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Treatment of O_3 with $Na_2S_2O_8$ by ANOVA Interpretation towards Degradation of Azo Dye

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ABSTRACT

Advanced oxidation processes (AOPs) especially ozonation method is widely studied in the wastewater treatment field. In this study, it highlighted about three main environmental issues in the world such as 1) proposing a method to overcome uncontrollable effluents from textile industries by using synthetic dyes; 2) creating an improvement of previous conventional method; 3) reduced process time by using statistical approach. To address with this issue, analysis of variance (ANOVA) from Response Surface Methodology (RSM) to study the performance of O_3 with the help of persulfate ($Na_2S_2O_8$) for treating one of azo dyes which is Reactive Green 19. This is due to there is very limited work done by statistical analysis on this study. Hence, ANOVA data would propose statistical models tailored to the data in 2D and 3D contour plots by knowing the three influenced parameters which is pH (6 to 10), persulfate concentration (30 to 70 mM) and contact time (4 to 20 min). Through the analysis, the result can be concluded that improvement of ozonation process with persulfate ($Na_2S_2O_8$) were statistically significant after all interactive effects gave a positive feedback towards responses. The obtained optimum conditions included a persulfate concentration (49 mM), initial pH (8.89) and contact time (18 min) with fixed initial concentration 100mg/L. The experimental results were corresponded well with predicted models colour removal rates which is 99%.

Keywords: Ozonation (O_3), Azo dye, Persulfate ($Na_2S_2O_8$), 2D and 3D Contour Plot, ANOVA.

1. INTRODUCTION

A great influential wastewater issues also involved a part of global economy mainly caused by continuously trends in fashion around the world including Malaysia. One of the industries that frequently involved in fashion trend is textile industry. Facts from Trabelsi-Souissi *et al*.[1] stated that industrialization contributes to the highest amount of wastewater that is extremely dangerous to the ecosystem. It can be as one of the bad precursors industries in the world due to their effluent consists of a high concentration of dyes and numerous of recalcitrant organic compounds investigated by Buthiyappan *et al*.[2]. In addition, Nimkar[3] studies had been explored the textile dyes have been composed such about 90% would stayed on fabric itself while their remaining 10% discharged into the effluent in manufacturing stages. After years, 90% portion in fabric itself could be end up with landfills and the water bodies also being affected in same terrible way during that fabric started degraded.

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Numerous applications of textile dyes are azo dyes which contain one or more N-N groups in their structures as stated by Kariyajjanavara *et al.*[4]. Statement from Chequer *et al.*[5] said that due to

presence method of dyeing cellulosic fibres (especially elongated fibres) with a high degree of attachment and high resistance against light and humidity caused it became high demands as compared to other classes of dyes. However, this study was extended by Phugare *et al.* [6] which stated that there are limitations treatments of this classification of dye due to its compounds were not biodegradable and their reductive cleavage could release aromatic amines where more toxic than the dyes themselves.

Several methods had been investigated to undergo the degradation of azo dyes specifically either by physical, biological and chemical treatments. After all, a lot of improvements can be generated to overcome the problems. It comes from most of conventional wastewater treatments that usually unable to ensure treated effluent quality meets the required standards due to the increasing complexity of textile discharges. Besides, conventional treatment processes unable to provide an effective treatment of wastewater due to adsorbent regeneration, excess sludge production and rapid fouling of the used membranes by Buthiyappan *et al.*[1]. Thus, to defeat today's challenges; a more potent wastewater treatment system is required immediately suggested by Tony *et al.*[7]. Hence, prior studies from Sandip *et al.*[8] said that in recent years, a feasible treatment among chemical technologies that has been appealed is the advanced oxidation processes (AOPs). AOPs used as an alternative technology based on the degradation of organic pollutants either by ozonation, Fenton, photo catalytic, wet air oxidation and others.

AOPs have been defined from Glaze *et al.*[9] as one of wastewater treatment process occur at room temperature and pressure that involved formation of hydroxyl radical (•OH) radicals in sufficient amount for wastewater purification. By using (•OH) radical as the second highest oxidation potential (E^0= 2.8eV) following by fluorine radicals (E^0 = 3.06eV), which are toxic and cannot be used for wastewater treatment. These elaborations from Hassaan *et al.*[10] unveiled that generation of •OH radical using AOPs such as a prior attention towards most researcher and technology developers. Therefore, one of the most suitable treatments which efficient for azo dye is ozonation process. It supported by Loeb *et al.*[11] evidences stated that ozonation was relatively easy to produce and does not contribute to any secondary pollution. The simplified reaction mechanism of ozone is given below in Eq. (1).

$$3O_3 + H_2O \longrightarrow 2\,\dot{O}H + 4O_2 \tag{1}$$

In spite of a powerful ozonation method, there still presence of some advantages in the wastewater treatment process. As examples are the limitation usage of types of dye, fully mineralization could not be achieved and the other radical that enhanced or disrupted the process not fully discovered yet. In addition, Abu Amr *et al.*[12] stated that ozonation process for treating wastewater still lacks some improvements. Based on recent studies by Stocking *et al.* [13], all AOPs process including ozonation have been influenced to the various parameters such as chemical dosages and ratios with other chemicals, contact time, reactor configuration, ozone dosage, temperature, pH, scavengers and type of pollutants. Sodium Persulfate, $Na_2S_2O_8$ which act as a catalyst in this study will release sulfate radicals which has a powerful oxidation of organics to enhance the performances for treating synthetic textile wastewater.

Prior researchs like Hussain *et al*.[14], Belgin *et al*.[15] and Petrucci *et al*.[16] substantiates the belief that Response Surface Methodology (RSM) such as Central Composite Design (CCD) is a useful scientific approach which has been successfully applied for optimizing advanced oxidation processes factors and other related multifactor problems. This approach supported by Raheem *et al*.[17] described the design of experiments and multiple regression analysis to evaluate the influence of multiple process

variables on response variables. Also, Fermoso *et al*.[18] said that the diagnostic verifying tests imposed by analysis of variance (ANOVA) could be disclosed the suitability of the intended model. Hence, Dutta *et al*.[19] statements concluded the main benefit of this method is by decreased number of experiment would be generated sufficient information and establishing the optimum conditions for desired responses.

As consequences, the four key goals for achieving main goal of this paper to investigate the performance of O_3 / $Na_2S_2O_8$ towards degradation of Reactive Green 19 as diazo dye. Firstly, by evaluating efficiency of colour removal on RG19 with presence of persulfate, $Na_2S_2O_8$. Next, this study interested to deep in statistical knowledge analyzed by ANOVA where by calculating their sum of square, mean square, degree of freedom and others. After that, by using CCD could be proposed a mathematical equation which is final regression model equation for colour removal of RG19. At last, all influenced parameters which is initial pH, persulfate concentration and contact time are been investigated towards their responses by optimum condition.

2. EXPERIMENTAL

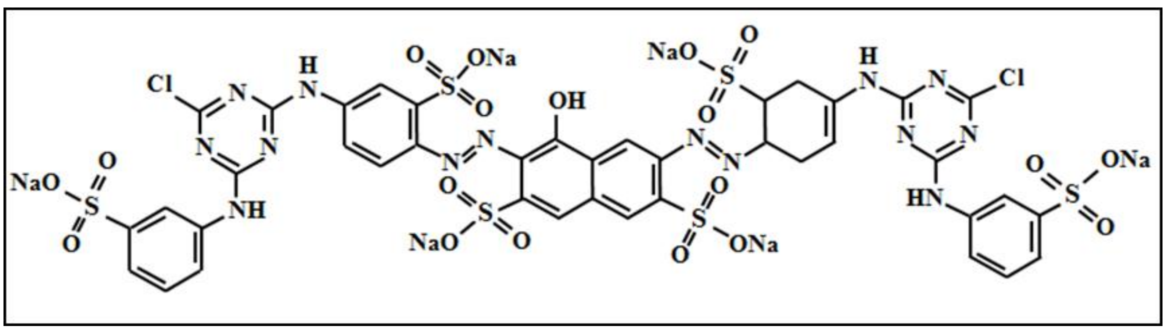

Figure 1. Molecular structure of Reactive Green 19.

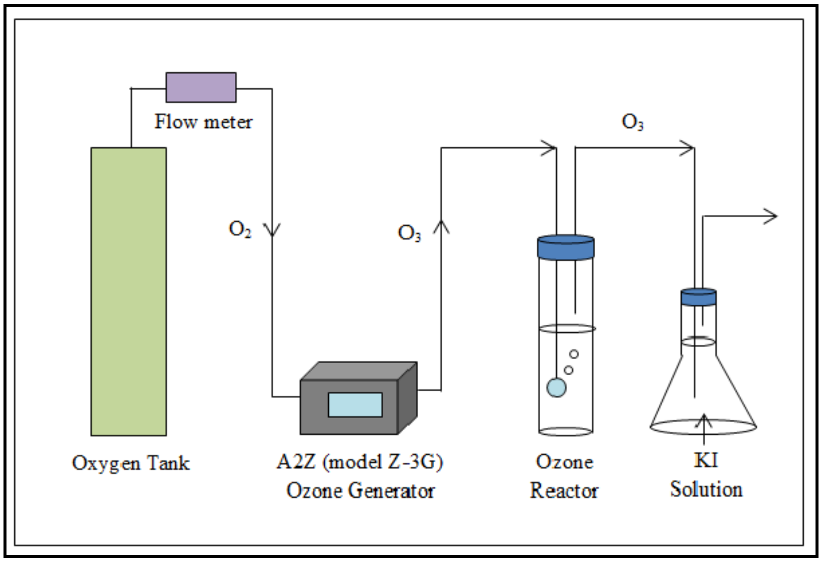

Figure 2. Schematic diagram of experimental set-up.

General procedures: Analytical grade RG19 dye obtained from Sigma-Aldrich was used for all this studies. The dye concentration used for the study was fixed 100mg/L. FIGURE 1 presents the molecular structure of RG19. RG19 has chemical formula of $C_{40}H_{23}Cl_2N_{15}Na_6O_{19}S_6$ and molecular weight is 1418.909 g/mol. The pH of the solutions was checked using a pH meter (Hannah Instruments H1223) and adjusted by adding concentrated H_2SO_4 or NaOH. 10g of dye will be dissolved in 1L ultrapure water for the preparation 10g/L concentration of the stock solution. During the semi-batch experiment, A2Z (model Z-3G) Ozone Generator was used to generate ozone gas through a constant supply of purified O_2. Ozone (O_3) would be continuously flow via a diffuser produced fine bubbles at constant rate supplied into 2 L dye sample. An ozone destructor which is 2% Potassium Iodide (KI) trap would be connected to 2 L of cylindrical glass reactor that equipped to the ozone generator. Then, before ozonation experiment started based on the condition, a certain desired condition of initial concentration of RG19, pH and persulfate concentration would be determined and 2 L/min O_2 flowed would applied through various contact time. The schematic diagram is shown in FIGURE 2.

Detection methods: For determination of colour removal as shown in Equation 2. The experiments were conducted at room temperature and samples were withdrawn at definite time intervals using UV–Vis spectrophotometer (MesuLabTM), Model ME - UV1100.

$$Colour, removal\,(\%) = (C_0 - C_t / C_0) \times 100\,\% \qquad (2)$$

$$Y = \beta_0 + \sum_{(i=1)}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{i=2}^{k} \beta_{ij} + X_i X_j + ei \qquad (3)$$

Response surface modeling: A compelling method such as Response surface methodology (RSM) used mathematical and statistical techniques to fit of a polynominal equation towards the experimental data by Jancic-Stojanovic *et al.*[20]. Optimum of operational variables for this ozonation process is the aim of the RSM. This is because statistical experimental designing with RSM can enhanced the process itself by would decreased the process variability, overall time taken as well as the overall cost Bezerra *et al.*[21]. RSM, Design-Expert® (Version 7.1.5) Stat-Ease, Inc., USA which is Central Composite Design with alpha type; face centered was used in the experimental design where each factor takes only three levels. Table 1 shows each of levels accordingly with operational variables value; where based on Moghaddam *et al.*[22] ;Y is the predicted response; k is the number of factors; β_i and χ_i are the coded variables; β_o is the offset term; β_i, β_{ii}, and β_{ij} are the first-order, quadratic, and interaction effects, respectively; i and j are the index numbers for factor; and e_i is the residual error.

Table 1 Experimental ranges and levels for parametric optimization process

Level of Value	(A) Persulfate concentration (mM)	(B) pH	(C) Contact time (min)
-1	30	6	4
0	50	8	12
1	70	10	20

3. RESULT AND DISCUSSION

3.1 Analysis of variance ANOVA Analysis for Response Surface Quadratic

Ozonation experiment with four process variables which is persulfate concentration (30-70 mM), pH (6-10) and contact time (4-20 min) were selected to investigate their influences on the colour removal % of RG19 (100 mg/L). These range intervals were determined based on preliminary experiments performances. Persulfate concentration which acts as catalyst to enhanced the efficiency of degradation of RG19.

For the above mentioned four variables, a set of 20 experiments is required in Table 2. Central Composite design is a 2^k full factorial which the central point and the star points are added. The star points were the sample points in which all the parameters but one are set at the mean level "m". The value of the remaining parameter is given in terms of distance from the central point. If the distance between the central point and each full factorial sample was normalized to 1, the distance of the star points from the central point can be chosen in different ways. Hence, in this study had been selected $\sqrt{k}/k$, the value of the parameter remains on the same levels of the 2^k full factorial (central composite faced, or CCF). This method elaborated by Emerson *et al.*[23] studies that stated it required three levels for each factor, namely l, m, h in which upper (+1), lower (-1) and central limit (0). The number of experiments required (N) is given by the expression: 2^k ($2^3 = 8$; star points) + 2k ($2 \times 3 = 6$; axial points) + 6 (center points; 6 replications).

The Table 2 shows that the difference of actual value and the predicted value was generated from the Equation 3 of the colour removal of RG19 (%). The residual show the difference between the actual value and the predicted value and it gave less value of difference between predicted and actual. The highest residual for colour removal stated in the data is at the 17th run that obtained 0.73 of residual value compared to the other runs while for lowest residual at the 6th and 12th run. It can be concluded that the residual only have slight number and can accept by the model because not more than 10.

Table 2 Experimental result of central composite design experiments

Run	Block	A	B	C	Colour Removal (%) Actual	Predicted	Residual
1	Day 1	30	6	4	92.4	92.84	-0.44
2	Day 1	50	8	12	99.5	98.98	0.52
3	Day 1	70	10	4	94.4	94.62	-0.22
4	Day 1	50	8	12	99.1	98.98	0.12
5	Day 1	70	6	20	98.8	98.76	0.041
6	Day 1	30	10	20	98.8	98.83	-0.029
7	Day 2	30	10	4	93.4	93.47	-0.073
8	Day 2	50	8	12	98.7	98.91	-0.21
9	Day 2	70	10	20	98.6	98.19	0.41
10	Day 2	70	6	4	94.7	94.70	-
11	Day 2	50	8	12	98.6	98.91	-0.31
12	Day 2	30	6	20	98.6	98.41	0.19
13	Day 3	50	10	12	99.5	99.59	-0.086
14	Day 3	50	8	12	99.7	99.84	-0.14
15	Day 3	70	8	12	99.6	99.83	-0.23
16	Day 3	50	6	12	99.7	99.49	0.61
17	Day 3	50	8	4	96.2	95.47	0.73
18	Day 3	50	8	12	99.6	99.84	-0.24
19	Day 3	30	8	12	99.5	99.15	0.35
20	Day 3	50	8	20	99.5	100.1	-0.61

Table 3 Analysis of variance table for colour removal

Source	Sum of Squares	Mean Squares	F Value	p-value Prob > F	Remarks
Block	19.78	9.89			
Model	81.64	9.07	34.68	< 0.0001	Significant
A – Persulfate concentration	1.16	1.16	4.42	0.0687	
B- pH	0.025	0.025	0.096	0.7651	
C – Contact time	53.82	53.82	205.76	< 0.0001	
AB	0.36	0.36	1.38	0.2737	
AC	1.36	1.36	5.20	0.0520	
BC	0.061	0.061	0.23	0.6414	
A^2	0.34	0.34	1.29	0.2885	
B^2	0.25	0.25	0.95	0.3573	
C^2	11.33	11.33	43.33	0.0002	
Residual	2.09	0.26			
Lack of Fit	2.00	0.40	13.35	0.0291	Significant
Pure Error	0.090	0.030			
Cor Total	103.51				

Table 4 Coefficient for colour removal

Coefficient	Response for Colour Removal Value
Standard Deviation	0.51
Mean	97.94
R-squared	0.9750
Prediction R-squared	0.5385

$$S\ S = \frac{N}{4}\left(_{Effect}^{2}\right) \quad (4)$$

$$SS_{\text{model}} = SA + SB + SC \quad (5)$$

$$SS_{residual} = SA + SB + SC \quad (6)$$

$$MeanSquare = \frac{SS}{df} \quad (7)$$

$$F_{value} = MS_{Model} / MS_{\text{Re}sidual} \quad (8)$$

Analysis of Variance (ANOVA) analysis was investigated in this study to make sure that the outcome suitable with statistical model is valid. Equation 4,5,6,7 and 8 accordingly showed that the generation equation calculated ANOVA table with statistical term. The generation of Sum of Squares, mean squares, F value and p-value is useful for tabulated an ANOVA table.

Based on Table 3, model that been discovered is the linear, quadratic, cubic and two-factor interaction (2FI). In addition, ANOVA analysis gave a significant term of the specific model by determined the probability F-value calculated from the data exceed its theoretical value. Hence, it surmised that when the p-value increases, the probability of the F-value will also decrease. The statistical significance was verified with adequate precision ratio and by the F test by Ghasempur *et al.*[24]. Significant term could be deduced when the probability is less than 0.05. The data presented clearly where all factors which is persulfate concentration, pH and contact time were located in significant term when their p-value less than 0.05. It was perceived that for colour removal gave lowest p-value as compared to other factor. Besides, pure error value gave less value which is 0.09 and 0.77 for colour removal respectively was determined lack of error in this analysis.

It can be approximated in Table 4, the summary statistic of ANOVA from the value of standard deviation, mean, R-Squared, and Predicted R-Squared. The standard deviation for colour removal showed that value of 0.51 with the mean value of 97.94. The coefficient calculated without the first point and then used to estimate the first point and calculate the residual for point one and squared residual are summed. Besides, based on Liu and Chiou [25] R-Squared is one of vital part in analysis that should be more closely to 1 to acquired validation and more acceptable which is 0.9750 from colour removal. This was supported the data due to it considered increasing the Predicted R-

Squared closer to the value 1 affected model reduction, response transformation and presence of outlier

3.2 Interpretation Final Regression Model Equation

Furthermore, the final regression model equation is a main key of each analysis for determination reliable of process and could be applied for the next experimental. It could be obtained from experimental results as followed Central Composite design for the three variables studied are shown in **Table 1**. In ozonation process, the individual and interactive effects of the selected three variables on the colour removal of the RG19 dye in an aqueous medium were investigated using CCD application. The experimental results were evaluated with RSM of Design-Expert® 8. The approximating functions of the colour removal obtained are shown as follows:

$$\text{Colour removal} = 99.24 + 0.34\,A + 0.050\,B + 2.32\,C - 0.21\,AB - 0.41\,AC - 0.087\,BC - 0.35\,A^2 - 0.30\,B^2 - 2.05\,C^2$$

where ,

A : (Persulfate concentration),
B : (pH) and
C : (Contact time) respectively.

3.3 3D Contour Plot between Independent Variable and Dependent Variables

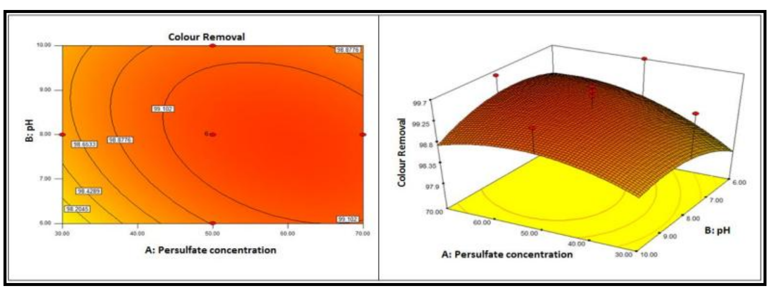

Figure 3. Response surface 2D and 3D contour plot for the interaction effect of persulfate concentration and pH by fixed of initial concentration for percentage of colour removal

From Figure 3, it appeared some peak from 3D response surface plot of interaction effect of persulfate concentration between pH at fixed concentration RG19 dye. Overall of 2D contour plots can be shown with optimize range colour which is orange to red colour scale. Hence, the optimize peak started showing their peak at (Persulfate concentration 50mM with pH 8). The graph showed that the colour removal (%) of RG19 increase gradually at these condition. The performances was little bit decreased when their pH less than 8 and the persulfate concentration less than 50mM. The data corroborated that the highest value pH and persulfate concentration could be retarded towards the performances removal. In general, colour removal proceeded in a satisfactory manner for persulfate concentration between 50-70mM and 40-60mM respectively. However, the reaction with a low concentration of persulfate 30mM and higher than 70mM was exhibited a slow reaction phenomenon. Thereby, more sulfate radicals are produced for oxidizing RG19 at intermediate concentration of persulfate supported by Weng and Tao [26], which resulted in achieving a higher degradation efficiency when sufficient contact time and suitable basic pH. In this reaction, Equation 9 stated the hydrolysis of persulfate where sulfate radicals were produced as $S_2O_8^{2-}$ reacting with hydroxyl radical that formed in the aqueous solution.

$$S_2O_8^{2-} + 2H_2O \longrightarrow HO_2^{-} + 2SO_4^{2-} + 3H^{+} \tag{9}$$

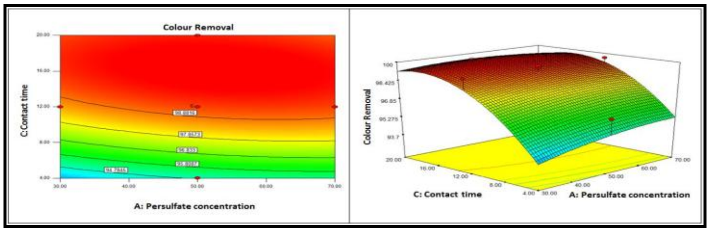

Figure 4. Response surface 2D and 3D contour plot for the interaction effect of persulfate concentration and contact time by fixed of initial concentration for percentage of colour removal.

Based on Figure 4, at the condition all range of persulfate concentration (30mM- 70mM) and starting 2 min of ozonation process was resulted the maximum colour removal of RG19. From the 3D surface plot, the longer the contact time, the higher amount of RG19 dye can be removed. Apparently, 98% (persulfate concentration 50mM, 12 min) colour removal was the highest value as compared to the lowest 94% (persulfate concentration 40mM, 4min). Therefore, from this analysis both variables affected colour removal but contact time gave a big contribution towards this process. The same effect was observed in the study reported previously from Zhou and He [27] where with increasing time, free radicals would be increased, which promoted the degradation rate. However, regardless of the experimental time, this interaction would be limited to the performance of radical itself either became scavenger or enhancer.

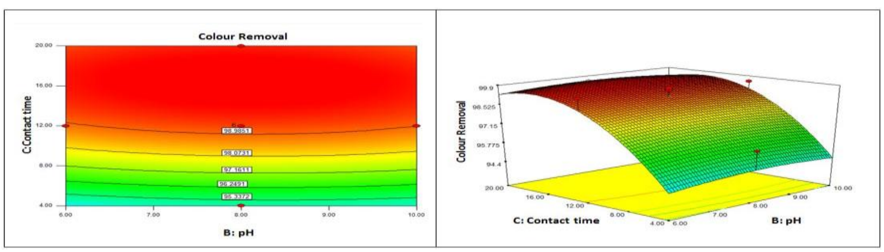

Figure 5. Response surface 2D and 3D contour plot for the interaction effect of pH and contact time by fixed of initial concentration for percentage of colour removal

Figure 5 showed the interaction of variables between pH and contact time. From the 3D surface plot, the shape of the curve seems like maximum outside the experimental region. This was because pH gave less affect towards colour removal but not for the contact time. That is the main reason for the resultant 3D plot in FIGURE 5. In order to get a clear picture of the interaction, 2D contour plot was also included as shown in same figure. From the figure, at constant initial concentration, efficiency of colour removal was increased up 98% and above when the contact time reached at 6 min above. Hence, it shows that the two variables have synergistic effect to enhance the colour removal.

In Beltran[28] study, it revealed at low pH values molecular ozone still remained while at high pH values hydroxyl radicals are produced from ozone decomposition. Thus, ozonation process stability would reduce with increasing more basic condition due to generation of secondary oxidants. In addition, Tehrani and Amini [29] described that dye chromophore stable to be attacked by hydroxyl radicals which have higher oxidizing potential and are less selective than molecular ozone for enhancing degradation efficiency at high pH values. Thus, selection pH of the solution as a influencing parameter absolutely important in ozonation process stated by Karami *et al.* [30] but independent of pH in the range 4-9 by Multani and Shah [31].

3.4 Desirability of Optimum Condition between Independent Variable and Dependent Variables

Table 6 Optimum condition for colour removal

Variables	Units	Optimum value
Persulfate Concentration	mM	49
pH	-	8.89
Contact time	min	18
Predicted Colour Removal	%	99.70
Experimental Colour Removal		98.30

Table 6 shows optimum condition for each of parameters that resulted a best value of colour removal. The efficiency of colour removal had been proved that this treatment could be decolorized azo dye efficiently.

4. CONCLUSION

This paper presents has investigated ozonation process various conditions of parameters showed the following results are significant and four respects conclusions could be drawn:

i. This study yielded a good value of colour removal compared with other experiments conducted on RG19. The performance of ozonation with presence of persulfate, $Na_2S_2O_8$ is proven can boost the performance of degradation.
ii. ANOVA which analysis of variance had been proved that the model are significant based on the p-value after calculated with sum of square, mean square, degree of freedom and others.
iii. Mathematical equation which is final regression model equation for colour removal of RG19 had been analyzed using Central Composite Design and could be applied for textile wastewater.
iv. All the parameters which initial pH, persulfate concentration and contact time gave different interactive effect accordingly based on the fundamental of wastewater knowledge. The statistical report showed the validation of optimum condition has been tested triplicate to get a best value both responses.

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