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STUDY OF SYNTHETIC DYE REMOVAL USING FENTON/TiO_2, FENTON/UV, AND FENTON/TiO_2/UV METHODS AND THE APPLICATION TO JUMPUTAN FABRIC WASTEWATER

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Abstract. Synthetic dyes were commonly used in textile industries such as Jumputan fabric industries in South Sumatera. Most of these industries were categorized as a home industry without a wastewater treatment plant, so the wastewater is released directly into waterbody. In general, the wastewater contains synthetic dyes, which are harmful to the environment and human body. Therefore, the wastewater needs to be treated before its release into the environment. Reactive Red 2 (RR2) is one of important synthetic dyes usually applied for colouring textile materials such as Jumputan fabric. The RR2 was used as a pollutant model in this research. The objective of the study is to compare the removal of RR2 by using Fenton/TiO_2, Fenton/UV, and Fenton/TiO_2/UV methods. Furthermore, the optimum conditions obtained were applied for the treatment of wastewater from Jumputan fabric industry. As a conclusion, the highest RR2 degradation of 100 % was reached by using the Fenton/TiO_2/UV method after 5 minutes of reaction. It was discovered that the optimum conditions were found when using $[Fe^{2+}]/[H_2O_2]$ molar ratio of 1:80, pH of 3, and TiO_2 concentration of 0.4 % (w/v). However, the application of the condition to the Jumputan wastewater treatment leads to Chemical Oxygen Demand (COD) removal of 94 % within 120 minutes of reaction.

Keywords: Reactive Red 2, Fenton reagent, Fenton/TiO_2, Fenton/UV, Fenton/TiO_2/UV, wastewater.

1. Introduction

Generally, the textile industry produces a large amount of waste water every year. Beside of the suspended solids, this wastewater has a high organic content characterized by high Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) values. The content of organic pollutants in wastewater is mostly derived from the use of chemicals in the process of colouring, dyeing, and washing textile materials. This is marked by the colour of the wastewater being discharged into the sewer. The coloured wastewater, besides being aesthetically displeasing, is also harmful to the environment. The presence of large amounts of colour can block the penetration of sunlight into a body of water, leading to a disruption of the balance of water ecosystems. Therefore, the textile industry wastewater must be treated properly.

The main source of pollution in textile industry wastewater is the presence of high concentrations of dyes. The textile industry generally uses synthetic dyes, such as procion, erionyl, and auramine, in the colouring process. In textile colouring procedures such as Batik, synthetic colouring agents used include indigosol, naphtol and rapid [1]. The reasons behind the use of synthetic dyes rather than the natural ones are the lower price, greater durability, easy obtainability and a wider variety of colour choices. These synthetic dyes are categorized as toxic and hazardous substances, whose presence in the water is not desirable because of the carcinogenic effects they cause. In addition, the colour changes have also reduced the water quality along with an increasing turbidity due to synthetic-dye pollutants.

For this reason, there is a need for a wastewater treatment technology that is simple and easy to apply in the textile industry, especially small and medium production plants, which are common Palembang. Several technologies have been developed to overcome wastewater problems that contain synthetic dyes, such as adsorption with activated carbon [2], coagulation-flocculation [3], photocatalysis including semiconductors [4], and a combination of physics and biology [5]. Physical processing using adsorbents, such as zeolite and activated carbon, only removes pollutants from liquid media into solid media, but does not destroy the pollutants themselves. Chemical processing involves the use of chemicals in large quantities and produces sludge, which must be separated at the end of the process, thus requiring further processing. Biological processing has been proven to reduce COD in large quantities, but requires a long time so the treatment of wastewater with this method generally requires a large land. An alternative method to handle textile industrial wastewater is by using Advanced Oxidation Processes (AOPs). AOPs are defined as the oxidation processes involving the generation of hydroxyl radicals (•OH) as powerful oxidizing agents, which can destruct the wastewater pollutants and transform them to less or even non-toxic products, thereby providing an ultimate solution for the wastewater treatment [6]. These processes offer a technology which can disintegrate the pollutants into less harmful components, and finally, to carbon dioxide and water. Therefore, the Fenton oxidation, one of the AOPs methods, was applied in this study to examine the Reactive Red 2 synthetic dye as a model pollutant.

The advantage of the AOP process with Fenton's reaction is that it has a short reaction time compared to other AOP processes. Hydrogen peroxide reagents are used only in small amounts, and can degrade organic components that are difficult to decompose [7]. Hydrogen peroxide is also environmentally friendly and easy to handle. The Fenton process is very promising among other AOPs, because this system provides a high reaction yield, which is able to produce hydroxyl radicals at a low cost and is easy to carry out [8–12]. In addition, Fe (iron) is widely available and non-toxic. The use of Fenton reagent does not require a special equipment, so the main advantage of the Fenton reagent method is the simplicity of the process itself [13].

Fenton Reagent is a solution consisting of hydrogen peroxide (H_2O_2) and iron catalyst (Fe^{2+}), which have high oxidation ability in oxidizing pollutants or wastewater. The Fenton reaction involves hydroxyl radicals produced from the oxidation reaction between H_2O_2 and Fe^{2+}. The use of the Fenton reagent involves complex reactions beginning with the H_2O_2 decomposition reaction with the assistance of Fe^{2+} catalyst. The mechanism of the reaction starts with Fe^{2+} initiating the reaction and catalysing the decomposition reaction of H_2O_2 to produce hydroxyl radicals (•OH) according to the reaction equation:

$$\mathrm{Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + \bullet OH} \tag{1}$$

The hydroxyl radical (•OH) is able to break down almost all organic compounds, 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 [14]:

$$\mathrm{\bullet OH + H_2O_2 \longrightarrow H_2O + HO_2\bullet} \tag{2}$$

$$\mathrm{Fe^{3+} + HO_2\bullet \longrightarrow Fe^{2+} + H^+ + O_2} \tag{3}$$

$$\mathrm{Fe^{2+} + HO_2\bullet \longrightarrow Fe^{3+} + HO_2^-} \tag{4}$$

$$\mathrm{Fe^{2+} + \bullet OH \longrightarrow Fe^{3+} + OH^-} \tag{5}$$

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

$$\mathrm{Fe^{3+} + H_2O} + hv \longrightarrow \mathrm{Fe^{2+} + H^+ + \bullet OH} \tag{6}$$

Reaction (6) is known as a Fenton-photo reaction (Fenton/UV) and followed by reaction (1). The •OH production is determined by the presence of light with an appropriate wavelength and hydrogen peroxide. In theory, by combining reactions (1) and (6), two moles of •OH will be produced per mole of hydrogen peroxide used [15]. Photocatalyst is a catalyst that works when absorbing a light of a specific wavelength. Photocatalysts are generally a semiconductors that have 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 [6]. This process occurs in the early stages of a photocatalyst reaction. Among many types of semiconductors, TiO_2 has become the preferred choice, especially in the form of anatase crystals as photocatalysts.

Commercially, TiO_2 powders are easy to obtain and have advantages, such as having high photocatalyst activity, non-toxicity, resistance to corrosion, and non-solubility in water. The TiO_2 also has a high light-absorption ability, which is characterized by the corresponding band gap energy (Eg) value, which is 3.2 eV for anatase structure. When a light with the hv energy equal to or greater than the band gap energy (Eg) is used, the electrons in the valence band have enough energy to be able to move or be excited to the conduction band and leave the positive hole (hv^+) in the valence band:

$$\mathrm{TiO_2} + hv \longrightarrow e^-_{cb} + hv^+_{vb} \tag{7}$$

Holes in the valence band can act with H_2O to produce hydroxyl radicals:

$$hv^+_{vb} + \mathrm{H_2O} \longrightarrow \mathrm{\bullet OH + H^+} \tag{8}$$

This reaction is one type of an advanced oxidation technique and is the beginning of the next photocatalytic reaction [6]. 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:

$$\mathrm{H_2O_2} + hv \longrightarrow 2\,\mathrm{\bullet OH} \tag{9}$$

Hydroxyl radicals, which become the character of AOPs, have high oxidation potential, so they can reduce COD levels in wastewater. 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 [16], palm oil processing industry [17], and pesticides [18]. In this study, the Fenton-based AOPs method is used to degrade Reactive Red 2 (RR 2) synthetic dyes. And it will be compared with the use of Fenton reagents and their combinations in processing RR 2 synthetic dyes. RR 2 is used as a model for synthetic dye wastewater because this dye is very commonly used in Palembang, the price is relatively cheap and can dissolve in water without heating. Traditional fabrics in Palembang always use a red touch in their main products. The purpose of this study is to treat RR 2 synthetic dye wastewater using the Fenton, Fenton/TiO_2, Fenton/UV, and Fenton/TiO_2/UV methods, and also to study the parameters that affect the COD and colour reduction. Furthermore, the best operating conditions are applied to treat the wastewater from Jumputan fabric home industry in Palembang.

2. Experimental

2.1. Material

In this study, Reactive Red 2 (RR 2) synthetic dye was obtained from dye suppliers of Fajar Kimia in Jakarta. The Titanium dioxide (TiO_2) catalysts were purchased from Sigma Aldrich. Whereas Sulphuric Acid (H_2SO_4), Sodium hydroxide (NaOH), Sodium Thiosulfate ($Na_2S_2O_3$), Fenton reagents in the form of Hydrogen peroxide (H_2O_2 30 % w/v) and Ferro sulphate ($FeSO_4$ 7 H_2O) were obtained from Merck. To adjust the pH, 0.1 M H_2SO_4 and 0.1 M NaOH were used. The UV source is obtained from a 15 watt UV lamp with a wavelength of 253.7 nm (UV-C).

2.2. Procedures

The treatment of RR 2 is carried out in a batch reactor equipped with UV lamps and mechanical stirrers. Synthetic dye wastewater is made by dissolving a certain amount of RR 2 into distilled water. The RR 2 initial concentration varied from 150-300 ppm. In this study, the Fenton reagent was made by H_2O_2 and $FeSO_4$ 7 H_2O with a molar ratio of 20:1-80:1, using 4 mM of $FeSO_4$ 7 H_2O. First, the COD and absorbance of RR 2 solution with a concentration of 150 ppm were measured. Then, the UV reactor was filled with the solution and set to a stirring speed of 500 ppm. Followed by an addition of $FeSO_4$ 7 H2O and setting the pH to 3 by adding 0.1 M H_2SO_4 or 0.1 M NaOH solution, before introducing H_2O_2.

2.2.1. Fenton/TiO_2 process

In the Fenton/TiO_2 process, the addition of 0.05 % (w/v) TiO_2 was carried out after adding the Fenton reagent into the reactor. The experiments were repeated with a varying RR 2 concentration, molar ratio of $[H_2O_2]/[Fe^{2+}]$, and TiO_2 concentration. The concentration of TiO_2 catalyst varied from 0.05 to 0.4 % (w/v). In this process, the reaction time starts when TiO_2 is added.

2.2.2. Fenton/UV process

The concentration of H_2O_2 varied with the fix concentration of $FeSO_4$ 7 H_2O to make the molar ratio of $[H_2O_2]/[Fe^{2+}]$ $20 : 1 - 80 : 1$. The experiments were repeated with varying RR 2 concentrations and molar ratios of $[H_2O_2]/[Fe^{2+}]$. In the Fenton/UV process, the reaction time starts when the UV lamp is turned on.

2.2.3. Fenton/UV/TiO_2 process

In the Fenton/UV/TiO_2 process, the concentration of TiO_2 catalyst varied from 0.05 to 0.4 % (w/v).The addition of TiO_2 was carried out after adding the Fenton reagent into the UV reactor. The experiments were repeated with varying RR 2 concentrations, molar ratios of $[H_2O_2]/[Fe^{2+}]$, and TiO_2 concentrations. In this process, the reaction time starts when TiO_2 is added and the UV lamp is turned on. The research was done on each process that was carried out. The solution samples were taken from the Fenton/TiO_2 process, the Fenton/UV process, and the Fenton/UV/TiO_2 process every 5 minutes to analyse the COD value and its absorbance. After taking samples from each process, 0.1 ml 1 N $Na_2S_2O_3$ was immediately added into each sample solution to stop the reaction [19].

3. Analyses

The pH measurement is done by using Hanna pH meter, the colour analysis through absorbance measurements using UV-Visible Genesys TM 20 Spectrophotometer, while the COD value was determined by titrimetric method (ASTM D-1252). The percentage of the RR 2 colour degradation is calculated based on the equation:

$$\%\,Color\ degradation = \frac{(A_0 - A_t)}{A_0} \cdot 100\,\% \quad (10)$$

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

$$\%\,COD\ removal = \frac{(COD_0 - COD_t)}{COD_0} \cdot 100\,\% \quad (11)$$

With COD_0 being COD at $t = 0$, COD_t being COD at $t = t$, and $t =$ time.

4. Results and discussion

The parameters analyszed in this study are colour 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. In textile industry wastewater, the presence of pollutants in the form of organic compounds is caused by the use of chemical dyes in the production process, such as colouring and dyeing, so thatresulting in the wastewater containings various chemicals [20]. Therefore, the COD value can be used as a determining parameter to determine changes in the pollutant content and quality of wastewater with a processing method used.

Fenton's oxidation, as indicated in the reaction equation (1), is a process that is very dependent on pH, because pH plays an important role in the •OH production mechanism in Fenton's reaction. Hydroxyl radicals can be formed efficiently under acidic conditions. At high pH, ferrous ions (Fe^{2+}) are unstable and will easily form ion ferries (Fe^{3+}) which tend to produce colloidal hydrosol complexes. This complex inhibits the hydroxyl radical production, in this form, iron ions catalysze the decomposition of Hydrogen peroxide to oxygen and water without producing hydroxyl radicals. While at pH 2-5, the solubility of Fe^{2+} is still high enough so that the hydroxyl radical can be produced [21]. In the study of the treatment of azo and reactive synthetic dyes, the colour removal and the highest COD were obtained at pH 3 [22–24]. Therefore, in this study, pH 3 was used in each experiment. In a previous study, Fenton reagent was used to treat RR 2 with a concentration of 150 ppm. As the a results, the photo-Fenton process was superior to Fenton process. In the Fenton process, during the 20 minutes of reaction, only 69 % of the colour reduction was obtained achieved using the molar ratio $[Fe^{2+}]/[H_2O_2]$ $1:20-1:80$. While the colour degradation of 99.9 % was achieved within 10 minutes of the reaction by using the photo-Fenton process with the molar ratio of at$[Fe^{2+}]/[H_2O_2]$ molar ratio ofbeing $1:80$ within 10 minutes of reaction [22]. The results of Fenton process are considered ineffective, therefore, the use of Fenton reagents needs to be combined with other advanced oxidation methods, namely UV light, TiO_2 catalyst, or photocatalyst of UV/TiO_2. The mechanism of the reaction proposed for the RR 2 degradation by using the Fenton reagent is as follows:

$$\begin{aligned} &C_9H_{10}C_{12}N_6Na_2O_7S_2 + \bullet OH \longrightarrow \\ &\qquad C_9H_{10}C_{12}N_6Na_2O_7S_2(-OH)+ \\ &\qquad\quad + \text{oxidized intermediates} + CO_2 \end{aligned} \tag{12}$$

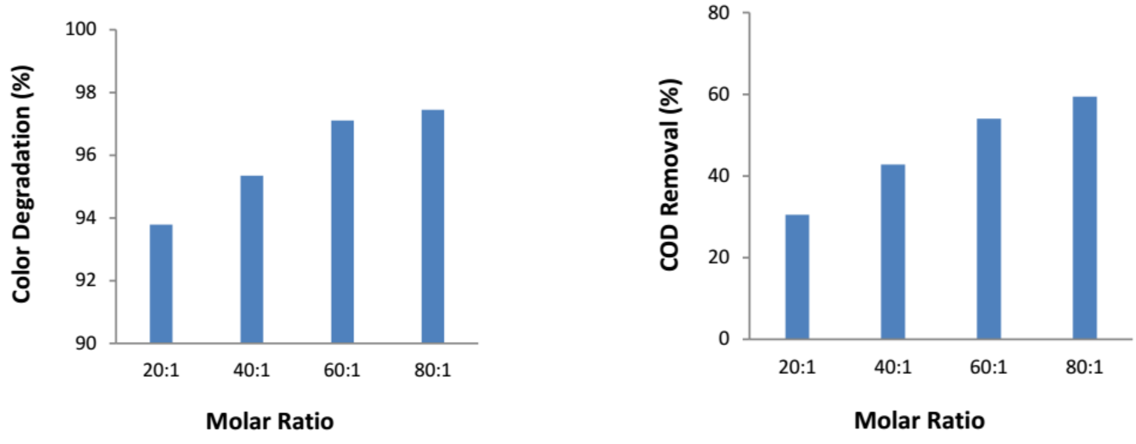
4.1. Effect of Fenton's reagent molar ratio

The Fenton reagent is a combination of chemicals that use hydrogen peroxide and iron catalysts. H_2O_2 and Fe^{2+} ions not only react to form hydroxyl radicals through the reaction equation (1), but both can also consume hydroxyl radicals through the reaction equation (2) and (5). The ratio of $[Fe^{2+}]/[H_2O_2]$ will affect the rate of production and the use of hydroxyl radicals [15]. Therefore, it is very important to use the right $[Fe^{2+}]/[H_2O_2]$ ratio in the treatment.

The effect of the molar ratio of the Fenton reagent on the RR 2 and COD degradation is shown in Figures 1a and 1b. It can be seen from figure 1 that the efficiency of colour degradation and COD removal are still increasing when the ratio of $[Fe^{2+}]/[H_2O_2]$ is increased to $80:1$. Further addition of H_2O_2 could possibly enhance the removal of COD. In the figure, it can be seen that the higher the Fenton molar reagent ratio is used in this study, the higher the colour and COD degradation is obtained. The RR 2 and COD highest degradation was achieved with the highest molar ratio of $1:80$, with the percentage of colour and COD degradation 97.5 % and 59.4 %, respectively.

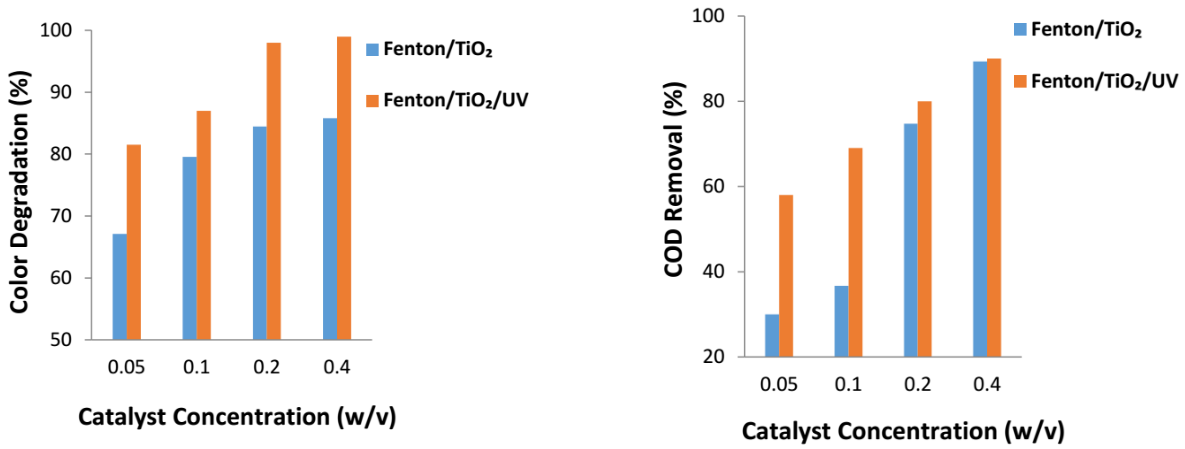
The importance of the ratio of $[H_2O_2]/[Fe^{2+}]$ in the treatment of carpet-colouring wastewater using Fenton reagents was investigated by [24]. In their study, it was reported that COD removal increased with an increase in the ratio of $[H_2O_2]/[Fe^{2+}]$ between 95 and 290, while the ratio above 290 caused a reduction in the COD removal. The highest COD removal was achieved at a ratio between 95 and 290 (g/g) which is equivalent to the molar ratio of 153-470 [24]. Other research regarding decolourization and mineralization of some commercial reactive dyes using Fenton reagents by both homogeneous and heterogeneous processes, and the process of homogeneous Fenton with UV light (Fenton/UV), has shown that the Fenton/UV homogeneous process is the most effective process. In this process, a high level of mineralization (78-84 %) and decolourization (95-100 %) has been achieved. Optimal operating conditions for efficient colour degradation in all investigated dyes (100 ppm concentration) were obtained when using a molar ratio of $[Fe^{2+}]/[H_2O_2]$ of 0.5 mM/20 mM or $1:40$ [23].

In the previous study, the use of Fenton reagent alone (molar ratio of $1:80$) in processing the RR 2 with a concentration of 150 ppm resulted in a 69 % of colour degradation. While the use of UV lamps and Fenton reagent with the same molar ratio is able to achieve a higher colour degradation of 97.5 % even though it is used at higher RR 2 concentrations (300 ppm). Thus, the Fenton/UV method provides a better results than the method using only Fenton. This is due to more hydroxyl radicals, which are initiated by the presence of UV light according to equation (9), being produced. The results of this study are in an agreement with the research on the degradation of Reactive Blue 19 dyes (RB 19) using AOPs. The study reported that the use of Fenton/UV (photo-Fenton) resulted in a greater degradation of RB 19 compared to the use of UV, H_2O_2, UV/H_2O_2, and Fenton reagent only. The UV/H_2O_2 process is effective enough to achieve a 91 % colour degradation, however, the downside being the required time – 3 h. The Fenton process gives > 98 % colour degradation in a few minutes, but the decrease of dissolved organic carbon content (DOC) is only 36.8 %. The most effective process is photo-Fenton, where the colour degradation of 99.4 % was reached and a decrease in dissolved organic



(a). (b).

Figure 1. Effect of Fenton reagent molar ratio on (a) RR 2 colour degradation (b) COD removal by using Fenton/UV method (RR 2 concentration of 300 ppm, pH 3, reaction time 5 min).



(a). (b).

Figure 2. Effect of TiO_2 catalyst concentration on (a) RR 2 colour degradation and (b) COD removal by Fenton/TiO_2 and Fenton/TiO_2/UV methods (Fenton reagent molar ratio of 1 : 80, RR 2 concentration of 150 ppm, pH 3, reaction time of 5 min).

carbon of 94.5 % was reached [25]. Thus, the achieved difference in colour degradation and the appropriate Fenton reagent molar ratio is strongly influenced by the chemical structure of the dye, the process used, and the type of pollutant treated.

4.2. Effect of TiO_2 catalyst concentration

The catalyst concentration is very important especially in its use together with the presence of photon sources (as the photocatalyst), such as UV light or sunlight. Because the excessive amount of catalyst can reduce the effectiveness of the oxidation itself where the catalyst can block the UV light to degradedegrading the pollutants [26].

The effect of the catalyst concentration on the colour degradation and COD removal can be seen in Figures 2a and 2b. The higher the catalyst concentration used in this study was, the greater the percentage of colour degradation and COD removal was achieved. This is in line consonance with the research conducted by [27], who studied the effect of the TiO_2 amount, pH, and temperature on the decolourization of C.I Reactive Red 2 using a system that involves ultraviolet-ultrasound-TiO_2. Their results indicate that the rate of decolourization rises constantly with the increase in the amount of TiO_2 catalyst used in the range of 0.5 − 2 g/l. Several studies have also shown that the rate of the decolourization rises with the increase in the amount of the catalyst used [4, 28–31]. The increase in the photocatalyst activity with the increase in the amount of catalyst used is an indication of a heterogeneous catalyst regime, because the fraction of light absorbed by the catalyst rises with the increase in the amount of the catalyst in the suspension [27]. But, the decolourization rate only slightly increases with the use of catalysts more in amountsthan larger than 2 g. This is due to the reductione of the photocatalytic activity due to the scattered and absorbed light.

The Fenton/TiO_2/UV method gives a 99 % of colour degradation and 90 % of COD removal. While the Fenton/TiO_2 method produced achieved a colour degradation and COD removal of 85.8 % and 88 %, respectively. The Fenton/TiO_2/UV method gives a better percentage of degradation than the Fenton/TiO_2 method because more hydroxyl radicals are produced in the presence of UV light. The presence of UV light can initiate the Fenton photo reaction (equation 6) and photocatalytic reaction (equation 8), which produces hydroxyl radicals. In addition, the presence of hydrogen peroxide as an oxidizing agent can also produce additional hydroxyl radicals under UV irradiation based on equation (9).

4.3. Comparative method of Fenton/TiO_2, Fenton/UV, and Fenton/TiO_2/UV

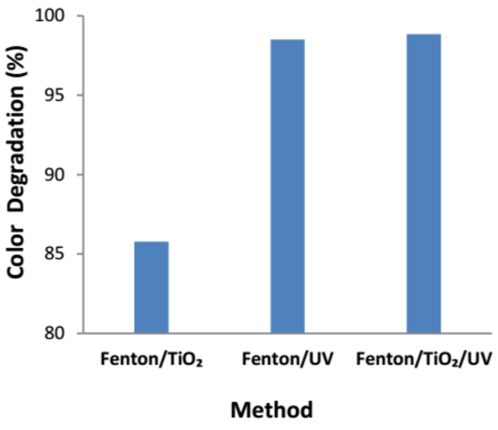
The treatment of the RR 2 with a concentration of 150 ppm using the Fenton/TiO_2, Fenton/UV, and Fenton/TiO_2/UV methods produced a percentage of color degradation at 85.8 %, 98.5 %, and 98.8 % colour degradation, respectively, as shown in Figure 3a. It can be concluded that the Fenton/TiO_2/UV method is a method that is superior to the Fenton/TiO_2 and Fenton/UV methods.

From Figures 3a and 3b, it can be seen that the use of UV becomes very important, because a very large increase in the percentage of the degradation compared to using the Fenton reagent only is obtained when using UV lamps compared to when adding TiO_2 catalysts. This can be seen by comparing the degradation percentage of the RR 2 and the removal of the COD achieved in the treatment with Fenton/TiO_2 and Fenton/UV methods. Treatment of the RR 2 with Fenton alone resulted in a degradation percentage of 69 % within 20 minutes. While the use of Fenton/TiO_2 and Fenton/UV methods resulted in the RR 2 degradation percentages of 85.8 % and 98.5 % within 5 minutes of reaction, respectively, within 5 minutes of reaction. Figure 3b shows a comparison of the three methods in reducing the COD value in the RR 2 with a concentration of 150 ppm. The COD removal of 81.2 %, 88 %, and 89.5 %, respectively, were achieved by using the Fenton/TiO_2, Fenton/UV, and Fenton/TiO_2/UV methods. The same as in colorAs in the colour degradation, the Fenton/TiO_2/UV method is a method that is superior to the Fenton/TiO_2 and Fenton/UV methods in reducing the COD. This is due to the use of Fenton/TiO_2/UV, the more hydroxyl radicals will produced, so thatresulting in more pollutants can be degraded which results in aand a decrease in the COD value. In the treatment of the black effluent and blue effluent from the textile industry, it was reported that the use of the photo-Fenton method with the help of UV lamps proved to provide the highest colour and COD degradation compared to the Fenton and Hydrogen peroxide methods only. In For the black effluent, colour and COD degradation reached 39 % and 84 %, respectively, while in for the blue effluent, colour and COD degradation were 56 % and 66 %, respectively [31]. In this study, the highest percentage of degradation was obtained by using the Fenton-photocatalytic (Fenton/TiO_2/UV) method, because of the increasing number of radical hydroxyls, caused by the presence of UV light and photocatalytic process (TiO_2/UV).In this study, the highest percentage of degradation was obtained by using the Fenton-photocatalytic (Fenton/TiO_2/UV) method, wherein the addition of radical hydroxyl besides being assisted by the presence of UV light, also came from the photocatalytic process (TiO_2/UV) involved in it.

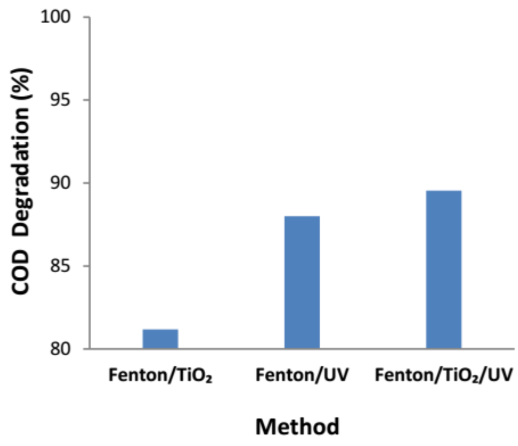
4.4. Treatment of jumputan fabric wastewater

To determine the effectiveness of the treatment method that has been studied, the best operating conditions that have been obtained in the treatment of the RR 2, namely the Fenton reagent molar ratio of 1 : 80, 0.4 % TiO_2 catalyst concentration, and pH of 3, are then applied to treat the Jumputan fabric wastewater coming from the centre of the textile home industry in Palembang. The percentage of the COD removal of Jumputan fabric wastewater using Fenton/TiO_2, Fenton/UV, and Fenton/TiO_2/UV methods is shown in Figure 4.

The highest COD removal of 94 % was obtained in the treatment of Jumputan fabric wastewater by using the Fenton/TiO_2/UV method. This is because, in this method, the hydroxyl radical is doubled, which is based on the reaction equation (1) and (6). In this case, there is a cycle between +2 and +3 oxidation numbers of the Fe element. The •OH production is determined by the presence of light with an appropriate wavelength and hydrogen peroxide. Theoretically, by combining equations (1) and (6), two moles of •OH can be produced per mole of hydrogen peroxide consumed. Shahwar et al., in their research on the effluent treatment of the textile industry, have compared the photo-Fenton method both using UV light and sunlight with other advanced oxidation processes (H_2O_2, Fenton, and ozonation) to see how the efficiency of colour and COD removal changes. It is reported that the photo-Fenton method assisted by sunlight is the most energy and cost effective treatment process (100 to 150 times lower than the UV/Fenton and ozone methods) among all the advanced oxidation processes studied in their study [31]. In the study, it was reported that the colour and COD degradation were 61 % and 85 %, respectively for the blue effluent, and 52 % and 88 %, respectively, for the black effluent, in 18 h of irradiation.



(a).



(b).

Figure 3. (a) RR 2 colour degradation and (b) COD removal by Fenton/TiO_2, Fenton/UV, and Fenton/TiO_2/UV methods (Fenton reagent molar ratio of 1 : 80, RR 2 concentration of 150 ppm, TiO_2 concentration of 0.4 %, pH 3, reaction time of 5 min).

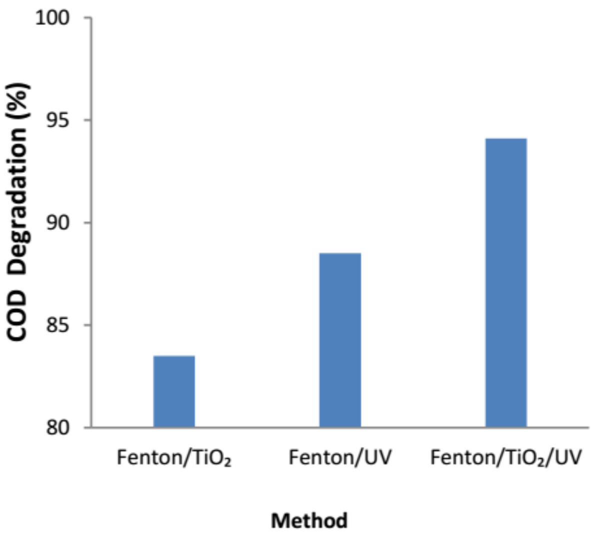


Figure 4. COD removal from the Jumputan fabric wastewater using Fenton/TiO_2, Fenton/UV, and Fenton/TiO_2/UV methods (Fenton reagent molar ratio of 1 : 80, pH of 3, 0.4 % TiO_2 catalyst concentration, reaction time of 120 min).

Thus, there is an opportunity for the Jumputan fabric wastewater treatment using the Fenton method with the aid of sunlight, although it will take a long time, but it will require less energy. In this case, the UV light source is replaced by sunlight, which is available abundantly throughout the year in Indonesia. The Fenton/TiO_2/UV method with the sunlight is one of the promising choices in treating textile industrial wastewater, considering the TiO_2 catalyst can be activated with the support of sunlight.

5. Conclusion

In this study, the Reactive red 2 (RR 2) synthetic dyes were treated by using Fenton-based of Advanced Oxidation Processes, namely, Fenton/TiO_2, Fenton/UV, and Fenton/TiO_2/UV. The effect of the molar ratio of the Fenton reagent, RR 2 initial concentration, and TiO_2 catalyst concentration on colour degradation and COD removal were studied. And the best operation condition was applied to the Jumputan fabric wastewater. From the results of the study, it can be concluded that the Fenton/TiO_2/UV method is superior to other methods with an achieved colour degradation and COD removal of 98.8 % and 94.1 %, respectively, using the Fenton reagent molar ratio of 1 : 80, pH of 3, and TiO_2 catalyst concentration of 0.4 % (w/v), in a reaction time of 5 minutes. This condition was applied to Jumputan fabric wastewater where the COD removal of 94.1 % was obtained in a reaction time of 120 minutes.

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