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Research Paper

Effect of Hydrogen Peroxide Addition Method on Fenton Oxidation of Sugarcane Vinasse

Nindia Noor Indah*[a], Riezky Gusti Fadhlillah[b], Amani Salsabil Husodo[a]

[a] *Department of Chemical Engineering, Faculty of Engineering, Universitas Pembangunan Nasional "Veteran" Jawa Timur, Jl. Raya Rungkut Madya No. 1, Surabaya 60294, Indonesia*
[b] *Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada, Jl. Grafika No. 2, Yogyakarta 55281, Indonesia*

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ABSTRACT: *Vinasse, a highly polluting byproduct generated during ethanol production, exhibited a very high chemical oxygen demand (COD) of 132,000 mg/L, making its treatment a critical environmental challenge. To reduce COD levels in vinasse, the Fenton process was employed in this study. The experiments were carried out for 1 hour in batches at atmospheric pressure and ambient temperature. The chemical reagents used for the reaction consisted of a 50%* H_2O_2 *solution and* $Fe(NO_3)_3{\cdot}9H_2O$*, with the key variable being the* H_2O_2 *addition method of direct addition (one-shot, 80 mL at t=0) and stepwise (gradually, 20 mL aliquots at t=0, 10, 20, 30 min). Samples were collected every 10 minutes for COD analysis. While both dosing methods demonstrated time-dependent COD removal, the stepwise addition proved to be significantly more efficient, achieving a maximum measured removal of 57.39% compared to 39.12% for the direct* H_2O_2 *addition method. Furthermore, biphasic kinetic modeling showed that the direct addition of* H_2O_2 *exhibited a rapid initial oxidation phase (*$k_1=0.0925\ min^{-1}$*) followed by a slower and almost stagnant phase (*$k_2=0.0005\ min^{-1}$*). In contrast, the stepwise addition resulted in a lower but more sustained degradation rate (*$k_1=0.0246\ min^{-1}$*;* $k_2\approx 0\ min^{-1}$*), indicating a more uniform oxidation behavior under stepwise oxidant loading.*

Keywords: *vinasse; Fenton; COD removal;* H_2O_2 *addition method*

1. INTRODUCTION

Sugarcane vinasse, an extremely polluting wastewater produced during the ethanol production process from molasses, is a serious environmental problem because it has an extreme organic load. Typical characteristics include COD levels of 70,000–139,000 mg/L, BOD exceeding 36,000 mg/L, a high turbidity, and an acidic pH [1]. At facilities such as Madukismo Plantation Center in Bantul, Yogyakarta, untreated vinasse discharge into the Bedog River far exceeding regulated discharge limits such as Daerah Istimewa Yogyakarta (DIY) Regulation No. 7/2016 (maximum COD 300 mg/L, BOD 100 mg/L) and the national limits set by the Ministry of Environment and Forestry [2]. Direct discharge of untreated vinasse leads to serious ecological degradation, such as eutrophication which reduces oxygen in water body, mass mortality of aquatic life, groundwater seepage into public wells, phytotoxicity to plants, and persistent foul odors from volatile organic compounds [3].

Effective treatment is necessary to significantly reduce COD and increase biodegradability, while ensuring regulatory compliance. Conventional methods will not be sufficient to handle wastewater with very high concentrations, so more advanced methods are being explored. Among these methods, Advanced Oxidation Processes (AOPs) offer a powerful solution by generating hydroxyl radicals (•OH) that decompose complex organic compounds, converting them to CO_2, water, and more biodegradable or harmless substances [4]. This nature is caused by the hydroxyl radicals' high reduction potential of 2.80 V that allows •OH to react

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Department of Chemical Engineering
Faculty of Industrial Technology
Universitas Muslim Indonesia, Makassar
Address
Jalan Urip Sumohardjo km. 05 (Kampus 2 UMI) Makassar- Sulawesi Selatan
e-mail : jcpe@umi.ac.id

Corresponding Author *
nindia_noor.tk@upnjatim.ac.id

instantaneously with the pollutant, with a rate constant of 10^6 - 10^{10} $M^{-1}s^{-1}$ [5]. Fenton oxidation stands out among other AOP methods due to its simplicity, low reagent costs, and rapid process [6].

Recent mechanistic studies have revealed additional high-valent iron pathways. Cohen et al. demonstrated the formation of $Fe^{IV}O^{2+}$ (ferryl) via an iron-peroxo intermediate, which is particularly significant at neutral pH where Fe(IV) competes with •OH oxidation [7]. However, under acidic conditions typical for vinasse, •OH remains the dominant oxidant. Fenton oxidation utilizes Fe^{2+} and H_2O_2 in an acidic environment (pH (3-4)) to produce hydroxyl radicals [8]. The reactions [9] include:

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

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

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

$$\bullet OH + H_2O_2 \rightarrow HO_2\bullet + H_2O \quad (4)$$

$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + H^+ + O_2 \quad (5)$$

$$Fe^{2+} + HO_2\bullet \rightarrow Fe^{3+} + HO_2^- \quad (6)$$

$$RH + \bullet OH \rightarrow R\bullet + H_2O \quad (7)$$

The main reactions of Fenton oxidation are Equations (1) and (2) [10]. These reactions keep the •OH radicals flowing so they can vigorously attack pollutants, pick up hydrogen by Equation (7), and add or remove electrons, all at very high rates [11].

Numerous studies on Fenton-treated vinasse have been conducted. Hakika et al. have optimized the conventional Fenton pretreatment on sugarcane vinasse (COD >100,000 mg/L) by varying pH (optimal 3.8), H_2O_2/COD mass ratio (0.62 g/g), and H_2O_2/Fe^{3+} ratio (50 g/g), achieving 48.10% COD reduction [12]. Guerreiro et al. used dissolved iron resulting from the previous coagulation/flocculation stage as catalyst in Fenton oxidation (H_2O_2 14.5 g/L without adding ferric ions) on biodigested vinasse, attaining 69.2% COD removal [13]. Although gradual (stepwise) H_2O_2 addition was found to be superior to the direct (one-shot) dosage, no kinetics on raw high-COD vinasse was reported. Most recently, Askarian et.al. optimized Fenton oxidation of molasses vinasse (pH 2.01, 24.98%v/v H_2O_2, Fe^{2+}/H_2O_2 0.01 g/g), achieving 50.2% COD removal [14]. No studies have examined the impact of reagent addition methods on Fenton reaction performance and kinetics, particularly on materials with very high COD values above 100 g/L.

A critical research gap exists regarding the effect of H_2O_2 addition methods on Fenton vinasse performance, including its radical efficiency and scavenging minimization. This study addresses these gaps by examining the direct versus stepwise addition (every 10 min for the first 30 min) of 50% H_2O_2 in a batch setting on Madukismo Plantation Center vinasse, measuring COD removal over time and the reaction kinetics. This study was designed as a preliminary comparative investigation focusing specifically on the effect of H_2O_2 addition strategy under controlled operating conditions. To minimize interference from multiple simultaneous variables, parameters such as temperature, Fe^{3+} concentration, and H_2O_2 ratio were maintained constant throughout the experiments.

2. RESEARCH METHOD

Sugarcane vinasse treatment via Fenton oxidation was investigated to evaluate the effects of H_2O_2 addition method on COD removal kinetics. Experiments followed a batch protocol at ambient conditions, with COD monitored over 60 min. COD analysis adhered to SNI 6989.73:2009 (closed reflux, titrimetric method) [15].

2.1. Materials and Equipments

Primary materials used were raw sugarcane vinasse (Madukismo Plantation Center Bantul, initial COD of 132,000 mg/L), hydrogen peroxide [H_2O_2 (CV Sentra Teknosains Indonesia, 50% w/w)], and iron(III) nitrate nonahydrate [$Fe(NO_3)_3\cdot 9H_2O$ (Merck, 98%)].

Fenton reaction employed a 500 mL beaker and digital overhead stirrer (IKA RW 20 digital, 220 rpm) on a stand (Figure 1).

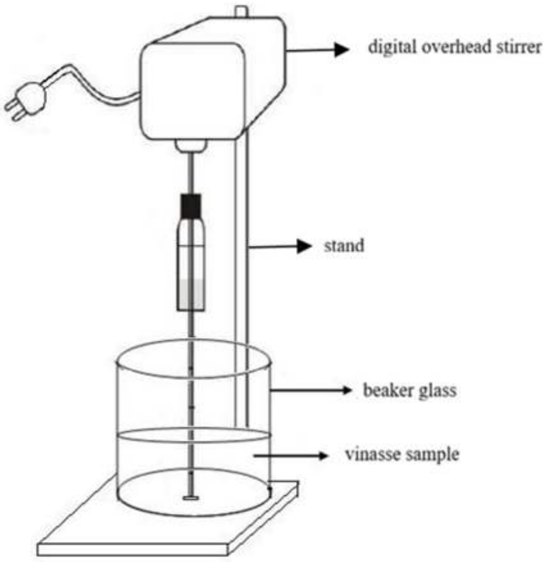


Figure 1. Fenton process apparatus

2.2. Research Procedures

2.2.1. Fenton Oxidation

Filtered vinasse (160 mL) was placed in a 500 mL beaker with 6.93 g $Fe(NO_3)_3 \cdot 9H_2O$. $Fe(NO_3)_3 \cdot 9H_2O$ was selected due to its high solubility and stable dissolution behavior under acidic reaction conditions. Compared to some ferrous salts such as $FeSO_4$ or $FeCl_2$, ferric nitrate also minimizes sulfate and chloride introduction into the reaction medium, which may influence radical reactions and secondary ionic composition. Furthermore, the use of Fe^{3+} salts allow Fenton oxidation pathways involving in situ Fe^{2+} regeneration during the reaction process as shown in Equation (2), allowing continuous hydroxyl radical generation throughout the oxidation process [16].

For direct addition, 80 mL 50% H_2O_2 was added one-shot at t=0. Meanwhile for stepwise addition, 20 mL 50% H_2O_2 was added gradually at t=0, 10, 20, 30 min (total 80 mL). Mixture was stirred at 220 rpm (ambient temperature, atmospheric pressure) for 60 min. Sample (0.2 mL) was then withdrawn every 10 min via 0.2 mL pipette for COD analysis.

2.2.2. COD Determination

Per SNI 6989.73:2009, sample was diluted to 100 mL volumetrically. The diluted sample of 10 mL was transferred to a 250 mL Erlenmeyer flask with the boiling stones and added 0.2 grams of HgSO4. Then, 5 mL of 0.25 N $K_2Cr_2O_7$ solution was added, and the mixture was stirred until homogeneous by gently rotating the flask. During 2 h reflux, 15 mL H_2SO_4-Ag_2SO_4 were added dropwise for the first 30 min via separatory funnel. The Erlenmeyer containing the sample solution was connected to a ball condenser and boiled on an electric stove. After 2 hours, the stove was turned off and the sample was cooled with a damp cloth to room temperature. The sample solution was diluted by adding 50 mL of distilled water, then titrated using 0.1 N FAS with 3 drops of ferroin indicator. The same steps were then carried out for the blank solution.

2.2.3. Kinetic Data Analysis

2.2.3.1. Pseudo-First-Order Kinetic

Organic degradation kinetics Fenton reactors follow second-order rate law:

$$-r_{COD} = k\, C_{\bullet OH}\, C_{COD} \qquad (8)$$

where:

$-r_{COD}$ = oxidation rate, mg/(L.min)

k = rate constant, L/(mg.min)
C_{COD} = COD concentration, mg/L
$C_{\bullet OH}$ = hydroxyl radical concentration, mg/L

With excess •OH, $C_{\bullet OH}$ remains nearly constant. Hence, the organic degradation kinetics can be simplified to pseudo-first-order kinetics:

$$-r_{COD} = k' \, C_{COD} \quad (9)$$

For batch reactor operation, COD mass balance yields:

$$\frac{dC_{COD}}{dt} = -k' \, C_{COD} \quad (10)$$

Integrating with $C_{COD} = C_0 \, (1 - x)$:

$$-ln(1 - x) = k' \, t + c \quad (11)$$

where:
x = COD removal
t = reaction time (min)
k' = pseudo-first-order rate constant (min^{-1})
c = integration constant

2.2.3.2. Pseudo-Second-Order Kinetic

An empirical pseudo-second-order kinetic model was evaluated to comparatively assess the fitting behavior of COD degradation during Fenton oxidation. Under this approach, the degradation rate:

$$-r_{COD} = k'' \, C_{COD}^2 \quad (12)$$

where:
k" = pseudo-second-order rate constant ($L.mg^{-1}.min^{-1}$)

For batch reactor operation, COD mass balance yields:

$$\frac{dC_{COD}}{dt} = -k'' \, C_{COD}^2 \quad (13)$$

$$\frac{1}{C_t} = \frac{1}{C_0} + k'' \, t \quad (14)$$

where:
C_0 = initial COD concentration (mg/L)
C_t = COD concentration at time t (mg/L)

2.2.3.3. Biphasic Kinetic

To further evaluate the degradation behavior of high-strength vinasse wastewater during the Fenton oxidation process, a biphasic kinetic model was also applied to describe the presence of readily oxidized and more resistant organic fractions. This model assumes that COD degradation occurs through two simultaneous oxidation phases with different apparent reaction rates, as expressed:

$$\frac{C_t}{C_0} = f \, e^{-k_1 t} + (1 - f) \, e^{-k_2 t} \quad (15)$$

where:
f = fraction of rapidly degradable organics
k_1 = apparent biphasic rate constant associated with the fast degradation phase (min^{-1})
k_2 = apparent biphasic rate constant associated of the slower degradation phase (min^{-1})

Model adequacy was evaluated using the coefficient of determination R^2, parity plots, and residual analysis between experimental and model-predicted COD values.

2.2.4. Oxidant Utilization Efficiency

Oxidant utilization efficiency was evaluated based on the number of COD removed per unit mass of H_2O_2 applied during the reaction process:

$$Oxidant\ utilization\ efficiency = \frac{COD_{removed}\ (g)}{H_2O_{2\,applied}\ (g)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

3. RESULTS AND DISCUSSION

3.1. COD Mass Removal Profiles

Raw vinasse contained 21,120 mg total COD (160 mL x 132,000 mg/L). Both H_2O_2 addition methods started from this identical mass basis, with all H_2O_2 (80 mL 50%) added by 30 min, reaching 240 mL final volume. Table 1 presents COD mass remaining and removal over 60 minutes.

Table 1. COD Mass Remaining and Removal During Fenton Treatment

Time (min)	**Direct H_2O_2 Addition**		**Stepwise H_2O_2 Addition**	
	COD mass (mg)	Removal (%)	COD mass (mg)	Removal (%)
10	16,714	20.86	20,714	1.92
20	13,714	35.06	16,500	21.88
30	13,714	35.06	12,857	39.12
40	13,714	35.06	12,857	39.12
50	12,857	39.12	12,857	39.12
60	12,857	39.12	12,000	43.18

Table 1 confirms that stepwise addition gives better COD removal (43.18% maximum versus 39.12%). The initial lag in stepwise addition COD removal (1.92% at 10 min) reflects gradual H_2O_2 dosing, yet surpasses one-shot performance by 60 min through sustained oxidation.

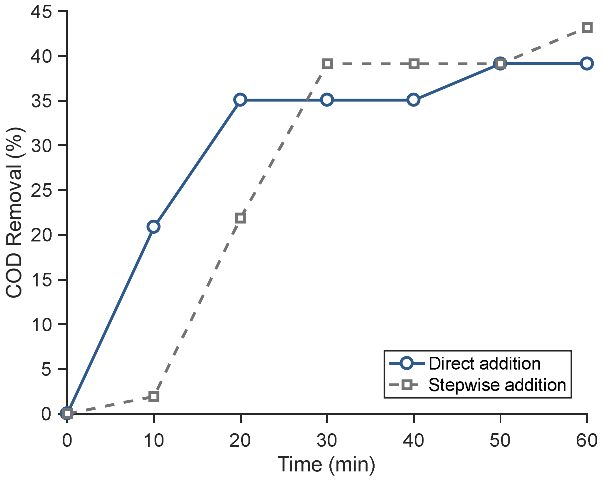


Figure 2. COD removal versus time

Figure 2 shows that the longer the reaction time, the higher the COD removal value. At the beginning of the Fenton reaction (0–20 min), the COD removal increases significantly and over time forms a relatively flat profile. This can occur because in the Fenton process, all Fe^{2+} ions react with H_2O_2 at a high-rate constant [17], resulting in the rapid formation of hydroxyl radical groups, which can facilitate the successful oxidation of organic compounds.

The stepwise H_2O_2 addition method achieved the highest corrected COD removal of 43.18%, higher than the achieved direct H_2O_2 addition method. This is consistent with previous research by Guerreiro et al., who observed organic compound reductions of 40.5% and 44.1% after 3 hours with gradual H_2O_2 addition (9.0 and 14.5 g/L, respectively), both of which exceeded the 40.2% reduction obtained when the 14.5 g/L dose was added directly all at once [13]. Esteves et al. [18] also reported that the stepwise addition of H_2O_2 for the different type of wastewater (olive mill wastewater) led to better COD removal of 55.7%, achieved by operating the process at $pH_0 = 3$, $[Fe^{3+}] = 1$ g/L, $Fe/H_2O_2 = 0.04$, and ambient temperature.

When H_2O_2 is added gradually, a more effective environment is created for the Fenton process, resulting in more hydroxyl radicals (•OH) being used to oxidize organic material in the wastewater [19]. This is because excessive amounts of H_2O_2 can cause a scavenging effect on hydroxyl radicals [20], as demonstrated in Equation (4) [21]. This reaction produces hydroperoxyl radicals (HO_2•), a weaker radical than hydroxyl radicals with reduction potential of 1.70 V [22]. Therefore, Equation (4) competes with Equation (7) and reduces the rate of organic material oxidation [23].

Beyond the scavenging effect, the imbalance between radical formation and iron regeneration further limits efficiency [16]. Hydroxyl radical formation in Equation (1) occurs rapidly ($k \approx 70\ M^{-1}s^{-1}$), while the reduction of Fe^{3+} back to Fe^{2+} in Equation (2) is much slower ($k \approx 0.01\ M^{-1}s^{-1}$) [24]. This large kinetic difference causes Fe^{2+} regeneration to be the rate-limiting factor during the reaction, especially at excessive instantaneous H_2O_2 concentrations. Consequently, direct addition of H_2O_2 can promote rapid initial radical formation followed by a decline in radical utilization efficiency as Fe^{2+} availability decreases and scavenging reactions become more dominant. This behavior was reflected in the direct addition, where COD removal increased rapidly to 35.06% in the first 20 minutes but then plateaued at 39.12% by 60 minutes, indicating a decline in oxidation activity after the initial reaction stage. In contrast, stepwise addition of H_2O_2 more closely synchronized peroxide availability with the Fe^{3+}/Fe^{2+} redox cycle, allowing for more sustained hydroxyl radical production and improved overall oxidation performance.

3.2. Kinetic Analysis

COD removal data at various reaction times were used to evaluate the degradation kinetics during the Fenton oxidation process. The degradation behavior of organic matter in wastewater systems is inherently complex due to the heterogeneous organic composition and the occurrence of multiple competing radical reactions. Therefore, a simplified kinetic estimate was initially evaluated using pseudo-first-order and pseudo-second-order models to describe the apparent oxidation behavior, as expressed in Equations (8) – (14).

To better reflect the presence of readily oxidized and more resistant organic fractions during the oxidation process, a biphasic kinetic model was also applied. This model assumes that COD degradation occurs through two simultaneous oxidation phases with different apparent degradation rates, allowing for a better representation of the non-uniform oxidation behavior observed in high-strength vinasse wastewater systems. The application of biphasic kinetic models in oxidative systems has also been reported in Fenton-like processes exhibiting time-dependent reaction behavior. A CaO_2-based Fenton-like system, for example, has been shown to follow biphasic kinetics in H_2O_2 release driven by diffusion- and reaction-controlled mechanisms, resulting in distinct fast and slow kinetic regimes [25]. Motivated by these observations, the biphasic approach was further evaluated in this study to capture the heterogeneous degradation behavior of vinasse wastewater under Fenton oxidation conditions.

Linear regression analysis was performed for pseudo-first-order and pseudo-second-order kinetic models, and nonlinear regression analysis was performed to estimate the biphasic kinetic parameters. The kinetic model parameters and coefficients of determination are summarized in Table 2.

Table 2. Comparison of kinetic model parameters for Fenton oxidation of vinasse wastewater

Kinetic Model	H_2O_2 Addition Method	Rate Constant	R²
Pseudo-first-order	Direct	$k' = 0.0072\ min^{-1}$	0.73
	Stepwise	$k' = 0.0104\ min^{-1}$	0.86
Pseudo-second-order	Direct	$k'' = 5 \times 10^{-7}\ L.mg^{-1}.min^{-1}$	0.77
	Stepwise	$k'' = 7 \times 10^{-7}\ L.mg^{-1}.min^{-1}$	0.87
Biphasic	Direct	$k_1 = 0.0925\ min^{-1}$ $k_2 = 0.0005\ min^{-1}$	0.98
	Stepwise	$k_1 = 0.0246\ min^{-1}$ $k_2 \approx 0\ min^{-1}$	0.90

The pseudo-first-order rate constant for the stepwise addition of H_2O_2 (0.0104 min^{-1}) was higher than that observed for the direct addition (0.0072 min^{-1}), indicating a faster degradation rate under the stepwise oxidant dosage. This increase suggests that the stepwise addition of peroxide can improve the efficiency of oxidant utilization by promoting more controlled hydroxyl radical formation and minimizing the accumulation of excess H_2O_2 that could contribute to radical scavenging reactions. Both the pseudo-first-order and second-order models showed only moderate fit, with R² values ranging from 0.73 to 0.86 and 0.77 to 0.87, respectively. The relatively limited fit performance of both models suggests that neither approach fully captures the complexity of COD degradation in vinasse wastewater under Fenton oxidation conditions. These deviations reflect the complex nature of the system, which involves heterogeneous organic constituents, simultaneous radical formation and consumption, and competing side reactions not explicitly represented in the simplified kinetic model.

To better represent this non-uniform degradation behavior, a biphasic kinetic model was applied and provided a significantly better fit, especially upon direct addition of H_2O_2 ($R^2 = 0.98$). The fast kinetic phase ($k_1 = 0.0925\ min^{-1}$) is associated with the rapid oxidation of readily degradable organic compounds, while the slow phase ($k_2 = 0.0005\ min^{-1}$) is associated with more recalcitrant constituents. In contrast, stepwise addition resulted in a lower rate constant of the fast phase ($k_1 = 0.0246\ min^{-1}$) and a negligible contribution of the slow phase ($k_2 \approx 0$), indicating that controlled oxidant dosage suppresses kinetic heterogeneity and reduces the pronounced biphasic behavior observed upon direct addition. In vinasse wastewater, the initial rapid oxidation is associated with the more reactive organic fraction, while the slower stages are associated with poorly biodegradable compounds such as melanoidins and phenolic structures [26].

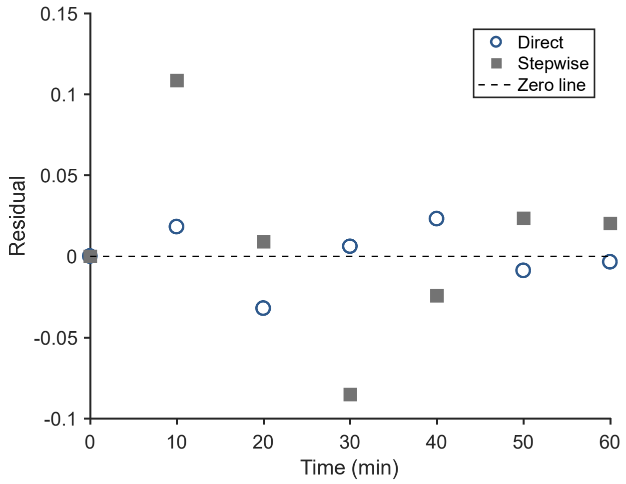
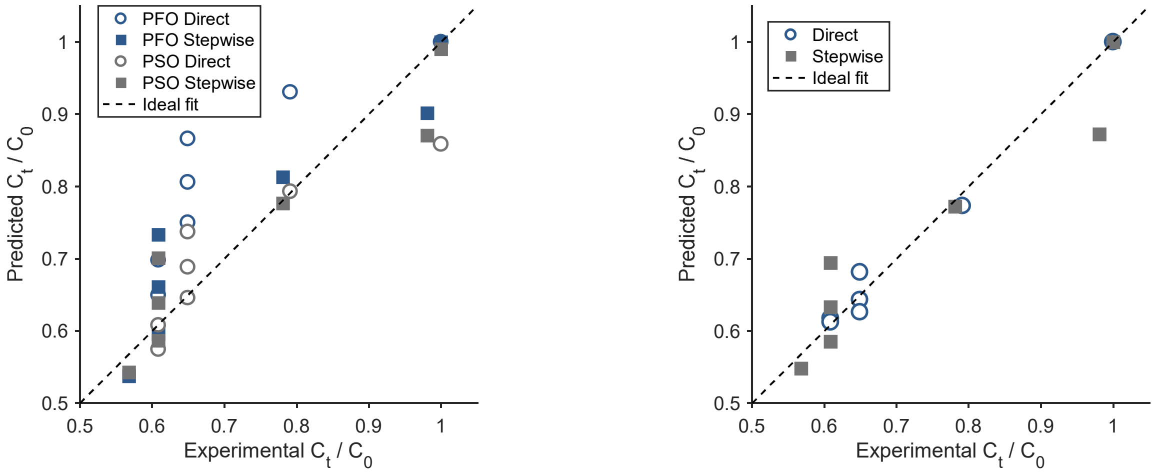


Figure 3. Residual plot for biphasic kinetic model

The reliability of the biphasic kinetic model was first evaluated using residual analysis as shown in Figure 3. The residuals were randomly distributed around the zero line for both direct and stepwise addition of H_2O_2, indicating no systematic deviation between experimental and predicted COD values. A slightly wider dispersion was observed at intermediate reaction times, corresponding to the transition between the fast and slow oxidation stages. This behavior reflects the progressive depletion of readily oxidized organic compounds, followed by an increase in the contribution of the more recalcitrant fraction during the final stages of the Fenton oxidation process.



(a) (b)

Figure 4. Parity plot for (a) pseudo-first-order and pseudo-second-order kinetics; (b) biphasic kinetic

The predictive performance of the pseudo-first-order, pseudo-second-order, and biphasic models was further assessed using parity plot analysis in Figure 4 (a) and (b). The pseudo-first-order and pseudo-second-order models showed significant deviations from the ideal 1:1 line, indicating limited ability to fully describe the complex degradation behavior of vinasse wastewater. In contrast, the biphasic model showed a closer agreement between experimental and predicted values, with data points clustered near the parity line for both direct and stepwise operating conditions. This confirms that the biphasic approach provides a more representative and reliable description of COD degradation kinetics under Fenton oxidation.

3.3. Oxidant Utilization Efficiency

The oxidant utilization efficiency as shown in Table 3 was assessed based on Equation (16).

Table 3. Oxidation utilization efficiency

H_2O_2 Addition Method	Total H_2O_2 Applied (g)	COD Removed (g)	Oxidant Utilization Efficiency (g COD removed/g H_2O_2)
Direct	47.88	8.26	0.1726
Stepwise	47.88	9.12	0.1905

The stepwise dosing strategy achieved an oxidant utilization efficiency of approximately 0.1905 g COD/g H_2O_2, slightly higher than that of direct addition (0.1726 g COD/g H_2O_2). This improvement indicates more effective oxidant utilization during the stepwise peroxide addition, potentially related to reduced excessive peroxide decomposition and lower radical scavenging behavior compared to direct dosing. However, the obtained oxidant utilization efficiency remained relatively low due to the very high organic strength and recalcitrant characteristics of the vinasse wastewater. These findings indicate that the Fenton process studied is more appropriately positioned as a partial oxidation pretreatment stage rather than as a standalone treatment method for direct discharge applications.

3.4. Practical Implications for Integrated Wastewater Treatment

Although the stepwise H_2O_2 addition improved COD removal performance compared to direct dosing, the final COD concentrations obtained after treatment remained relatively high due to the very high initial organic load of vinasse wastewater. This observation suggests that the Fenton oxidation process investigated in this study may not be sufficient as a stand-alone final treatment method for direct discharge applications. Instead, this process is more appropriately positioned as a pretreatment stage for high-strength vinasse wastewater treatment systems by reducing the organic load prior to downstream treatment processes.

In practical wastewater treatment applications, Fenton pretreatment can be integrated with subsequent biological processes such as anaerobic digestion, activated sludge treatment, or aerobic biodegradation systems. Partial oxidation during the Fenton stage can convert complex and recalcitrant organic compounds into smaller, more biodegradable intermediates, thereby improving substrate accessibility for microbial degradation in downstream biological units. Furthermore, reducing the initial organic shock load can contribute to improved stability and efficiency of biological treatment performance [27].

Several previous studies have also proposed integrating advanced oxidation processes with biological treatment for high-concentration wastewater. Such hybrid treatment strategies are generally considered more economical and operationally feasible than relying solely on advanced oxidation for complete pollutant removal [28]. The proposed integrated treatment scheme combining Fenton pretreatment and biological treatment for high-strength vinasse wastewater is shown in Figure 5.

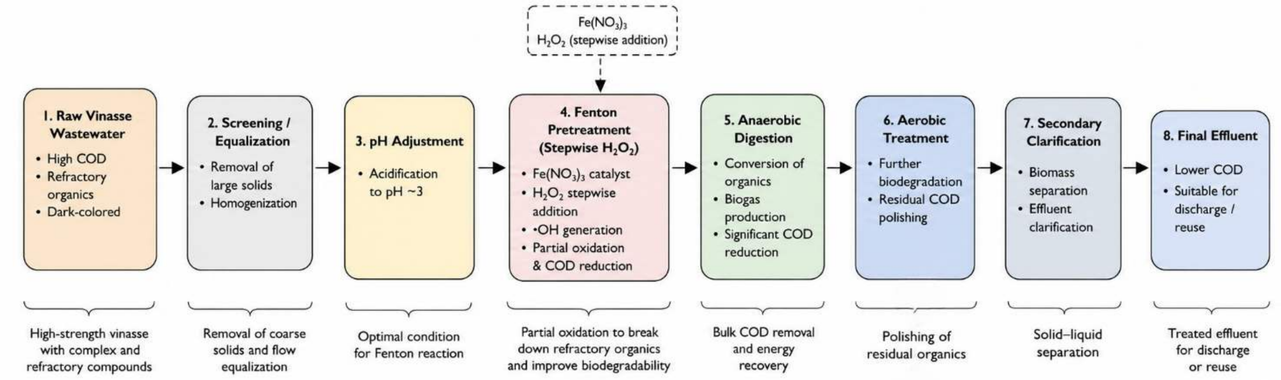


Figure 5. Proposed integrated treatment scheme for high-strength vinasse wastewater

The proposed system begins with equalization and screening to homogenize the wastewater characteristics and remove coarse solids, ensuring stable operation of the downstream process. Acidification is applied before the Fenton stage to provide optimal conditions for hydroxyl radical formation and iron catalyst stability. The stepwise Fenton process was chosen as the primary pretreatment step due to its superior performance in COD degradation and oxidant utilization.

Following Fenton oxidation, anaerobic digestion is introduced as the primary biological treatment step, utilizing the high organic content of vinasse for biogas production. The partial oxidation achieved in the Fenton stage enhances the biodegradability of the wastewater, thereby increasing the efficiency of anaerobic treatment. Finally, an aerobic purification step is included to further reduce residual biodegradable organics and stabilize the effluent quality before discharge.

4. CONCLUSION

Fenton oxidation effectively reduced COD in high-concentration sugarcane vinasse wastewater (132,000 mg/L), achieving the study's objective of evaluating the effect of the H_2O_2 addition method on degradation performance. The stepwise addition demonstrated higher COD removal efficiency (43.18%) compared to direct addition (39.12%), indicating improved process performance under controlled oxidant delivery. COD degradation behavior in this study is best described by a biphasic kinetic model, characterized by an initial rapid oxidation stage (k_1) followed by a slower degradation stage (k_2). This biphasic behavior reflects the heterogeneous nature of vinasse organic matter, where readily degradable compounds are rapidly oxidized, while poorly degradable fractions persist and degrade more slowly. These findings suggest that stepwise dosing combined with a biphasic representation provides a more appropriate framework for describing Fenton oxidation in high-concentration wastewater and may enhance its application as a pretreatment step prior to biological treatment. Further studies should focus on optimizing operational conditions and integration with biological treatment systems for full-scale applications.

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