



## DEGRADATION OF REACTIVE RED 2 BY FENTON AND PHOTO-FENTON OXIDATION PROCESSES

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### ABSTRACT

In many developing countries such as Indonesia, one of a great potential area which will continue to grow is textile industry. These industries usually utilized artificial color, also known as synthetic dyes, in their manufacture production. The synthetic dyes contained in wastewater generated from textile industrial processing were refractory to degrade and toxic to human. The Reactive Red 2, as one of the important synthetic dye was used as a model organic pollutant in this research. However, Advanced Oxidation Processes (AOPs) have shown great potential in treating pollutant such as the treatment of textile dyes. In this study, degradation of RR 2 was examined by using Fenton and photo-Fenton oxidation processes, as one of  $\text{H}_2\text{O}_2$ -based AOPs. The RR2 concentration of 150-300 ppm,  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio of 1:20-1:80, and reaction time of 0-20 minutes were investigated on the degradation of dye in term of color and Chemical Oxygen Demand (COD) removal. The degradation of color and COD were strongly influenced by the initial concentration of dye, the  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio, and the reaction time. The color degradation of 69% was reached within 20 minutes of reaction by using Fenton process for all molar ratio of 150 ppm of RR 2 concentration usage. While the color degradation of 99.9% was obtained only in 10 minutes of reaction by using photo-Fenton process at  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio of 1:80, and also a maximum COD degradation of 95% was achieved when using RR 2 concentration of 150 ppm within 10 minutes of reaction.

**Keywords:** synthetic dye, fenton, photo-fenton, advanced oxidation processes.

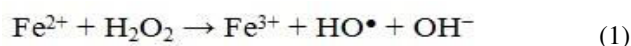
### INTRODUCTION

Wastewaters from textile and dye industries are highly colored with large concentrations of organic matter. Direct discharge of textile industry wastewater into the receiving water body causes serious environmental pollution. The release of synthetic color is very problematic to aquatic life and toxic to living organism [1]. Hence, it is desired to look for alternative process for the treatment of this kind of wastewater to reduce their environmental impact.

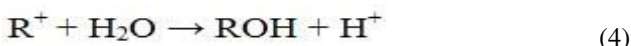
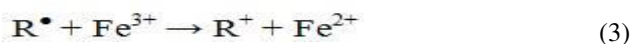
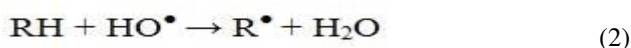
Azo dyes are characterized by containing one or more azo group ( $-\text{N}=\text{N}-$ ) bound to an aromatic ring. It has to be emphasized that due to their complicated and steady molecular structure, they are usually difficult to remove or inefficiency to remove from wastewater by using conventional physical, chemical and biological treatment methods [2]. Reactive Red 2 (RR 2) was classified as reactive azo dyes, which difficult to decompose in nature because of they have a strong covalent bond.

On the other hand, Advanced Oxidation Processes (AOPs), based on the generation of hydroxyl radicals ( $\text{HO}^\bullet$ ) with great oxidizing potential can be a good choice to treat this type of wastewater because of their powerful oxidizing capability to oxidize numerous organic compounds finally to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Among the various AOPs, application of Fenton's reagent is more attractive for several reasons, Fe is widely available,  $\text{H}_2\text{O}_2$  is easy to handle and excess decomposes to environmentally safe products, additionally the simplicity of equipment and the mild operation conditions and also short reaction time are another competitive advantages of Fenton-based oxidation processes like Fenton and photo-Fenton [3].

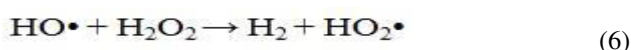
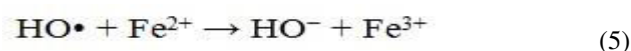
Fenton's reagent oxidation is a homogeneous catalytic oxidation process using a mixture of hydrogen peroxide and ferrous ions. An interesting technology to produce  $\text{HO}^\bullet$  radicals via the Fenton reagent is initiated by the proper combination of ferrous iron and peroxide (Equation. (1)).



The ferrous ion initiates and catalyzes the decomposition of  $\text{H}_2\text{O}_2$ , resulting in the generation of hydroxyl radicals,  $\text{HO}^\bullet$  [4]. The hydroxyl radicals are capable of rapidly attacking organic substrates (RH) and cause chemical decomposition of these compounds by H-abstraction and addition to C-C unsaturated bonds [5]:



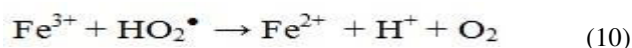
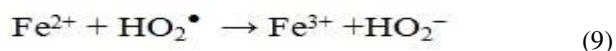
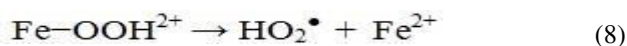
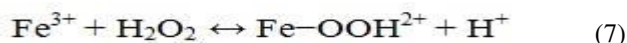
Several competing reactions which include  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{H}_2\text{O}_2$ , hydroxyl radicals, hydroperoxyl radicals and radicals derived from the substrate, may also be elaborated. Hydroxyl radicals may be scavenged by reacting with  $\text{Fe}^{2+}$  or hydrogen peroxide:



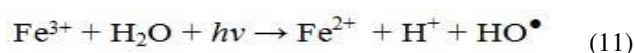
$\text{Fe}^{3+}$  formed through reactions (1) and (5) can react with  $\text{H}_2\text{O}_2$  following a radical mechanism that



involves hydroxyl and hydroperoxyl radicals, with regeneration of  $\text{Fe}^{2+}$  [6]:

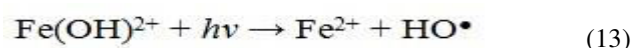


When irradiated with light of suitable wavelength (180-400 nm), that is, ultraviolet and some visible light,  $\text{Fe}^{3+}$  can catalyze the formation of hydroxyl radicals:



This is called photo-Fenton reaction and is followed by reaction (1). Hence, iron becomes cycled between the +2 and +3 oxidation state. The  $\text{HO}^\bullet$  production is determined by the availability of light of suitable wavelength and  $\text{H}_2\text{O}_2$ . In theory, by combination of reaction (1) and (11), two moles of  $\text{HO}^\bullet$  should be produced per mole  $\text{H}_2\text{O}_2$  consumed [7].

In the absence of photons, the accumulation of  $\text{Fe}^{3+}$  and its complexation with carboxylate species appears to be the principal drawback for Fenton processes due to the reduction of the degradation rates [8]. A combination of  $\text{H}_2\text{O}_2$  and UV irradiation with  $\text{Fe}^{2+}$ , or photo-Fenton process, can significantly enhance decomposition of many refractory organic compounds. Fenton reagent can completely decolorize and partially mineralize textile dyes rather rapidly. Katsumata and co-worker reported that the acceleration of photo-Fenton process for the decomposition of organic compounds is believed to have the capacity of photolysis of iron aqua complex,  $\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$  (to be  $\text{Fe}(\text{OH})^{2+}$  in the succulent form), to provide a new important source of  $\text{HO}^\bullet$  radicals. Further, the photolysis of  $\text{Fe}(\text{OH})^{2+}$  regenerates  $\text{Fe}^{2+}$  which is can be shown in Equation. (12) and (13), this means that photo-Fenton reaction would need low  $\text{Fe}^{2+}$  concentration compared with the Fenton process. Besides,  $\text{Fe}(\text{OH})^{2+}$  can absorb light at wavelengths up to 410 nm, which is the usual wavelength range provided by UV lamp [9].



In the present research, Fenton and photo-Fenton processes were applied to degrade RR 2, which is one of reactive azo dyes commonly present in textile wastewater. The objective of this study is to analyze the feasibility of degradation of RR 2 by Fenton and photo-Fenton processes. Many factors affecting degradation of color of dye. The influence of initial concentration of dye, the  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio, and the reaction time which affect the efficiency of both processes were also

investigated in this study. The progress of degradation of RR 2 was monitored in term of color and COD degradation.

## MATERIALS AND METHODS

### Chemicals and materials

The Reactive Red 2 dye obtained from Fajar Setia Dyestuff in Jakarta and used without further purification. Hydrogen peroxide ( $\text{H}_2\text{O}_2$  30% w/w), ferrous sulphate catalyst ( $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ ) and other chemicals were purchased from Sigma Aldrich. The initial pH of the solution was adjusted by adding diluted sulphuric acid ( $\text{H}_2\text{SO}_4$ ) or sodium hydroxide ( $\text{NaOH}$ ). Measurement of pH was obtained from a Hanna instrument pH meter.

### Experimental details

The degradation of RR2 dyes were carried out in batch operation in an UV reactor with the working volume of 9.6 l as shown in Figure-1. Dyes solution was prepared in distilled water, the initial RR 2 concentration was varied between 150-300 ppm. For every experiment performed, the reactor was initially loaded with RR 2 aqueous solution, adding ferrous sulphate catalyst, following by adjusting pH value of 3 with 0.1 or 0.01 M of  $\text{H}_2\text{SO}_4$  and 0.1 M of  $\text{NaOH}$  solution. Concentration of hydrogen peroxide was varied while the ferrous sulphate concentration was kept constant to make the  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio of 1:20-1:80. Continuous mixing was maintained by means of mechanical stirrer. In Fenton process the reaction time was recorded when the  $\text{H}_2\text{O}_2$  solution was added, for photo-Fenton process it is recorded when a 15 watt of UV lamp is turned on. The wavelength of UV lamp is 253.7 nm which is in the range of wavelength emitted by UV C. Samples of the dye solution were withdrawn every 5 minutes during the course of the reaction and analyzed.

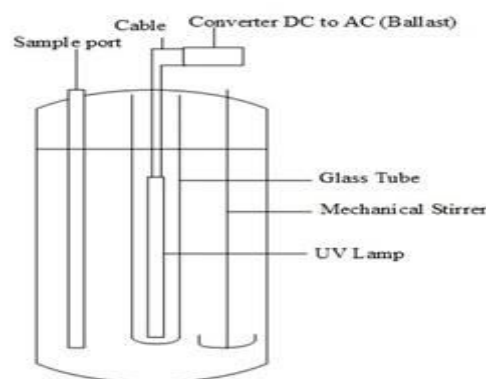


Figure-1. UV reactor.

### Analytical method

The samples were taken periodically for analysis of color and COD degradation. Color degradation was determined by UV/Vis Spectrophotometer while COD degradation was determined by titrimetric method. The COD degradation percentage is define as follows:



$$\text{COD degradation (\%)} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100 \% \quad (14)$$

Where  $\text{COD}_0$  is initial concentration of COD (mg/l) and  $\text{COD}_t$  is the concentration of COD (mg/l) at reaction time  $t$  (min). If  $A_0$  is initial absorbency of sample solution and  $A_t$  is the absorbency of sample solution at reaction time  $t$  (min), the color degradation percentage of dye can be represented by:

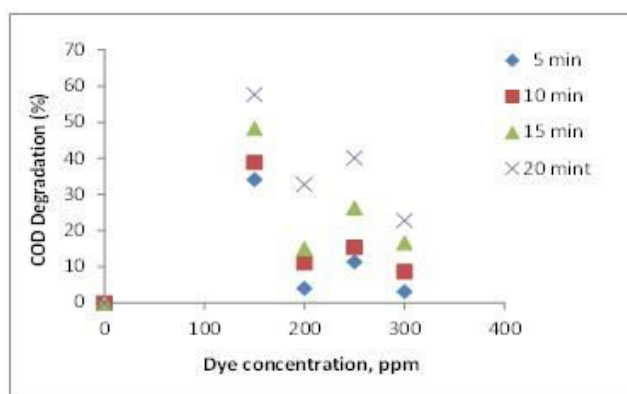
$$\text{Color degradation (\%)} = \left[ 1 - \left( \frac{A_t}{A_0} \right) \right] \times 100 \% \quad (15)$$

## RESULTS AND DISCUSSION

In the previous research about Decolorization and Mineralization of Reactive Blue 4 and Reactive Red 2 by Fenton oxidation process, the optimal operating condition were found at pH 3 which is the highest color degradation of 99.8% was attained [1]. In another study by Kusic and co-worker on Fenton type process for minimization of organic content in colored wastewater, two reactive dyes namely C.I Reactive Blue 49 and C.I. Reactive Blue 137 with azo chromophore were used as model organic pollutants, and the best results were also achieved at pH of 3 with the color removals of 92-98.5% [10]. The optimum pH was also observed in the range of 3.0-4.0 in the study of the Decolorization of Direct Blue 15 by Fenton process [11]. Therefore, in order to get a high degradation of dyes, further experiments in this study were conducted at pH of 3.

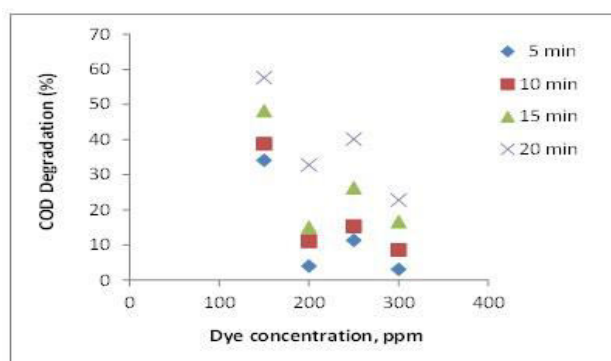
### Effect of initial dye concentration

The effect of initial dye concentration of aqueous solution RR2 on Fenton and photo-Fenton processes were investigated, since pollutant concentration is an important parameter in wastewater treatment. As a result of preliminary research in this study, by using Fenton process and the smallest initial concentration of 150 ppm, a color degradation of only 69% was found within 20 minutes of reaction in all  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio usage. So the remain only report the degradation of RR 2 by photo-Fenton process. The influence of the concentration in photo-Fenton process is illustrated in Figure-2 and 3.



**Figure-2.** Effect of initial dye concentration on COD degradation,  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio of 1:20.

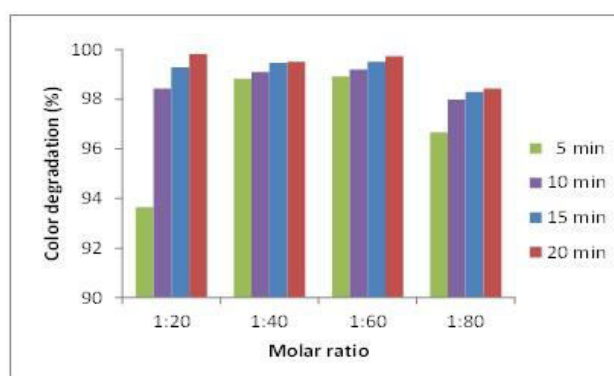
From both figures, it is evident that the percentage of COD degradation decreases with increasing initial dye concentration. Increasing the initial dye concentration from 150 to 300 ppm decreases the COD degradation from 57.6% to 22.8% by using  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio of 1:20. And similarly when using  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio of 1:40, the color degradation also decreases from 90.6% to 30.5%, in 20 minutes of reaction. The increase in dye concentration increases the number of dye molecules and not the OH radical concentration.



**Figure-3.** Effect of initial dye concentration on COD degradation,  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio of 1:40.

### Effect of $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ molar ratio

Both, the ferrous ion ( $\text{Fe}^{2+}$ ) and  $\text{H}_2\text{O}_2$  not only react to form hydroxyl radicals by reaction in Equation. (1), but are also scavengers of hydroxyl radicals by reactions (5) and (6). The ratio of  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  should affect the rates of hydroxyl radical production and scavenging. Hence it is important to use the optimum  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  ratio (Parson, 2004). In the previous research, the maximum color degradation of 99.8% was achieved by Fenton process of 100 ppm of RR 2 at maximum molar ratio of 1:20 within 60 min of reaction. Here, at the same molar ratio but higher concentration of 150 ppm, the same color degradation percentage of 99.8% can be achieved within only 20 min of reaction by photo-Fenton process.

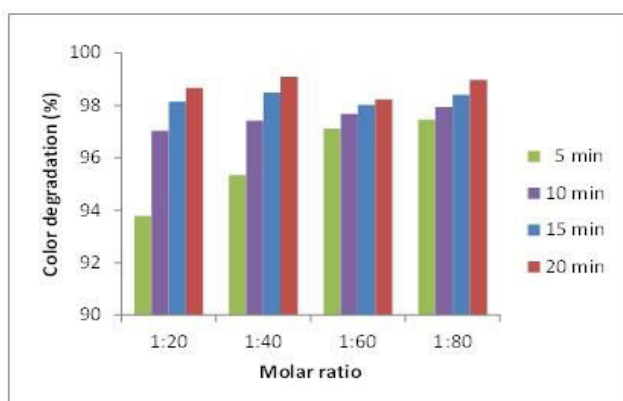


**Figure-4.** Effect of  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio on color degradation, RR 2 concentration of 250 ppm.



The employment of the UV lamp benefits the azo reactive dye degradation. The UV lamp, though has little power (15 W), is very useful in photo-Fenton process to increase the dye degradation. It could be explained because in the presence of photon provided by the UV lamp, there is more hydroxyl radicals generated, according to Equation. 12 and 13, which result in faster degradation of RR 2.

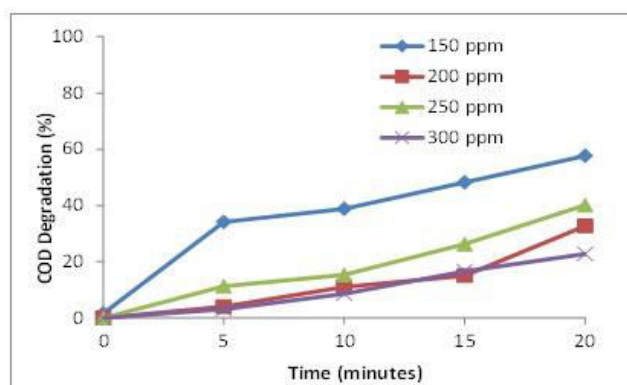
Effect of  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio on degradation of higher concentration of RR 2 were demonstrated in Figure-4 and 5. As can be seen in the figures, within 20 min of reaction, the color degradation of more than 98% can be accomplished for all of ratio molar usage. It is clear that the  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio have a little effect on color degradation at high concentration of RR 2.



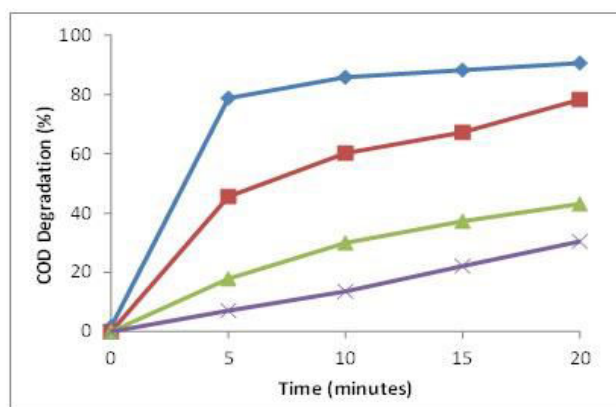
**Figure-5.** Effect of  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio on color degradation, RR 2 concentration of 300 ppm.

#### Effect of reaction time

The effect of reaction time at different dye concentration on COD degradation was illustrated in Figure-6 and 7. COD degradation percentage increase as increasing time, while the smallest RR 2 concentration got the highest COD degradation as shown in Figure-6 and 7. To make the economic wastewater treatment plant, it is need to utilize a lower reactant concentration and a shorter reaction time.



**Figure-6.** Effect of reaction time on COD degradation,  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio of 1:20.



**Figure-7.** Effect of reaction time on COD degradation,  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio of 1:40.

The COD degradation increase with increasing reaction time. The color degradation of 99.9% was obtained only in 10 minutes of reaction by using photo-Fenton process at  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio of 1:80, and also a maximum COD degradation of 95% was achieved when using RR 2 concentration of 150 ppm within 10 minutes of reaction. The COD result from this operational condition have fulfilled the environmental quality standard of wastewater discharge in Indonesia.

From the result of this study, photo-Fenton process was superior to Fenton process. In photo-Fenton process, two moles of hydroxyl radical should be produced per mole of  $\text{H}_2\text{O}_2$  consumed based on Equation. (1) and Equation. (11). Then generated hydroxyl radicals attack the organic pollutant and oxidize to the less harmful component to finally form  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . In this process, with the UV lamp assisted, more hydroxyl radicals is available so make the reaction faster.

#### CONCLUSIONS

Fenton and photo-Fenton processes lead to complete degradation of RR 2 synthetic dye in relatively short time. Photo-Fenton process was superior to Fenton process. The color degradation of 69% was reached within 20 minutes of reaction by using Fenton process for all molar ratio of 150 ppm of RR 2 concentration usage. While the color degradation of 99.9% was obtained only in 10 minutes of reaction by using photo-Fenton process at  $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$  molar ratio of 1:80, and also a maximum COD degradation of 95% was achieved when using RR 2 concentration of 150 ppm within 10 minutes of reaction.

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