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Influence of Nutrient Impregnated into Zeolite Addition on Anaerobic Digestion of Palm Oil Mill Effluent (POME)

M Mellyanawaty[1], F M A Chusna[2], H Sudibyo[2], N Nurjanah[1], W Budhijanto[2,*]

[1] Department of Environmental Engineering, Faculty of Engineering, Universitas Muhammadiyah Tasikmalaya, Tasikmalaya, 46196 Indonesia

[2] Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Yogyakarta 55281 Indonesia

[*]Corresponding author: wiratni@ugm.ac.id

Abstract. Palm oil mill effluent (POME) was wastewater generated from palm oil milling activities which was brownish liquid, acidic with pH 3-4, and contained soluble materials which were hazardous to the environment. It was characterized by high organic loading (COD 40,000–60,000 mg/L). According to its characteristics, POME was identified as a potential source to generate renewable energy through anaerobic digestion. In other words, a combination of wastewater treatment and renewable energy production would be an additional advantage to the palm oil industries. Methanogenesis was the rate limiting step in anaerobic digestion. In the conventional anaerobic digester, it required large reactors and long retention time. The addition of microbial immobilization media was to improve anaerobic reactor performance in term of higher organic removal and methane production. Additionally, better performance could lead to reduction of reactor volume and shorter retention time in high rate anaerobic digester. The loading of essential microorganism nutrient into the media might increase the affinity of bacteria to attach and grow on the media surface.

Activating or inhibition effects of natural and modified zeolite addition in anaerobic digestion of POME was studied in batch reactors using erlenmeyer of 1,000 mL at COD concentrations of about 8,000 mg/L. Zeolite was impregnated with nickel and magnesium at concentrations of 0.0561 mg Ni/g zeolite and 0.0108 mg Mg/g zeolite. The effect of the different zeolite addition was determined by the measurement of soluble COD (sCOD), Volatile Fatty Acids (VFAs) and biogas production. Greater effect of modified zeolite was observed in zeolite impregnated with nickel with a 54% increase of biogas production. Meanwhile, the modified zeolite impregnated with magnesium had no positive impact to the methanogenic bacteria activities.

1. Introduction

Indonesia is one of the largest palm-oil-producing countries in the world. Domestic production of palm oil had increased in the last few years. Thereby, the palm oil waste which was the by-product of palm milling process also increased. Huge quantities of waste were generated from palm oil industry. One of which was palm oil mill effluent (POME). The fresh POME is a hot, acidic (with pH between 1–5), and brownish colloidal suspension with a high amount of total solids (40,500 mg/L). It also contained high organic material with the level of Chemical Oxygen Demand (COD) was about 50,000 mg/L and Biochemical Oxygen Demand (BOD) was about 25,000 mg/L [1]. As the consequence, the generation of POME had created environmental issue for the palm oil industry. According to its high organic loading, POME could become a promising source for biogas production and potentially boosted up the renewable energy sector.

One preferred process to utilize POME as the energy source was anaerobic digestion. Anaerobic digestion has considerable advantages during the process such as minimum sludge production, less energy demand, no unpleasant odor and low microorganism nutrient requirements [2]. It implied that the level of COD and BOD in POME was also reduced as the biogas was produced. During the process of converting POME into methane, carbon dioxide, and water, there were three steps comprising of hydrolysis, acidogenesis (including acetogenesis) and methanogenesis [3]. Hydrolysis as the first step was the reaction where complex organic matters (i.e. carbohydrates, proteins, lipids) were degraded into sugar, amino acid, and fatty acids. In the second step, acidogenic bacteria converted these sugar, fatty acids, and amino acids into organic acids which mainly consisted of acetic acid. The product from acetogenesis step would be converted by methanogenic bacteria into methane and carbon dioxide as final products.

In anaerobic digestion process, one common problem was the slow growth of methanogenic bacteria which made the methanogenesis be the rate limiting step. Accordingly, in the conventional anaerobic digesters, it required longer retention time and followed by larger reactor dimension [4]. Nevertheless, several methods were developed to optimize the anaerobic digestion process by preventing the loss of bacterial biomass by using a support, a material to which the microbes attached [5]. Natural zeolite was selected as the immobilization media because it had large surface area and contained essential mineral for the anaerobic microbe's growth such as potassium, iron, etc. [6]. In this study, the impregnated minerals were nickel and magnesium. They would be impregnated into zeolite as immobilization medium. Hopefully, the impregnation could enhance and stimulate the microorganism activities. The aim of this study is to investigate the effect of the modified zeolite to the anaerobic digestion of POME using the effluent of biodiesel digester as inoculum. This study was preliminary research to evaluate the effect of mineral/nutrient addition into zeolite as immobilization media.

2. Methodology/experimental

2.1. POME and Inoculum Characterization

The palm oil mill effluent (POME) as substrate was collected from PT. Perkebunan Nusantara VII, Lampung. The table 1 showed the characteristics of POME used in this study. The inoculum used in this anaerobic process was digested biodiesel waste produced by the biodiesel industry operating in East Java with the COD of 1,400 mg/L, the VFA concentration of 300 mg/L, and pH of 8.17.

Table 1. Characteristics of Lampung Palm Oil Mill Effluent (POME)

Parameter	Value	Unit
pH	4.09	-
Chemical Oxygen Demand	10,000 – 16,000	mg/L
Protein	0.15	%
Nitrogen	0.0295	%
Fe	0.258	mg/L
Phosphate	37.175	mg/L
Phenol	≤ 0.0001	mg/L
Oil and grease	115	mg/L
Potassium	1,459.86	mg/L
Sulphate	1,032.93	mg/L
Ammonia	125	mg/L

2.2. Modified and Natural Zeolite
The natural zeolite with particles size of 1–2 mm was obtained from Tasikmalaya, West Java, Indonesia. Nickel and magnesium cations were impregnated to the natural zeolite surface. Zeolite was homo-ionized with NaCl 1 N for 24 hours before washed with aquadest and was soaked with NiSO4 and $MgCl_2$ solution for 24 hours. The initial concentrations of $NiSO_4$ and $MgCl_2$ were 200 mg/L for each. Thereafter, the modified zeolite was used as the immobilization media in anaerobic reactors.

The nickel and magnesium level inside the zeolite was determined by mass balance from the Ni^{2+} and Mg^{2+} level reduction of the solution before and after impregnation using ICP method (Perkin Elmer Optima 8300). The calculated Ni^{2+} and Mg^{2+} concentrations inside the solid were 0.0561 mg Ni/g zeolite and 0.0108 mg Mg/g zeolite respectively.

2.3. Anaerobic Batch Reactor
One liter Erlenmeyer flasks were modified to be used as batch anaerobic reactors equipped with a rubber cap with a glass pipe for measuring gas pressure and a drain pipe for liquid sampling port in the bottom part. It was connected through gasometer for gas measurement (figure 1). The gasometer was filled with acidic salt water to reduce biogas solubility [7]. A mixture of diluted POME (sCOD 8,000 mg/L) and inoculum with volumetric ratio of 3:1 was added. The anaerobic digestion process was conducted for 30 days.

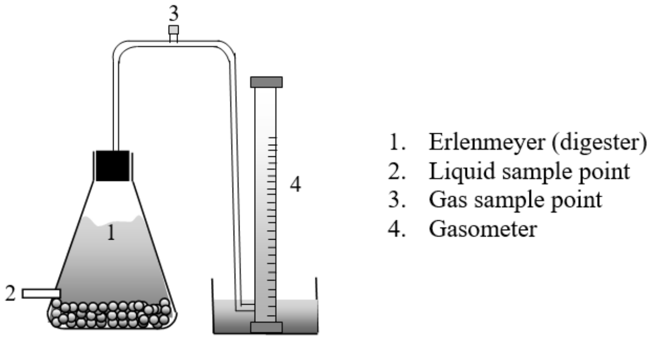

Figure 1. Anaerobic Digestion Batch Reactor

2.4 Analytical Methods
The volume of biogas was calculated following the gasometer equation from study by Walker et al [7]. The sCOD was used as a measure of the oxygen equivalent of the organic content inherently of a sample that is susceptible to oxidation by a strong chemical oxidant. In this study, the closed reflux method of COD analysis and VFA analysis method used procedures explained by APHA [8]. The procedures for COD analysis consisted of equipment preparation, sample and reagent preparation and reading method. For equipment preparation, the COD analysis required the reflux instrument which consisted of Digital Reactor Block heater HI 839800 and Hach DR 900 colorimeter. The pH was measured using Lutron pH meter PH-208. Meanwhile, the biogas composition was determined by gas chromatography Shimadzu GC 8A, Japan.

2.5 Batch Anaerobic Digestion
Three experimental sets of batch reactors were conducted in anaerobic digestion in which each contained different immobilization medium. The label of each reactor following the sCOD concentration was used and the nutrient was impregnated into the zeolite. The table 2 showed the label of the entire reactors in this experiment.

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Table 2. The Label of the Anaerobic Digester (Reactor)

Reactor No.	$sCOD_{initial}$ (mg/L)	Cation	Type of immobilization media
1	8,000	-	8Z (Control)
2	8,000	Ni	8Z-Ni
3	8,000	Mg	8Z-Mg

3. Results and discussion

3.1 Results

The figure 2 shows the results obtained by the sCOD measurements in the process of anaerobic digestion of POME using zeolite as immobilization media. The significant sCOD removal was occurred from day 0 to day 8. At day 8 onwards, the sCOD concentration levels decreased slightly. The sCOD removal efficiency for the reactor 8Z, 8Z-Ni, and 8Z-Mg were 43.69%, 53.40%, and 60.52% respectively. The high sCOD efficiency removals indicated that the complex organic matter was decomposed and converted by microorganisms into methane and carbon dioxide as the final product of anaerobic digestion. Acidogenic microorganisms degrade the organic materials only until the production of VFAs which were also organic matter. Generally, the addition of nutrient which was used in this study i.e: Ni^{2+} and Mg^{2+}, provided the sCOD removal higher than control.

The effect of the addition of nickel and magnesium ion into natural zeolite as immobilization medium over the production of VFAs during the anaerobic process could be seen in figure 3. The production of VFAs significantly occurred in first 4 days. At day 4, the concentration of VFAs were between 3,400–4,260 mg/L. These values significantly increased from 2,143 mg/L. Reactor 8Z-Ni produced VFAs higher than 8Z indicating that nickel in the zeolite could stimulate the acidogenic microorganisms activities. However, the reactor 8Z-Mg produced VFAs lower than 8Z indicating that the activity was not improved after magnesium ion was added into the zeolite pores.

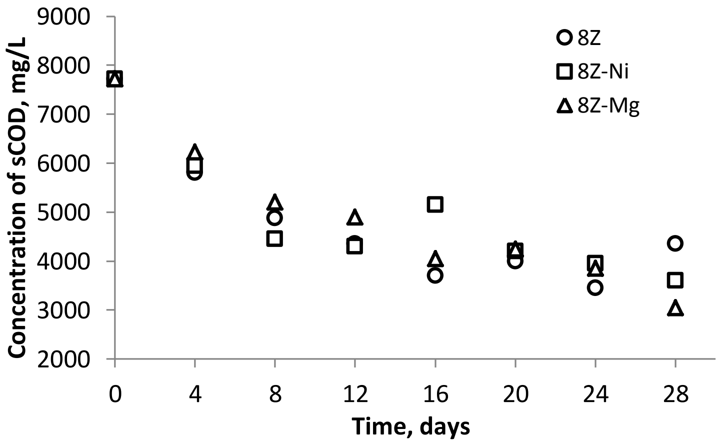

Figure 2. Concentration of sCOD during the Anaerobic Digestion of POME Using Immobilization Medium

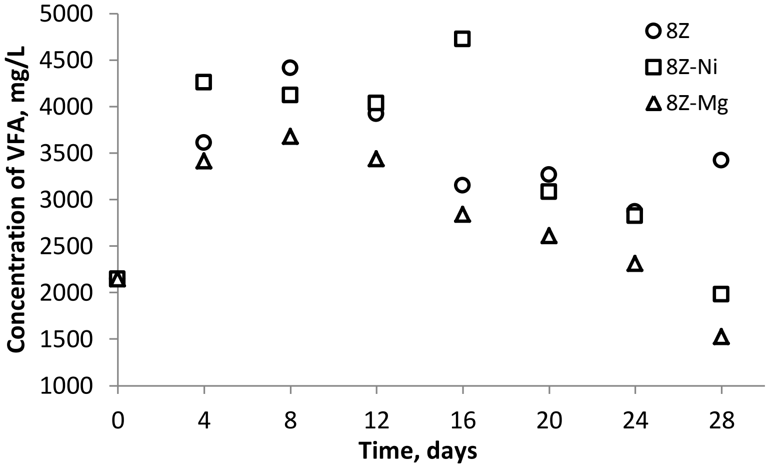

Figure 3. Production of VFAs during the Anaerobic Digestion of POME using Immobilization Medium

The biogas production was evaluated by measuring the total biogas and methane production. The anaerobic digestion batch trials with nickel in zeolite provided the highest biogas production as shown in figure. 4. However, reactor 8Z-Mg produced biogas lower than control. During the process, reactor 8Z, 8Z-Ni, and 8Z-Mg obtained the cumulative biogas production as many as 550.05 mL, 850.07 mL, and 256.74 mL respectively.

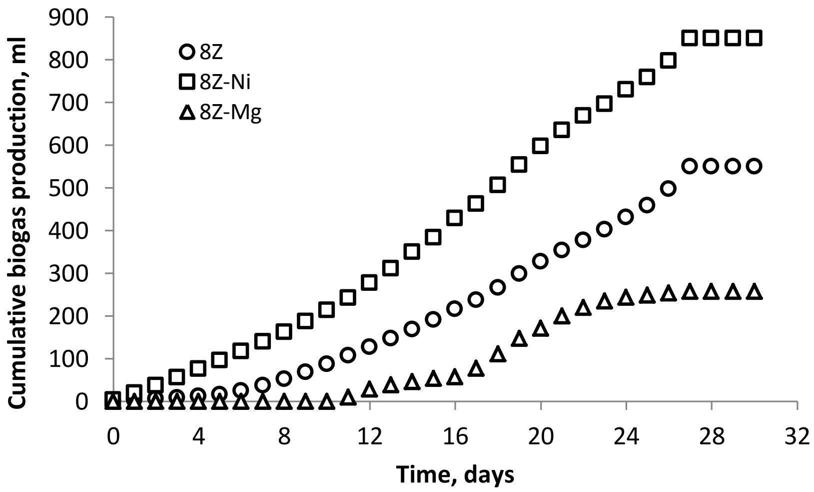

Figure 4. Cumulative Biogas during the Anaerobic Digestion of POME using Immobilization Medium

3.2 Discussion

The presence of nickel in the zeolite, in this study, enhanced the production of biogas as large as 54%. The presence of nickel in anaerobic digestion processes could increase acetate utilization rate of methanogenic bacteria. Similarly, Milán et al. [9] observed the modified zeolite with nickel increase the methanogenic specific activity by 2.8 times in anaerobic digestion of piggery waste. Nickel was a unique micronutrient for methanogenic bacteria. It stimulated the conversion of acetic acid into methane and carbon dioxide by a mixed methanogenic population [3]. The addition of material with ion exchange capacity (e.g. bentonite, phosphorite, and zeolites) or inorganic absorbent material (e.g. clay, manganese oxides) to anaerobic digester had shown good results [10–13].

Meanwhile, the presence of magnesium into the zeolite decreased the production of biogas by 53%. Similarly, Uludag-Demirer et al. [12] had investigated the effect of $MgCl_2$, $Mg(OH)_2$, and Na_2HPO_4. The result showed no improvement in the methane production yield of the anaerobic digester. The physical phenomenon observed during and after the anaerobic digestion was the formation of precipitate. The precipitate was ammonium magnesium phosphate ($MgNH_4PO_4.6H_2O$) or struvite. Study by Miles and Ellis [14] explained that struvite was a mineral which often precipitated from wastewater during anaerobic digestion when ammonium, phosphate, and magnesium ions were released. In high concentrations of dissolved magnesium, orthophosphates, and ammonia ions, there was strong potential for formation of struvite in the biological treatment of organic wastes. A high magnesium concentration was found in potential substrates for anaerobic (co-)digestion olive oil mill wastewater. In high concentration, magnesium became inhibitory on the anaerobic digestion process [15].

Research by Romero-Guiza et al [15] and Perez Rodriguez et al [16] reported that the bentonite support impregnated with Mg^{2+} caused struvite crystal appeared whose size remains similar with time. This attributed to the fact that the precipitates were formed from magnesium exchange ions transferred to the solution which took place over a very short period of time. It could be interpreted that the presence of Mg^{2+} on the zeolite as immobilization medium in anaerobic digestion of POME did not affect the biogas production. It likely promoted the struvite precipitation. Further study related to the struvite formation during and after anaerobic digestion of POME could be exciting.

4.Conclusion

A major stimulation to microorganism in anaerobic reactor was observed after the addition of immobilization medium. The impregnation of nickel ion into natural zeolite improved the anaerobic reactor performance. On the other hand, magnesium-ion-impregnated natural zeolite only slightly influenced the AFBR performance. To sum up, the application of nickel-ion-impregnated natural zeolite opened the possibility to allow AFBR to perform as efficient as possible and might lead to the considerable reduction of volume reactor for the future design of AFBR.

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Abbreviations

POME	Palm Oil Mill Effluent
AFBR	Anaerobic Fluidized Bed Reactor
sCOD	Soluble Chemical Oxygen Demand
VFA	Volatile Fatty Acid