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BIOGAS ENHANCEMENT USING AIR STRIPPING PRE-TREATMENT PROCESS IN ANAEROBIC DIGESTION

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ABSTRACT

Biogas is a form of renewable energy that could be a turning point in economic progress, and palm oil mill effluent (POME) is one of its primary sources in Malaysia. Due to the concerns regarding the quality of biogas from POME, this study was done to improve its quality by using the air-stripping method as the pre-treatment process in the wastewater treatment pond from the mill. Additionally, this procedure was recognised as one of the methods that can reduce the concentration of the chemical oxygen demand (COD), total suspended solids (TSS), and ammoniacal nitrogen (NH_3-N) in the POME. The experiment was carried out using an air-stripping lab scale model with different pH levels and stripping times at consistent operational temperatures and flow rates. The experimental results showed that the higher removal efficiencies of COD, TSS, and NH_3-N are 22.5%, 50%, and 92.8%, respectively, at pH of 12 and fourth days of the air stripping process. The highest biogas production rate is 5.54 ml/h on the first day of stripping time. It can be concluded that the reduction of NH_3-N enhanced biogas production.

Keywords: *air stripping, anaerobic digestion, biogas, palm oil mill effluent*

INTRODUCTION

The number of palm oil plants is growing every year, which causes a rise in the waste or effluent discharge from fresh fruit bunches. About 31% of the world's output and 53% of the world's exports come from Malaysia, which helps the domestic market thrive [1]. Due to its massive abundance and disposal issues, palm oil mill effluent (POME) is recognised as one of the significant issues in every palm oil mill factory. Direct discharge from POME on land results in soil waterlogging, killing vegetation on contact and clogging, and direct discharge to the waterways can cause water depletion, which results in aquatic pollution [2].

Anaerobic digestion is recognised as one of the effective ways of coping with agricultural waste and sewage sludge. In Malaysia, the conventional ponding method is still commonly used for POME handling due to Malaysia's constant weather and topographical area, which is more suitable for the ponding system. At the same time, the remaining mills opt for open digesting tanks [3]. POME is one of the sources that has a higher potential for biogas production, which is generated through the anaerobic process. It involves breaking organic matter without oxygen (Figure 1) [4]. Biogas can be utilised in combined heat and power (CHP) operations, or it can be converted into electricity using a combustion engine, fuel cell, or gas turbine, and the generated electricity can be consumed on-site or supplied to the electric grid. It contains roughly 70% of methane, 30% to 40% of carbon dioxide and the rest is labelled with other gases [5]-[6]. Methane gas emitted from untreated POME has a 25 times higher chance of causing greenhouse gas emissions (GHG), which has a higher risk of causing global warming [7]. According to Shahidul et al. [8], methane is a heat and energy source currently appearing as a Global Warming Potential (GWP) contributing to

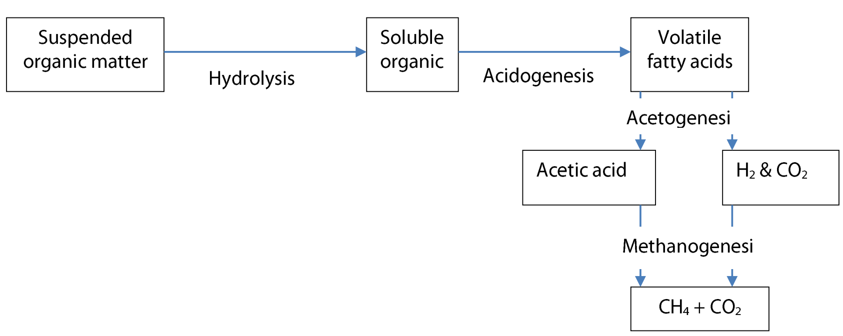

Figure 1 Process flow of biogas generation from anaerobic process

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climate change. Another substance inside the POME, ammoniacal nitrogen, adds to the creation of harmful methane emissions, which hinders the production of high-quality biogas [9]. The substantial reduction of ammoniacal nitrogen (NH_3-N) inside the POME resulted in safer and cleaner methane gas, preserving the environment. Air-stripping is one of the most efficient and cost-effective techniques to reduce NH_3-N [10].

Air stripping is a process that involves bringing a liquid into close contact with a gas, usually air, for some undesirable volatile substances present in the liquid phase to be released and carried away by the gas [11]. These processes are resulting a situation where a lot of the treated water surface area is exposed to the air, which encourages the transfer of contaminants from the liquid phase to the gaseous phase. Direct entry, such as urban wastewater discharges, and indirect entry, such as agricultural operations, are ways that ammonium nitrogen (NH_4^+) can enter aquatic ecosystems [12]. In the air-stripping process, ammonium ions were first transformed into free ammonia (FA) as part of the ammonia stripping process [13]. Next, FA diffuses from the bulk of the liquid phase to the interface between the liquid and gaseous phases, then crosses the interface and diffuses into the gaseous phases, and lastly, diffuses into the bulk of the gas phase. The system is then finished by removing the gas using the stripping agent.

According to Equation 1, the ammonium ion exists in equilibrium in aqueous solutions as the aqueous form (NH_4^+) and gaseous form (NH_3). By increasing pH and changing ammonium ion (NH_4^+) to ammonia gaseous form (NH_3), the stripper mechanism in ammonium elimination can be increased [14]. The effectiveness of ammonia removal is affected by several factors, including pH, the air-to-water (G/L) ratio, the temperature of the water and the surrounding environment, contact time and stripping time, column height, wastewater NH_4^+ concentration, hydraulic wastewater loading, and packing depth [14]. Since pH and stripping time are the two main parameters in the air stripping process, this study will focus more on pH and stripping time [15].

$$NH_4^+ + OH- \leftrightarrow NH_3 + H_2O \tag{1}$$

Conventional ammonia stripping processes are typically performed at a temperature between room temperature and 50˚C [16]. The airflow rate of air stripping is one of the parameters that significantly affected ammonia removal efficiency besides pH and temperature [10]. However, the interaction between air flow rate, pH and temperature considerably affected ammonia removal efficiency by simultaneously increasing air flow rate and temperature or air flow rate and pH [10]. Increased air flow rates did not significantly influence ammonia removal efficiency at lower temperatures, whereas raising the starting pH increased ammonia removal efficiencies. If the air stripping process was carried out at a low air flow rate, increasing the temperature and initial pH had no discernible effect on the ammonia removal efficiencies. However, increasing the temperatures and initial pH increases ammonia removal efficiencies at the higher air flow rate. Unlike temperature and pH, the airflow rate does not affect the FA concentration in the liquid phase. Rather than that, increasing the air flow rate maintains the FA concentration gradient between the liquid and gaseous phases, which is the driving force behind ammonia mass transfer. Besides that, ammonia recovery increases when the air flow rate is increased. It also increases the interfacial area, allowing for greater diffusion of gaseous ammonia from the liquid to the gas phase. On the other hand, increased flow rates can decrease liquid temperature, foaming, and liquid phase evaporation [10],[17].

Hence, the objective of this study is to identify the best pH and stripping time to enhance the quality of the biogas production (CH_4 +CO_2) from the POME while reducing the generation of COD, TSS, and NH_3-N by using air stripping pre-treatment process.

METHODOLOGY

Experimental Flow

The study was started by collecting the POME sample from the palm oil factory close to the study area. The air stripping process was run on the POME sample (lab scale) to treat and reduce the ammonium ion in the POME by adjusting the pH and stripping time. Once the air stripping process was done, the anaerobic process took about seven days without any other process running. A new nalophan bag was attached to the glass bottle to collect the biogas gas during the anaerobic process. Hence, no other gases, except biogas, will be trapped inside the nalophan bag. Then, the amount of collected biogas (CH_4 +CO_2) gas was measured using the water displacement method.

Site Selection

The samples were collected from the POME wastewater treatment plant at Felda Lepar Hilir 3 Palm Oil Mill, Gambang, Kuantan, Pahang, Malaysia (Figure 2). An anaerobic pond was chosen as the main point in this study since it is the pond where the highest biogas is generated.

Air Stripping Process

The air stripping process was run by using 550 ml of POME sample in a 1 L glass bottle with an attached 5 L nalophan bag at the top of the bottle. The experiment was set up in a 35°C water bath with an aerator that supplied 4L/min air flow rate, as shown in Figure 3. The experiments' temperature is adjusted using a water bath method while the nalophan bag traps ammonia gas arising from the pre-treatment process from release to the environment. The purpose of the nalophan bag is to prevent the contaminated gases from being released in the building/closed area where the experiment is being set up. All the connections between the silicone tube with a bottle and the nalophan bag are secured so that no gases escape into the surrounding area. Each experiment was run at the same temperature and with the same amount of POME sample. Sodium hydroxide solution was added to the POME sample, and the pH values were set at 8, 10, and 12 with the stripping time of 2, 3, and 4 days [10],[15],[17]. During the aeration process, the gases trapped in the nalophan bag will be released into the open area once the bag is complete to prevent pressure build-up. After that, the treated POME was tested for its pH, COD, TSS and NH3-N. Then, the parameter test results were compared before and after the air stripping pre-treatment process.

Figure 2 Site sampling point at Felda Lepar Hilir 3

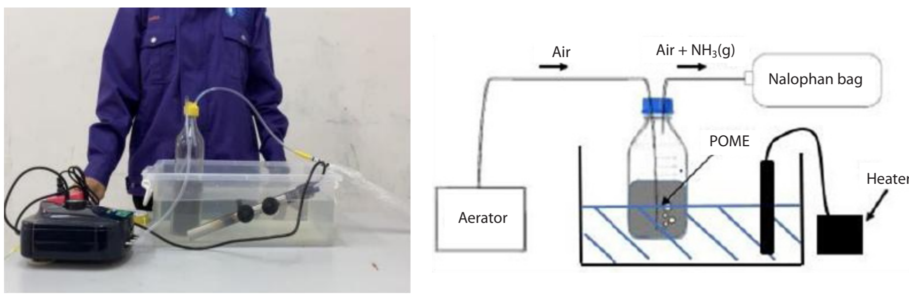

Figure 3 The experimental setup for air stripping pre-treatment

Preliminary Test

COD Test

The HI 839800 COD digestion reactor is used in the COD parameter test. The experiment started by preheating the COD reactor to 150°C, and the safety shield was placed in front of the reactor. Firstly, 2 mL of POME samples were diluted with 70 mL of distilled water because it is a high-concentration sample. The caps from two COD Digestion Reagent Vials were removed, and the first vial was held at a 45-degree angle. 2 mL of diluted sample was added to the vial using a clean volumetric pipette, and the second vial was used as a blank by adding 2 mL distilled water to the vial using a clean volumetric pipette. The vials were then capped tightly and wiped with a clean towel. The vials were inverted gently several times to mix and placed in the preheated COD Reactor for 2 hours. The reactor was then turned off, and the vials were waited for 20 minutes to cool at 120°C or less. Each vial was inverted several times while still warm and was placed into a rack to be cooled at room temperature, and then a DR 5000 Spectrophotometer was used to get the reading.

Total suspended solid (TSS)

The experiment started with the preparation of a glass-fibre disk. The filtration apparatus inserted the glass fibre with a wrinkled side up. Then, the disk was applied with a vacuum and washed with three successive 20 mL portions of reagent-grade water. The suction was continued to remove all traces of water. Then, the filter was removed from the filtration apparatus, transferred to an inert aluminium dish, and kept in the oven for drying at 103°C to 105°C for 1 hour. After 1 hour, the aluminium dish was kept in the desiccator to cool and balance the temperature and weight. The analytical balance was turned on, and the result was recorded with the filter and aluminium dish (in unit mg). Then, the filtering apparatus and filter were assembled, and the suction process was begun. The filter was wet, and a small volume of distilled water was used to seat it. In a beaker, the POME sample was stirred with a magnetic stirrer at a speed that allowed it to shear larger particles. While stirring, a 5 mL sample was transferred onto the seated glass fibre using a measuring cylinder. The filter was washed with three successive 10 mL volumes of distilled water, allowing complete drainage between washing and suction, and was continued for about 3 min after filtration was complete. After that, the filter was removed from the filtration apparatus and transferred to the aluminium dish as a support. The filter was dried for at least 1 hour at 103°C to 105°C in an oven, cooled in a desiccator to balance temperature and weighed. The weight of the filter, dish and residue were recorded as (unit in mg), and the drying, cooling, desiccating, and weighing cycle was repeated until a constant weight was obtained.

Ammoniacal nitrogen (NH_3-N)

DR 5000 Spectrophotometer was used to measure the concentration of NH_3-N in the POME samples.

Anaerobic Digestion Experiments

The anaerobic digestion process was taking part after the air-stripping pre-treatment process. This process was run to collect the biogas generated from the air-stripping pre-treatment process, as seen in Figure 4. During this process, no process was involved other than the anaerobic process. A glass bottle containing treated POME was detached from the aerator. During the detachment, the seal was tightly closed to prevent escaping gas from coming out of the bottle. All digesters were filled with sufficient nitrogen gas to purge oxygen to create an anaerobic condition. Then, the nalophan bag was attached to a silicon tube connected to the treated bottle to trap the biogas. The same water bath method was applied throughout the process. Another bottle was prepared for control purposes. The condition for the control bottle was set the same as the tested bottle but without undergoing an air stripping pre-treatment process. After seven days of anaerobic digestion, the biogas generation from treated and raw POME was compared using the water displacement method, while the biogas composition was measured using the portable gas detector.

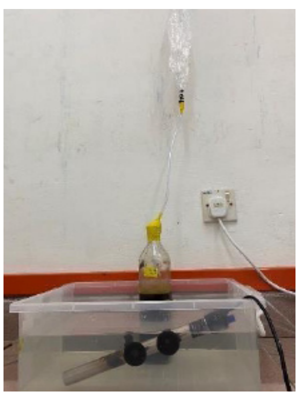

Figure 4 Anaerobic digestion process

Water Displacement

The water displacement method was used to measure the biogas production. A container full of water was used for the water and gas displacement process. The generated biogas will replace the water by pressing the nalophan bag, and water will slowly come out of the container since no element can occupy the same space simultaneously. The following formula was used to calculate the biogas production rate collected in the anaerobic digestion process.

$$\text{The volume of biogas} = \text{Volume water before} - \text{Volume water after pressing nalophan bag} \quad (2)$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad (3)$$

P = Pressure, V = Volume, T = Temperature,

where,

Temperature inside the glass bottle, T2 = 35°C @ 308.15 K
Water Pressure at 308.15K (Pwater) = 5.63 kPa
Total Pressure (Pwater + Pbiogas) = 101.3 kPa
Biogas Pressure (Pbiogas = Ptotal – Pwater), P1 = 95.67 kPa

$$\text{Rate of biogas production} = \frac{\text{Volume of dry biogas production (ml)}}{\text{Time taken (h)}} \quad (4)$$

RESULTS AND DISCUSSION

Effect of Air Stripping on the Reduction of COD, TSS and NH_3-N

This study investigated the performance of air stripping by adjusting the pH and stripping time to reduce the COD, TSS and NH_3-N of POME and enhance the quality of the biogas. The temperature of palm oil mill effluent is 45˚C since fresh fruit bunches (FFB) are sterilised using steam to remove the palm fruit from the bunch, and also deactivates any enzymes during the processing at the mill, while the pH of POME samples taken from Felda Lepar Hilir 3 Palm Oil Mill was 4.71 which is below the standard discharge limit by the Malaysian Department of Environment (DOE).

The results before and after the treatment can be seen in Table 1. This study conducted the air stripping pre-treatment of POME at pH 8, 10 and 12. Typically, conventional air stripping operations are carried out at a pH range of 10 – 12 [16]. Similarly, with air stripping time, the air stripping of POME was conducted for 1, 2, 3 and 4 days. The air stripping pre-treatment, conducted at an initial pH of 12 and 4 days of stripping time, resulted in the largest reduction of COD, TSS, and NH_3-N concentration. The results showed that COD, TSS, and NH_3-N removal efficiencies were 22.5%, 50% and 92.8%, respectively. The air stripping process effectively reduces COD in the POME since the aeration process will increase the dissolved oxygen in the wastewater; hence, the microorganisms or bacteria in the POME will break down organic compounds present in wastewater into carbon dioxide and water in the presence of air. Also, the bubbles from the aeration process will trap the suspended solids, decreasing the TSS concentration.

The decrease in NH_3-N concentration in POME can be seen starting from day 1 of the experiment when 0.34 mg/L was at pH 8, 0.27 mg/L was at pH 10, and 0.11 mg/L was at pH 12. From the result in Table 1, the ammonia reduction decreased simultaneously with time, and day 4 recorded a higher reduction of NH_3-N with 0.10 mg/L at pH 8, 0.07 mg/L at pH 10 and 0.03 mg/L at pH 12. In comparison of pH value, higher pH contributes to the highest reduction of NH_3-N, with pH 12 and day 4 recording the lowest concentration of NH_3-N with almost 93% reduction, where most of the NH_3-N being oxidised into ammonia gases by using air stripping process. This research's findings are supported by previous studies in which higher ammonia removal rates were obtained after 12 hours of air stripping, with the efficiency of the process increasing from 6.6% to 98% as the pH increased from 9.4 to 12.38 [14]-[15].

Figure 5 summarises all the data for comparison. According to Santos et al. [11], with a high pH value, air stripping may remove 92.8% of the NH_3-N at a rate of 4 to 9 days. Kinidi et al. [14] also stated that pH becomes insignificant when the pH value exceeds

Table 1 Results of COD, TSS and NH_3-N of POME before and after air stripping pre-treatment

Stripping Time (Day)	pH		COD (mg/L)		TSS (mg/L)		NH_3-N (mg/L)	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
1		7.47		977		2854		0.34
2		7.38		7.93		1027		969
	8		1027		3400		0.42	
3		7.93		912		3400		0.27
4		7.58		874		2196		0.10
1		7.84		973		2383		0.27
2		7.69		980		2379		0.20
	10		1027		3400		0.42	
3		8.25		851		1965		0.10
4		8.18		802		1976		0.07
1		7.85		1017		1970		0.11
2		7.72		869		1949		0.09
	12		1027		3400		0.42	
3		7.93		806		1798		0.07
4		8.13		795		1700		0.03

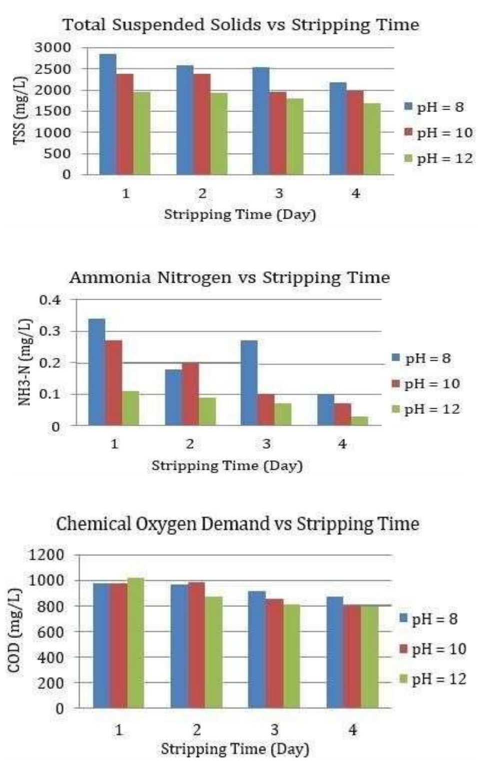

Figure 5 Graph of chemical oxygen demand (COD), total suspended solid (TSS) and ammoniacal nitrogen (NH_3-N) removal

10.5, but the additional sodium hydroxide solution boosts the process of NH_3-N removal inside the POME. The statements from the previous study supported the findings of this project.

Chemical Oxygen Demand

The samples of POME taken from Felda Lepar Hilir 3 palm oil mill consist of 1027 mg/L COD. After the air stripping pre-treatment, the COD reading in POME samples decreased. The overall COD removal rate was in the range of 1% to 22.5%. The highest COD removal rate was 22.5%, achieved under a pH value of 12 and a stripping time of 4 days. The lowest removal rate was 1%, under the condition of pH value 12 at one day of stripping time. pH value and stripping time influence the removal of COD. When pH was increased, the ammonia fraction also increased, resulting in higher removal efficiency and mass transfer rate. Air stripping also improved COD removal, which may improve the volume of biogas released. Thus, increased pH and stripping time resulted in higher COD removal in air stripping pre-treatment. COD is an estimation of oxygen necessary to oxidise the organic matter in wastewater and the amount of oxygen used by organic matter in boiling acid potassium dichromate solution. If COD levels in wastewater are high, aerobic and anaerobic biological treatment, filtration, coagulation, and flocculation should be utilised to remove organic and inorganic particles. However, the air stripping pre-treatment in this study is not fully treated in the POME sample since it is just a pre-treatment process.

Total Suspended Solid

POME typically consists of 40,500 – 75,000 mg/L of suspended solids. The samples of POME used in this study contain 3400 mg/L of total suspended solids. After the air stripping pre-treatment, the reading of TSS in POME samples decreased. The overall TSS removal rate was 16% to 50% after air stripping pre-treatment. The highest TSS removal rate was 50%, achieved under the condition of a pH value of 12 and a stripping time of 4 days. The lowest removal rate was 16%, under pH value eight, at one day of stripping time. Air stripping removes contaminants from water by contacting clean air with the contaminated water, causing the Volatile Organic Compounds and other contaminants to move from the water into the air. Based on the results analysis, the highest TSS removal of POME was at pH value 12 after four days of the air stripping process, which removed 50% of TSS. Hence, pH value and stripping time influence the TSS removal. According to Kanidi et al. [14]xx, the average removal rate increases with increasing stripping time. Under the same stripping time, the average removal rate increases with increasing pH during the air stripping pre-treatment process. Hence, higher pH and stripping time increase the potential of TSS removal. However, the TSS of POME is still high according to the standard limit set by the DOE since it needs further treatment.

Ammonia Nitrogen

Typically, POME consists of 250 – 120 mg/L of NH_3-N. The sample used in this research consists of 0.42 mg/L of NH_3-N. After being treated by air stripping pre-treatment, the reading of NH_3-N decreased. The removal rate of NH_3-N after POME was treated was 19% to 92.8%. Steps in the ammonia stripping process start with converting ammonium ions (NH_4^+) to free ammonia (FA). Then, the diffusion of FA from the bulk liquid phase to the interface between the liquid and gaseous phase is followed by the transfer of FA across the interface into the gaseous phase and, finally, the diffusion of FA into the bulk gas phase. The gas used for stripping (also called the stripping agent) containing FA is finally removed from the system. In aqueous solutions, the ammonium ion exists in equilibrium in its aqueous form (NH_4^+) and gaseous form (NH_3). The stripper removes ammonium by increasing the pH and converting ammonium ion (NH_4^+) to ammonia gaseous form (NH_3). When pH was increased, the ammonia fraction also increased, resulting in higher removal efficiency and mass transfer rate [14].

pH

Air stripping at natural pH was applied to observe the efficiency of the process of removing COD and TSS. Three pH values were selected in conducting air stripping pre-treatment of POME, which are 8, 10 and 12. After the air stripping process was completed between 1 to 4 days of stripping time, the pH of all samples decreased to pH 7 to 8 ± 0.18. This study shows that the final pH values decreased due to the removal of free ammonia gas. The treated POME has a suitable pH for anaerobic digestion to produce biogas. The optimum pH range in an anaerobic digester is 6.8 to 7.2. However, the process can tolerate a range of 6.5 up to 8.0. At a pH of 3.5 to 4.5, the wastewater has a lot of organic matter in it. Anaerobic digestion could be a good way to clean up wastewater with a lot of organic material. It also makes less sludge and generates biogas, a renewable energy source. A neutral pH is usually suitable for anaerobic microorganisms to work in a pH lower than 5; the metabolism of methanogenic communities could be slowed down.

Production of Biogas

Biogas production can be obtained through a treated anaerobic digestion process. In order to obtain high-quality biogas production, a few factors need to be considered. The factors include hydraulic retention time, pH value and ammonia removal during the air-stripping treatment process. Ammonia removal is successfully achieved during the initial phase of this study through the air stripping process with a proper pH value and the duration of stripping time. This is supported by Kinidi et al. [14], where the reduction of ammonia removal can enhance the performance of the anaerobic digestion process, thus boosting the quality of the biogas.

However, the air stripping process has its disadvantages; since it is a process where it flows the moving air with a specific flow rate through contaminated water such as POME, chicken manure, and wastewater, the water will evaporate into gases form hence, decreasing the volume of POME [18]. In this study, the POME volume decreases from 550 ml in its original state to 400 ml, depending on the duration of the stripping time, which would affect the collection of biogas production since the volume of POME for anaerobic digestion was inadequate. The same experiment was run to test the production of the biogas from POME, and the result can be seen in Figure 6.

As a result, the longer the retention time, the lesser the rate of biogas produced. However, it contains high-quality gases since the ammonia removal efficiency is high. Ammonia removal is successfully achieved through the air stripping process with the proper pH value and the duration of stripping time. This is supported by Kinidi et al. [14], where a high reduction of ammonia removal can enhance the performance of the anaerobic digestion process, thus boosting the production of biogas.

According to Loh et al. [19], 1 m^3 of POME can produce around 28 m^3 of biogas. On the laboratory scale, it can produce approximately 0.00040 m^3 and above. In this study, the minimum volume of biogas collected is 420 ml at pH = 8 with a hydraulic retention time of 4 days and the highest data collected is at pH = 12, and hydraulic retention time is one day with the volume of biogas production is 930 ml. This is supported by Shi et al. [20], where shorter stripping time is desirable as it is directly related to reducing capital cost and increasing process efficiency.

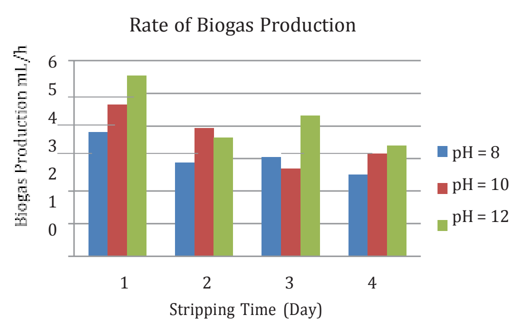

Figure 6 Rate of Biogas Production

CONCLUSIONS

This research has identified the performance of air stripping in reducing COD, TSS, and NH_3-N to treat POME for the anaerobic digestion process. Around 22.5% of COD, 50% of TSS and 92.8% of NH_3-N were removed. The result also showed that air stripping conditions, such as stripping time and pH, play significant roles in the efficiency of ammonia removal, which needs to be removed to improve the quality of the biogas. Almost 93% of NH_3-N were released after four days of air stripping pre-treatment process at pH 12, and around 5.54 ml/h of biogas were produced after day one of air stripping with pH 12. For future recommendations, it is advisable to manipulate the temperature up to 50°C since the temperature difference affected biogas production. This is because the air stripping pre-treatment and anaerobic digestion process is undergone at high temperatures. This research was run at a temperature of 35°C for safety reasons. Lastly, the catalyst can be introduced during the anaerobic process to stimulate the bacteria inside the sample since it can also improve biogas generation from POME.

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