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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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.

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 dyeing 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 used to treat textile wastewater (Azmi 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).

Referring 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).

$$\text{active species} + \text{contaminants} \rightarrow \text{intermediates} \rightarrow CO_2 + H_2O \tag{1}$$
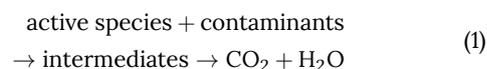
The application of Fenton reaction in removing organic contaminants in dye wastewater needs further evaluation to be eventually implemented in a wider range of industries. In this work, the used dye wastewater was taken from coloring activity of a traditional fabrics industry in Gamplong, Sleman, Yogyakarta. 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 (H_2O_2) from Merck and naturally Fe_2O_3 (hematite) and Fe_3O_4 (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 Fe_2O_3 or Fe_3O_4 catalyst was then added to a 500 ml-three-neck flask containing the solution. Then, a 5.8 mL of H_2O_2 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.

$$\% \text{ Absorbance reduction} = \left(\frac{Ai - Ao}{Ao}\right)100\% \qquad (2)$$

$$\frac{dA}{dt} = -kA^n \qquad (3)$$

where Ai is the absorbance at certain time, Ao 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 $HgSO_4$ and 3-5 boiling stones, (ii) 2.5 mL of sulfuric acid reagent and (iii) 15 mL of 0.25 N $K_2Cr_3O_7$ 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 $K_2Cr_2O_7$ 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.

$$\text{COD} = \frac{(A_v - B_v)N_{FAS}8000}{V} \qquad (4)$$

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

3. RESULTS AND DISCUSSION

3.1 Performance of Fenton reaction using easy recoverable catalyst of Fe_3O_4

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 CO_2 and H_2O (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. Fe_3O_4 has a relatively strong magnetic force. The strong magnetic force makes it possible for the Fe_3O_4 catalyst to be recollected by using a magnet to be able to be used for other oxidation processes. The illustration of the reusability of Fe_3O_4 can be seen in

FIGURE 1. Side to side comparison between sample before and after being reacted with Fenton Process.

FIGURE 2. Demonstration of catalyst separation by using magnet.

TABLE 1. Color removal efficiency for oxidation processes using Fe_3O_4 and Fe_2O_3 catalyst at different temperatures.

Temperature (°C)	% Color removal	
	Fe_3O_4	Fe_2O_3
30	89.49	80.82
50	97.41	94.06
70	98.48	98.50
90	98.96	99.44

Figure 2 where the figure shows the easiness of the Fe_3O_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_3O_4 catalyst usage, the data derived from Fenton reaction using Fe_2O_3 catalyst is used as the basis of comparison. Figure 3a and 3b shows the comparison of color removal rate and effectiveness between Fe_2O_3 and Fe_3O_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_2O_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_2O_3 and Fe_3O_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_3O_4 catalyst demonstrated a higher color degradation rate than that of the reaction using Fe_2O_3 catalyst in 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_3O_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_2O_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_2O_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).
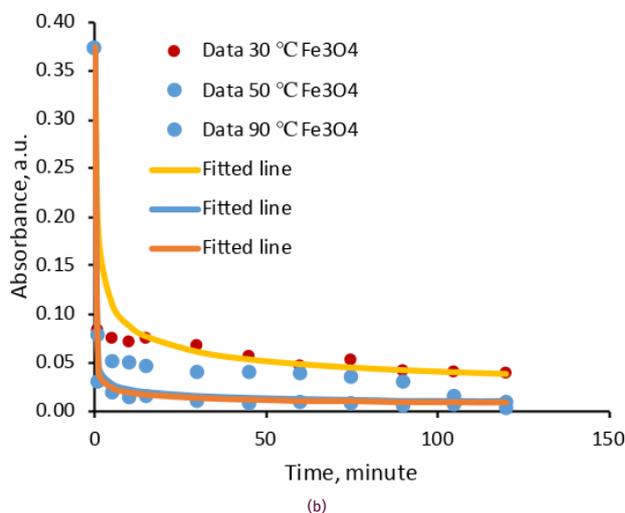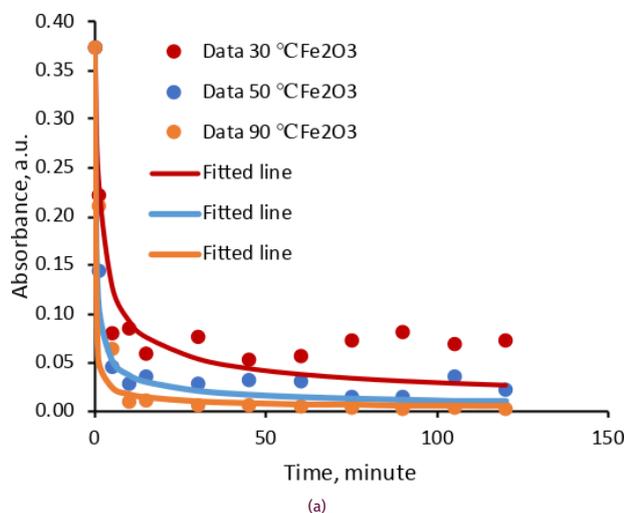

(a)

(b)

FIGURE 3. Effect of reaction temperature on color removal of dye wastewater by Fenton oxidation using Fe_2O_3 and Fe_3O_4 catalyst at 30 to 90°C temperature.

Furthermore, Figure 3 also shows the fluctuation of absorbance measurement for oxidation process using Fe_2O_3 catalyst 30 and 50°C, and this case is not seen for oxidation process using Fe_3O_4 catalyst at any given temperature. This is possibly due to the reaction complexity of oxidation using Fe_2O_3 catalyst. To produce ·OH radical, unlike oxidation process using Fe_3O_4 which mechanism is direct, oxidation process using Fe_2O_3 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 Fe_2O_3 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 Fe_2O_3 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 Fe_2O_3 than Fe_3O_4. 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 Fe_3O_4 and Fe_2O_3 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 H_2O_2, the iron positive charge, either Fe^{2+} (ferrous) or Fe^{3+} (ferric), becomes the ion which breaks down as well as activate H_2O_2 to produce ·OH radicals. Without the presence of the catalyst, H_2O_2 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 Fe_3O_4 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 Fe^{2+} and Fe^{3+} present, they would most likely react with hydrogen peroxide and generate ·OH to further degrade the pollutants. Catalysts, however, as Fe^{2+} and Fe^{3+} donor in the reaction has to be in proportional concentration because too much catalyst could lead to the Fe^{2+} and ·OH recombination which hindered the oxidation of organic pollutants (Li et al. 2009). The ·OH radicals are trapped by Fe^{2+} in excess as shown in the reaction of Equation 5 according to literature (Bouasla et al. 2010).
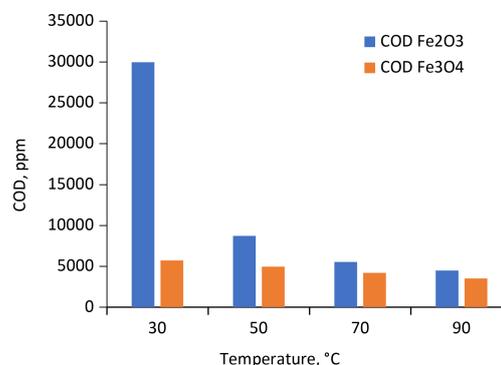
FIGURE 4. Comparison of COD values at the end of reaction after treatment using Fe_2O_3 catalyst and Fe_3O_4 catalyst with variation in reaction temperatures.

TABLE 2. Constant parameters to determine the color removal rate for Oxidation using Fe_3O_4 and Fe_2O_3 catalyst with variation in reaction temperature.

Temperature (°C)	Color removal rate constants (k) / minute-1	
	Fe_3O_4	Fe_2O_3
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 Fe_3O_4 and Fe_2O_3 catalyst at different catalyst loading.

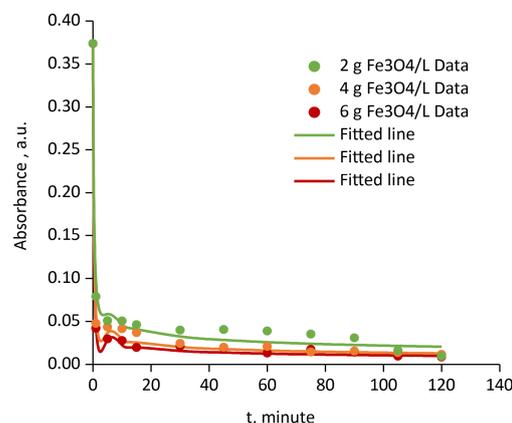| Catalyst loading (g/L)	% Color removal	
	Fe_3O_4	Fe_2O_3
2	97.41	94.06
4	96.87	95.99
6	97.67	98.56

FIGURE 5. Correlation between absorbance and time for Fe_3O_4 based Fenton reaction with varied catalyst loadings. Reaction temperature: 50°C.

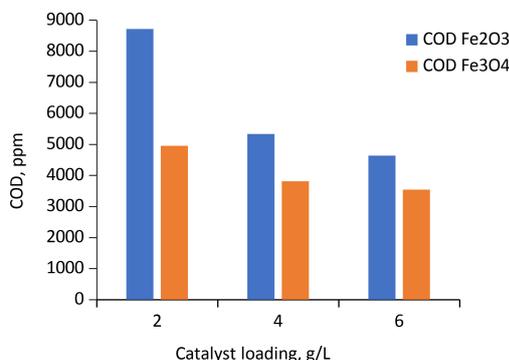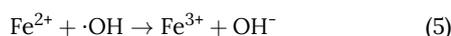FIGURE 6. Comparison of COD values at the end of reaction after treatment using Fe_3O_4 catalyst and Fe_2O_3 catalyst with variation in catalyst loading.

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- \qquad (5)$$

Correspondingly, the increase in catalyst loading would also increase COD removal (Figure 6). For oxidation process using Fe_3O_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_2O_3 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_3O_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_3O_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_3O_4 catalyst is easy to be recover by simple separation using magnet. The result hopefully can be scaled up 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.

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