

# UV/Fenton photo-oxidation of Drimarene Dark Red (DDR) containing textile-dye wastewater

**T Hudaya\*, J Anthonios and E Septianto**

Chemical Engineering Department, Parahyangan Catholic University,  
Ciumbuleuit 94 Bandung, Indonesia

E-mail : t.hudaya@unpar.ac.id / t\_hudaya@yahoo.com.au

**Abstract.** Textile dye wastewater contains organic pollutants which are non-biodegradable, characterized by low BOD/COD ratio of typically  $< 0.01$ . Therefore to treat such wastewater, the destructive wastewater treatment methods which can be utilized are the Advanced Oxidation Processes (AOPs). One of the AOPs method which is the  $\text{UV}/\text{H}_2\text{O}_2/\text{Fe}^{2+}$  (or UV/Fenton) offers not only relatively low cost but also quite effective (in terms of color removal and reaction time) treatment. This particular research aimed to optimize the conditions of UV/Fenton photo-oxidation process for Drimarene Dark Red containing textile-dye wastewater. The two main operating conditions to be optimized were the initial concentration of  $\text{H}_2\text{O}_2$  ranged between 0.022–0.078 %-w and the mol ratio of  $\text{Fe}^{2+} : \text{H}_2\text{O}_2$  was varied from 1 : 13 up to 1 : 45, using the Central Composite Design experimental matrix. The photo-oxidation was carried out at the optimum pH of 3 from some previous experiments. The best processing conditions of the photo-oxidation of Drimarene Dark Red (DDR) were found at the initial concentration of  $\text{H}_2\text{O}_2$  at 0.050%-w and the mole ratio  $\text{Fe}^{2+} : \text{H}_2\text{O}_2$  of 1 : 22. Under these conditions, the measured 2<sup>nd</sup> order pseudo-rate constant was  $0.021 \text{ M}^{-1}.\text{min}^{-1}$ . The DDR color removal of 90% was surprisingly achievable within only 10 minutes reaction time.

## 1. Introduction

Several type of wastewaters come from industrial activity often cause negative as well as serious impact not only to the natural environment, but also to community due to its non-biodegradable and sometimes toxic in nature. Such wastewater can easily be found in Indonesia, especially in heavily populated West Java region. Common problems related to rivers pollution in this area are mostly originated from textile-dye water discharge, if improperly treated to meet the regulation.

Due to its toxic and non-biodegradable characteristics [1], dye containing wastewater can not be easily dealt with commonly used biological treatment. Therefore, as one of the tertiary treatments, Advanced Oxidation Processes (AOPs) offer an alternative yet excellent method of treating such wastewater by effectively oxidizing the dye pollutants. This method can easily and rapidly destroy the non-biodegradable content (with BOD/COD ratio of typically  $< 0.01$ ) in the wastewater into simpler compounds or intermediates which later on become biodegradable (BOD/COD ratio  $> 0.1$ ), and thus can be further treated by cheaper conventional biological methods [2], such as using aeration or activated sludge pond.

Various AOPs have something in common, which is the generation of  $\bullet\text{OH}$  (hydroxyl) radicals whose standard reduction potential is only less positive than Fluorine [3]. Therefore, these radicals will act as very potent oxidizing agents capable of degrading almost any organic pollutants. Hydroxyl radicals may be produced via several ways, but normally by combining UV radiation with common oxidizing agents (such as  $\text{H}_2\text{O}_2$  or  $\text{O}_3$ ). However, without UV present those radicals may also be generated if certain oxidizing agents meet a catalyst. For example,  $\text{O}_3$  (ozone) in alkaline condition or the combination of  $\text{H}_2\text{O}_2$  with  $\text{Fe}^{2+}$ , well known as Fenton reagent, may also yield  $\bullet\text{OH}$  radicals [4].

This research explored the use of UV with Fenton reagent altogether for treating textile-dye (Drimarene Dark Red / DDR) containing wastewater. The combination of UV with Fenton reagent might offers rapid and effective degradation of the dye pollutant due to the synergetic effect of both



elements which produced more  $\bullet\text{OH}$  radicals than separate UV/  $\text{H}_2\text{O}_2$  or Fenton reagent as normally used. In addition, the use of  $\text{Fe}^{2+}$  catalyst to significantly promote the degradation capability of UV/  $\text{H}_2\text{O}_2$  system brought attractive economical advantage in comparison to similar process using ozone as additional oxidizing agent, which required expensive capital related cost for the ozone generator.

## 2. Materials and Methods

### 2.1. Materials

The DDR containing wastewater was prepared by dissolving 2,5 g dye in 50 L of water resulting in 50 ppm concentration, as normally found in similar (real) textile-dye wastewater. The wastewater was initially mixed with a certain amount of  $\text{H}_2\text{O}_2$  (50%-w) solution and the pH of the mixture was adjusted to 3 (with 2N  $\text{HNO}_3$ ) as the optimum pH for treating similar textile-dye using UV/  $\text{H}_2\text{O}_2$  method [5].

### 2.2. Photo-oxidation

The mixture was then fed into a 50 L column photo-reactor equipped with 5 low pressure UV lamp (75 Watt each) and  $\text{Fe}^{2+}$  ( $\text{FeSO}_4$ ) solution was subsequently added to the reactor before the UV irradiation began. The mixture was processed batch wisely for 90 minutes, and samples (10 mL each) were withdrawn during the photo-oxidation process within the reactor. Those samples were treated with excess thiosulfate solution to deactivate the remaining  $\text{H}_2\text{O}_2$  and then centrifuged prior to spectrophotometer analyses (at  $\lambda = 525$  nm).

### 2.3. Experimental design

The effect of the two main variables, namely  $\text{H}_2\text{O}_2$  initial concentration and the  $\text{Fe}^{2+} : \text{H}_2\text{O}_2$  mole ratio, were investigated using Central Composite Design [6] to determine the optimum conditions, under which the highest reaction rate constant was achievable. Within the experimental design matrix, the center point was at 0.05 %-w  $\text{H}_2\text{O}_2$  and ratio of 1 : 20, with 4 replications.

## 3. Results and Discussions

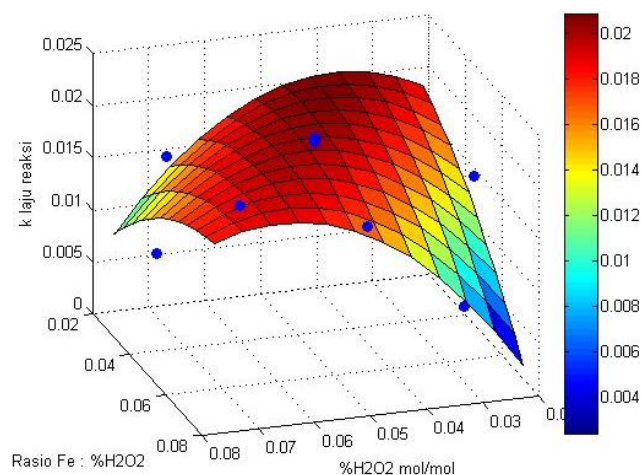
### 3.1. Response variable and the optimum conditions

The response variable selected as the measure of DDR removal effectiveness was the reaction rate constant, which appeared to follow the pseudo 2<sup>nd</sup> order kinetic rather than the pseudo 1<sup>st</sup> order commonly applicable for UV/  $\text{H}_2\text{O}_2$  system [5]. The DDR concentration profiles against reaction time showed a 'long tail' or a typical 2<sup>nd</sup> order reaction curve. The results of the calculated 2<sup>nd</sup> order reaction constants at various experimental conditions were summarized in Table 1.

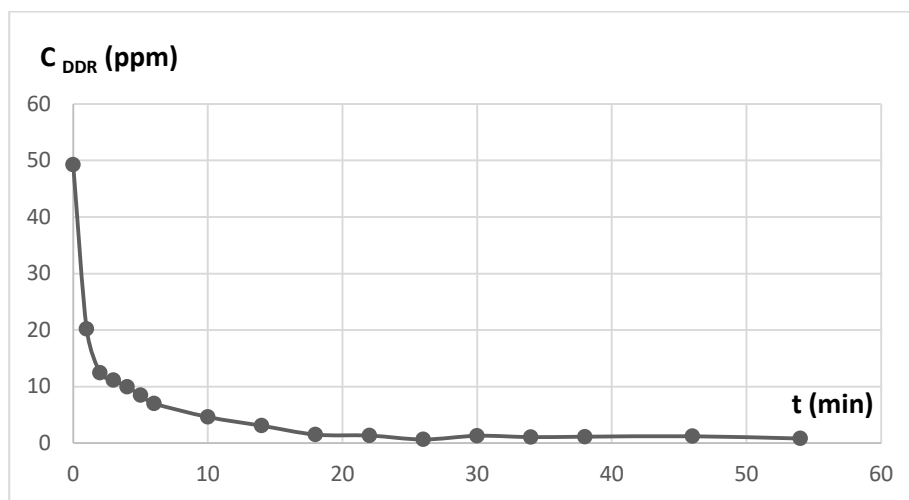
Those results were then fitted to the 1<sup>st</sup> order as well as 2<sup>nd</sup> order response surface model. The multi linear regression for both models revealed that the response surface followed 2<sup>nd</sup> order model with  $R^2$  of 0.986 compared to that of 1<sup>st</sup> order of 0.899. Furthermore, using the 2<sup>nd</sup> order model the partial derivatization with respect to both  $x_1$  and  $x_2$  resulted in the optimum conditions of 0.0504 %-w  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+} : \text{H}_2\text{O}_2$  ratio of 0.0446 (or 1 : 22.4) under which the reaction rate constant was predicted as  $0.021 \text{ M}^{-1} \cdot \text{min}^{-1}$ . The 3-D plot of the results presented in Table 1 was shown in Figure 1, and a validation run was also carried out to confirm the model prediction on the optimum conditions above. The validation result showed an excellent agreement with the 2<sup>nd</sup> order response surface model prediction.

**Table 1.** The 2<sup>nd</sup> order reaction constant at various conditions

RUN	Coded Variable		Rate Constant [M <sup>-1</sup> .min <sup>-1</sup> ]
	x <sub>1</sub> (% H <sub>2</sub> O <sub>2</sub> )	x <sub>2</sub> (Fe <sup>2+</sup> : H <sub>2</sub> O <sub>2</sub> )	k
1	-1	-1	0,0179
2	-1	1	0,0073
3	1	-1	0,0164
4	1	1	0,0195
5	0	0	0,0207
6	0	0	0,0205
7	0	0	0,0183
8	0	0	0,0208
9	1,414	0	0,0115
10	-1,414	0	0,0154
11	0	1,414	0,0178
12	0	-1,414	0,0189

**Figure 1.** The 3-D plot of the experimental results

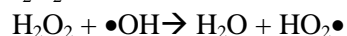
Under those optimum conditions, the DDR removal in the wastewater was found to be very rapid as shown in Figure 2. Within only 10 minutes reaction time, the DDR content removal reached 90% and after 20 minutes (97% removal) the DDR concentration showed a plateau which was typical for reactions with 2<sup>nd</sup> order kinetics.



**Figure 2.** The DDR concentration profile under optimum conditions

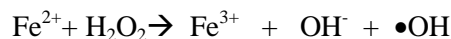
### 3.2. The effect of $H_2O_2$ concentration

The 3-D plot revealed that the initial  $H_2O_2$  concentration had a significant role, especially at relatively high  $Fe^{2+} : H_2O_2$  ratio, to the DDR removal effectiveness. At lower  $H_2O_2$  concentration, the increasing  $H_2O_2$  concentration brought dramatic advantage due to the high concentration of  $\bullet OH$  radicals formed due to the interaction of  $H_2O_2$  with both UV and especially more abundant  $Fe^{2+}$ . This fact would finally led to much more quicker DDR degradation which translated to significantly higher  $k$  was observed, for example run 4 had  $k$  value 2.7 times larger than run 2 due to the increasing % $H_2O_2$  at relatively high  $Fe^{2+} : H_2O_2$  ratio. However, at higher  $H_2O_2$  concentration, the increasing  $H_2O_2$  concentration led to a detrimental DDR removal performance, i.e. run 9 showed much lower  $k$  value (around  $\frac{1}{2}$ ) than that of run 8. Excessive  $H_2O_2$  concentration resulted in a drawback to the DDR degradation / removal because the  $H_2O_2$  itself was reactive to the  $\bullet OH$  radicals producing a much less potent  $HO_2\bullet$  radicals (reduction potential of 1.7 V compared to 2.8 V of  $\bullet OH$  radicals) to destroy the pollutant [7]. The reaction between  $H_2O_2$  with the  $\bullet OH$  radicals was as follow:



### 3.3. The effect of $Fe^{2+} : H_2O_2$ ratio

In general, the effect of the  $Fe^{2+} : H_2O_2$  ratio had similar trend with that of  $H_2O_2$  concentration to the DDR degradation effectiveness. An optimum value of around 1 : 22 was ideal ratio for the treatment. Increasing  $Fe^{2+}$  concentration was initially beneficial since it was needed for  $\bullet OH$  radical generation essential for the DDR degradation. The reaction between  $Fe^{2+}$  and  $H_2O_2$  was outlined by Tang [4] as follow:



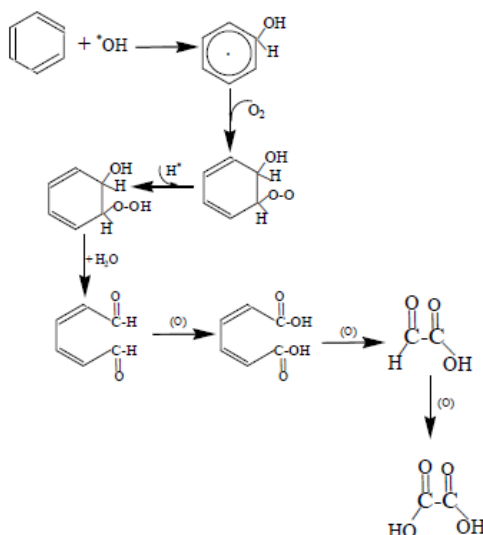
However, at excessive level of  $Fe^{2+}$  concentration the UV light available for  $\bullet OH$  radical production was partially consumed / absorbed by the  $Fe^{3+}$  (as the product of above reaction) and eventually lower the degradation rate constant. Therefore, it was imperative to operate the degradation under those optimum conditions, so that the treatment could be carried out as effective as possible, in terms of both time and cost.

### 3.4. DDR photodegradation mechanism

The DDR structure had many aryl (benzene) rings as well as several  $-N=N-$  bonds (azobridges) which were known as chromophores [8] responsible for the color of the dye since they contain delocalized electrons able to absorbed some spectrum of the visible light. During the photodegradation, the  $\bullet OH$  radicals would initiate the attack to such groups by electrophilic addition

to the  $\Pi$  bonding [4] yielded intermediate radicals which would experience further degradation into simpler species.

The mechanism of the degradation of the aryl ring by  $\bullet\text{OH}$  radical had been published in several literatures. For example, Christina [9] explained a series of reaction led to the ring opening and oxalic acid as the final product, as shown in Figure 3 below.



**Figure 3.** The mechanisms of aryl ring degradation by  $\bullet\text{OH}$  radical

The aromatic ring would initially turned into hydroxycyclohexadienyl as the result of electrophilic addition. This radical could further react with dissolved  $\text{O}_2$  producing unstable hydroxyhydroperoxide which later yield an aliphatic dialdehyde after water molecule elimination step. Subsequently, the dialdehyde species would be further oxidized into glyoxal and finally oxalic acid.

#### 4. Conclusions

The UV/Fenton photo-oxidation process was proven to be effective for treating Drimarene Dark Red (DDR) containing textile-dye wastewater. An optimization using Central Composite Design experimental matrix revealed that the photo-oxidation at pH 3 was best carried out at the initial concentration of  $\text{H}_2\text{O}_2$  at 0.050%-w and the mole ratio  $\text{Fe}^{2+} : \text{H}_2\text{O}_2$  of 1 : 22. Under these conditions, the measured 2<sup>nd</sup> order pseudo-rate constant was  $0.021 \text{ M}^{-1} \cdot \text{min}^{-1}$  and the DDR color removal of 90% was surprisingly achievable within only 10 minutes reaction time. The experimental results also showed that it was imperative to operate the degradation under those optimum conditions, so that the treatment could be carried out as effective as possible, in terms of both time and cost.

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