






Impact of feed pH on biogas generation from liquid waste of tapioca starch industry through anaerobic digestion assisted by microbial electrolysis cell

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ABSTRACT

The amount of liquid waste from the tapioca flour industry in Indonesia is quite high. Because of its high organic content, the waste is suitable for use as a biogas feedstock. The purpose of this research was to examine the impact of feed pH on the biogas generation from tapioca liquid waste via anaerobic digestion (AD) combined with microbial electrolysis cell (MEC-AD). The results revealed that the MEC-AD increased biogas yield up to 1.85 times compared to the AD alone. Then, in MEC-AD, the optimum feed pH was 7. At a feed pH of 7, biogas yields generated from AD and MEC-AD processes were 190.30 mL/g-COD_{added} and 340.58 mL/g-COD_{added}, respectively. Furthermore, MEC-AD removed a higher chemical oxygen demand (COD) content (43 %) compared to AD alone (37 %). Consequently, it can be concluded that the optimum conditions were the MEC-AD at a feed pH of 7. The existence of MEC in AD enhanced the values of maximum biogas yield (A), biogas generation rate (μ), and adaptation time (λ). The MEC-AD at feed pH 7 had μ , λ , and λ of 340.58 mL/g-COD_{added}, 170.00 mL/g-COD_{added}/day, and 0.00 days, respectively.

Keywords: anaerobic digestion, biogas, microbial electrolysis cell, pH, tapioca liquid waste.

INTRODUCTION

Based on the National Energy General Plan (RUEN), new and renewable energy (NRE) is targeted to meet national energy needs by a dominant percentage in 2050 (Syaichurrozi et al., 2023). In 2025 and 2050, bioenergy is expected to contribute 36.6% and 39.3%, respectively, to the total renewable energy needs (Syaichurrozi et al., 2023). Biogas, one of the types of NREs, can be processed from organic materials through anaerobic digestion (AD). Biogas is an eco-friendly energy source, which can then be used for various needs (Budiyo et al., 2023). Biogas can be used

directly in the form of gas (Budiyo, Riyanta, et al., 2021) or can be converted into electricity and heat (Sumardiono et al., 2023). In addition, the slurry of the biogas digester can be applied as organic fertilizer (Putri et al., 2012).

In Indonesia, one of the most prevalent wastes is tapioca liquid waste that can be utilized as a raw material for biogas generation. In the tapioca industry, it takes 4 tons of cassava tubers and 16 m³ of water to produce 1 ton of tapioca flour and by-products, including 1200 kg of cassava pulp, 1600 kg of fruit peel, and 17 m³ of liquid waste (Situmorang and Manik, 2018). Solid waste in the form of cassava pulp can be utilized as a feedstock

for making bioethanol (Arnata et al., 2021). Fruit peels are usually used for animal feed (Lounglawan et al., 2011), while liquid waste in some small industries is still dumped directly into rivers without any treatment, causing environmental damage (Sánchez et al., 2017).

Tapioca liquid waste usually has high biological oxygen demand (BOD), chemical oxygen demand (COD), and total suspended solid (TSS) contents (Sulistiyowati et al., 2023). As stated by Virunanon et al. (2013), tapioca liquid waste contains COD of 20,433 mg/L and BOD of 9750 mg/L. Hence, tapioca liquid waste is forbidden to be discharged to the environment directly because it contributes to environmental pollution. On the other hand, due to its organic matter, tapioca liquid waste is suitable to be utilized as a raw material for biogas.

The biogas generation can be enhanced by integrating AD with microbial electrolysis cell (MEC), thereby creating a synergistic effect that optimizes biogas yield (Syaichurrozi et al., 2024). In the MEC-AD, the electrodes (anode and cathode) are placed directly into the biogas reactor. This configuration facilitates the concurrent operation of both MEC and AD processes inside a single reactor. A low electric current is provided to facilitate the bioelectrochemical reaction. When an electric current is applied, electrochemically active microorganisms degrade organic compounds at the anode, thereby producing protons (H^+), carbon dioxide (CO_2), and electrons (e^-) (Yu et al., 2018). Subsequently, H^+ , CO_2 , and e^- undergo conversion into methane (CH_4) via a methanogenesis process based on direct interspecies electron transfer (DIET) (Wang et al., 2022). In addition, methane can also be generated via a methanogenesis process based on indirect interspecies electron transfer (IIET). On the other hand, in AD alone, the methane is only formed via the IIET pathway (Syaichurrozi et al., 2024). Thus, adding MEC to the AD process will boost the degradation of organic compounds, which will in turn increase the generation of biogas.

The MEC-AD technique has previously been used by Syaichurrozi et al. (2024) in the treatment of tofu wastewater by the addition of iron (Fe). The MEC-AD technique successfully improved biogas yield by 14.4–114.5% and improved pollutant removal efficiency by 1.09 to 1.63-fold than the AD alone. Khomariah et al. (2024) also used the MEC-AD technique in treating artificial tapioca liquid waste by the addition of urea. They

found that by adding 1.5 g of urea, MEC-AD generated a biogas yield 2.5-fold higher than the AD. Considering the information mentioned above, it is noteworthy that the utilization of MEC-AD to convert real tapioca liquid waste to biogas has yet to be explored.

One of the critical factors impacting biogas yield is feed pH. The feed pH level serves as a fundamental determinant for the activity of anaerobic bacteria (Kafle et al., 2013). Consequently, it is essential to analyze the impact of feed pH on the MEC-AD process. In this research, the feed pH was systematically varied between 5 and 8. This research represents a novel exploration, as the application of MEC-AD technology for producing biogas from real tapioca liquid waste at various feed pHs has not previously been examined. Thus, the primary goal of the present research was to increase biogas generation from real tapioca liquid waste by employing the MEC-AD technology at various feed pH levels.

MATERIALS AND METHODS

Materials

The tapioca liquid waste was taken from the settling stage of the home-scale tapioca flour manufacturing process. The tapioca liquid waste contained COD of 3628 mg- O_2 /L, volatile fatty acids (VFAs) of 1644.71 mg-acetic acid/L, and pH of 3.79. The current research used fresh cow rumen fluid as inoculum. It was collected from a slaughterhouse in Cilegon, Indonesia. The cow rumen fluid had COD of 9733 mg- O_2 /L, VFAs of 1973 mg-acetic acid/L, and pH of 6.48. Black carbon graphite plates with 99.9% purity were used as electrodes with a dimension of length×width×thickness of 4.1×2.3×0.4 cm.

Experimental set-up

The anaerobic reactor was constructed from a 600 mL Erlenmeyer flask that had a working volume of 500 mL. Electrodes were placed in the reactor with an inter-electrode distance of 1.1 cm. The anode and cathode were linked to the direct current (DC) power source's positive and negative terminals, respectively. The voltage was maintained at a constant level of 1 volt throughout the experiment. This voltage level was chosen by following the previous research (Syaichurrozi

et al., 2024). The initial current density in this study was 3.26 A/m^2 or 0.15 A/m^3 . Rubber stoppers were used to close the reactor and preserve anaerobic conditions. The volume of the resulting biogas per day was recorded by employing the liquid displacement method. Each digester was linked to a glass cylinder-shaped gas collector via a connecting pipe. Furthermore, each gas collector was submerged in a saturated salt solution to facilitate accurate measurement. The biogas formed by the reactor was collected in the glass cylinder and pushed the liquid downwards. The detailed experimental setup at the laboratory scale is presented in Figure 1.

Experimental design and research procedure

The ratio of tapioca liquid waste to rumen was 80:20v/v. Subsequently, 5 N NaOH solution was introduced to adjust the liquid pH to 5, 6, 7, and 8

for both AD and MEC-AD processes. The experimental design employed in this research is detailed in Table 1. The experiment was carried out at room temperature (1 atm, 25–30 °C) and batch system. The experiment was stopped when biogas was no longer formed. Biogas volume and electrical current were recorded daily. The liquid displacement technique was used to record the biogas volume. The electrical current was measured using a multi-meter. Liquid samples ($\pm 10 \text{ mL}$) were taken every four days for the analysis of pH, VFAs, and COD. Biogas samples ($\pm 5 \text{ mL}$) were taken every four days for the GC-TCD analysis.

Analyses

Liquid pH

The pH was recorded with a digital pH meter, which was calibrated using buffer solutions before its use to ensure accurate measurements.

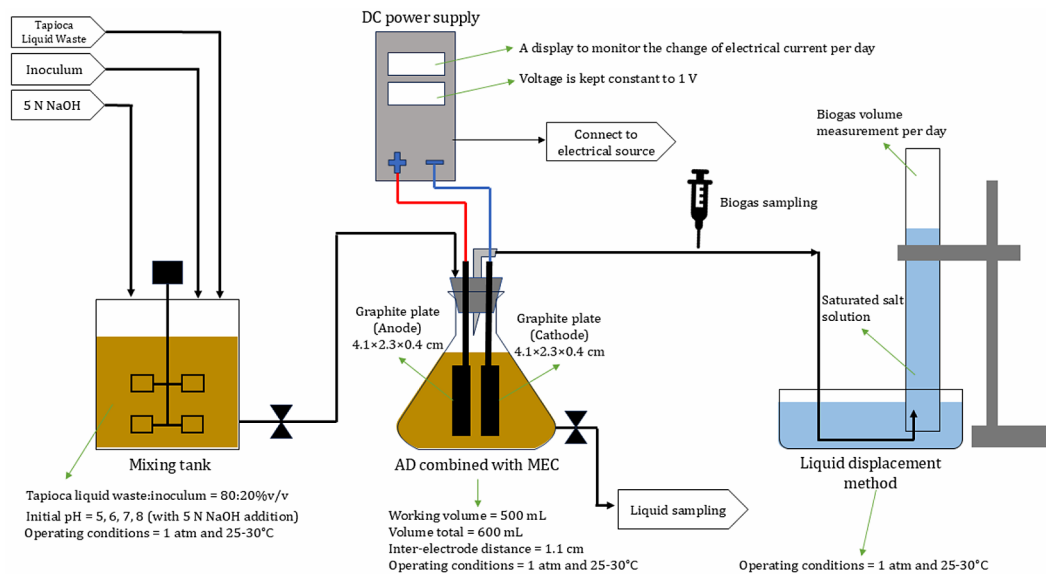


Figure 1. Laboratory scale MEC-AD set-up

Table 1 Experimental design

Process	Digester code	Tapioca liquid waste volume (mL)	Rumen volume (mL)	Feed pH
MEC-AD	A	400	100	5.0±0.2
MEC-AD	B	400	100	6.0±0.2
MEC-AD	C	400	100	7.0±0.2
MEC-AD	D	400	100	8.0±0.2
AD	E	400	100	5.0±0.2
AD	F	400	100	6.0±0.2
AD	G	400	100	7.0±0.2
AD	H	400	100	8.0±0.2

VFAs

The VFAs were analyzed through a steam distillation method (Syaichurrozi et al., 2024). A 2 mL liquid sample was diluted into a 100 mL volumetric flask to the limit and put into a 500 mL Erlenmeyer. After that, 100 mL of distilled water and 5 mL of H₂SO₄ 50 % were added. Subsequently, the Erlenmeyer flask was attached to the distillation apparatus and heated. The sample in the Erlenmeyer flask will evaporate, then the steam that passes through the condenser will be condensed and collected into a 250 mL Erlenmeyer flask. When as much as 100 mL of distillate was collected, the distillation procedure was stopped. Furthermore, the distillate was titrated with 0.05 N sodium hydroxide with an indicator of phenolphthalein. The VFA concentration was subsequently calculated utilizing Equation 1.

$$\text{VFAs} \left(\frac{\text{mg} - \text{acetic acid}}{L} \right) = \frac{V_{\text{NaOH}} \times N_{\text{NaOH}} \times BM_{\text{Acetic acid}} \times 1000}{V_{\text{Sample}} \times F_{\text{Recovery}}} \quad (1)$$

COD removal

The COD was analyzed using the closed reflux and spectrophotometry. The COD reactor (Hanna H1839800), COD meter (Hanna H183399), and COD High Range Plus reagent were utilized in this procedure. The COD removal value was quantified through Equation 2.

$$\text{COD removal (\%)} = \frac{\text{COD}_{\text{initial}} - \text{COD}_{\text{final}}}{\text{COD}_{\text{initial}}} \times 100\% \quad (2)$$

Methane content

Methane and carbon dioxide contents in biogas were analyzed with a GC-TCD instrument. Then, the actual methane and carbon dioxide percentages were calculated using Equations 3 and 4.

$$\text{CH}_4(\%) = \frac{\% \text{CH}_4}{(\% \text{CH}_4 + \% \text{CO}_2)} \times 100\% \quad (3)$$

$$\text{CO}_2(\%) = \frac{\% \text{CO}_2}{(\% \text{CH}_4 + \% \text{CO}_2)} \times 100\% \quad (4)$$

Biogas yield

The biogas yield (mL/g-COD_{added}) was quantified by dividing the resulting biogas volume (mL) by the initial COD mass (g) of the tapioca

liquid waste. This biogas calculation technique was adapted from previous research (Syaichurrozi et al., 2024).

Kinetics analysis

The kinetics of biogas production assumes that the biogas generation rate in a batch system follows the specific growth rate of bacteria in the reactor (Syaichurrozi et al., 2013). Thus, the modified Gompertz model was used to simulate the biogas generation evolution. In addition, the modified Gompertz model also results in a higher accuracy than the first-order kinetic model (Budi-yono et al., 2014b). The equation of this kinetic model is presented in Equation 5. The Mean Absolute Percentage Error (MAPE) was employed as an objective function, and the optimization was conducted with the help of Microsoft Excel. The equation of MAPE is shown in Equation 6.

$$y(t) = A \cdot \exp \left\{ -\exp \left[\frac{\mu \cdot e}{A} (\lambda - t) + 1 \right] \right\} \quad (5)$$

$$\text{MAPE} = \sum_{t=1}^n \left| \frac{y_i - \hat{y}_i}{y_i} \right| \times 100\% \quad (6)$$

where: $y(t)$ is cumulative of biogas yield at time t (mL/g-COD_{added}), A is the maximum biogas yield that can be achieved (mL/g-COD_{added}), μ is maximum biogas production rate (mL/g-COD_{added}/day), λ is lag time (days), e is 2.718282, t is the operating time (days), y_i is the experimental biogas yield, and \hat{y}_i is the modeled biogas yield.

RESULTS AND DISCUSSION

Biogas generation

The results indicated that variations in the feed pH exerted a significant effect on both daily and cumulative biogas yields. The profiles of daily and cumulative biogas yields recorded throughout the experiment are exhibited in Figure 2 (A and B). Figure 2(A) depicts the fluctuations in daily biogas yields across all variations of feed pH. Notably, high daily biogas yield was observed between days 1 and 4, by the peak daily biogas yield of 165.17 mL/g-COD_{added} occurring on day 1 in the MEC-AD at pH 7. However, a decline in daily biogas yield occurred from day 8 to 16 across all variations of feed pH. Biogas production will increase until the optimum time and then decrease gradually until the AD process

ends (Matin et al., 2024). Figure 2 (B) shows the cumulative biogas yields. The AD process at feed pHs of 5, 6, 7, and 8 produced total biogas yields of 263.11, 136.43, 190.30, and 199.82 mL/g-COD_{added}. Hence, the feed pH of 5 generated the highest biogas yield. The acidogenic bacteria thrive in acidic conditions, while the methanogenic bacteria thrive in neutral conditions. Therefore, the biogas generated at a feed pH of 5 might have low quality (low methane content and high CO₂ content), although its biogas yield was high. Meanwhile, the MEC-AD process at feed pHs of 5, 6, 7, and 8 produced total biogas yields of 166.64, 252.88, 340.58, and 220.72 mL/g-COD_{added}. These data indicate that the MEC-AD process afforded a greater total biogas yield in comparison to the AD alone. The MEC-AD enhanced total biogas yield up to 1.85 times compared to the AD process. Comprehensively, the highest total biogas yield was achieved at a feed pH of 7 in the MEC-AD process, namely 340.58 mL/g-COD_{added}. It means that neutral environmental conditions had a positive effect on biogas production because methanogenic bacteria can grow well at pH ranges from 6.8 to 7.2 (Buyukkamaci and Filibeli, 2004). In

the MEC-AD, when the electric current flowed, electrochemically active microorganisms grew and then converted organic matter to H⁺, CO₂, and e⁻ at the anode. Furthermore, they were converted into biogas at the cathode via DIET-based methanogenesis. Besides that, in MEC-AD, the biogas was also generated via IIET-based methanogenesis (Syaichurrozi et al., 2024). Conversely, in AD, biogas was only produced through IIET-based methanogenesis (Syaichurrozi et al., 2024). Therefore, MEC-AD formed more total biogas yield than AD did.

Some previous studies support the findings of the present study. Previous research revealed that the MEC-AD in treating activated sludge effluent at different voltages (0.3–0.9 V) produced 27.2–44.8% more methane yield than AD alone (Joicy et al., 2022). Khomariah et al. (2024) also used the MEC-AD technique in treating artificial tapioca wastewater with the addition of urea and found that MEC-AD with the addition of 1.5 g urea produced the highest biogas yield of 268.8 mL/g-COD_{added}. When compared to the control (without urea), MEC-AD generated a biogas yield 2.5 times greater than AD alone.

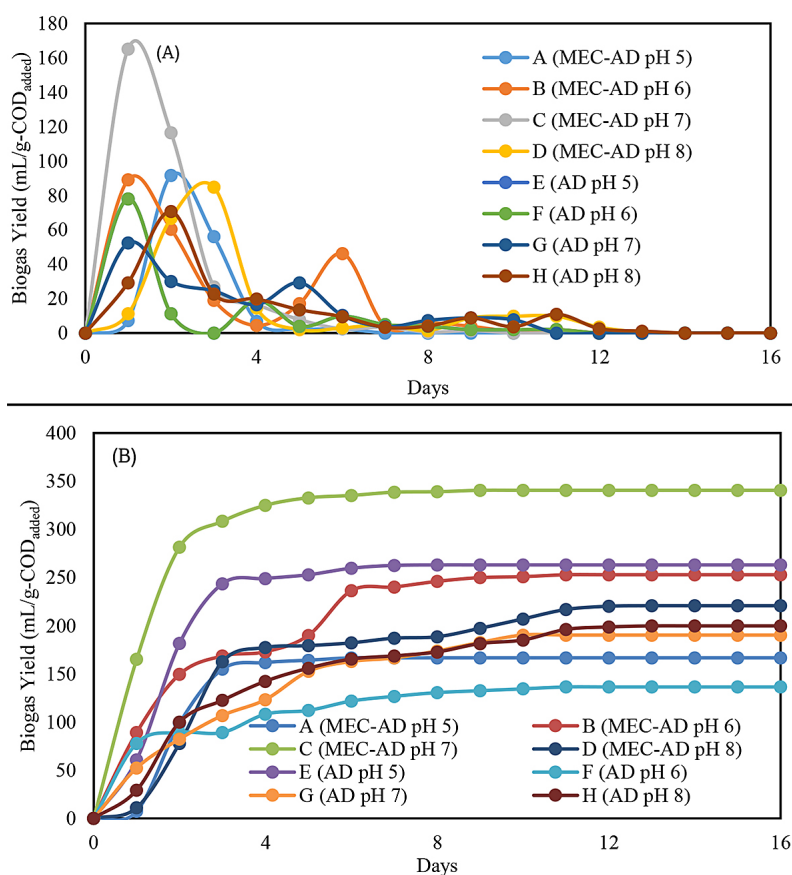


Figure 2. Biogas yield profile (A) daily, (B) cumulative

pH and volatile fatty acids (VFAs)

Liquid pH and VFA concentration are important parameters in the AD and MEC-AD because they greatly affect bacterial growth. The findings that pH affects anaerobic processes were also reported by Carlini et al. (2015) in biogas generation using poultry manure and cheese whey wastewater as substrates. Generally, pH decreases until a certain day, after which it increases until the end of digestion time (Budiyono et al., 2021). The feed pH affected the liquid pH profile and the accumulation of VFAs in the reactor (Figure 3). In both AD and MEC-AD, the liquid pH in the reactor tended to decrease from days 0 to 8 (Figure 3(A)). This was caused by the VFA accumulation in the reactor (Figure 3(B)). The decrease in pH was caused by acidogenic bacteria that produced acetic acid, hydrogen gas, carbon dioxide, and several other organic acids (Budiyono et al., 2014a). After day 8, the liquid pH tended to increase due to a decrease in VFAs. This decrease in VFAs occurred because methanogenic bacteria utilized VFAs to produce biogas (Syaichurrozi et al., 2016). In the AD and MEC-AD at feed pHs of 5, 6, 7, and 8,

the highest VFA concentration occurred on day 4, namely 6184, 10,124, 6184, and 10,131 mg acetic acid/L in AD, while 5263, 9449, 6075, and 9210 mg acetic acid/L in MEC-AD, respectively. After day 16, only a small amount of biogas was formed in the AD process, and the concentration of VFAs remained high. In contrast, the concentration of VFAs in MEC-AD was significantly lower because more of them were converted into biogas. The accumulation of VFAs in MEC-AD was less than that of AD, which helps to preserve pH stability (Xu et al., 2020). Therefore, the total biogas yield in MEC-AD was greater than in AD. Based on this, the MEC-AD with a feed pH of 7 is the optimum condition for processing tapioca liquid waste into biogas.

COD removal

Figure 4 shows that variations in feed pHs affected the level of COD removal in both the AD and MEC-AD. The COD removal in the AD at feed pHs of 5, 6, 7, and 8 was 29, 24, 37, and 14%, respectively. Meanwhile, the MEC-AD at feed pHs of 5, 6, 7, and 8 had COD removals of 34, 25, 43,

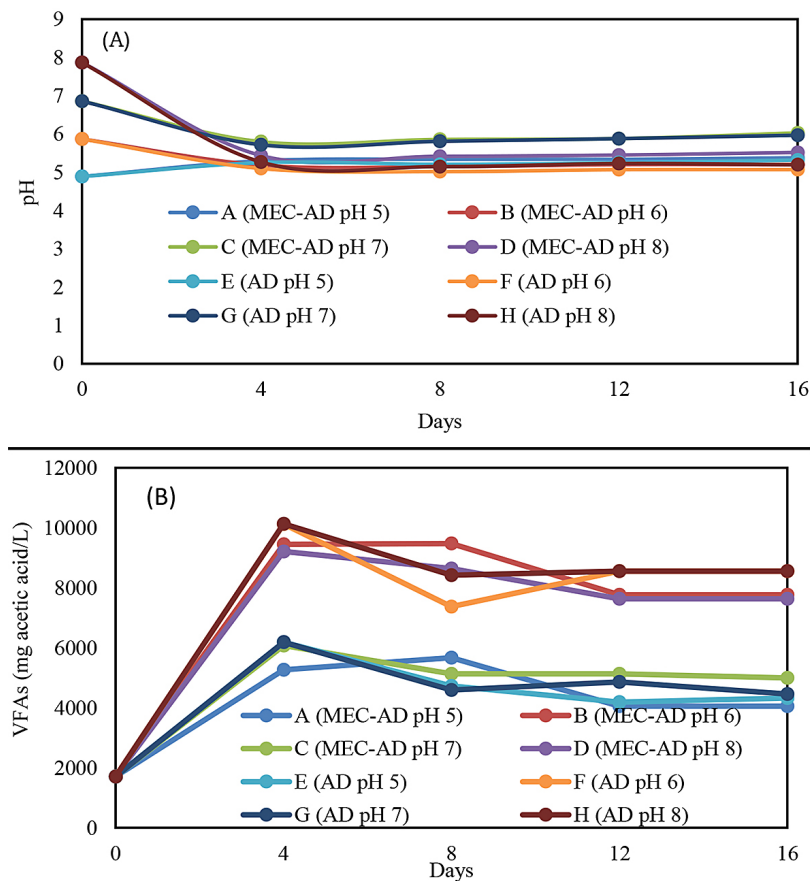


Figure 3. (A) pH profile, (B) VFA profile

and 20%, respectively. The MEC-AD had a higher COD removal compared to the AD at various feed pHs. This was because the MEC-AD improved biogas yield and reduced COD more effectively (Lee et al., 2017). Then, MEC-AD at a feed pH of 7 generated a higher COD removal compared to MEC-AD at feed pHs of 5, 6, and 8. This was because at a feed pH of 7, bacteria grew well in the digestion. The presence of MEC assistance in AD also increases the number of hydrolytic microorganisms so that more organic compounds can be hydrolyzed (Syaichurrozi et al., 2024). In accordance with this research, previous research revealed that the MEC-AD process in treating cow dung waste and aloe vera skin at 0.6 V achieved a higher COD removal (64.83%) compared to the AD (47.66%) (Xing et al., 2021). Furthermore, Syaichurrozi et al. (2024) also revealed that the MEC-AD process at a voltage of 1 V generated

higher COD and TSS removal efficiencies, namely 1.09 to 1.63 times, than the AD. In theory, the relationship between COD removal and biogas formation is such that increases in COD removal correlate with greater biogas formation. In detail, this study found that there is an inconsistency in the relationship between COD removal and biogas. Therefore, the authors made Figure 5 to see the correlation generally. Based on Figure 5, generally, the higher the biogas yield, the higher the COD removal was obtained. The highest COD removal was 43% obtained from MEC-AD at a feed pH of 7. It shows that there was remaining organic matter in the substrate. There are some reasons to explain this phenomenon. First, the anaerobic bacteria may die due to unfavorable conditions such as too low pH level, lack of nutrients, and the presence of toxic compounds. Second, the remaining organic matter may not be easily consumed by bacteria.

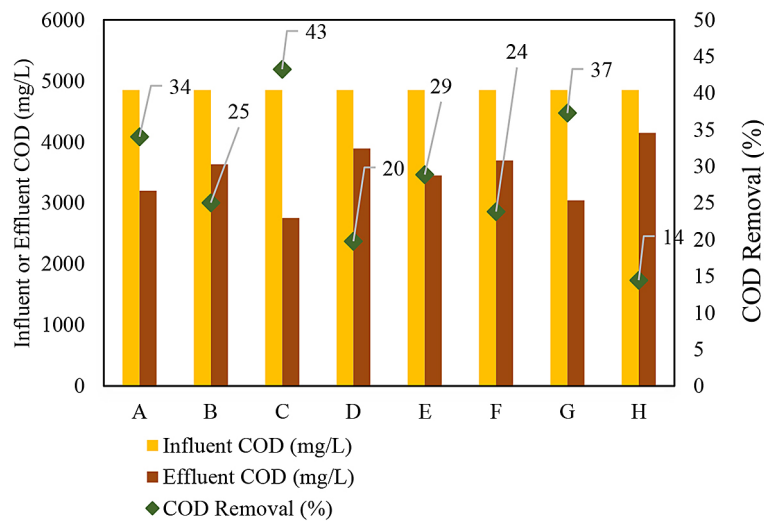


Figure 4. COD removal

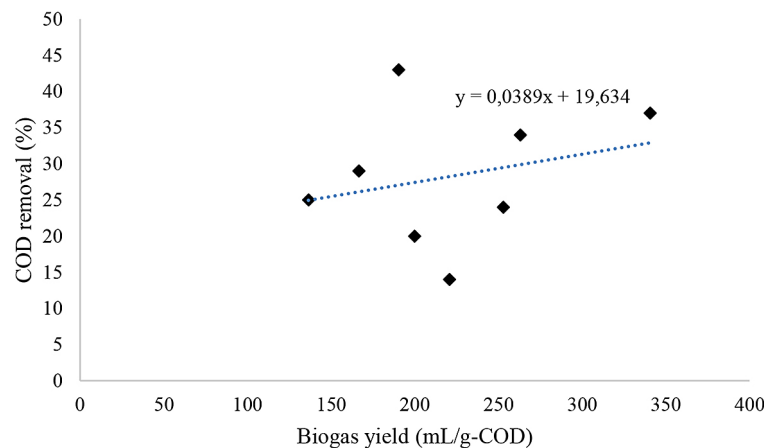


Figure 5. Correlation between biogas yield and COD removal

Methane content

The results of methane content in MEC-AD at a feed pH of 7 and AD at a feed pH of 7 are shown in Table 2. On days 4 and 8, the MEC-AD at a feed pH of 7 produced greater methane content (37.372–48.214%) compared to AD at a feed pH of 7 (7.621–44.659%). Hence, it means that the MEC-AD improved the methane content. The existence of MEC in AD modified the microbial community, leading to an enhancement in biogas production (Wang et al., 2022). In previous research conducted by Zhao et al. (2021), MEC-AD at a voltage of 0.6 V on a protein substrate improved the abundance of fermentation bacteria by 46.7% at the anode and increased hydrogenotrophic methanogenic bacteria by 84.3% at the cathode. At the cathode, hydrogenotrophic methanogenic bacteria were much more dominant because this methanogen converted hydrogen, carbon dioxide, and electrons into methane through a DIET pathway. Meanwhile, the methanogenic bacteria produced methane through an IIET pathway (Fudge et al., 2021). In MEC-AD, methane was produced via DIET and IIET pathways. On the other hand, in AD, methane was only produced through IIET-based methanogenesis (Syaichurrozi et al., 2024). As a result, MEC-AD afforded biogas with a higher methane percentage than AD did.

Kinetics analysis

The biogas evolution was simulated by utilizing a modified Gompertz model. Under batch conditions, the biogas evolution aligns with the growth rate of bacteria in the reactor (Sumardiono et al., 2021). The constants are comprehensively detailed in Table 3. Figure 6 depicts the plot between the experimental and simulated data derived from the modified Gompertz model.

The MEC-AD in prediction produces a greater total biogas yield (A) than AD alone. Then, in prediction, the highest total biogas yield was achieved in an MEC-AD process at a feed pH of 7, namely 340.58 mL/g-COD_{added}. This showed that neutral environmental conditions had a positive impact on the biogas formation.

The MEC-AD also enhanced the μ value across a range of feed pH levels. It means that the MEC-AD successfully augmented microbial activity, thus increasing the daily biogas generation. The highest μ value was reached in MEC-AD at a feed pH of 7, namely 170.00 (mL/g-COD_{added}/day). In the context of this study, as the value of A increased, the value of μ also increased. In other words, the potential for total biogas yield was expected to increase along with the acceleration of the biogas generation rate (Syaichurrozi et al., 2024).

The kinetic constant λ serves as an indicator of the adaptation period necessary for anaerobic

Table 2. Methane content

Process	Day	Percentage (%)	
		CH ₄	CO ₂
MEC-AD pH 7	4	48.214	51.786
	8	37.372	62.288
AD pH 7	4	44.659	55.341
	8	7.621	92.379

Table 3. Kinetic constants of biogas output

Digester	A (mL/g-COD _{added})	μ (mL/g-COD _{added} /day)	λ (days)	MAPE (%)
A (MEC-AD pH 5)	166.64	109.78	1.08	0.264
B (MEC-AD pH 6)	252.90	59.00	0.00	5.978
C (MEC-AD pH 7)	340.58	170.00	0.00	1.056
D (MEC-AD pH 8)	207.11	83.34	1.06	6.029
E (AD pH 5)	263.11	133.09	0.55	0.600
F (AD pH 6)	136.45	31.03	0.00	7.032
G (AD pH 7)	190.48	36.16	0.00	4.416
H (AD pH 8)	197.20	42.73	0.40	5.979

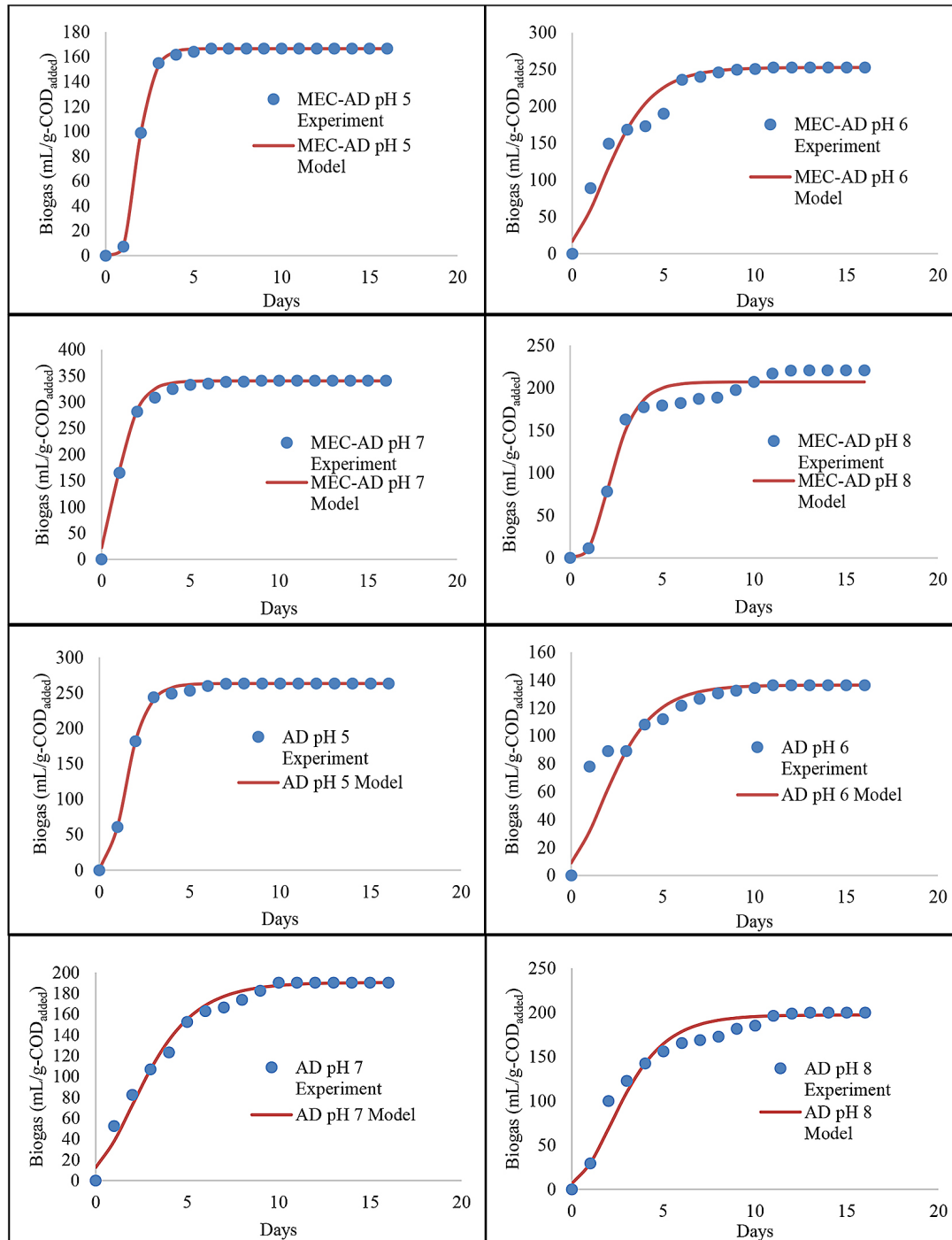


Figure 6. Fitting between experimental data and modeled data

microorganisms before the biogas is generated (Syaichurrozi et al., 2016). The λ value in the MEC-AD tended to be greater than AD. The combination of MEC-AD resulted in a λ value of 0.00–1.08 days and the AD had a λ value of 0.00–0.55 days. It means that the presence of an electric current requires a long delay time for methanogenic microorganisms to acclimate to the substrate (Syaichurrozi et al., 2024). Previous research by Zou et al. (2021) revealed findings

similar to the current study, indicating that the MEC-AD led to improvements in A , μ , and λ . In the absence of MEC, the AD exhibited values of A , μ , and λ measuring 431.8 mL/g-TS, 28.7 mL/g-TS/day, and 0.673 days. When MEC was employed at a voltage range of 0.3 to 1.5 V, the A , μ , and λ values were 486.2 to 605.4 mL/g-TS, 32.4 to 40.8 mL/g-TS/day, and 0.996 to 1.216 days, respectively. Furthermore, research by Syaichurrozi et al. (2024) also found that MEC-AD for

treating tofu wastewater with the iron addition of 0–600 mg/L at a voltage of 1 V produced greater A, μ , and λ values than AD alone.

Comparison of this study with previous research

The MEC-AD process has previously been applied to the treatment of various substrates such as tofu wastewater (Syaichurrozi et al., 2024), protein (Bovine Serum Albumin) (Zhao et al., 2021), activated sludge waste (Joicy et al., 2022), synthetic tapioca wastewater (Khomariah et al., 2024), glucose (Choi et al., 2017), mixed substrates composed of cattle manure and aloe vera peel waste (Xing et al., 2021). The novelty of the current research lies in the substrate used in the MEC-AD process. MEC-AD successfully improved biogas and methane generation, as well as achieving higher organic matter removal efficiency across the different substrates tested compared to AD alone.

In the MEC-AD process, applied electrical voltage (current density) also significantly influences biogas production. Previous research by Choi et al. (2017) varied the voltages of 0.5 V, 0.7 V, 1.0 V, and 1.5 V (or current densities of 5.84, 12.28, 19.04, and 2.36 A/m³). The research demonstrated that a voltage of 1 V (current density of 19.04 A/m³) improved methane yield by 1.3-fold compared to AD alone. At voltages higher and lower than 1 V (current density of 19.04 A/m³), methane production declined. Conversely, Xing et al. (2021) and Joicy et al. (2022) revealed that a voltage of 0.6 V yielded higher biogas production than 1 V. In research by Xing et al. (2021), the voltage of 0.6 V had an initial current density

of about 1–2 A/m². These studies used different substrates and inoculum, which may account for the varying conclusions regarding the optimum voltage in the MEC-AD process. This suggests that voltage is a critical factor in MEC-AD performance. This study used a voltage of 1 V (or initial current density of 3.26 A/m² or 0.15 A/m³). Therefore, future research should investigate voltage or current density variation to determine the optimum MEC-AD voltage specifically for tapioca liquid waste treatment.

Furthermore, the type of electrode also affects the microbial communities at the electrodes responsible for methane generation. Previous research by Xiaomei et al. (2022) revealed that MEC-AD with a Ni/Co-NC cathode generated a higher methane production compared to MEC-AD with a carbon cathode. Thus, electrode modification in the MEC-AD process for treating tapioca liquid waste warrants further investigation.

Energy analysis

Figure 7 illustrates the electric current profile throughout the MEC-AD process. In this study, the MEC-AD was operated at a constant voltage of 1 V. Variations in electric current during the MEC-AD process were caused by changes in the conductivity of the liquid. The initial current was approximately 77 μ A. The final current values for MEC-AD at feed pH levels of 5, 6, 7, and 8 were 62, 57, 53, and 66 μ A, respectively (Figure 7). The electric current tended to decrease towards the end of the process, indicating a reduction in organic pollutants in the liquid and an increase in the liquid's electrical resistance (Syaichurrozi et al., 2024). Energy analysis was essential to be conducted to

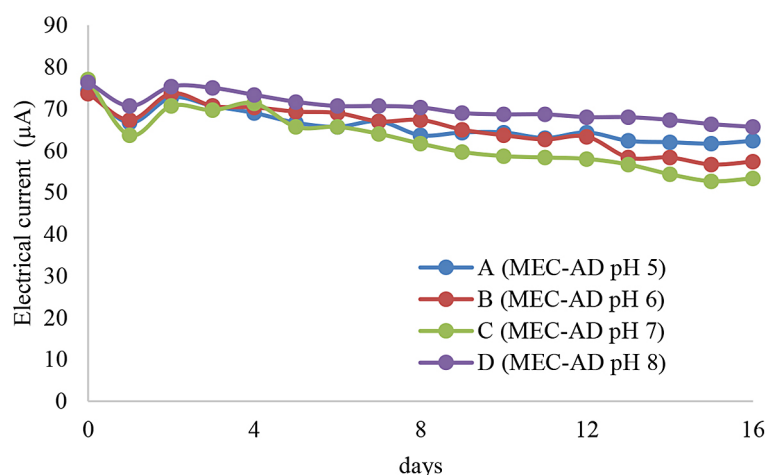


Figure 7. Electric current profile on MEC-AD

investigate the feasibility of the MEC-AD process. The input energy required to treat 1 L of tapioca liquid waste can be quantified using Equation 7.

$$Energy_{input} (J) = Voltage (V) \times Current (A) \times t (s) \quad (7)$$

The resulting methane can be converted to generate energy. The energy output from methane combustion is estimated using Equation 8 (Kanellos et al., 2024).

$$Energy_{output} (J) = [68\% \times 817,970 (J/mol) \times \text{Methane} (L)] / 22.4 L/mol \quad (8)$$

Subsequently, the net energy surplus is quantified using Equation 9:

$$Energy_{surplus} (J) = energy_{output} (J) - energy_{input} (J) \quad (9)$$

Thus, the energy surplus generated from AD and MEC-AD is 123.5 and 275.6 J, respectively, which shows that the addition of MEC can increase the energy surplus by around 152.1 J (or 2.2 times).

CONCLUSIONS

The effect of various feed pHs of 5, 6, 7, and 8 on biogas generation using AD and MEC-AD processes was conducted. The AD at feed pHs of 5, 6, 7, and 8 produced total biogas yields of 263.11, 136.43, 190.30, and 199.82 mL/g-COD_{added}. Then, the MEC-AD procedure at feed pHs of 5, 6, 7, and 8 produced total biogas yields of 166.64, 252.88, 340.58, and 220.72 mL/g-COD_{added}, respectively. This indicated that the MEC-AD led to a total biogas yield 1.85 times greater than AD alone. Specifically, the MEC-AD at a feed pH of 7 resulted in a COD removal of 43% which was higher than AD at the same feed pH (37%). Furthermore, the methane content in MEC-AD was found to be greater than that in AD. The presence of MEC contributed to an improvement in the values of A, μ , and λ . In the case of MEC-AD at a feed pH of 7, the A, μ , and λ values were 340.58 mL/g-COD_{added}/day, and 0.00 days, respectively. The prospect research that can be conducted in the future is research on the effect of various voltage (current density) levels and modification of electrodes in MEC-AD of tapioca liquid waste. In addition, the biogas purification treatment can be conducted to increase the methane content in the resulting biogas.

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REFERENCES

1. Arnata, I. W., Gunam, I. B. W., Anggreni, A. A. M. D., Wijaya, I. M. M., Sartika, D. (2021). Utilization of solid tapioca waste for bioethanol production by co-fermentation of baker's and tapai yeast. *IOP Conference Series: Earth and Environmental Science*, 724(1), 1–7. <https://doi.org/10.1088/1755-1315/724/1/012058>
2. Budiyo, B., Matin, H. H. A., Yasmin, I. Y., Priogo, I. S. (2023). Effect of pretreatment and C/N ratio in anaerobic digestion on biogas production from coffee grounds and rice husk mixtures. *International Journal of Renewable Energy Development*, 12(1), 209–215. <https://doi.org/10.14710/ijred.2023.49298>
3. Budiyo, B., Riyanta, A. B., Sumardiono, S., Jos, B., Syaichurrozi, I. (2021). Optimization of parameters for biogas production from bagasse using taguchi method. *Polish Journal of Environmental Studies*, 30(5), 4453–4461. <https://doi.org/10.15244/PJOES/129914>
4. Budiyo, B., Syaichurrozi, I., Suhirman, S., Hidayat, T., Jayanudin, J. (2021). Experiment and modeling to evaluate the effect of total solid on biogas production from the anaerobic co-digestion of tofu liquid waste and rice straw. *Polish Journal of Environmental Studies*, 30(4), 3489–3496. <https://doi.org/10.15244/PJOES/127277>
5. Budiyo, Syaichurrozi, I., Sumardiono, S. (2014a). Effect of total solid content to biogas production rate from vinasse. *International Journal of Engineering, Transactions B: Applications*, 27(2). <https://doi.org/10.5829/idosi.ije.2014.27.02b.02>
6. Budiyo, Syaichurrozi, I., Sumardiono, S. (2014b). Kinetic model of biogas yield production from vinasse at various initial pH: Comparison between modified gomperz model and first order kinetic model. *Research Journal of Applied Sciences, Engineering and Technology*, 7(13).
7. Buyukkamaci, N., Filibeli, A. (2004). Volatile fatty acid formation in an anaerobic hybrid reactor.

- Process Biochemistry*, 39(11), 1491–1494. [https://doi.org/10.1016/S0032-9592\(03\)00295-4](https://doi.org/10.1016/S0032-9592(03)00295-4)
8. Carlini, M., Castellucci, S., Moneti, M. (2015). Biogas production from poultry manure and cheese whey wastewater under mesophilic conditions in batch reactor. *Energy Procedia*, 82, 811–818. <https://doi.org/10.1016/j.egypro.2015.11.817>
9. Choi, K., Kondaveeti, S., Min, B. (2017). Biore-source technology bioelectrochemical methane (CH₄) production in anaerobic digestion at different supplemental voltages. *Bioresource Technology*, 245(September), 826–832. <https://doi.org/10.1016/j.biortech.2017.09.057>
10. Fudge, T., Bulmer, I., Bowman, K., Pathmakanthan, S., Gambier, W., Dehouche, Z., Al-Salem, S. M., Constantinou, A. (2021). Microbial electrolysis cells for decentralised wastewater treatment: The next steps. *Water (Switzerland)*, 13(4). <https://doi.org/10.3390/w13040445>
11. Joicy, A., Seo, H., Lee, M.-E., Kim, D.-H., Cho, S. K., Ahn, Y. (2022). Enhanced methane production using pretreated sludge in MEC-AD system: Performance, microbial activity, and implications at different applied voltages. *International Journal of Hydrogen Energy*, 47(96), 40731–40741. <https://doi.org/10.1016/J.IJHYDENE.2022.07.154>
12. Kaffle, G. K., Kim, S. H., Sung, K. I. (2013). Ensiling of fish industry waste for biogas production: A lab scale evaluation of biochemical methane potential (BMP) and kinetics. *Bioresource Technology*, 127, 326–336. <https://doi.org/10.1016/J.BIORTECH.2012.09.032>
13. Kanellos, G., Tremouli, A., Arvanitakis, G., Lyberatos, G. (2024). Boosting methane production and raw waste activated sludge treatment in a microbial electrolysis cell-anaerobic digestion (MEC-AD) system: The effect of organic loading rate. *Bioelectrochemistry*, 155, 108555. <https://doi.org/10.1016/J.BIOELECTCHEM.2023.108555>
14. Khomariah, N., Syaichurrozi, I., Kurniawan, T. (2024). Enhanced biogas production from tapioca wastewater through the microbial electrolysis cell-assisted anaerobic digestion process at various urea additions. *Jurnal Bahan Alam Terbarukan*, 13(2), 146–155. <https://doi.org/10.15294/jbat.v13i2.12860>
15. Lee, B., Park, J. G., Shin, W. B., Tian, D. J., Jun, H. B. (2017). Microbial communities change in an anaerobic digestion after application of microbial electrolysis cells. *Bioresource Technology*, 234, 273–280. <https://doi.org/10.1016/J.BIORTECH.2017.02.022>
16. Lounglawan, P., Khungaew, M., Suksombat, W. (2011). Silage production from cassava peel and cassava pulp as energy source in cattle diets. *Journal of Animal and Veterinary Advances*, 10(8), 1007–1011. <https://doi.org/10.3923/JAVAA.2011.1007.1011>
17. Matin, H. H. A., Damarjati, B. Y., Shidqi, M. I. G., Budiyo, B., Othman, N. H., Wahyono, Y. (2024). Biogas production from the potato peel waste: Study of the effect of C/N ratio, Em-4 bacteria addition and initial Ph. *Revista de Gestao Social e Ambiental*, 18(6), 1–21. <https://doi.org/10.24857/rgsa.v18n6-039>
18. Putri, D. A., Saputro, R. R., Budiyo, B. (2012). Biogas production from cow manure. *International Journal of Renewable Energy Development*, 1(2), 61–64. <https://ijred.cbior.id/index.php/ijred/article/view/3805>
19. Sánchez, A. S., Silva, Y. L., Kalid, R. A., Cohim, E., Torres, E. A. (2017). Waste bio-refineries for the cassava starch industry: New trends and review of alternatives. *Renewable and Sustainable Energy Reviews*, 73(February 2016), 1265–1275. <https://doi.org/10.1016/j.rser.2017.02.007>
20. Situmorang, A., Manik, Y. (2018). Initial sustainability assessment of tapioca starch production system in Lake Toba area. *IOP Conference Series: Materials Science and Engineering*, 337(1). <https://doi.org/10.1088/1757-899X/337/1/012044>
21. Sulistyowati, L., Andareswari, N., Rahmat Hidayatullah, R., Amri Komarudin, N., Yolanda, Y., Rahmat, R., Amri, N., Hidayatullah, R. R., Komarudin, N. A. (2023). Liquid waste treatment for sustainable tapioca industry: A comparison between biogas and liquid sugar. *ASEAN Journal on Science and Technology for Development*, 40(1), 2. <https://doi.org/10.61931/2224-9028.1001>
22. Sumardiono, S., Adisukmo, G., Hanif, M., Budiyo, B., Cahyono, H. (2021). Effects of pretreatment and ratio of solid sago waste to rumen on biogas production through solid-state anaerobic digestion. *Sustainability* 2021, 13(13), 7491. <https://doi.org/10.3390/SU13137491>
23. Sumardiono, S., Matin, H. H. A., Sulistianingias, I., Nugroho, T. Y., Budiyo, B. (2023). Effect of physical and biological pretreatment on sugarcane bagasse waste-based biogas production. *Materials Today: Proceedings*, 87, 41–44. <https://doi.org/10.1016/J.MATPR.2023.01.372>
24. Syaichurrozi, I., Budiyo, B., Sumardiono, S. (2013). Predicting kinetic model of biogas production and biodegradability organic materials: Biogas production from vinasse at variation of COD/N ratio. *Bioresource Technology*, 149. <https://doi.org/10.1016/j.biortech.2013.09.088>
25. Syaichurrozi, I., Murtiningsih, I., Angelica, E. C. et al. (2024). A preliminary study: Microbial electrolysis cell assisted anaerobic digestion for biogas production from Indonesian tofu-processing wastewater at various Fe additions. *Renewable Energy*, 234, 121203. <https://doi.org/10.1016/J.RENENE.2024.121203>
26. Syaichurrozi, I., Rusdi, R., Hidayat, T., Bustomi, A.

- (2016). Kinetics studies impact of initial pH and addition of yeast *saccharomyces cerevisiae* on biogas production from Tofu Wastewater in Indonesia. *International Journal of Engineering*, 29(8), 1037–1046.
27. Syaichurrozi, I., Sarto, S., Sediawan, W. B., Hidayat, M. (2023). Effect of Fe addition on anaerobic digestion process in treating vinasse: Experimental and kinetic studies. *Periodica Polytechnica Chemical Engineering*, 67(1), 127–140. <https://doi.org/10.3311/PPCH.20611>
 28. Virunanon, C., Ouephanit, C., Burapatana, V., Chulalaksananukul, W. (2013). Cassava pulp enzymatic hydrolysis process as a preliminary step in bio-alcohols production from waste starchy resources. *Journal of Cleaner Production*, 39, 273–279. <https://doi.org/10.1016/j.jclepro.2012.07.055>
 29. Wang, X. T., Zhang, Y. F., Wang, B., Wang, S., Xing, X., Xu, X. J., Liu, W. Z., Ren, N. Q., Lee, D. J., Chen, C. (2022). Enhancement of methane production from waste activated sludge using hybrid microbial electrolysis cells-anaerobic digestion (MEC-AD) process – A review. *Bioresource Technology*, 346, 126641. <https://doi.org/10.1016/J.BIORTECH.2021.126641>
 30. Xiaomei, Z., Rujing, L., Jun, X., Yingying, H., Xinying, Z., Li, X. (2022). Enhanced methane production by bimetallic metal–organic frameworks (MOFs) as cathode in an anaerobic digestion microbial electrolysis cell. *Chemical Engineering Journal*, 440, 135799. <https://doi.org/10.1016/J.CEJ.2022.135799>
 31. Xing, T., Yun, S., Li, B., Wang, K., Chen, J., Jia, B., Ke, T., An, J. (2021). Coconut-shell-derived bio-based carbon enhanced microbial electrolysis cells for upgrading anaerobic co-digestion of cow manure and aloe peel waste. *Bioresource Technology*, 338, 125520. <https://doi.org/10.1016/J.BIORTECH.2021.125520>
 32. Xu, X. J., Wang, W. Q., Chen, C., Xie, P., Liu, W. Z., Zhou, X., Wang, X. T., Yuan, Y., Wang, A. J., Lee, D. J., Yuan, Y. X., Ren, N. Q. (2020). The effect of PBS on methane production in combined MEC-AD system fed with alkaline pretreated sewage sludge. *Renewable Energy*, 152, 229–236. <https://doi.org/10.1016/J.RENENE.2020.01.052>
 33. Yu, Z., Leng, X., Zhao, S., Ji, J., Zhou, T., Khan, A., Kakde, A., Liu, P., Li, X. (2018). A review on the applications of microbial electrolysis cells in anaerobic digestion. *Bioresource Technology*, 255, 340–348. <https://doi.org/10.1016/J.BIORTECH.2018.02.003>
 34. Zhao, L., Wang, X. T., Chen, K. Y., Wang, Z. H., Xu, X. J., Zhou, X., Xing, D. F., Ren, N. Q., Lee, D. J., Chen, C. (2021). The underlying mechanism of enhanced methane production using microbial electrolysis cell assisted anaerobic digestion (MEC-AD) of proteins. *Water Research*, 201(May). <https://doi.org/10.1016/j.watres.2021.117325>
 35. Zou, L., Wang, C., Zhao, X., Wu, K., Liang, C., Yin, F., Yang, B., Liu, J., Yang, H., Zhang, W. (2021). Enhanced anaerobic digestion of swine manure via a coupled microbial electrolysis cell. *Bioresource Technology*, 340. <https://doi.org/10.1016/J.BIORTECH.2021.125619>