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Anaerobic acetogenic treatment of palm oil mill effluent for COD removal

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Abstract. Palm oil mill effluent (POME) is a form of wastewater that is dark brownish and contains a high concentration of contaminants such as chemical oxygen demand (COD). Conventional biological treatments, such as ponding, are widely utilized and require large amounts of land to be occupied for extended periods to cure POME efficiently. The goal of this research is to examine the effect of 5, 7, and 9-day hydraulic retention times on the COD removal of POME in a batch mode utilizing anaerobic acetogenic treatment followed by anaerobic polishing. The findings indicate that increasing HRT improves the removal efficiency of POME treatment. COD had a removal efficiency of 53%, 63%, and 62% for 5,7, and 9 days, respectively. Seven and nine HRT days performed better than five HRT days. This study establishes the suitability of the anaerobic acetogenic process for the treatment of POME.

1. Introduction

Malaysia is one of the world's major producers and exporters of palm oil [1]. One of the most serious problems with POME is that it contains significant amounts of highly contaminated compounds. Water is consumed in significant quantities during the milling process of palm oil production. To produce one tonne of crude palm oil, around six to seven tonnes of water are required, with more than half of the volume being disposed of as palm oil mill wastewater (POME) [2]. One of the major drawbacks of POME is its high concentration of highly polluting compounds as it is more than 100 times as compared that of municipal wastewater [3]. POME has a high chemical oxygen demand, according to reports [4]. As a result, discharging POME into a stream may result in environmental pollution. Thus, an efficient and effective treatment technique should be developed to minimise the negative consequences associated with the discharge of nontreated POME into bodies of water.

2. Literature Review

Numerous biological, physical, and chemical procedures have been proposed as methods of POME therapy, but only a handful have been approved by the industry [5]. Physical and chemical processes can create several difficulties, including expensive installation and operating costs as well as the usage of many chemicals [6], which may not be appropriate for widespread application [7]. Given the biodegradability nature of POME, it was suggested that the most suited treatment technique would be a biological one [8].

When utilized properly, anaerobic treatment is a renewable energy source that can dramatically reduce greenhouse gas emissions related to palm oil production. During the anaerobic digestion process, POME can be employed as the primary source of anaerobic digestion biogas, such as CO_2 and CH_4, to be produced. Anaerobic digestion may also contribute in reducing the total cost of final sludge disposal by reducing the amount of oxygen required [9].

Anaerobic treatment has the advantage of weakening waste through the use of anaerobic microbes, which makes it more environmentally friendly. This four-step biological process begins with hydrolysis and goes through acidogenesis, acetogenesis, and methanogenesis before ending up with methanogenesis. Anaerobic digestion begins with hydrolysis, which is the first stage of the process. Anaerobic bacteria, which are present in this step complex but do not require oxygen, degrade organic molecules in the absence of oxygen [10]. Carbohydrates are transformed into sugar or alcohol, proteins into amino acids, and fats into fatty acids as part of this transformation process [11]. The acidogenic digestion stage is the second stage of anaerobic digestion. Acidogenesis is sometimes referred to as fermentation in scientific circles [11]. Fermentative organisms will use the hydrolysis products as substrates for their activities [12]. The other active microorganisms involved in the acetogenesis process use the acidogenic products as substrates for their growth and reproduction. Methanogenic bacteria convert non-methanogenic materials into methanogenic substrates through their process. Bacteria that produce methane can be found in the environment. The hydrogen-producing acetogenic bacteria are another type of bacterial species that oxidises volatile fatty acids and alcohol to produce methanogenic substrates such as acetate, hydrogen, and carbon dioxide, which are subsequently utilised to power the creation of methane [11]. A distinctive feature of methanogen's metabolism is that it grows solely on the energy and carbon sources H_2/CO_2 or acetate, rather than on any other energy or carbon sources. It is possible to produce methane in one of two ways during this step either by reducing CO_2 in the presence of hydrogen, which is accomplished by two distinct types of bacteria, acetotrophic bacteria and hydrogenotrophic bacteria, or by splitting up acetic acid molecules, which results in the production of carbon dioxide and methane [13]. Microorganisms with distinct physiologies and nutritional requirements are responsible for each of the four processes [14].

Over 85% of Malaysian palm oil mills have installed a ponding system for the treatment of palm oil mill effluent [15]. Ponding systems can be split into two types: anaerobic ponds and facultative or aerobic ponds. Anaerobic ponds are those that do not have any oxygen. It is necessary to have a substantial area of land to successfully process the POME using this approach, which generally takes a long period (up to four months). As a result, there has been a rise in interest in alternate production strategies that could partially or completely replace the ponding system. Anaerobic acetogenic treatment can be completed in a single or two-stage procedure. It is feasible to bring the anaerobic treatment to a close at the acetogenic stage by shortening the methanogenic phase. To minimise H_2-consuming bacteria, a variety of techniques have been tried, including biokinetic management (low pH and short HRT), heat shock treatment, chemical inhibitors, and oxygen purging [16]. As a result of disrupting these systems, the interaction of microorganisms with their environment is disrupted, allowing for the creation of acetogenic bacteria to occur.

Anaerobic acetogenic treatment techniques have been utilized to treat wastes that contain an abnormally high proportion of biodegradable material, such as food wastes [17-18]. The anaerobic acetogenic treatment technique is effective at removing COD from textile effluent [19-20].
However, the use of anaerobic acetogenic treatment for POME treatment is quite limited. This research aims to determine the effect of HRT on COD elimination when used in conjunction with an anaerobic acetogenic treatment procedure coupled with the aerobic condition for POME.

3. Materials and Methods

In Johor, POME samples were collected from an anaerobic pond of the Felda Kulai Palm Oil Mill. To ensure that there are no big debris or inert contaminants were present in the sludge before it was used in this experiment, it was sieved to a size of 1.0 mm. Approximately once a week, samples were collected and stored in a cool chamber with a temperature of less than 4°C.

In a 5L class beaker, a batch experiment was undertaken. A specific volume of anaerobic sludge and POME were added to the glass beaker, with a mixture volume of 2L The beakers were under anaerobic acetogenic conditions for 4,6, and 8 days, then the aerobic condition was applied for 24hr for each HRTs used, thus the completed cycle for each HRTs can be referred to 5, 7, and 9 HRT.

The pH was adjusted to be between 6.5 and 6.8. The pH adjustment was achieved using 2N hydrochloric acid (HCL) and 1N sodium hydroxide (NaOH) (beaker A), while another beaker was used without adjusting the pH (beaker B). Both beakers (A and B) underwent the same operational condition except for the pH difference.

The experiment was carried out at room temperature (26-30 °C). To provide good contact between bacteria and pollutants, a magnetic stirrer was used, which rotated at a speed of 50 revolutions per minute, and the beakers were covered with aluminium foil as illustrated in Figure 1.

In addition, a fine air bubble diffuser was used at a superficial air velocity of 1.5 cm/s. Every day of the anaerobic acetogenic treatment process, the dissolved oxygen content was adjusted to 2.0 mg/L, resulting in daily oxygen purification. It is necessary to perform a brief oxygen purging period (3-5 minutes) once daily during the anaerobic acetogenic treatment process to raise the concentration of dissolved oxygen to 2.0 mg/L. While the experiment was taking place, the pH and dissolved oxygen (DO) levels were monitored with a portable pH/DO metre (Horiba Ltd.). The volumetric exchange rate (VER) of the system, which was set at 50%, was used. Aluminium foils were used to cover the beakers, which helped to generate anaerobic conditions and eliminate evaporation in the lab. Specifically, the beakers were run for 40, 49, and 45 days, for 5, 7, and 9 days HTR, respectively.

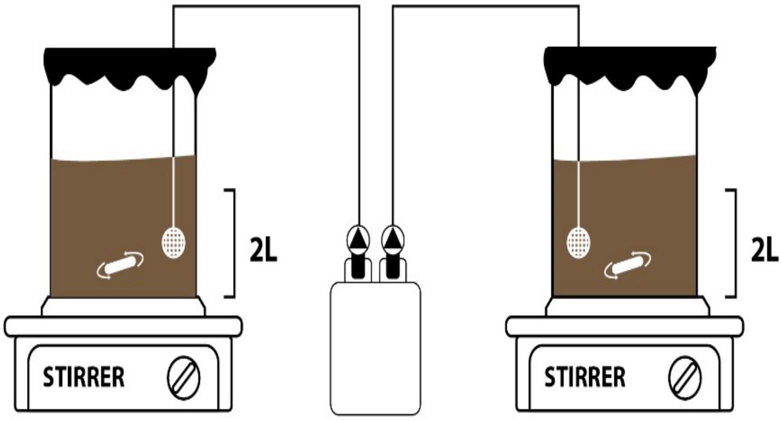

Figure 1. Experimental setup.

To assess the sample, it was centrifuged at 6,000 rpm for 15 minutes at room temperature. The ability of the COD to remove pollutants from the influent and effluent was determined by comparing the two samples. Using Standard Methods for the Examination of Water and Wastewater, COD was measured analytically [21]. ANOVA one-way was performed by using Microsoft Excel to anayles the data satitically.

4. Results and discussion

Figure 2 depicts the COD concentration profile in the influent, effluent, and removal performance of the anaerobic acetogens treatment process coupled with the aerobic condition during the 5 HRT experiment. The COD concentration in the influent was 2252 mg/L.

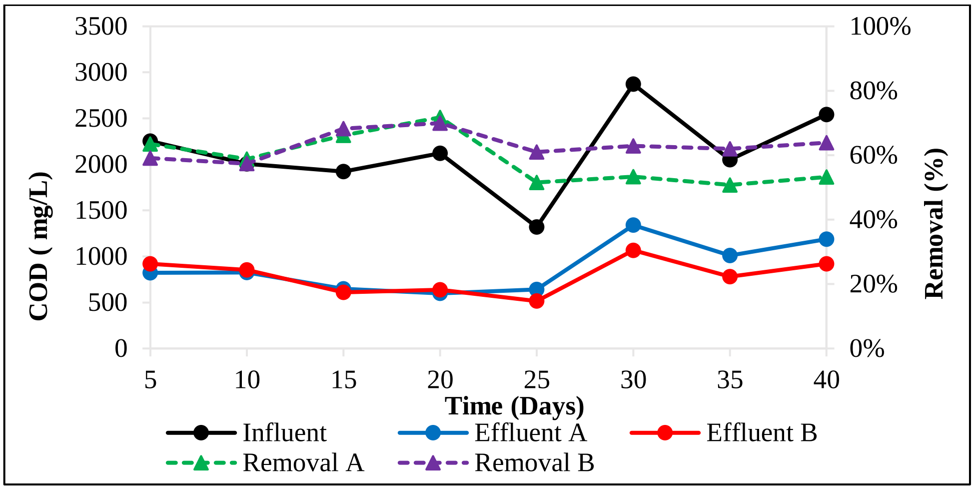

Figure 2. Profile of COD at 5 HRT.

HRT affects the performance of the system. To demonstrate the effect of HRT, it was predicted that pollutants from POME might be degraded with varying degrees of removal effectiveness under anaerobic acetogenic conditions if the HRT was just 5, 7, or 9 days long. The HRT should be sufficient to ensure that the number of dead microorganisms in the batch system does not exceed the number of new microorganisms generated in the batch system [22].

As indicated in Figure 2, COD elimination was successful in all batch tests. It was observed a decrease in COD elimination performance at the start of the experiment. This observation could be explained by the time required for bacteria to adjust to the altered environmental conditions caused by the acetogenic treatment process. In comparison to beaker A, beaker B removed a bigger amount of COD. This observation could be explained by the effect of the pH values used as a starting point (8.46), as the pH in beaker B was not adjusted, but the pH in beaker A was adjusted. The results suggested that as compared to beaker B, the pH adjustment may greatly improve COD removal. pH variations in the biodigester have a substantial effect on numerous parts of the complex bacterial metabolism [23].

Figure 2 shows that despite a momentary improvement in the COD removal capability of both beakers after four cycles, beakers A and B eliminated COD at rates of 52 and 63 percent, respectively, by the end of the process. Although COD removal between both beakers slightly differed, the *p*-value from ANOVA analysis indicated a significant difference with a *p*-value of less than 0.05 as shown in Table 1.

Table 1. ANOVA OF COD removals between beakers A and B for 5 HRT.

Source of Variation	**SS**	**df**	**MS**	**F**	**p-value**	$\mathbf{F}_{\text{critical}}$
Beaker A vs Beaker B	0.023	1	0.023	83.44	9.6E-05	5.987

The absence of COD indicates that there was significant biological activity occurring during the batch experiment's operation. On the other hand, the decrease in COD elimination may be attributable to a modest accumulation of VFA. During acetogenesis, the total volatile fatty acid concentration in the system may increase to such a level that it has minimal influence on COD elimination [24]. Earlier studies revealed that an anaerobic reactor operating at an HRT of fewer than ten days could result in a VFA rise of between 10% and 25% [25] it may account for the minor decline in removal performance during the first 20 days of the experiment.

However, air purification may help mitigate the effect of VFA. Damayanti, Sarto, Astiti, and Budhijanto [26] found that air purification reduced VFA accumulation; this could be because as air is introduced into the system, methanogenic microorganisms use VFA for self-maintenance. However, despite the relatively quick conversion of COD to VFA due to the presence of these methanogenic bacteria, there is no accumulation of VFA in the environment [26]. Because these microorganisms are sensitive to air injected into the beaker, they view the environment as toxic and hazardous. As a result, to survive, they consume the VFA before the formation of biogas [26].

For beaker A, two inhibitors of methanogenesis were used: pH and air. Beaker A consumed VFA at a slower pace than beaker B, which may have resulted in beaker A having a greater accumulation of VFA than beaker B as a result of this difference in consumption rates. The previous result may have an impact on the eradication of COD in the future. The fact that COD removal was more prevalent in the B beaker than in the A beaker could be explained by this.

Figure 3 shows the results of an experiment with 7 HRT, which revealed that beaker B had much more removals than beaker A. Beakers A and B achieved maximal COD removal after 42 days; COD removal in beaker A exceeded 65 percent and COD removal in beaker B exceeded 76 percent. Microorganisms were provided sufficient time to break down contaminants as a result of the increase in HRT. Although COD removal between both beakers slightly differed, the p-value from ANOVA analysis indicated a significant difference with a *p*-value less than 0.05 with a *p*-value of 0.003 as shown in Table 2.

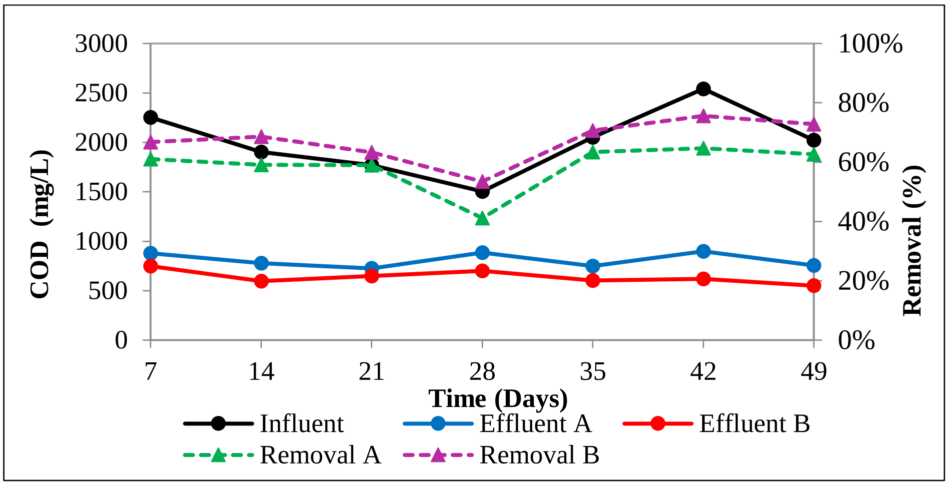

Figure 3. Profile of COD at 7 HRT.

Table 2. ANOVA OF COD removals between beakers A and B for 7 HRT.

Source of Variation	**SS**	**df**	**MS**	**F**	**p-value**	**$F_{critical}$**
Beaker A vs Beaker B	0.013	1	0.013	37.23	0.003	7.70

Between days 9 and 18, both beakers exhibited an increasing trend (Figure 4). Despite a brief decrease in both beakers on day 27, COD elimination remained large and stable throughout both beakers, reaching 62% and 76% for beakers A and B, respectively. Similarly, the obtained *p*-value of the COD removal between beakers A and B was less than 0.05 as shown in Table 3.

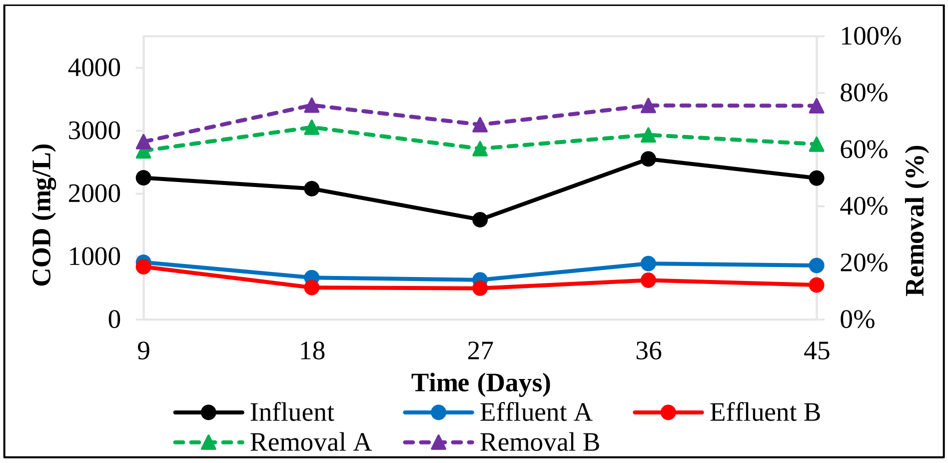

Figure 4. Profile of COD at 9 HRT.

Table 3. ANOVA OF COD removals between beakers A and B for 9 HRT.

Source of Variation	SS	df	MS	F	p-value	$F_{critical}$
Beaker A vs Beaker B	0.017	1	0.017	6.602	0.03	5.31

7 and 9 HRT days outperform 5 HRT days. The results indicate that increasing HRT increases the efficiency of POME therapy elimination. This conclusion validated previous findings [22] showing HRT affects COD removal. There was, however, no significant difference in removal performance between 7 and 9 HRT. Because increasing HRT from 7 to 9 days had only a modest influence on COD elimination performance, it is recommended to select suitable HRT to provide enough contact time between substrate and microorganisms and prevent the accumulation of VFA.

5. Conclusion

The combination of anaerobic and aerobic acetogenic processes was used to treat POME. According to the preliminary investigation, COD can be decomposed by anaerobic acetogenic followed by an aerobic process. It was revealed that various HRTs affected the performance of anaerobic acetogenic therapy. Superior removal performance was reported at 7 and 9 HRT.

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