Fenton Oxidation using Easily Recoverable Catalyst of Magnetite (Fe$_3$O$_4$) as an Efficient Approach to Treatment of Rhodamine B Dyeing Effluent in Traditional Fabrics Industry

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KEYWORDS
Chemical oxygen demand (COD)
Colorimetry
Dye wastewater
Fenton reaction
Fe$_3$O$_4$ catalyst

ABSTRACT A direct release of dye wastewater to a water environment without pre-treatment could cause negative impacts. To solve them, an effective method for degrading wastewater contaminants is needed. In this research, the Fenton reaction using Fe$_3$O$_4$ catalyst for removal of wastewater contaminants taken from a traditional fabrics industry was studied. For this purpose, reaction temperature was varied in the range of 27–90°C. Furthermore, catalyst concentration was also varied in the range of 2–6 g/L solution. The results showed that increasing both temperature and catalyst concentration will increase the performance of the Fenton reaction in degrading wastewater contaminants. The contaminant degradation was measured by detecting chemical oxygen demand and inspecting the color of wastewater. The highest reduction of color intensity was 98.96% at 90°C temperature and 2 g Fe$_3$O$_4$/L solution.

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1. INTRODUCTION

Textile industries are regarded notoriously as the main contributor to dye pollution among other industries due to it’s dying as the main process. Approximately 10–15% of the dyes are lost in the wastewater during the dying process (Zollinger 2003). The textile industry contributes to 93% of total manufacturing industrial wastewater. Especially, a traditional industry produces a significant amount of dye wastewater due to lack of proper wastewater treatment. The untreated wastewater containing dye when is dumped to local streams and rivers, it can cause problems such as local water supplies exhausting, visible aquatic environment physical change, and aquatic biota poisoning (Natalija Koprivance 2007). If these problems are left untreated, worse wastewater conditions will be unavoidable then furthermore create negative impacts on humans and other living creatures as well.

Because of their complicated structure, dyes are difficult to be treated by municipal waste treatment. Physical and chemical methods including chemical precipitation, flocculation, adsorption, ion-pair extraction, photolysis, electrochemical treatment, chemical reduction, and chemical oxidation are generally electrochemically used to treat textile wastewater (Azmì et al. 1998; Zhao et al. 2013; Parsa et al. 2014; Ariyanto et al. 2019). The commonly used existing methods have several disadvantages. Most of these methods are high sludge and by-products, ineffective, expensive, produce side reactions, and not suited to degrade all dyes (Krull et al. 1998).

Reffing to the problems of the existing methods, new solutions or existing methods improvement are required to meet industrial need in decreasing dye pollution in wastewater. Heterogeneous Fenton reaction using iron oxide catalyst has gained attention recently due to its efficiency in removing recalcitrant organic contaminants under a wide range of pH for instance for Remazol Black B (de Souza et al. 2010), Sulphur Black (Sarto et al. 2019), and Methylene Blue (Amelia et al. 2019). Fenton reaction relies on the advanced process of oxidation to reduce organic pollutants which a general reaction follows Equation 1 (Isari et al. 2018). Forms of iron oxide catalyst can be Fe$_2$O$_3$ (hematite) or Fe$_3$O$_4$ (magnetite). However, Fe$_3$O$_4$ catalyst has an advantage of easy separation using magnet (Álvarez-Torrellas et al. 2018).

$$\text{active species + contaminants} \rightarrow \text{intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (I)$$

The application of Fenton reaction in removing organic contaminants in dye wastewater needs further evaluation to be eventually implemented in a wider range of industries. In this work, the used dye wastewater was taken from coloring activity of a traditional fabrics industry in Gamping, Sleman, Yogyakarta. The aims of the study are to assess the efficiency of Fenton reaction using Fe$_3$O$_4$ catalyst in degrading organic pollutants in real dyeing effluent and to analyze the influences of several variables consisting of various temperatures and catalyst concentrations towards Fenton reaction-based degradation of dye wastewater. For comparison, Fe$_2$O$_3$ catalyst was also employed.

2. MATERIALS AND METHODS

2.1 Materials

The main materials used for the research are industrial dye wastewater with main component of Rhodamine B from a
traditional fabrics industry in Gamplong village, Sleman, Yogyakarta. The other materials are a 50% hydrogen peroxide (H₂O₂) from Merck and naturally Fe₃O₄ (hematite) and Fe₂O₃ (magnetite) catalysts.

2.2 Procedures

Evaluation of Fenton reaction-based dye wastewater degradation was conducted by three steps consisting of the Fenton reaction step, colorimetry analysis, and chemical oxygen demand (COD) analysis (open reflux method). This was based on the procedures described in literature (Akbar 2019; Prabandari 2019).

2.2.1 Fenton reaction procedure

Wastewater sample was taken about 200 mL and poured into a 500 ml-three-neck flask. Then, the temperature was adjusted by turning on the heater. The Fe₂O₃ or Fe₃O₄ catalyst was then added to a 500 ml-three-neck flask containing the solution. Then, a 5.8 mL of H₂O₂ was poured into the solution. To control solution pH by 3.0, HCl was added to the solution. The sample was stirred by using a stirrer motor with a constant velocity of 200 rpm for 2 hours. Liquid samples were taken periodically for colorimetry analysis. For temperature variation experiment, the used temperatures were 27, 50, 70 and 90°C and amount of catalyst was fixed to 2 g/L. For the catalyst concentration variation experiment, the reaction temperature was set to 50°C while concentration of catalyst was varied to 2, 4 and 6 g/L.

2.2.2 Colorimetry analysis

When Fenton reaction was conducted, a liquid sample was taken about 7 mL for every certain time ranging from 1st to 120th minute. The liquid was filtered using a syringe filter to remove solid catalyst. The sample was then analyzed directly by using spectrophotometry UV/Visible (UV-Vis Shimadzu Mini 1240). Absorbance analysis was performed at 560 nm wavelength.

Percentage of color intensity reduction and kinetics of color degradation were evaluated using Equations 2 and 3, respectively.

\[
\% \text{ Absorbance reduction} = \left( \frac{A_i - A_0}{A_0} \right) \times 100\% \tag{2}
\]

\[
\frac{dA}{dt} = -kA^n \tag{3}
\]

where \(A_i\) is the absorbance at certain time, \(A_0\) is the absorbance prior to reaction, \(k\) is degradation constant and \(n\) is the degradation order.

2.2.3 Open reflux method procedure for COD analysis

The COD analysis was based on SNI 6989.73:2009. In the end of Fenton reaction, about 25 mL of sample was taken by using a volumetric pipette and added to a 250 ml Erlenmeyer flask. Sequence addition of chemicals were then performed (i) 0.5 gram of HgSO₄ and 3-5 boiling stones, (ii) 2.5 mL of sulfuric acid reagent and (iii) 15 mL of 0.25 N K₂Cr₂O₇ solution. For every addition, the solution was homogenized carefully. Erlenmeyer flask was then set to reflux conditions. Sulfuric acid reagent was then added to the funnel from the upper side of the condenser drop by drop. The upper part of the condenser was closed by using a funnel to prevent materials from going outside the system during the heating. Then the condenser was chilled, and the inner part was washed by using 25 mL of distilled water. The reflux condenser was deconstructed after being chilled and the solution was diluted by adding 50 mL of distilled water. The blank solution was prepared by using distilled water and being treated similarly with the sample.

The solution that has been treated with the open reflux method can then be titrated. About 2-3 drops of ferroin indicator were added and excessive K₂Cr₂O₇ was titrated using 0.25 N FAS. Titration was stopped if the solution started to change from blueish-green to reddish-brown for the first time. COD (in ppm) was evaluated using Equation 4.

\[
\text{COD} = \frac{(A_v - B_v)N_{\text{FAS}} 8000}{V} \tag{4}
\]

where \(A_v\) is FAS volume for standard solution titration (mL), \(B_v\) is the FAS volume for sample titration (mL) and \(N_{\text{FAS}}\) is the FAS normality (N).

3. RESULTS AND DISCUSSION

3.1 Performance of Fenton reaction using easy recoverable catalyst of Fe₃O₄

Usage of the catalyst is advantageous based on its performance in accelerating the process of dye degradation in the wastewater using Fenton processes. The post-treatment result compared to pre-treatment condition can be seen in Figure 1. It can be seen that based on visual appearance, the color of the wastewater is removed significantly after Fenton process. The general reaction of contaminant degradation follows Equation 1 where contaminant reacts with active species of radicals producing intermediates and then final products of CO₂ and H₂O (Isari et al. 2018).

One of the most highlighted advantages of Fe₃O₄ usage in the oxidation process in wastewater effluent treatment is simple separation using magnet. Fe₃O₄ has a relatively strong magnetic force. The strong magnetic force makes it possible for the Fe₃O₄ catalyst to be recollected by using a magnet to be able to be used for other oxidation processes.

The illustration of the reusability of Fe₃O₄ can be seen in

![FIGURE 1](image303x78 to 533x290)

FIGURE 1. Side to side comparison between sample before and after being reacted with Fenton Process.
Demonstration of catalyst separation by using magnet.

Figure 2 where the figure shows the easiness of the Fe\textsubscript{3}O\textsubscript{4} catalyst to be separated with the solution simply by attaching the magnet to the surface of the solution container.

3.2 Effect of temperature on the dye degradation

The effect of reaction temperature on decolorization and COD removal of wastewater was investigated by varying reaction temperatures at 30 (room temperature), 50, 70, and 90°C during oxidation with a catalyst loading of 2 g/L. To assess the efficiency of Fe\textsubscript{3}O\textsubscript{4} catalyst usage, the data derived from Fenton reaction using Fe\textsubscript{2}O\textsubscript{3} catalyst is used as the basis of comparison. Figure 3a and 3b shows the comparison of color removal rate and effectiveness between Fe\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{3}O\textsubscript{4} catalyst in Fenton oxidation as a function of time with the variation of reaction temperature. It can be seen that increasing reaction temperature had a positive effect on the color removal of dye wastewater. This is because raising the temperature affects the reaction between H\textsubscript{2}O\textsubscript{2} and iron catalyst by improving the generation rate of ∙OH (Sun et al. 2009; Emami et al. 2010). Other than that, increasing the temperature would also increase the possible collisions between -OH and organic compounds in wastewater due to higher kinetic energy of the molecules and therefore enhancing the decolorization of wastewater. The degradation efficiency for Fenton oxidation using Fe\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{3}O\textsubscript{4} catalysts, as reflected in the percentage of color removal at the end of the reaction, is shown in Table 1.

It is apparent from Figure 3 that both catalysts were effective in dye decolorization, and had similar color removal efficiencies at the end of the reaction. However, the reaction using Fe\textsubscript{3}O\textsubscript{4} catalyst demonstrated a higher color degradation rate than that of the reaction using Fe\textsubscript{2}O\textsubscript{3} catalyst at the initial stages of reaction. This is likely due to the immediate formation of hydroxyl radical which degrading the pollutants into smaller molecules (Wang 2008). Hence, in the case of reaction using Fe3O4 catalyst, the initial rate of mineralization is faster.

For oxidation process using Fe\textsubscript{3}O\textsubscript{4} catalyst, the color removal already reached 89.49% after 120 minutes of reaction at room temperature, and only slightly higher than oxidation process using Fe\textsubscript{2}O\textsubscript{3} catalyst at the same condition i.e. 80.82%. Although the color removal efficiency was best at 90°C for both oxidation mechanisms, the color removal showed a significant increase when the reaction temperature was raised from 30 to 50°C. This is because a higher reaction temperature could lead to H\textsubscript{2}O\textsubscript{2} decomposition. Therefore, no significant amount addition of organic pollutants which could be converted into water, carbon dioxide, and inorganic compounds due to the insufficient amount of -OH radical (Han et al. 2011).

| Temperature (°C) | % Color removal Fe\textsubscript{3}O\textsubscript{4} | % Color removal Fe\textsubscript{2}O\textsubscript{3} |
|-----------------|---------------------------------|---------------------------------|
| 30              | 89.49                           | 80.82                           |
| 50              | 97.41                           | 94.06                           |
| 70              | 98.48                           | 98.50                           |
| 90              | 98.96                           | 99.44                           |

TABLE 1. Color removal efficiency for oxidation processes using Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{2}O\textsubscript{3} catalyst at different temperatures.
Furthermore, Figure 3 also shows the fluctuation of absorbance measurement for oxidation process using Fe₂O₃ catalyst 30 and 50°C, and this case is not seen for oxidation process using Fe₃O₄ catalyst at any given temperature. This is possibly due to the reaction complexity of oxidation using Fe₂O₃ catalyst. To produce -OH radical, unlike oxidation process using Fe₃O₄ which mechanism is direct, oxidation process using Fe₂O₃ must undergo an intermediate step to produce hydroperoxyl radical first. This radical reported having lower oxidation capability than -OH as the main oxidizing agent (Malik and Saha 2003). Thus, for oxidation process using Fe₂O₃ catalyst, there is a higher chance of forming intermediate products that further will not be oxidized at a lower temperature. This is also supported by several studies that resulted that the chemistry and kinetics of the oxidation of organic compounds by oxidation process using Fe₂O₃ catalyst system have not been well elucidated (Wang 2008).

Another important take is the color removal rate expressed by constant and the function of absorbance. The experiments have shown that the rate of color removal is much slower when using Fe₂O₃ than Fe₃O₄. Table 2 shows the change of rate constants (k) as the temperature increased. It shows for both mechanisms that higher reaction temperature resulted in higher rates of color removal in dye wastewater, indicated by the higher k values. The color removal orders respective to absorbance with Fe₃O₄ and Fe₂O₃ were 4 and 2.93, respectively.

For COD, the removal efficiency gradually increased with an increase in the reaction temperature, with the initial COD of dye wastewater was 38400 ppm (Figure 4). This happens because the increase in reaction temperature would generate more -OH radical due to the higher kinetic energy of the molecules. Raising the temperature also enhances the interaction between the pollutants, -OH, and catalyst. Consequently, there will be more organic compounds to be degraded.

### 3.3 Effect of catalyst loading on the dye degradation

Iron catalyst plays an important role in the oxidation. When reacts with H₂O₂, the iron positive charge, either Fe²⁺ (ferrous) or Fe³⁺ (ferric), becomes the ion which breaks down as well as activate H₂O₂ to produce -OH radicals. Without the presence of the catalyst, H₂O₂ needs more activation energy to convert to -OH, and therefore degradation of the pollutant will not reach the optimum result.

To see the effect of catalyst loading in the oxidation process, a series of experiments were conducted at varied loading of Fe₂O₃ catalyst with different concentrations from 2.0, 4.0, and 6.0 g/L. The reaction was set at 50°C to dismiss the effect of temperature in investigating how catalyst loading affected the decolorization as well as COD removal of dye wastewater. The result is shown in Figure 5.

As shown in Figure 5, the addition of catalyst loading would increase color removal rate in the first minutes, represented by the steepness of the curve. Although the higher catalyst loading added to wastewater would increase the color removal efficiency, from Table 3 it can be concluded that there is no significant increase in color removal efficiency as it already reached 97.41% and 94.06% for both catalysts, respectively.

The extent of color degradation increased with increasing catalyst loading because when more Fe²⁺ and Fe³⁺ present, they would most likely react with hydrogen peroxide and generate -OH to further degrade the pollutants. Catalysts, however, as Fe²⁺ and Fe³⁺ donor in the reaction has to be in proportional concentration because too much catalyst could lead to the Fe²⁺ and -OH recombination which hindered the oxidation of organic pollutants (Li et al. 2009). The -OH radicals are trapped by Fe²⁺ in excess as shown in the reaction of Equation 5 according to literature (Bouasla et al. 2010).

### Table 2. Constant parameters to determine the color removal rate for Oxidation using Fe₃O₄ and Fe₂O₃ catalyst with variation in reaction temperature.

| Temperature (°C) | Color removal rate constants (k) / minute⁻¹ | Fe₃O₄ | Fe₂O₃ |
|------------------|---------------------------------------------|-------|-------|
| 30               |                                             | 51.96 | 4.82  |
| 50               |                                             | 360.58| 22.40 |
| 70               |                                             | 3483.70| 29.02 |
| 90               |                                             | 5613.90| 132.73|

### Table 3. Color removal efficiency for oxidation processes using Fe₃O₄ and Fe₂O₃ catalyst at different catalyst loading.

| Catalyst loading (g/L) | % Color removal | Fe₃O₄ | Fe₂O₃ |
|------------------------|-----------------|-------|-------|
| 2                      |                 | 97.41 | 94.06 |
| 4                      |                 | 96.87 | 95.99 |
| 6                      |                 | 97.67 | 98.56 |

![Comparison of COD values at the end of reaction after treatment using Fe₂O₃ catalyst and Fe₃O₄ catalyst with variation in reaction temperatures.](image)

![Correlation between absorbance and time for Fe₃O₄ based Fenton reaction with varied catalyst loadings. Reaction temperature: 50°C.](image)
Fe\(^{2+}\) + \cdot \text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^– \quad (5)

Correspondingly, the increase in catalyst loading would also increase COD removal (Figure 6). For oxidation process using Fe\(_2\)O\(_4\) catalyst, COD removal efficiency increased as much as 23.06% when the catalyst loading was doubled from 2.0 g/L. The difference was not significant when the catalyst loading was tripled to 6 g/L, resulted in only 28.51% in COD removal. As a comparison, oxidation process using Fe\(_3\)O\(_4\) reaches a more significant increase in COD removal efficiency even though the COD values at any variation of catalyst loading were still higher than oxidation process using Fe\(_2\)O\(_4\). The COD removal efficiency raised from 38.79% to 46.81% when the catalyst loading was added from 4.0 to 6.0 g L\(^{-1}\).

4. CONCLUSION

Decreasing contaminants in dye wastewater by using oxidation process and Fe\(_3\)O\(_4\) catalyst is efficient due to the significance of decreased contaminants measured by color degradation and COD value. The colorimetry revealed an efficient color degradation up to 98% when the temperature condition at 50°C. The COD value could tremendously decrease up to 3500 ppm from original value of 38400 ppm. Furthermore, Fe\(_3\)O\(_4\) catalyst is easy to be recover by simple separation using magnet. The result hopefully can be used to solve problems of untreated dye wastewater not only in Indonesia, but also across South East Asian countries. Especially by seeing the rampant traditional dyeing industries that need supports for wastewater treatment in the region.

ACKNOWLEDGMENTS

The authors thank Dr. Macarena Munoz of Universidad Autonoma Madrid for the gift of the sample of catalysts. The authors would also like to thank Gamplong’s traditional industry owner for providing the sample for the research.

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