Removing BOD, COD, and Decolorization of Batik Cual Wastewater using Fenton Mechanism

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Article Info

ABSTRACT

During the production of batik cual, thick-colored wastewater is produced. Unfortunately, the wastewater could damage the environment if it is disposed of without specific processing. The Fenton method is an advanced oxidation process (AOPs) that can degrade organic dyes found in liquid waste. In this research, the researchers studied the Fenton mechanism’s application to the batik cual wastewater treatment. The Fenton’s reagent used was H₂O₂ with FeSO₄·7H₂O. Some of the experimental wastewater treatment parameters were the values of biological oxygen demand (BOD), chemical oxygen demand (COD), the degradation efficiency of difficult to decompose organic materials, and the color degradation efficiency in batik cual wastewater. The results show that the Fenton mechanism’s efficiency of removing color from batik cual wastewater is up to 97.8%. COD and BOD removal efficiencies are 76.3% and 75.2%, and the degradation efficiency of difficult to decompose organic matter is 76.8%. Also, the researchers found that the higher amounts of FeSO₄·7H₂O increase the removal parameters effectiveness. Therefore, the Fenton mechanism can effectively improve the quality of wastewater in batik cual production.

INTRODUCTION

The cual woven cloth is one of Bangka Belitung’s cultural identity products that is often used as a souvenir icon for tourists (Damayanti & Ferdiana, 2020). Recently, the cual woven fabric artisans are innovating to produce batik-type cual (called as batik cual). This effort is made to reduce production costs so that people can easily purchase the cual. Therefore, the transformation of woven fabrics into batik has made cual famous among tourists and can be applied to various office/school uniforms (Ayan et al., 2018; Tomohardjo et al., 2018).

Besides providing positive values for regional economic growth, the increase in batik cual production harms the environment (Gusa et al., 2020). It can be a severe problem because some batik artisans use synthetic dyes in the production process. The batik synthetic dyes’ wastewater will damage the environment because it has high toxicity, is non-biodegradable, and can have carcinogenic and mutagenic properties (Lestari & Windyartini, 2020; Rahmadyanti & Febriyanti, 2020). Batik wastewater usually has high color content, chemical oxygen demand (COD), biological oxygen demand (BOD), and some difficult to decompose organic matters (Buthiyappan et al., 2016; Galih et al., 2020; Khalik et al., 2018).

The methods to process textile waste are biological methods (Bhatia et al., 2017; Shoukat et al., 2019), physicochemical methods (adsorption) (Babaei et al., 2017; H. Zhang et al., 2018), coagulation (Dalvand et
Several previous researchers have carried out the application of the Fenton method in degrading batik wastewater. However, most of these studies only use a single type of dye from batik and only focus on reducing the wastewater color (Qin et al., 2018; Setyaningtyas et al., 2019). In practice, batik wastewater contains complex dyes. Also, BOD and COD problems need to be solved besides the color problems.

In this research, the Fenton mechanism in real batik *cual* wastewater was investigated. Several parameters observed were BOD, COD, the number of organic compounds that were difficult to decompose, and the color concentration. The Fenton mechanism's performance is highly dependent on the amount of reagent used in the oxidation process. Therefore, the researchers investigated Fenton's reagent amount in degrading pollutants. This research aims to provide information regarding the effective dosage of Fenton's reagent in batik *cual* wastewater treatment.

**METHOD**

Batik *cual* wastewater used in this study was taken from *cual* batik artisan in Pangkalpinang City, Bangka Belitung Islands. In one production, batik *cual* artisans can produce about 20 liters of wastewater. To treat batik *cual* wastewater, the researchers used the Fenton method. The Fenton method was carried out by mixing 100 ml of batik *cual* wastewater with Fenton's reagent consisting of 1 ml of hydrogen peroxide (H₂O₂) and FeSO₄·7H₂O with mass variations of FeSO₄·7H₂O ranging from 0.1, 0.2, 0.3, 0.4, up to 0.5 grams. The oxidation process using the Fenton method was carried out for 24 hours and continued with the measurement of BOD, COD, the number of organic compounds that were difficult to decompose, and the concentration of residual wastewater's color. The BOD value is determined by the difference between the dissolved oxygen on the first day of incubation (DO₀) and the dissolved oxygen after five days of incubation (DO₅). The dissolved oxygen measurement was carried out with a DO-meter. COD measurements were carried out using the digestion reactor method. Digestion solution and sulfuric acid are mixed into the sample and then heated in
The digestion reactor. The COD concentration was determined using a UV-Vis spectrophotometer (HACH DR 2600) based on a calibration curve at a wavelength of 600 nm. The UV-Vis spectrophotometer was used to measure the color concentration of the sample. The measurement process began by creating a calibration curve determined from the absorbance value at the wavelength that can produce the highest absorbance peak for the standard solution. Furthermore, the absorbance of the sample is measured at this wavelength and the color concentration value is calculated based on the resulting calibration curve (Nandiyanto et al., 2018). The method schematic of this research is shown in Figure 1.

RESULTS AND DISCUSSION

In Figure 2, a comparison between batik cual wastewater and standard freshwater is presented. Batik cual wastewater is dark bluish-purple color because various synthetic dyes are used, such as remazol, naphthol, or indigosol. Therefore, if batik cual wastewater is disposed of in the aquatic environment, it will disturb the organisms because it blocks sunlight for the photosynthesis process.

After the Fenton mechanism was carried out using the H$_2$O$_2$ reagent with variations in the amount of FeSO$_4$.7H$_2$O for 24 hours, various transformation of batik cual wastewater occur as shown in Figure 3. After the Fenton treatment, batik cual wastewater has a more transparent color. The decolorization process occurred from initially dark bluish-purple to bluish-purple. With the Fenton treatment with 0.5 gr of FeSO$_4$.7H$_2$O reagent, the wastewater has become more transparent, almost like a standard freshwater. It shows that the Fenton mechanism is effective for decolorizing batik cual wastewater. The more FeSO$_4$.7H$_2$O used in Fenton treatment, the more significant the decolorization process will be.

![Figure 3. The Results of the Fenton Mechanism in Batik Cual Wastewater Based on Mass Variations of FeSO$_4$.7H$_2$O](image)

The decolorization process of batik cual wastewater through the Fenton mechanism occurred due to the formation of free radicals such as HO$^-$ (hydroxyl radicals) and HO$_2^-$ (hydreroxyl radicals) during the Fenton oxidation process. Hydroxyl radical is an oxidizing agent with an electrochemical oxidation potential value up to 2.80 V. This value is higher than other oxidizing agents such as ozone (2.08 V), hypochlorite (1.49 V), and chlorine (1.36 V) (Hassaan & Nemr, 2017). The formed free radicals are reactive to pollutants in batik cual wastewater which are generally composed of various organic compounds. Free radicals will attack organic compounds in batik cual wastewater, thus the decolorization process occurs. The radical formation in the Fenton mechanism occurs in a very complex process. However, the simple explanation for the reaction is proposed by the Haber-Weiss through the reaction (Kremer, 1999):

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{OH}^- \quad (1)$$

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ \quad (2)$$

The net effect of this chemical reaction is that H$_2$O$_2$ is disproportionation to form two
different oxygen-radical species with water as a by-product,

\[ 2\text{H}_2\text{O}_2 \rightarrow \text{HO}^* + \text{HO}_2^* + \text{H}_2\text{O} \quad (3) \]

In the Fenton reaction, there is a conversion process of Fe\(^{2+}\) ion (ferrous ion) to Fe\(^{3+}\) (ferric ion) and vice versa when the iron ion reacts to \(\text{H}_2\text{O}_2\). Each phase produces radicals that play a role in the degradation process of pollutants in wastewater. Also, iron in the Fenton reaction can act as a catalyst in the hydroxyl formation process. Schematically, the conversion cycle of ferrous ion to ferric ion in the presence of hydrogen peroxide is shown in Figure 4.

![Figure 4. The Conversion Cycle of Ferrous Ion to Ferric Ion in Fenton Reaction](image)

During the measurement process using a UV-Vis spectrophotometer, the highest absorbance peaks for all standard batik cual wastewater in various concentrations occurring at a wavelength of 699 nm. Therefore, based on the Lambert-Berth law, there is a linear relationship between absorbance (\(A\)), concentration (\(c\)), molar absorption coefficient (\(\varepsilon\)), and the optical length path of the solution (\(l\)) (Nandiyanto et al., 2018):

\[ A = c\varepsilon l \quad (4) \]

Then, a linear relationship between absorbance and concentration of batik cual wastewater is shown in Figure 5. The color concentration of the wastewater with absorbance at wavelength 699 nm fulfills the linear relationship that satisfies \(y = 0.0168x + 0.0123\), where \(x\) is the wastewater color concentration, and \(y\) is the absorbance value. The coefficient of the linear equation is excellent, i.e., \(R^2 = 0.9975\). Thus, the calibration curve can be used to measure the color concentration of wastewater in this study.

![Figure 5. UV-Vis Spectrophotometer Calibration Curve to Detect the Color Concentration of Wastewater](image)

The results of absorbance value of batik cual wastewater using the Fenton mechanism are shown in Table 1. Through the absorbance value, the color concentration value of the waste can be determined according to the calibration curve in Figure 5. The calculations show that the waste color concentration has decreased significantly after the Fenton mechanism was performed. The color concentration value of wastewater after the Fenton mechanism ranged from 6.78% to 2.20%. The 0.5 gr of FeSO\(_4\).7H\(_2\)O can reduce the color concentration of the wastewater by 2.20%. It is in line with the results of the batik cual wastewater shown in Figure 3 that the resulted wastewater was more transparent than the raw wastewater.
The Fenton method can reduce up to 97.8% of the batik cual wastewater’s color. With the similar dosage of H₂O₂, the degradation effectiveness was higher than the degradation of a single dye i.e. methylene blue as conducted by Liu et al. (2013). In her research, Liu used 10 mg/liter of H₂O₂ of methylene blue solution resulted in the effectiveness of 93.1% (Liu et al., 2013). This research used a higher dose of FeSO₄·7H₂O. The higher amount of FeSO₄·7H₂O concentration increases Fe²⁺ which acts as a catalyst to decompose H₂O₂ and produce hydroxyl radicals. Also, Fe²⁺ or Fe³⁺ ion can serve as a coagulant agent. Thus, they may bind the color pollutant molecules of batik cual wastewater, both in raw pollutant and after the oxidation process (Setyaningtyas et al., 2019). However, when the amount of FeSO₄·7H₂O catalyst is sufficient, the addition of more catalyst does not have a significant effect due to the limited amount of H₂O₂.

Figure 6 shows the results of COD measurements from batik cual wastewater after the application of Fenton mechanism. The Fenton mechanism is effective in reducing the COD value of the batik cual wastewater. Initially, the wastewater’s COD value was 104 mg/L. Then, it decreased to 24.7 mg/L after the Fenton mechanism was applied. Also, the higher amount of FeSO₄·7H₂O used in the Fenton mechanism effectively reduced the COD levels. It occurred because more ferrous ions can generate hydroxyl radicals. Compared to hydroperoxyl radicals generated by ferric ions, hydroxyl radicals are more aggressive in destroying organic pollutants. The conversion of ferrous ions to ferric ions (and vice versa) increased the process reaction time. Thus, the high amount of FeSO₄·7H₂O as a catalyst will accelerate the degradation of pollutants in batik cual wastewater.

Compared to the other methods of AOPs, such as UV, UV/Fe²⁺, and UV/H₂O₂, the Fenton (Fe²⁺/H₂O₂) method is the most effective to degrade COD in textile wastewater. The effectiveness is determined by the ratio of COD degraded to the electrical energy needs. The Fenton method does not require electrical energy to work, but it can degrade COD around 80% (Buthiyappan & Abdul Raman, 2019). In this research, the effectiveness of COD degradation reached 79.3%. In several other studies, it was also stated that UV radiation can increase the Fenton method’s effectiveness in degrading COD (GilPavas et al., 2017; Pérez et al., 2002). The photo-Fenton method is considered more effective because of the continuous generation of reactive oxygen species, especially hydroxyl radicals.

Besides COD, Figure 7 presents the BOD levels in the batik cual wastewaters. There was a BOD decrease due to the Fenton mechanism. Initially, the raw wastewater’s BOD value was 35 mg/L. After the application of Fenton mechanism, the value decreased to 8.6 mg/L. There was an increase in the organic matter’s oxidation (related to

### Table 1. The Absorbance Value Measurement and the Color Concentration value Calculation of the Wastewater

| FeSO₄·7H₂O (gr) | Absorbance (a.u) | Wastewater Color Concentration (%) |
|-----------------|------------------|-----------------------------------|
| 0.1             | 0.072            | 3.69                              |
| 0.2             | 0.115            | 6.24                              |
| 0.3             | 0.124            | 6.78                              |
| 0.4             | 0.051            | 2.44                              |
| 0.5             | 0.047            | 2.20                              |

Figure 6. Relationship between the COD removal of batik cual wastewater and the amount of FeSO₄·7H₂O in the Fenton mechanism

Figure 7. Relationship between the BOD removal of batik cual wastewater and the amount of FeSO₄·7H₂O in the Fenton mechanism
aspects of biological oxygen) by radicals produced in the Fenton mechanism.

![Graph](image1.png)

**Figure 7.** The Relationship between the BOD Removal and the amount of FeSO₄·7H₂O in the Fenton Mechanism

By definition, COD is related to the amount of oxygen needed to break down all organic material contained in a liquid. Meanwhile, BOD is related to measuring the amount of oxygen required by microorganisms to decompose organic matter in aerobic conditions (readily decomposable organic matter). Therefore, the difference between COD and BOD provides information on the amount of organic matter that is difficult to decompose in wastewater (Atima, 2015). To observe the amount of non-biodegradable organic matter remaining in the waste after the Fenton mechanism, the researchers calculated the difference between COD and BOD as shown in Figure 8. The Fenton mechanism effectively reduced the amount of difficult to decompose organic material. The greater the use of FeSO₄·7H₂O, the smaller the difference between COD and BOD will be which indicates that the amount of the difficult to decompose organic matter remaining in the wastewater is low.

![Graph](image2.png)

**Figure 8.** The Relationship between COD and BOD with the Amount of FeSO₄·7H₂O in the Fenton Mechanism

**CONCLUSION AND SUGGESTION**

Without any processing, the batik *cual* wastewater has a very thick color. The Fenton mechanism helps decolorizing the wastewater. Through the Fenton mechanism, batik *cual* wastewater became significantly more transparent. Quantitatively, the color removal efficiency reached 97.8%. The Fenton mechanism also reduced the COD and BOD levels in batik *cual* wastewater. The efficiency of COD removal reached 76.3%, while BOD removal efficiency reached 75.2%. Besides, the Fenton mechanism degraded difficult to decompose organic matter. The organic pollutants in batik *cual* wastewater was reduced by the Fenton mechanism because the ferrous ions from FeSO₄·7H₂O can generate hydroxyl radicals that damage pollutant compounds. The more FeSO₄·7H₂O added to the wastewater, the more effective the Fenton treatment will be. In further research, it is interesting to integrate the batik *cual* wastewater treatment method through the Fenton mechanism with other methods such as filtration and other AOPs methods to reduce the use of FeSO₄·7H₂O catalyst.
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