and Mohamed Hasnain I,2006. Relationship between Volatile Fatty Acid and Alkalinity in Anaerobic Digestion of Food Waste.

Ibrahim, A. Yeoh,B.G,Cheah, S.C,Ma, A.N,Ahmad, S.Chew,T.Y. Raj.R and Wahid M.J.A,1984. Thermophilic anaerobic contact digestion of palm oil mill effluent.*Water Science and Technology* **17**, 155-165.

Kaparaju P., Buendia, I., Ellegaard and L.Angelidakia l,2008.Effect of mixing on the methane production during thermphilic anaerobic digestion of manure:lab scale pilot-scale studies.*Bioresources Technology* **99**, 4919-4928.

Karim, K., Hoffmann, R., Klasson, T., Al-Dahhan, M.H., 2005. Anaerobic digestion of animal waste: waste strength versus impact of mixing. *Bioresource Technology* **96**, 1771–1781,Elsevier.

Kementerian Tenaga Air and komunikasi , 2005. The regional forum on sustainable energy, Retrieved on 10 March, 2010 from http://www.kettha.gov.my/system/print_details.asp?tt=NEWS&newsid=239&PrintVersion=yes

Kim, M., Ahn, Y.-H., Speece, R.E., 2002. Comparative process stability and efficiency of anaerobic digestion; mesophilic vs. thermophilic. *Water Research* **36**, 4369–4385,Elsevier.

K.M Ostrem, K. Millrath and N.J Themelis, 2004. Combining Anaerobic Digestion and Waste-to-energy,12 North American waste to energy conference (NAWTEC 12).

Lenntech,2010.Solid retention time, Retrieved on 20 March 15,2010 from http://www.lenntech.com/wwtp/srt.htm

Leslie Grady Jr.,C.P.Daigger, G.T., Lim, H.C,1999.Biological Wastewater Treatment, second ed. CRC Press. Revised & Expanded.

Lim C.H , E.Salleh and P.Jones, 2006.Renewable energy policy and initiatives in Malaysia. ALAM CIPTA, Intl.J. on sustainable Tropical Research & Practise. Vol. 1 (Issue 1):pp. 33-44

Ling L.Y ,2007. Treatability of palm oil mill effluent (POME) using black liquor in anaerobic treatment process Thesis, University Sains Malaysia.

L.Wang, X.D. Wang and K. Fukushi, 2008. Effect of operational conditions on ultrafiltration membranes by natural water. *Desalination* **229**.

Ma, A.N., Cheah, S.C., Chow, M.C., 1993. Current status of palm oil processing wastes management. In: Waste Management in Malaysia: Current Status and Prospects for Bioremediation, pp. 111–136.

M.A de la Rubia, M.Perez, L.I Romero and D.Sales,2006. Effect of solids retention time (SRT) on the pilot scale anaerobic thermopilic sludge digestion.*Process biochemistry* **41** (2006) 79-86.Elsevier.

M.Cai et al, S.Zhao and H.Liang,2010.Mechanism for the enhancement of ultrafiltration and membrane cleaning by different ultrasonic frequencies.*Desalination* **263** (2010) 133-138.

M. Clara, N. Kreuzinger, B. Strenn O. Gans and H. Kroiss, 2004. The solids retention time of a suitable design parameter to evaluate the capacity of wastewater treatment plants to remove micropollutants.*Water research* **39** (2005) 97 -106.

M.F. Basri,2010.Improved biogas production from palm oil mill effluent by a scale down anaerobic treatment process.*World J Microbiol Biotechnol* (2010) **26**:505-514.Springer Science.

Michael H.Geradi, 2003.The microbiology of anaerobic digesters.John Wiley and Sons,Inc. Hoboken, New Jersey.

Michael H.Geradi, 2006.Waste Water Bacteria. John Wiley and Sons,Inc.Hoboken,New Jersey.

M.O Lamininen, H.W. Walker, L.K. Weavers,2004.Mechanism and factors influencing the ultrasonic cleaning of particle-fouled ceramic membranes. *Journal of membrane science* **237** (2004) 213-223.

M.O Lamminen, H.W.Walker and L.K Weavers,2006. Cleaning of particle-fouled membranes during cross-flow filtration using embedded ultrasonic transducer system. *Journal of membrane Science* **283** 225-232.

Najafpour, G.D.,Zinatizadeh, A.A.L, Mohamed, A.R,Hasnain Isa.M.,Nasrollahzadeh H.,2006.High-rate anaerobic anaerobic digestion of palm oil mill effluent in an upflow anaerobic sludge-fixed film bioreactor.*Process Biochemistry* **41**, 370-379.

NA Ludin, MA MBakri, M Hashim, B Sawilla, Ir NR Menon and H Mokhtar ,2006. Palm Oil Biomass for Electricity Generation in Malaysia, Pusat Tenaga Malaysia, Malaysia Palm Oil Board , SIRIM Berhad.

N.H Abdurahman, Y.M. Rosli, N.H. Azhari,2011. Developement of membrane anaerobic system for plam oil mill effluent treatment. *Desalination* **266** (2011)208-212.

N.H Abdurahman, 2010.Kinetic study of sewage sludge treatment by an Anaerobic Digestion, *Journal of Applied Sciences* **10** (2010) (3):226-230.

N.H Abdurahman, 2011.Ultrasonicated membrane anaerobic system (UMAS) for POME treatment. LAP Lambert Academic Publishing, Germany.

Norman N. Li, Anthony G. Fane, W.S Winston Ho and M. Takeshi, 2008, Advanced membrane Technology and Applications.John Wiley & Sons, New Jersey.

Poh P.E and Chong M.F, 2009. Development of anaerobic digestion methods for palm oil mill effluent (POME) treatment. *Bioresource Technology* **100** (2009) 1-9.

Poh P.E and Chong M.F,2010. Biomethanation of Palmi Oil Mill Effluent (POME) with thermophilic mixed culture cultivated using POME as a substrate. *Chemical Engineering Journal* **164** (2010) 146-154.

P.Sui, X. Wen and X.Huang,2008. Feasibility of employing ultrasound for on-line membrane fouling control in an anaerobic membrane reactor. *Desalinaiton* **219** (208)203-123.

Ramakrishna. S, Ma Z. and M.Takeshi, 2011.Polymer membrane biotechnology, Imperial College Press,London.

S.Sung and H.Santha, 2003.Performance of temperature-phased anaerobic digestion (TPAD) system treating dairy cattle wastes. *Water research* **37** (2003) 1628-1636.

S.S Raja and K.Premjit,2005. Treatment of Palm oil mill effluent using membrane technology. University Malaya.

Tong, S.L.Jaafar, A.B,2006. POME Biogas capture, upgrading and utilization.*Palm Oil Engineering Bulletin* **78**,11-17.

T.Y.Wu, A.W.Mohammad, J.Md. Jahim and N.Anuar,2007. Palm Oil Mill Effluent (POME) treatment and bioresources recovery using ultrafiltration membrane: Effect of pressure on membrane fouling. *Biochemical Engineering Journal* **35** (2007) 309-317.

Ugoji, E.O,1997.Anaerobic digestion of palm oil mill effluent and its utilization as fertilizer for environmental protection.*Renewable Energy* **10**, 291-294.

V.S Marcos, L.C Carlos Augusto, 2005.Biological Waste Treatment in Warm Climate Regions. IWA publishing.

Wang Q.H, K. Massaaki, O.Hiroaki and K.Yasuhiko, 1999.Degradation of volatile fatty acids in highly efficient anaerobic digestion. *Biomass and Bioenerg* **16** (1999). 407-416.

Yacob S.Hassan, M.A. Shirai, Y.Wakisaka and M.Subash, 2006.Baseline study of methane emmision from open digesting tanks of Palm Oil Mill Effluent treatment. *Chemosphere* **59** (2005) 1575-1581.

Yacob,S.,Hassan, M.A Shirai, Y.Wakisaka and M.Subash.S,2005.Baseline methane emission from open digesting tanks of palm oil mill effluent treatment. *Science of the total environment* **366**,187-196.

Y.J. Zhang,Y.Li,Q.X.Li,N.X.Jun,M.Z.Jian and Z.J. Zhang,2007. Integration of biological method and membrane technology.*Journal environmental science* **20** (2008).558-564. Elsevier.

APPENDIX A

RESULT & DISCUSSION

Experimental Data

Table 4.1: Chemical Oxygen Demand Profile

	Untreated	Treated	Permeate	% Removal
1	20650	9550	2250	89.10
2	27400	20450	2550	90.69
3	25700	17405	2331	90.93
4	23950	15250	1820	92.40
5	23600	13700	3000	87.29
6	21200	10250	1060	95.00
7	12550	8650	1440	88.53
8	6150	1960	1138	81.49
9	5620	1820	936	83.34
10	5780	2980	1224	78.82
11	4780	1500	974	79.62
12	4360	961	809	81.44
13	3460	1030	847	75.52

Table 4.2: Biological Oxygen Demand Profile

BOD	Untreated	Treated	Permeate	%
1	861	832.5	529.5	38.50
2	1123.5	1066.5	673.5	40.05
3	1647.5	1600	860	47.80
4	2247	2049	1131	49.67
5	2255	2006	999	55.70
6	2544	1758	654	74.29
7	807	594	276	65.80
8	831	462	360	56.68
9	781	456	332	57.49
10	772.5	435	365	52.75
11	759	420	327.5	56.85

12	642	459	276	57.01
13	639	426	264	58.68

Table 4.3: Total Suspended Solid Profile

Day 1		Before	After	Difference	mg/L	TSS	%
U	1	0.1534	0.2692	0.1158	11580	12080	99.67
	2	0.1525	0.2783	0.1258	12580		
T	1	0.1524	0.198	0.0456	4560	9950	
	2	0.151	0.2049	0.0539	5390		
P	1	0.1521	0.1525	0.0004	40	40	
Day 2		Before	After	Difference	mg/L	TSS	%
U	1	0.1528	0.3214	0.1686	16860	18270	99.78
	2	0.1527	0.3495	0.1968	19680		
T	1	0.1521	0.246	0.0939	9390	10765	
	2	0.1536	0.275	0.1214	12140		
P	1	0.1522	0.1526	0.0004	40	40	
Day 3		Before	After	Difference	mg/L	TSS	%
U	1	0.1539	0.3701	0.2162	21620	18580	99.17
	2	0.1536	0.309	0.1554	15540		
T	1	0.1545	0.3168	0.1623	16230	15225	
	2	0.154	0.2962	0.1422	14220		
P	1	0.1521	0.1552	0.0031	155	155	
Day 4		Before	After	Difference	mg/L	TSS	%
U	1	0.1542	0.3791	0.2249	22490	21515	99.77
	2	0.1549	0.3603	0.2054	20540		
T	1	0.1528	0.2965	0.1437	14370	13600	
	2	0.1533	0.2816	0.1283	12830		
P	1	0.1533	0.1538	0.0005	50	50	
Day 5		Before	After	Difference	mg/L	TSS	%
U	1	0.1525	0.2754	0.1229	12290	20360	97.54
	2	0.1538	0.2381	0.0843	8430		
T	1	0.1533	0.3252	0.1719	17190	19940	
	2	0.1524	0.3793	0.2269	22690		
P	1	0.1518	0.1618	0.01	1000	1000	

Day 6		Before	After	Difference	mg/L	TSS	%
U	1	0.1545	0.2489	0.0944	9440	9330	98.71
	2	0.1534	0.2456	0.0922	9220		
T	1	0.1535	0.2472	0.0937	9370	6170	
	2	0.1516	0.1813	0.0297	2970		
P	1	0.1515	0.1527	0.0012	120	120	
Day 7		Before	After	Difference	mg/L		%
U	1	0.1525	0.1857	0.0332	3320	3085	99.67
	2	0.1531	0.1816	0.0285	2850		
T	1	0.1528	0.1902	0.0374	3740	3590	
	2	0.152	0.1864	0.0344	3440		
P	1	0.1531	0.1533	0.0002	20	20	
Day 8		Before	After	Difference	mg/L		%
U	1	0.1536	0.1838	0.0302	3020	3065	97.71
	2	0.1535	0.1846	0.0311	3110		
T	1	0.1545	0.1885	0.034	3400	3055	
	2	0.1544	0.1815	0.0271	2710		
P	1	0.1539	0.1546	0.0007	70	70	
Day 9		Before	After	Difference	mg/L		%
U	1	0.1526	0.1843	0.0317	3170	3895	95.38
	2	0.1512	0.1974	0.0462	4620		
T	1	0.1522	0.1838	0.0316	3160	3285	
	2	0.1532	0.1873	0.0341	3410		
P	1	0.1528	0.1546	0.0018	180	180	
Day 10		Before	After	Difference	mg/L		%
U	1	0.1525	0.2102	0.0577	5770	6095	98.52
	2	0.1529	0.2171	0.0642	6420		
T	1	0.1537	0.1704	0.0167	1670	2425	
	2	0.1534	0.1852	0.0318	3180		
P	1	0.1517	0.1526	0.0009	90	90	
Day 11		Before	After	Difference	mg/L		%
U	1	0.153	0.1793	0.0263	2630	2760	95.29
	2	0.1532	0.1821	0.0289	2890		
T	1	0.1521	0.1862	0.0341	3410	2300	
	2	0.1528	0.1647	0.0119	1190		
P	1	0.152	0.1533	0.0013	130	130	

Day 12		Before	After	Difference	mg/L		%
U	1	0.1529	0.1803	0.0274	2740	2420	91.32
	2	0.1509	0.1719	0.021	2100		
T	1	0.1523	0.1734	0.0211	2110	2350	
	2	0.152	0.1779	0.0259	2590		
P	1	0.1508	0.1529	0.0021	210	210	
Day 13		Before	After	Difference	mg/L		%
U	1	0.1511	0.1672	0.0161	1610	1580	91.77
	2	0.1521	0.1676	0.0155	1550		
T	1	0.1518	0.1676	0.0158	1580	1560	
	2	0.1518	0.1672	0.0154	1540		
P	1	0.1495	0.1508	0.0013	130	130	

Table 4.4: Volatile Suspended Solid

Day 1		After	Difference	mg/L	VSS	VSS Fraction	%
U	1	0.1738	0.0954	9540	10300	78.97350993	100
	2	-	-	-			
T	1	0.1849	0.0131	1310	2375	23.86934673	
	2	0.1705	0.0344	3440			
P	1	0.1525	0	0	0	0	
Day2		After	Difference	mg/L		VSS	%
U	1	0.2011	0.1203	12030	13660	74.76737822	100
	2	0.1966	0.1529	15290			
T	1	0.1701	0.0759	7590	9300	86.39108221	
	2	0.1649	0.1101	11010			
P	1	0.1526	0	0	0	0	
Day 3		After	Difference	mg/L		VSS	%
U	1	0.2053	0.1648	16480	13910	74.86544672	99.28
	2	0.1956	0.1134	11340			
T	1	0.1944	0.1224	12240	11410	74.94252874	
	2	0.1904	0.1058	10580			
P	1	0.1532	0.002	100	100	6.451612903	

Day 4		After	Difference	mg/L		VSS	%
U	1	0.2116	0.1675	16750	16030	74.50615849	99.81
	2	0.2072	0.1531	15310			
T	1	0.1925	0.104	10400	9970	73.30882353	
	2	0.1862	0.0954	9540			
P	1	0.1535	0.0003	30	30	60	
Day 5		After	Difference	mg/L		VSS	%
U	1	0.1825	0.0929	9290	15800	77.60314342	95.88
	2	0.1762	0.0619	6190			
T	1	0.1909	0.1343	13430	15290	76.68004012	
	2	0.2078	0.1715	17150			
P	1	0.1553	0.0065	650	650	65	
Day 6		After	Difference	mg/L		VSS	%
U	1	0.1819	0.067	6700	6640	70.33898305	99.25
	2	0.1798	0.0658	6580			
T	1	0.1728	0.0744	7440	4790	77.63371151	
	2	0.1599	0.0214	2140			
P	1	0.1522	0.0005	50	50	41.66666667	
Day 7		After	Difference	mg/L		VSS	%
U	1	0.1619	0.0238	2380	2210	71.636953	99.55
	2	0.1612	0.0204	2040			
T	1	0.1631	0.0271	2710	2590	72.1448468	
	2	0.1617	0.0247	2470			
P	1	0.1532	1E-04	10	10	50	
Day 8		After	Difference	mg/L		VSS	%
U	1	0.1685	0.0153	1530	1965	64.11092985	97.96
	2	0.1606	0.024	2400			
T	1	0.1621	0.0264	2640	2195	71.84942717	
	2	0.164	0.0175	1750			
P	1	0.1542	0.0004	40	40	57.14285714	
Day 9		After	Difference	mg/L		VSS	%
U	1	0.1609	0.0234	2340	2855	73.29910141	96.15
	2	0.1637	0.0337	3370			
T	1	0.1619	0.0219	2190	2315	70.4718417	
	2	0.1629	0.0244	2440			
P	1	0.1535	0.0011	110	110	61.11111111	

Day 10		After	Difference	mg/L		VSS	%
U	1	0.1607	0.0495	4950	4750	82.32235702	98.74
	2	0.1716	0.0455	4550			
T	1	-	-	-	2180	89.89690722	
	2	0.1634	0.0218	2180			
P	1	0.152	0.0006	60	60	66.66666667	
Day 11		After	Difference	mg/L		VSS	%
U	1	0.1602	0.0191	1910	1980	75.2851711	97.47
	2	0.1616	0.0205	2050			
T	1	0.1572	0.029	2900	1905	82.82608696	
	2	0.1556	0.0091	910			
P	1	0.1528	0.0005	50	50	38.46153846	
Day 12		After	Difference	mg/L		VSS	%
U	1	0.1606	0.0197	1970	1730	71.48760331	97.68
	2	0.157	0.0149	1490			
T	1	0.1587	0.0147	1470	1665	70.85106383	
	2	0.1593	0.0186	1860			
P	1	0.1525	0.0004	40	40	19.04761905	
Day 13		After	Difference	mg/L		VSS	%
U	1	-	-	-	1160	73.41772152	93.10
	2	0.156	0.0116	1160			
T	1	0.1562	0.0114	1140	1130	72.43589744	
	2	0.156	0.0112	1120			
P	1	0.15	0.0008	80	80	61.53846154	

Table 4.5: Methane gas composition

Day	% Gas
1	28
2	45
3	56
4	70
5	74
6	81.5
7	79.6
8	78
9	82.14
10	80.3
11	79.6
12	76.9
13	77.7

Table 4.6: pH

	U	T	P
1	7.2	7.11	7.81
2	7.01	6.98	7.77
3	6.96	6.86	7.72
4	7.22	7.40	7.84
5	7.23	7.35	8.14
6	7.32	7.38	8.06
7	7.41	7.48	7.98
8	7.35	7.43	8.05
9	7.29	7.37	8.00
10	7.44	7.52	8.17
11	7.48	7.81	8.27
12	7.34	7.44	8.12
13	7.43	7.52	8.26

Table 4.7: Membrane flux

	Permeate volume (L)	Flux (L/m3.h)	% reduction
1	2.24	9.33	0
2	2.03	8.46	0.09375
3	1.81	7.54	19.19642857
4	1.83	7.63	18.30357143
5	2.44	10.17	0
6	2.26	9.42	7.37704918
7	2.15	8.96	11.8852459
8	1.88	7.83	22.95081967
9	1.66	6.92	31.96721311
10	1.58	6.58	35.24590164
11	1.52	6.33	37.70491803
12	1.55	6.46	36.47540984
13	1.52	6.33	37.70491803