

Enhancing Vinasse Treatment Efficiency using Electro-Fenton: The Role of Electrode Thickness and Power Supply Voltage

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Abstract.

The production of ethanol from molasses generates vinasse as a by-product of the distillation process. Vinasse waste produced by PT Energi Agro Nusantara contains COD and BOD levels of 910.5 ppm and 460.5 ppm, respectively, which significantly exceed the maximum limits set by wastewater quality standards, necessitating treatment. One treatment method is the use of Advanced Oxidation Processes (AOPs), which utilize hydroxyl radicals to oxidize organic pollutants in vinasse. One such process is the electro-Fenton process. In this study, 500 ml of vinasse was placed in a beaker and stirred for 90 minutes. A 25 ml addition of hydrogen peroxide was made, with a 2 cm gap between the iron electrode plates. Voltage variations of 3V, 6V, 9V, and 12V, along with electrode thicknesses of 2 mm, 3 mm, 4 mm, 5 mm, and 6 mm, were tested. COD and BOD levels were analyzed using the titrimetric method. The results showed that increasing the voltage and electrode thickness reduced COD and BOD levels, while the percentages of COD and BOD removal increased. The highest voltage (12V) and electrode thickness (6 mm) yielded the lowest final COD and BOD values of 163.5 ppm and 88.9 ppm, respectively, with COD removal at 82% and BOD removal at 81%.

Keywords: Vinasse, Elektro-fenton, COD and BOD.

1. INTRODUCTION

Bioethanol production in Indonesia has grown rapidly in recent years, primarily using molasses as the raw material. Vinasse, the main byproduct of bioethanol production, presents environmental challenges due to its high organic load, with biochemical oxygen demand and chemical oxygen demand often exceeding 100 g/L (Hakika et al., 2019; Rahmawati et al., 2020). Its recalcitrant compounds resist biological treatments, necessitating advanced oxidation processes such as electro-Fenton for effective remediation (Hakika et al., 2022).

Electro-Fenton mineralizes persistent pollutants and improves biodegradability by generating hydroxyl radicals ($\bullet\text{OH}$) via catalytic decomposition of electrogenerated H_2O_2 by Fe^{2+} (Afolabi et al., 2022; Nidheesh et al., 2023). This process is suitable for distillery wastewater, which has Chemical Oxygen demand (COD) greater than 50,000 mg/L, Biological Oxygen demand (BOD) greater than 30,000 mg/L, and recalcitrant phenolics resistant to anaerobic digestion (Covarrubias-Del-Toro et al., 2023; Minnalkodi Senguttuvan et al., 2024; Wijayanti et al., 2024). Treatment via electro-Fenton reduces environmental impact, enabling biological treatment or safe discharge (Widyastuti et al., 2021) with studies showing significant reductions in COD and color under optimized conditions.

In an electrochemical cell, electro-Fenton regenerates Fe^{2+} cathodically and produces H_2O_2 , sustaining $\bullet\text{OH}$ without continuous iron dosing (Klidi et al., 2019; Patil et al., n.d.) Contrasts with conventional Fenton, which needs precise reagent dosing and generates more sludge (GilPavas & Correa-Sánchez, 2019). Electro-Fenton excels in treating high-organic-load wastewaters, outperforming traditional Fenton (Isiaka & Olaniran, 2021). It detoxifies distillery effluents, boosts biodegradability, and enhances biogas yield; for example, Fenton pretreatment added 0.1 Nm^3 of biogas per m^3 of biomethanated wastewater (Bhoite & Vaidya, 2020; Hakika et al., 2022). Applications span leather, hospital, pharmaceutical, textile, and leachate wastes (Borba et al., 2018), and low-cost iron electrodes improve sludge biogas via altered pH, conductivity, and soluble COD (Feki et al., 2020). These benefits promote pollutant reduction and energy recovery from byproducts. The efficacy of electro-Fenton is further enhanced in coupled electro-Fenton/anodic oxidation systems, where both cathodic and

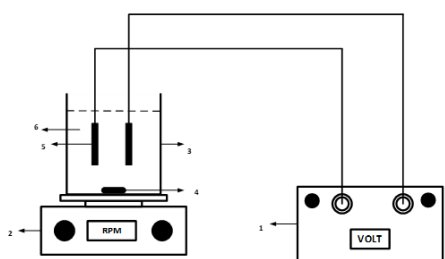
anodic reactions contribute to the oxidative degradation of organic pollutants, thereby increasing mineralization efficiency (Garcia-Rodriguez et al., 2022).

This study examines the effects of voltage and electrode thickness on electro-Fenton for vinasse treatment. Optimizing these maximizes $\bullet\text{OH}$ production and mass transfer, improving degradation of vinasse organics. Furthermore, the systematic exploration of these parameters is crucial for developing a cost-effective and scalable electro-Fenton system capable of achieving significant reductions in both BOD and COD from vinasse (Khatri & Garg, 2020).

II. METHODS

Material and Equipment

The materials used in this research include vinasse waste from PT Energi Agro Nusantara (ENERO), iron electrodes, and 30% hydrogen peroxide (H_2O_2). The experimental setup utilized a 500 mL beaker as the reactor, equipped with iron electrodes and a controlled power supply to facilitate the electro-Fenton process. The experimental setup consisted of a DC power supply to regulate current and voltage, a magnetic stirrer to ensure homogeneity, and pH and temperature probes for continuous monitoring. The experimental setup for the electro-Fenton process is depicted in Figure 1, illustrating the primary components and their arrangement.



Caption

1. Powersupply
2. Magnetic Stirrer
3. Beaker Glass
4. Magnet
5. Iron Electrode Pair
6. Waste Solution

Fig 1 Electro-fenton reactor setup

Experimental Setup

The experimental setup treated vinasse by varying the voltage (3V;6V,9V, and 12V), and electrode thickness (2mm, 3mm, 4mm, 5mm, and 6mm), with constant stirring speed (250 rpm), sample volume (500 mL), reaction time 90 minutes, electrode spacing of 2 cm, and Hydrogen peroxide (H_2O_2) volume of 25 mL.

Experimental Procedure

The experimental procedure involved the following steps: First, the electrodes were cleaned, dried, and weighed before and after the process. Next, the electro-Fenton reactor was assembled with the electrodes spaced at a fixed distance. The vinasse sample was then added to the reactor, followed by H_2O_2 . Subsequently, the magnetic stirrer and power supply were activated, and the reaction proceeded for 90 minutes. Finally, COD and BOD values of the treated sample were determined using titration methods.

III. RESULTS AND DISCUSSION

Initial characterization of the raw vinasse revealed a high initial COD concentration of 910.50 ppm and BOD of 460.55 ppm, underscoring the need for effective pretreatment prior to discharge. The vinasse waste exhibited a pitch-black, cloudy appearance and a very unpleasant odor, as confirmed by analysis conducted at the Surabaya Industrial Research and Consultation Laboratory.

The Effect of Electro Fenton Process on Chemical Oxygen Demand (COD) Levels

Voltage, a key operating parameter in the electro-Fenton process, significantly influences reactions at the anode and cathode of the electrochemical cell. Figure 2 shows the effects of voltage and various electrode thicknesses on COD levels.

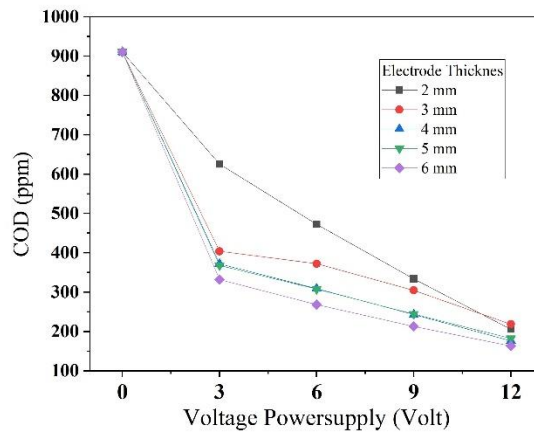


Fig 2. Effect of Power supply voltage on COD concentration

Fig 2 illustrates that as the voltage increases, the COD levels in vinasse decrease significantly. This reduction occurs because voltage directly influences the current produced, which is directly proportional according to Faraday's First Law, stating that the mass of a substance produced or liberated at an electrode is proportional to the electric charge passed through the electrolyte (Nabilah et al., 2025). Consequently, higher voltages generate more ions, leading to increased formation of hydroxyl radicals (Nguyen et al., 2021). Notably, a 12-volt system proved most effective, reducing COD to 163.65 ppm at a 6 mm electrode thickness. Furthermore, as shown in Figure 2, the COD reduction efficiency was higher for thicker electrodes than for thinner ones. This indicates that thicker electrodes enhance mass transfer and reaction kinetics for hydroxyl radical generation in the electro-Fenton process. Moreover, the thicker the electrode plate, the greater its electrostatic attraction to ions, which further promotes hydroxyl radical formation.

To better understand the effect of voltage on COD removal percentage, Figure 3 plots voltage versus COD removal.

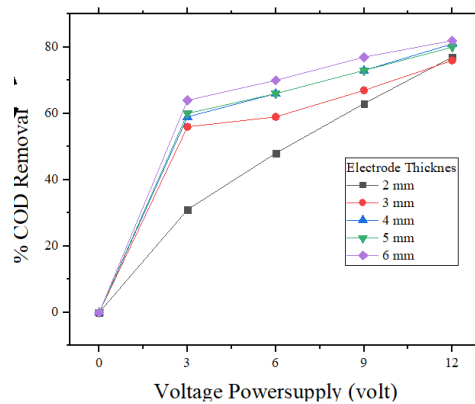


Fig 3. The relation of Power Supply voltage on Percentage COD removal

Fig 3 confirms that higher applied voltages yield higher COD removal percentages, owing to increased ion production, which promotes greater hydroxyl radical generation (Atmaca & Beyazıt, 2020). For instance, at 3 V with 2 mm electrode thickness, COD removal reached 31%, compared to 82% at 12 V with 6 mm thickness. The Electro-Fenton process is an advanced oxidation method that utilizes hydroxyl radicals ($\bullet\text{OH}$) as strong oxidizing agents to degrade organic pollutants. This process involves the reaction between ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2), generating hydroxyl radicals, which play a crucial role in breaking down complex organic compounds (Casado, 2019). The formation of hydroxyl radicals occurs when Fe^{2+} reacts with H_2O_2 , producing Fe^{3+} , hydroxyl ions (OH^-), and hydroxyl radicals ($\bullet\text{OH}$) (He & Zhou, 2017). The Fe^{3+} ions are then reduced back to Fe^{2+} at the cathode, ensuring a continuous catalytic cycle. Organic pollutants (RH) are oxidized through interaction with hydroxyl radicals, leading to their degradation into simpler, less harmful compounds. Additionally, iron plays a mediating role in oxidation, ensuring the sustainability of the reaction process (Rahmawati et al., 2020).

The Effect of Electro Fenton Process on Biological Oxygen Demand (BOD) Levels

The effects of power supply voltage on BOD level and BOD removal percentage are shown in Fig 4 and fig 5.

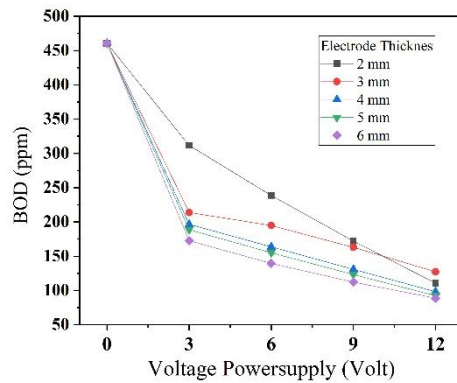


Fig 4 The effect of voltage power supply on BOD reduction

Fig 4 illustrates the relationship between voltage and BOD reduction at varying electrode thicknesses. As the applied voltage increases in the electro-Fenton process, BOD levels decrease more substantially

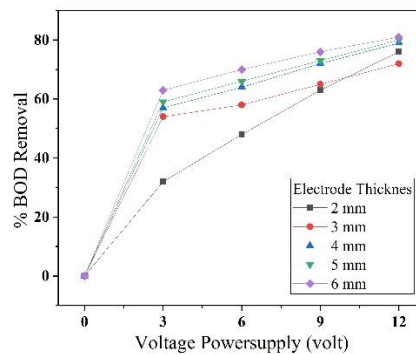


Fig 5 The effect of power supply voltage on BOD removal percentage

Fig 5 proves that as the applied voltage increases in the electro-Fenton process, BOD levels decrease more substantially. For instance, at 3 V with 2 mm electrode thickness, BOD reduction is only 32%; however, it rises to 76% at 12 V with the same thickness. This improvement occurs because higher voltages generate more hydroxyl radicals ($\bullet\text{OH}$) via the Fenton reaction, thereby degrading organic compounds in vinasse waste (Nguyen et al., 2021). Voltage variation thus significantly enhances BOD reduction efficiency by accelerating oxidation and vinasse degradation, consistent with prior research (Atmaca & Beyazıt, 2020). Electrode thickness also plays a crucial role by increasing the surface area available for the Fenton reaction. As shown in the figures, 6-mm electrodes at 12 V achieve an 81% reduction in BOD. This aligns with findings that optimal thickness improves process efficiency by facilitating more reactions on the electrode surface. Overall, optimizing both voltage and electrode thickness maximizes BOD reduction in the electro-Fenton process.

pH profile during Electro-Fenton Process

Acidity or pH is a critical parameter in the electro-Fenton process, profoundly influencing the efficiency of hydroxyl radical ($\bullet\text{OH}$) generation, ion stability, and the overall degradation of organic pollutants; suboptimal pH can lead to iron precipitation or reduced Fenton reaction rates. Continuous monitoring of pH provides insights into reaction dynamics, including acidification from production during decomposition. The pH profile as a function of reaction time at varying voltages is shown in Figure 6.

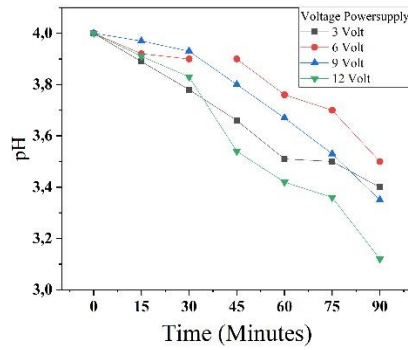


Fig 6 The pH profil during Fenton process

Fig 6 illustrates the effect of electro-Fenton reaction time on the pH of vinasse waste at varying voltages. The graph shows that the pH fluctuates at 15-minute intervals but overall decreases. This occurs because the electro-Fenton process generates ions, lowering the pH and rendering the solution more acidic. Key reactions involve the decomposition of to produce highly reactive hydroxyl radicals ($\bullet\text{OH}$), with ions catalyzing the breakdown of into these radicals in the Fenton reaction. This reaction also produces additional ions, further contributing to the decline in pH. Thus, the solution pH becomes increasingly acidic during the electro-Fenton process due to elevated ion concentrations. In the Fenton reaction, Fe^{2+} ions act as catalysts to produce H_2O_2 , which then decomposes into hydroxyl radicals (Babuponnusami & Muthukumar, 2014). Additionally, the Fenton reaction also produces H^+ ions, contributing to the decrease in pH (Zhang & Zhou, 2019). Therefore, it can be concluded that during the electro-Fenton process, the solution tends to become more acidic due to an increase in H^+ concentration.

Temperature profile during the Electro-Fenton Process

The reactor temperature during the electro-Fenton process was monitored to determine whether the reaction releases or requires heat. The temperature profile during the electro-Fenton process is shown in Fig7.

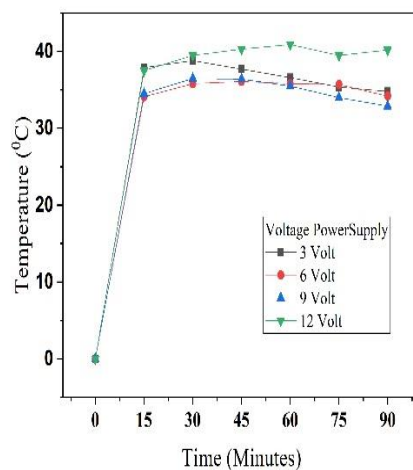


Fig 7 The temperature profile during fenton process

Fig 7 illustrates the relationship between reaction time and temperature during the electro-Fenton process using 3-mm-thick electrodes at varying voltages. The temperature rises notably at the 15- and 30-minute intervals, then declines from 45 to 90 minutes. These initial fluctuations stem from vigorous chemical reactions that produce substantial amounts of hydroxyl radicals ($\bullet\text{OH}$) and heat. The early temperature increases are further attributed to intensified exothermic reactions. At 12 V, the rise is more pronounced due to the higher electric current; per Ohm's Law, higher current generates more electrical energy, which is converted to thermal energy, raising the solution temperature. The optimal temperature for the electro-Fenton process is approximately 35°C (Nidheesh et al., 2023). These variations result from the underlying reactions and applied operational conditions.

IV. CONCLUSION

This study indicates that the Advanced Oxidation Process (AOPs) method, combining electrolysis and Fenton's reaction (Electro-Fenton), can be effectively used to treat Vinasse waste. However, the number of parameters affecting the treatment efficiency in this method is quite large. Therefore, several parameters, such as the electro-Fenton process duration, H₂O₂ concentration, and electrode distance, need to be determined. Other parameters, such as power supply voltage and electrode thickness, are varied. Based on the results, the optimal operating conditions for the electro-Fenton process in Vinasse treatment are a power supply voltage of 12 volts, electrode thickness of 6 mm, and a treatment time of 90 minutes. Under these conditions, a reduction of approximately 82% in COD and 81% in BOD was achieved.

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