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Biomethanation of Palm Oil Mill Effluent (POME) by Membrane Anaerobic System (MAS) using POME as a Substrate

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***Abstract*—**The direct discharge of palm oil mill effluent (POME) wastewater causes serious environmental pollution due to its high chemical oxygen demand (COD) and biochemical oxygen demand (BOD). Traditional ways for POME treatment have both economical and environmental disadvantages. In this study, a membrane anaerobic system (MAS) was used as an alternative, cost effective method for treating POME. Six steady states were attained as a part of a kinetic study that considered concentration ranges of 8,220 to 15,400 mg/l for mixed liquor suspended solids (MLSS) and 6,329 to 13,244 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 2 to 13 kg COD/m^3/d. throughout the experiment, the removal efficiency of COD was from 94.8 to 96.5% with hydraulic retention time, HRT from 400.6 to 5.7 days. The growth yield coefficient, Y was found to be 0.62gVSS/g COD the specific microorganism decay rate was 0.21 d^{-1} and the methane gas yield production rate was between 0.25 l/g COD/d and 0.58 l/g COD/d. Steady state influent COD concentrations increased from 18,302 mg/l in the first steady state to 43,500 mg/l in the sixth steady state. The minimum solids retention time, θ_c^{min} which was obtained from the three kinetic models ranged from 5 to 12.3 days. The k values were in the range of 0.35 – 0.519 g COD/ g VSS • d and μ_{max} values were between 0.26 and 0.379 d^{-1}. The solids retention time (SRT) decreased from 800 days to 11.6 days. The complete treatment reduced the COD content to 2279 mg/l equivalent to a reduction of 94.8% reduction from the original.

***Keywords*—**COD reduction; POME; Kinetics; Membrane; Anaerobic; Monod, Contois equation.

I. Introduction

PALM oil mill effluent (POME) is an important source of inland water pollution when it is released into local rivers or lakes without treatment. POME contains lignocellulolic wastes with a mixture of carbohydrates and oil. Its chemical oxygen demand (COD) and biochemical oxygen demand (BOD) are very high; COD values greater than 80,000 mg/l and; acidic pH values 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 [1-3]. (POME) is a brownish colloidal suspension, characterised by high organic content, and high temperature (70-80 °C) [4]. Most commonly, palm oil mills use anaerobic digestion for the primary treatment [5-6]. More than 85% the POME producers in Malaysia have adopted the ponding system for POME treatment [7] due to its low capital and operating costs. Disadvantages of this system include its large land area requirement and long retention time (1-2 months). High treatment POME treatment would reduce treatment costs by increasing the digestion rate and eliminating the need for cooling facilities prior to biological treatment [8]. Membrane separation techniques have proven to be an effective method for separating biomass solids from digester suspensions and recycling them to the digester [9]. Several studies using membrane anaerobic processes to treat a variety of wastewaters [10-14] found that membrane anaerobic system (MAS) processes retained and due to long solids retention times liquefied and decomposed all particulate matter. To accurately and precisely design bioreactor, it is important to have values for the relevant kinetic parameters. These parameters depend on the substrate type, microorganisms and temperature. The three widely used kinetic models considered in this study are shown in Table 1. The purposes of the present work are to study the performance of (MAS) in treating POME and producing methane and to determine the kinetic parameters of the process, based on three known models; Monod [15], Contois [16], and Chen & Hashimoto [17].

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TABLE I
MATHEMATICAL EXPRESSIONS OF SPECIFICS SUBSTRATE UTILIZATION RATES FOR KNOWN KINETIC MODEL

Kinetic Model	Equation 1	Equation 2
Monod (1949)	$U = \frac{k\ S}{k_s + S}$	$\frac{1}{U} = \frac{K_s}{K}(\frac{1}{S}) + \frac{1}{k}$
Contois (1959)	$U = \frac{U_{\max} \times S}{Y(B \times X + S)}$	$\frac{1}{U} = \frac{a \times X}{\mu_{\max} \times S} + \frac{Y(1+a)}{\mu_{\max}}$
Chen & Hashimoto (1980)	$U = \frac{\mu_{\max} \times S}{Y\ K\ S_o + (1-K)\ S\ Y}$	$\frac{1}{U} = \frac{Y\ K\ S_o}{\mu_{\max}\ S} + \frac{Y(1-K)}{\mu_{\max}}$

II. MATERIALS AND METHODS

Raw POME was treated by MAS in a laboratory digester with an effective 50-litre volume. Fig. 1 presents a schematic representation of the (MAS) which consists of a cross flow ultra-filtration membrane (CUF) apparatus, a centrifugal pump, and an anaerobic reactor. 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 two membranes was 0.024 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 clear PVC with an inner diameter of 15 cm and a total height of 100 cm. The operating pressure in this study was maintained between 1.5 and 2.5 bars by manipulating the gate valve at the retentate line after the CUF unit.

A. Palm oil mill effluent

Raw POME samples were collected from a palm oil mill in Kuantan city-Malaysia. The wastewater was stored in a cold room at 4ºC 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).

B. Bioreactor operation

Performance was evaluated under six steady-states with influent COD concentrations ranging from (18,302 to 47,143 mg/l) and organic loading rates (OLR) between (2 and 13 kg COD/m^3/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.

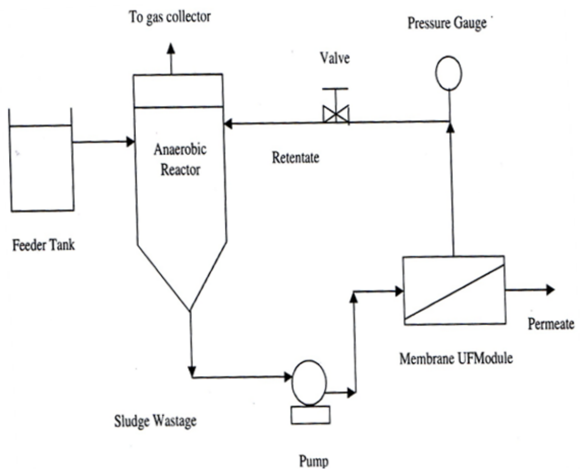

Fig. 1 Experimental set-up

A 20-litre water displacement bottle was used to measure the daily gas volume. The produced biogas contained only CO_2 and CH_4, so the addition of sodium hydroxide solution (NaOH) to absorb CO_2 effectively isolated methane gas (CH_4).

TABLE II
SUMMARY OF RESULTS (SS: STEADY STATE)

Steady State (SS)	1	2	3	4	5	6
COD feed, mg/L	18302	20196	26087	34524	40000	43500
COD permeate, mg/L	641	808	1096	1588	2040	2279
Gas production (L/day)	288	294	312	342	380	395
Total gas yield, L/g COD/day	0.25	0.36	0.59	0.74	0.78	0.83
% Methane	74.2	72.6	69.7	70.8	69.1	68.7
Ch_4 yield, l/g COD/day	0.27	0.29	0.46	0.56	0.54	0.58
MLSS, mg/L	8220	9200	10140	11640	13300	15400
MLVSS, mg/L	6329	7268	8051	9428	11172	13244
% VSS	77.00	79.00	79.40	81.00	84.00	86.00
HRT, day	400.6	63.6	20.4	11.6	8.86	5.70
SRT, day	800	200	100	35.6	20.8	11.6
OLR, kg COD/m^3/day	2	5	7	9	11	13
SSUR, kg COD/kg VSS/day	0.254	0.266	0.284	0.295	0.316	0.381
SUR, kg COD/m^3/day	0.74	1.64	3.30	6.67	8.80	10.48
Percent COD removal	96.5	96.0	95.8	95.4	94.9	94.8

TABLE III
RESULTS OF THE APPLICATION OF THREE KNOWN SUBSTRATE UTILIZATION MODELS

Model	Equation	R^2 (%)
Monod	$U^{-1} = 2025\ S^{-1} + 3.61$ $K_s = 498$ $K = 0.350$ $\mu_{Max} = 0.260$	97.1
Contois	$U^{-1} = 0.306\ X\ S^{-1} + 2.78$ $B = 0.111$ $u_{Max} = 0.344$ $a = 0.115$ $\mu_{Max} = 0.380$ $K = 0.519$	96.2
Chen & Hashimoto	$U^{-1} = 0.0190\ S_o\ S^{-1} + 3.77$ $K = 0.006$ $a = 0.006$ $\mu_{Max} = 0.278$ $K = 0.374$	97.5

III. RESULTS AND DISCUSSION

A. Semi-continuous membrane anaerobic system (MAS) performance

Table 2 summarizes MAS 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 1 by using a linear relationship; the coefficients are summarized in Table 3. At steady-state conditions with influent COD concentrations of 18,302-43,500 mg/l, MAS 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 8,220 mg/l whereas the MLVSS concentration was 6,329 mg/l, equivalent to 77% 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 86% of the MLSS. This indicates that the long SRT of MAS facilitated the decomposition of the suspended solids and their subsequent conversion to methane (CH_4); this conclusion supported by [14]. The highest influent COD was recorded at the sixth steady-state (43,500 mg/l) and corresponded to an OLR of 13 kg COD/m^3/d. At this OLR the, MAS achieved 94.8% COD removal and an effluent COD of 2279 mg/l. This value is better than those reported in other studies on anaerobic POME digestion [18-19]. The color of treated POME (permeate) by MAS was very clear compared to the raw POME, Fig.2. The three kinetic models demonstrated a good relationship (R^2 > 96.2%) for the membrane anaerobic system treating POME, as shown in Figs. 3, 4 and 5. The Monod 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 > 96.2%) in this study suggests that the MAS process is capable of handling sustained organic loads between 2 and 13 kg m^3/d.

Fig. 2 Treated POME (permeate)

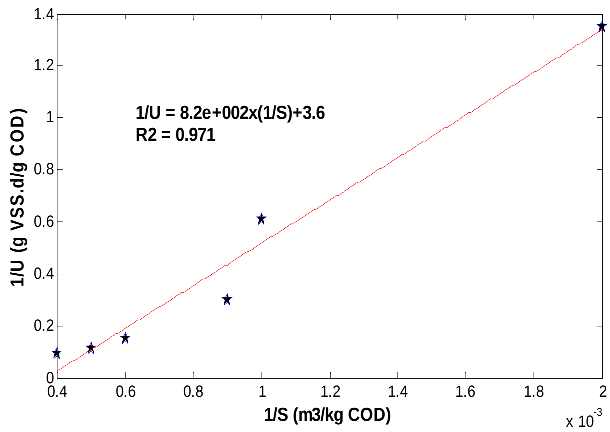

Fig. 3 Monod model

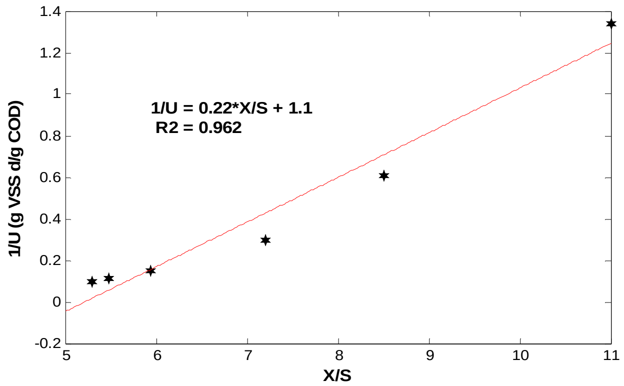

Fig. 4 Contois model

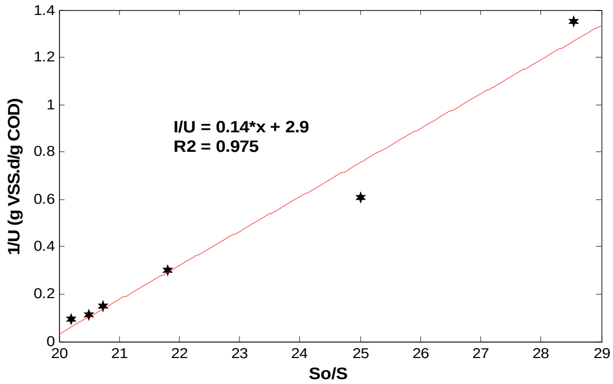

Fig. 5 Chen and Hashimoto model

Fig.6 shows the percentages of COD removed by MAS at various HRTs. The removal of COD is reflected in the rise in biomass concentration, as the dissolved organics were converted into new cells. COD removal efficiency increased as HRT increased from 5.7 to 400.6 days and was in the range of 94.8% - 96.5%. This result was higher than the 85% COD removal observed for POME treatment using anaerobic fluidized bed reactors [20] and the 91.7-94.2% removal observed for POME treatment using MAS [21]. The COD removal efficiency did not differ significantly between HRTs of 400.6 days (96.5%) and 63.6 days (96.0%). On the other hand, the COD removal efficiency was reduced shorter HRTs; at HRT of 5.7 days, COD was reduced to 94.8%. 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.

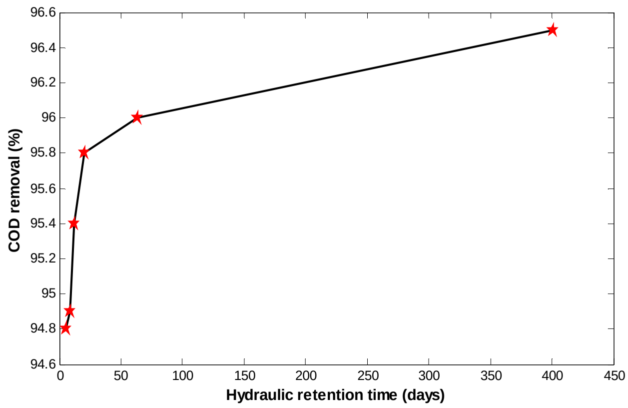

Fig. 6 COD removal efficiency of MAS under steady-state conditions with various hydraulic retention times

B. Determination of bio-kinetic coefficients

Experimental data for the six steady-state conditions in Table 2 were analyzed; kinetic coefficients were evaluated and are summarized in Table 3. Substrate utilization rates (SUR); and specific substrate utilization rates (SSUR) were plotted against OLRs and HRTs. Fig. 7 shows the SSUR values for COD at steady-state conditions HRTs between 5.7 and 400.6 days. SSURs for COD generally increased proportionally HRT declined, which indicated that the bacterial population in the MAS multiplied [22]. 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 0.260 and 0.380 d^{-1}. All of the kinetic coefficients that were calculated from the three models are summarized in Table 3. The small values of μ_{max} are suggestive of relatively high amounts of biomass in the MAS [23]. According to [24], 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.

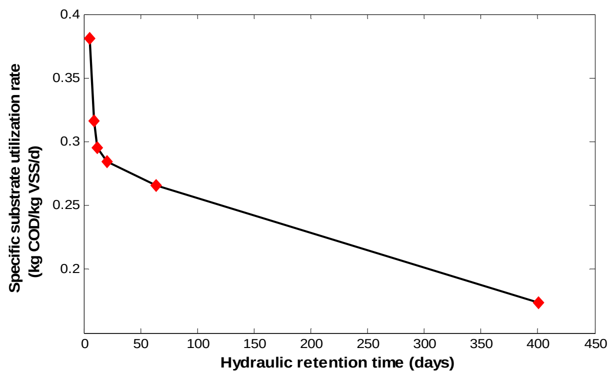

Fig. 7 Specific substrate utilization rate for COD under steady-state conditions with various hydraulic retention times

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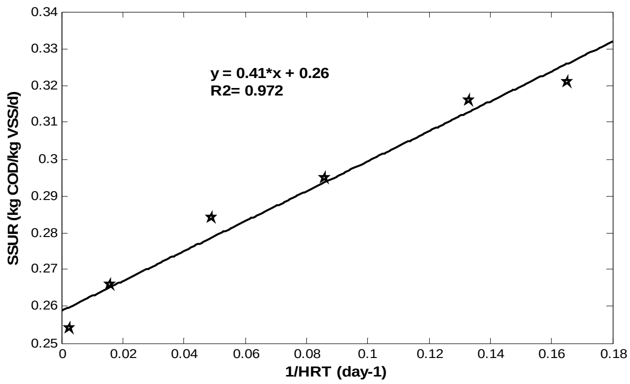

Fig. 8 Determination of the growth yield, Y and the specific biomass decay rate, b

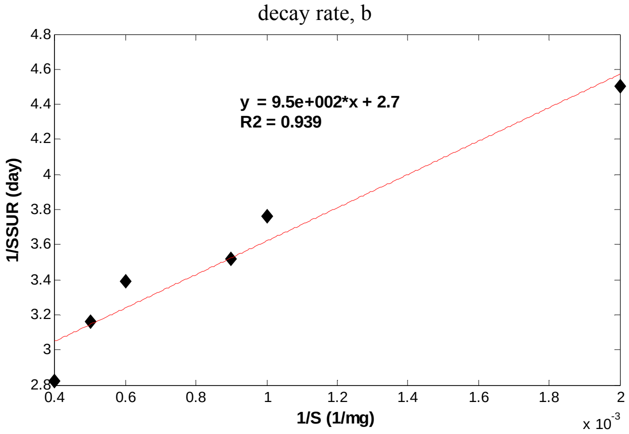

Fig. 9 Determination of the maximum specific substrate utilization and the saturation constant, K

IV. 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. 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 68.7% to 74.2% and the methane yield ranged from 0.27 to 0.58 CH_4/g COD/d. Biogas production increased with increasing OLRs from 0.27 l/g COD/d at 2 kg COD/m^3/d to 0.83 l/g COD/d at 13 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. Fig.11 shows the relationship between normalized effluent COD and SRT at different HRTs with an influent COD concentration of 43,500 mg/l. The normalized effluent COD decreases with increasing SRT.

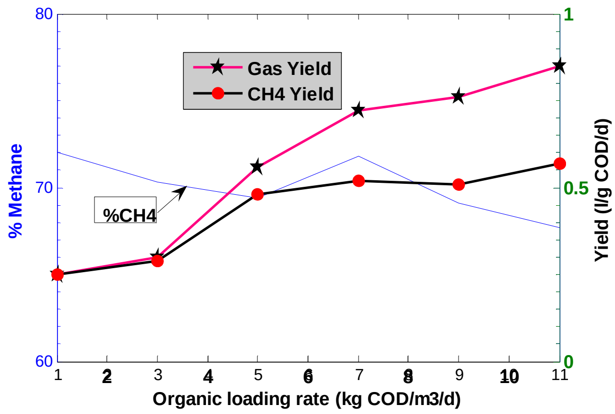

Fig. 10 Gas production and methane content

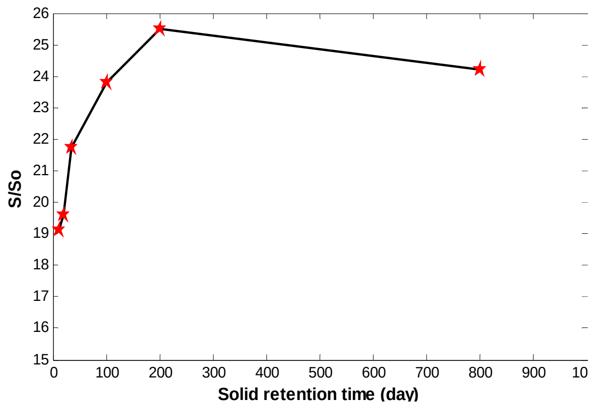

Fig. 11 Normalized COD concentration as a function of solids retention time

V. Conclusions

The MAS seemed to be adequate for the biological treatment of undiluted POME, since reactor volumes are needed which are considerably smaller than the volumes required by the conventional digester. MAS were found to be a successful biological treatment system that achieved high COD removal efficiency in a short period of time. The overall substrate removal efficiency was very high-about 96.5%. The gas production, as well as the methane concentration in the gas, were satisfactory and, therefore, could be considered as an additional energy source for the use in the palm oil mill.

Nomenclature

Symbol	Definition
COD	chemical oxygen demand (mg/l)
LR	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
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)
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)
b	specific microorganism decay rate (day^{-1})
Y	growth yield coefficient (gm VSS/gm COD)

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