Decreasing COD Levels and Colors of Textile Industrial Waste with Electro-fenton Method

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To cite this article:

Received: April 25, 2021; Accepted: May 11, 2021; Published: October 5, 2021

Abstract: The wastewater from the coloring process in the textile industry threads and fabrics generally contains Azo compounds and organic pollutants which are difficult to decompose biologically and require a long time. The handling of these organic pollutants can be carried out with alternative advanced oxidation processes (AOPs) technology including the Electro-Fenton method. This study aims to obtain optimum operating conditions reduction of chemical oxygen demand (COD) and color in textile industry wastewater using the Electro-Fenton method. Processing is done by using the Electro-Fenton Method in batches with a time variation of 30, 60, 90, 120, 180 minutes. Using variations of electrical voltage of 6 volts with electrode distance is 2cm, 7 volts with electrode distance is 4cm, 8 volts with electrode distance is 6cm, variations of fenton doses based on the ratio of the molar ratio of \( \text{H}_2\text{O}_2:\text{FeSO}_4 \) of (10:0.1), (10:0.2), (10:0.3). In addition to batching, this study also carried out a continuous Electro-Fenton experiment using electric voltage and electrode distance and the best contact time of the batch process. Based on the research, the processing efficiency of COD and Color in the textile industry wastes produced using the Electro-Fenton method of 94.1%, and 99.2%, respectively, on the ratio of the molar ratio of \( \text{H}_2\text{O}_2:\text{FeSO}_4 \) 10:0.1 with a voltage of 7 volt and 4 cm electrode distance in 180 minutes contact time and pH condition 4.

Keywords: Wastewater, Textile Industry, Electro-Fenton, Chemical Oxygen Demand, Color

1. Introduction

In this modern era, clothing is a very important requirement for everyone. Cain, which is the main ingredient in making clothes, must go through a long process to become a cloth that is ready for use. In the process, the textile industry as an industry whose income must pay attention to factors related to sanitation in the textile industry environment and sanitation of the surrounding environment. Waste The textile industry generally uses synthetic dyes for reasons of being inexpensive, durable, easy to obtain and easy to use. But the waste produced is still colored and difficult to degrade. Most of the industries are textile industries which generally do not have good waste treatment. The wastewater originating from the household textile industry is a dye of organic compounds which if channeled into a body of water will reduce dissolved oxygen levels for aquatic organisms, because the oxygen is actually used to oxidize organic compounds contained in these dyes [4].

This textile industry waste is a waste from the yarn color dyeing process from PT. Sorin Setosa in the Krian area, East Java. The samples that have been taken are then tested to have a high COD value in the sample which is up to 2890.31 mg/L.

If this liquid waste is disposed of without treatment first, pollution will be difficult to avoid, especially pollution in the waters because the liquid waste still contains a lot of coloring agents and supporting substances for the dyeing process. These dyes can disrupt aesthetics and the process of penetrating water bodies, thus disrupting the photosynthesis process of aquatic plants. Decreasing water quality with increasing turbidity of water caused by dye pollution will disturb the balance of photosynthesis with the obstruction of light entering the waters, and the emergence of mutagenic and carcinogenic effects of these dyes [1].

2. Advanced Oxidation Process Method

Waste treatment can be divided into 3 processing, namely primary processing, secondary processing and tertiary...
processing [25]. However, many of the processes that have been carried out are still experiencing deficiencies, so that further processing is needed so that the waste can reach the prescribed quality standards. Advanced oxidation process or known as AOPs (Advanced Oxidation Process) is one alternative technology that has been successfully used for pretreatment methods for biological process wastewater treatment [20]. AOPs is a process of generation of free radicals that are very effective in destroying substances organic chemistry. AOPs that will be used in this study is the "Fenton" system, which consists of the reaction of H₂O₂ with Fe²⁺ in forming OH. The Fenton reaction involves several stages where free hydroxyl (OH) and hydroxyperoxyl (HO₂) radicals are intermediate results which are the key to Fenton's system [24].

At present the hybrid system consists of different oxidation combination processes, such as Oxidation-Fenton, Photo-Oxidation, Electro-Oxidation which aims to improve the efficiency of the method of electrochemistry. The mechanism chosen in this study was Electro-Fenton. The mechanism itself is to combine the Electrocoagulation process with Fenton Reaction and carried out together, the results are quite good in purifying wastewater [2]. In this research method, Electro-Fenton is carried out in batches and simulations of continuous reactor circuits based on kinetics data obtained from batch reactor experiments.

This study aims to obtain optimum operating conditions in textile industry wastewater treatment using advanced oxidation alternative technology based on AOPs with batch electro-Fenton method and continuous reactor circuit simulation based on kinetics data obtained from batch reactor experiments. Next, a study of the performance of Electro-Fenton in the degradation of COD content and color in the wastewater of the textile industry will be conducted.

Characteristics of Yarn Dyeing Waste

Liquid waste from the textile color dyeing process is a source of water pollution which is quite high if no waste treatment is carried out. Textile dyes are generally made from azo compounds and derivatives which are benzene groups. It is known that benzene groups are very difficult to degrade, even if possible it takes a long time [18]. There are various kinds of chemical dyes used in coloring batik and textiles, including indigosol, naptol and rapid.

Rapid color substances are commonly used for rapid fast type lines. This dye is a mixture of naptol components and stabilized diazocium salt. Naptol dyes are a textile dye that can be used to dye quickly and have a strong color [14].

Diazonium is one group of azo dye derivatives with two azo groups (-N=N-) which bind to an aromatic amine. Generally rapid that is widely used is rapid red, because the color is bright and not found in the indigosol group [14].

Waste from textile dyes containing azo is difficult to decompose with biological processes and takes a long time [5]. This is due to the existence of a double bond (-N=N-) on azo compounds. This double bond (-N=N-) must be broken down in order to describe the environmental pollution caused [9]. The most worrying in coloring using diazonium salts is the effect of mutagenicity and carcinogenicity [16].

An alternative decomposition of diazo double bonds (–N=–N) in rapid color waste is with AOPs (Advanced Oxidation Processes). AOPs methods have been widely applied with various pollutant decomposition results with various advantages. Therefore, the effectiveness of this technology is carried out on the derivative dye "Azo Rapid" in the hope that it can provide efficiency in decreasing the color value higher than other methods with a relatively short time [12].

Electrocoagulation Method

Currently hybrid systems consist of different oxidation processes, such as Fenton oxidation, Photo-Oxidation, Electro-Oxidation, often used to improve the efficiency of the electrochemical method. In the Electro-Fenton method, the mechanism of electro-coagulation and Fenton is carried out together, and the results obtained are quite good in the treatment of polluting wastewater [2].

3. Electro-Fenton Method

In general, there are two different Electro-Fenton applications. The first is the Electro-Fenton system where Fenton reagents (Fe²⁺ and H₂O₂) are added to the reactor from the outside, and use an inert electrode which has a high enough catalytic. The second is the Electro-Fenton system where H₂O₂ is added from the outside, and Fe²⁺ is provided at the expense of the anodize [2].

This study aims to obtain optimum operating conditions in degrading COD content and color of textile industrial wastewater by using the AOPs processing method of Electro-Fenton.

This research was conducted in two stages, namely experiments in a batch reactor and continuous reactor simulation based on kinetics data obtained from batch reactor experiments. The reactor model used is a continuous stirred-tank reactor according to [6] which is equipped with a magnetic stirrer as a stirrer and is called a stirred continuous fenton photo reactor. The effect of the feed flow rate on reactor performance is expressed as the residence time of feed in the reactor to the percentage decrease in the content of organic matter in waste. The feed residence time is the ratio of the reactor volume to the volumetric flow rate of the feed.

Electro-Fenton Chemical Reactions

The Electro-Fenton method produces Fe²⁺ and/or H₂O₂ with an electrochemical process. The carbon felt cathode, carbon-PTFE O₂ diffusion, BDD, reduces O₂ with the following equation (...) [11].
During the Electro-Fenton process, molecular oxygen and iron anodes are electrolyzed oxidized by the cathode to produce hydrogen peroxide and iron ions according to reactions (1) and (2):

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$  

(1)  

Iron anodes are oxidized with the following (...) equation:

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$  

(2)  

•OH radicals obtained from simultaneous electrochemical reduction O$_2$ with the presence of iron ions as catalysts [19].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH$$  

(3)  

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$  

(4)  

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$$  

(5)  

With this reaction hydroxyl radicals can form which, if large and strong, can degrade organic compounds. The constant rate of reaction of iron ions with hydrogen peroxide (H$_2$O$_2$) itself is high which makes it possible to produce a more stable decrease, and provides an advantage with the increased biodegradability during the process [22].

For color degradation the mixture between peroxide (H$_2$O$_2$) and ferrous ions or Fe (II) or iron (II) can produce hydroxyl radicals as the following reaction.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH$$  

(6)  

$$HO + Dye \rightarrow Dyes \text{ are oxidized} + H_2O$$  

(7)  

The addition of Fe$^{2+}$ and H$_2$O$_2$ can increase the decrease in COD and color values. The hydroxyl radicals formed by the reaction between iron ions [II] (Fe$^{2+}$) and H$_2$O$_2$ destroy the existing dye molecules to be smaller [7].

Substances found in this artificial waste are Azo derivatives. Azo dyes have a special bond, namely the double bond of Nitrogen (-N=N-). The result of decreasing the color absorbance value indicates that the hydroxyl radical formed from the Fenton reagent reaction will attack the azo group bond on the dye molecule [23].

**4. Research Methods**

**4.1. Research Materials**

Waste water comes from the textile industry, yarn dyeing, Fero Sulfate (FeSO$_4\cdot7H_2O$), Sulfuric Acid (H$_2$SO$_4$), Hydrogen Peroxide (H$_2$O$_2$).

**4.2. Research Equipment**

The glass reactor measures 0.2 m x 0.2 m x 0.3 m with a total volume of 12 liter reactors. The reactor is adjusted to the sample volume of 6 liters, power supply, reservoir, discharge regulator and outlet tub, stirring magnet and magnetic stirrer, iron electrode and stainless steel, pH meter to measure sample pH at the beginning and end of the process, analytical scales used to weigh FeSO$_4\cdot7H_2O$.

**4.3. Ways of Working**

A. Preliminary Research

Acidification of wastewater becomes the specified pH. The fenton reaction takes place at acidic pH<5, and the optimal
Electro-Fenton process takes place at pH 3-5. So before the wastewater is put into the reactor it is conditioned at acidic pH 4. Acidification of used wastewater $\text{H}_2\text{SO}_4$.

Reactor Process Batch Variation of Electric Voltage and Electrode Distance

Add as much as 6 liters of waste into the reactor.

$\text{H}_2\text{O}_2$ and $\text{FeSO}_4$ are inserted into the reactor which already contains waste based on the ratio of $\text{H}_2\text{O}_2$: $\text{FeSO}_4$ (M/M): 10:0.2. The waste is stirred with a magnetic stirrer at a speed of 200 rpm for 30 minutes.

Current variations of 6 Volts (Electrode Distance 2 cm), 7 Volts (Electrode Distance 4 cm), and 8 Volts (Electrode Distance 6 cm) electrolysis time are 30, 60, 90, 120, and 180 minutes and each electrode is immersed in an area of 0.15 m x 0.10 m.

After the electrolysis is complete, then the floc is formed and allowed to settle until perfect. Samples in the form of clear water were taken to test the pollutant levels.

Waste samples that have passed the Electro-Fenton test will be deposited 2-4 hours so that the sediment drops completely and then tested the COD and color parameters.

Process Reactor Batch Fenton Dose Variations

The same is done with the previous variation, but the voltage is set at 6 volts, the electrode distance is 4cm, with the electrolysis time and stirring for 30, 60, 90, 120, and 180 minutes.

A variation of the molarity of $\text{H}_2\text{O}_2$: $\text{FeSO}_4$ (M/M) 10:0.10, 10:0.20, 10:0.30 was carried out.

B. Continuous Reactor System Process

Conducted with an electro-Fenton process continuously (continuous), where the results of time, variations in current strength and distance of the best electrodes will be used to run the continuous reactor in order to determine the discharge and running time.

In this experiment the sampling time was carried out in the processing time for 60,120,180,240 and 300 minutes.

Test samples were carried out on the flow of wastewater flowing at the specified time from the reactor outlet.

Waste samples that have passed the Electro-Fenton test will be deposited for 2-4.

5. Results and Discussion

5.1. Electric Voltage Variation and Electrode Distance of Batch Reactors

In the Electro-Fenton process with variations in the voltage and electrode distance, the aim is to determine how much influence the Electro-Fenton process in batches has on COD and color reduction in textile industry waste.

In the process of electrocoagulation it has a great influence on the amount of stress and contact time. The greater the voltage, the stronger current, and the contact time, the greater the decrease or decrease in the content in the waste. [17].

Based on the data obtained the highest COD reduction results at 6volt electrical voltage variation and 2cm electrode distance with 180 minute contact time which is equal to 92.9% of the initial COD. Meanwhile, the lowest reduction of chemical oxygen demand (COD) was at a variation of 7volt electrical voltage and 4cm electrode distance with a contact time of 30 minutes which was 63.3% of the initial concentration.

The decrease percentage is seen increasing from the contact time of 60 to 180 minutes. This is because the longer the contact time that continues in the Electro-Fenton process will produce more OH radicals, so that it can oxidize organic matter into a simpler element and can improve processing efficiency [21]. The OH formation reaction - more than the $\text{H}^+$ ion makes the pH in the Electro-Fenton process become more alkaline, so that at 180 minutes the base gain is obtained from pH 4 to an average of 9.7.

Based on the data obtained the highest color reduction results on the variation of 8 volt electric voltage and 6 cm electrode distance with a contact time of 180 minutes which is equal to 99.5% of the initial color. While for the lowest color reduction at 7 volt electric voltage variation and 4 cm electrode distance with 30 minutes contact time which is equal to 31.5% of the initial concentration.
5.2. Fenton Batch Reactor Dosage Variations

The Electro-Fenton process with fenton dosage variations aims to determine how much influence the batch Electro-Fenton process has in reducing COD and color in textile industry waste.

In this variation the molarity ratio of $\text{H}_2\text{O}_2$: $\text{FeSO}_4$ (M/M) was varied to 10: 0.10, 10: 0.20, 10: 0.30. By setting an electric voltage of 7 volts with a 4cm electrode distance.

Addition of the molar ratio of $\text{FeSO}_4$ would accelerate the reaction so that it could increase the percent allowance [24]. Comparison of too high molar $\text{FeSO}_4$ ratios will cause dissolved iron ions and decrease percent color removal, but if the ratio of $\text{FeSO}_4$ molar ratio is too low it will result in self saving OH, so the ratio of molar ratio $\text{H}_2\text{O}_2$: $\text{FeSO}_4$ must be in a balanced state.

![Figure 7. Relationship between decreased COD levels (%) with fenton doses and contact time (minutes).](image)

It can be seen that the highest reduction in chemical oxygen demand (COD) is indicated by the molarity ratio of $\text{H}_2\text{O}_2$: $\text{FeSO}_4$ of 10: 0.1 with a contact time of 180 minutes which is equal to 94.1% from the initial chemical oxygen demand (COD) with the voltage set 7 volts and the electrode distance that has been set is 4 cm. While the lowest decrease was shown by the molarity ratio of $\text{H}_2\text{O}_2$: $\text{FeSO}_4$ of 10: 0.2 at 30 minutes, which is 63.3%. The percentage of decrease is seen to increase from the contact time of 60 to 120 minutes.

![Figure 8. Relationship between decreasing color content (%) and fenton dose and contact time (minutes).](image)

5.3. Continuous Electro-fenton Study

The process in continuous Electro-Fenton research is an experiment with the best average results from batches. With the average batch yield, the voltage determined is 6 volts with a 2cm electrode distance with a cross section area of 10 cm x 15 cm. Determination of $\text{H}_2\text{O}_2$: $\text{FeSO}_4$ is also determined which is 10: 0.1 Determination of contact time is 1 hour. With 6 liter x 5 waste sampling, the total waste in the reservoir is 30 liters, and the discharge is 0.1 liters per minute with the following calculations:

Discharge calculation:
\[ \text{Discharge (Q)} = \frac{\text{Volume (V)}}{\text{time (T)}} = \text{m}^3/\text{minute} \]

![Figure 9. Relationship between a decrease in COD level (%) and contact time (minutes) in a continuous Electro-Fenton process.](image)

It can be seen from the graph that with increasing processing time it will increase the efficiency of decreasing color absorbance. The percentage decrease will increase starting from the exposure time of 10 minutes to 120 minutes. The best result of this process is the molarity ratio of $\text{H}_2\text{O}_2$: $\text{FeSO}_4$ of 10: 0.1 at the contact time of 180 minutes which is equal to 99.2% of the initial color.

While the lowest decrease was shown in the molarity ratio of $\text{H}_2\text{O}_2$: $\text{FeSO}_4$ of 10: 0.3 at 30 minutes, which is 12.9%. The electrical voltage and electrode distance in this study have been set at 7 volts and 4 cm. The presence of more OH-formation reactions is also from the H+ ion making the pH in the fenton process to be more alkaline, so that at 180 minutes the pH increases from 4 to an average of 9.7.

![Figure 9. Relationship between a decrease in COD level (%) and contact time (minutes) in a continuous Electro-Fenton process.](image)
charged Fe(OH)_2 colloid because the surface binds H^+ ions. In this Electro-Fenton process it is maximized by fenton combination ie Decayed Fe^{2+} can increase the performance of the Fenton reagent in reducing COD [10].

During the Fenton Electrical process, molecular oxygen and iron anodes are electrolyzed reduced by the cathode to produce hydrogen peroxide and iron ions according to reactions (4.1) and (4.2):

\[ \text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+} \] (10)

On the surface of the electrode the iron anode is oxidized with the following equation:

\[ \text{Fe}^{3+} + 2(\text{OH})^- \rightarrow \text{Fe(OH)}_2 \] (11)

\[ \text{Fe(OH)}_2 + \text{X} \rightarrow \text{Deposition Floc} + \text{H}_2\text{O} \] (12)

Whereas on this Electro-Fenton OH radical is produced from the formation of fenton reagents, so that it can oxidize organic matter into a simpler element and can improve processing efficiency [21]. The oxidation process of organic molecules with Fenton reagents has a process, namely organic molecules are decomposed rapidly continuously due to the speed of formation of OH radicals from the reaction of H_2O and Fe^{3+} [3]. As organic molecules are decomposed quickly, suspended solids will also be eroded due to the formation of Fe(OH)_3 iron ions which will bind the decomposed solids (X) to waste. So that suspended solids are also precipitated at alkaline pH. [21] The Fenton reaction itself can be explained by chemical reactions like the following:

- OH radicals are obtained from simultaneous electrochemical reduction of O_2 with the presence of iron ions as catalysts [19].

\[ \text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{OH}^- + \text{OH}^- \] (13)

\[ \text{OH}^- + \text{RH} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{X} \] (14)

\[ \text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3 \] (15)

\[ \text{Fe(OH)}_3 + \text{X} \rightarrow \text{Deposition Floc} \] (16)

In dye degradation if it is more efficient in acidic media because of better sensibility than the protonated form for the oxidation process. For all compounds, organic dye loss is visually significant according to the charge obtained from electrolysis. The electrophilic addition of OH • to the azo double bond causes breaking up quickly. Rapid clarification of the solution has to do with the bond (-N=N-) reinforcing this suggestion. Detection of degradation products such as hydroquinone confirms this hypothesis. The breakdown of
azo bonds is responsible for the loss of chromophoric characteristics and results in the formation of aromatic intermediates [13]. The result of decreasing the color absorbance value indicates that the hydroxyl radical formed from the Fenton reagent reaction will attack the azo group bond on the dye molecule [23].

The degradation of azo dyes not only breaks the azo bond, but also the degradation of the aromatic ring. The COD measurements in this study indicate that the reaction follows a decrease by means of total mineralization (reduction in Azostain substances). It must also be mentioned that the final degradation products are mineral ions such as NH₄⁺, NO₃⁻, and SO₄²⁻ according to the groups of substituents included in the initial molecule, as well as CO₂ and H₂O [15].

Example Azobenzene mineralization through oxidative reactions by hydroxyl radicals follows equation (17) [8]:

\[
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH} \\
\text{C}_6\text{H}_4\text{N}_2\text{O}_6 + 68 \text{OH}^- \rightarrow 12\text{CO}_2 + 38\text{H}_2\text{O} + 2\text{H}^+ + 2\text{NO}_3^- \tag{18}
\]

It can be seen that the average reduction in COD and color is quite effective. But the settling floc will always increase with the length of the processing time. The sediment floc generally still has a fairly high water content and becomes mud. For this reason, the mud in the reactor must be considered more. Further processing needs to be carried out regarding mud during the process for further research. Because Electro-Fenton can be a pre-treatment processing, sludge treatment that can be recommended is thickening or sludge thickening, sludge stabilization, sludge dewatering, sludge drying and others. The main purpose of sludge treatment is to reduce the volume of sludge by separating water from the sludge before being discharged, so as to facilitate transportation problems.

In determining the processing method, it should be based on the characteristics of the waste to be processed. If the waste to be treated has the characteristics of organic matter, it is more effective to use a chemical method because of the organic content present in waste, especially staining waste is difficult to decompose by biological methods because it has a series of stable chemical compounds. So it can be concluded that processing using a combination of Electro-Fenton is more effectively applied to wastes that have characteristics of organic materials and many chemicals contained therein.

6. Conclusion

From the results of the research and discussion conducted, conclusions can be drawn as follows:

In Electro-Fenton in batch variations on electrical voltage and electrode distance. The best results in this study were 6 volt electricity voltage and 2cm electrode distance with a COD reduction percentage of 92.9%. For color, the best results of this variation were 8 volt electricity voltage and 6 cm electrode distance with a 99% color reduction percentage. 5%. In this study the molarity ratio was determined H₂O₂: FeSO₄ 10: 0.2.

Electro-Fenton in batches of Electro-Fenton fenton dose variations in batches. The best results in this study were the ratio of molarity of H₂O₂: FeSO₄ 10: 0.1 with a percentage of COD reduction of 94.1%. For color, the best result of this variation is the molarity ratio of H₂O₂: FeSO₄ 10: 0.1 with a color reduction percentage of 99.2%. In this study the voltage and electrode distance were determined, namely 7 volt and 4 cm.

In a continuous Electro-Fenton trial, the best results in this study were 5 hours/300 minutes contact time with a COD reduction percentage of 83.2%. For color, the best result of this variation is the contact time for 5 hours/300 minutes with a color reduction percentage of 92.9%. In this study the voltage and electrode distance were determined from the best results from Electro-Fenton in batches with variations in electrical voltage and electrode distance of 6 volt and 2 cm, while the molarity ratio was determined H₂O₂: FeSO₄ 10: 0.1. It can be concluded in this Electro-Fenton study, that the closer the electrode distance is, the more current is strong, so that more H₂O₂ is formed to help the reaction of Fenton and Fe(OH)₂ as coagulants to help reduce organic pollutants. At Fenton, it can be seen that the addition of the right molar ratio of H₂O₂: FeSO₄ will accelerate the reaction thereby increasing the percent decrease. If the dose of fenton with a high ratio of molarity will cause dissolved iron ions, reagent fenton is unstable and the precipitate formed will disturb the electrolysis process in decreasing the percent decrease.

References


