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Decreasing COD in Sugarcane Vinasse Using the Fenton Reaction: The Effect of Processing Parameters

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Received: 26 September 2019; Accepted: 21 October 2019; Published: 24 October 2019

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Abstract: An experiment on Fenton degradation of sugarcane vinasse was carried out to determine its effect on the wastewater characteristics. Vinasse, a by-product of distillation in the bioethanol industry, contains high organic matter, as the value of chemical oxygen demand (COD) is >100,000 mg/L and BOD_5 is 31,250 mg/L. The Fenton reaction is one of the advanced oxidation process (AOP) methods which has been widely applied for the treatment of wastewater containing organic pollutants and contaminants. This method utilizes hydroxyl radical ($^{\bullet}OH$) produced from the catalyzing reaction between Fe^{2+} or Fe^{3+} and hydrogen peroxide. The effect of pH, the ratio of [H_2O_2] and [COD], and the ratio of [H_2O_2] to [Fe^{3+}] were studied in this research to evaluate the Fenton reaction. Results from this experiment showed that treatment of vinasse using the Fenton reaction decreased the COD value to 48.10%, and its biodegradability enhanced almost two times at a pH value of 3.8, a ratio of [H_2O_2] to [COD] of 0.62, and a ratio of [H_2O_2] to [Fe^{3+}] of 50 (g/g), which demonstrated that the Fenton treatment was effective to reduce organic matter of sugarcane vinasse. Three kinetic models (first order, second order, and Behnajad–Modirshahla–Ghanbery (BMG) kinetic model) were used to evaluate the degradation of the COD value. On the basis of the value of R^2 (coefficient of determination), we suggested that BMG represented the best kinetic model. This study finds that the Fenton treatment is able to mitigate the environmental impacts of sugarcane vinasse.

Keywords: advanced oxidation process; Fenton reaction; sugarcane vinasse; chemical oxygen demand; BMG kinetic model

1. Introduction

Sugarcane vinasse, also known as distillery wastewater, slop or stillage, is a by-product from the distillation using by the bioethanol industry for the fermentation of molasses. This wastewater poses a serious environmental concern because vinasse is discharged from the industry in large quantities. From this industry, around 9 to 14 L of vinasse is generated for each liter of bioethanol produced [1]. The characteristics of sugarcane vinasse depend on its feedstock and many aspects of the bioethanol production process, but, generally, sugarcane vinasse is in an acidic condition (pH 3–5), dark brown in color, and contains high organic matter causing a large chemical oxygen demand (COD) ranging from 100,000 to 150,000 mg/L [1,2]. These characteristics cause sugarcane vinasse to have negative environmental impacts such as contaminating surface water and soil. This high COD value can result in depletion of dissolved oxygen in the river or water sources, which can harm the aquatic flora and fauna. Some recalcitrant compounds in vinasse, such as phenols, sulfate, and heavy metals, also have pollution potential in the soil. Thus, this wastewater should not be disposed directly into the environment [3–5].

Some treatment methods have been proposed in order to reduce the toxicity of sugarcane vinasse through the degradation of organic matter into more simple substances, for example, a biological treatment, which is commonly used to treat organic wastewaters. Nevertheless, some persistent and toxic compounds are not removed using a biological treatment, and it also inhibits the biodegradation process as some microorganisms are sensitive to the toxic compounds [6]. A biological treatment is also not effective for sugarcane vinasse treatment due to its low biodegradability. Therefore, a further treatment method is necessary to treat this wastewater.

Advanced oxidation processes are treatment methods which have the potential to oxidize various kinds of organic compounds based on the generation of hydroxyl radicals ($^{\bullet}OH$). Hydroxyl radical is a very strong and nonselective oxidant (±2.8 V) which is capable of degrading a wide range of contaminants and pollutants, especially organic pollutants [7]. The Fenton reaction, one of the advanced oxidation processes (AOPs) could be used as an alternative, as this method is very popular for its efficiency to treat wastewater with recalcitrant pollutants. The Fenton process is also easy to run, has a short reaction time, and is less expensive as compared with other AOP methods, such as ozone or ultrasound radiation [8,9].

The Fenton reaction has been widely applied for the treatment of various wastewaters because of its eco-friendly characteristics [10]. Another benefit of this method is its ability to degrade organic compounds to carbon dioxide (CO_2), water (H_2O), and inorganic ions. The Fenton oxidation mechanism generates hydroxyl radicals ($^{\bullet}OH$) from the catalyzing reaction between ferrous or ferric ion (Fe^{2+}/Fe^{3+}) and hydrogen peroxide (H_2O_2) under acidic conditions (pH 2–6). The overall reactions of the Fenton process are as presented in the following equations [11,12]:

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

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

$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + H^+ + O_2 \quad (3)$$

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^- \quad (4)$$

$$H_2O_2 + \bullet OH \rightarrow HO_2\bullet + H_2O \quad (5)$$

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \quad (6)$$

$$\bullet OH + HO_2\bullet \rightarrow O_2 + H_2O \quad (7)$$

$$\bullet OH + \text{organics} \rightarrow \text{products} \quad (8)$$

The Fenton reaction has been used to reduce the organic load or toxicity of different wastewaters, for example, from the chemical industry, textile, pharmaceutical, paper pulp, and olive mills [13–16]. Some researchers also have applied the Fenton reaction for vinasse treatment in their experiments, such as de Heredia [2] and Guerreiro [17]. Their experiments obtained COD removal up to 80% and 63%, respectively, which demonstrates that the Fenton reaction is capable of reducing organic matter in vinasse, however, the values of COD in these experiments were quite low, ranging only from 5000 to 20,000 mg/L. In this experiment, the COD value of sugarcane vinasse is extremely high (more than 100,000 mg/L), and this value could be challenging to carry out the Fenton process. Furthermore, in this experiment, the Fenton reaction is expected to increase the biodegradability of sugarcane vinasse, so that, in the future, it can be applied as a pretreatment method before biological process. Organic compounds of sugarcane vinasse can be degraded to simpler and biodegradable forms after the Fenton reaction. In these way, a biological process such as anaerobic digestion can convert the biodegradable compounds into a more valuable product, for example, biogas. Therefore, it is important to verify the effectiveness of the Fenton treatment on sugarcane vinasse. The effectiveness of the process depends on the initial pH, the ratio of $[H_2O_2]$ to [COD], and the ratio of $[H_2O_2]$ to $[Fe^{3+}]$.

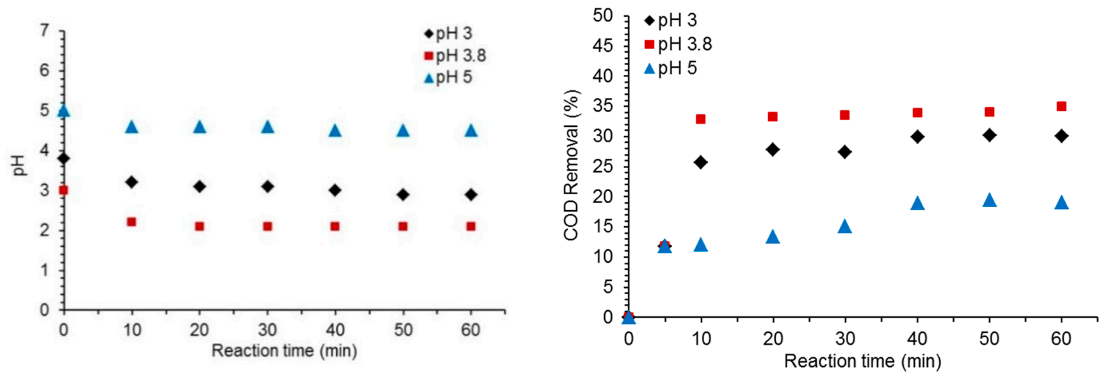
The aim of this work is to evaluate the Fenton reaction for treatment of sugarcane vinasse as an alternative in order to find an efficient and economically viable method for sugarcane vinasse treatment. The performance of the treatments was assessed and evaluated in terms of the COD removal value. The target of this study is to reduce the COD of sugarcane vinasse and improve its biodegradability. In order to evaluate the reaction kinetic of the COD degradation process, the experimental data were also subjected to the first order, second order, and Behnajady–Modirshahla–Ghanbery (BMG) kinetic models.

2. Results and Discussion

The results showed that during the Fenton process $^{\bullet}OH$ was produced and the COD value of sugarcane vinasse was reduced. The formation of $^{\bullet}OH$ depends on several factors such as initial pH, the ratio of [H_2O_2] to [COD], and the ratio of [H_2O_2] to [Fe^{3+}]. It was also demonstrated that the Fenton reaction increased the biodegradability of sugarcane vinasse so that it can be further degraded by biological treatment. Therefore, the effects of those three parameters were investigated.

2.1. Effect of Initial pH

The Fenton reaction is a pH dependent process because pH plays an important role in the mechanism of $^{\bullet}OH$ generation in the Fenton reaction [18]. The effect of the initial pH value of vinasse on the COD removal by the Fenton reaction was studied in the pH range of 3 to 5 by adding HNO_3 or NaOH to adjust the pH value. The experiment was conducted to investigate the influence of pH on the degradation process efficiency and find the optimum pH. The results obtained are presented in Figure 1A showing the profile of pH during the Fenton reaction, and Figure 1B showing that residual COD removal varies with the pH value of the solution. As shown in Figure 1B, the experiment at pH 3.8 has the best COD removal value (34.9%) as compared with the experiments at pH 3 and 5, which reached 30.1% and 19.1%, respectively. Theoretically, the optimum pH for the Fenton reaction would be 3 to 4 because, in this pH range, hydrogen peroxide was in the most stable condition [19]. At a pH > 4, generation of hydroxyl radical in solution is inhibited due to precipitation of $Fe(OH)_3$, and thus the concentration of dissolved Fe^{3+} decreased. As the amount of catalysts in the Fenton reaction decreased, the oxidation efficiency of the Fenton process was also reduced [20,21].



(A) (B)

Figure 1. The pH profile (**A**) and removal of chemical oxygen demand (COD) (**B**) by the Fenton reaction at different pH for the ratio of [H_2O_2] to [COD] = 0.12 (g/g) and the ratio of [H_2O_2] to [Fe^{3+}] = 50 (g/g).

An acidic condition is needed for the Fenton reaction to produce the hydroxyl radicals. Figure 1B shows that a rapid degradation rate of COD was observed at a pH of 3.8 and three experiments, during 1 h reaction time, indicating production of hydroxyl radicals ($^{\bullet}OH$) within a short time. However, when the pH is too low than its optimum value, Fe^{3+}, is difficult to be reduced to Fe^{2+}. As stated by Duesterberg, the redox cycling of iron species between Fe(III) to Fe(II) is enhanced at a pH around 4.0 [22]. This condition caused the degradation rate of COD to decrease since the production of $^{\bullet}OH$

was reduced. In addition, a low pH solution has a high concentration of H^+ which tends to consume $^{\bullet}OH$ and form water according to the following reaction [13,23,24]:

$$\bullet OH + H^+ + e^- \rightarrow H_2O \quad (9)$$

As a consequence, the oxidation rate decreased and the degradation rate of organic matter for a pH of 3 was slower than a pH of 3.8. This result is in agreement with the findings from a previous report by Varma [18]. Varma conducted research on using Fenton oxidation to treat distillery wastewater (COD = 160 g/L diluted 100 times into 1.6 g/L) in the pH range of 2 to 7. This study determined that an optimum pH for the Fenton reaction is 4 with COD removal efficiency reaching 92%. Hence, a pH of 3.8, which was the uncontrolled pH of raw sugarcane vinasse, was recommended as the optimum operating pH in this work.

2.2. *Effect of the [H_2O_2] to [COD] Ratio*

Determination of the favorable amount of the Fenton reagent is highly important because excess H_2O_2 could scavenge hydroxyl radical and would increase the cost of wastewater treatment. Meanwhile, an inadequate amount of H_2O_2 could not provide enough hydroxyl radical needed for the Fenton process [25]. The H_2O_2 dosage depends heavily on the initial COD value. Generally, a higher initial COD requires more H_2O_2 and, due to the cost of H_2O_2, the optimum concentration of H_2O_2 should be determined. The effect of the [H_2O_2] to [COD] ratio on COD removal, ranged from 0.12 to 0.62 at a pH of 3.8 and the ratio of [H_2O_2] to [Fe^{3+}] = 50, was investigated. The results are presented in Figure 2A,B.

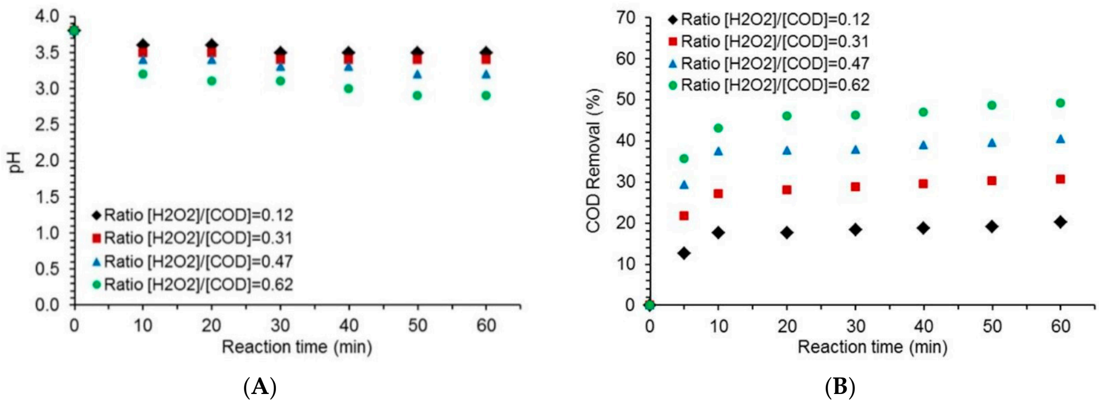


Figure 2. The pH profile (**A**) and removal of COD (**B**) by the Fenton reaction at different [H_2O_2] to [COD] ratios for pH = 3.8 (without adjustment) and the ratio of [H_2O_2] to [Fe^{3+}] = 50 (g/g).

As shown in Figure 2B, the removal efficiency of the COD value increased as a consequence of increasing the [H_2O_2] to [COD] ratio. The highest removal efficiency occurred at the highest ratio (0.62) with a removal percentage of 49.2%. At ratios of 0.12, 0.31, and 0.47 the removal efficiencies were lower as they obtained 20.2%, 30.6%, and 40.4%, respectively. This resulted because the higher the concentration of hydrogen peroxide, the faster the formation of hydroxyl radical ($^{\bullet}OH$) would be produced. At a higher ratio, an abundant amount of $^{\bullet}OH$ would react with more organic substances and increase degradation rate. This statement is consistent with an earlier study conducted by de Heredia [26] which observed the effect of the Fenton reaction as a treatment in the wine distillery industry with less organic matter (COD = 15–16.5 g/L, pH = 3.76). Various ratios of [H_2O_2] to [COD], ranging from 0.05 to 4.5 (g/g) have been studied. A similar trend of results was obtained, and it was stated that greater doses of hydrogen peroxide led to higher removals of COD. From de Heredia's study, the Fenton reaction with the highest ratio of [H_2O_2] to [COD] demonstrated a COD removal of 77%.

The COD degradation during the Fenton process indicated rapid removal during the first 15 min, followed by slower degradation until 60 min. In this experiment, first, Equation (2) would happen, followed by Equation (1) to produce $^{\bullet}OH$ in fast reaction and reduce the concentration of H_2O_2 in the solution. After being generated, almost all $^{\bullet}OH$ would react with organic substances and degrade them, however, the excessive amount of $^{\bullet}OH$ could react with H_2O_2 in solution, as stated in Equation (5), to produce $HO_2^{\bullet}$ which had a weaker ability than hydroxyl radical. It also caused H_2O_2, as the provider of $^{\bullet}OH$, to be depleted [16,20]. Therefore, the production of $^{\bullet}OH$ was ceased and the degradation rate of organics gradually decreased.

For the range of $[H_2O_2]$ to [COD] ratio values used in this experiment, which were 0.12 to 0.62, it is found that the optimal H_2O_2 concentration is 0.62, which was the highest $[H_2O_2]$ to [COD] ratio, however, since this ratio reached only 49.2% of COD removal efficiency, it is suggested that the ratio can still be increased to obtain higher removal efficiency.

2.3. Effect of the $[H_2O_2$ to $[Fe^{3+}]$ Ratio

The concentration of ferric ion (Fe^{3+}) dosage is also important because of its role as a catalyst during the Fenton reaction. In this study, iron dosage is presented as the ratio of $[H_2O_2]$ to $[Fe^{3+}]$. To study the effect of this parameter, the investigation was carried out in the range of $[H_2O_2]$ to $[Fe^{3+}]$ ratio = 50, 37.5, and 25 at a pH condition of 3.8 and the ratio of $[H_2O_2]$ to [COD] was kept constant at 0.62. A lower value of the $[H_2O_2]$ to $[Fe^{3+}]$ ratio means a higher concentration of iron was added in solution. Results from this investigation are shown in Figure 3A for the pH profile and Figure 3B for the COD removal. From Figure 3B, the obtained results show that, after 60 min of Fenton reaction, the value of the COD removal increased only slightly, as higher amounts of ferric ion were added into the solution. The COD removal for the $[H_2O_2]$ to $[Fe^{3+}]$ ratio = 25, which is the lowest ratio, is 51.66%. This value is only slightly above the ratio of 37.5 (48.33%) and the ratio of 50 (48.10%). Thus, the use of extra ferric ion, in this study, had a negligible effect on the COD removal of sugarcane vinasse.

Despite the insignificant effect, a higher iron salt concentration in the system increased the degradation rate of sugarcane vinasse, because ferric ion plays a role as catalysts during the Fenton reaction. According to Equation (2), during the Fenton reaction, first, Fe^{3+} is converted to Fe^{2+}, and, then, Fe^{2+} reacts with hydrogen peroxide to generate $^{\bullet}OH$, as shown by Equation (1). Therefore, a high amount of ferric ion (Fe^{3+}) would also increase the amount of ferrous ion (Fe^{2+}) converted and eventually enhanced the production of $^{\bullet}OH$. Similar results have also been obtained by Hadavifar [27] and Rodrigues [28] who studied the effect of iron dosage in the degradation of distillery effluent (COD = 12–39 g/L) using Fenton oxidation and stated that the removal efficiency is higher with increasing iron dosage, which is attributed to the availability of more oxidants. However, an excessive amount of Fe^{2+} could bring a negative impact because this ion also reacts with hydroxyl radical based on Equation (4), causing hydroxyl radicals to be scavenged and reducing the degradation rate of the COD [29].

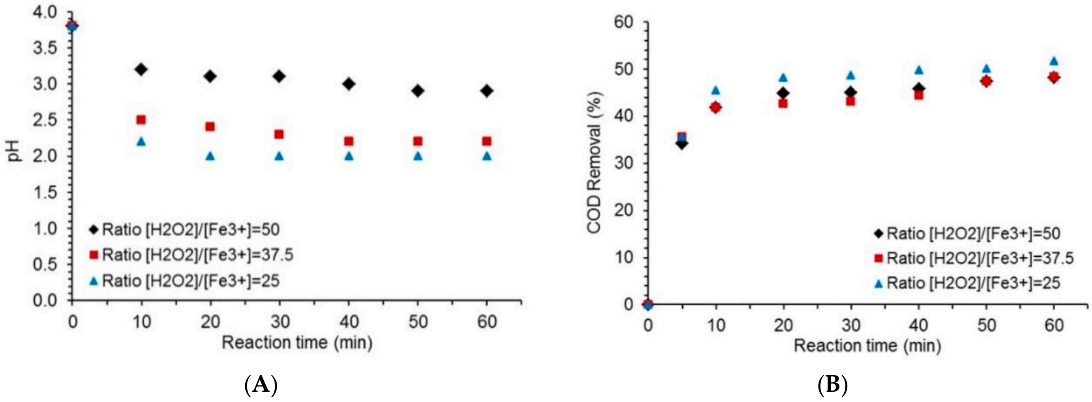


Figure 3. The pH profile (**A**) and removal of COD (**B**) by the Fenton reaction at different $[H_2O_2]$ to $[Fe^{3+}]$ ratios for pH = 3.8 (without adjustment) and the ratio of $[H_2O_2]$ to [COD] = 0.62 (g/g).

The dosage of iron salt concentration is also an important parameter for a large-scale Fenton treatment due to the application costs of iron salt. In addition, if the iron concentration is high, there is production of sludge from iron complex which increases the total dissolved solid (TDS) value of the wastewater, and therefore further treatment is required for iron removal at the end of the process. Consequently, the optimum ratio of [H_2O_2] to [Fe^{3+}] should be selected carefully. It is preferable to choose a smaller but sufficient concentration of iron which can achieve high COD removal. In this study, the ratio of [H_2O_2] to [Fe^{3+}] = 50 is considered as the optimum value for iron concentration as it successfully reduced 48.10% of the COD of sugarcane vinasse.

2.4. Biodegradability Enhancement

The ratio of BOD_5 to COD is commonly used to show the biodegradability index of wastewater. The biodegradability index can help to indicate the ability of wastewater to go through biodegradation. If the value of the BOD_5 to COD ratio is in the range between 0.4 and 0.8, wastewater can be taken into consideration as readily biodegradable [30,31]. In this study, the initial value of the measured BOD_5 to COD ratio of raw sugarcane vinasse was equal to 0.29, indicating that raw sugarcane vinasse is non-biodegradable since the value is lower than 0.4. This could be caused by the complex composition of sugarcane vinasse, which is composed of biorecalcitrant organic components [32].

After the Fenton process, the biodegradability index of sugarcane vinasse increased, as presented in Figure 4. The values of the BOD to COD ratio of treated vinasse after the Fenton process for ratios of 0.31, 0.47, and 0.62 were higher than 0.4, except for the ratio 0.12 where the BOD_5 to COD ratio was still below 0.4. The obtained value of the BOD_5 to COD ratios 0.12, 0.31, 0.47, and 0.62 were 0.344, 0.401, 0.422, and 0.477, respectively. Thus, based on the ability of the Fenton reaction to enhance vinasse's biodegradability, we suggest that the Fenton process could be used to treat sugarcane vinasse. This result is in accordance with findings reported by Guerreiro [17], Rodrigues [28], and Pouran [33]. Their studies demonstrated that the Fenton treatment successfully and significantly improved the biodegradability of vinasse and recalcitrant wastewaters, by about 60% to 70%. From these results, it is also proposed that treated sugarcane vinasse can be further degraded by a biological treatment, such as anaerobic digestion, to be converted into biogas. By increasing the biodegradability, production of biogas could also be enhanced.

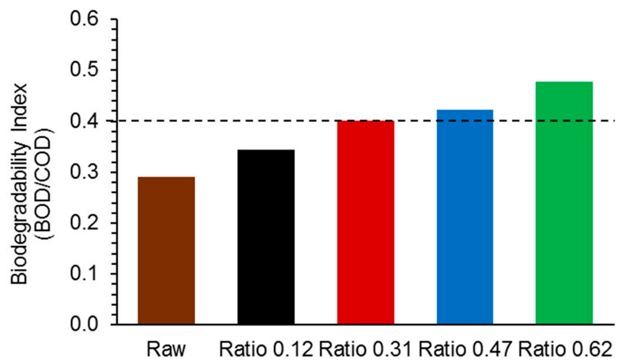


Figure 4. BOD5 to COD ratio of initial and treated sugarcane vinasse at different [H_2O_2] to [COD] ratios.

2.5. Kinetic of COD Degradation

During the Fenton reaction, the degradation of organic matter in sugarcane vinasse could be described quantitatively by reaction kinetics. In this study, the calculation of reaction kinetics used various [H_2O_2] to [COD] ratios to explain the effect of H_2O_2 dosage as the $^{\bullet}OH$ provider on degradation kinetics of organic matter in sugarcane vinasse. The degradation of the organic matter was represented in terms of the COD considering that this parameter reflects the overall concentration of organic matter [29,32]. From the results, as presented in Figure 2B, it is shown that the degradation rates were dependent on the dosage of H_2O_2 because higher COD removal was achieved with increasing [H_2O_2] to [COD] ratios due to increased generation of hydroxyl radical.

Data obtained from the experiment were tested using three kinetic models, first order, second order, and BMG kinetic model. Some researchers have reported that the BMG model has effectively predicted degradation of the Fenton process [20,24,34]. By applying the equations in Table 1 below, the three kinetic models at different [H_2O_2] to [COD] ratios during the 15 min Fenton reaction were calculated. The kinetics were calculated only based on the 15 min reaction because fast oxidation occurred in that range of time followed by slower oxidation in the last 45 min. The results are represented in Table 2 and Figure 5.

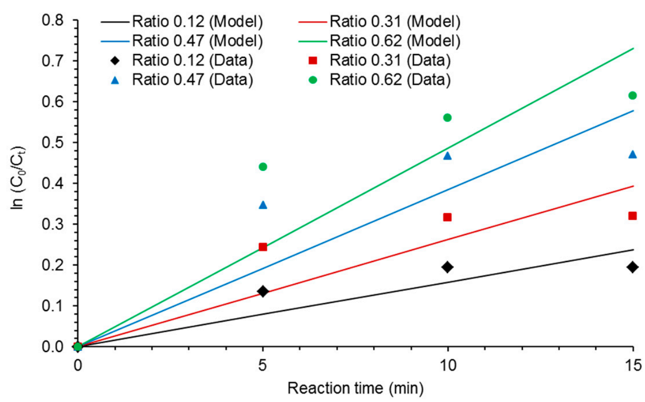
Table 1. Linear form of the kinetic models.

Kinetic Model	Equation	
First order	$ln\frac{C_0}{C_t} = k_1 \cdot t$	(10)
Second order	$\frac{1}{C_t} - \frac{1}{C_0} = k_2 \cdot t$	(11)
BMG model	$\frac{t}{1-(C_t/C_0)} = m + b \cdot t$	(12)

For Equations (10)–(12), C_0 and Ct are showing COD concentration (mg/L) of sugarcane vinasse at initial (t = 0) and time t (min), respectively; k_1 is first order kinetic parameter (min^{-1}); k_2 is second order kinetic parameter ($L \cdot mg^{-1} \cdot min^{-1}$); m (min) and b are two characteristic constants of BMG kinetic model which represent the relation between oxidation capacity and reaction kinetics.

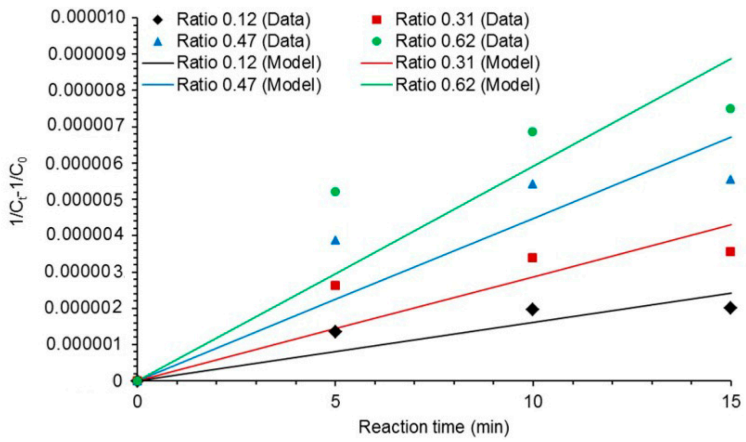
Table 2. Comparison of first order, second order, and BMG kinetic models for COD degradation at different [H_2O_2] to [COD] ratios.

Kinetic Model	Ratio of [H_2O_2] to [COD]			
	0.12	**0.31**	**0.47**	**0.62**
First order kinetic				
k_1 (min^{-1})	0.0158	0.0262	0.0385	0.0487
R^2	0.8221	0.7804	0.7964	0.8272
Second order kinetic				
k_2 ($L \cdot mg^{-1} \cdot min^{-1}$) × 10^{-6}	0.160	0.286	0.448	0.591
R^2	0.8390	0.8058	0.8230	0.8403
BMG kinetic model				
1/m (min^{-1})	0.0650	0.1428	0.2015	0.3511
1/b	0.2225	0.3224	0.4345	0.5129
R^2	0.9809	0.9957	0.9919	0.9912

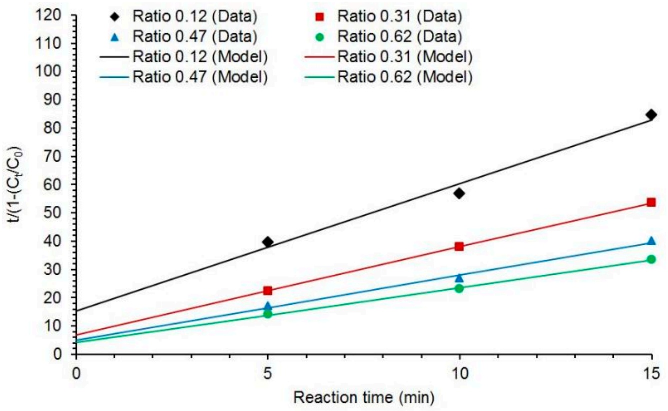


(A)

Figure 5. *Cont.*



(**B**)



(**C**)

Figure 5. Kinetic models for COD degradation at different [H_2O_2] to [COD] ratios: (**A**) first order, (**B**) second order, and (**C**) BMG.

The results show that as the ratio of [H_2O_2] to [COD] increased, most of the kinetic values for every kinetic model also increased linearly with the [H_2O_2] to [COD] ratio. For instance, the value of k_1 for the first order kinetic increased from 0. 0158 to 0.0487 (Figure 5A), while the value of k_2 for the second order reaction kinetic increased from 0.160×10^{-6} to 0.591×10^{-6} (Figure 5B) as the ratio went up from 0.12 to 0.62. For the BMG model, the same case also happened, i.e., by increasing the ratio of [H_2O_2] to [COD], the value of two constants (1/m and 1/b) also increased from 0.1695 to 0.3511 and 0.1481 to 0.4496, respectively. The meaning of 1/m in this model is related to initial reaction rate, while the value of 1/b represents the maximum theoretical conversion that could have been achieved after infinite reaction time, namely, the maximum oxidation capacity. Hence, the higher value of 1/m means the initial degradation rate is faster. If the value of 1/b is high, it means that higher removal is achieved. These results indicated that the degradation rate during the the Fenton reaction was faster at higher [H_2O_2] to [COD] ratios because of more generation of $^{\bullet}$OH.

The oxidation of organic compounds in sugarcane vinasse by the Fenton reaction, in this study, can be divided into two phases. The first phase is attributed to the rapid reaction that occurs for the first 15 min and represents fast generation of $^{\bullet}$OH from the catalytic reaction of H_2O_2 and Fe^{2+} which is more available during the initial stages of the reaction, and, afterwards, it directly degrades organic substances. The second phase is the slower reaction when t = 15 to 60 min and indicates a lower rate of generation of $^{\bullet}$OH. In previous studies related to the degradation of wastewater by the Fenton reaction, similar behavior was also observed, such as works by Zhang [20] and Santana [35]. The reaction profile of their experimental data showed a very fast reaction followed by a slower one and they suggested, based on this behavior, that degradation of organics by Fenton oxidation is not suitable to be modeled by first order or second order kinetics because the fitting of experimental data with those models would not be good. Thus, the BMG model was proposed by some authors because it was the best model to describe the Fenton oxidation process at different reaction conditions [24,36,37].

In this study, the kinetics calculation was done for the first 15 min reaction which represents the fast phase. From Table 2, it is shown that the values of 1/m as constants that indicate the reaction rate from the BMG model are higher than the rate constants for both first order (k_1) and second order (k_2) kinetics. For this reason, the BMG model gives a better correlation related to faster reaction rate as compared with first and second order kinetics. This may explain the behavior of the Fenton reaction in which an abundant amount of $^{\bullet}OH$ oxidized organic matters. As a result, the COD significantly decreased in a short time. Furthermore, the fitting of experimental data to the first order and second order kinetic models was not good enough since the values of R^2, which show correlation coefficient for both models, were slightly low. Meanwhile, the experimental data of COD degradation fitted well to the BMG kinetic model, as the value of R^2 was very high and close to 1, ranging from 0.9809 to 0.9957. Accordingly, we concluded that the COD degradation of sugarcane vinasse by the Fenton process, in this study, was best explained by the BMG kinetic model.

3. Materials and Methods

3.1. Materials and Reagents

The raw sugarcane vinasse used in this study was collected from PS Madukismo, a bioethanol industry of molasses located in Yogyakarta, Indonesia. The characteristics of this wastewater are presented in Table 3.

Table 3. Chemical properties of raw vinasse.

Parameters	Unit	Value
COD	mg/L	132,250
BOD_5	mg/L	31,250
pH	-	3.80
Iron	mg/L	128.10
Sulfate	mg/L	3275.53
Phenol	mg/L	4.64
Appearance	-	Dark brown

Hydrogen peroxide (H_2O_2) with a concentration of 30% wt was obtained from PT Peroksida Indonesia Pratama (PIP), and ferric nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$), as the source of ferric ion, was provided by Merck. Nitric acid (HNO_3) and sodium hydroxide (NaOH) used for pH adjustment were at analytical grade.

3.2. Experimental Setup

In each experiment, raw sugarcane vinasse was treated to the Fenton treatment at an ambient temperature (29 ± 1 °C) in batch mode with varying pH (3, 3.8, and 5) dosages of H_2O_2 and iron. Due to the fluctuating amount of the COD value of raw sugarcane vinasse, the H_2O_2 dosage was presented as a ratio of [H_2O_2] to [COD] (0.12, 0.31, 0.47, and 0.62 g/g) while the ratio of [H_2O_2] to [Fe^{3+}] was 50, 37.5, and 25 (g/g). Low values of initial iron concentration were used in this work because iron already exists in raw sugarcane vinasse. Moreover, a higher concentration of iron is suggested to be avoided as it can lead to complications caused by precipitation of ferric iron species. To evaluate the influence of pH, the concentrations of H_2O_2 and iron salt were maintained constant, vice versa.

Raw sugarcane vinasse was put in a beaker and stirred by a magnetic stirrer. The pH was adjusted using HNO_3 (for pH 3), without adjustment (pH 3.8), and NaOH (pH 5). Subsequently, the required quantities of source of iron/Fe^{3+} (as $Fe(NO_3)_3{\cdot}9H_2O$) was, first, added into the sugarcane vinasse solution, followed by H_2O_2. Reaction time was started by the addition of hydrogen peroxide with constant stirring (200 rpm) until 60 min and then stopped. Every ten minutes, following the start of each reaction, a sample was withdrawn for analysis. The pH of treated sample was adjusted to 7 by NaOH 1 M to interrupt the reactions. The COD values of sugarcane vinasse, before and after the Fenton treatment, were measured by closed reflux colorimetric method with a spectrophotometer, whereas BOD_5 value was identified and quantified using standard methods. The value of pH was measured using a pH meter.

3.3. Kinetic Modeling

The results of COD degradation were tested using three kinetic models, first order, second order and Behnajady–Modirshahla–Ghanbery (BMG) model which were derived from Behnajady et al. [38]. The mathematical model of the BMG kinetic model is shown in Equation (13) [39], and the linear form of the three kinetic models is as indicated in Table 1 in Section 2.5.

$$\frac{C}{C_0} = 1 - \frac{t}{m + bt} \tag{13}$$

To evaluate the linear model, the value of the coefficient of determination (R^2) for each model is compared.

4. Conclusions

The Fenton process was investigated to treat sugarcane vinasse and it was revealed that the Fenton reaction was efficient for reduction of COD and enhancement of biodegradability of sugarcane vinasse. It was observed that in the evaluations performed, reaction medium with pH = 3.8, the ratio of $[H_2O_2]$ to [COD] = 0.62, and the ratio of $[H_2O_2]$ to $[Fe^{3+}]$ = 50 obtained more promising results, as it reached an efficiency of 48.10% in COD removal. The BMG kinetic model fitted well to experimental data for COD reduction and it was the best model to explain the kinetic reaction of the Fenton process as compared with first and second order kinetic models. The results of this study show that the Fenton reaction has the potential to be used as a sugarcane vinasse treatment method in order to remediate organic compounds into simple components and increase its biodegradability. It is also suggested that the Fenton process could be used as a pretreatment method of sugarcane vinasse to be followed by a biological treatment such as anaerobic digestion to produce biogas, because, based on biodegradability index value, its biodegradability was improved. The Fenton reaction can also be applied as one of alternative method for sugarcane vinasse pretreatment in order to increase biogas production.

Author Contributions: Conceptualization, S.S.; methodology, S.S., A.M., M.H., D.C.H.; validation, S.S., A.M. and M.H.; investigation, D.C.H.; writing—original draft preparation, D.C.H.; writing—review and editing, S.S., A.M., M.H.; visualization, D.C.H.; supervision, S.S., A.M., M.H.; funding acquisition, S.S.

Funding: This research was funded by the Direktorat Penelitian Universitas Gadjah Mada through "Rekognisi Tugas Akhir (RTA) 2019" Program under grant number: 3342/UN1/DITLIT/DIT-LIT/LT/2019. The APC was funded by the Direktorat Penelitian Universitas Gadjah Mada.

Acknowledgments: The authors would like to thank Direktorat Penelitian Universitas Gadjah Mada for the research funding through "Rekognisi Tugas Akhir (RTA) 2019" Program, and PS Madukismo Yogyakarta who kindly provides the sugarcane vinasse for this study.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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