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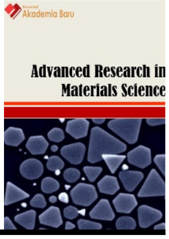

Optimization of Ozonation Process Implemant Sodium Persulfate using Azo Dyes

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ABSTRACT

Ozonation (O_3) process aided with other oxidants can be a best method for degradation compounds that presented by azo dyes specifically Acid Orange 52 (AO52). Numerous application of AO52 had been applied in textile industries, cosmetic and pharmaceutical industries. In this work, integration of hydroxyl radical with sulfate radical can enhanced the production of radical useful for colour and COD removal mechanism. It had been proven when its performance of ozonation + persulfate process better than ozonation process only. The effects of operational conditions had been investigated including the fixed initial concentration of AO52, initial pH of the AO52 (2-6), Na2S2O8 / sodium persulfate concentration (25-65mM) and contact time (3-25min) on the colour and chemical oxygen demand removal efficiency. By predicting both of responses efficiency, Central Composite Design (CCD) had been applied to achieve the optimization of ozonation process with Na2S2O8 / sodium persulfate concentration, second-order polynomial equation was proposed. Good agreement of experimental values were found which is (Colour removal; R2 = 0.6615, COD removal; R2 = 0.5453), which proves the appropriateness of the model employed. Hence, success of CCD suggested the optimum conditions of ozonation process at (pH 6,65mM Na2S2O8 / sodium persulfate concentration, 25min). Both of process efficiency as a function of independent variables was shown specifically by mathematical modelling equation, interactive effect by cube plot, normal probability plot and ramp. However, the statistical tests are supported also with UV-Vis spectra evolution through each condition. By getting an optimum value, it could be applied in any dyes that contains same organic molecule. Furthermore, the new ozonation approach had been modified based on their factor achievement especially presence of Na2S2O8 /sodium persulfate concentration to improve the degradation performances.

Keywords:
Acid orange 52(AO52), ozonation, sulfate radical, CCD

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1. Introduction

Recently, the rapid on-going development of industrial world used of different type of chemicals are been explored just only to meet the trends of fashion requirement. One of the big issues was textile industry processes had been consumed on average about 150 L of water per kilogram of cloth

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processed. Thus, it had been caused discharge of coloured textile effluent into the environment in which it's either carcinogenic and/or teratogenic health effects [22]. Practically, this was due to the process had been generated a large flows effluents which contain high COD, large amount of suspended solids, largely fluctuating pH, high temperature, unbound colourants, dye impurities, auxiliaries and surfactants. As instances of the harmful effluents, azo dyes has been assigned for approximately 70% of all dyestuffs used worldwide by weight, causing them as the largest group of dyes released into the environment. Hence, the degradation process of these dyes and intermediate products completely from dye effluent are crucial to reduce their final discharge flowing to the environment.

As a result, international consensus concerning discharging textile effluent with respect to legislation especially for usage of azo dyes in many countries unfortunately including Malaysia. Therefore, this problem must be immediately to overcome this excess compound appealed around the world where must be considered to their consumption and discharge effluent [10]. This due to this issue was getting recognition from scientists all over the world about their negative effects towards photosynthetic aquatic plant and water bodies [7, 9]. It has been conclusively shown azo dyes required a suitable and efficient method for their degradation process. Therefore, the application of azo dyes treatment techniques was increasing including physical, biological and chemical processes had been investigated. Result from Sukanchan [20] studies have been identified that advanced oxidation processes (AOPs) like ozonation process as one of the efficient chemical process for most of dyes.

However, this method has a number of limitations as example only resulted in significant colour removal, costly if applied in actual field and unable fulfilled the discharge standard of effluents in term of chemical oxygen demand (COD) [15] Advanced oxidation processes (AOPs) are involved in situ generation of very powerful oxidizing agent such as hydroxyl radical (second highest powerful oxidant after the fluorine) and efficiently for removal of recalcitrant organics from the wastewater [12]. Among the AOPs, ozonation process can performed well in decolourization due to it occur easy and fast reaction; less harmful; sludge are not formed; decomposition process can convert easily into oxygen and water; and need little space is required [19].The mechanism of this radical is by attacking organic molecules by either abstracting a hydrogen atom or adding hydrogen atom to the double bonds. Hence, if complete mineralization had been completed, formation of different structure of intermediates with lower molecular weight or carbon dioxide and water would occur [3]. Therefore, the selective radicals can be generated by oxidizing agent such as by hydrogen peroxide, $Na_2S_2O_8$/sodium persulfate, ozonation and homogenous or heterogeneous catalyst. The main limitation to another study was investigators are kept suggested several approach to enhance hydroxyl radical production.

This view is supported from this researcher, who argues that hydroxyl radicals are non-selective in nature and able to perform well without any other additives with a wide range of contaminants [18]. However, AOPs unable to undergoes complete mineralization due to this limitation. By coupling AOPs with $Na_2S_2O_8$/sodium persulfate can be as the most latest improvement to overcome this drawback. In this paper, the integration of oxidation efficiency, ozonation aided with sodium persulfate would obtain a better efficiency of optimum condition in colour and COD removal. Unfortunately, this method of analysis has a number of limitations studies which unable to know their best of optimum condition, have only focussed on other types of dyes, different experimental condition and aims.

According Buthiyappan *et al.*, [25], many factors had been contributed to the efficiency of dyes degradation such as classes of dye, concentration of solution, temperature, contact time, pH and selection of catalyst. Now, researchers usually delve into applying more extensive statistical mathematical tools and user friendly methods for analysing complex experimental results. To this end, a rigorous approach attempted the response surface methodology (RSM) which is Central Composite Design (CCD) that widely used in many industries for technological operations which provide superior optimization in experimental conditions. CCD in the form of a 2^3 full factorial design was used to develop mathematical equations which utilized for maximizing or minimizing different independent variables by evaluating the effects of multiple factors and their interactions on one or more response variables simultaneously. It would be constructed for performance of the AO52 removal by providing a clear visual aid to improving quantitative evaluation of the integration process of ozonation. In this evaluation, initial pH of AO52, $Na_2S_2O_8$/ sodium persulfate concentration and contact time as the factors affecting the colour and COD removal performance were studied. Consequently, the objectives of this work were to compare performances of ozonation and ozonation + sodium persulfate process, to evaluate the mathematical equation, reconsidering the performances of normal probability plot residual and understanding the interactive effects of different parameters by cube plot dimensional. This data and results could reveal the process of optimization through their ramp suggestion and would improvement in the works already done by researchers.

2. Methodology

2.1 Chemicals and Preparation of Dye Solution

Acid Orange 52, AO52 (Fluka Analytical) as stated in Figure 1, sodium hydroxide, NaOH (HmbG), sulphuric acid, H_2SO_4 (95-98%, Fisher Chemical) and $Na_2S_2O_8$/ sodium persulfate (Sigma Aldrich) has been used along this research. AO52 has been selected due to its low biodegradability and lack of effective treatment. Ultrapure water from Elga Pure-Lab Option-Q water system had been used for the preparation of solutions. When required according condition, the pH of the solution was adjusted using 1M of H_2SO_4 and NaOH. Initial dye concentration was adjusted and as constant variable at 100 mg L^{-1} by dilution with ultrapure water.

2.2 Ozonation Experiment

Combination of ozonation has been selected in this study was the combination of ozonation process and sodium persulfate. The experimental setup shown in Figure 2 comprised of an oxygen cylinder (99.8% of oxygen concentration), ozone generator (A2ZZ-3G), 2L of glass measuring cylinder as ozone reactor and KI trap. Constant ozone gas was supplied from the bottom of the reactor through a diffuser at a dosage of 2L/min of O_2 inflow at $10g/m^3$ of O_3 generation.

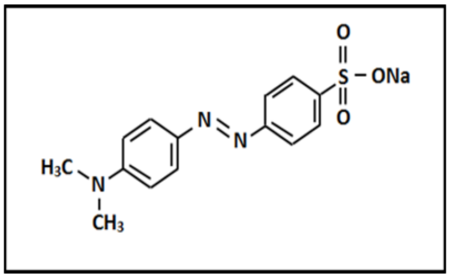

Fig. 1. Molecular structure of AO52

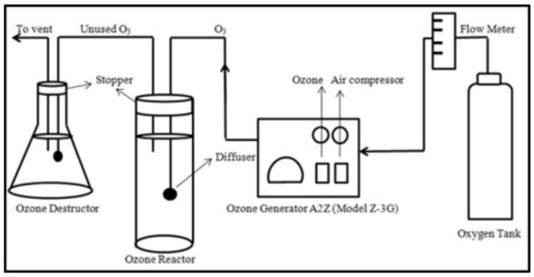

Fig. 2. Schematic diagram of ozonation set-up

In ozonation experiment, AO52 with same concentration (100mg/L) undergoes different condition of initial pH (2-6), $Na_2S_2O_8$/sodium persulfate concentration (25-65mM) and contact time (3-25min) were used to investigate their effects towards colour and COD removal. For determination of colour, COD removal as shown in Equation 1 and UV-Vis spectra analysis, the experiments were conducted at room temperature and samples were withdrawn at definite time intervals.

2.3 Analytical Methods

The solution pH adjusted by Hanna Instrument HI223 pH meter while for absorbance measurements were performed using a UV–Vis spectrophotometer (MesuLabTM), Model ME - UV1100 at wavelengths ranging from 200–800 nm. The maximum visible region (λ max 456 nm) was used as a base to follow AO52 decolourization, using a quartz cuvette. Chemical oxygen demand (COD) was determined with the closed reflux, calorimetric method using HACH DR200 COD reactor and were measured by using HACH DR2800 Spectrophotometer.

$$Colour\ and\ COD\ Removal\ (\%) = [((C_O - C_t)/\ C_O) \text{ x } 100] \qquad (1)$$

2.4 Experimental Design

All runs were suggested followed the range as stated in Table 1. It statistically processed using Central Composite Design which helped to optimize the process and obtained good enough precision. Data were acquired from the ozonation experiment and then assessed using RSM (Response Surface Methodology), Design-Expert® (Version 7.1.5) Stat-Ease, Inc., USA). For designing experiments and obtaining optimum conditions for desirable responses, RSM is one of the mathematical and statistical techniques [11].The application of RSM had been applied in different branches of scope like Anupam *et al*., [1] studies for optimization of various factors for degradation in different pollutants. This current study, three factors with two responses had been applied in Central Composite Design (CCD) based on RSM was used in 20 run of experiments where consist 8 factorial points, 6 axial points and 6 replicates of center points at 5 levels of each variable. The center points were utilized to define the experimental error and the reproducibility of the data.

The experimental plan was based on three factors referred to as face centered central composite design. In this study, the selection of this design as the experimental design because it is more precise for estimating factor effects [21]. Hence, the interaction effect between factors can be evaluated and optimized in the full factor space. It was done to optimize independent variables in this study (A: initial pH), (B: $Na_2S_2O_8$/sodium persulfate concentration) and (C: contact time). The five levels of values for the independent variables were explicit of their coded and uncoded forms in Table 1. The value of independent variables were expressed in their coded as -1, 0, +1 interval shows the low, center, and high level of each variable, respectively. Based on the preliminary screening analysis [17], the range and levels used in this experiment are constructed in Table 1.

2.5 Optimization and Statistical Analysis

By determining the approximately optimum condition, Design Expert software had been predicted the variation of conditions which is independent variables to optimize interest study. The desired goal for each variable was chosen. The optimal of ozonation + persulfate process conditions were chosen based on the condition of attaining highest colour and COD removal for each run. The Design Expert software overlaying all the responses to obtained the optimal condition. Moreover, the optimal condition that depended on the independent variables was also obtained using the predicted equations determined by RSM. By employing the polynomial regression equation, the response surface behaviour was examined for the response function (Y). The generalized response surface model is shown below (Equation 2)

$$\mathrm{Y} = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} \mathrm{X}_i^2 + \sum_{i=1}^{k-1} \quad \sum_{i=2}^{k} \beta_{ij} X_i X_j + e_i \tag{2}$$

where *Y* represents the response variables to be modeled; β_o is a constant, β_i, β_{ii} and β_{ij} are the linear, quadratic and cross-product coefficients, respectively. X_i and X_j are the levels of the independent variables. *k* is the number of variables and *e* is the random error of the model. The statistical significance of the term in the regression equations and best fitted model of response can be achieved by highlighting various statistical parameters such as multiple correlation coefficients (R^2). The fitted polynomial regression equation was expressed in the form of cube plots in order to illustrate the relationship between responses and the experimental variables used.

Table 1
Experimental ranges and levels for parametric optimization process

Symbol	Factor	Goal	Range and level			Response			
			-1	0	+1				
A	Initial pH	In range	2	4	6	1	Colour Removal	%	Optimize
B	($Na_2S_2O_8$) Sodium persulfate concentration	In range	25	45	65	2	COD Removal	%	Optimize
C	Contact time	In range	3	14	25				

3. Results and Discussions

3.1 Differentiate of Ozonation and Ozonation + Sodium Persulfate Process

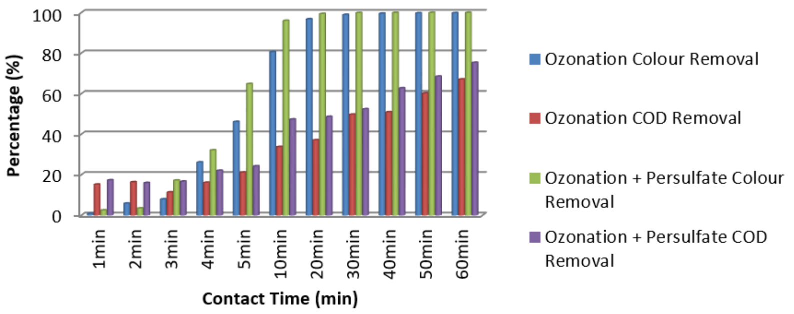

Fig. 3. Difference of ozonation and ozonation + sodium persulfate process

In ozonation + persulfate process, sodium persulfate was introduced into ozonation process towards AO52 (500mg/L), which significantly enhanced the performances of ozonation as stated in Figure 3 and provided sulfate radical reaction in degradation process itself , that making ozonation + persulfate process more efficient based on colour and COD removal than ozonation only. With the increasing contact time of process, the decolourization inclined slightly and remained above 90% at 10 min and above. Colour and COD removal rate for both processes increased persistently with increasing contact time and no inhibition process was occurred. However the decolourization rate in ozonation + persulfate process was much higher as compared to ozonation process only due to the average increment was about 31%, which indicated that sodium persulfate might play a synergistic role in the degradation process. As high concentration of AO52 was composed various compound in their structure that make it needed longer contact time to decolourize completely. Equations below showed a comparison how these radical performed in the process [12, 8].

Ozonation process (1) $3O_3 + H_2O \rightarrow 2OH^{\bullet} + 4O_2$

Ozonation + Persulfate process $3O_3 + H_2O \rightarrow 2OH^{\bullet} + 4O_2$ and $S_2O_8^{2-} + 2H^+ + 2e^- \rightarrow 2HSO_4^-$

Ozonation + persulfate process gained the highest COD removal at 60 min 75% removal as compared to ozonation process was only about 65%. By introducing sodium persulfate in the ozonation process, it unable to accelerate an accomplished 100% COD removal as compared to colour removal performance. COD Removal average increment of ozonation + persulfate was about 19.85% only. This due to decolourization with ozone would occur rapidly due to the rapid destruction of conjugated chains of dye molecules that functionally for colour only [22]. Furthermore, Yao *et al.,* [23] stated that mineralization effectiveness usually varies numerously with the type of constituents contain in the wastewater.

3.2 Central Composite Design Application

The design of experimental data in Table 2 obtained for this response based on CCD matrix. List of 20 run had been analysed by investigated each run with semi-batch ozonation + persulfate process. Their responses had been determined after calculated the average of triplicate data. Therefore, these data had been compared with the predicted as suggested by CCD. However, there was presented illogical value when the colour removal predicted more than 100% at Run 6, 12, 15, 16, 17 and 20.

3.3 Model Fitting and Statistical Analysis

All three independent variables and responses, a quadratic polynomial model was selected and fitted well as suggested by the software. Each response can be represented by a mathematical equation that correlated the response surface as stated in Equation 5 and 6. The optimum condition degradation AO52 was determined by CCD under RSM. Based on the results, higher coefficients of determination for colour and COD removal were (R^2 =0.6615) and (R^2 = 0.543), which confirmed that the quadratic polynomial models are highly significant and acceptable to interpret actual relationship between the responses and variables tested. Furthermore, the calculated R^2 values for studied responses variables got within good range. Hence, there is a close agreement between the experimental values and the theoretical values predicted by the proposed models. The final empirical regression model of the relationship between three tested variables for colour and COD removal were obtained can be expressed using the following equations:

Colour removal =

$$94.47 + 5.00\,A - 3.74\,B + 7.55A\,B - 6.27\,AC + 4.68\,BC - 4.96\,A^2 - 4.6\,B^2$$

R-squared = 0.6615

COD removal =

$$25.37 + 3.66A + 2.05B + 8.47AB + 3.77AC + 3.87BC + 0.99A^2 - 3.39B^2$$

R-squared = 0.5453

where A, B and C are initial pH, $Na_2S_2O_8$/ sodium persulfate concentration and contact time respectively. A negative sign in each equation represented an antagonistic effect of the variables and a positive sign represents a synergistic effect of the variables.

Table 2
Percentage of colour and COD removal

Run	A:pH	B: Sodium Persulfate Concentration	C: Contact time	Colour removal (%)		COD removal (%)	
				Experimental	Predicted	Experimental	Predicted
1	4	45	14	99.81	99.55	17.90	25.54
2	2	25	3	68.32	63.46	20.34	23.04
3	2	65	25	99.40	92.04	13.62	19.88
4	6	65	3	74.70	69.17	11.89	19.16
5	6	25	25	99.35	87.62	17.65	22.90
6	4	45	14	99.07	99.55	21.31	25.54
7	6	65	25	99.28	104.60	53.70	51.68
8	4	45	14	99.22	99.55	44.78	25.54
9	2	65	3	19.33	31.52	7.01	2.44
10	6	25	3	63.11	70.93	11.46	5.88
11	4	45	14	99.80	99.55	24.23	25.54
12	2	25	25	99.26	105.25	31.58	24.98
13	4	45	3	77.99	68.37	14.85	15.03
14	4	45	14	99.86	99.55	19.46	25.54
15	6	45	14	98.91	103.04	38.20	33.29
16	4	25	14	99.31	102.10	18.97	23.21
17	4	45	25	99.18	106.97	35.15	32.26
18	2	45	14	98.99	93.03	23.77	25.97
19	4	65	14	99.24	94.62	34.25	27.30
20	4	45	14	99.33	102.99	23.21	28.64

3.4 Normal Probability Plot of Studentized Residual for Colour and COD Removal

The normal probability plot for colour and COD removal of AO52 were showed in Figure 4 and 5. In this part, the normal probability plot has been indicated that residuals followed a normal distribution. It was apparently shown that residual can be assumed to fit which all runs already scattered followed a straight line that showing errors. Thus, the data collected can support the relevance of the empirical model. Models are reliable has been accepted [13]. Different colour of data had been explained through their rank of the performances in which red (optimum), green (average) and blue (lowest) based on data in Table 2.

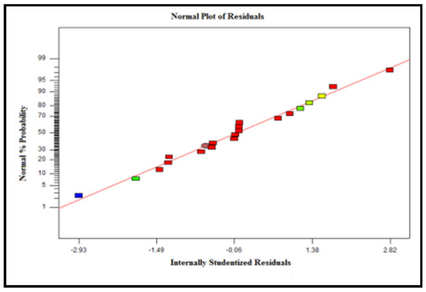

Fig. 4. Normal probability plot of colour removal

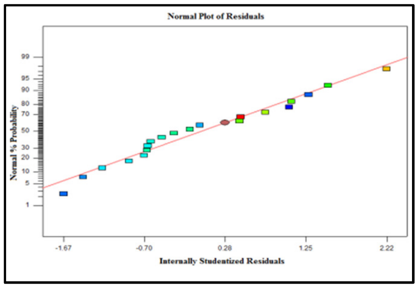

Fig. 5. Normal probability plot of COD removal

3.5 Interactive Effects of Different parameters

Figure 6 presents the cube plots of colour removal of AO52 dye synthetic wastewater. The data in Figure 6 indicates that at condition (pH 6, 25mM, 3min) resulted highest colour removal which is 97%. Strong evidence of AO52 decolourization can be achieved within 3minutes and found that at (pH 2, 65mM) gave lowest percentage of decolourization which is 57%. It was possible to hypothesise that combination of too high acidic condition with highest $Na_2S_2O_8$/sodium persulfate concentration may give a negative effect towards response. It is because the contribution of unlimited hydrogen ions gave badly influenced to the performance of radicals to breakdown the dye structure. Mamun and their co-workers stated that the oxidants might enhance the degradation of dye because it able to generate number of trapped electrons which can prevents recombination and generates oxidizing radicals. However, tendency of AO52 to be degraded was retarded due to high acidic solutions (pH less than 3). This happened due to high concentration of proton which resulting in lower degradation efficiency (Mamun, Aswr & Fahmida, 2017). The effect of $Na_2S_2O_8$/sodium persulfate concentration strongly affected colour removal efficiency at medium concentration 25-45mM but barely effect the removal efficiency at high concentration 65mM. The colour removal was ranged from 63.11% to 99.81%.

Based on Figure 7 the effect of initial pH, $Na_2S_2O_8$/sodium persulfate concentration and contact time on the COD removal was presented. The results, as seen in Figure 7, indicated that about 44% COD removal can be achieved as the condition stated at (pH 2, 65mM, 25 min). The cube plots model exhibited that longer contact time required to enhance the efficiency of COD removal that stated 44.78% in Run 8 as compared to Run 9 which was only 7.01%. There are similarities in significant of contact time as a factor between the present study and those described in ozonation such as crucial factor [24]. On the other hand, $Na_2S_2O_8$ /sodium persulfate had been proved that COD removal of

AO52 can exceeds about 44.78% only in 14min in acidic condition rather than the other ozonation only studies needed 150 min for 44.57% respectively [2].

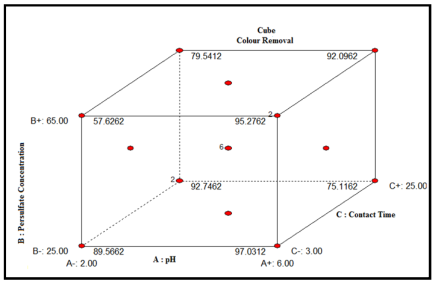

Fig. 6. Cube plots of colour removal

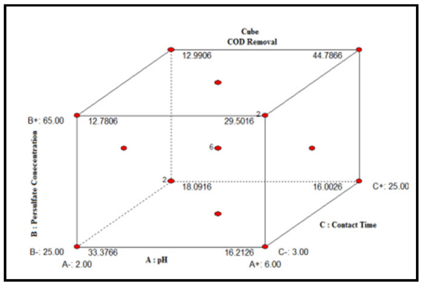

Fig. 7. Cube plots of COD removal

After all, the optimum conditions of ozonation + persulfate process suitable at (pH 6, 65 mM $Na_2S_2O_8$ / sodium persulfate concentration, 25 min) as stated in Figure 8. In particular, the ozonation + persulfate process of AO52 azo dyes has gained considerable condition due to the facts:

- ≤ 65mM $Na_2S_2O_8$ / sodium persulfate concentration: Enhanced hydroxyl radicals in ozonation process by inducing sulfate radical.
- High acidic pH: According to Tizaoui and Grima [22], increase production of hydroxyl radicals was significant which boost a faster colour removal and H-N-R group of the dye molecule deprotonates, which makes the sites more reactive for the electrophilic attack by ozone. In addition, it more susceptible to electrophilic attacks by molecular ozone and possibly hydroxyl radicals. Unfortunately, at very low acidic pH; the production of hydroxyl radicals from ozone decomposition was negligible because of the very low concentration of hydroxide ions (the initiator of ozone decomposition) make it had been proceed solely through molecular ozone reaction (direct mechanism).
- Longer contact time: This parameter could not give same feedback performances towards colour and COD removal. Since ozonation process itself a fast process that induced the colour removal 100% rapidly when it needs less breakage of compound while COD removal difficult to achieve 80-100% due to it needs longer time to undergo the mineralization process for eliminating all organic products along the process.

3.6 Process of Optimization

The priority of operating cost is a vital issue to be considered for each implementation of wastewater treatment method [4]. Thus, optimum condition for ozonation aided with $Na_2S_2O_8$ /sodium persulfate with minimum contact time was desired by achieving both of significant responses. Moreover, the frequent initial concentration of wastewater is about 100mg/L that suited with the optimum condition. In present study, by taking operational condition "within range" while for the response as "maximum" to attain maximum efficiency of colour and COD removal approximately 92.09% and 44.77% respectively. The desirability function is achieved 0.855 for the mentioned conditions as optimum. Thus, the validation experiment was done to accomplish, verified and proved the findings which revealing with predicted response values of the mathematical model. The results of predicted and experimental parameter were shown in Table 3 were found within the range and to be not statistically different at 95% confidence level. Based on the optimum conditions, the actual values of colour removal 90% as compared to predicted 92% and 40% for actual COD removal than 44% of its predicted value.

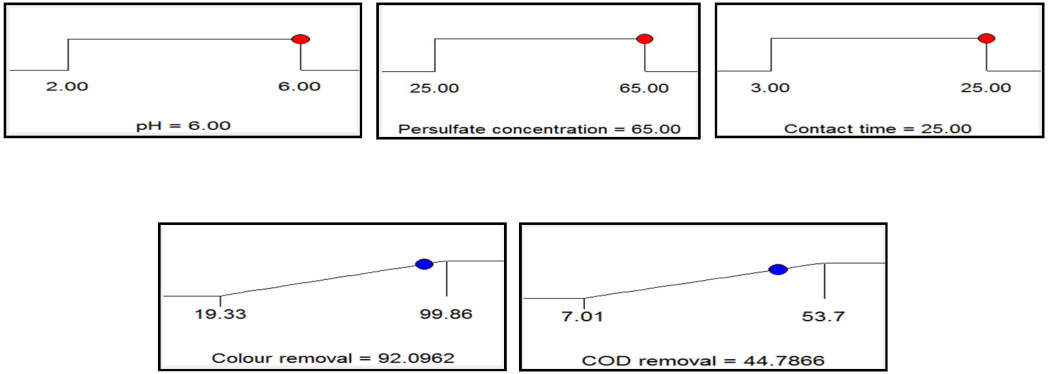

Fig. 8. Optimum condition derived by RSM for AO52 degradation

Table 3
Percentage of colour and COD removal

Variables	Units	Optimum value
Initial pH		6
$Na_2S_2O_8$ /sodium persulfate concentration	mM	65
Contact time	Min	25
Predicted AO52 Removal	%	92
Actual AO52 Removal		90
Predicted COD Removal		44
Actual COD Removal		40

UV-Vis Spectra Changes

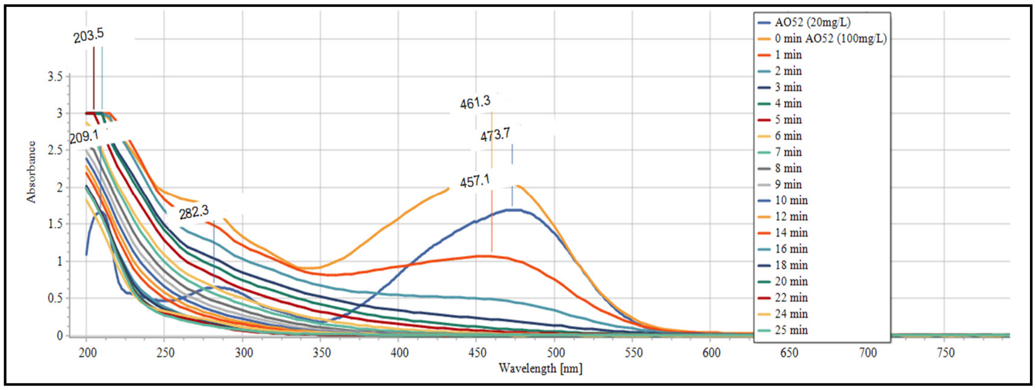

Fig. 9. The evolution of absorbance with reaction time

Analysis Figure 9 in which UV–Vis absorption spectra along degradation AO52 in aqueous solutions can be shown by using UV–Vis spectrophotometer (MesuLabTM), Model ME - UV1100. Molecular and structural characteristic of AO52 with $Na_2S_2O_8$/sodium persulfate concentration was clarified through UV–vis spectra. Based on the performances of degradation dye solution through its contact time (1min - 25min) were depicted in Figure 8 for enhancing ozonation experiment. Before ozonation process, the absorption spectrum of AO52 in ultrapure water was characterized by one main band in the visible region 474 nm (20 mg/L). It can be prove through its maximum absorption which is 461 nm at 100mg/L was attributed based on its conjugated structure constructed by azo bond. Besides that, other bands were formed in the ultraviolet region located at 282 nm as benzene structures in the molecule.

Along ozonation towards AO52 (100mg/L), the structure had been decreasing which indicated the decomposition of AO52 due to the fragmentation of the azo links by direct ozone attack. Other than that, a new band at wavelength of 203 and 209 nm had been appeared. This had been supported through this study that it was considered suggesting the formation of by- products/intermediates and it was proven through aromatic fragment degradation in the dye molecule [2].

4. Conclusion

This research has investigated by ozonation aided with $Na_2S_2O_8$/sodium persulfate degradation of AO52 under various conditions, the following results are significant and five respects conclusions could be drawn:

(1) Performances of ozonation + persulfate process greater than ozonation process only.

(2) AO52 was successfully degraded by ozonation aided with $Na_2S_2O_8$/sodium persulfate. Its degradation achieved the optimum condition of ozonation with according condition (pH 6,65mM $Na_2S_2O_8$/sodium persulfate concentration, 25min). The decolorization increased with an increase of contact time.

(3) Mathematical equation of colour and COD removal of AO52 had been modelled using Central Composite Design and could be analysed their normal probability plot residual.

(4) In this work, it demonstrated based on statistical analysis degradation of AO52 was significantly accelerated under the oxidative conditions, while its degradation efficiency was higher based on interactive effects of different parameters by cube plot dimensional.

(5) This data and results could reveal the process of optimization through their ramp suggestion and would be as improvement in the works already done by researchers. The process of degradation AO52 undergoes C-N cleavages that produced the various intermediates.

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