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Ultrasonic Membrane Anaerobic System (UMAS) for Palm Oil Mill Effluent (POME) Treatment

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1. Introduction

Palm oil mill effluent (POME) is an important source of inland water pollution when released into local rivers or lakes without treatment. The production of palm oil, however, results in the generation of large quantities of polluted wastewater commonly referred as palm oil mill effluent (POME). In the process of palm oil milling, POME is generated through sterilization of fresh oil palm fruit bunches, clarification of palm oil and effluent from hydro-cyclone operations [1]. POME is a viscous brown liquid with fine suspended solids at pH ranging between 4 and 5 [2]. In general appearance, palm oil mill effluent (POME) is a yellowish acidic wastewater with fairly high polluting properties, with average of 25,000 mg/l biochemical oxygen demand (BOD), 55,250 mg/l chemical oxygen demand (COD) and 19,610 mg/l suspended solid (SS). This highly polluting wastewater can cause several pollution problems. Anaerobic digestion is the most suitable method for the treatment of effluents containing high concentration of organic carbon such as POME [1]. Anaerobic digestion is defined as the engineered methanogenic anaerobic decomposition of organic matter. It involves different species of anaerobic microorganisms that degrade organic matter [3]. In the anaerobic process, the decomposition of organic and inorganic substrate is carried out in the absence of molecular oxygen. The biological conversion of the organic substrate occurs in the mixtures of primary settled and biological sludge under anaerobic condition followed by hydrolysis, acidogenesis and methanogenesis to convert the intermediate compounds into simpler end products as methane (CH_4) and carbon dioxide (CO_2) [4], [5], and [6]. Therefore, the anaerobic digestion process offers great potential for rapid disintegration of organic matter to produce biogas that can be used to generate electricity and save fossil energy [7]. The suggested anaerobic treatment processes for POME include anaerobic suspended growth processes, attached growth anaerobic processes (immobilized cell bioreactors, anaerobic fluidized bed reactors and anaerobic filters), anaerobic blanket processes (up-

flow anaerobic sludge blanket reactors and anaerobic baffled reactors), membrane separation anaerobic treatment processes and hybrid anaerobic treatment processes.

Over the past 20 years, the technique available for the treatment of POME in Malaysia has been biological treatment, consisting of anaerobic, facultative and aerobic pond systems [8, 9]. Anaerobic digestion has been employed by most palm oil mills as their primary treatment of POME [10]. More than 85% of palm oil mills producers in Malaysia have adopted the ponding system for POME treatment [11] due to its low capital and operating costs, while the rest opted for open digesting tanks [12]. These methods are regarded as conventional POME treatment method whereby long retention times and large treatment areas are required. High-rate anaerobic bioreactors have also been applied in laboratory-scaled POME treatment such as up-flow anaerobic sludge blanket (UASB) reactor [13]; up-flow anaerobic filtration [14]; fluidized bed reactor [15, 16] and up-flow anaerobic sludge fixed-film (UASFF) reactor [2]. Anaerobic contact digester [12] and continuous stirred tank reactor (CSTR) have also been studied for POME treatment [17]. Other than anaerobic digestion, POME has also been treated using membrane technology [14, 18, 19], [20] and [21]. (POME's) chemical oxygen demand (COD) and biochemical oxygen demand (BOD) are very high; COD values greater than 80,000 mg/l and; pH values in the acidic range between (3.8 and 4.5) are frequently reported and the incomplete extraction of palm oil from the palm nut can increase COD values substantially. The effluent is non-toxic because no chemicals are added during the oil extraction process [22, 23, and 24]. (POME) is a brownish colloidal suspension, characterised by high organic content, and high temperature (70-80 $^\circ$C) [25]. Most commonly, palm oil mills have already suggested use of anaerobic digesters for the primary treatment [26, 27]. The three widely used kinetic models considered in this study are shown in Table 1. The traditional ways for wastewater treatment from both economic (high cost) and environmental (harmful) disadvantages, this paper aims to introduce a new design technique of ultrasonic-membrane anaerobic system (UMAS) in treating POME and producing methane and to determine the kinetic parameters of the process, based on three known models; Monod [28], Contois [29] and Chen and Hashimoto[30].

Kinetic Model	Equation 1	Equation 2
Monod	$U = \dfrac{k\,S}{k_s + S}$	$\dfrac{1}{U} = \dfrac{K_s}{K}(\dfrac{1}{S}) + \dfrac{1}{k}$ [28]
Contois	$U = \dfrac{U_{max} \times S}{Y(B \times X + S)}$	$\dfrac{1}{U} = \dfrac{a \times X}{\mu_{max} \times S} + \dfrac{Y(1 + a)}{\mu_{max}}$ [29]
Chen & Hashimoto	$U = \dfrac{\mu_{max} \times S}{Y\,K\,S_o + (1 - K)\,S\,Y}$	$\dfrac{1}{U} = \dfrac{Y\,K\,S_o}{\mu_{max}\,S} + \dfrac{Y(1 - K)}{\mu_{max}}$ [30]

Table 1. Mathematical expressions of specifics substrate utilization rates for known kinetic models

2. Materials and methods

Raw POME was treated by UMAS in a laboratory digester with an effective 200-litre volume. Figs. 1&2 presents a schematic representation of the ultrasonicated-membrane anaero-

bic system (UMAS) which consists of a cross flow ultra-filtration membrane (CUF) apparatus, a centrifugal pump, and an anaerobic reactor. 25 KHz multi frequency ultrasonic transducers (to create high mechanical energy around the membrane to suspends the particles) connected into the MAS system. The ultrasonic frequency is 25 KHz, with 6 units of permanent transducers and bonded to the two (2) sided 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 ºC, 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 4 bars by manipulating the gate valve at the retentate line after the CUF unit.
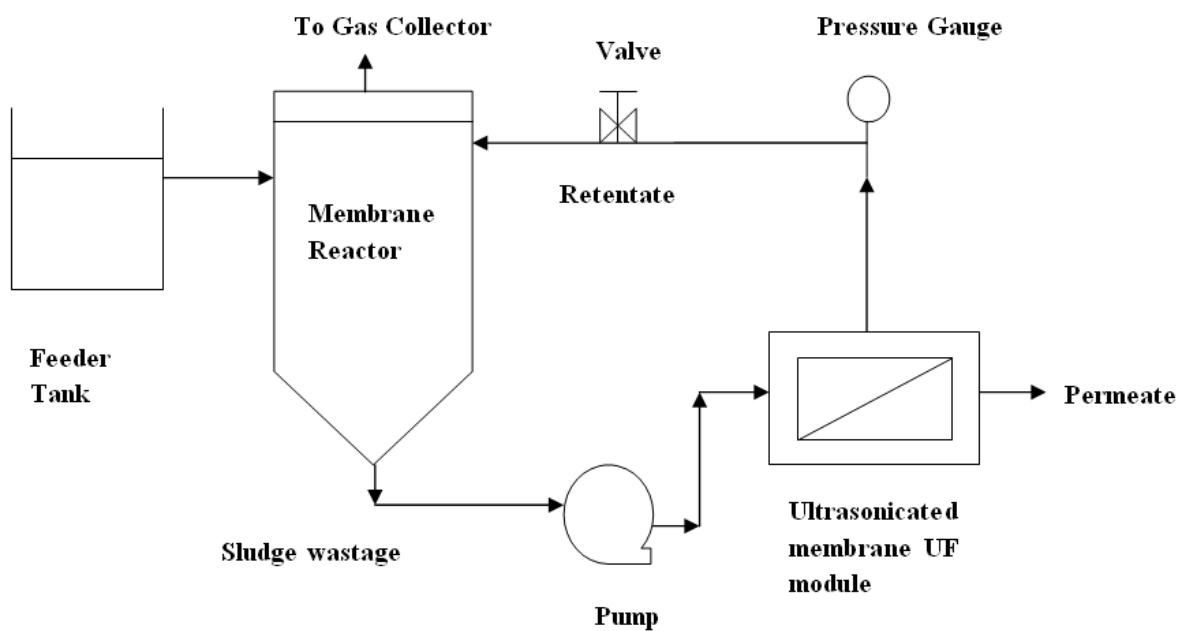

Figure 1. Experimental set-up

Figure 2. Schematic for Ultrasonicated membrane anaerobic system (UMAS)

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 analysed for chemical oxygen demand (COD), total suspended solids (TSS), pH, volatile suspended solids (VSS), substrate utilisation rate (SUR), and specific substrate utilisation rate (SSUR).

2.2. Bioreactor operation

The ultrasonicated membrane anaerobic system, UMAS Performance was evaluated under six different inflow conditions (six steady-states) with influent COD concentrations ranging from (67,000 to 91,400 mg/l) and organic loading rates (OLR) between (0.5 and 9.5 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 CO_2 and CH_4, in order to collect pure CH_4, the addition of sodium hydroxide solution (NaOH) will absorb CO_2 effectively and the remaining will be methane gas (CH_4).

Steady State (SS)	1	2	3	4	5	6
COD feed, mg/L	67000	79000	82400	86000	90000	91400
COD permeate, mg/L	980	1940	1650	1980	2200	3000
Gas production (L/d)	280.5	357	377	395	470	540
Total gas yield, L/g COD/d	0.29	0.38	0.65	0.77	0.82	0.88
% Methane	79	75.5	70.2	71.8	70.6	68.5
CH_4 yield, l/g COD/d	0.29	0.32	0.50	0.54	0.56	0.59
MLSS, mg/L	12960	13880	15879	17700	20000	25600
MLVSS, mg/L	10091	10950	12624	14638	17000	22528
% VSS	77.86	78.89	79.50	82.7 0	85.00	88.00
HRT, d	480.3	76.40	20.3	8.78	7.36	5.40
SRT, d	860	320	132	32.6	14.56	10.6
OLR, kg COD/m^3/d	0.5	1.5	3	5.5	8.5	9.5
SSUR, kg COD/kg VSS/d	0.185	0.262	0.266	0.274	0.315	0.321
SUR, kg COD/m3/d	0.0346	0.8454	3.3028	5.6657	7.7753	9.4528
Percent COD removal (MAS)	**96.5**	**96.0**	**95.8**	**95.4**	**94.9**	**94.8**
Percent COD removal (UMAS)	**98.5**	**97.5**	**98.0**	**97.7**	**97.6**	**96.7**

Table 2. Summary of results (SS: steady state)

Model	Equation	R^2 (%)
Monod	$U^{-1} = 2025 S^{-1} + 3.61$ $K_s = 498$ $K = 0.350$ $\mu_{Max} = 0.284$	98.9
Contois	$U^{-1} = 0.306 X S^{-1} + 2.78$ $B = 0.111$ $u_{Max} = 0.344$ $a = 0.115$ $\mu_{Max} = 0.377$ $K = 0.519$	97.8
Chen & Hashimoto	$U^{-1} = 0.0190 S_o S^{-1} + 3.77$ $K = 0.006$ $a = 0.006$ $\mu_{Max} = 0.291$ $K = 0.374$	98.7

Table 3. Results of the application of three known substrate utilisation models

3. Results and discussion

3.1. Semi-continuous Ultrasonic-Membrane Anaerobic System (UMAS) performance

Table 2 summarises UMAS performance of six inflow rates all (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 1 by using a linear relationship; the coefficients are summarised in Table 3. At steady-state conditions with influent COD concentrations of 67,000-91,400 mg/l, UMAS performed well and the pH in the reactor remained within the optimal working range for anaerobic digesters (6.7-7.8). At the first steady-state, the MLSS concentration was about 12,960 mg/l whereas the MLVSS concentration was 10,091 mg/l, equivalent to 77.9% of the MLSS. This low result can be attributed to the high suspended solids contents in the POME. At the sixth steady-state, however, the volatile suspended solids (VSS) fraction in the reactor increased to 88% of the MLSS. This indicates that the long SRT of UMAS facilitated the decomposition of the suspended solids and their subsequent conversion to methane (CH_4); this conclusion supported by [31] and [32]. The highest influent COD was recorded at the sixth steady-state (91,400 mg/l) and corresponded to an OLR of 9.5 kg COD/m^3/d. At this OLR the, UMAS achieved 96.7% COD removal and an effluent COD of 3000 mg/l. This value is better than those reported in other studies on anaerobic POME digestion [33, 34]. The three kinetic models demonstrated a good relationship (R^2 > 99%) for the membrane anaerobic system treating POME, as shown in Figs. 2-5. 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_o). In Monod model, however, S is independent of S_o. The excellent fit of these three models (R^2 > 97.8%) in this study suggests that the UMAS process is capable of handling sustained organic loads between 0.5 and 9.5 kg m^3/d.
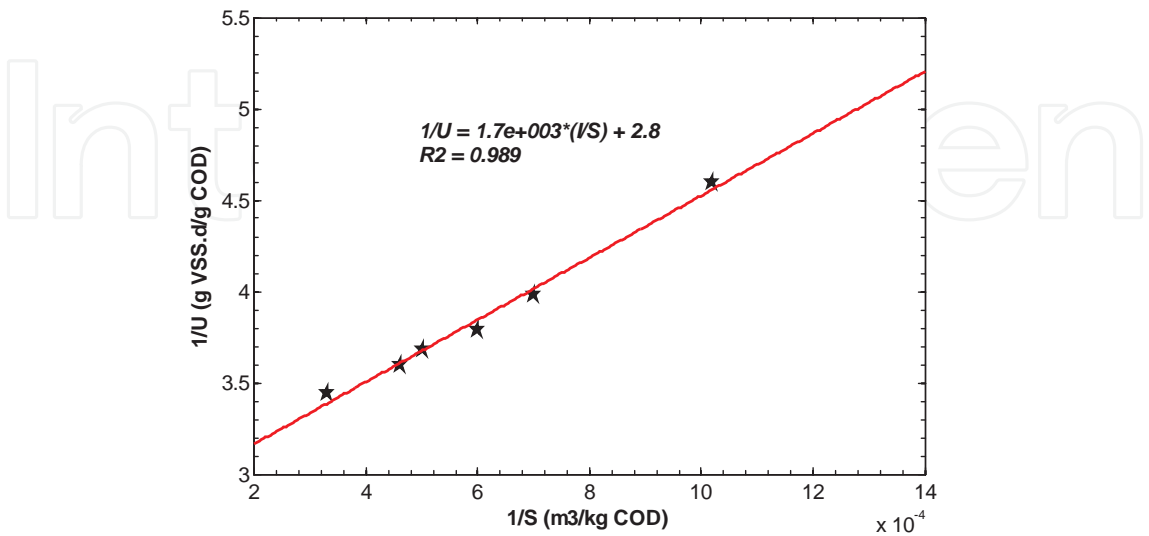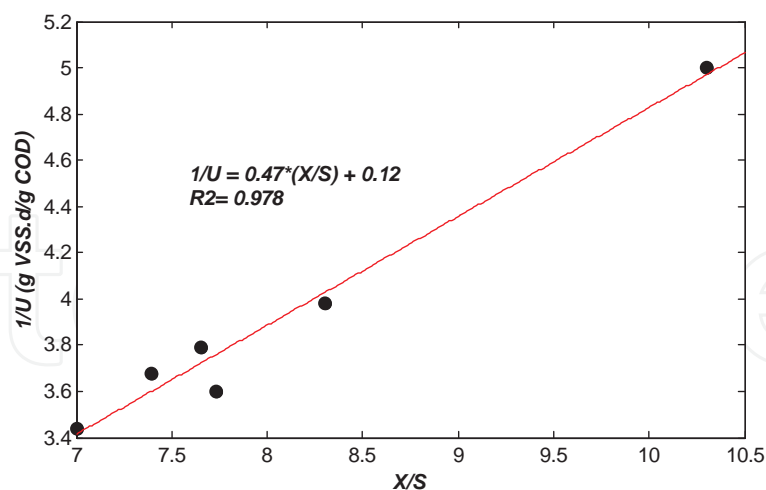

Figure 3. The monod model.

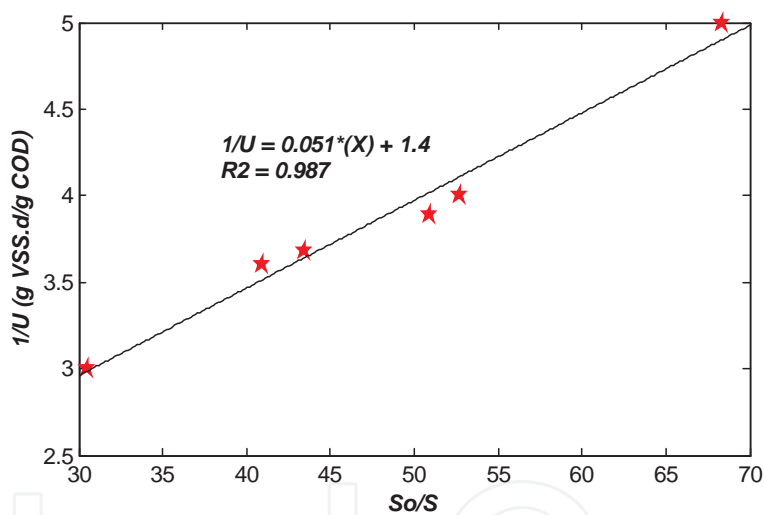**Figure 4.** The Contois model.

Figure 5. The Chen and Hashimoto mdel.

Fig.6 shows the percentages of COD removed by UMAS at various HRTs. COD removal ef‐
ficiency increased as HRT increased from 5.40 to 480.3 days and was in the range of 96.7 % -
98.5 %. This result was higher than the 85 % COD removal observed for POME treatment
using anaerobic fluidised bed reactors [35] and the 91.7-94.2 % removal observed for POME
treatment using MAS [36]. The COD removal efficiency did not differ significantly between
HRTs of 480.3 days (98.5%) and 20.3 days (98.0%). On the other hand, the COD removal effi‐
ciency was reduced shorter HRTs; at HRT of 5.40 days, COD was reduced to 96.7 %. As
shown in Table 2, this was largely a result of the washout phase of the reactor because the
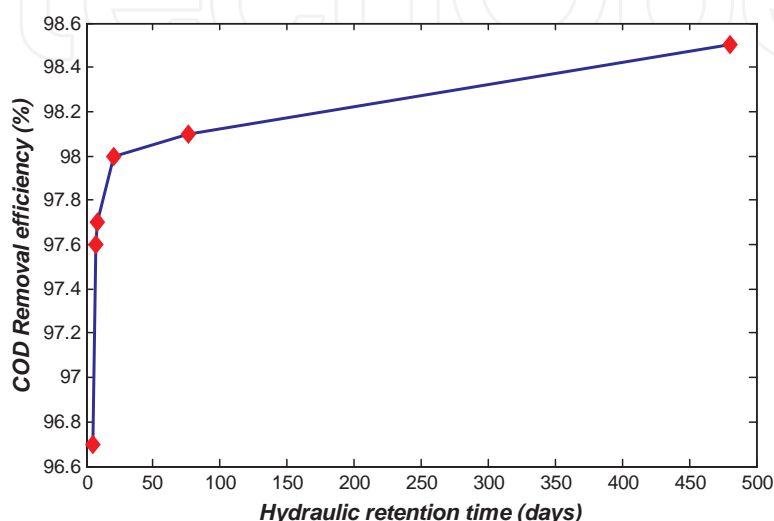biomass concentration increased in the system.

Figure 6. COD removal efficiency of UMAS under steady-state conditions with various hydraulic retention times.

3.2. Determination of bio-kinetic coefficients

Experimental data for the six steady-state conditions in Table 2 were analysed; kinetic coefficients were evaluated and are summarised in Table 3. Substrate utilisation rates (SUR); and specific substrate utilisation rates (SSUR) were plotted against OLRs and HRTs. Fig. 7 shows the SSUR values for COD at steady-state conditions HRTs between 5.40 and 480.3 days. SSURs for COD generally increased proportionally HRT declined, which indicated that the bacterial population in the UMAS multiplied [37]. 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. 8 and 9. Maximum specific biomass growth rates (μ_{max}) were in the range between 0.248 and 0.474 d^{-1}. All of the kinetic coefficients that were calculated from the three models are summarised in Table 3. The small values of μ_{max} are suggestive of relatively high amounts of biomass in the UMAS [38]. According to [39], 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.
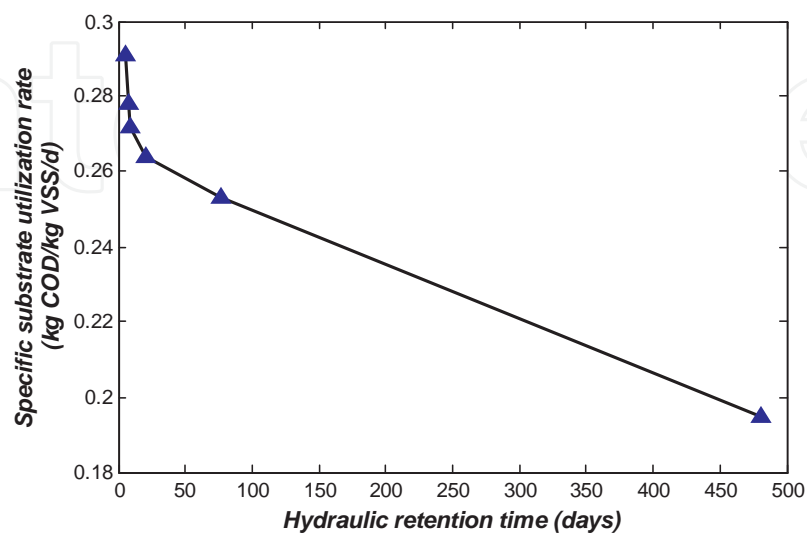
Figure 7. Specific substrate utilization rate for COD under steady-state conditions with various hydraulic retention times.
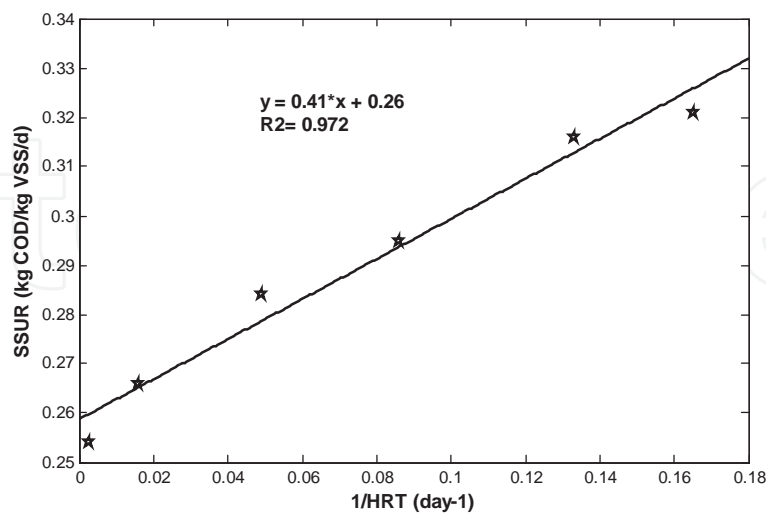

Figure 8. Determination of the growth yield, Y and the specific biomass decay rate, b

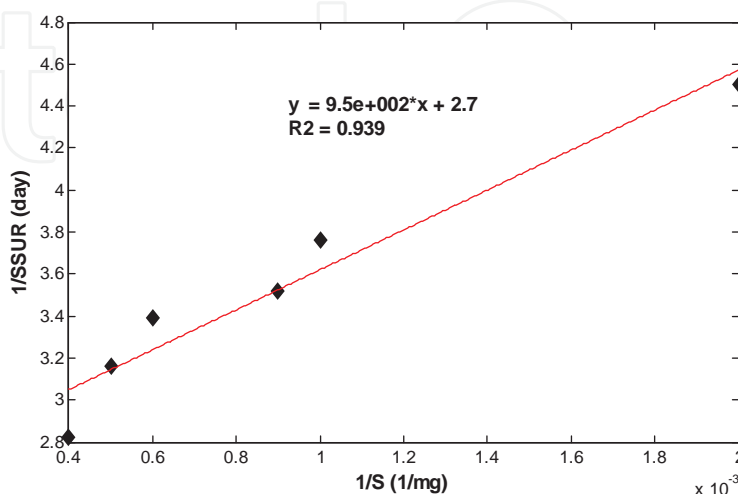$$y = 9.5e+002*x + 2.7$$
$$R2 = 0.939$$

Figure 9. 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) (by addition of NaOH) 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. 10 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 68.5% to 79% and the methane yield ranged from 0.29 to 0.59 CH_4/g COD/d. Biogas production increased with increasing OLRs from 0.29 l/g COD/d at 0.5 kg COD/m^3/d to 0.88 l/g COD/d at 9.5 kg COD/m^3/d. The decline in methane gas content may be attributed to the higher OLR, which favours the growth of acid forming bacteria over methanogenic bacteria. In this scenario, the higher rate of carbon dioxide; (CO_2) formation reduces the methane content of the biogas.
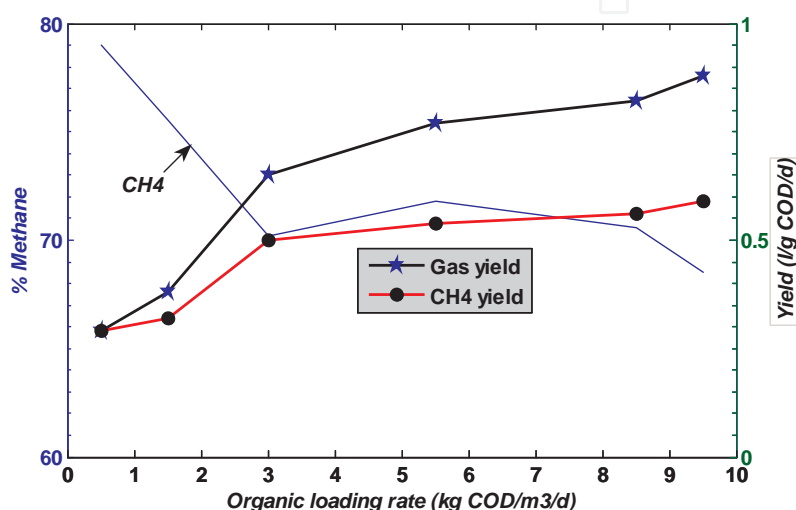
Figure 10. Gas production and methane content

5. Conclusions

The ultrasonic membrane anaerobic system, UMAS seemed to be adequate for the bio-logical treatment of undiluted POME, since reactor volumes are needed which are considerably smaller than the volumes required by the conventional digester. UMAS were found to be an improvement and a successful biological treatment system that achieved high COD removal efficiency in a short period of time (no membrane fouling by introduction of ultrasonic). The overall substrate removal efficiency was very high-about 98.5%. The gas production, as well as the methane concentration in the gas was satisfactory and, therefore, could be considered (the produced methane gas) as an additional energy source for the use in the palm oil mill. Preliminary data on anaerobic digestion at 30 °C in UMAS showed that the proposed technology has good potential to substantially reduce the pollution load of POME wastewater. UMAS was efficient in retaining the biomass.The UMAS process will recover a significant quantity of energy (methane 79%) that could be used to heat or produce hot water at the POME plant.

Appendix A. nomenclature

COD: chemical oxygen demand (mg/l)

OLR: organic loading rate (kg/m^3/d)

CUF: cross flow ultra-filtration membrane

SS: steady state

SUR: substrate utilization rate (kg/m^3/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

UMAS: Ultrasonicated 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)

S_o = influent substrate concentration (mg/l)

X = micro-organism concentration (mg/l)

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

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

: 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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