

Effect of Organic Loading Rate on the Performance of Ultrasonic-Assisted Membrane Anaerobic System (UAMAS) in Treating Palm Oil Mill Effluent (POME)

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Abstract: The primary objective of this study was to evaluate the effects of organic loading rate (OLR) on the performance of ultrasonic-assisted membrane anaerobic system (UAMAS) in treating Palm Oil Mill Effluent (POME), based on the following indicators: (i) methane gas contents; (ii) chemical oxygen demand (COD) removal efficiency; and (iii) effluent variability (phenol, suspended solids, volatile fatty acids, and pH stability). Six steady states were attained as a part of a kinetic study that considered concentration ranges of 15,830 to 21,600 mg/l for mixed liquor suspended solids (MLSS) and 9,450 to 18,200 mg/l for mixed liquor volatile suspended solids (MLVSS). Kinetic equations from Monod, Contois and Chen & Hashimoto were employed to describe the kinetics of POME treatment at organic loading rates ranging from 0.5 to 15 kg COD/m³/d. The removal efficiency of COD was from 93 to 98.7 % with hydraulic retention time, HRT of 4 days. The growth yield coefficient, Y was found to be 0.59 g VSS/g COD the specific microorganism decay rate was 0.26 d⁻¹ and the methane gas yield production rate was between 0.264 l/g COD/d and 0.47 l/g COD/d.

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1.0 Introduction

Palm oil mill effluent (POME) waste is characterized by a high content of organic matter and pathogenic organisms. The disposal of POME without adequate treatment can cause a drastic effect on the environment and human health. Typically, 1.0 ton of crude palm oil production requires 5.0-7.5 ton of water; over 50.0 % of which ends up as POME. Moreover, POME was high in organic content (COD 50.0 g/l, BOD 25.0 g/l) and contains appreciable amounts of plant nutrient (Borja et al., 1996; Singh et al., 1999; Ahmad et al., 2005). If discharged, the untreated POME can cause considerable environmental problems. With increasing demand for energy and cost effective environmental protection, anaerobic digestion biotechnology has become the focus of worldwide attention (Singh et al., 1999). Moreover, it offers a positive environmental impact since it combines waste stabilization with net fuel production and allows the use of the effluent as fertilizer. POME consists of various suspended components. POME nutrient content is too low for aerobic treatment process, but sufficient for anaerobic process (Chin et al., 1996). According to the most common characteristics of this waste, anaerobic digestion could be considered one of the most promising treatment alternatives (Kimchie et al., 1988; Hobson and Shaw, 1973; Hobson, 1974, 1981, 1992; Sanchez et al., 1995; Baader, 1990; Yang and

Gan, 1998; Parkin and Owen, 1986). In anaerobic wastewater treatment, loading rate plays an important role. In the case of nonattached biomass reactors, where the hydraulic retention time is long, overloading results in biomass washout. This, in turn, leads to process failure. Fixed film, expanded and fluidized bed reactors can withstand higher organic loading rate. Even if there is a shock load resulting in failure, the system is rapidly restored to normal. In comparison to a CSTR system, fixed film and other attached biomass reactors have better stability. Moreover, high degree of COD reduction is achieved even at high loading rates at a short hydraulic retention time. Several studies using membrane anaerobic processes to treat a variety of wastewaters (Fakhru'l et al., 1994; Nagano et al., 1992). Table 1 gives the recommended COD loading rates with various reactor configurations. Anaerobic fluidized bed appears to withstand maximum loading rate compared to other high rate reactors. The three widely used kinetic models considered in this study are shown in Table 2. This paper aims to introduce a new technique of ultrasonic-assisted-membrane anaerobic system (UAMAS) in treating POME as well as producing high methane (no membrane fouling) and to determine the kinetic parameters of the process, based on three known models; (Monod, 1949), Contois (1959) and Chen and Hashimoto (Chen et al., 1980).

Table 1: Recommended COD loading rates with various reactor configurations

Anaerobic reactor type	Start up period	Channeling effect	Effluent recycle	Gas separation device	Carrier packing	Typical loading rates (kg COD/m ³ day)	HRT (d)
CSTR	-	Not present	Not required	Not required	Not essential	0.25-3	10-60
UASB	4-16	Low	Not required	Essential	Not essential	10-30	0.5-7
Anaerobic filter	3-4	High	Not required	Beneficial	Essential	1-4	0.5-12
AAFEB	3-4	Less	Required	Not required	Essential	1-50	0.2-5
(AFB)	3-4	Non-existent	Required	Beneficial	Essential	1-100	0.2-5

Table 2: Mathematical expressions of specific substrate utilization rates for known kinetic models

Kinetic Model	Equation 1	Equation 2
Monod	$U = \frac{k S}{k_s + S}$	$\frac{1}{U} = \frac{K_s}{K} \left(\frac{1}{S} \right) + \frac{1}{k}$ [14]
Contois	$U = \frac{U_{\max} \times S}{Y(B \times X + S)}$	$\frac{1}{U} = \frac{a \times X}{\mu_{\max} \times S} + \frac{Y(1+a)}{\mu_{\max}}$ [15]
Chen & Hashimoto	$U = \frac{\mu_{\max} \times S}{Y K S_o + (1-K) S Y}$	$\frac{1}{U} = \frac{Y K S_o}{\mu_{\max} S} + \frac{Y(1-K)}{\mu_{\max}}$ [16]

2. Materials and methods

Raw POME was treated by UAMAS in a laboratory digester with an effective 200-litre volume. Fig. 1 presents a schematic representation of the ultrasonic-assisted membrane anaerobic system (UAMAS) which consists of a cross flow ultra-filtration membrane (CUF) apparatus, a centrifugal pump, and an anaerobic reactor. 25 KHz multi frequency ultrasonic transducers connected into the MAS system. The ultrasonic frequency is 25 KHz, with 6 units of permanent transducers and bonded to the two (2) sides of the tank chamber and connected to one (1) unit of 250 watts 25 KHz Crest's Genesis Generator. The UF

membrane module had a molecular weight cut-off (MWCO) of 200,000, a tube diameter of 1.25 cm and an average pore size of 0.1 μm . The length of each tube was 30 cm. The total effective area of the four membranes was 0.048 m². The maximum operating pressure on the membrane was 55 bars at 70 °C, and the pH ranged from 2 to 12. The reactor was composed of a heavy duty reactor with an inner diameter of 25 cm and a total height of 250 cm. The operating pressure in this study was maintained between 2 and 6 bars by manipulating the gate valve at the retentate line after the CUF unit.

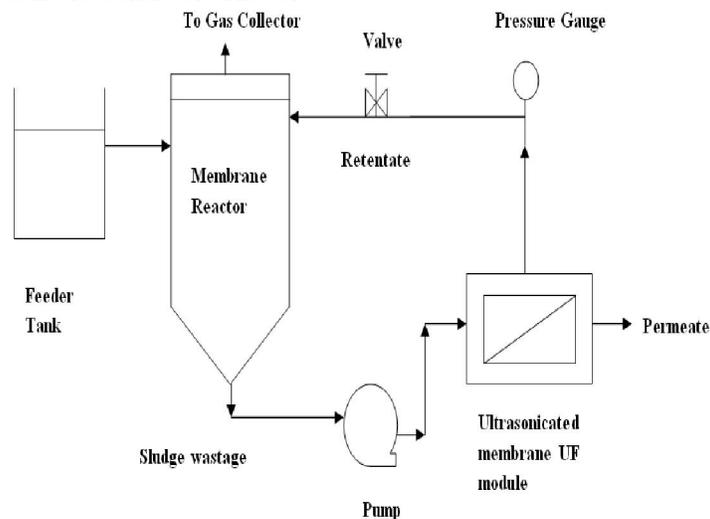
**Fig.1.** Experimental set-up of UAMAS



Fig. 2. Experimental schematic for UAMAS

2.1 Palm oil mill effluent

Raw POME samples were collected from a palm oil mill in Kuantan-Malaysia. The wastewater was stored in a cold room at 4°C prior to use. Samples analyzed for chemical oxygen demand (COD), total suspended solids (TSS), pH, volatile suspended solids (VSS), substrate utilization rate (SUR), and specific substrate utilization rate (SSUR).

2.2 Bioreactor operation

The ultrasonic-assisted membrane anaerobic system, UAMAS Performance was evaluated under six

steady-states with influent COD concentrations ranging from (57,000 to 77,000 mg/L) and organic loading rates (OLR) between (0.5 and 15 kg COD/m³/d). In this study, the system was considered to have achieved steady state when the operating and control parameters were within ± 10% of the average value. A 20-litre water displacement bottle was used to measure the daily gas volume. The produced biogas contained only CO₂ and CH₄, so the addition of sodium hydroxide solution (NaOH) to absorb CO₂ effectively isolated methane gas (CH₄).

Table 3: Summary of results (SS: steady state)

Steady State (SS)	1	2	3	4	5	6
COD feed, mg/L	57000	62000	70600	63000	69200	77000
COD permeate, mg/L	741	1860	2824	4410	3668	5390
Gas production (L/d)	277.8	334.4	381	484	520	580
Total gas yield, L/g COD/d	0.473	0.361	0.445	0.430	0.374	0.290
% Methane	77	74.0	71.8	68.4	73.0	67.8
Ch ₄ yield, l/g COD/d	0.470	0.431	0.411	0.394	0.295	0.264
MLSS, mg/L	15830	14815	16169	19400	21000	21600
MLVSS, mg/L	9450	11200	13000	15481	17325	18200
% VSS	60.00	75.60	80.40	79.8 0	82.50	84.00
HRT, d	16.00	12.00	8.00	6.00	5.00	4.00
SRT, d	860	320	132	32.6	14.56	10.6
OLR, kg COD/m ³ /d	0.5	2.0	4	11.0	13.0	15.0
SSUR, kg COD/kg VSS/d	0.198	0.240	0.261	0.281	0.290	0.320
SUR, kg COD/m ³ /d	0.346	0.852	3.424	6.281	8.552	9.867
Percent COD removal (UAMAS)	98.7	97.0	96.0	93.0	95.0	93.0
VFA feed (mg/L)	360	490	740	870	1300	1480
VFA permeate (mg/L)	402	510	794	940	920	870

Table 4: Results of the application of three known substrate utilization models

Model	Equation	R^2 (%)
Monod	$U^{-1} = 2025 S^{-1} + 3.61$ $K_s = 498$ $K = 0.372$ $\mu_{Max} = 0.261$	95.1
Contois	$U^{-1} = 0.306 X S^{-1} + 2.78$ $B = 0.111$ $u_{Max} = 0.346$ $a = 0.115$ $\mu_{Max} = 0.482$ $K = 0.567$	99.4
Chen & Hashimoto	$U^{-1} = 0.0190 S_o S^{-1} + 3.77$ $K = 0.006$ $a = 0.006$ $\mu_{Max} = 0.351$ $K = 0.383$	98.6

3. Results and discussion

3.1. Semi-continuous ultrasonic-assisted membrane anaerobic system (UAMAS) performance

After a short and successful start up period of UAMAS, Table 3 summarizes the UAMAS performance at six steady-states, which were established at different HRTs and influent COD concentrations. The kinetic coefficients of the selected models were derived from Eq. (2) in Table 2 by using a linear relationship; the coefficients are summarized in Table 4. In this study, the UAMAS pH was maintained in an optimum range (6.8-7) to minimize the effects on methanogens that might biogas production, while the influent COD concentrations was increased from 57,000 to 77,000 mg/L (at six steady states). The organic loading rate, OLR was adjusted by gradually increasing the influent COD and decreasing the HRT. The COD removal efficiencies between 93-98.7% were achieved (Table 3). During this period, influent COD was adjusted in order to obtain OLR values between 0.5 and 15 kg COD/m³/d. a significant

correlation was noted to exist between the influent and effluent COD ($R^2:0.994$), and increasing influent COD resulted in a deterioration of effluent quality in terms of COD, which varied between 741 and 5,390 mg/L, as shown in Fig.3. During the experimental operation period, the initial OLR was set at 0.5 kg COD/m³/d and HRT of 16 days. The OLR then increased to 2.0, 4.0, 11.0, 13.0 and 15.0 kg COD/m³/d by reducing the HRT to 16.0, 12.0, 8.0, 6.0, 5.0, and 4.0 days, correspondingly. At the first steady state, the MLSS concentration was about 15,830 mg/L whereas the MLVSS concentration was 9,450 mg/L, equivalent to 60% of the MLSS. This low result can be attributed to the high suspended solids contents in the POME. At the six steady-states, however, the volatile suspended solids (VSS) fraction in the reactor increased to 84% of the MLSS. This indicates that the long SRT of UAMAS facilitated the decomposition of the suspended solids and their subsequent conversion to methane (CH₄); this conclusion supported by (Nagano et al., 1992).

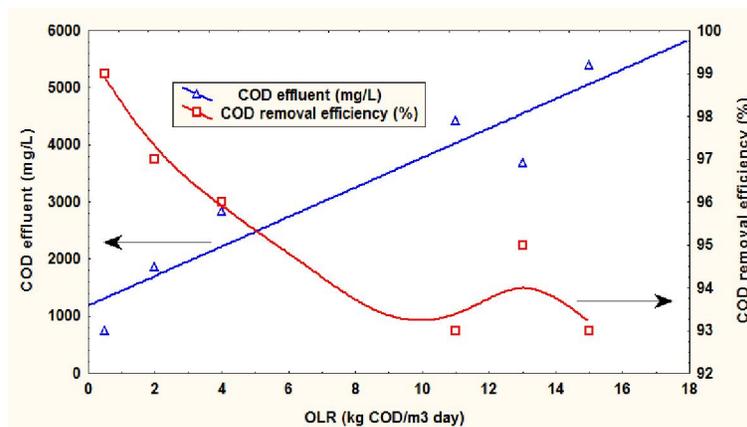


Fig.3: Relationship between OLRs and COD removal efficiency and effect of OLRs on the effluent COD (straight line).

The hydraulic retention time, HRT was determined to be a crucial design criterion, particularly for the treatment of POME effluent with concentrated influent COD. Fig.4 shows the percentages of COD removal efficiency by UAMAS at various HRTs. Short HRT values (4 days) resulted in poor COD removal efficiency (93%) compared to high HRT (16 days) of COD removal of 98.7%. This result was higher than the 85% COD removal observed for POME treatment using anaerobic fluidized bed reactors (Idris et al., 1998) and the 91.7-94.2% removal observed for POME treatment using MAS (Fakhru'l Razi et al., 1999), and the 93.6-97.5% removal observed for

POME treatment using MAS (Abdurahman et al., 2011). At 35°C temperature, the optimum HRT was found to be 16 days giving the highest average COD removal of 98.7%. However, biogas production was highest 16 days HRT and significantly different from that at 12, 8, 6, 5, and 4 days HRT. This was due to the fact that at low HRT with high OLR, the organic matter was degraded to volatile fatty acids (VFA). The HRTs were mainly influenced by the ultra-filtration, UF membrane influx-rates which directly determined the volume of influent (POME) that can be fed to the reactor

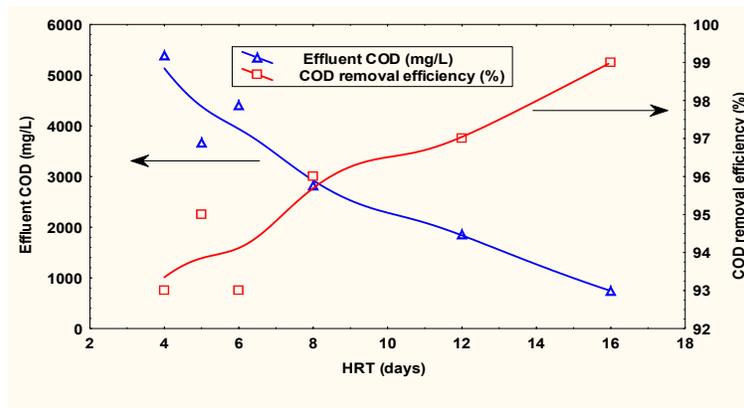


Fig.4: Effect of HRT on COD removal efficiency and effluent COD

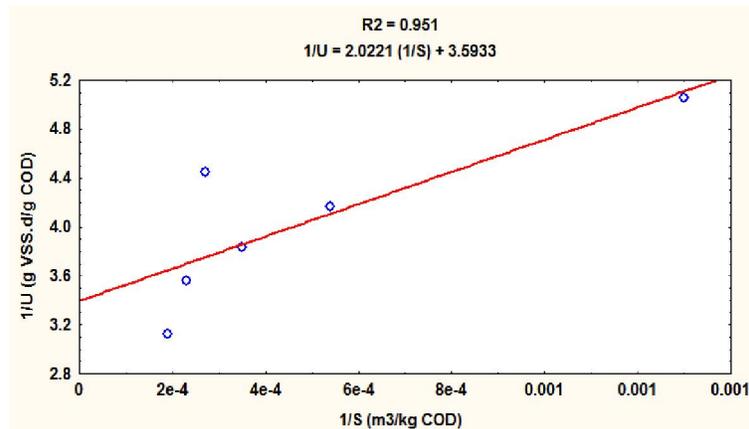


Fig.5. Monod model

The three kinetic models demonstrated a good relationship ($R^2 > 99\%$) for the Ultrasonic assisted membrane anaerobic system treating POME, as shown in Figs. 5-7. The Contois and Chen & Hashimoto models performed better, implying that digester performance should consider organic loading rates. These two models suggested that the predicted

permeate COD concentration (S) is a function of influent COD concentration (S_0). In Monod model, however, S is independent of S_0 . The excellent fit of these three models ($R^2 > 99.4\%$), this study suggests that the UAMAS process is capable of handling sustained organic loads between 0.5 and 15.0 kg m³/d.

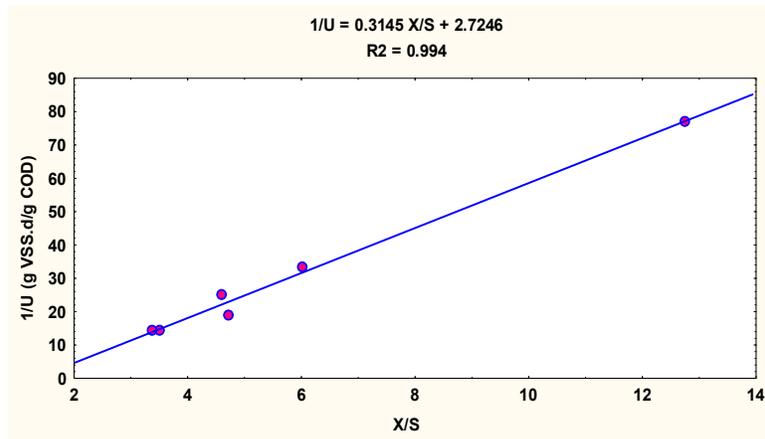


Fig.6. Contois model

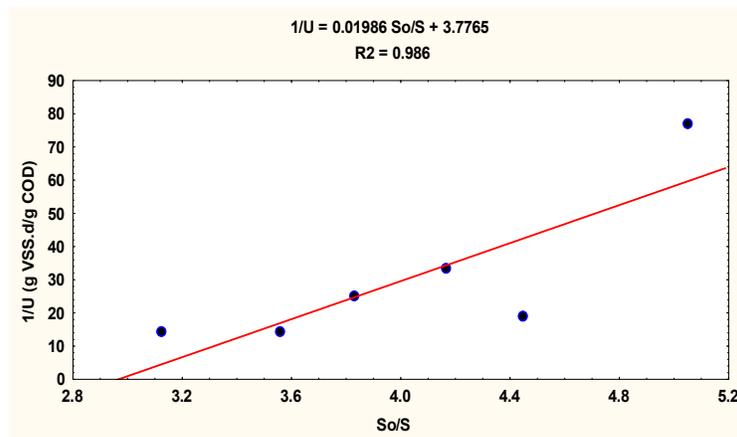


Fig.7. Chen and Hashimoto model

Volatile fatty acids (VFAs) in the influent and effluent were also measured throughout the study. Depending upon the dilution factor, the levels of VFAs in the influent varied between 360 and 1,480 mg/L (Table 3). The measurement of the VFAs indicated that some of the influent COD could be attributed to the VFAs in the effluent, which occurred at concentrations between 402 and 940 mg/L (Fig.4).

3.2 Determination of bio-kinetic coefficients

Table 3 shows the six steady-state results obtained under the different experimental conditions studied for UAMAS. The kinetic coefficients were evaluated and are summarized in Table 4. Substrate utilization rates (SUR) and specific substrate utilization rates (SSUR) were plotted against OLRs as shown in Figure. 8. The SURs had generally increased with increasing OLRs which indicated that the bacterial population in the UAMAS had multiplied (Abdullah et al., 2005). This augmentation of the biomass concentration had led to a matching

rise in specific substrate utilization rates, SSURs, signifying that the increasing rate of influent COD fed into the reactor was matched by the rate of COD consumption by the bacteria populations. The bio-kinetic coefficients of growth yield (Y) and specific micro-organic decay rate, (b); and the K values were calculated from the slope and intercept as shown in Figs. 9 and 10. Maximum specific biomass growth rates (μ_{max}) were in the range between 0.261 and 0.482 d^{-1} . All of the kinetic coefficients that were calculated from the three models are summarized in Table 4. The small values of μ_{max} are suggestive of relatively high amounts of biomass in the UMAS (Zinatizadeh et al., 2006). According to (Grady et al., 1980), the values of parameters μ_{max} and K are highly dependent on both the organism and the substrate employed. If a given species of organism is grown on several substrates under fixed environmental conditions, the observed values of μ_{max} and K will depend on the substrates.

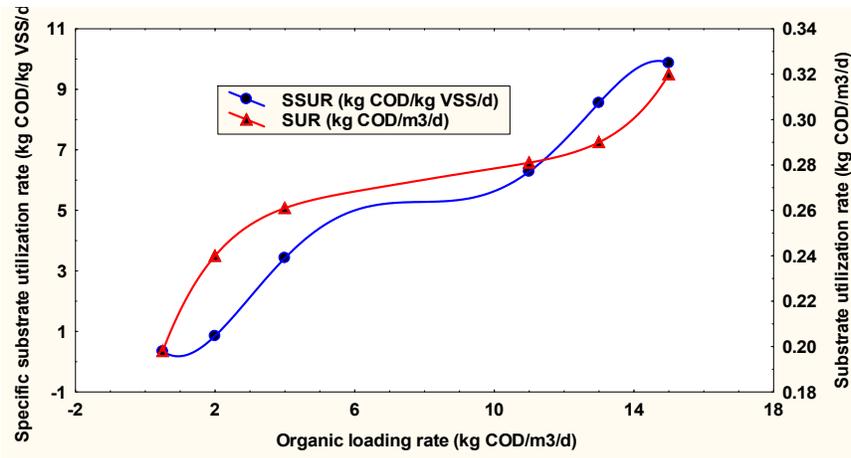


Fig.8. Organic loading rate Vs. SUR & SSUR

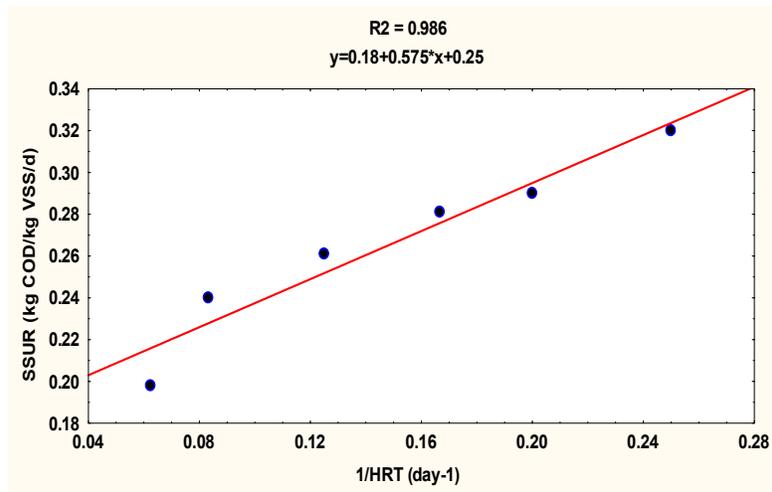


Fig.9. Determination of the growth yield, Y and the specific biomass decay rate, b

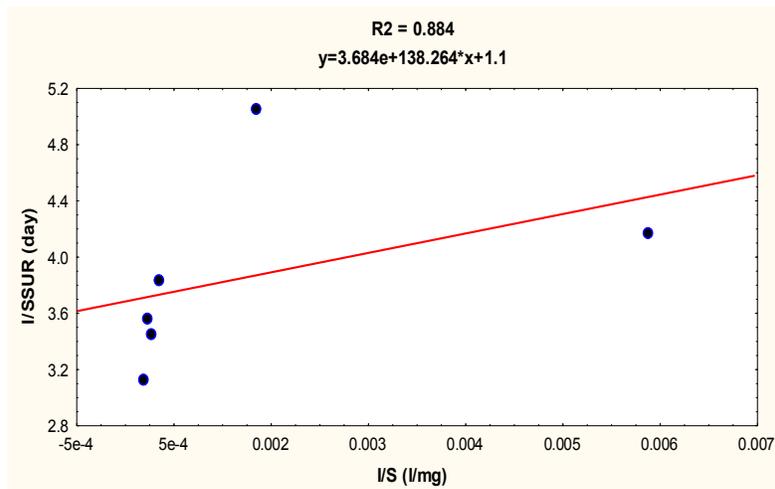


Fig.10. Determination of the maximum specific substrate utilization and the saturation constant, K

4. Gas production and composition

Many factors must be adequately controlled to ensure the performance of anaerobic digesters and prevent failure. For POME treatment, these factors include pH, mixing, operating temperature, nutrient availability and organic loading rates into the digester. In this study, the microbial community in the anaerobic digester was sensitive to pH changes. Therefore, the pH was maintained in an optimum range (6.8-7) to minimize the effects on methanogens that might biogas production. Because methanogenesis is also strongly affected by pH, methanogenic activity will decrease when the pH in the digester deviates from the optimum value. Mixing provides good contact between microbes and substrates, reduces the resistance to mass transfer, minimizes the build-up of inhibitory intermediates

and stabilizes environmental conditions. This study adopted the mechanical mixing and biogas recirculation. Fig. 11 shows the gas production rate and the methane content of the biogas. The methane content generally declined with increasing OLRs. Methane gas contents ranged from 67.8% to 77% and the methane yield ranged from 0.264 to 0.47 CH₄/g COD/d. The declining methane content may be attributed to the higher organic loading rate which favours growth rate of the acid forming bacteria over the methanogenic bacteria. Thus the methane conversion process was adversely affected with reducing methane content and this has led to the formation of carbon dioxide at a higher rate. The gas production showed an increase from 277.8 to 580 Litres per day during the study.

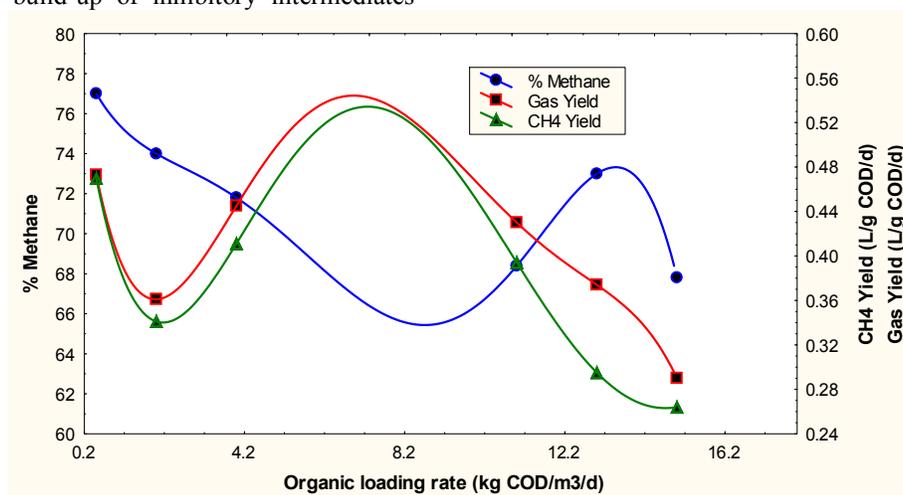


Fig.11. Gas production and methane content

5. Conclusions

The UAMAS bioreactor was found to be an improvement and a successful biological treatment process to achieve a high COD removal efficiency in a short period of time (no membrane fouling by introduction of ultrasonic). Palm oil mill effluent wastewater containing between 57,000 mg/L and 77,000 mg/L of COD was treated in 200-L UAMAS operated at 35 °C. The best COD removal (98.7%) for POME treatment in UAMAS reactor has obtained at an OLR of 0.5 kg m⁻³ d⁻¹ and HRT of 16 days. The VFA production in UAMAS and methane production in UAMAS increased with the increasing OLR. The maximum VFA accumulation of 1480 mg/L was achieved at OLR of 15 kg COD/m³/d and HRT of 4 days in UAMAS reactor. Nevertheless, the maximum gas production was 580 L/d at OLR of 15 kg COD/m³/d. The UAMAS produced a biogas containing 77% methane. The high degree of methanization suggested that most of soluble and suspended organics in Palm oil mill effluent (POME)

wastewater were degraded during treatment in the UAMAS.

Appendix A. Nomenclature

COD: chemical oxygen demand (mg/l)
 OLR: organic loading rate (kg/m³/d)
 CUF: cross flow ultra-filtration membrane
 SS: steady state
 SUR: substrate utilization rate (kg/m³/d)
 TSS: total suspended solid (mg/l)
 MLSS: mixed liquid suspended solid (mg/l)
 HRT: hydraulic retention time (day)
 SRT: solids retention time (day)
 SSUR: Specific substrate utilization rate (kg COD/kg VSS/d)
 MAS: Membrane An aerobic System
 UAMAS: Ultrasonic-assisted Membrane Anaerobic System
 MLVSS: mixed liquid volatile suspended Solid (mg/l)
 VSS: volatile suspended solids (mg/l)
 MWCO: molecular weight Cut-Off
 BLR: biological loading rate
 U = specific substrate utilisation rate (SSUR) (g COD/G VSS/d)
 S = effluent substrate concentration (mg/l)
 S₀ = influent substrate concentration (mg/l)

X = micro-organism concentration (mg/l)

μ_{\max} : Maximum specific growth rate (day^{-1})

K: Maximum substrate utilisation rate (COD/g/VSS.day)

K_s : Half velocity coefficient (mg COD/l)

X: Micro-organism concentration (mg/l)

b = specific microorganism decay rate (day^{-1})

Y = growth yield coefficient (gm VSS/gm COD)

T: time

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