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Effect of Initial PH Adjustment on Acetogenic Treatment of Palm Oil Mill Effluent

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Abstract. The waste produces from the palm oil industries either in liquid or solid forms have significant impact on the environment. Palm oil mill effluent (POME), is comprised of organic compounds which can be treated through aerobic and anaerobic degradation process. The current treatment technology of POME is mostly dependent on biological treatment process. These processes require large acreage of land and always associated with production of the greenhouses gases particularly carbon dioxide and methane gases. Hence, enhancement of the existing approach in POME treatment is very much required. The aim of this research is to investigate the effect of initial pH adjustment on the treatment of POME under acetogenic condition. Initially, a suitable hydraulic retention time of four days was used in a reactor system, equipped with continuous stirring process set at a mixing rate of 50 rpm. Analyses of color, chemical oxygen demand (COD), ammonia nitrogen, nitrite, and nitrate removal were measured. The results showed that the removal performance of COD, color, ammonia nitrogen, nitrite and nitrate were 38%, 29%, 53%, 52% and 92%, respectively. This study demonstrates that acetogenic process is a suitable and reliable environmental process in treating the POME.

Keywords: Palm Oil Mill Effluent; Palm Oil Treatment; Anaerobic; Acetogenic.

INTRODUCTION

The world demand for fit to be eaten oil is growing along with population. The world population is expected to develop from 7 billion in 2011 to 9 billion via 2043 (Wong et al., 2019). Thus, the dependence on oil including palm oil will proceed to rise to fulfil the increasing global demand. Malaysia and Indonesia together contributes about 85–90% of total global production (Choong et al., 2018). Palm oil processing consumes a large volume of water and also generates a large volume of wastewater. To produce a single tonne of crude palm oil, as much as 7 tonnes of water are used, with roughly more than half of it ending up as POME (Ahmad et al., 2003). In 2012, roughly 20 million tonnes of crude palm oil was produced (Zaied et al., 2019). This lead to a considerably high amount of water being used, and most of it ending up as POME which is extremely dangerous for the environment. POME is a very polluted wastewater. POME is acidic, dark and brownish in color. It is characterized with high in organic content with average values of 25,000 mg/L biochemical oxygen demand

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(BOD) and 50,000 mg/L chemical oxygen demand (COD), 18 000 mg/L, 40500 mg/L total solid (TS), and 4000mg/L oil and grease (Alhaji et al., 2016). Thus, an efficient and effective treatment system should be applied in order to prevent the adverse impact that may take place if the improper treated POME is release to the water bodies.

LITERATURE REVIEW

In Malaysia, ponding system is widely adopted for POME treatment in palm oil mills industry (Ahmad et al., 2003). However, ponding systems require prolong hydraulic retention time (HRT) in the range of 100–120 days, large area needed. Ponding system for POME treatment usually consisted of one or more anaerobic and aerobic ponds. Thus, ponding system is commonly associated with the emission of greenhouse gases (GHGs) including CO_2 and CH_4 (Lee et al., 2019). Many attempts have been conducted in laboratory scaled to treat POME such as anaerobic filtration, fluidized bed reactor, up-flow anaerobic sludge blanket (UASB), up-flow anaerobic sludge fixed-film (UASFF), continuous stirred tank (CSTR), anaerobic contact digestion (Poh et al., 2009; Ohimain et al., 2017), anaerobic sequencing batch (ASBR) (Ahmed et al., 2015). However, these techniques are not typically applied in a practical or industrial setting, due to them costing more than the conventional techniques using anaerobic digestion system (Lam et al., 2011). In Malaysia, one of the most popular techniques used for POME treatment is ponding (Ma et al., 1985). The name of the system originates from the use of several ponds with different purposes such as anaerobic, facultative and algae (aerobic) ponds (Hassan et al., 2004). Most high strength wastewater including POME requires both anaerobic treatment followed by aerobic degradation process in order to obtain better overall treatment efficiency (Trisakti et al., 2015).

Anaerobic digestion is a biochemical process involving four steps starting with hydrolysis, acidogenesis, acetogenesis and methanogenesis. Hydrolysis is the first stage of anaerobic digestion process is also known as the depolymerization process of organic matters. In this step complex organic compounds are breaking down by different anaerobic microorganisms without the presence of oxygen (Wong et al., 2019). This essential step is the usage of strict anaerobes such as bacteroides, clostridia and facultative bacteria such as streptococci (Christy et al., 2014). The importance of this particular step, relates to the size of the organic molecules being too large, and require for them to be broken down into smaller molecules (Poh et al., 2009; Lam et al., 2011).

The second step of anaerobic digestion is called the acidogenic stage. Acidogenesis is sometimes referred as fermentation process (Lam et al., 2011). The organic monomers produced from hydrolysis process will then be utilized as substrates by fermentative organisms (Demirel et al., 2008). The products produced in the acidogenic phase are consumed as substrates for the other active microorganisms in acetogenesis process. Acetogenesis bacteria are used to convert products into methanogenic substrates. The substrates are then oxidized to acetate, carbon dioxide, and or hydrogen (Khanal, 2008; Lam et al., 2011). Methanogen has an unusual type of metabolism because they use H_2/CO_2 or acetate as energy and carbon sources for growth. Methane production in the fourth step occurs in two ways either by reduction of carbon dioxide with hydrogen by two groups of bacteria are involved in the process acetotrophic and hydrogenotrophic or using a split of acetic acid molecules to generate carbon dioxide and methane (Christy et al., 2014). All microorganisms in the four processes have different physiology and nutritional requirements that control the metabolic activities (Olvera et al., 2012).

Methanogens are weak microbes and sensitive to environmental changes (Li et al., 2007). Since the methanogen are categorized as strict anaerobes, the production of methane gas by methanogens can be usefully inhibited by air-exposure (Omil et al., 1997). Different methods have been used to inhibit H_2-consuming bacteria, including biokinetic control (low pH and short HRT), heat shock treatment, chemical inhibitors and oxygen purge (Chae et al., 2010). When these processes are altered, the behaviour and physiology of the microorganisms also change relative to their environment (Chae et al., 2010), and build up of acetogenic bacteria can be achieved. Optimization of acetogenic process requires the variation of operational conditions to break down complex organic compounds into hydrogen, carbon dioxide and acetate (Khandaker et al., 2019). Thus, the anaerobic system is manipulated for termination at the acetogenic process by inhibiting the methanogenic stage. Acetogenic reactors have been used to treat waste with high and readily biodegradable content, such as food waste (Fascetti et al., 1998; Fang et al., 2000; Ferchichi et al., 2005) and textile wastewater (Khandaker et al., 2017). To date, no study has been carried out to investigate the effect of acetogenic condition for POME treatment. The objective of this study is to clarify the impact of short HRT of four days and initial pH adjustment at 6.0 on acetogenic condition for POME treatment toward the reduction of color, COD, ammonia nitrogen, nitrite and nitrate.

MATERIALS AND METHODS

The POME samples collected from an anaerobic pond of the palm oil industry in Felda Kulai, Johor, Malaysia. The samples were sieved using a 1.0 mm mesh to remove large debris and inert impurities, and then stored at 4 °C prior to experimental work. Anaerobic sludge is used as the source of sludge biomass that was taken from the palm oil mill. The design of the reactor used in this study was based on Sarker et al. (2018) and Khandaker et al. (2019) with several modifications. The experimental work was conducted in a 2 L glass column with a height of 193mm and a diameter of 130 mm. The system operated with a working volume of 1 L. In this study, four days HRT was used to evaluate the effect of anaerobic acetogenic condition on degradation of organic matters in POME. The initial mixed liquor suspended solid (MLSS) concentration was 2,000 mg/L. In order to assure a well mixed condition of the biomass and the wastewater, the wastewater was mixed throughout the experimental work using a magnetic stirrer rotated at 50 rpm. The volumetric exchange rate of the system was set at 50% and the pH was initially adjusted to 6.0 using 2 N hydrochloric acid (HCl) for acetogenic treatment process. The reactors were purged once on a daily basis by adjusting the dissolved oxygen concentration to 2.0 mg/L. Aeration was conducted using an air pump with a superficial air velocity of 0.5 cm/s. To increase dissolved oxygen concentration to 2.0 mg/L, short oxygen purging time is used (3-5) minutes. The treatment system was operated under room temperature. The properties of fed samples were examined every four days. HORIBA/pH/DO meter model was used in order to measure the POME pH level. The final effluent was centrifuged for 15 min at 6,000 rpm to separate the liquid and solid phases for further analysis. The sample was then analyzed for COD, color, ammonia nitrogen, nitrate, and nitrite. The parameters were carried out according to Standard Methods for the Examination of Water and

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Wastewater (APHA, 2005). The analytical tests followed the procedures as given in the Hach Water Analysis Handbook (Hach, 1997).

RESULTS AND DISCUSSION

POME samples collected from the anaerobic pond were characterized as shown in Table 1.

Table 1: Summary of essential characteristics of POME

Parameter	Value
COD mg/L	1174
Color ADMI	1040
pH	7.19
Ammonia nitrogen mg/L	354
Nitrite mg/L	101
Nitrate mg/L	30

At the initial stage of the experiment the pH was adjusted to 6 in order to ensure the successful development of anaerobic digestion condition. Wong et al. (2019) stated that pH 6.8-7.8 is considered as optimum operating range for anaerobe cultures. In anaerobic acetogenic process, the anaerobic reaction is manipulated to enhance the acetogenic process by limiting the methanogenic process (Khandaker et al., 2019). The inhibition of methanogenic process limits the reaction to anaerobic acetogenesis and eliminates the emission of methane, which is a greenhouse gas (Khandaker et al., 2019). Thus, low pH increases the activity of acidogens, and reduce the activity of methanogens (Wong et al., 2019).

The anaerobic acetogenic reactors were operated for five cycles (20 days). The performance of the experiment was determined on the basis of COD, color, ammonia nitrogen, nitrite and nitrate removal. At the beginning of the experiment, COD removal percentage was 34% which then reduce to 22% in the second cycle of the experimental run. The removal efficiency increased to over 38% at the end of the experiment, indicating an acclimation period is essential for biodegradation by gradually exposing the microbial community to potential inhibition of methanogenic bacteria (Metcalf et al., 2003). During acetogenesis, the total volatile fatty acid may increase in the system until it reached a stable condition that affects COD removal.

The removal percentage of color depends on microbial ability, either to consume color causing compounds such as lignin or to produce biological products such as enzymes to remove color (Hamisan et al., 2009). Based on Figure 1, the percentage of color removal was low. The final removal for color was only about 32%. There was an increment of only 20 % when compared to the initial removal performance of color.

The trend of ammonia nitrogen removal is also depicted in Figure 1. The average removal of ammonia nitrogen was 53%. The removal was about 66% during the startup phase and decreased to approximately 53% at the end of the experiment run. The findings suggested that oxidation of ammonia occurred by ammonia oxidizing bacteria (AOB) during the anaerobic acetogenic treatment with a periodic shock of oxygen (Bellucci et al., 2011).

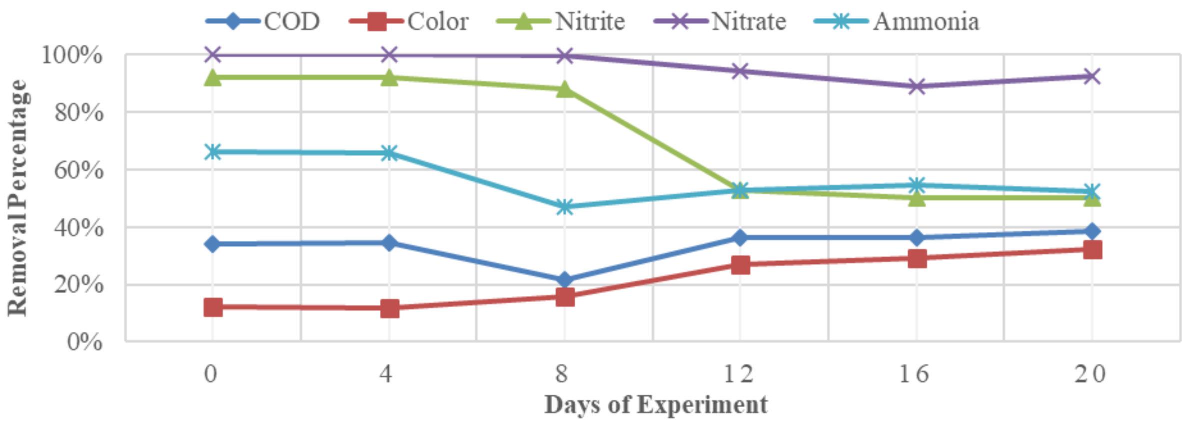

Figure 1: Percentage Removal of COD, Color, Nitrate, Nitrite, and Ammonia

During startup, the percentage removal of nitrite and nitrate were 92% and 100%, respectively (Figure 1). The removal of nitrite decreased to approximately 52% at the end of the experiment run. The low removal percentage of nitrite could be due to the adaptation of anaerobic acetogenic bacteria with the reactor's environment, as well as experimental conditions.

The removal of nitrate was high throughout most of the experimental run. There was only a slight decrease at the end of the experiment. Due to the existence of dissolved oxygen (as low as 1.0 mg O_2/L), the removal of nitrogen would cause the nitrite and nitrate to be converted from ammonia. Consequently, if oxygen were to be removed, denitrification occurs, in which the nitrate will be converted and reduced to nitrogen and nitrogen oxide (Ying et al., 2010; Rahimi et al., 2011). Thus, daily purging of oxygen for a short time allows nitrogen removal to take place in a single reactor in which the influent ammonium nitrogen is nitrified and then denitrified.

CONCLUSION

The study successfully demonstrated the convincing reduction in biodegradable matters by the implementation of acetogenic condition. The process requires periodic purging with oxygen, unlike the aerobic process that requires constant aeration and consumption of a substantial amount of energy. Anaerobic acetogenic process is a suitable environmentally friendly technique for pollutant removal from POME since the potentially emission of the greenhouse gases (GHG) are limited. Culture acclimation and HRT plays a significant role in the stability of the removal performance of the compounds measured in this study. With controlled air injection and adjustment of the pH, the acetogenic stage can be conducted in anaerobic digestion. Ultimately, this article presents information that can aid in enhancing the anaerobic microbial consortium performance.

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REFERENCES

[1] Ahmad, A. L., Ismail, S., & Bhatia, S. (2003). Water recycling from palm oil mill effluent (pome) using membrane technology. *Desalination, 157*, 87-95.

[2] Ahmed, Y., Yaakob, Z., Akhtar, P., & Sopian, K. (2015). Production of biogas and performance evaluation of existing treatment processes in palm oil mill effluent (POME). *Renewable and Sustainable Energy Reviews, 42*, 1260-1278.

[3] Alhaji, M. H., Sanaullah, K., Lim, S.-F., Khan, A., Hipolito, C. N., Abdullah, M. O., Bhawani, S. A., & Jamil, T. (2016). Photocatalytic treatment technology for palm oil mill effluent (POME)–A review. *Process Safety and Environmental Protection, 102*, 673-686.

[4] APHA. (2005). Standard methods for the examination of water and wastewater. In *American Public Health Association (APHA)*. Washington, DC, USA: American Public Health Association.

[5] Bellucci, M., Ofiţeru, I. D., Graham, D. W., Head, I. M., & Curtis, T. P. (2011). Low-dissolved-oxygen nitrifying systems exploit ammonia-oxidizing bacteria with unusually high yields. *Appl. Environ. Microbiol., 77*(21), 7787-7796.

[6] Chae, K.-J., Choi, M.-J., Kim, K.-Y., Ajayi, F. F., Chang, I.-S., & Kim, I. S. (2010). Selective inhibition of methanogens for the improvement of biohydrogen production in microbial electrolysis cells. *International Journal of Hydrogen Energy, 35*(24), 13379-13386.

[7] Choong, Y. Y., Chou, K. W., & Norli, I. (2018). Strategies for improving biogas production of palm oil mill effluent (POME) anaerobic digestion: A critical review. *Renewable and Sustainable Energy Reviews, 82*, 2993-3006.

[8] Christy, P. M., Gopinath, L., & Divya, D. (2014). A review on anaerobic decomposition and enhancement of biogas production through enzymes and microorganisms. *Renewable and Sustainable Energy Reviews, 34*, 167-173.

[9] Demirel, B., & Scherer, P. (2008). The roles of acetotrophic and hydrogenotrophic methanogens during anaerobic conversion of biomass to methane: a review. *Reviews in Environmental Science and Bio/Technology, 7*, 173-190. doi:10.1007/s11157-008-9131-1

[10] Fang, H. H., & Yu, H. (2000). Effect of HRT on mesophilic acidogenesis of dairy wastewater. *Journal of environmental engineering, 126*(12), 1145-1148.

[11] Fascetti, E., D'addario, E., Todini, O., & Robertiello, A. (1998). Photosynthetic hydrogen evolution with volatile organic acids derived from the fermentation of source selected municipal solid wastes. *International Journal of Hydrogen Energy, 23*, 753-760.

[12] Ferchichi, M., Crabbe, E., Gil, G.-H., Hintz, W., & Almadidy, A. (2005). Influence of initial pH on hydrogen production from cheese whey. *Journal of biotechnology, 120*(4), 402-409.

[13] Hach. (1997). *Hach Water analysis handbook* (3rd ed.). USA: Hach Company.

[14] Hamisan, A., Abd-Aziz, S., Kamaruddin, K., Shah, U. M., Shahab, N., & Hassan, M. (2009). Delignification of oil palm empty fruit bunch using chemical and microbial pretreatment methods. *International Journal of Agricultural Research, 4*(8), 250-256.

[15] Hassan, M. A., Yacob, S., Shirai, Y., & Hung, Y.-T. (2004). *Handbook of Industrial and Hazardous Waste Treatment* (2 ed.). U.S.A.: Marcel Dekker, INC.

[16] Khanal, S. K. (2008). Overview of anaerobic biotechnology. *Anaerobic biotechnology for bioenergy production: Principles and applications*, 1-27.

[17] Khandaker, N., & Rio, F. (2019). *Acetogenesis : A Novel Energy Efficient Operation of Textile Effluent Treatment Plants (ETPS)*. Bangladesh: Century Publications.

[18] Khandaker, N., Sarkar, M., & Rahman, S. D. (2017). Acetogenic pretreatment of textile wastewater for energy conservation. *International Journal of Science and Research (IJSR), 6*(9), 59-62.

[19] Lam, M. K., & Lee, K. T. (2011). Renewable and sustainable bioenergies production from palm oil mill effluent (POME): win–win strategies toward better environmental protection. *Biotechnology Advances, 29*(1), 124-141.

[20] Lee, J., Ng, C. A., Lo, P. K., & Bashir, M. J. K. (2019). Enhancement of renewable electrical energy recovery from palm oil mill effluent by microbial fuel cell with activated carbon. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 41*(21), 2662-2674. doi:10.1080/15567036.2019.1568638

[21] Li, C., & Fang, H. H. (2007). Fermentative hydrogen production from wastewater and solid wastes by mixed cultures. *Critical Reviews in Environmental Science and Technology, 37*(1), 1-39.

[22] Ma, A., & Ong, A. S. (1985). Pollution control in palm oil mills in Malaysia. *Journal of the American Oil Chemists' Society, 62*(2), 261-266.

[23] Metcalf, & Eddy. (2003). *Wastewater engineering: Treatment and Reuse* (4 th ed.). Boston: McGraw Hill Companies Inc.

[24] Ohimain, E. I., & Izah, S. C. (2017). A review of biogas production from palm oil mill effluents using different configurations of bioreactors. *Renewable and Sustainable Energy Reviews, 70*, 242-253.

[25] Olvera, J. d. R., & Lopez, A. (2012). *Biogas production from anaerobic treatment of agro-industrial wastewater*. Rijeka: InTech.

[26] Omil, F., Elferink, S. O., Lens, P., Pol, L. H., & Lettinga, G. (1997). Effect of the inoculation with Desulforhabdus amnigenus and pH or O_2 shocks on the competition between sulphate reducing and methanogenic bacteria in an acetate fed UASB reactor. *Bioresource technology, 60*(2), 113-122.

[27] Poh, P., & Chong, M. (2009). Development of anaerobic digestion methods for palm oil mill effluent (POME) treatment. *Bioresource technology, 100*(1), 1-9.

[28] Rahimi, Y., Torabian, A., Mehrdadi, N., & Shahmoradi, B. (2011). Simultaneous nitrification–denitrification and phosphorus removal in a fixed bed sequencing batch reactor (FBSBR). *Journal of Hazardous Materials, 185*, 852-857.

[29] Sarker, S. R., Rabbi, F., Ahmed, F., & Khandaker, N. (2018, 11-13 December 2017). *Development of a novel anaerobic reactor for treating textile dyeing wastewater*. Paper presented at the International conference on Energy, Environment and Economics, Edinburgh.

[30] Trisakti, B., Manalu, V., Taslim, I., & Turmuzi, M. (2015). Acidogenesis of Palm Oil Mill Effluent to Produce Biogas: Effect of Hydraulic Retention Time and pH. *Procedia Social and Behavioral Sciences, 195*, 2466 – 2474.

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[31] Wong, L. P., Isa, M. H., Bashir, M. J., & Chin, Y. H. (2019, 23–26 April 2019). *Effect of hydraulic retention time on volatile fatty acid production and organic degradation in anaerobic digestion of palm oil mill effluent.* Paper presented at the AIP Conference Proceedings, Malaysia.

[32] Ying, C., Umetsu, K., Ihara, I., Sakai, Y., & Yamashiro, T. (2010). Simultaneous removal of organic matter and nitrogen from milking parlor wastewater by a magnetic activated sludge (MAS) process. *Bioresource technology, 101*, 4349-4353.

[33] Zaied, B., Siddique, M., Zularisam, A., Ahmad, M., & Salih, Y. (2019). Biomethane Production from Anaerobic Codigestion of Palm Oil Mill Effluent with Cattle Manure: A Review. *Asian Journal of Chemistry, 31*(11), 2413-2424.