

# The performance and decolourization kinetics of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> oxidation of reactive green 19 dye in wastewater

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**Abstract.** The degradations characteristic of azo dye Reactive Green 19 (RG19) was investigated using advanced oxidation process (AOPs). It was evaluated based on colour and chemical oxygen demand (COD) removal. The effect of operational parameters such as initial dye concentration, initial dosage of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), contact time, and pH was also being studied. The samples were treated by ozonation (O<sub>3</sub>) and peroxone O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process. Advanced oxidation processes (AOPs) involve two stages of oxidation; firstly is the formation of strong oxidant and secondly the reaction of organic contaminants in water. In addition, the term advanced oxidation is referring to the processes in which oxidation of organic contaminants occurs primarily through reactions with hydroxyl radicals. There are several analyses that use to determine the efficiency of the treatment process, which are UV-Vis absorption spectra, COD, Fourier Transform Infrared (FT-IR), and pH. The results demonstrated that the ozone oxidation was efficient in decolourization and good in mineralization, based on the reduction of colour and COD. Additionally, results indicate that H<sub>2</sub>O<sub>2</sub> is able to perform better than ozonation in order to decolourize the dye wastewater with 0.5 mL H<sub>2</sub>O<sub>2</sub>/L dye dosage of H<sub>2</sub>O<sub>2</sub> at different initial concentration, initial pH, with contact time.

## 1 Introduction

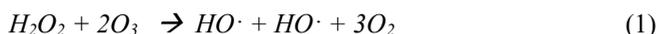
The industrial wastewater pollution is a serious problem that impacts negatively on the environment especially water resources. The biggest industrial wastewater comes from textile, leather, paper and other dyeing industries. The treatment of industrial wastewater poses significant problems in wastewater treatment industry. However, the AOPs have become the most promising procedures to treat dye-containing in terms of effective decolourization and degradation of the refractory pollutants [1]. Nearly all AOPs are based on the generation of reactive species, hydroxyl radicals which degrade a broad range of organic pollutants quickly and non-selectively. The generation commonly accelerated by a

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combination of oxidants (ozone (O<sub>3</sub>) or H<sub>2</sub>O<sub>2</sub>), irradiation (UV light), and catalysts (metal ions or photocatalysts). The oxidation potential of hydroxyl radicals (2.80V) exceeds that of O<sub>3</sub> (2.08V).

The textile industry is one of the largest industries in the world in terms of its output or production and employment [2]. The dye is a colorant which can be used to dye textile fibers, which means that it has an affinity to the material to which it is applied. Dye in wastewater of textile industry mainly generated from the wet-processing originates from washing and bleaching [3]. Dyes are widely used in the textile industries due to favourable characteristics, such as intense colour, water fastness, and uncomplicated application techniques. In the industries, the azo are among the most common synthetic dyes both in terms of the number and amount produced with azo bond groups [4]. The azo dye wastewaters are high biological oxygen demand (BOD) and COD content that impact visible colour, obstruct light penetration and oxygen transfer into water bodies. Besides, azo dyes account for approximately 60-70% of all dyes used in food and textile manufacture [5]. O<sub>3</sub> reacts directly with pollutants via ozonolysis and through radical reaction [6]. Typically, ozonation rarely produces complete mineralization to carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O), but leads to partial oxidation products such as organic acid, aldehydes, and ketones where oxygen is introduced into carbonyl sites within the product molecules [7]. The peroxone (O<sub>3</sub> with H<sub>2</sub>O<sub>2</sub> oxidation) is used basically for the contaminants which conventional oxidation is difficult and consumes large amounts of oxidant [8]. The reaction comprises of O<sub>3</sub> dissolution and H<sub>2</sub>O<sub>2</sub> addition (Equation 1).

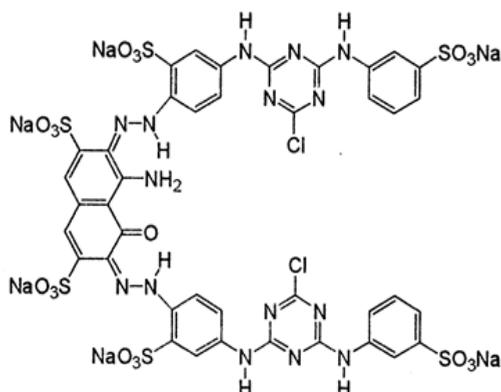


The H<sub>2</sub>O<sub>2</sub> is relatively inexpensive and readily available chemical oxidant [9], and the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> can be easily be automated. The independence of the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> from any light source (UV irradiation) gives a specific benefit to this process, that can be used in high turbidity or dark wastewater [8]. The O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> of synthetic dye highly depended on the pH. The O<sub>3</sub> decomposed rate was increased with pH, as more H<sub>2</sub>O<sub>2</sub> was dissociated into HO<sub>2</sub><sup>-</sup>. For this reason pH 11 was considered to be the most suitable pH for the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> treatment [10]. Moreover, complete discoloration achieved for vinyl sulphone dyes of Reactive Blue 220 and Reactive Yellow 15 in 90 min, and experience more difficulty in decolourization [11]. The COD values obtained were also below the allowed limit, but exceeded the allowed limit value of the other dyes. Therefore, it is obvious that performance of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> depends on the type of dyes. Therefore, in order to get the most suitable and economical process, it is important that appropriate contact time, H<sub>2</sub>O<sub>2</sub> dosage, and pH are being determined.

## 2 Materials and methods

### 2.1 Materials

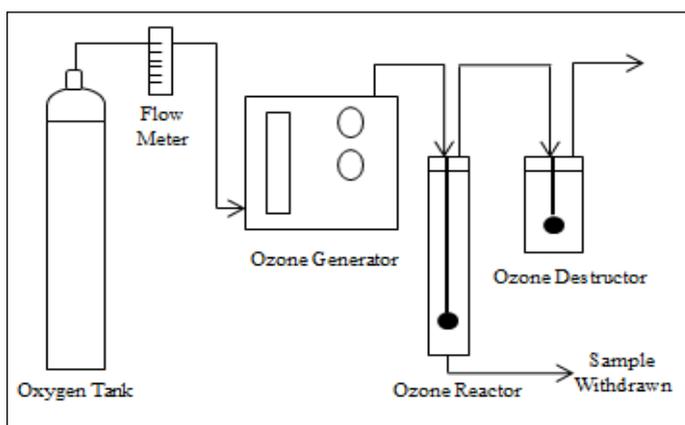
The analytical grade diazo RG19 was selected as a model due to its common application in industries obtained from Sigma-Aldrich. Its molecular weight and the molecular formula are 1,418.94g and C<sub>40</sub>H<sub>23</sub>C<sub>12</sub>N<sub>15</sub>Na<sub>6</sub>O<sub>19</sub>S<sub>6</sub>, respectively. The appropriate weight of dye will be dissolved in ultrapure water for the preparation of the stock solution. In order to prepare 5,000 mg/L concentration of the stock solution, 5 g RG19 will be dissolved in 1 L of ultrapure water. Figure 1 shows the molecular structure of RG19.



**Fig. 1.** Molecular structure of RG19.

### 2.1 Experimental Setup

The  $\text{O}_3$  was generated in a laboratory scale cylindrical glass reactor from purified  $\text{O}_2$  with a total volume of 2 L, equipped with  $\text{O}_3$  destructor. The  $\text{O}_2$  will continue introduced into ANA-13 A2ZZ-3G Ozone Generator to produce  $\text{O}_3$  gas into the reactor. Thus, the gas continues flow through a diffuser and produce fine bubbles at constant flow rate supplying to 2 L dye sample. Predetermined  $\text{H}_2\text{O}_2$  dosage will be added to the dye sample just before  $\text{O}_3$  entered the reactor. The 2% of potassium iodide (KI) will trap the leftover  $\text{O}_3$ . Figure 2 shows the schematic diagram of experimental set-up.



**Fig. 2.** Schematic diagram of experimental set-up for  $\text{O}_3$  and  $\text{O}_3/\text{H}_2\text{O}_2$ .

### 2.3 Experimental Procedure

Constant  $\text{O}_3$  flow rate has been applied, with different dosage of 0.25, 0.50, 0.75 and 1.00 mL  $\text{H}_2\text{O}_2/\text{L}$  dye at pH 7. Moreover, the  $\text{O}_3$  and optimum  $\text{H}_2\text{O}_2$  dosage were applied to the study of the effects of pH (3, 5, 7, 9, 11), together with the initial concentration of 100, 300, 500 mg/L. The experiments were conducted at room temperature with different contact time of 0, 1, 2, 3, 4, 5, 10, 15, and 20 minutes. Finally, the samples were withdrawn at definite intervals for analyses.

## 2.4 Analytical Method

The KI titration will use to determine the  $O_3$  flow rate dye samples. UV-Vis spectrophotometer will be used to analyse the colour and dye concentration of the dye samples. The value of COD will be tested before and after treatment by  $O_3/H_2O_2$  oxidation with the standard APHA method. HACH DR200 COD reactor and DR2800 spectrophotometer will be used to react and take the COD reading in terms of mg/L, respectively. The FT-IR (Spectrum 400 FT-IR/FT-Nir Perkin Elmar) spectroscopy is used to identify and compare the basic functional group of the dye samples before and after  $O_3/H_2O_2$ . The pH of the samples will be adjusted and measured by using Hanna Instrument HI 2211 pH meter.

## 3 Results and discussions

### 3.1 Percentage of Colour Removal

Fig. 3 shows the percentage removal for RG19 that has been treated with  $H_2O_2$  in the dosage 0.5 mL  $H_2O_2/L$  dye with ozonation for different contact time. For the comparison between the two experiment result  $O_3$  and  $O_3/H_2O_2$ , the graph below shows that the decolorization of RG19 is faster with the presence of  $H_2O_2$ . This is because, when  $H_2O_2$  is added into the ozonation system, the decomposition of  $O_3$  into hydroxyl radical is accelerated the process and shift the process entirely to an AOP [12]. Therefore, with the more number of hydroxyl radicals, they can attack the azo bond faster than breaking down the sulphonate group and naphthalene ring in dye [13]. Fig. 4 shows the colour removal result for RG19 treated with  $O_3/H_2O_2$  with different dosage of  $H_2O_2$  in the different contact time. According to the graph dosage, 0.5 mL  $H_2O_2/L$  dye is the suitable dosage for due to the faster decolourization of RG19 compared to other. Thus, 0.5 mL  $H_2O_2/L$  dye was selected as the optimum dosage and the dosage has been used to treat RG19 for higher concentration (300 and 500 mg/L).

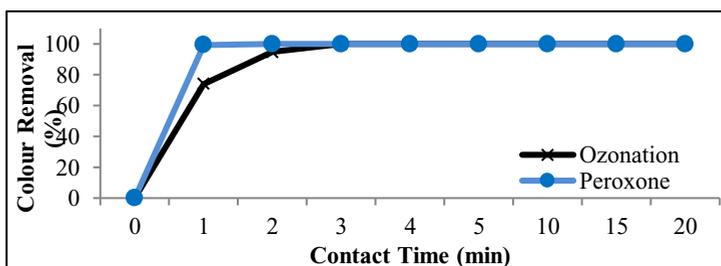


Fig. 3. Colour Removal for RG19 Treated with Ozonation and  $O_3/H_2O_2$  of 100 ppm of RG19.

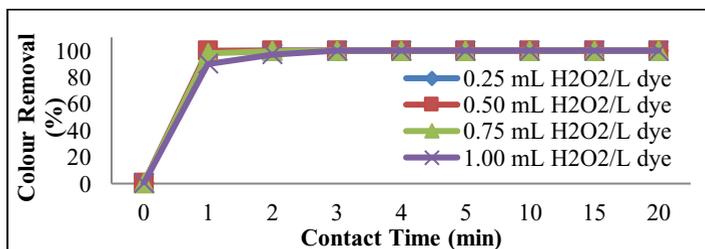


Fig. 4. Colour Removal for 100 ppm of RG19 for Peroxone with Different Dosage of  $H_2O_2$ .

### 3.2 COD Results

Fig. 5 shows the COD result for different dye treatment in the contact time 0, 1, 2, 3, 4, 5, 10, 15, and 20 minutes. According to the graph shown, the treatment with  $O_3/H_2O_2$  has higher COD reading compared to treatment with  $O_3$  only. This is because that  $H_2O_2$  can interfere with COD analysis by consuming oxidation reagent, for example,  $K_2Cr_2O_7$ . Thus it is lead to the overestimating of COD measurements [14]. Generally, the addition of  $H_2O_2$  during ozonation may enhance the rate of COD degradation compared to treatment without the interference of  $H_2O_2$ . Fig. 6 shows the COD result for RG19 treated with  $O_3/H_2O_2$  in a different dosage of  $H_2O_2$  with different contact time. According to the graph below, higher dosage of  $H_2O_2$  can give a higher reading of COD value. Therefore, the results show that  $H_2O_2$  is not suitable to remove COD compared to ozonation. This is because of its radical scavenging effect [14].

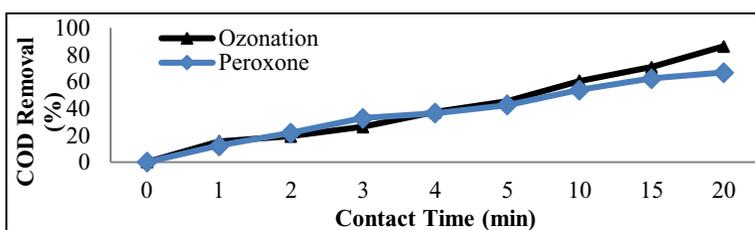


Fig. 5. COD for Treated RG19 with  $O_3$  and  $O_3/H_2O_2$ .

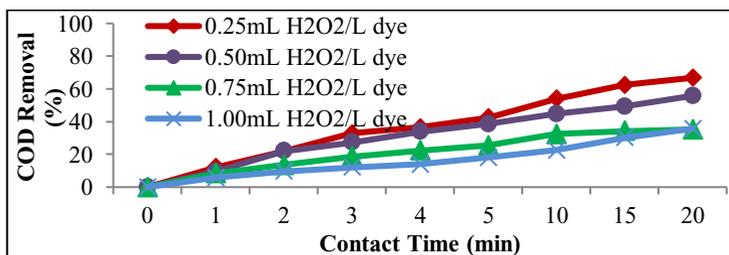


Fig. 6. COD for Treated RG19 with  $O_3/H_2O_2$  with Different Dosage of  $H_2O_2$ .

Fig. 7 shows the COD result for RG19 treated with  $O_3/H_2O_2$  in optimum dosage with different concentration of dye. According to the graph shown below, the higher concentration of RG19 can give the given value of COD. In addition, it is also shown that longer treated contact time give the lower value of COD. This can explain that longer period of treatment gives higher ability to treat dye. Thus, less residual COD found as most of them have been oxidized to  $H_2O$  and  $CO_2$  [15].

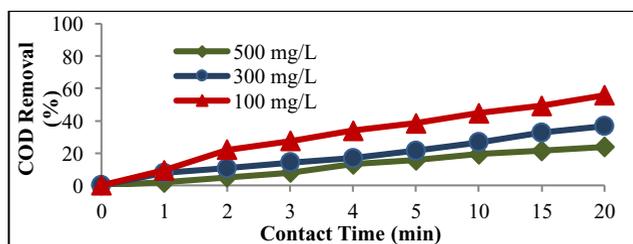


Fig. 7. COD Removal for Treated RG19 with  $O_3/H_2O_2$  in Optimum Dosage of  $H_2O_2$  with Different Concentration of RG19.

### 3.3 FT-IR Spectra

Fig. 8 (a) below shows the FT-IR result for RG19 for ozonation in different contact times 0, 10, and 20 minutes in form of split view. We can observe that some of the absorption peaks will be shifted slightly or disappeared after the ozonation for some period of time. By observing 0 min treatment process, peak at  $1,500\text{ cm}^{-1}$  can be seen, which indicates the presence of azo bond in the RG19. But, it is shown that as the time of treatment increase the azo bond has been shifted and disappeared. Besides, benzene ring that represents in peak  $1,600\text{ cm}^{-1}$  to  $1,400\text{ cm}^{-1}$  has been decreasing with the treatment period of ozonation. Benzene ring has been oxidized by hydroxyl ion. Around peak  $1,180\text{ cm}^{-1}$  that represent sulphonate group, it is decreased after ozonation from 0 to 20 minutes. this shows that it has been mineralized.  $3,400\text{ cm}^{-1}$  to  $3,000\text{ cm}^{-1}$  show a very weak peak that represents carboxylic acid. Fig. 8 (b) below shows the FTIR result for RG19 treated with  $\text{O}_3/\text{H}_2\text{O}_2$  in different contact time in form of split view. For  $\text{O}_3/\text{H}_2\text{O}_2$  treatment, it is almost similar to ozonation for the peak absorption peak. However, the peak for representing each functional groups are stronger than the ozonation process. This happens due to the addition of  $\text{H}_2\text{O}_2$  in the process.

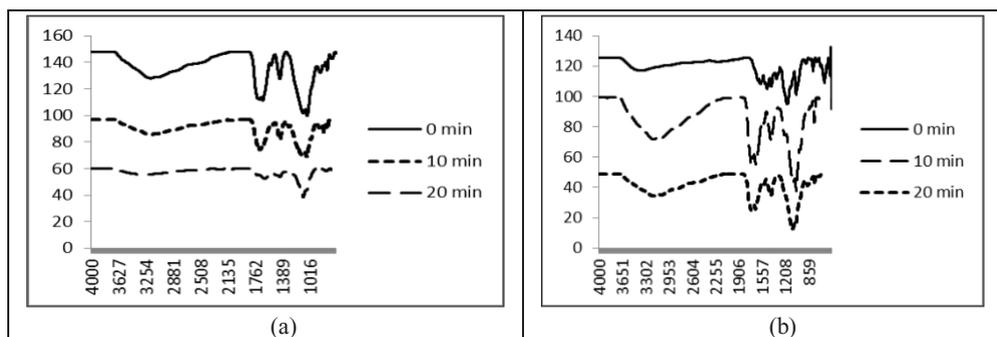


Fig. 8. FTIR Split View for RG19 Treated with a)  $\text{O}_3$ , b)  $\text{O}_3/\text{H}_2\text{O}_2$ .

### 3.4 Effect of pH

Fig. 9 shows the pH of treated sample of RG19 for the different dosage of  $\text{H}_2\text{O}_2$  treated with peroxone in the contact time 0, 1, 2, 3, 4, 5, 10, 15 and 20 minutes. Based on the graph,  $1.0\text{ mL H}_2\text{O}_2/\text{L dye}$  give the lowest pH and  $1.5\text{ mL H}_2\text{O}_2/\text{L dye}$  give the highest pH of treated sample compared to other. The  $\text{O}_3/\text{H}_2\text{O}_2$  of synthetic dye highly depended on the pH. The  $\text{O}_3$  decomposed rate was increased with pH, as more  $\text{H}_2\text{O}_2$  was dissociated into  $\text{HO}_2^-$  [8]. Therefore, in order to get the most suitable and economical process, it is important that appropriate contact time,  $\text{H}_2\text{O}_2$  dosage, and pH are being determined. Figure 10 shows the COD value against dosage of  $\text{H}_2\text{O}_2$  with different initial pH. According to the graph below initial pH, 11 give the lower COD value and initial pH 3 give the higher COD value. Therefore, initial pH 11 proves that pH 11 is the most suitable initial pH of RG19 to be treated compared to others.

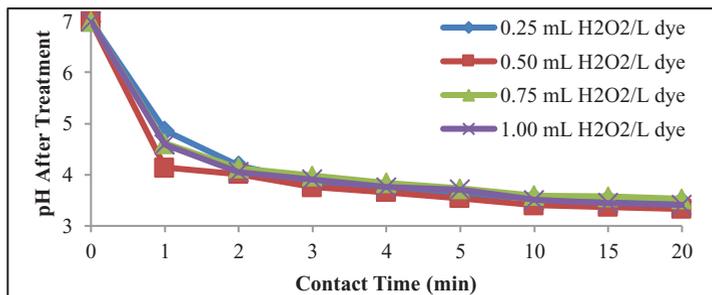


Fig. 9. pH After Treatment versus Contact Time with Different Dosage of H<sub>2</sub>O<sub>2</sub>.

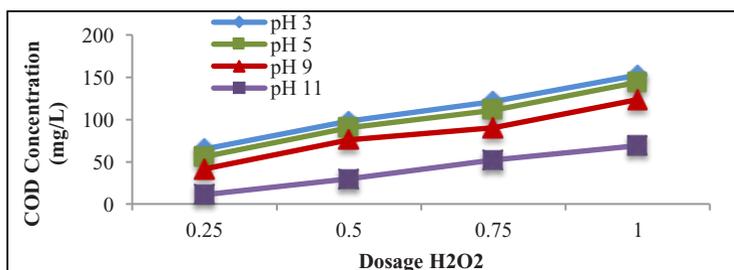


Fig. 10. COD Concentration versus Dosage of H<sub>2</sub>O<sub>2</sub> from Different Initial pH.

## 4 Conclusions

In conclusion, ozonation and AOPs are able to remove colour from dye wastewater. It is decolourised azo dyes by breaking the azo bond and degrades the organic matter to become small fragments of an organic compound. In addition, by comparing ozonation and AOP, the addition of H<sub>2</sub>O<sub>2</sub> in the treatment process can enhance the efficiency of colour removal and degradation process. This is explained that H<sub>2</sub>O<sub>2</sub> able to enhance the decomposition of O<sub>3</sub> into hydroxyl radicals. In addition, from the UV-Vis result shows that 0.5 mL H<sub>2</sub>O<sub>2</sub>/L dye is the optimum dosage of H<sub>2</sub>O<sub>2</sub> to treat RG19. This is because it gives faster time to decolourized RG19; give the lower value of COD; and able to decolourized the high concentration of dye. The degradation of dye can be seen from the wavelength scan. It is shown that AOPs has faster degradation of wavelength compared to ozonation. For COD value, AOPs has the higher value compared to ozonation due to the presence of H<sub>2</sub>O<sub>2</sub> in the treatment. Besides, initial pH 11 gives the lower COD value compared to others. The same trend happens on FTIR results, the absorption peak for AOPs is stronger than ozonation. However, AOPs presence lower peak azo bond compared to ozonation indicates that azo bond has been breaking more during AOPs treatment process. Therefore, in order to get the most suitable and economical process, it is important that appropriate contact time, H<sub>2</sub>O<sub>2</sub> dosage, and pH are being determined.

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