The effect of reactive red 2 initial concentration on COD and colour degradation by using Fenton, Fenton/TiO₂, Fenton/UV, and Fenton/TiO₂/UV methods

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Abstract. One area that is developing in Indonesia is in the area of textile industry. These industries absorb a lot of labor and contribute to the country's foreign exchange but have a negative impact in the form of wastewater produced. The wastewater produced generally contains synthetic dyes such as Reactive Red 2 (RR2). This synthetic coloring material will pollute the environment if it is not well treated first before being discharged into the environment. In this study, RR2 will be used as a pollutant model. RR2 will be treated by several methods. Pollutant concentration is an important parameter in determining the most appropriate treatment method. The purpose of this research was to study the effect of RR2 initial concentration on reducing COD and color using Fenton, Fenton/TiO₂, Fenton/UV, and Fenton/TiO₂/UV methods. RR2 concentration was varied between 150-300 ppm. As the results, RR2 concentration from 150-300 ppm does not significantly affect the percentage of color degradation. However, at high concentration of 250 and 300 ppm, the percentage of COD degradation decrease by increasing concentration of RR2. When using 150 ppm of RR2, the highest COD and color degradation of 98.8 % and 89.5 %, respectively were achieved by using the Fenton/TiO₂/UV methods.

1. Introduction

One of industry that is growing rapidly in Indonesia is the textile industry. The textile sector is the main non-oil and gas export commodity from Indonesia. The existence of the textile industry has absorbed a lot of labor and generated foreign exchange for the country. No doubt this industry has made a positive contribution to the Indonesian economy. However, every industrial activity must have a side effect in the form of the production of waste, including wastewater from the textile industry. The main source of wastewater in the textile industries is on the use of dyes [1], it is because the textile dyes may be composed of various chemicals, toxins, heavy metals, pharmaceuticals, petroleum based oils, and greases, that are difficult to decompose [2]. The textile industries use a lot of synthetic dyes such as procion, erionyl and auramin [3] because of its relatively cheap price, long-lasting color, more various of color choices and easy to use compare to natural dyes [4]. Textile dyes may interfere the aesthetics, which is immediately visible from the wastewater generated. The colored wastewater will decrease the incoming sunlight into the water body and will inhibit the photosynthesis process. Moreover, it will disrupt the balance of the ecosystem. The synthetic dyes also have the character of carcinogenic and mutagenic material [4].

The Fenton reagents involve the application of ferrous ions (Fe²⁺) to react with hydrogen peroxide (H₂O₂) producing hydroxyl radicals (•OH) with the powerful oxidizing ability to degrade organic...
pollutants in wastewater [5] otherwise there is no energy needed in terms of activating hydrogen peroxide because the reaction takes place at room temperature and atmospheric pressure [6]. Fenton’s reagent is a solution of hydrogen peroxide with dissolved ferrous iron as a catalyst. It is used to oxidize organic contaminant found in industrial wastewaters [7]. The oxidation method with Fenton reagent has been applied for processing various kinds of industrial wastewater containing toxic organic compounds such as olive oil processing industry [8], palm oil processing industry [9], and pesticides [10]. The mechanism of the reaction starts with Fe^{2+} initiating the reaction and catalyzing the decomposition reaction of H_2O_2 to produce hydroxyl radicals (\textcolor{red}{^\bullet}OH) according to the reaction equation:

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \textcolor{red}{^\bullet}\text{OH}
\] (1)

Hydroxyl radical (\textcolor{red}{^\bullet}OH) is able to break down almost all organic compounds, typical application is the destruction of organic solvents that are resistant to biological oxidation such as phenols, formaldehyde, methylene chloride and chlorinated solvents [11]. It will react with dissolved components, and initiate successive reactions through a series of oxidation processes so that the component is degraded. Although involving complex reactions, generally the reactions that occur in Fenton reagents are as follows [12]:

\[
\textcolor{red}{^\bullet}\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^+
\] (2)

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

\[
\text{Fe}^{2+} + \text{HO}_2^+ \rightarrow \text{Fe}^{3+} + \text{HO}_2^-
\] (4)

\[
\text{Fe}_2^+ + \textcolor{red}{^\bullet}\text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^-
\] (5)

If illuminated with a light of an appropriate wavelength (180-400 nm), i.e. ultraviolet and some visible light, Fe^{3+} can catalyze the formation of hydroxyl radicals:

\[
\text{Fe}^{3+} + \text{H}_2\text{O} + \text{hv} \rightarrow \text{Fe}^{2+} + \text{H}^+ + \textcolor{red}{^\bullet}\text{OH}
\] (6)

Photocatalyst is a catalyst that works when given a certain wavelength of light. Photocatalysts are generally a semiconductor that has a full valence band and an empty conduction band such as TiO_2. The TiO_2 is a catalyst that is often used in the photocatalysis process because of its superiority. If the semiconductor is subjected to a certain wavelength of light, the electrons will be excited from the valence band to the conduction band to produce a hole in the valence band [13]. This process occurs in the early stages of a photocatalyst reaction. Among the many types of semiconductors, until now TiO_2 has become a choice especially in the form of anatase crystals as photocatalysts.

\[
\text{TiO}_2 + \text{hv} \rightarrow \text{e}^-_{\text{cb}} + \text{h}^+_{\text{vb}}
\] (7)

\[
\text{h}^+_{\text{vb}} + \text{H}_2\text{O} \rightarrow \textcolor{red}{^\bullet}\text{OH} + \text{H}^+
\] (8)

This reaction is one type of advanced oxidation processes and is the beginning of the next photocatalytic reaction [13]. If there are other oxidizing agents such as Hydrogen peroxide or ozone, additional hydroxyl radicals can be produced under UV irradiation. For example Hydrogen peroxide separated in the presence of UV light produces two hydroxyl radicals:

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \textcolor{red}{^\bullet}\text{OH}
\] (9)
Hydroxyl radicals which become the character of AOPs have high oxidation potential, so they can reduce COD levels in wastewater. In this case the Fenton reagent serves as a degradator of pollutant or contaminant compounds that are difficult to degrade. The purpose of this study is to study the effect of RR2 initial concentration on degradation of COD and color by using Fenton, Fenton/TiO$_2$, Fenton/UV, and Fenton/TiO$_2$/UV methods. In addition, the results will be compared to determine the most effective method.

2. Materials and method

2.1. Materials

Reactive Red 2 (RR2) synthetic dye used in this research was obtained from dyes suppliers of Fajar Kimia in Jakarta. Titanium dioxide (TiO$_2$) catalysts was purchased from Sigma Aldrich. Sulfuric Acid (H$_2$SO$_4$), Sodium hydroxide (NaOH), Sodium Thiosulfate (Na$_2$S$_2$O$_3$), Hydrogen peroxide (H$_2$O$_2$ 30% w/v), and Ferro sulfate (FeSO$_4$.7H$_2$O) were obtained from Merck. To adjust the pH 0.1 M H$_2$SO$_4$ and 0.1 M NaOH was used. The UV source is obtained from a 15 watt UV lamp with a wavelength of 253.7 nm (UV-C).

2.2. Procedure

The treatment of RR2 is carried out in a batch reactor equipped with mechanical stirrers and UV lamps. Synthetic dye wastewater is made by dissolving a certain amount of RR2 into distilled water. RR2 initial concentration was varied from 150 to 300 ppm. In this study, Fenton reagent was made with FeSO$_4$.7H$_2$O and H$_2$O$_2$ molar ratio of 1: 80 by using 4 mM of FeSO$_4$.7H$_2$O.

First, measure COD and absorbance of RR2 solution with a concentration of 150 ppm. Add the solution to the UV reactor. Set the stirring speed to 500 ppm. Add FeSO$_4$.7H$_2$O and set the pH to 3 by adding a solution of 0.1 M H$_2$SO$_4$ or 0.1 M NaOH. Next add H$_2$O$_2$ to make a comparison of $\frac{[\text{Fe}^{2+}]}{[\text{H}_2\text{O}_2]}$ 1: 80. In the Fenton/TiO$_2$ process, the addition of 0.4% (w/v) TiO$_2$ was carried out after adding the Fenton reagent to the reactor. Then repeat the experiment by varying RR2 concentration.

In the Fenton process the reaction time starts when H$_2$O$_2$ is added. In the Fenton/TiO$_2$ process, the reaction time starts when TiO$_2$ is added. In the Fenton/UV process the reaction time starts when H$_2$O$_2$ is added and the UV lamp is turned on. Whereas in the Fenton/UV/TiO$_2$ process, the reaction time starts when TiO$_2$ is added and the UV lamp is turned on. The solution sample was taken every 5 minutes to analyze the COD value and its absorbance. After taking the sample immediately add 0.1 ml 1 N Na$_2$S$_2$O$_3$ into the sample solution to stop the reaction [14].

2.3. Analysis

The UV-Visible GenesysTM 20 Spectrophotometer was used to analyze the color through absorbance measurements, while the COD value was determined by titrimetric method. pH measurement is done by using pH meter (Hanna instrument). The percentage of RR2 color degradation is determined by following equation:

$$\% \text{color degradation} = \left(\frac{A_0-A_t}{A_0}\right) \times 100\%$$

(10)

With $A_0$ is color absorbance at $t = 0$, $A_t$ is color absorbance at $t = t$, and $t = $ time. While the percentage of COD degradation is calculated by following equation:

$$\% \text{COD degradation} = \left(\frac{\text{COD}_0-\text{COD}_t}{\text{COD}_0}\right) \times 100\%$$

(11)

With COD$_0$ is COD at $t = 0$, COD$_t$ is COD at $t = t$, and $t = $ time.
3. Results and discussion

The parameters analyzed in this study are color and COD. The COD value represents the amount of total oxygen needed to decompose organic and chemical compounds that are chemically dissolved in a wastewater. The proposed mechanism of the reaction for RR2 degradation by using Fenton reagent is as follows:

\[ \text{C}_9\text{H}_{10}\text{C}_{12}\text{N}_6\text{Na}_2\text{O}_7\text{S}_2 + \cdot\text{OH} \rightarrow \text{C}_9\text{H}_{10}\text{C}_{12}\text{N}_6\text{Na}_2\text{O}_7\text{S}_2(-\text{OH}) + \text{oxidized intermediates} + \text{CO}_2 \]  

(12)

In the previous study, the use of Fenton reagent alone (molar ratio of 1:80) in processing RR2 with a concentration of 150 ppm resulted in 69 % of color degradation. While the use of UV lamps and Fenton reagent with the same molar ratio is able to achieve a higher color degradation of 97.5 % even though it is used at higher RR2 concentrations (300 ppm). Thus the Fenton/UV method provides better color degradation than using Fenton method alone. This is due to the Fenton/UV method, more hydroxyl radicals are produced, which are initiated by the presence of UV light according to equation (9).

The effect of initial concentration of RR2 dye solution needs to be investigated because the pollutant concentration is an important parameter in wastewater treatment [15]. By knowing how much concentration can be charged to a processing method, it can be known the efficiency of the method. Because the purpose of any wastewater treatment is the fulfilment of environmental quality standards at the end of processing, before wastewater is discharged into the environment. In this study, the initial concentration of RR2 varied from 150-300 ppm with a molar ratio of 1:80.

In Figure 1 (a), it can be seen that the Fenton/TiO₂/UV method gives the highest percentage of color degradation compared to the Fenton/UV or Fenton/TiO₂ methods. In the use of RR2 with an initial concentration of 150 ppm, the color degradation were 85.8 %, 98.5 %, and 98.8 % by using the Fenton/TiO₂, Fenton/UV, and Fenton/TiO₂/UV methods respectively. However, in general, variations in RR2 concentration from 150-300 ppm do not significantly affect the percentage of color degradation in each processing method. The formed hydroxyl radicals will break the double bond on the procion red into a simpler compound and so the color will degrade in the wastewater, which was originally red to became clear [16].

As can be seen in Figure 1 (b), the COD degradation were 81.2%, 88%, and 89.5 % by using the Fenton/TiO₂, Fenton/UV, and Fenton/TiO₂/UV methods respectively were obtained when using RR2
initial concentration of 150 ppm. Obviously, the Fenton/TiO$_2$/UV method also gave the highest percentage of COD degradation compared to the Fenton/UV and Fenton/TiO$_2$ methods as shown in Figure 1 (b). This is caused, in the Fenton/TiO$_2$/UV method, the hydroxyl radical produced is more than in the Fenton/UV or Fenton/TiO$_2$ method. The use of Fenton/TiO$_2$/UV can produce hydroxyl radicals according to equation (1), (6), and (8). In the use of concentrations of RR2 of 250 and 300 ppm, a significant difference in COD degradation was obtained from each method. The COD degradation of 86%, 50%, and 16%, respectively, were achieved by the Fenton/TiO$_2$/UV, Fenton/TiO$_2$, and Fenton/UV methods, when using a concentration of RR2 of 300 ppm. In this case, the Fenton/UV and Fenton/TiO$_2$ method looks less effective than Fenton/TiO$_2$/UV, probably because of the concentration of RR2 and TiO$_2$ catalyst which is high enough to block UV light from initiating the oxidation reaction according to equations (6), (8), and (9), thus inhibiting the formation of hydroxyl radicals.

![Figure 2](image-url)  
**Figure 2.** COD degradation by using Fenton/TiO$_2$, Fenton/UV, and Fenton/TiO$_2$/UV methods when using initial RR2 concentration of (a) 250 ppm and (b) 300 ppm (Fenton reagent molar ratio of 1:80, pH 3, 0.4% TiO$_2$ catalyst concentration, and reaction time of 5 min)

Figure 2 (a) and (b) compare the COD degradation by using Fenton/TiO$_2$, Fenton/UV, and Fenton/TiO$_2$/UV methods. From both figures, it is clear that the highest COD degradation was achieved when applying Fenton/TiO$_2$/UV method. This is because this method produces the most hydroxyl radical according to equation (1), (6), and (8). The percentage of COD degradation decrease by increasing initial RR2 concentration from 250 to 300 ppm, as can be seen in both figures. For example, in Fenton/TiO$_2$ method, the COD degradation percentage of 34% was obtained by using initial concentration RR2 of 250 ppm as demonstrated in Figure 2 (a), while the COD degradation percentage of 14% was obtained by using initial concentration RR2 of 300 ppm as shown in Figure 2 (b). This result is in agreement with other research conducted by Agustina and Ang (2012). In their study, increasing the initial concentration of Reactive Blue 4 from 20 to 200 ppm decreases the decolorization from 94.5% to 81%, and similarly for Reactive Red 2, increasing the initial concentration from 20 to 200 ppm decreases the decolorization from 100% to 91.5%, within 60 minutes of reaction [17]. The increase in dye concentration increases the number of dye molecules but not the number of hydroxyl radical. That is why the percentage of degradation decrease with increasing the initial dye concentration.
4. Conclusion
In this study Reactive red 2 (RR2) synthetic dye was treated by using Fenton-based of Advanced Oxidation Processes, namely, Fenton, Fenton/TiO₂, Fenton/UV, and Fenton/TiO₂/UV. The effect of RR2 initial concentration on COD and color degradation were studied. From the study, it was found that RR2 concentration from 150-300 ppm do not significantly affect the percentage of color degradation. However, at high concentration RR2 of 250 and 300 ppm, the percentage of COD degradation decrease by increasing concentration of RR2. The Fenton/TiO₂/UV method is superior to other methods with the highest COD and color degradation, using Fenton reagent molar ratio of 1:80, pH of 3, and TiO₂ catalyst concentration of 0.4% (w/v), in a reaction time of 5 minutes. When using 150 ppm of RR2, the highest COD and color degradation of 98.8 % and 89.5 %, respectively were achieved by using the Fenton/TiO₂/UV methods.

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