Treatment of Palm Oil Mill Effluent (POME) using Membrane Anaerobic System (MAS)

M S Hybat¹, N H Abdurahman¹*, Z H Yasmeen¹, Z Jemaa¹ and N H Azhari²

¹Faculty of Chemical and Process Engineering Technology, College of Engineering Technology, Universiti Malaysia Pahang, 26300 Kuantan, Pahang, Malaysia.
²Faculty of Pure and Applied Science International University of Africa Khartoum, Sudan

*E-mail: nour2000_99@yahoo.com

Abstract. The directly discharged of Palm Oil Mill Effluent (POME) into the river causes environmental hazards due to the biochemical oxygen demand (BOD) and high Chemical Oxygen Demand (COD). The main issue of the traditional methods for POME treatment is that are not suitable for high suspended solid wastewaters and their gas production is less efficient at a high treatment volume. Therefore, in this study Membrane Anaerobic System (MAS) was used as alternative effective method for treating POME. The result obtained from the six steady states with concentration ranging from 11,048 to 15,700 mg/L for the MLSS, while the MLVSS recorded a concentration range between 10,540 and 17,600 mg/L. Moreover, the COD removal efficiency and HRT recorded from 94 to 97% and 150 to 10 days, respectively. Also, the coefficient of microorganism yield, decay rate, and the produced methane gas were obtained as 0.52g VSS/g COD, 0.31 day⁻¹ and 0.182 to 0.564 l/g, respectively. 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 13 kg COD/m³/day. POME were characterized using Transform Infrared (FTIR) spectroscopy, in the regions of 900 to 1740 and 2800 to 3400 cm⁻¹. Scanning Electron Microscope (SEM), the obtained result confirmed the potential of Membrane Anaerobic System (MAS) for the efficient treatment of POME effluent.

1. Introduction

Palm oil mill effluent is usually associated with palm oil processing which uses large volume of wastewater at high COD, BOD, and high temperatures, 80 to 90 °C [1]. In the recent years, the palm oil industry has been growing rapidly in Malaysia. Palm oil has been the most produced and consumed vegetable oil in the world, and it has been widely used in the field of cosmetics, hygiene, and food products due to its high oxidative stability, affordable price, and efficient production. However, Palm Oil Mill Effluent (POME) is immersive of Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) at high level which is discharged into the river and land before treatment at 75–85°C. Previous studies reported that POME had high contents of organic matter melanoid which are generated from the fresh fruit bunches during the sterilization process, and carotene pigment as well as other compounds such as polyphenol compounds, polyalcohol, etc. The physicochemical characteristics of raw POME which was used in this current work was thick with a dark brownish colour and oily with a viscous texture. Its obnoxious odour is usually dangerous to both aquatic life and human beings [2]. Traditional methods which were adopted in order to treat the problem of waste effluent (POME) could not obtained methane. Thus, the main drawback of these traditional methods is that it is not suitable at
high Organic Loading Rate (OLR), at which these methods were rated [3-4]. In addition, POME has low PH which is hard to be treated by conventional methods [5-6]. The traditional method of anaerobic digestion is the regular primary treatment of POME [7-8] and it was found that ponding system for POME treatment adopted more than 85% of the POME, due to its low capital and operating costs [9]. However, this system has disadvantages such as large land area requirement and long retention time [10]. Therefore, this study intends to use membrane separation techniques to overcome the above-mentioned problems.

MAS has shown economic viability, good ability in recycling high biomass solids and has long solid retention time that leads to degrade all particulate matter. In addition, the proposed method is effective for separating high biomass solids from digester. The kinetic equations in table 1 were found to be applicable to the anaerobic treatment of palm oil mill effluent.

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

| Kinetic Model         | Equation 1                                      | Equation 2                                      |
|-----------------------|-------------------------------------------------|-------------------------------------------------|
| Monod                 | \[ U = \frac{kS}{K_s + S} \]                    | \[ \frac{1}{U} = \frac{K_s (1) + 1}{k} \]      |
| Contois               | \[ U = \frac{U_{\text{max}} \times S}{Y (B \times X + S)} \] | \[ \frac{1}{U} = \frac{a \times X}{\mu_{\text{max}} \times S} + \frac{Y (1 + a)}{\mu_{\text{max}}} \] |
| Chen & Hashimoto      | \[ U = \frac{\mu_{\text{max}} \times S}{Y K S_o + (1 - K) S Y} \] | \[ \frac{1}{U} = \frac{Y K S_o}{\mu_{\text{max}} S} + \frac{Y (1 - K)}{\mu_{\text{max}}} \] |

### 2. Materials and Methods

In this study, the sample were collected from a near local palm oil mill in Lepar Hilir, Kuantan, Malaysia. Temperature ranged from 75 °C to 90 °C and the wastewater was stored in a cooled room at 4 °C before it was used in this experimental study. An effective volume of 60-litre of row pome was treated in the laboratory digester by using MAS consisting of a Cross-flow Ultra-Filtration membrane (CUF) apparatus, pump, and anaerobic reactor shown in figure 1. By gravity flow, the feed system was designed to provide continuous addition of feed volume from feeder tank. The type of membrane of this design was used in the UF membrane module which 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 °C, and the pH ranged from 2 to 12. In this study, the operating pressure was maintained between 1.5 and 2.5 bars by manipulating the gate valve at the retentate line after the CUF unit.
2.1. Analysis
Samples were analysed for Chemical Oxygen Demand (COD), Mixed Liquid Suspended Solids (MLSS were determined by using dichromate reflux (HACH Water Analysis method)), Total Suspended solid (TSS), Volatile Suspended Solids (VSS), Substrate Utilization Rate (SUR), Specific Substrate Utilization Rate (SSUR), and pH were determined by the pH meter.

2.2. Bioreactor operation
The performance was evaluated under six steady states as running digester at constant temperature, feed input, output, and gas. The process was evaluated by Organic Loading Rates (OLR) between 0.5 and 13kg COD/m3/d, alongside COD concentrations ranging from 72,100 to 84,400mg/L. The condition of steady state was considered acceptable in this study when the operating and control parameters were within ± 10% of the averages. The gas volume was measured daily by using a 20-litre water displacement bottle. J-tube gas analyzer was used to perform this analysis, as shown in figure 1 above. The method assumed that the biogas produced CO₂ and CH₄ gases, and then the sodium hydroxide solution (NaOH) was added to absorb CO₂. The remaining volume was methane gas (CH₄).

3. Result and discussion
The applicability of three substrate utilization kinetic models (Monod, Contois, and Chen, and Hashimoto) were tested and tabulated in table 2 linear relationship and the coefficients. The six steady states were achieved when feed COD, TSS, VSS, PH reactor, and permeate were within increased 10% variation of each average. The data for six steady states were summarized in Table 3. In this study the steady states were taken between 9 and 13 days to achieve steady state after each new organic loading rate during the six steady states, the organic loading rate increased from 0.5 to 13kg/COD/m3/d corresponding to the highest influent COD which was recorded at the sixth steady state (84,800mg/L), the steady state conditions with influent COD concentration of 72,100-84,800 mg/L and pH within the optimal working range for anaerobic digesters (6.7-7.8) achieved good performance of MAS.

In addition, the Volatile Suspended Solids (VSS) fraction in the reactor rose to 90.6% of the MLSS. This indicates that the long solid retention times and SRT of MAS are beneficial to the anaerobic contact process over the conventional process because of the ability to work well in different SR. Also, it predicted the decomposition of the suspended solids and the conversion to (CH₄). Table 2 shows that the MLVSS concentration was 14226 mg/L, whereas MLSS concentration was 15700 mg/L; this result was low due to high amount of suspended solids contents in the POME. At six steady states the MAS signified 95% COD removal during an effluent COD of 84800. This value is better than that which was reported by [11].

Thus, this study observed six steady states with an Organic Loading Rate (OLR) of 13 kg COD/m³ daily. The highest influent COD was recorded at the sixth steady state (84800mg/L). The value
was better than those reported in other studies on anaerobic POME digestion [12,13]. It also found that the Volatile Suspended Solids (VSS) fraction in the reactor increased to 90.6% of the MLSS. This indicates a conversion of the suspended solids to (CH₄). The Hydrolytic Retention Time (HRT) for the first steady state was too high. This may be attributed to very little amount of feeding to the system in the first steady state, S1.

However, the three kinetic models by Monod and Chen and Hashimoto demonstrated an acceptable relationship (R² > 90%) for the membrane anaerobic system treating POME, as shown in figures 2 to 4. Based on the result of this study, the three kinetic models by Monod and Chen, and Hashimoto showed a better performance, implying that digester organic loading rates quantify and rationalize the digester operation.

Table 2. Results of the application of three known substrate utilization models

| Model            | Equations                        | R² (%) |
|------------------|----------------------------------|--------|
| Monod            | \( U^{-1} = 2025 \times S^{-1} + 3.6 \) \( K_s = 498 \) \( K = 0.350 \) \( \mu_{MAX} = 0.259 \) | 0.99   |
| Contois          | \( U^{-1} = 0.306 \times S^{-1} + 2.78 \) \( B = 0.111 \) \( \mu_{MAX} = 0.344 \) \( a = 0.115 \) \( \mu_{MAX} = 0.384 \) \( K = 0.519 \) | 0.9993 |
| Chen & Hasimoto  | \( U^{-1} = 0.0190 \times S^{-1} + 3.77 \) \( K = 0.006 \) \( a = 0.006 \) \( \mu_{MAX} = 0.277 \) \( K = 0.374 \) | 0.9998 |

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

| Steady State (SS) | 1    | 2    | 3    | 4    | 5    | 6    |
|-------------------|------|------|------|------|------|------|
| COD feed, mg/L    | 72,100 | 73,400 | 75,400 | 78,900 | 81,700 | 84,800 |
| COD permeate, mg/L| 1250  | 1420  | 1865  | 2393  | 3412  | 3608  |
| Gas production (L/d) | 280   | 290   | 313   | 352   | 370   | 399   |
| Total gas yield, L/g COD/d | 0.26 | 0.33 | 0.45 | 0.69 | 0.77 | 0.83 |
| % Methane         | 70   | 71.3 | 68   | 67.8 | 70.1 | 68   |
| CH₄ yield, l/g COD/d | 0.182 | 0.235 | 0.306 | 0.467 | 0.539 | 0.564 |
| MLSS, mg/l        | 11,048 | 12,410 | 13,750 | 14,680 | 14,800 | 15,700 |
| MLVSS, mg/L       | 9,0593 | 10,450 | 12,054 | 13,054 | 13,262 | 14,226 |
| % VSS             | 82   | 84.2 | 87.6 | 88.9 | 89.6 | 90.6 |
| HRT, d            | 150  | 73.0 | 25   | 13.1 | 11.6 | 10.0 |
| SRT, d            | 200  | 100  | 70   | 50.0 | 30.0 | 15.0 |
| OLR, kg COD/m³/d  | 0.5  | 1    | 3    | 6    | 7    | 10   |
| SSUR, kg COD/kg VSS/d | 0.152 | 0.182 | 0.274 | 0.427 | 0.586 | 0.664 |
| SUR, kg COD/m³/d  | 0.472 | 0.8997 | 3.3028 | 5.6657 | 7.7753 | 9.4528 |
| Percent COD removal | 97.0  | 96.7 | 96.2 | 95.7 | 95.6 | 95   |
Figure 2. The Monod model

Figure 3. The Contois model.
3.1. Gas Production and Composition

To achieve accurate and good result, and to prevent the failure of the performance of anaerobic digester, factors such as pH, temperature, mixing, organic loading rate and nutrient availability must be controlled. Methanogenic activity will decline with the pH in the system of digester perversities from the optimum level (6.8 - 8). In addition, to reduce the resistance of mass transfer and obtain better contact between substrate and microbes by mixing, as shown in figure 5, the observed methane content decreased from 0.26 to 0.81/g COD/d while the OLR decreased from 0.05 to 13 kg COD m⁻³ because the acid bacteria grew more than methanogenic bacteria. In addition, figure 6, showed COD removal efficiency from 95% to 97% increasing, while the HRT increased from 10 to 150 days due to the increasing in contact time between waste water and granular sludge and enhanced COD removal.

Figure 4. Chen and Hashimoto model

Figure 5. Organic loading rate (kg COD/m³/day)
3.2. Characterization of POME
Characterization is a tool which has to do with the development, control and optimization of the wastewater processes by the characterization of the activated sludge. The physical and chemical properties of wastewater (POME) were characterized using various analytical techniques such as Scanning Electron Microscope (SEM) and Fourier Transform Infrared (FTIR) spectroscopy.

3.3. Elemental composition and spectrum analysis of the POME (SEM-EDXS) micrographs imaging of POME
The SEM showed the morphology of untreated and treated POME while the EDXs showed the propositional elemental composition spectrum demonstrated by the micrograph imaging and elemental analysis of untreated and treated POME. Figures 7 shows the micrographic imaging of the treated and untreated POME. Thus, Figure 7 (b) showed irregular disperse rod- shape and rough surface image in the bacteria cell of the composite for untreated POME. In this figure also, an external density can be noticed in the hall surface, where this observation is similar to [14]. In addition, the surface showed pore indicating that the gas bubbles were generated in the process inside the reactor. The study used the reactors at high loading rates, which justified the greatest quantity of morphologies observed when compared to [15]. However, in a complex network the appearance of the microorganisms was like noodles and they were connected to each other where Bello et al., has a similar observation [16]. On the other hand, Figure 7 (a) presents that the observed treated POME had smooth surface and had close pores compared with figure 8, which may indicate the interparticle bridging and effective degradation of the particles. Obviously, the two images can be presented and observed in various textural features between the networks of structures.

SEM-EDX was employed to further ascertain the composition of the formed elemental peak along with others. Figure 8 reveals the elemental composition of the treated and untreated POME. Table 4 shows the major elements observed during the SEM experiment such as carbon and oxygen. In addition, Saphira et al., 2018, they traced amount of phosphorus, sulphur, potassium and calcium that appeared in this result [17]. The high concentration of carbon and low concentration of sulphur is an indication that the sludge can be used as biomass energy source for power generation. The presence of a significant quantity of carbon provided active surface for the attachments of the organic pollutants to the surface of the composite. Over all, the difference in elements composition peak indicated in the POME treatment further affirmed the biodegradation potential of the model. In row POME, the result presented a
concentration of NH3eN which is an evidence of the importance of the treatment of POME before it was discharged into the river or land to avoid the eutrophication phenomenon. The toxic elements such as cd2 and pb2 in row pome are hazardous in the water and to human health [18].

![Figure 7. Scanning Electron Microscope (SEM) (a) before treated 500XK POME (b) treated POME](image)

![Figure 8. Elemental composition (a) after treatment (b) before treatment](image)

| Element   | Weight % Before | Weight % After |
|-----------|-----------------|----------------|
| Oxygen    | 48              | 54             |
| Sodium    | 18              | 12.637         |
| Magnesium | 4.421           | 2.415          |
| Silicon   | 0.567           | 0.299          |
| Chlorine  | 14.2            | 9.527          |
| Cadmium   | 0.231           | 0              |
| Potassium | 17.858          | 15.583         |

Table 4: Characteristics of POME before and after treatment

3.4. Fourier Transform Infrared (FTIR) spectroscopy

The Fourier Transform Infrared (FTIR) spectroscopy was used to discover the functional groups which were presented in the POME samples. FTIR works on the concept of absorption, or emission of solid liquid, or gas. In addition, FTIR has in a wide range ability to collect high resolution data process. Also, FTIR at times, can measure intensity over a narrow range of wave lengths. In this study, FTIR spectra of POME before and after treatment are shown in figure 9. The spectra of row POME in Figure 9(a) showed that the broad spectrum absorption observed at 3391.1m⁻¹ was designated to OH stretching. 
vibrations in intra molecular H [18]. On other hand, figure 9(b) shows that the Pome after treatment showed that a broad absorption band at 3391 cm$^{-1}$ was reduced to 3250 cm$^{-1}$ due to the completed digestion process of POME. However, due to the consumed component of lipid and fat, the shoulder peak 2855 cm$^{-1}$ disappeared in figure 9(b) after treatment. In addition, the band attributed to C-O-C vibrations in esters was obtained at 1088.75, having the same result as [19]. The absorption spectrum between 1130 and 1260 cm$^{-1}$ POME after treatment were similar for lignin [18]. In addition, two absorptions band appear between1449 and 1417cm$^{-1}$ related to the methyl asymmetric CH, designated to the effective degradation of the particle in the model [20].

Figure 9. FTIR for POME (a) before treatment (b) after treatment
4. Conclusion
MAS has been found to be a successful alternative treatment system that achieved high COD removal efficiency (94%-97%) in a short period of time and the recovery of methane CH₄ for energy would be an additional valuable of the process (67.8-70.3%). Therefore, MAS is a good alternative for treating high strength wastewaters. The proposed kinetic equations have been found to be applicable to the anaerobic treatment of Palm Oil Mill Effluent (POME). MAS has been able to operate at a high SRT and has been quite tolerant of variations in influent COD loadings. The SEM characterization and FTIR analysis supported the success of modification with the increase in a peak at C=H group, C=C, O-H and the presence of C=O.

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Nomenclatures
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 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)
Sᵣ 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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