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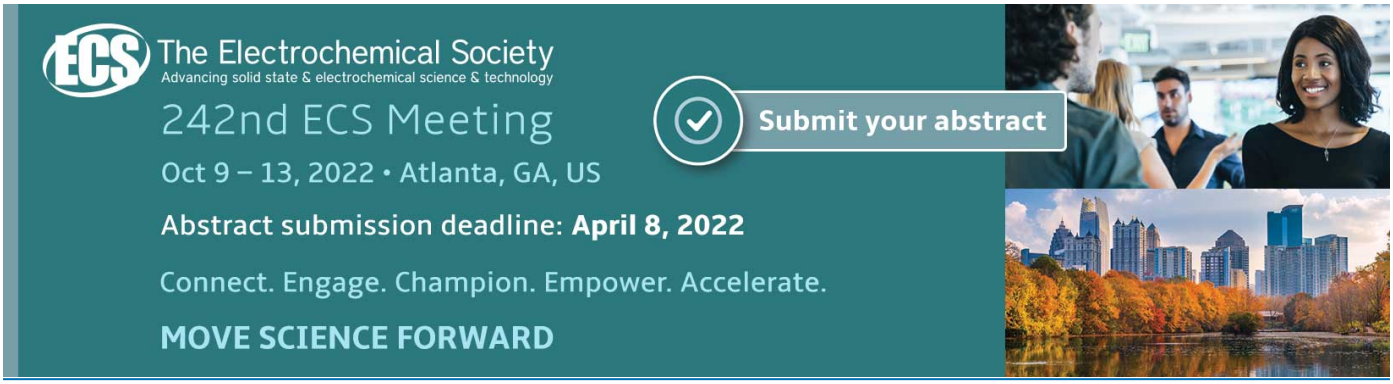

Influence of fenton pretreatment on anaerobic digestion of sugarcane vinasse: effect of H_2O_2 dosage

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Abstract. Sugarcane vinasse is one of the resources with a high potential for biogas production. However, its high value of COD (>100 g/L) and poor biodegradability could present substrate inhibition during anaerobic digestion. Thus, pretreatment techniques seem necessary for improving the process efficiency and enhancing biogas yield from sugarcane vinasse. In this study, the pretreatment process has been carried out using Fenton reagent, which utilizes the hydroxyl radical produced from the catalyzing reaction between hydrogen peroxide and Fe^{2+} or Fe^{3+}. Sugarcane vinasse as substrate was pretreated using Fenton reaction at different doses of 30% H_2O_2 within the range of 15 to 80 g/L. Through Fenton pretreatment, the biodegradability of sugarcane vinasse and biogas production was markedly increased. The optimum dose of H_2O_2 for Fenton pretreatment of biogas production from sugarcane vinasse was 60 g/L. At this pretreatment condition, the cumulative biogas yield was 124.39 mL/g sCOD, and the methane content was 52.6%. The methane content of biogas from Fenton-pretreated vinasse increased approximately four times higher (from 11.3% to 52.6%) compared to the untreated sugarcane vinasse as control. These results indicate that Fenton pretreatment can be applied to improve substrate biodegradability and enhance biogas production from sugarcane vinasse.

1. Introduction

Recently, the importance of ethanol biorefineries has arisen as some countries are starting to switch from fossil fuel to biofuel, particularly bioethanol. Ethanol has several advantages over fossil fuel, such as being a relatively low-cost alternative fuel, less harmful to the environment, and coming from a renewable resource. To gradually shift from fossil-based fuels to alternative fuels, bioethanol can be one of the best options [1]. However, during bioethanol production, each liter of ethanol generated about 15 liters of distillery wastewater, also known as vinasse. Vinasse produced by the ethanol industry contains high organic matter causing a large chemical oxygen demand (COD) and biological oxygen demand (BOD) value. It also has various chemical compositions, which mostly depend on the raw material used in bioethanol production, such as sugars (sugarcane, sugar beet, and molasses), starch (corn, wheat, grains), or cellulose (forest product). Its main characteristics are dark brown color, acidic pH (3.5–5.0), high organic matter concentration (COD > 100,000 mg/L) and salinity (K, Ca, Mg) [2]. These characteristics could direct to environmental problems, therefore adequate treatment is necessarily required.

Based on its characteristics, the organic matter in sugarcane vinasse could be used as raw material for biogas production through anaerobic digestion. Anaerobic digestion is considered a promising method for treating wastewater such as vinasse due to the energy recovery by biogas production [3].

Applying anaerobic digestion as a treatment for vinasse in ethanol plants could provide some advantages. For example, the digestate could still be used as a mixture for fertilizers on the sugarcane fields, and the produced biogas could be generated to electricity as one of the energy sources for the plant. However, the anaerobic digestion process of vinasse should be carefully assessed first, especially concerning the characteristics of vinasse. The ratio BOD_5/COD of vinasse is considerably low (BOD_5:COD=0.29), and this condition could affect the effectiveness of anaerobic digestion. The BOD_5/COD ratio term used to show biodegradability indicates the ability of organic substances and materials to be broken down into simpler substances through the action of microorganisms. Also, due to the complex nature of vinasse and the presence of recalcitrant compounds and inhibitors, the anaerobic digestion of vinasse could be hindered by substrate inhibition [4]. Therefore, pretreatment before anaerobic digestion is required to overcome this problem.

Investigation of many kinds of pretreatment methods for AD has been conducted by some researchers, for example, water dilution, physical and chemical pretreatments. Pretreatment using water dilution could increase biogas production [5]. However, dilution is not suggested to be applied because of the great amount of water needed for the process. It can also cause volume expansion resulting in larger reactor volume needed. In other previous studies, physical approaches such as comminution, steam-explosion, extrusion, and irradiation have been carried out and positively affected biogas yield [6–8]. Another pretreatment method using chemicals, e.g., alkaline treatment, acid treatment, wet oxidation, and ionic liquids, has also been reported to increase methane yield from biogas production [9–11]. Based on the results from those different studies, chemical methods are mostly selected because they have better efficiency and faster rates and are usually less expensive [12]. Fenton reaction has been widely applied for the treatment of various wastewaters. This method is reported as effective alternatives for converting wastewater contaminants into simpler compounds that can be treated biologically [13]. Under acidic conditions (pH 2–6), it produces the hydroxyl radical (•OH) from the catalyzing reaction between Fe2+ or Fe3+ and hydrogen peroxide. The mechanism of the Fenton reaction is shown in equation (1)-(2) below.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^+ \quad (2)$$

Besides its ability to effectively degrade organic compounds, the Fenton reaction also has some advantages, such as easy and simple operation and short reaction time. Meanwhile, some drawbacks from this method include the requirement of pH adjustment for specific wastewater in neutral or alkaline conditions and the formation of sludge at the end of the reaction due to the precipitation of iron ions [14]. Nevertheless, by applying the Fenton reaction as a pretreatment method to detoxify vinasse, these drawbacks can be considered as a benefit because vinasse is acidic (has a pH of 3-4), so pH adjustment is unnecessary. The iron sludge formed at the end of the Fenton reaction can be further utilized as additional trace elements during biogas production, which will be carried out through anaerobic digestion, so in this case, effluent separation after Fenton pretreatment is not required.

Treatment of sugarcane vinasse by applying Fenton reaction has been done by some researchers [15,16]. Overall, this method was proved to be effective in removing the COD and some organic pollutants. However, those studies were focused only on removing pollutants from vinasse. Study about the effect of Fenton as a pretreatment method for anaerobic digestion from vinasse is still limited. By applying this method for pretreatment, the organic compounds in sugarcane vinasse are objected to be further degraded by hydroxyl radical and make them more biodegradable. Thus, the Fenton reaction can be an interesting alternative as a chemical oxidation pretreatment method to convert biorecalcitrant organics to more readily biodegradable intermediates, followed by anaerobic digestion of these compounds generate more biogas [17,18]. The aim of this study is to investigate the effect of Fenton pretreatment on the anaerobic batch digestion of sugarcane vinasse by using different doses of H_2O_2 of Fenton reaction ranging from 15 to 80 g/L. The effect of Fenton treatment on biogas production was compared with the results obtained from untreated vinasse.

2. Materials and method

2.1. Materials

Raw sugarcane vinasse used in this study was collected from the bioethanol plant from molasses fermentation in Yogyakarta, Indonesia. It was collected insufficient amount for all tests performed and stored in the refrigerator. Its characteristics are reported in table 1.

Table 1. Characteristics of raw vinasse.

Parameters	Unit	Value
TCOD	mg/L	129,250
sCOD	mg/L	99,750
BOD_5	mg/L	31,250
pH	-	3.80 $\pm$ 0.1
Total Nitrogen	mg/L	420

Hydrogen peroxide solution (30% wt) was obtained from PT Peroksida Indonesia Pratama (PIP), and ferric nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$) as the source of ferric ion was obtained from Merck. The pH adjustment has been carried out by using NaOH (analytical grade). The digesters for anaerobic digestion were inoculated with anaerobic sludge from a biogas reactor in Boyong Village, Yogyakarta. The sludge used as inoculum was obtained from a mesophilic anaerobic reactor in operation in a cow dung digester and the samples collected had concentrations of volatile solids (VS) of 56,000 mg/L.

2.2. Fenton pretreatment

Fenton pretreatment was performed in a batch reactor containing 1 L of raw vinasse at ambient temperature and pressure. The pH of vinasse was 3.8, and there was no adjustment for pretreatment. Fe^{3+} catalyst under the form of ferric nitrate ($Fe(NO_3)_3.9H_2O$) was added using a ratio of 0.02 g Fe^{3+} per gram of H_2O_2 added and stirred until dissolved. Subsequently, H_2O_2 was added in vinasse solution at different doses (15 g/L; 40 g/L; 60 g/L; and 80 g/L). The reaction time started by adding hydrogen peroxide with constant stirring (200 rpm) until 60 minutes and then stopped. The pH of the vinasse solution was raised to 7$\pm$0.1 using NaOH 5M to quench the reaction.

2.3. Anaerobic digestion

After Fenton pretreatment, pretreated sugarcane vinasse from each different H_2O_2 dosage was used as a substrate for anaerobic digestion, while untreated vinasse was used as a control. To compare the effect of Fenton pretreatment with dilution (to decrease COD value) in anaerobic digestion from sugarcane vinasse, an additional digester containing diluted sugarcane vinasse was also included, following the lowest COD value after Fenton pretreatment. Anaerobic digestion was performed in batch-type laboratory-scale reactors. Digester conical flasks of volume 2000 mL with a provision to collect biogas at room temperature ($\pm$29°C) were used. The working volume of the substrate for each digester was 1000 mL. The sludge volume as inoculum added to each flask was calculated to maintain a ratio of $sCOD_{(pretreated\ vinasse)}$:$VS_{(sludge)}$=5:1. The initial pH of the pretreated vinasse was adjusted to 7$\pm$0.1 with NaOH solution (5M). To remove air from the headspace of the digester and maintain the anaerobic conditions, the digester was purged with Nitrogen. Flasks were sealed with rubber stoppers and aluminum seals and then incubated at room temperature ($\pm$29°C). The anaerobic digestion was carried out for 32 days or until there was no production of gas. The volume of biogas produced from the digester was measured using a water displacement unit connected directly to the biodigester. The biogas sampling was collected at the end of anaerobic digestion using a syringe and injected into a vacutainer tube to determine the content of methane (CH_4).

2.4. Analytical methods

Parameters such as concentration of chemical oxygen demand (TCOD), soluble chemical oxygen demand (sCOD), biological oxygen demand (BOD_5), volatile solids (VS), and total Nitrogen were quantified according to standard methods while pH was determined using a pH meter (Hanna HI-98107). Parameter sCOD was carried out after filtration using 0.45 µm filter paper. The content of methane (CH_4) in biogas was determined using Gas Chromatography (Shimadzu GC-8A).

3. Result and discussion

In the Fenton process, H_2O_2 plays an essential role as the dominant hydroxyl radical (•OH) source. However, H_2O_2 also has been known to be toxic to bacteria and living cells. Thus, it is important to select an optimum concentration of H_2O_2 due to the treatment efficiency and treatment cost of the Fenton process and the operation of anaerobic digestion.

3.1. Substrate pretreatment using Fenton reaction

Experiments with four different dosages of H_2O_2 (15 g/L; 40 g/L; 60 g/L; and 80 g/L) were conducted to study the effect of H_2O_2 dosage. Other reaction conditions such as pH; ($Fe(NO_3)_3.9H_2O$) dosage; temperature; stirring speed, and the reaction time was fixed at 3.8; 0.02 g Fe^{3+} per gram of H_2O_2 added; ±29°C; 200 rpm and 60 minutes, respectively. During the Fenton reaction, hydroxyl radical was produced by the catalytic reaction between hydrogen peroxide and Fe^{2+}/Fe^{3+}. It was used to oxidize organic matter in sugarcane vinasse. Organic matter in this study was represented in terms of TCOD, considering that this parameter reflects the overall concentration of organic matter. Thus, the effect of Fenton pretreatment was evaluated from the value of TCOD before and after Fenton reaction. Figure 1 shows the removals of the COD value of sugarcane vinasse during Fenton pretreatment.

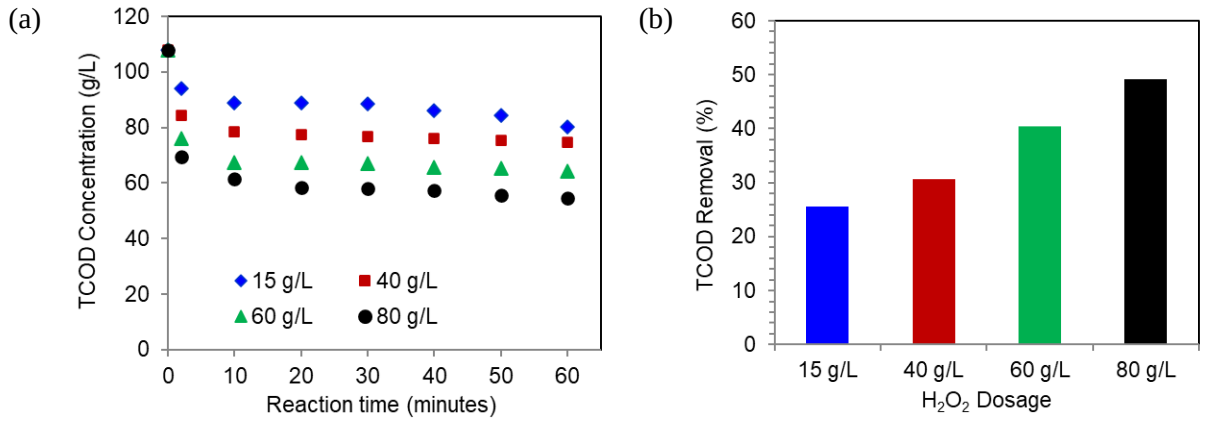

Figure 1. Effect of the dosage of H_2O_2 on the: (a) degradation of TCOD and (b) TCOD removal of sugarcane vinasse by Fenton process.

As presented in figure 1(a), it indicated that conducting Fenton pretreatment significantly decreased the TCOD value of sugarcane vinasse. All TCOD values of sugarcane vinasse pretreated by Fenton reaction at different dosages of H_2O_2 decreased from 129,25 g/L to some extent. The TCOD values after Fenton treatment at H_2O_2 dosage of 15 g/L; 40 g/L; 60 g/L; and 80 g/L were 80.25 g/L; 74.75 g/L; 64.25 g/L; and 54.75 g/L, respectively. For the Fenton process, a higher dosage of H_2O_2 increases the TCOD removal of sugarcane vinasse, as shown in figure 1(b). The addition of H_2O_2 concentration in the Fenton system increased the hydroxyl radical (•OH) production rate. This •OH reacts rapidly with organic matter in sugarcane vinasse and decomposes into more simple compounds [19]. As a result, the TCOD concentration was reduced. The highest percentage of TCOD removal occurred at H_2O_2 dosage of 80 g/L with 49.19% TCOD removed.

3.2. Effect of Fenton pretreatment on anaerobic digestion

This study compared the effectiveness of biogas and methane production from untreated and treated sugarcane vinasse. The efficiency of biogas production was evaluated using biogas yield (the calculated biogas production per gram of sCOD added, mL/g sCOD), methane content in the biogas (%), and methane yield (the calculated methane production per gram of sCOD added, mL/g sCOD). All variables and experiment data from the results are shown in table 2. The daily and cumulative biogas yields (mL/g sCOD) during anaerobic digestion from all variables are shown in figures 2(a) and 2(b), respectively.

Table 2. Effect of Fenton pretreatment on total biogas yield and methane composition.

Parameter	**Untreated Vinasse**	**Diluted Vinasse**	**H_2O_2 15 g/L**	**H_2O_2 40 g/L**	**H_2O_2 60 g/L**	**H_2O_2 80 g/L**
Initial sCOD (g/L)	97.95	53.62	76.92	73.24	64.07	53.62
sCOD/N ratio	233:1	128:1	183:1	174:1	153:1	128:1
Final pH	6.2	6.4	6.7	6.9	7.2	6.8
Total biogas yield (mL/g sCOD)	12.34	14.82	31.12	59.96	124.39	21.08
Methane composition (%)	11.32	1.64	7.37	37.57	43.18	-
Total methane yield (mL CH_4/g sCOD)	11.1	5.4	21.5	31.37	80.09	-
sCOD removal (%)	19.89	31.90	25.94	26.09	33.25	22.01

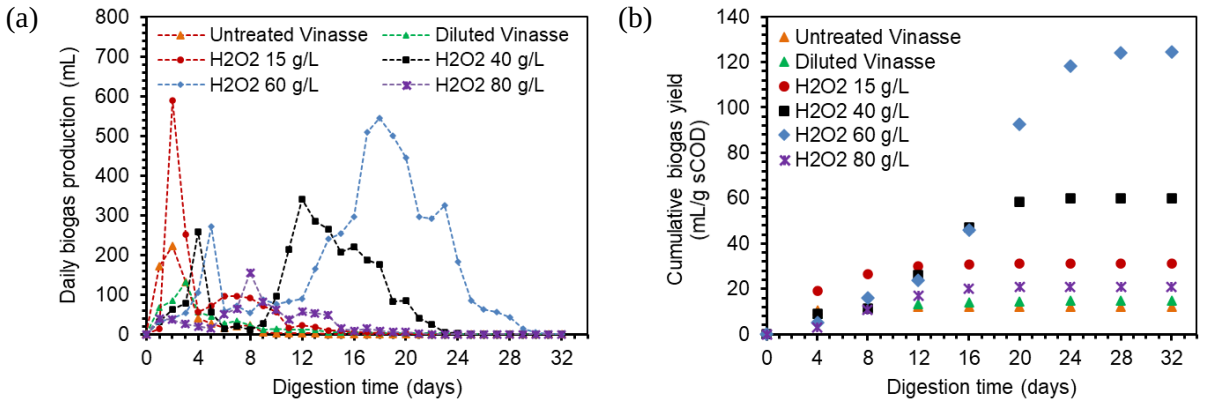

Figure 2. Effect of Fenton pretreatment with different dosages of H_2O_2 on: (a) daily biogas production and (b) cumulative biogas yield during anaerobic digestion of sugarcane vinasse.

Figure 2 presents daily and cumulative biogas yields of untreated and Fenton-pretreated substrate of sugarcane vinasse during 32 days of digestion time. All digesters produced biogas from the first day of anaerobic digestion operation. Biogas production of Fenton-treated sugarcane vinasse under H_2O_2 dosage of 15 g/L; 40 g/L; 60 g/L; and 80 g/L yielded 31.12 mL; 59.96 mL; 124.39 mL; and 21.08 mL biogas from 1 g sCOD, respectively. Meanwhile, biogas production from untreated sugarcane vinasse and diluted sugarcane vinasse gave only 12.34 mL and 14.82 mL biogas, respectively. From figure 2, it is clear that Fenton pretreatment positively affects anaerobic digestion as biogas production from vinasse with Fenton pretreatment for all H2O2 dosage conditions was higher than vinasse without pretreatment (untreated and diluted vinasse). The cumulative biogas yield during digestion also increased significantly with increasing H_2O_2 dosage.

During anaerobic digestion, substrate inhibition possibly happened in untreated vinasse digester because the COD value was too high (COD>100 g/L). This caused overloading of the substrate, where organics would be quickly hydrolyzed and acidified, leading to a high accumulation of volatile fatty acids (VFA). This might also affect the balance of hydrolysis, acidogenesis and methanogenesis process during anaerobic digestion, so biogas production was disrupted [20,21]. The digestion time of untreated sugarcane vinasse was also very short since it only produced biogas in 13 days, while other digesters

last longer. Anaerobic digestion of diluted vinasse digester occurred in 23 days, H_2O_2 15 g/L digester in 20 days, H_2O_2 40 g/L digester in 24 days, H_2O_2 60 g/L digester in 30 days, and H_2O_2 60 g/L digester in 21 days. Biogas production from Fenton-pretreated substrate overall was lower than untreated digester initially, but it gradually overtook the volume of the untreated digester after eight days. After Fenton pretreatment, organic compounds in sugarcane vinasse were broken down into more simple fractions and smaller molecules. These fractions were easier to degrade during digestion time than the original organic matter in untreated vinasse and tended to produce more biogas [22]. Methane percentages obtained from GC analysis for all digesters are shown in figure 3.

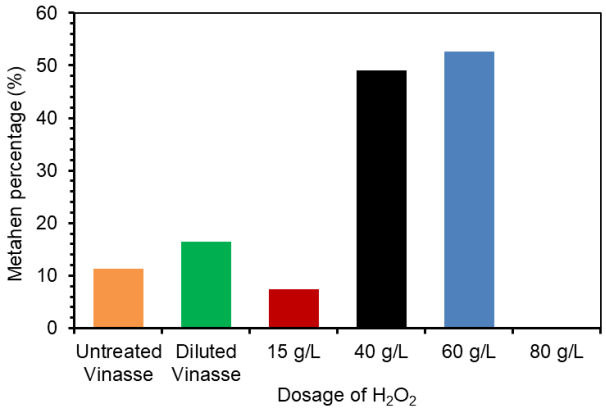

Figure 3. Percentage of methane content in biogas in different dosages of H_2O_2.

The highest methane content was achieved by digester with an H_2O_2 dosage of 60 g/L. It generated 52.6% of CH_4, while the methane content for other digesters were 11.3% (untreated vinasse); 16.4% (diluted vinasse); 7.35 (digester with H_2O_2 dosage of 15 g/L); 49.1% (digester with H_2O_2 dosage of 40 g/L); and 0% (digester with H_2O_2 dosage of 80 g/L). Although digester with an H2O2 dosage of 80 g/L yielded biogas, it didn't generate any methane. This possibly happened because the anaerobic digestion at that condition was inhibited by the excess of hydrogen peroxide in the Fenton-pretreated substrate. This reason was also supported by the works of other researchers, which observed inhibition of microbial metabolism during anaerobic digestion because of the great amounts of residual H_2O_2 in the system [23,24]. Even though Fenton pretreatment at condition H_2O_2 dosage of 80 g/L gave the highest TCOD removal, it does not positively affect anaerobic digestion. Therefore, conducting Fenton pretreatment at this condition was not beneficial for enhancing biogas production from sugarcane vinasse.

From the experiment, Fenton-treated vinasse with an H_2O_2 dosage of 60 g/L obtained the highest total biogas yield of 124.39 mL/g sCOD. Digester with this condition also generated the highest methane content in biogas (52.6%). Thus, Fenton pretreatment with an H_2O_2 dosage of 60 g/L was suggested to be an optimal condition for the generation of biogas and methane from sugarcane vinasse in this research. In this study, Fenton pretreatment exhibited high performance in reducing organic matters in sugarcane vinasse by oxidizing it and producing more simple and biodegradable compounds. In other words, Fenton pretreatment enhanced the biodegradability of sugarcane vinasse to be readily converted into biogas by anaerobic digestion. These results agree with other studies that observed that the Fenton process improved substrate biodegradability and enhanced anaerobic digestion efficiency [25,26].

4. Conclusion

This research studied the application of the Fenton reaction as substrate pretreatment of biogas production from sugarcane vinasse with investigating the effect of H2O2 dosage during Fenton pretreatment. The optimum H_2O_2 dosage of Fenton pretreatment for anaerobic digestion from sugarcane vinasse was at the addition of 60 g/L H_2O_2, which resulted in a total biogas yield of 124.39 mL/g sCOD. The methane content increased approximately four times higher (from 11.3% to 52.6%) than untreated sugarcane vinasse. It indicated that Fenton pretreatment improved the biodegradability of sugarcane vinasse enhanced biogas production. However, the initial dosage of H_2O_2 during Fenton pretreatment

for biogas production should be selected carefully because the residual H_2O_2 in the system could inhibit anaerobic digestion.

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