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Degradation of Congo Red in batik wastewater using fenton reagent under visible rays

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Abstract. Congo Red is one of synthetic dyes used in the process of making batik. Batik wastewater which contained Congo red leads to environmental pollution. Fenton reagent can be used to degrade Congo red based on formation of hydroxyl radicals ($\bullet OH$). Hydroxyl radical is able to decompose Congo red compound through oxidation process. Fenton reagent is a mixture from hydrogen peroxide (H_2O_2) with Fe^{2+} ions produced from $FeSO_4$ compounds. The function of visible rays in H_2O_2/Fe^{2+} system is to accelerate and increase the formation of hydroxyl radicals. The formation of hydroxyl radicals are affected by pH condition in the solution. The purpose from this research is to degrade Congo red in batik wastewater using fenton reagent under visible rays. The parameters varied were H_2O_2 concentration, $FeSO_4$ weight and pH. The results showed that visible rays in the system can increase Congo red degradation in batik wastewater. The decrease level of Congo red using fenton/Vis is 63% with added up H_2O_2 50 ppm, $FeSO_4$ 0.2 gram with visible light irradiation for 7 hours. The optimum pH conditions for fenton/Vis system is pH 2 with decrease level of Congo red is 98.19%.
Keywords: Congo red, batik wastewater, degradation, fenton reagent.

1. Introduction

The development of batik industry in Indonesia is currently progressing quite rapidly. It can cause a positive impact that is improving people's welfare. However, activities in the field of clothing is also a negative impact on the environment that is environmental pollution. Environmental pollution due to batik industrial waste is currently quite apprehensive. Colored wastes produced by the batik industry can cause damage to aquatic ecosystems due to the high concentrations of organic compounds contained therein [1].

One of the synthetic dyes contained in batik waste is Congo red. The presence of Congo red on water bodies has a serious effect on the life of microorganisms even at relatively low concentrations [2]. A large amount of Congo red in water can cause a decrease in dissolved oxygen levels. Reduced levels of dissolved oxygen in aquatic systems will disrupt the living ecosystems of animals and plants in water, also can kill live aerobic bacteria [3].

Pollution of Congo red in the waters can cause taste and odor, and at certain concentrations can cause the death of organisms in the waters. In addition, if it consumed can cause health problems in humans such as disorders of the brain, lungs, kidneys and spleen and can cause failure of blood circulation and death due to respiratory failure. Due to that reason we need a processing, as an effort to reduce levels of Congo red in waste water so that it becomes safe for the environment [4].

Some technology has been done for Congo red waste treatment, among others, by the method of physical processing of adsorption, filtration and reverse osmosis. Chemical processing methods are ion
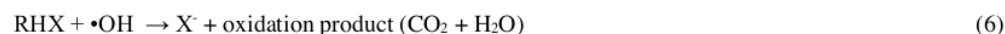
exchange and extraction, as well as biological treatment methods namely aerobic and anaerobic processes [5]. However, according to Dakhil [6] the method requires several stages of the process, chemicals, and produce residues that are harmful to health.

One of the innovative technologies to degrade Congo red is the Advanced Oxidation Processes (AOPs) method, with a harmless, eco-friendly, and CO_2 and H_2O end result. AOPs are systems based on the very strong oxidative properties of hydroxyl radicals (•OH). This radical can be produced from a combination of hydrogen peroxide with a ferro ion (Fe^{2+}) commonly referred to as the Fenton reagent [7].

Combined method of hydrogen peroxide and visible light is the most studied method and tried to treat various types of liquid waste. Hydrogen peroxide (H_2O_2) is an agent that has strong oxidizing properties that capable to oxidizing mixture of salt and not salt in aqueous media. Visible light (Vis) is also capable of triggering the breaking of bonds in organic compounds. The combination of both treatments, hydrogen peroxide and visible light can result in a more efficient and faster process for solving the problems of pollutants [8].

Fenton reagents may act as oxidizing agents and coagulants in the liquid waste treatment process. The fenton reagent is a mixture of the ferro (Fe^{2+}) ions as a catalyst and the H_2O_2 as an oxidizing reagent. The Fenton reagent is a very strong oxidizing agent for organic contaminants because it produces a hydroxyl radical having a large reducing potential value of 2.8 V. This reagent is an effective reagent for wastewater treatment [8].

The iron (II) ion in the fenton reagent acts as a catalyst to accelerate the decomposition of hydrogen peroxide to form a hydroxyl radical. The mechanism of the fenton reaction is shown in the equation below [9] :

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + •OH + OH^- \tag{1}$$

$$•OH + H_2O_2 \rightarrow H_2O + HO_2• \tag{2}$$

$$Fe^{3+} + HO_2• \rightarrow Fe^{2+} + H^+ + O_2 \tag{3}$$

$$Fe^{2+} + HO_2• \rightarrow Fe^{3+} + HO_2^- \tag{4}$$

$$Fe^{3+} + OH^- \rightarrow Fe^{2+} + •OH \tag{5}$$

$$RHX + •OH \rightarrow X^- + \text{oxidation product } (CO_2 + H_2O) \tag{6}$$

(RHX= organic compound)

The photofenton process is a development of the fenton process by adding ultraviolet lights to accelerate and multiply the hydroxyl radicals formed. This process ($Fe^{2+}/H_2O_2/Vis$) implicates hydroxyl radical (•OH) formation by hydrogen peroxide photolysis (H_2O_2/Vis) and Fenton (Fe^{2+}/H_2O_2) reaction. The presence of visible light causes the ferrite ion (Fe^{3+}) formed in the fenton reaction to be converted back into ferrous (Fe^{2+}) ions with the formation of a new hydroxyl radical [10].

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + •OH + H^+ \tag{7}$$

2. Methodology

2.1. Effect of H_2O_2 Concentration on Congo Red Degradation
A total of 500 mL of Congo red samples added to the beaker glass, followed by H_2O_2 solution with concentration variations of 10, 20, 30, 40, 50, 60, and 100 ppm. The sample stirred for 8 hours in the dark room, then taken as much as 10 ml and measured the Congo red level at maximum wavelength. This was also done for the H_2O_2 system with irradiation for 8 hours. Hence, the optimum concentration of H_2O_2 obtained.

2.2. Effect of FeSO₄ Weight Increase on Congo Red Degradation

A total of 500 mL of Congo red samples added into a beaker glass, then added with $FeSO_4.7H_2O$ powder with a weight variation of 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; and 1 gram. The sample stirred for 8 hours in the dark room, then taken as much as 10 mL and measured the Congo red level at maximum wavelength. This was also done for $FeSO_4/H_2O_2$ system with irradiation for 8 hours. Hence, the optimum weight of $FeSO_4.7H_2O$ obtained.

2.3. Influence of Radiation Exposure Time of the H₂O₂/FeSO₄ (Fenton) System on Congo Red Degradation

A total of 500 mL of batik wastewater sample added into beaker glass then added $FeSO_4.7H_2O$ powder at optimum weight and H_2O_2 at optimum concentration. The mixture stirred in the dark room for 8 hours. Every hour sample captured 10 mL and measured the Congo red level at maximum wavelength. This was also done for the $FeSO_4/H_2O_2/Vis$ system so that the optimum time obtained.

2.4. Effect of pH on Fenton and Fenton/Vis Systems on Congo Red Degradation

A total of 500 mL of batik wastewater sample (at the optimum condition of $FeSO_4/H_2O_2$ and $FeSO_4/H_2O_2/Vis$) plus H_2SO_4 and/or NaOH then stirred to obtain a solution of variation pH 2, 3, 4, 5, 6 then irradiated Vis during optimum time. Samples took as much as 10 mL and measured the Congo red level at maximum wavelength.

3. Results and Discussion

3.1. Variation of H₂O₂ Concentration

Reduced levels of Congo red using H_2O_2 system and H_2O_2/Vis system are each done by varying the concentration of H_2O_2. This system is performed in dark spaces (without visible light radiation) and with Vis radiation. The results of Congo red degradation for H_2O_2 and H_2O_2/VIS systems are shown in Fig. 1:
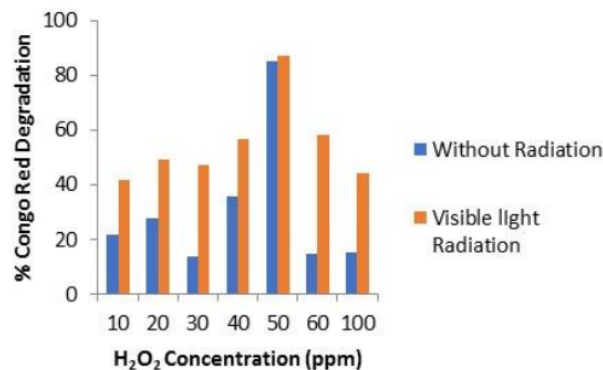

Figure 1. Effect of H_2O_2 Concentration on Congo Red Degradation.

The hydrogen peroxide compound is one of the strong oxidizing agents because it has a reduction potential value of 1.78 V. The reaction between hydrogen peroxide and Congo red in batik liquid waste is an oxidation-reduction reaction. Hydrogen peroxide is reduced to water while Congo red will oxidize to ketones and aliphatic carboxylic acids [11] The H_2O_2/Vis system uses visible light radiation to break the O-O bonds in hydrogen peroxide to produce hydroxyl radicals (•OH). According to Deng and Zhao (2015) the reaction of (•OH) formation is shown in the reaction below:

$$H_2O_2 + Vis \rightarrow \bullet OH + \bullet OH \tag{8}$$

Based on Fig. 1 it is seen that the greater the concentration of H_2O_2 is added, the Congo red degradation will increase as more OH is formed. However, the addition of too much H_2O_2 concentration causes Congo red degradation to be less effective, because of the reduced number of OHs formed. Excess H_2O_2 reacts with •OH to form a hydroperoxyl radical having a lower reduction potential value than OH at 1.70 V [7]. The reaction of hydroperoxyl radical formation is shown in the equation:

$$H_2O_2 + •OH \rightarrow HO_2• + H_2O \qquad (9)$$

$$HO_2• + •OH \rightarrow H_2O + O_2 \qquad (10)$$
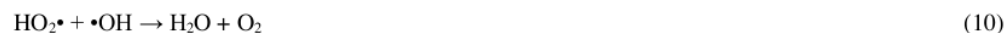
3.2. FeSO₄ Weight Variation
Degradation of Congo red or decreased Congo red level in batik wastewater in this system is done by varying $FeSO_4$ weight.
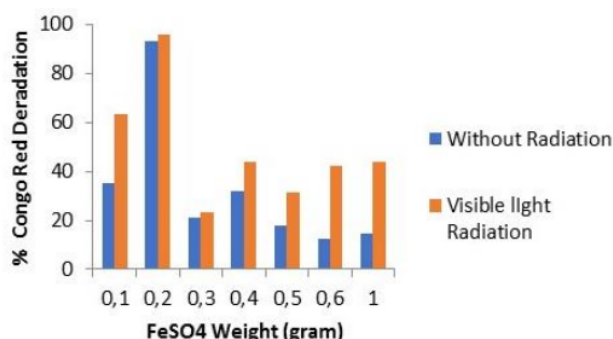

Figure 2. Effect of $FeSO_4$ Weight on Congo Red Degradation.

Based on Fig. 2 it is seen that the more $FeSO_4$ addition to the waste then the percentage of Congo red degradation will be greater. The reaction occurring in the $FeSO_4$ system is shown in the equation [12]:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (11)$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad (12)$$

$$Fe^{3+} + Congo\ red \rightarrow complex\ Fe^{3+}\text{-Congo red} \qquad (13)$$

Fe^{2+} and Fe^{3+} ions serve as coagulant so they can bind to the Congo red form a complex. In addition to the amount of $FeSO_4$ added, Vis radiation can also help increase the percentage reduction in Congo red levels in batik waste due to photo Fenton reactions that produce •OH. With oxygen in the environment and the system, Fe^{2+} ions will oxidize to Fe^{3+} while oxygen will be reduced to water [10]. Based on Fig. 2 it is also seen that the more $FeSO_4$ added to the $FeSO_4$/Vis system, the greater the percentage of Congo red degradation. However, if the addition of $FeSO_4$ too much will decrease Congo red percent degradation and it is less effective. The more $FeSO_4$ added after its optimum weight, the rest of ferrous ion will oxidized and produce Fe^{3+}, and this Fe^{3+} ions will made another complex with Congo red and lead degradation processes to less effective.

3.3. The Time of Light Irradiance is Seen in H₂O₂/FeSO4 (Fenton)
In the $FeSO_{4/}H_2O_2$ (Fenton) system performed without irradiation and by varying the irradiation time.
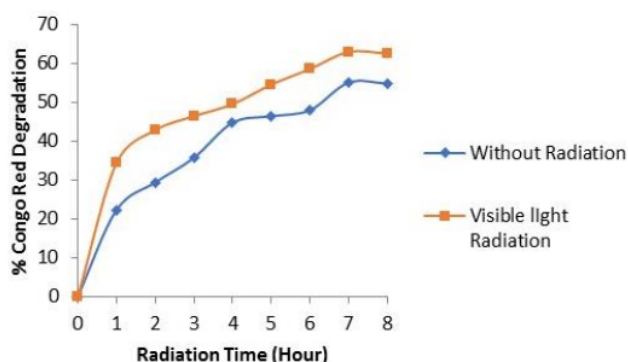
Figure 3. Influence of Radiation Time on Fenton System to Congo Red Degradation

Fig. 3 shows that irradiation with visible light can increase the percentage of Congo red degradation in batik wastewater. The longer irradiation time the percent degradation of Congo red increases sharply. Prolonged exposure time causes the interaction between $FeSO_4/H_2O_2$ with the visible rays to be more effective so that more •OH radicals are generated. The number of radicals •OH which causes many reactions between radicals •OH with Congo red compounds is more effective, so that the content of Congo compounds in wastewater is decreasing. After 7 hours' irradiation time the Congo red level decrease significantly. This is because the Congo red contained in the wastewater may react with other compounds present in the waste to form an intermediet compound [2]. According to Babuponnusami and Muthukumar [10] the decrease in Congo red content in the effluent by oxidation process using fenton will occur in competition with other organic compounds contained in the waste. The formed OH radicals not only oxidize the Congo red but also other organic substances such as the dye present in the batik waste. This resulted in decreased Congo red in batik liquid waste did not reach 100% [13].

3.4. Variations of pH in Fenton and Fenton/UV Systems
The final step in this research is the determination of the optimum pH for phenol degradation in batik liquid waste using fenton and photo Fenton process. The purpose of determining the optimum pH is to determine the best condition of the system to obtain the best percent degradation [8].
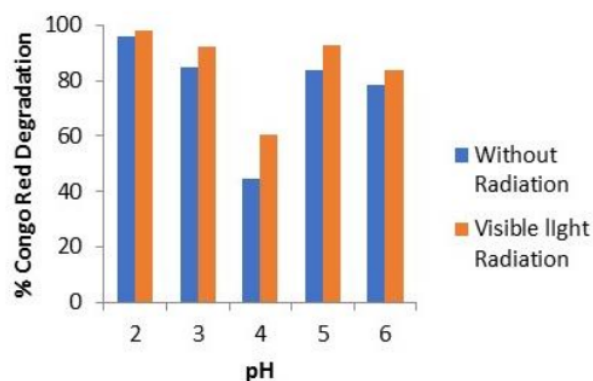

Figure 4. Effect of pH on Fenton and Fenton/Vis systems on phenol degradation.

The pH value is one of the factors that affect the ability of fenton reagents in oxidizing phenols. The best pH conditions were obtained by looking at the highest percentage of phenol degradation. According to Fig. 4, the best pH obtained in the fenton and fenton/Vis systems is pH 2. According to Hadjltaief *et al*. [14] at low pH conditions can increase the degradation of phenol. This is because at low pH with pH = 3, fenton reagents will produce more OH radicals. According to El Haddad *et al*. [15] at a pH above 4 fenton reactions becomes less efficient due to the dissolved fraction of Fe^{2+} ions decreasing. Whereas in pH conditions above 5, more hydroxy iron is formed and causes hydrogen peroxide to lose the ability to oxidize because it decomposes into water (H_2O) and oxygen (O_2). According to Setiyanto *et al*. [16] the reaction of hydrogen peroxide at pH <2 is:

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \tag{14}$$

The reaction of hydroxy formation of iron at pH> 5 is as follows [15]:

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^- \rightarrow Fe(OH)_3 \tag{15}$$
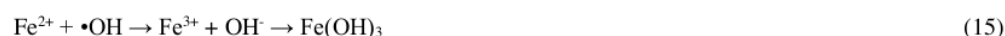
In this condition, the less hydroxyl radical ($\bullet OH$) formed, processes for fenton and photofenton is lack effective, resulting in less degradation of the phenol.

4. Conclusion
Based on the research results, the decrease of phenol content in batik waste using fenton reagent more effectively with the aid of visible light radiation (visible) compared without radiation of light. The optimum concentration of H_2O_2 was 50 ppm while the optimum $FeSO_4$ was 0.2 gram with the decrease of phenol level for H_2O_2, H_2O_2/Vis, $FeSO_4$ and $FeSO_4$/Vis respectively by 85.37%; 87.19%; 93.14%; and 95.86%. The decrease of phenol level in Fenton and Fenton/UV system obtained optimum time is 7 hours with decrease of phenol content respectively by 55,11% and 63%. This happened because a Congo red solution used for H_2O_2 optimum concentration and $FeSO_4.7H_2O$ weight optimum measurement but a batik wastewater used for fenton and fenton/vis measurement. The optimum pH conditions in the process of decreasing the phenol content using Fenton and Fenton/UV are pH 2 with percent degradation for each system is 95.99% and 98.19%.

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