## THE EFFECT OF MAGNESIUM SULFATE ADDITION ON VOLATILE SOLID DESTRUCTION AND CHEMICAL OXYGEN DEMAND REDUCTION OF FOOD WASTE ANAEROBIC DIGESTION

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## ABSTRACT

Process instability often occurs in anaerobic digestion (AD) due to inhibitors, such as the high sodium content in food waste. Recent studies have reported that magnesium can reduce the sodium ion's toxicity towards methanogens. This study aimed to analyze the effect of magnesium addition to Volatile Solids Destruction (VSD), Chemical Oxygen Demand (COD) reduction, and biogas production in AD of food waste. The experiment consisted of two phases, the control phase and the experimental phase, without and with MgSO<sub>4</sub>, respectively. The control phase results were: average COD reduction, VSD, and methane yield up to 80.9%, 87.6%, 340 mL CH<sub>4</sub>/gr VS/day, respectively. The experimental phase results were: average COD reduction, VSD, and methane yield up to 78.5%, 83.9%, 125 mL CH<sub>4</sub>/gr VS/day, respectively. Overall, the study's results showed that MgSO<sub>4</sub> had a negative impact on VSD and methane yield. The addition of MgSO<sub>4</sub> seemed to cause instability in the AD system, which resulted in a decrease in the WSD value and a decrease in the methane concentration.

Keywords: Biogas; COD; Inhibition; Methane; Solid waste; VSD

## 1. INTRODUCTION

Waste management is a fundamental process for finding solutions to the problems arising from waste produced by individuals and industry (Pongrácz, 2002). Society's awareness of environmental issues is considered to drive the search for waste disposal methods that are alternatives to landfills (Shukor et al., 2018). Anaerobic digestion (AD) is a widely used domestic waste processing method that is able to convert various biodegradable waste materials into energy (Wijayanti et al., 2018) through a biological anaerobic process that converts organic matter into biogas and digestate (Lin et al., 2018). In comparison to other aerobic technology, anaerobic processes, such as AD, offer several advantages, including low energy use and low sludge production; moreover, the produced biogas can function as an energy source. Furthermore, the anaerobic process does not have a strong odor because the process is carried out in an enclosed space (Abdel-Shafy & Richardson, 1996).

However, operational problems, such as instability in the system and fluctuating biogas productivity, are disadvantages of AD (Lin et al., 2018). Failure to maintain the balance between acid bacteria and methanogen bacteria is known to be the main cause of instability in the system (Demirel & Yenigün, 2002). Furthermore, various elements, such as sodium (Na), are believed

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to inhibit AD processes (Chen et al., 2008). The amount of Na concentration that can cause inhibition can vary. This is influenced by the type of feedstock and the operating parameters, which might be different in each reactor (Anwar et al., 2016). According to Alhraishawi and Alani (2018), an NaCl concentration of 3,100 mg/L or more has the potential to inhibit AD processes.

To counter Na toxicity, a mechanism known as antagonism can be implemented (Kugelman & McCarty, 1965). Antagonism is achieved by the presence of another cation that reduces the toxicity of other types of cations, which can reactivate enzymes that have been damaged due to an excess amount of the toxic cation. This may induce a stimulatory effect from one type of cation, which, in this case, is magnesium (Mg), which could act as an antagonist cation against Na (Kugelman & McCarty, 1965). The study conducted by Bashir and Matin (2004) found that the handling of Na inhibition at a concentration of 9,000 mg/L can be done by adding Mg, which can reduce the toxic effects of Na. Hence, in our study, we further analyzed the effect of the addition of Mg on Na toxicity in anaerobic waste treatment. Toward that end, we evaluated the following parameters: Volatile Solids Destruction (VSD) and Chemical Oxygen Demand (COD) reduction. Both VSD and COD reduction represent the efficiency of the AD process in reducing organic matter, depending on the methods and concentrations used in the process.

The increase in VSD is related to the increased production of biogas (Anwar et al., 2016). According to Budiyono et al. (2013), in an AD system, COD is consumed through microbial activity and is converted into methane (CH<sub>4</sub>). Both of these parameters are important because they represent the performance of the AD process.

### 2. MATERIALS AND METHODS

### 2.1. Inoculum, Feedstock, and Chemicals

The inoculum used in this study was a mixture of cow manure and water with a ratio of 1:1. Cow manure was obtained from a cattle farm in Bandung, West Java. The feedstock used in this study was a combination of a substrate, in the form of food waste, and a co-substrate, in the form of cow manure. Food waste was obtained from the waste treatment facility at the University of Indonesia. Cow manure was obtained from a cattle farm in Depok, West Java. The ratio of the substrate and co-substrate mixture is 9:1. This ratio is considered to be suitable because it enables the AD system to be more stable because better alkalinity conditions can be obtained (Siregar and Priadi, 2017). The Mg used by Bashir and Matin (2004) did not come in compound form. In our study, we selected magnesium sulfate (MgSO<sub>4</sub>) as the Mg<sup>2+</sup> source since it is less expensive and readily available. Moreover, MgSO<sub>4</sub> is also highly soluble (Dogterom et al., 2018). In our study, the concentration of MgSO<sub>4</sub> that was added was 200 mg/l. The concentration was obtained from the ratio based on the study conducted by Bashir and Matin (2004) who overcame the Na toxicity at 9,000 mg/L with the addition of 500 mg/L of Mg. The concentration of MgSO<sub>4</sub> used in our study is considered to be a non-inhibitory concentration, based on the study conducted by Grady et al. (1999).

### 2.2. Acclimatization Phase

The acclimatization phase was done over a period of 80 days in which the Organic Loading Rate (OLR) value increased gradually from 1 kg VS/m<sup>3</sup> per day to 10 kg VS/m<sup>3</sup> per day to acclimate the inoculum to the substrate. During acclimatization, the pH and temperature were monitored (data not shown). COD and VS monitoring was performed during the last week of the acclimatization phase. Biogas production was also observed through the concentration of CH<sub>4</sub> in the biogas and the volume of biogas. This phase ended when the COD reduction reached 50%, the effluent quality parameters were stable, and biogas was consistently produced (Lopez et al., 2013).

## 2.3. Operational Phase

In the operational phase, the OLR value remained constant at 10 kg VS/per day with a food waste-to-cow manure VS ratio of 9:1 (Tassakka et al., 2019; Siregar and Priadi, 2017). The operational phase was divided into a control phase and an experimental phase, using the same reactor. The control phase was conducted over a period of 29 days to obtain the effluent parameter data, which will represent the AD performance without the addition of MgSO<sub>4</sub>. The experimental phase was conducted over a period of 21 days to obtain the effluent parameter data, which will represent the AD performance with the addition of MgSO<sub>4</sub>. During the operational phase, the COD reduction, VSD, and biogas production were monitored to analyze the performance of the AD reactors with and without the addition of MgSO<sub>4</sub>, according to the research study's objectives.

# 3. RESULTS AND DISCUSSION

## 3.1. Feedstock Characteristics

The characteristics of the feedstock are listed in Table 1. The Na concentration in the feedstock used in the operational phase of the study was 3,280 mg/L. In our study, the Na concentration is in the range that has the potential to cause inhibition in the AD process (Alhraishawi & Alani, 2018). The MgSO<sub>4</sub> concentration in the feedstock is still considered to be the non-inhibitory concentration required for microbial growth (Grady et al., 1999; Radhakrishnan, 2011). However, the total solids (TS) content of feedstock is very high, which could lead to an inhibition in mass transfer (Abbassi-Guendouz et al., 2012). The VS content of the feedstock was 94.1%; thus, the feedstock has a higher potential to generate a high quantity of biogas (Orhorhoro et al., 2017). The analysis also showed high COD content (up to 497,500 mg/L), which is beneficial as the source of substrate for bacteria (Ashish & Oprakash, 2014). The alkalinity value of the feedstock was 2,250 mg CaCO<sub>3</sub> /L, which indicates a greater capacity for resisting pH changes (Martínez-Alvarez et al., 2018); therefore, the stability in the AD system could be maintained.

Parameters	Feedstock
Na (mg/L)	3,280
Mg (mg/L)	160
TS (%)	31.4
VS (%TS)	94.1
COD (g/L)	497.5
Alkalinity (mg CaCO <sub>3</sub> /L)	2,250

Table 1 Feedstock characteristics

## 3.2. Mg Addition Effects

On average, the VSD obtained in the control phase was  $87.6\% \pm 0.03\%$ ; this is significantly higher (p < 0.05) than the average VSD obtained during the experimental phase, which was  $83.9\% \pm 0.04\%$  (Figure 1a). The average decline of VSD in the experimental phase may be caused by the microorganisms that have not adapted to the addition of MgSO<sub>4</sub> concentrations that force them to remain in the stationary phase (Llorens et al., 2010; Klauck & Hengge, 2012). In an AD system, an acetoclastic methanogen is one of the microorganisms classified as being very sensitive to changes in environmental conditions (Hajarnis & Ranade, 1993; Ahring et al., 2001). If the acetoclastic methanogen activity and metabolism are disrupted, there is the potential for acetate to accumulate in the AD system, which decreases VSD efficiency. VSD seems to be weakly correlated to pH (P = 0.35); a sharp decrease in the VSD value to 76% on day 6 in the experimental phase also simultaneously demonstrated a pH with a minimum value of 5, as shown in Figure 1c.

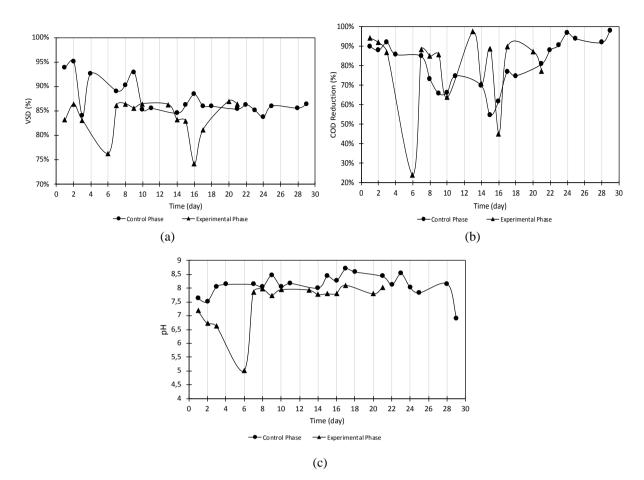


Figure 1 (a) VSD in the control and experimental phases; (b) COD reduction in the control and experimental phases; (c) pH fluctuation in the control and experimental phases

As shown in Figure 1b, in the experimental phase, the data fluctuations in COD reduction appear to be similar to the fluctuations in the VSD values. When the COD reduction is at its lowest level (24%), the VSD value is also at its lowest level (76%). However, unlike the VSD results, the COD reduction obtained in the experimental phase (78.5%  $\pm$  0.2%), was not significantly different (p = 0.66) than the COD reduction obtained in the control phase (80.9%  $\pm$  0.12%).

The CH<sub>4</sub> yield obtained in the experimental phase was  $339\pm156.5$  mL CH<sub>4</sub>/gr VS/day. This value is significantly lower (p < 0.05) than the CH<sub>4</sub> yield obtained in the control phase, which was  $125\pm107.2$  mL CH<sub>4</sub>/gr VS. As seen in Figure 2a, fluctuations in the CH<sub>4</sub> yield data due to the addition of MgSO<sub>4</sub> can be attributed to the instability of the AD process because the methanogenic microorganisms have not adapted to the presence of new compounds in the AD system causing their metabolism to be impaired, as previously mentioned. Similar to other organisms, methanogens will react and adapt to changes in environmental conditions (Rother et al., 2011). Moreover, interference with methanogens can be caused by the presence of hydrogen sulfide, which can inhibit CH<sub>4</sub> production (Kavuma, 2013), where the formation of hydrogen sulfide in the AD system occurs through sulfate reduction due to the addition of MgSO<sub>4</sub> in its sulfate form. Hydrogen sulfide is toxic to living organisms, and it can inhibit enzyme formation in certain types of microorganisms (Kushkevych, 2016). Furthermore, competition can occur between sulfate reducing bacteria (SRB) and methanogens, in which SRB will use sulfates as electron recipients in the metabolic process (Boshoff et al., 2004).

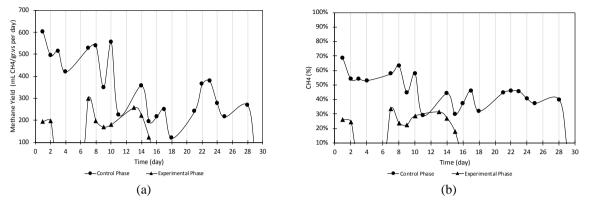


Figure 2 (a) Methane yield in the control and experimental phases; (b) CH<sub>4</sub> in the control and experimental phases

As shown in Figure 2b, the CH<sub>4</sub> concentration in the biogas produced in the control phase was significantly different from the CH<sub>4</sub> concentration in the biogas produced in the experimental phase (p < 0.05), which had the average percentage of  $16.1\% \pm 0.13\%$ . Conversion of CO<sub>2</sub> to methane is primarily carried out by hydrogenotrophic methanogen (Zabranska & Pokorna, 2018); thus, if the concentration of CO<sub>2</sub> in the system increases, it is likely that hydrogenotrophic methanogen metabolism will be inhibited. Based on the results of the correlation test, the CH<sub>4</sub> concentration has a strong positive correlation with VSD (P = 0.64). This condition is in accordance with the findings reported by Anwar et al. (2016), which explains that the reduction in VS reduction efficiency is related to a decrease in CH<sub>4</sub> gas production. As shown in Figures 2b, 2b, the CH<sub>4</sub> concentration and the biogas yield obtained in the experimental phase decreased to as low as 0% on day 6, 16, and 17.

### 4. CONCLUSION

The results of this experiment demonstrated that the addition of MgSO<sub>4</sub> did not improve the performance of the AD process. The addition of a significant amount of MgSO<sub>4</sub> caused a significant decrease in VSD (p < 0.05), as seen in the VSD value of 83.9%  $\pm$  0.04% obtained in the experimental phase and the VSD value of 87.6%  $\pm$  0.07% obtained in the control phase. Moreover, the addition of MgSO<sub>4</sub> caused a significant decrease in the CH<sub>4</sub> yield of 125±107.2 mL CH<sub>4</sub>/gr VS/day obtained in the experimental phase and the CH<sub>4</sub> yield of 339±156.5 mL CH<sub>4</sub>/gr VS/day obtained in the control phase. However, in this experiment, the addition of MgSO<sub>4</sub> did not significantly influence the efficiency of COD reduction, as seen in the COD reduction of 78.5%  $\pm$  0.2% in the experimental phase and the COD reduction of 80.9%  $\pm$  0.12% in the control phase. Further study on the synergistic effect of MgSO<sub>4</sub> must be analyzed in a complex food waste AD environment.

### 6. ACKNOWLEDGEMENT

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