Enhanced Biogas Production from Sugarcane Vinasse using Electro-Fenton as Pre-treatment Method

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Abstract. High concentration of organic matter in the sugarcane vinasse is potential as a biogas feedstock, but its a very high organic matter (expressed by chemical oxygen demand (COD), >100,000 mg/L) disturbs the biological activity during anaerobic digestion (AD). The maximum COD concentration in vinasse that is recommended as an initial condition of biogas feedstock is ±75,000 mg/L. Furthermore, complex characteristics of vinasse make it necessary to be pre-treated before it is converted to biogas. Therefore, an advanced oxidation process (AOP) such as electro-Fenton (EF) is applied as a pre-treatment method in the AD of vinasse. The goal of this study was to investigate the effect of pre-treatment of vinasse using the EF method on biogas production. The process of EF was conducted with a variation of voltage (4, 6, 8 V) under the batch system and constant operating conditions such as treatment time, initial pH, the ratio of [H₂O₂] to [COD], and distance between electrodes. Moreover, the process of AD was run using anaerobic digesters having a volume of 2 L under the batch system at room temperature. The AD was conducted for 40 days. The results showed that the best EF could decrease the COD as much as 81.14% at 4 V with constant operation conditions (treatment time of 60 min, initial pH of 4.34, a ratio of [H₂O₂] to [COD] of 0.6 and distance electrodes of 3 cm). Furthermore, the pre-treatment of EF increased biogas volume successfully (6.02 L). The applicability of the first-order, second-order, and Behnajady-Modirshahla-Ghanbery (BMG) was investigated to evaluate the removal of the COD value. This primary concern is that the electro-Fenton treatment is favorable to decrease the organic matter of sugarcane vinasse.

Keywords: sugarcane vinasse, electro-Fenton, chemical oxygen demand, anaerobic digestion, biogas

1. Introduction

The production of bioethanol from molasses yields vinasse as a result of distillation. Each liter of ethanol makes about 10-15 L of vinasse [1]. Enormous sugarcane vinasse from that industry is turning into a matter of extraordinary concern because of its high concentration of BOD and COD (ranging from 100,000-150,000 mg/L). The high concentration of BOD and COD can cause negative ecological effects when disposed directly to the environment. Moreover, other characteristics of vinasse have an acidic condition (pH 3-5), corrosive, dark brown in color, and present recalcitrant compounds and inhibitors that hinder its biodegradation [1,2]. In fact, a high concentration of organic matter in the sugarcane vinasse is potential as a biogas feedstock, but it is a very high...
organic matter disturbs the biological activity during anaerobic digestion. The maximum recommended COD concentration in which vinasse waste can be converted into biogas optimally is 74,182.50 mg/L [3]. If the COD above the value, the pH condition will be drop at the beginning of the fermentation stage so that microbial activity is disrupted and biogas production is inhibited [3,4]. To limit those effects, proficient and monetarily reasonable cycles for vinasse pre-treatment are required before converted into biogas.

Advanced Oxidation Processes (AOPs) are eco-accommodating techniques and ongoing days it got more consideration for wastewater treatment. The electro-Fenton method is a promising innovative treatment of wastewater [5]. This method depends on the continuous electro generation of H$_2$O$_2$ at an appropriate cathode by the decrease of broke up oxygen or air alongside the expansion of iron as a catalyst for produce oxidant OH onsite electrochemically through Fenton’s reaction. In other words, the reaction between H$_2$O$_2$ and Fe$^{3+}$ produces hydroxyl radical, a non-selective strong oxidant which is fit for corrupting a wide scope of organic pollutant substances and toxins in wastewater. The general reaction of the electro-Fenton cycle are showed in the equations below [5–7]:

\[
\begin{align*}
O_2 + 2H^+ + 2e^- & \rightarrow H_2O_2 \\
Fe & \rightarrow Fe^{3+} + 2e^- \\
Fe^{2+} + H_2O_2 & \rightarrow Fe^{3+} + OH + OH^- \\
Fe^{3+} + H_2O_2 & \rightarrow Fe^{2+} + HO_2^- + H^+ \\
Fe^{3+} + HO_2^- & \rightarrow Fe^{2+} + H^+ + O_2 \\
H_2O_2 + OH^- & \rightarrow HO_2^- + H_2O \\
Fe^{2+} + HO_2^- & \rightarrow Fe^{3+} + HO_3^- \\
2 H_2O_2 & \rightarrow 4H^+ + O_2 + 4e^- \\
\text{products} & \rightarrow \text{products}
\end{align*}
\]

Electro Fenton Process (EFP) incorporates both electrochemical and Fenton treatment techniques and every strategy is an amazing and compelling technique for the treatment cycle. In contrast with Fenton’s reagent, EFP is more effective, ecologically benevolent, responds well with organics, and does not deliver optional toxins and poisonous mixes during oxidation. However, it likewise has a few impediments like EFP ought to be kept up in acidic conditions, H$_2$O$_2$ presence may disturb to microorganism (if the reaction time is short), during electro-Fenton reaction little flocs were seen that flocs set aside more or huge effort to settle [7].

The objective of this study is to evaluate the effectiveness of the electro-Fenton process for reducing chemical oxygen demand (COD) in vinasse and then investigate the enhanced biogas production from the EFP pretreated vinasse. Furthermore, to investigate the reaction process of electro-Fenton, it was carried out using three kinetics models, such as first-order, second-order, and Behnajady-Modirshahla-Ghanbery (BMG).

2. Material and Method

2.1 Materials and Chemicals

Vinasse utilized in this research was gathered from a bioethanol industry of molasses. The bioethanol industry situated in Yogyakarta, Indonesia (PT. Madubaru). The Physico-chemical characteristics of vinasse utilized in the research are given in Table 1.

| Parameters      | Unit | Value    |
|-----------------|------|----------|
| COD             | mg/L | 126,750  |
| BOD$_5$         | mg/L | 32,250   |
| Phenol          | mg/L | 4.64     |
| Sulfat          | mg/L | 5        |
| pH              | -    | 4.2-4.5  |
| Appearance      |      | Dark brown |

Hydrogen peroxide (H$_2$O$_2$) with a concentration of 30% wt was obtained from PT Peroksida Indonesia Pratama and the iron electrodes had a length × width × thickness dimension of 25 cm × 2 cm × 0.3 cm as the source of ferric ion.
The inoculum used in this study was digested cow manure that obtained from cattle breeding in Turgo, Yogyakarta, Indonesia.

2.2 Electrolytic Systems

The test device used in this study was a batch mode containing five fundamental compartments (Figure 1): an electro-Fenton cell (made of pyrex glass with an effective volume of 1213 ml), a DC power supply with the range of 1-1.4 A for electrical current and 4, 6, 8 V of voltage [8], the iron electrodes in equal dimensions of 2 cm × 5 cm (surface-active immersed in wastewater), a motor digital stirrer with steady blending 300 rpm and a thermometer.

![Figure 1. Experimental apparatus of electro-Fenton.](image)

2.3 Experimental Setup

2.3.1 Electro-Fenton Setup. All electro-fenton response time was begun by the addition of hydrogen peroxide with consistent blending (300 rpm) until 60 min and afterward halted. Hydrogen peroxide was added and the power supply was turned on to initiate the reaction. The example was taken at regular intervals (every 10 minutes) then an example was separated for investigation. The pH treated example was acclimated to 7 by NaOH 5 M to stop the reaction. The COD estimation of sugarcane vinasse, when the electro-Fenton treatment, were estimated by Balai Besar Teknik Kesehatan Lingkungan dan Pengendalian Penyakit (BBTKLPP) Yogyakarta while the BOD$_5$ was investigated and measured utilizing standard strategies. The estimation of pH was estimated utilizing a pH meter.

2.3.2 Biogas Setup. Anaerobic digesters were made from Erlenmeyer glasses which have a volume of 2 L. The Erlenmeyer glasses were stopped with elastic attachment and were outfitted with a valve for biogas measurement. Anaerobic digesters were worked in a batch system and at room temperature. The volume of biogas is determined based on the exhaustion of water in the gasometer. Vinasse was diluted by using faucet water with a proportion of vinasse: water of 1:3. Furthermore, initial pH for all substrates was adjusted to become 7.0 by the addition of NaOH 10 N. Digested cow manure or inoculum as methanogenic microorganisms supplier was added into the digester as much as 30% v/v absolute volume. Biogas produced was estimated once every 2 days at regular intervals to know biogas production. Also, the substrate pH was investigated once every 2 days to realize the pH profile every day using the digital pH meter. In this study, vinasse as a biogas feedstock was not the same as pretreatment vinasse. The samples were not utilized because of stored for too long (due to the Covid-19 pandemic).
2.4 Kinetic Modeling of Biogas

The decrease in COD concentration during electro-Fenton process was modeled through three kinetics models, i.e. first-order, second-order and Behnajady-Modirshahla-Ghanbery (BMG) [9,10]. To assess the linear model, the estimation of the coefficient of assurance ($R^2$) for each model is thought about [11]. The linear type of the first-order, second-order and BMG was shown in table 2:

| Kinetic Model       | Equation                        |
|---------------------|---------------------------------|
| First-order         | $\ln \frac{C_0}{C_t} = k_1 t$  |
| Second-order        | $\frac{1}{C_t} - \frac{1}{C_0} = k_2 t$ |
| BMG                 | $\frac{t}{1 - (C_t / C_0)} = m + b t$ |

3. Results and discussion

This study was conducted in two stages, namely the electro-Fenton pre-treatment stage and the biogas stage. The first stage aimed to determine the effectiveness of the electro-Fenton method as a vinasse waste pre-treatment method in degrading COD concentrations. Furthermore, the second stage was presented to determine the effect of the first experiment on biogas production (the results of the first experiment were used as biogas feedstock).

Electro-Fenton is a decrease of wastewater strategy dependent on the continuous electro generation of $H_2O_2$ at an appropriate cathode and anode by the decrease of dissolved oxygen or air alongside the expansion of an iron catalyst to the treated solution to produce hydroxyl radical [12–14]. With these considerations, the parameter to be reviewed in this study was current density with each current variable being looked at its effectiveness in the form of biogas production.

3.1 Effect of Voltage

The study was conducted on different voltage (4, 6, 8 V). Each voltage resulted in an electrical current (EC) range 1-2.4 A. The EC was the main boundary, which impacts the reaction rate of electrochemical cycles [15]. The impact of applied EC to decrease COD removal was investigated by electrolyzing the vinasse at the original pH of vinasse at various voltage and the outcomes have appeared in Figure 3.
Figure 3. Removal of chemical oxygen demand (COD) by the electro-Fenton process at different voltages.

The graph compares three voltages in terms of COD removal from 0 to 60 min. It is noticeable that despite some fluctuations, over the reaction time as a whole the removals rose in both 4 V and 6 V at the first of time. In contrast, at 8 V saw dramatic fall of COD removal at initial time and began to rise again after 20 min. The highest COD removal of 81% was acquired, namely at 4 V (2 A) with a reaction time of 40 min, but when EC exceeded this level, no increase was observed. One of the reasons may be that there are decomposition of organic components occurs in the solution and final by-products in the sludge, so that increasing the EC up to more than 2 A could not lead to more COD removal.

The electrical production of Fe$^{2+}$ consequently producing hydroxyl radical in the reactor had a direct connection with applied EC. Consequently, it is recommended that the EC is kept restricted to forestall unfriendly impacts, for example, heat generation and higher energy utilization. Figure 4 below shows the electro-Fenton optimization using a simple method.

Figure 4. Influence of voltage and reaction time on COD removal based on SN ratio.
The line graphs show that the optimum condition to degrade the COD concentration is at a voltage of 4 with a reaction time of 40 min.

### 3.2 Kinetic Models of COD Removal

The kinetic model of COD removal by the electro-Fenton method is complex attributable to a few phases of response during the cycle[10]. Three kinetic models, first-order, second-order and Behnajady-Modirshahla-Ghanbery (BMG) for fitting the experimental information have been utilized. The kinetic models were determined just dependent on the 30 min for reactions since fast oxidation happened in that range of time. Moreover, in the last 30 min occurred slow oxidation. To evaluate the linear model, the estimation of the coefficient of assurance ($R^2$) for each model is thought about. In other words, the coefficient has equal to 1 ($R^2 \approx 1$). The outcomes are presented in Table 3 and Figure 5.

#### Table 3. The results of kinetic model comparison for decreasing COD concentration of sugarcane vinasse at first-order, second-order and BMG.

| Kinetic Model         | Voltage | 4 V   | 6 V   | 8 V   |
|-----------------------|---------|-------|-------|-------|
| First order kinetic   |         |       |       |       |
| $R^2$                 |         | 0.4667 | 0.5446 | 0.5621 |
| Second order kinetic  |         |       |       |       |
| $R^2$                 |         | 0.5153 | 0.3929 | 0.5448 |
| BMG kinetic model     |         |       |       |       |
| $R^2$                 |         | 0.9928 | 0.9986 | 0.9686 |
3.3 Biogas Enhancement

Biogas is a mixture of several gases consisting of methane (CH₄), carbon dioxide (CO₂), and other minor gases. Biogas is produced through an anaerobic degradation process by microorganisms or anaerobic digestion (AD). The decomposition of organic material to biogas through 4 stages, namely hydrolysis, acidogenesis, acetogenesis, and methanogenesis [16].

This study was done to evaluate the effect of the electro-Fenton process as a pre-treatment of sugarcane wastewater as the initial substrates (represented by COD). High concentration of organic matter in the sugarcane vinasse is potential to be used as a biogas feedstock, but it is very high organic matter (expressed by COD >100,000 mg/L) disturbs the biological activity during anaerobic digestion (AD). The maximum COD concentration in vinasse that is recommended in biogas production is ±75,000 mg/L. Therefore, pre-treatment using electro-Fenton is expected to reduce the COD concentration until the suitable level which is 75,000 mg/L.

Variation of voltage (4, 6, 8 V) as a supply catalyst caused a change in solid concentration and COD content of substrates. The biogas substrate used in this study was sugarcane vinasse without pre-treatment and the results of pre-treatment for 1 hour of vinasse at various voltages. The biogas production from pretreated and raw sugarcane vinasse is shown in Figure 6. Unpretreated (raw) sugarcane vinasse had the lower biogas production rate than other variables. From Figure 6, it was resumed that the order of the biogas production rate is: Raw<8 V<4 V<6 V. Biogas began to form on the first day for all variables. In all pretreated variables, biogas was increased gradually and ran...
out on the 40th day. While, in variable unpretreated (raw) vinasse, biogas formation rate rose slowly until the 9th day, then biogas production was decreasing and was completely discharged at 11th day. The total biogas formed at 4 V, 6 V, 8 V, and raw was 6.014; 6.341; 4.942; 1.353 L respectively.

**Figure 6.** Effect of treated (at various voltages) and untreated vinasse on biogas production rate.

Biogas at 4 and 6 V is greater than 8 V and raw vinasse. This is because the COD values in the 4 and 6 V are lower than the 8 V and raw variables. The total biogas in the treated vinasse waste was 4 to 5 times greater than the unpertreated vinasse. This was due to the high concentration of COD in untreated vinasse. Additionally, this was brought about by movement of acidogenic and methanogenic bacteria. The more organic compounds entered into digesters caused the faster acidogenic bacteria growth rate. Organic compounds will be converted into fatty acid and it made pH decline. Whereas, methanogenic bacteria could not grow well at low pH. This condition caused biogas production low.

Figure 7 below shows that composition of biogas 8th day with the assumption only CH₄ and CO₂ are present in the biogas.

**Figure 7.** Gas and methane production on treated and untreated vinasse.
The chart depicts the methane composition of less than 30% in each variable. The methane test was only carried out on the 8th day, this was because the samples were not suitable for testing (stored more than 3 months or during a covid-19 pandemic). In essence, figure 7 is presented to prove methane in biogas even though the percentage is small.

4. Conclusion
The EF cycle was researched to treat sugarcane vinasse and it was uncovered that the EF response was effective to lessen COD. The outcome demonstrated that the best EF could decrease the COD as much as 81.14% at 4 V. The BMG kinetic model fitted well to test information for COD decrease and it was the best model to clarify the active response of the EF cycle as contrasted with first-order and second-order models. The outcome of this investigation demonstrates that the EF response can be utilized as a technique for preparing sugarcane vinasse to increase its biodegradability as confirmed by the production of biogas. Furthermore, the pretreatment of EF increased biogas volume successfully (6.02 L).

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References
[1] España-Gamboa E, Mijangos-Cortes J, Barahona-Perez L, Dominguez-Maldonado I, Hernández-Zarate G and Alvarez-Gaviria I 2011 Vinasses: Characterization and treatments Waste Manag. Res. 29 1235–50
[2] Bergmann J C and Sallet L P 2018 Technological Advancements in 1G Ethanol Production and Recovery of By-Products Based on the Biorefinery Concept 73–95
[3] Syaihurstrozi I and Sumardiono S 2014 International Journal of Engineering Effect of Total Solid Content to Biogas Production Rate from Vinasse 27 177–84
[4] Parsaei M, Kiani Deh Kiani M and Karimi K 2019 A review of biogas production from sugarcane vinasse Biomass and Bioenergy 122 117–25
[5] Oturan M A and Brillas E 2007 Electrochemical Advanced Oxidation Processes (EAOPs) for Environmental Applications 25 1–18
[6] Lin H and Lin H 2016 Removal of organic pollutants from water by electro-Fenton and electro-Fenton like processes To cite this version: HAL Id: tel-01336262
[7] Davamnejad R and Hosseinitabar P 2016 Application of Iron Electrode in Textile Industry Wastewater Treatment Using Electro-fenton Technique: Experimental and Statistical Study 29 887–97
[8] Rahmani A R, Nematollahi D, Azarian G, Godini K and Berizi Z 2015 Activated sludge treatment by electro- Fenton process: Parameter optimization and degradation mechanism Korean J. Chem. Eng. 32 1570–7
[9] Behnajady M A, Modirshahla N and Ghanbary F 2007 A kinetic model for the decolorization of C. I. Acid Yellow 23 by Fenton process 148 98–102
[10] Nazari P, Tootoonchian P and Setayesh S R 2019 Efficient degradation of AO7 by ceria-delafoisite nanocomposite with non-inert support as a synergistic catalyst in electro-fenton process Environ. Pollut. 252 749–57
[11] Hakika D C, Sarto S, Mindaryani A and Hidayat M 2019 Decreasing COD in sugarcane vinasse using the fenton reaction: The effect of processing parameters Catalysts 9
[12] Pushpalatha M and Krishna B M 2017 Electro-Fenton Process for Waste Water Treatment A Review Int. J. Adv. Res. Ideas Innov. Technol. 3 439–51
[13] Guerreiro L F, Rodrigues C S D, Duda R M, de Oliveira R A, Boaventura R A R and Madeira L M 2016 Treatment of sugarcane vinasse by combination of coagulation/flocculation and Fenton’s oxidation J. Environ. Manage. 181 237–48
[14] Yavuz Y 2007 EC and EF processes for the treatment of alcohol distillery wastewater 53 135–40
[15] Babuponnusami A and Mithukumar K 2012 Advanced oxidation of phenol: A comparison between Fenton, electro-Fenton, sono-electro-Fenton and photo-electro-Fenton processes Chem. Eng. J. 183 1–9
[16] Wardani N A 2020 Seleksi Inokulum untuk Peruraian Anaerob Termofilik Limbah Vinasse