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Detoxification of Distillery Wastewater by AOP Fenton for the Enhancement of Biogas Production

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Abstract

Distillery wastewater from the bioethanol industry contains a high level of organic content which can be converted into biogas. However, the presence of toxic compounds in this wastewater could inhibit biogas production. Therefore, prior detoxification of distillery wastewater is required. Fenton, one of the Advanced Oxidation Process (AOP) methods, was selected due to its high performance to degrade organic pollutants, short reaction time, and the process is simple and easy. Additionally, this method can also be used as a pretreatment for biogas production. This paper aims to study the improvement of biogas production from distillery wastewater by applying AOP Fenton as a pretreatment method. The experiment consists of two stages, the first was application of AOP Fenton to the distillery wastewater in order to determine its effect on the concentration of COD and some toxic compounds such as phenol and sulfate. The second stage was biogas production through anaerobic digestion process, which was carried out under two conditions of raw materials: (i) distillery wastewater without pretreatment of AOP Fenton as a control and (ii) distillery wastewater that has been treated with AOP Fenton as pretreatment. Results show a remarkable decrease in COD concentration by 45%, phenol (63%), and sulfate (18,6%) from distillery wastewater after applying AOP Fenton. It implies that the application of AOP Fenton significantly detoxified distillery wastewater. As a biogas pretreatment, this method also increased biogas production by 33% higher, from 2.399 mL (without pretreatment) to 3.191 mL (with pretreatment). It indicates that AOP Fenton increased the biodegradability of distillery wastewater. Thus, it was easier to be converted into biogas.

INTRODUCTION

Along with the global outbreak of the coronavirus (Covid-19), there has been a significant surge in demand for alcohol in order to meet the needs of sterilization or sanitation. Alcohol or ethanol, as a raw material used in the manufacture of alcohol-based hand sanitizers, disinfectants, and antiseptics, is one of the essential compounds in handling the Covid-19 pandemic. This condition causes several ethanol industries to increase their production capacity, especially in Indonesia. Most of the bioethanol factories in Indonesia use molasses (sugarcane molasses) as raw material because the production costs are considerably low (Setyawati et al., 2015). On the other hand, the bioethanol industry from molasses produces liquid waste that can harm the environment if disposed directly into the water body. This liquid waste, also known as distillery wastewater or vinasse, has high organic matter content with the value of chemical oxygen demand (COD) concentration is more than 150,000 mg/L. It is also acidic (pH 3.5–5) with dark brown color and unpleasant odor. The volume of

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liquid waste generated from bioethanol industry is also one of the challenging factors in processing this wastewater because the production of 1 liter of bioethanol will produce 8–15 liters of wastewater (España-Gamboa et al., 2011; Janke et al., 2015; Rodrigues Reis and Hu, 2017).

Based on its characteristics, distillery wastewater is potential to be converted into biogas through the anaerobic digestion process as it is a biodegradable waste and contains high organic compounds. However, the biodegradability index (BOD_5/COD ratio) of this wastewater is considerably low (0.2–0.4) because the COD concentration is too high. In order to be easily broken down biologically, the recommended value of biodegradability index should be more than 0.4 (Rodriguez-Couto et al., 2021). The presence of toxic compounds in distillery wastewater such as phenol and sulfate can also inhibit the anaerobic digestion process. In addition, the value of the Carbon/Nitrogen (C/N) ratio of distillery wastewater is relatively low. The ratio of C/N of organic compounds is one of the crucial parameters during anaerobic digestion process in order to maintain nutrients balance and stability (Damayanti et al., 2019; Moset et al., 2012; Syaichurrozi and Rusdi, 2020). Therefore, it is necessary to detoxify the distillery wastewater prior to being used as biogas raw material so that biogas production can be successfully carried out.

Distillery wastewater can be detoxified using physical, biological, and chemical treatment. Several options of chemical methods have been implemented to treat this wastewater, including Fenton, which is one of the advanced oxidation processes (AOP) methods. AOP Fenton is a catalytic oxidation process using a mixture of hydrogen peroxide (H_2O_2) and ferrous (Fe^{2+}) or ferric ions (Fe^{3+}) to produce hydroxyl radicals (•OH) (Neyens and Baeyens, 2003). Hydroxyl radicals are free radicals that are highly reactive and have high oxidation-reduction potential (+2.33 V), higher than ozone (+2.07 V) and H_2O_2 itself (+1.36 V) (Bacardit et al., 2007; Pilli and Tyagi, 2015). These hydroxyl radicals would attack and destroy the organic pollutants and toxic compounds in wastewater.

In this study, AOP Fenton is selected to detoxify distillery wastewater because this method has been known as an effective technology and has been proven to degrade organic pollutants in various kinds of wastewater successfully. It has the main advantage of degenerating contaminants into simpler and safer compounds such as CO_2, H_2O, and inorganic salts. Other benefits of this method are that the reaction time is short, no additional external energy is needed, and the application is simple and convenient. Despite its advantages, Fenton has some shortcomings, including the potential for sludge generated after the reaction and the narrow working pH range. Several studies have reported that Fenton reaction is working optimally under acidic conditions, specifically in the pH range of 3–5 (Amelia et al., 2021; Rossi, 2014). However, the specific range is beneficial to this study because the pH of distillery wastewater is also acidic (3–4), so there is no need to do any pH adjustment during the application of AOP Fenton treatment to this wastewater. Therefore, this method is considered suitable to be implemented as a detoxification treatment for distillery wastewater (Hakika et al., 2019).

This research aims to study the effect of AOP Fenton to detoxify distillery wastewater and investigate its result during biogas production. The experiment consisted of two stages; the first stage was the application of AOP Fenton to the distillery wastewater in order to detoxify the toxic compounds, especially sulfate and phenol. The next stage is biogas production from distillery wastewater which was conducted by comparing two conditions of distillery wastewater: (i) without AOP Fenton pretreatment and (ii) with AOP Fenton pretreatment to examine the effect of AOP Fenton as a pretreatment method on the biogas production.

MATERIALS AND METHODS

Materials

Distillery wastewater as raw material was obtained from one of the bioethanol industries in Yogyakarta with characteristics as shown in Table 1.

Table 1. Characteristics of distillery wastewater.

No	Parameter	Value
1	COD (mg/L)	150,840
2	BOD_5 (mg/L)	31,250
3	pH	3.80
4	Sulfate (mg/L)	3.27
5	Phenol (mg/L)	4.65

The inoculum was taken directly from an active biogas reactor treating cow dung in Boyong Village, Pakem, Sleman Yogyakarta. The characteristics of the inoculum are shown in Table 2.

Table 2. Characteristics of inoculum.

No	Parameter	Value
1	Total solid (TS) (mg/L)	75,665
2	Volatile solid (VS) (mg/L)	56,000
3	pH	6.90

The chemicals used as reagents in this study were Hydrogen peroxide (H_2O_2) 30%wt (PT Peroksida Indonesia Pratama), $Fe(NO_3)_3.9H_2O$ 98% (Sigma Aldrich), Sodium hydroxide (NaOH) flake 97% (Sigma Aldrich), and aquadest.

Methods

AOP Fenton

The first stage of the experiment was run in batch operation. One liter of distillery wastewater was poured into the reactor followed by 3.62 grams of $Fe(NO_3)_3.9H_2O$. The solution was mixed until the iron salt dissolved. H_2O_2 with a ratio of $COD:H_2O_2=0.5$ (g/g) was added afterward. Fenton reaction was carried out for 60 minutes with constant stirring (200 rpm). After 60 minutes, the pH of the solution was increased to 7 using NaOH to stop the reaction.

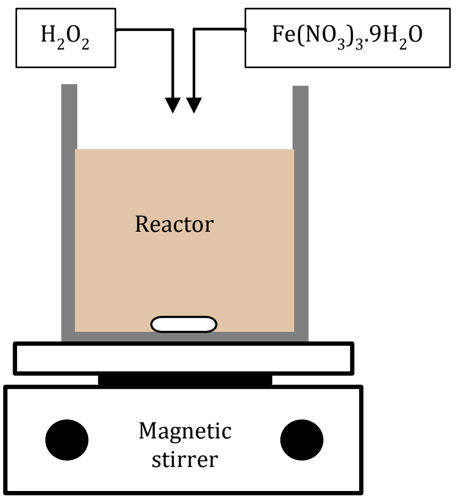


Figure 1. Experimental setup of detoxification of distillery wastewater by AOP Fenton.

Biogas Production

The experiment in the second stage was carried out using two (2) batch digesters. The first digester was filled with substrate from distillery wastewater without AOP Fenton as a control, and the second digester was filled with substrate from distillery wastewater with AOP Fenton. Distillery wastewater as a substrate was mixed with inoculum with a ratio of substrate:inoculum (RSI) 2:1. The pH of the mixture was then adjusted to neutral conditions (pH 7) using NaOH. Anaerobic digestion was carried out at room temperature for approximately 32 days (until biogas production stopped).

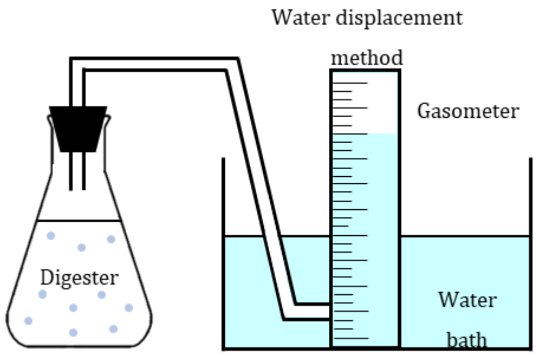


Figure 2. Experimental setup of biogas production from distillery wastewater.

Data Analysis

The sampling point of AOP Fenton (first stage) was taken at the beginning (t=0) and the end of the reaction (t=60 minutes). The samples were collected and several parameters were measured: pH, the concentration of COD, sulfate, phenol, Total Carbon, and Total Nitrogen. In the second stage, biogas volume was measured every two (2) days using water displacement method.

RESULTS AND DISCUSSION

Detoxification of Distillery Wastewater Using AOP Fenton Method

In this study, the COD parameter was chosen to represent the concentration of organic matter in distillery wastewater. The concentration of phenol and sulfate compounds in distillery wastewater before and after AOP Fenton treatment was also measured.

Figure 3 shows that AOP Fenton was able to detoxify distillery wastewater from bioethanol industry. This is indicated by the decrease in COD concentration by as much as 45% and the reduced concentration of toxic compounds, in this case are

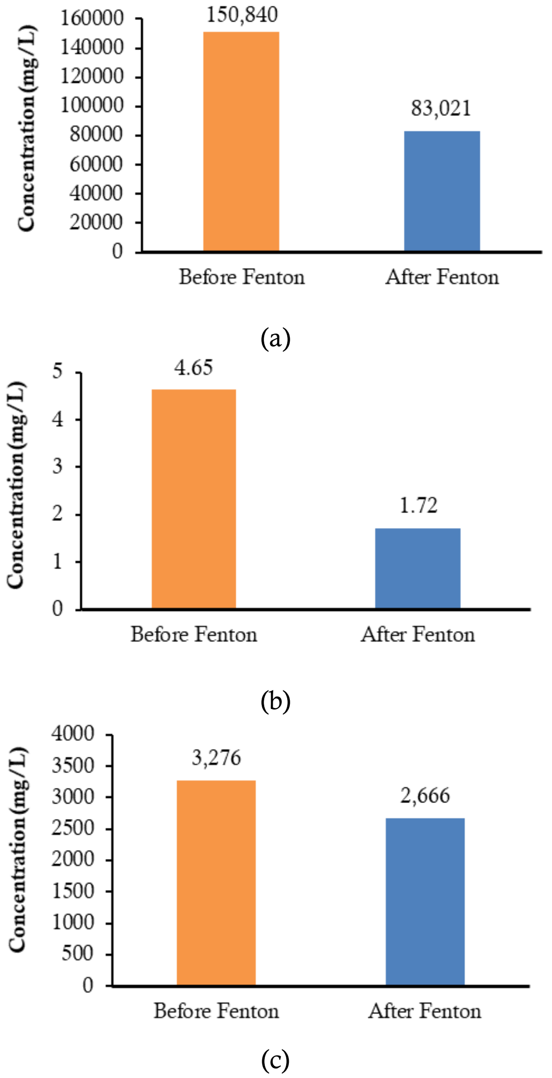


Figure 3. The concentration of: (a) COD, (b) phenol, and (c) sulfate in distillery wastewater before and after AOP Fenton.

phenol (63%) and sulfate (18.6%) in distillery wastewater after AOP Fenton was applied. During the Fenton reaction, equations (1) and (2) occur as follows:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^+ \quad (1)$$

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

Equation (1) occur first followed by Equation (2) to produce hydroxyl radical (•OH) quickly. At the beginning of the reaction, the presence of Fe^{3+} and Fe^{2+} ions in the solution will immediately decompose H_2O_2 into •OH. Subsequently, •OH reacts with organic compounds in solution and degrades these compounds. The decrease in COD, phenol, and sulfate concentration of distillery wastewater in this study occurred as a result of further oxidation process of hydroxyl radicals that attack these organic materials and toxic compounds, so that they are broken down into simpler compounds (Chen et al., 2020; Pérez et al., 2002).

In addition, the effect of AOP Fenton treatment on the value of C/N ratio of distillery wastewater was also observed. The C/N ratio of distillery wastewater before and after AOP Fenton treatment can be seen in Figure 4.

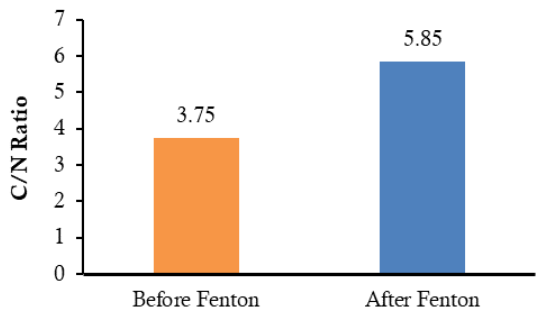
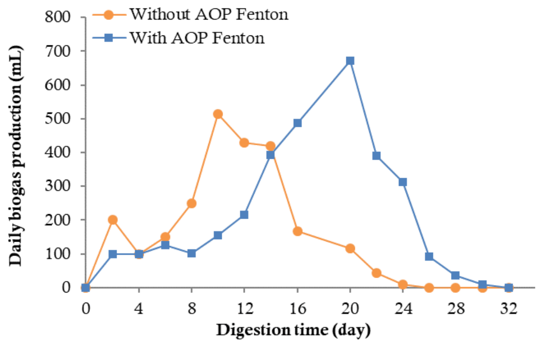


Figure 4. C/N ratio of distillery wastewater before and after AOP Fenton.

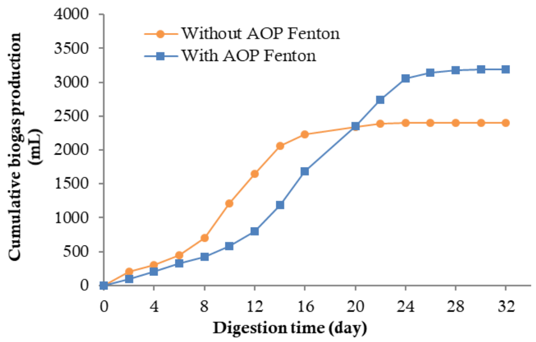
The ratio of C/N of distillery wastewater increased by 56% (from 3.75 to 5.85) after being treated by AOP. The C/N ratio indicates the ratio of carbon and nitrogen content in substrate as an important source of nutrients required by microorganisms during anaerobic digestion process. Carbon is the primary energy source for microbial activities, while nitrogen is needed by microbes for the growth and development of cell structures. If carbon and nitrogen content in the substrate is low, the process of anaerobic digestion will run slowly (Khanal et al., 2019). Therefore, the value of the C/N ratio in distillery wastewater is essential and has to be considered because the distillery wastewater will be used as a biogas substrate after being treated by AOP Fenton.

Biogas Production from Distillery Wastewater

After being treated by AOP Fenton, distillery wastewater proceeded to the next stage, which was biogas production through anaerobic digestion. To compare the effect of AOP Fenton treatment on biogas production, the anaerobic digestion process from distillery wastewater as a raw material was carried out under two conditions: (i) distillery wastewater without AOP Fenton (as a control), and (ii) distillery wastewater which has been pretreated using AOP Fenton. The volume of daily and cumulative biogas production from these two conditions were observed for 32 days (until there was no gas production) as shown in Figure 5.



(a)



(b)

Figure 5. Profile of: (a) daily volume and (b) cumulative volume biogas production from distillery wastewater.

Experiment results showed that digester with distillery wastewater which has been treated using AOP Fenton generated 3,191 mL of biogas. This result is 33% higher than biogas production from distillery wastewater without AOP Fenton treatment which only produced 2,399 mL of biogas. This low gas production was due to the concentration of organic matter (represented by COD) in distillery wastewater without AOP Fenton treatment was too high and causing the digester overload. Thus, the process of anaerobic digestion was hindered and could not occur in optimal conditions (Hallaji et al., 2018; Widyastuti et al., 2021). On the other hand, digester with substrate from distillery wastewater which has been pretreated using AOP Fenton yielded more biogas. Higher biogas production from this substrate indicated that detoxification method using AOP Fenton increased the biodegradability of distillery wastewater. As a result, the distillery wastewater became easier to be biologically degraded through anaerobic digestion process. This led to better conditions for anaerobic digestion so that more substrate could be converted into biogas than the one without AOP Fenton treatment.

Based on the value of the C/N ratio obtained from this study, distillery wastewater that has been pretreated with AOP Fenton has a higher C/N ratio than distillery wastewater without pretreatment. The C/N ratio is one of the critical parameters that can determine the amount of biogas produced. In general, increasing the C/N ratio until its optimum condition during anaerobic digestion positively affects the volume of biogas. According to Cerón (2019), a high C/N ratio can encourage an increase in microbial activity during the anaerobic digestion process, thereby the volume of biogas produced also increases.

Results achieved in this study are in agreement with previous findings from Nagarajan & Ranade (2020) which applied physical treatment by hydrodynamic cavitation to detoxify distillery wastewater before being utilized into biogas. Hydrodynamic cavitation pretreatment helped in breaking down the recalcitrant compounds from distillery wastewater such as phenol and melanoidins. This pretreatment led to more digestible COD and enhanced higher biomethane yield (10 – 22%) from the treated wastewater. Other than physical treatment, biological treatment also provided successful method to detoxify distillery wastewater by using white rot fungi (*Trametes versicolor*) to eliminate the phenolic compounds and melanoidins (España-Gamboa et al., 2017). It mentioned that the removal of phenols presents on distillery wastewater resulted higher biogas flow (from 1,102 mL to 2,370 mL) and methane content (from 65% to 74%) in the biogas.

CONCLUSION

AOP Fenton successfully detoxified distillery wastewater. The COD concentration of distillery wastewater after AOP Fenton treatment was reduced by 45%. The concentrations of other toxic compounds that can inhibit biogas production through anaerobic digestion, which are phenol and sulfate, were also reduced by 63% and 18.6%, respectively. The ratio of C/N in distillery wastewater also increased from 3.75 to 5.85. The application of AOP Fenton as a pretreatment method for biogas production from distillery wastewater enhanced biogas production by increasing 33% biogas produced from 2,399 mL (without AOP Fenton) to 3,191 mL (with AOP Fenton). It indicates that AOP Fenton degraded organic matter in distillery wastewater into more easily biodegradable compounds.

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