Optimization of Anthraquinone Dye Wastewater Treatment using Ozone in the Presence of Persulfate Ion in a Semi-batch Reactor

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Abstract. The degradation of anthraquinone dye Reactive Blue 19 by using O₃ and O₃ / S₂O₈²⁻ in the advanced oxidation processes is studied to investigate the performance of these two systems. The response surface method with a Box-behnken Design was successfully applied to identify the relationship between operating variables such as initial concentration, S₂O₈²⁻ dosage and contact time in order to determine the optimum operating condition. The quadratic model for the percentage COD removal (response) proved to be significant for the degradation of the dye. The COD removal efficiency under Box-behnken Design and experimental test were found to be 96.2% and 83.9% under the optimum conditions. Furthermore, the result obtained showed that the O₃ / S₂O₈²⁻ system is more effective than the O₃ only in treating the Reactive Blue 19.

1. Introduction
In recent year, due to the development in many industries such as light and heavy industries, it brings the higher potential effect to the environment. Even though, these industries can give the benefits to the economy around the world, but the creation of the pollutant from these industries will produce the large amount of waste that harmful to human and environment. Industrial wastewater such as textile industries will bring the higher potential to the water pollution due to their development in industries. It is because the dyes use in industrial wastewater is very extensive and these industrial become the largest contributor to the industrial effluent. More than 11% of dyes lost in effluent during manufacturing and application processes from the 450,000 tons of organic dyes that annually produced by the worldwide [1]. Anthraquinone dye is one of the examples of dyes that have been used widely especially in the textile industry. As the decolorization anthraquinone dye is one of the serious problems that give a big effect to the environment, this issue has gotten much attention due to their recalcitrant nature [2]. Due to longer time needed of removing dye residue from the textile wastewater by conventional wastewater treatment methods such as carbon adsorptions, coagulation, advanced oxidation processes (AOPs) become the most suitable procedures to treat textile wastewater containing...
dye residue in terms of effective decolourization and reduction of the refractory pollutants. In recent year, the ozonation and AOPs involving ozone in combination with hydrogen peroxide (O$_3$/H$_2$O$_2$), photolytic H$_2$O$_2$ oxidation (UV radiation with H$_2$O$_2$) and advanced Fenton have been the new technology to treat dyes textile and dyestuff industrial effluent. Thus, the ozone-based concept has been extended to the oxidation processes with sulfate radicals (SO$_4^{•-}$), namely ozone-persulfate (O$_3$/S$_2$O$_8^{2–}$) treatment. It uses the powerful hydroxyl or sulfate radicals as a major oxidizing agent and has some operational advantage over conventional processes such as wide pH range, low cost of oxidant precursors (Ammonium sulphate or Sodium persulphate), no post-treatment steps and complete mineralization of pollutants into harmless products (Abdul Aziz et al., 2014).

The study focused on the optimization of the treatment process by using Design Expert (DoE) software. Among different types of programs provide in DoE Expert, this study will use the Response Surface Methodology (RSM) due to their effectiveness and widely used in environmental engineering for optimization processes. In other hand, RSM is a statistical method which is efficient to predict the best performance with a minimum number of experiments [3]. This research mainly focusses on the efficiency of O$_3$ and O$_3$/S$_2$O$_8^{2–}$ in AOPs for treating anthraquinone dye wastewater, to determine the effect of the operational parameters of ozone based AOPs treatment performance. Finally, to identify the optimum operational parameter for COD removal by using Box-behnken Design (BBD) under RSM.

2. Methodology

2.1. Materials and Methods
The analytical grade anthraquinone dye Reactive Blue 19 (RB19) was selected as model due to its common application in industries obtained from Sigma-Aldrich. Other chemicals used were reagent grade and were obtained from R&M and HmbG manufactures. The 10,000 mg/L concentration of stock solution was prepared by using 10 g of RB19 by dilution in 1 L volumetric flask with distilled water. The pH of aqueous solution was adjusted by using 0.1 M Sodium hydroxide (NaOH) and 0.1 M Hydrochloric acid (HCl) solution until desired pH was obtained.

2.2. Experimental Procedure
The semi-batch reactor system consists of the four important equipment in the experimental ozonation setup which an oxygen tank, ozone generator, glass reactor and KI trap reactor. Ozone was generated from a pure oxygen in a ozone generator and continuously bubbled in the liquid bulk with a gas diffuser by applied 2 L/min of flow rate at room temperature. Ozone applications were carried out in a cylindrical glass reactor with the 2 L working volume. The different dye concentration of 100, 300 and 500 mg/L were added into the glass reactor. For the (O$_3$/S$_2$O$_8^{2–}$) system, the varying S$_2$O$_8^{2–}$ dosage from 2 to 6 g would be added to the sample in glass reactor. The treatment was identified at different contact times which were 0, 1, 2, 3, 4, 5, 10, 15 and 20 min. Thus, the remaining ozone leaving the reactor was destroyed in a 2 L conical flask containing 2% KI solution. The samples were withdrawn at definite time interval to determine the pH and COD analysis.

2.3. Analytical Methods
The sample of the RB19 was measured by using Hanna Instrument H1233. The COD concentration was identified by using DR2800 spectrophotometer. The test value obtained from experiment are presented as the average of two measurement. Thus, the efficiency COD removal was determined by using the following equation:

\[
\text{COD removal \%} = \frac{C_0 - C_t}{C_0} \times 100
\]  

Where, $C_0$ is referring to the initial dye concentration (mg/L) while $C_t$ is referring to the final dye concentration (mg/L).
2.4. Experimental Design

Design Expert® 7.1.5 version software was used for the statistical design of experiments and data analysis. Box-Behnken experimental design was applied to optimize the COD removal of the RB19 (response) to investigate the effect of operating parameter on COD removal efficiency. Three factors were chosen as independent variables such as initial dye concentration, contact time and dosage and thus 17 runs were conducted by RSM to optimize the chosen variables. The ranges of independent variables were evaluated based on a set preliminary of experiment and each of the independent variable was varied over three levels and the range of the independent variable as presented in Table 1.

Table 1: O₃ and O₃/Ｓ₂Ｏ₈²⁻ parameters and their level

| Variable         | Factor | -1  | +1  |
|------------------|--------|-----|-----|
| Dye Concentration| A      | 100 | 500 |
| Contact Time     | B      | 0   | 20  |
| Dosage S₂O₈²⁻   | C      | 0   | 6   |

3. Results and Discussion

The efficiency of the O₃ and O₃/Ｓ₂O₈²⁻ were successfully identified in the current study. As shown in Figure 1, the efficiency O₃/Ｓ₂O₈²⁻ in COD removal occurred faster that in O₃ alone, indicating that the sulfate radical still an ability to oxidize the target pollutants despite the increase in S₂O₈²⁻ dosage even though the excess amount of S₂O₈²⁻ will consume hydroxyl radical and inhibit the reaction. The effectiveness on percentage COD removal for both systems were evaluated at 0, 1, 2, 3, 4, 5, 10, 15 and 20 min of reaction time. For a given time, an increase in contact time has resulted in an increase in COD removal. RSM was successfully applied in this study to identify the relationship between a set of controllable experiment factors and observed results. The initial dye concentration, contact time, pH and S₂O₈²⁻ dosage play an important role that influence the percentage COD removal of RB19. The complete design matrix are shown in Table 2.

Figure 1. COD Removal for the O₃ and O₃/Ｓ₂O₈²⁻ treatment at the different contact time

Table 2. Experimental Design Matrix for the % COD Removal of RB19 by the BBD

| Run | Initial Dye Concentration (mg/L) | Contact Time (min) | Dosage of S₂O₈²⁻ | % COD Removal  |
|-----|----------------------------------|--------------------|------------------|---------------|
| 1   | 300.00                           | 20.00              | 6.00             | 39.10         |
| 2   | 100.00                           | 20.00              | 3.00             | 71.96         |
| 3   | 300.00                           | 0.00               | 6.00             | 2.00          |
| 4   | 500.00                           | 20.00              | 3.00             | 9.00          |
| 5   | 100.00                           | 0.00               | 3.00             | 4.00          |
| 6   | 300.00                           | 10.00              | 3.00             | 6.15          |
| 7   | 100.00                           | 10.00              | 6.00             | 63.00         |
3.1. Experimental Design

Table 3 shows the statistical significance of the quadratic model evaluated through ANOVA for % COD Removal of RB19. The final of the mathematical equation as justified by RSM in term of coded factors was given below in Equation 2.

\[
\% \text{COD Removal} = 6.20 - 16.31A + 17.32B + 5.21C - 15.24AB - 7.24AC + 2.66BC + 15.64A^2 - 0.099B^2 + 10.79C^2
\]  \tag{2}

| Source              | Sum of Square | Degree of Freedom | Mean Square | F Value | p-value Prob>F |
|---------------------|---------------|-------------------|-------------|---------|----------------|
| Model               | 7516.91       | 9                 | 835.21      | 164.57  | <0.0001        |
| A-Dye Concentration | 2126.82       | 1                 | 2126.82     | 419.06  | <0.0001        |
| B-Contact Time      | 2398.82       | 1                 | 2398.82     | 472.66  | <0.0001        |
| C-Dosage of S\textsubscript{2}O\textsubscript{8}^-  | 217.05        | 1                 | 217.05      | 42.77   | <0.0003        |
| AB                  | 929.03        | 1                 | 929.03      | 183.05  | <0.0001        |
| AC                  | 209.67        | 1                 | 209.67      | 41.31   | <0.0004        |
| BC                  | 28.25         | 1                 | 28.25       | 5.57    | 0.05054        |
| A\textsuperscript{2}  | 1029.77       | 1                 | 1029.77     | 202.90  | <0.0001        |
| B\textsuperscript{2}  | 0.041         | 1                 | 0.041       | 8.090E-003 | 0.9309        |
| C\textsuperscript{2}  | 490.32        | 1                 | 490.32      | 96.61   | <0.0001        |
| Residual            | 35.53         | 7                 | 5.08        |         |                |
| Lack of Fit         | 35.50         | 3                 | 11.83       | 1893.40 | <0.0001        |
| Pure Error          | 0.026         | 4                 | 6.250E-003  |         |                |
| Car Total           | 7552.43       | 16                |             |         |                |

The model F value of 7516.91 shown in the Table 3 implies that the model is significant for the degradation of RB19 (response). In addition, the value of “Prob > F” less than 0.0500 indicate the model terms are significant while the value greater than 0.1000 indicate the model terms are not significant for the degradation of RB 19. In this case, A, B, C, AB, AC, A\textsuperscript{2}, and C\textsuperscript{2} are the significant parameters. The Lack of Fit F-value of 1893.40 implies the Lack of Fit is significant in this present study. In other hand, based on the ANOVA results, the model obtained a high R\textsuperscript{2} value of 0.9953 and it is in reasonable agreement with the Adj R\textsuperscript{2} value of 0.9892. Based on the value of R\textsuperscript{2} and Adj R\textsuperscript{2} are close to 1.0, it can explain that the regression model provides a very good explanation of the relationship between the independent variables and response.

3.2. Effect of the Independent Variable (Dye Concentration, Contact Time, and S\textsubscript{2}O\textsubscript{8}^- Dosage) on the Response (%COD Removal)

As presented in Figure 2, the 3D plot shows the effect of contact time and dye concentration on the COD removal that given by the BBD. In this case, it can explain that the efficiency of the degradation of RB19 can be performed by increasing the contact time, followed by the decreasing of the dye
concentration. Thus, the contact time play an important role in degradation rate of the RB19. In other hand, the percentage COD removal decreased as the initial dye concentration increased because of the non-availability of sufficient hydroxyl radicals. The expected reason is that because of the •OH concentration is not increase correspondingly when the initial dye concentration increased.

![Figure 2](image2.png)

**Figure 2.** Effect of Contact Time and Dye Concentration on the % COD Removal of RB19

Figure 3 clearly showed the effectiveness of the % COD Removal by increasing the contact time and dosage of $S_2O_8^{2-}$. The maximum of the COD Removal given by the BBD reached until 96.2% at 20 min of experimental time and by using 5.98 g of the $S_2O_8^{2-}$ dosage. Thus, the improvement of the percentage COD removal of RB 19 can be enhanced by using the higher contact time and dosage. The relationship between the contact time and $S_2O_8^{2-}$ acts as the important parameters in order to obtain the higher performance of the % COD Removal. Thus, the efficiency of the oxidation during ozonation was improved by using persulfate reagent in this study. The $S_2O_8^{2-}$ releases sulfate radical in $O_3/S_2O_8^{2-}$ which has powerful oxidation of organics as presented in Equation 3 and 4 [4].

$$S_2O_8^{2-} + 2H^+ + 2e^- \rightarrow 2HSO_4^- \quad (3)$$

$$SO_4^{2-} + HO^- + SO_4^- \rightarrow OH^- \quad (4)$$

![Figure 3](image3.png)

**Figure 3.** Effect of $S_2O_8^{2-}$ Dosage and Contact Time on %COD Removal of RB19

The 3D plot in Figure 4 summarized the effect of $S_2O_8^{2-}$ dosage and dye concentration on COD Removal of RB 19. As can be seen, the percentage removal reached the higher performance when the $S_2O_8^{2-}$ increased with the decreasing of the dye concentration. The employing of $S_2O_8^{2-}$ dosage can obtain higher performance in COD removal efficiency of RB19.
3.3. Effect of pH

The solubility of ozone is affected by the pH, and the result on the percentage COD removal in O₃ and O₃ / S₂O₈²⁻ treatment is given in Figure 5. As can be seen on the plotted graph, the degradation rate of the RB19 increased as the pH increase from 3 to 11. Generally, lower efficiency of the degradation of the RB19 under acidic condition because of the O₃ molecule itself was one of the main reactive. In other hand, the rate of O₃ decomposition to secondary oxidants such as hydroxyl radical increased as the solution become more alkaline [5]. Initial pH 11 shows much decrease of COD concentration within 10 min of ozonation compared to other pH. Thus, the obtained results indicate that the process effectiveness increases significantly when applied alkaline pH due to formation of hydroxyl radical which have much potential stronger oxidizing ability than the molecular ozone under the acidic condition. In addition, for the O₃ / S₂O₈²⁻ system, the removal efficiency of COD also improves with increased pH to 11 because S₂O₈²⁻ was more active at high pH. Thus, pH 11 is the optimum pH to treat the RB19 in AOPs.

3.4. Model Optimization Process and Confirmation

The result optimization by BBD under RSM showed the excellent correspondence between the predicted and experimental values in COD removal efficiency. To achieve the highest performance, the desired goal of each operation condition was set as the ‘minimum’ for the dye concentration, while the contact time was set as a ‘maximum’ and for the S₂O₈²⁻ dosage was set ‘in the range’ in the software optimization step. In other hand, the % COD removal as response was defined as maximum to obtain the maximize COD removal efficiency. Table 4 shows the optimum value predicted from the RSM and experimental value for the process parameters for the maximum COD removal.
Table 4. The efficiency of COD removal at optimum value of each of the independent variables

| Parameters                  | Optimum Value Predicted by RSM | Experimental Value |
|-----------------------------|---------------------------------|--------------------|
| Dye Concentration           | 100 mg/L                        | 100 mg/L           |
| Contact Time                | 20 min                          | 20 min             |
| \(S_2O_8^{2-}\) dosage      | 5.98 g                          | 6 g                |
| Efficiency of the % COD removal | 96.24                           | 83.87              |

4. Conclusion
In the current research, the performance of the \(O_3\) and \(O_3 / S_2O_8^{2-}\) in AOPs for the RB19 dye wastewater was investigated. Based on experimental result, by employing the \(S_2O_8^{2-}\) dosage, it can enhance the effectiveness of the process treatment compared to the process with \(O_3\) alone. The optimum value from the experimental test for each parameter (initial dye concentration, contact time, pH, dosage) were found 100 mg/L, 20 min, 11 and 6 g respectively. Thus, from the experimental design by using BBD, the optimum value predicted for the initial dye concentration is 100 mg/L, followed by the 20 min for the contact time, while 5.98 g for the \(S_2O_8^{2-}\) dosage. The percentage COD removal for both two experiment were 83.9% and 96.2%, respectively under the optimal condition. Based on the analysis of variance ANOVA, it showed the high coefficient of determination value (\(R^2 = 0.9953\), \(\text{adj } R^2 = 0.9892\)), therefore it is ensuring a satisfactory adjustment of the second-order regression model with the experimental data.

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