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**BIOMETHANATION OF PALM OIL MILL EFFLUENT (POME) BY ULTRASONIC-
ASSISTED MEMBRANE ANAEROBIC SYSTEM (UMAS)**

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ABSTRACT

This study mainly focussed on methane production (CH₄) from palm oil mill effluent (POME) by using Ultrasonic Membrane Anaerobic System (UMAS). Design of anaerobic reactor was applied in order to design experimental work which was 100 L volume digester of Ultrasonic Membrane Anaerobic System (UMAS). The parameters of UMAS such as COD, BOD, pH, TSS and VSS were studied. Reactor was operated under ambient temperature within the range ~30 to 35 °C. POME continuous up-flow feeding from the side flow into the anaerobic reactor and effluent samples has taken from the reactor after 5 hours for analysis of the parameters at each batch of HRT. The start-up of the UMAS reactor was involved step increasing in influent organic volumetric loading rates from higher retention time to lower retention time of 392.16, 128.21, 119.05, 111.11, and 98.04 days. The acclimatization was done within 4 to 9 days to allow all the microorganisms present in the mixed liquor perfectly acclimatized to the new environmental. Mixture of methane and carbon dioxide gases produced was collected by using syringe. NaOH or KOH was filled in the syringe in order to adsorb the carbon dioxide (CO₂) from the methane gas. The developed UMAS was effective process that has more excellent performance in methane production by encountering the membrane fouling hence decreased the retention time. The amount of methane gas obtained was about 92 %. The COD content can be reduced up to 87.22 % reduction from the original by complete treatment.

KEYWORDS: UMAS, Membrane, COD reduction, HRT, Methane gas, POME.

INTRODUCTION

Palm oil mill effluent (POME) is the wastewater which is generated during the production process of palm oil. POME is a non-toxic thick brownish liquid waste, which has an unpleasant odour. It contains high amounts of total solids, oil and grease, with high concentration of COD and BOD. (Faisal and Unno, 2001; Najafpour et al., 2006; Borja and Banks, 1994; Choorit and Wisarnwan, 2007) About 0.67 tonne of POME is generated for every tonne of fresh fruit bunch (FFB) processed. POME is a colloidal suspension that contains 95-96 % of water, 0.6-0.7 % of oil and grease and 4-5% of total solids including 4-5% suspended solids originated from the mixture of sterilized condensate, separator sludge and hydrocyclone wastewater (Borja, R., Banks, C.J., , 1994c.). It is a thick brownish color liquid and discharged at a temperature between 80 and 90 °C. It is fairly acidic with pH ranging from 4.0-5.0.

POME is a highly polluting wastewater with high chemical oxygen demand (COD) and biochemical oxygen demand (BOD) in which can caused severe

pollution to the environment, typically pollution to water resources. Thousands of tons of landfill waste that produce methane can be eliminate by using methane digesters because the landfill wastes may cause global warming and the reduction of fossil fuels for the purpose of transportation (Abdurahman, N. H., Rosli, Y. M., Azhari, N. H., & Tam, S. F., 2011). 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 (Droste, R. L., (1997).). According to (Lam, M. K., & Lee, K. T., (2011).) nowadays palm oil millers have two choices in running biogas plants which are: (a) methane produces can be converted into electricity and fed into power grid, owned by Tenaga Nasional Bhd (TNB) and (b) methane produced can be injected into the pipeline, owned by Gas Malaysia Sdn Bhd.

Anaerobic digestion is one of the most widely used processed in the world and aims to stabilize the bio solid waste such as from the agro and municipal waste

to industrial waste as well as for the treatment of organic sludge in wastewater treatment facilities (Björnsson, 2000; Hartman and Ahring, 2005; Davidsson et al, 2007; Lin et al, 2011). Ultrasound has been widely used as a method for cleaning materials because of the cavitation phenomenon and proved to be able to enhance membrane permeability of solvent and permeate through membrane, facilitate improved separation rate and mitigate membrane fouling effectively in-cross flow filtration of macromolecules (Okahata and Naguchi, 1983; Kabayash et al., 1999; Li et al, 2002; Kobayashi et al., 2003; Muthukumaran et al., 2005). The advantages of this process are the low-energy requirement involved in ultrasound and high binding capacity of the polymers (Chaufer and Deratani, 1988; Noble, R. D. & Stern, S. A., (1995).). The first objective of this study is to evaluate the application of UMAS in wastewater treatment. The second objective is to examine the efficiency of UMAS in the production of methane by treating POME compared to MAS. The third objective is to produce methane gas (CH₄) by investigating the kinetic parameters of UMAS.

MATERIALS AND METHODS

Materials (Feed Substrates)

The feed substrate (raw POME) samples were obtained from (Dominic Square) LKPP, Pahang and adjusted from a COD concentration ranging from 540 to 5472 mg/L to the desired COD concentration

(approximately 900 to 3000 mg/L). Initial characterizations of the raw samples such as COD, BOD₅, TSS, VSS, pH and turbidity will be measured.

Table 1: The Characteristics of the Raw POME obtained from LKPP, Pahang

Parameter	Concentration
COD (mg/L)	900-3000
BOD ₅ (mg/L)	500-2000
TSS (mg/L)	30
Ammoniacal Nitrogen (mg/L)	400
Nitrate (mg/L)	15
pH	5-13

**Except pH, all other parameters are in mg/L*

Methods

The schematic diagram of UMAS reactor is shown in Figure 1. The UMAS reactor consists of a cross flow ultra-filtration membrane (CUF) apparatus, a centrifugal pump, and an anaerobic digester. The anaerobic digester reactor design configuration is depicted in Figure 1. The reactor was composed of clear PVC with an inner diameter of 15 cm and a total height of 100 cm. The working volume was 50.0 litres and aluminium foils were used to cover up the whole surface of reactor in order to prevent reaction between the POME and the light. The operating pressure for this study was maintained to 5 bars by manipulating the gate valve at the retentive line after the CUF unit.

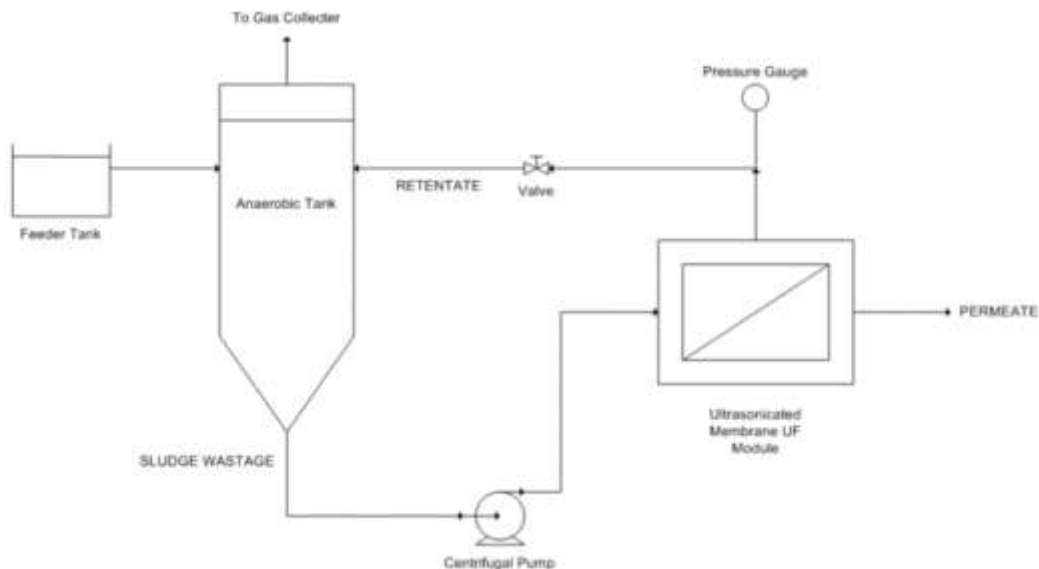


Figure 1 : Experimental Set-up

Reactor was operated under ambient temperature (~30-35 °C). POME is continuous up-flow feeding from the side flow into the anaerobic reactor. HRT was adjusted volumetrically through controlling the flow rate of the influent feed. Effluent samples were taken from the reactor after 5 hours for analysis at each batch of HRT with the manual pump. The samples were subjected to the analysis of the following parameters such as COD, pH, alkalinity, suspended solids and volatile suspended solids based on the Gerardi, M.H. the standard methods for water and wastewater analysis. (Gerardi, M.H., 2006.). The start-up of the UMAS reactor involved step increasing in influent organic volumetric loading rates from higher retention time of 30, 25, 20, 15, 10 and 5 days. The acclimatization phase was used to feed flow-rate of 0.375L which correspond to the HRT of 4 days for about 9 days to allow all the microorganisms present in the mixed liquor perfectly acclimatized to the new environmental.

DETERMINATION OF PARAMETERS

Determination of Biochemical Oxygen Demand (BOD₅)

Dilution water is prepared by adding 1 mL of each phosphate buffer, magnesium sulphate, calcium chloride, ferric chloride solution into 1 L volumetric flask. Distilled water is added to 1 L. For determination BOD₅, 10 mL of POME is diluted to 300 mL in a 500 mL beaker. The pH value is adjusted to the range of 6.5-7.5 by adding acid or alkali. All prepared samples are controlled in 300 mL incubation bottle respectively. Dissolved oxygen (DO) concentration is measured for each sample by using Dissolved Oxygen Meter and all the data are tabulated in a table. Water is added to the flared mouth of bottle and cover up by aluminium foil. All the bottles are kept in BOD incubator for five days by setting the temperature to 20 °C. Final DO value is measured after five days later.

Determination of Total Suspended Solid (TSS)

A filter disk is dried in the oven at 103 °C to 105 °C for 1 hour, cooled in desiccators and is weight. Filtering apparatus is assembled to begin suction. The filter is wet with a small volume of distilled water to seat it. 50 mL of water sample (mixed to ensure homogeneity) is pipette onto center of filter disc in a Buchner flask by using gentle suction (under vacuum). Filter is washed three successive 10 mL volumes of distilled water, allowing complete drainage between washings, and suction process is continued for about 3 min after filtration is complete. Filter is carefully removed from filtration apparatus and is transferred to

aluminium weighing dish/crucible dish as a support. The sample is dried at least 1 hour at 103 °C to 105 °C in an oven, then is allowed to cool in desiccator to balance temperature and weigh. The cycle of drying, cooling, desiccating, weighing are repeated until a constant weight is obtained.

Determination of Volatile Suspended Solid (VSS)

The sample from TSS testing is continuously heated in furnace at 550 °C for about half an hour. Then the sample is allowed to cool in desiccator to balance temperature and weigh.

Determination of Chemical Oxygen Demand (COD)

100 mL of wastewater sample is homogenized for 30 seconds in a blender. Notice here that homogenization time need to be increased if the samples containing large amounts of solids. The homogenized sample is poured into a 250 mL beaker and is stirred gently with a magnetic stir plate. This step is done for the 200 – 15 000 mg/L sample or to improve accuracy and reproducibility of the other ranges. Both of these steps are omitted if the sample does not contain suspended solid. COD reactor is preheated to 150 °C and the safety shield is placed in front of the reactor. The caps are removed from two COD Digestion Reagent Vials (20-1500 ppm). The first vial is hold at a 45° angle. A clean volumetric pipette is used to add 2.00 mL of sample to the vial. This is the prepared sample. The same procedure is repeated for the second vial but 2.00 mL of de-ionized water is pipette to the vial instead of the wastewater. This is the blank. The vials are cap tightly, rinsed with de-ionized water and are wiped with a clean paper towel. The vials are hold by the cap over a sink and gently invert for several times to mix. The vials are placed and preheated in the preheated COD Reactor. After heated the vials for two hours, the vials are allowed to cool to 120 °C for about 20 minutes. Each vial is inverted for several times while still warm, and then are allowed to cool down at room temperature. For setting up the COD Reactor, program for 435 COD HR (High Range/High Range Plus) is selected. The outside of the vials need to be cleaned with a damp towel followed by a dry one to remove fingerprints. 16 mm adapter is installed and the blank is placed into the adapter.

Determination of Ammonia-Nitrogen and Nitrate-Nitrogen

In the ammonia-nitrogen part, Ammonia Salicylate Powder Pillow and Ammonia Cyanurate Reagent Powder Pillow were added to the wastewater samples while NitraVer 5 Nitrate Reagent Powder Pillow was

added for the determination of nitrate. After two hours, wastewater samples reading were recorded.

RESULTS & DISCUSSION

Results

The prepared syringe was used to measure the daily gas volume. The produced biogas contained only CO₂ and CH₄, so a portion sodium hydroxide solution

(NaOH) was added into the syringe to absorb the CO₂ affectively by isolating the CH₄ gas. There are some different parameters were studied through this study such as COD, BOD, TSS and VSS. The biological treatment (anaerobic system) is incorporated with ultrasonic to treat POME and this combination gave high COD removal rate up to 87.22 % only in a short time. The amount of methane gas obtained was about 92 %.

Table 2: Initial Measurements of POME

Parameters	Initial Measurement
pH	5.01
Temperature (°C)	35.0
COD (mg/L)	2560.0
BOD (mg/L)	183.0
TSS (mg/L)	231.5
VSS (mg/L)	189.02
Methane Production (%)	0.0

Ultrasonic Membrane Anaerobic System (UMAS) Performance

Table 3: Summary Results of UMAS Performance

Steady state	COD permeate	% Methane	Ammonia Nitrogen	HRT	COD Removal (%)	TSS Removal (%)	BOD Removal (%)
1	795	-	387.04	393.54	91.77	87	85.30
2	802	-	380.52	392.67	91.69	87.34	83.76
3	835	-	380.02	245.34	91.35	87.89	82.09
4	868	-	370.45	222.09	91.01	88.56	80.56
5	872	-	365.78	198.05	90.96	88.92	80.40
6	969	94	341.23	185.26	89.77	89.73	78.09
7	988	93	293.45	183.01	89.77	89.88	76.52
8	1096	87	282.15	128.22	88.65	90.02	76.32
9	1195	92	281.03	124.34	87.62	90.35	76.14
10	1234	92	279.65	104.55	87.22	91.21	76.10

All are unit mg/L except HRT (day), Methane and COD, TSS and BOD Removal in %

Table 3 summarizes UMAS performance at five steady states, which were established at different influent of COD concentrations. At first steady state, the TSS concentration was about 14.8 mg/L compared to the last run which is 18.7 mg/L. this indicates that the long solid retention time (SRT) of UMAS assisted

the decomposition of the suspended solids and their subsequent conversion to methane gas. The highest COD was recorded at the fifth steady-state (1234 mg/L). At this organic loading rate (HRT) the UMAS achieved 87.22 % COD removal. The color of treated POME (permeate) by UMAS was very clear compare to the raw POME as shown in Appendix A.1.

DISCUSSIONS

COD Removal with Hydraulic Retention Time

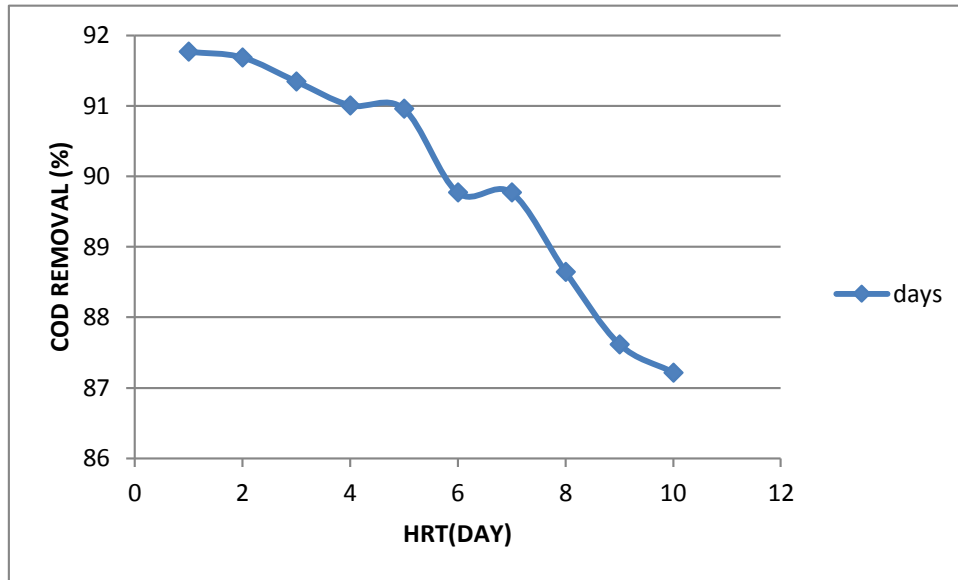


Figure 2 COD Removal by UMAS with various retention times

Figure 2 shows the COD removal by UMAS with various retention times. As the HRT increased from 104.55 to 393.54 days, the COD removal also increased. COD removal was reduced as the HRT decreased on the tenth steady state which is about 87.22 % as a result of washout phase in the reactor since the concentration in the system has increased. The COD removal observed for POME treatment

reported by (Alvarado-Lassman, A., Rustrían, E., García-Alvarado, M.A., Rodríguez-Jiménez, G.C.,Houbron, E., , 2008.) was about 80-90 % by using inverse flow anaerobic fluidized bed while 78-94 % COD removal observed using fluidized bed reactor in treating POME was reported by (Borja, R., Banks, C.J., , 1995b).

TSS Removal with Hydraulic Retention Time

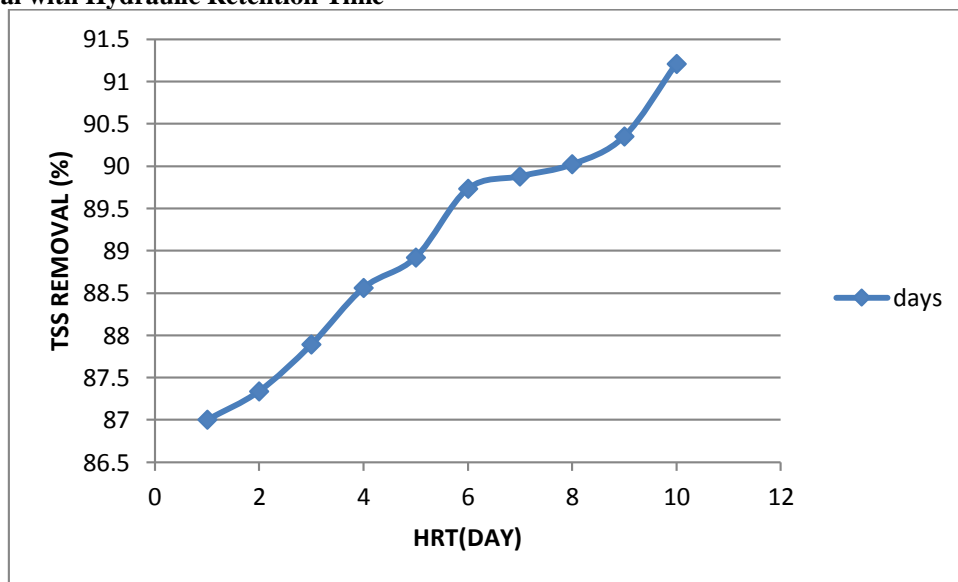


Figure 3: TSS Removal by UMAS with various retention times

Figure 3 shows the data for TSS permeate collected of UMAS under steady-state conditions with various hydraulic retention times. At first steady state, the TSS removal was about 87.0 % compared to the last run which is 91.21 %. This indicates that the long solid

BOD Removal with Hydraulic Retention Time

retention time (SRT) of UMAS assisted the decomposition of the suspended solids and their subsequent conversion to methane gas.

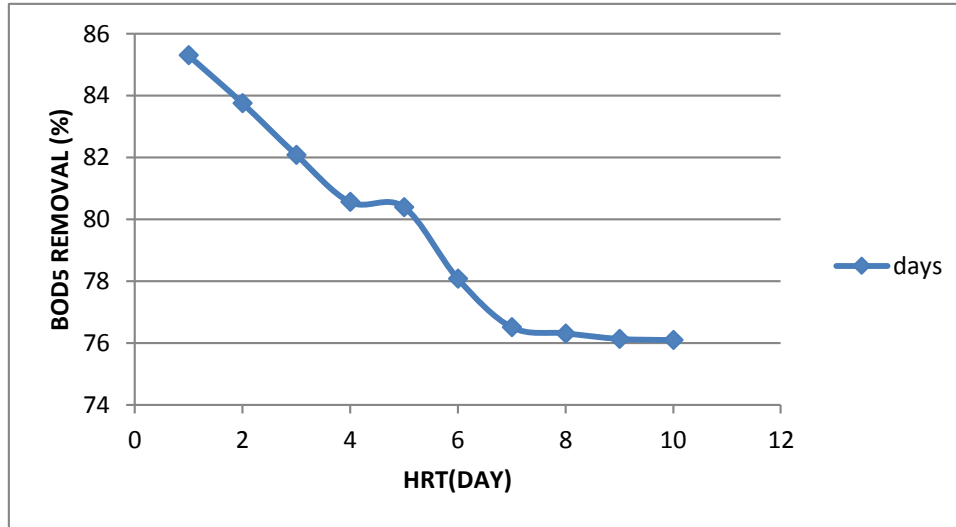


Figure 4: BOD Removal by UMAS with various retention times

Figure 4 shows the BOD collected of UMAS under steady-state conditions with various hydraulic retention times. The BOD removal collected for once in each 4 days was decreased as HRT increased from 104.55 to 393.54 days and was in the range of 85.3 – 76.1 %. As the HRT decreased, the BOD will be decreased.

CONCLUSIONS

The designed Ultrasonic Membrane Anaerobic System (UMAS) was found to be an effective method in treating POME as the volume of reactor required was smaller than conventional method. This combination treatment was successfully treated POME by removing COD about 87.22 % only in a short time. The ultrasonic membrane anaerobic system, UMAS seemed to be adequate for the biological treatment of undiluted slaughterhouse wastewater, since reactor volumes are needed which are considerably smaller than the volumes required by the conventional digester. In addition, the amount of methane gas captured was 92 % which was quite high and satisfactory.

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APPENDICES



FIGURE 1: Obtained raw sample (POME) at the discharge point



FIGURE 2: POME inside the reactor (acclimatization phase)



Figure 3: POME before treated



Figure 4: POME after treated



Figure 5: Filter paper before (TSS test)



Figure 6: Filter paper after dried for one hour (TSS test)