

Preliminary screening oxidative degradation methyl orange using ozone/ persulfate

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Abstract. The present study focusing on the performances of advanced oxidation process by using ozonation method towards Methyl Orange based on the efficiency of colour removal and Chemical Oxygen Demand (COD) removal. Factorial design with response surface methodology (RSM) was used to evaluate the interaction between operational conditions, such as pH, initial concentration, contact time and persulfate dosage to obtain the optimum range conditions using a semi-batch reactor. The range of independent variables investigated were pH (3-11), initial concentration (100-500mg/L), contact time (10-50min) and persulfate dosage (20-100mM) while the response variables were colour removal and COD removal of Methyl Orange. The experimental results and statistical analysis showed all the parameters were significant. Thus, from this findings, optimization of operational conditions that had been suggested from the ozone/persulfate RSM analysis were (pH 3, 100 mg/L, 50min, 60mM) that would be produced 99% Colour Removal and 80% COD Removal and help in promoting an efficient ozonation process. The effect list data that showed the most contributed effects to increase the percentages of colour removal were pH and persulfate dosage whereas the contact time and initial concentration had the highest positive effects on the COD removal. Other than that, the interaction between pH, contact time and persulfate dosage were found to be the most influencing interaction. Therefore the least influencing interaction was interaction between persulfate dosage and pH. In this study, the correlation coefficient value R^2 for colour removal and COD removal of Methyl Orange were $R^2= 0.9976$ and $R^2= 0.9924$ which suggested a good fit of the first-order regression model with the experimental data.

1 Introduction

Main traits to determine the textile wastewater based on their colour intensity and chemical oxygen demand (COD) content, large amount of suspended solids, condition of pH and bio toxicity which can cause harmful towards water environment [1]. Current environmental issues either encountered by developed and under developed countries over the world

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associated with residual dye content or residual colour in treated textile effluents are always a concern for each textile operations because they are directly discharged from sewage treatment works and commercial textile operations.

Textile industries discharged large volumes of residual dye which contributed a significant effect towards environmental pollution [2]. Due to its complex aromatic structures, it can stand as refractory in nature and resistant to the degradation environmental activities, consequently threaten the environment especially towards human and aquatic organisms. Azo dyes containing wastewater must be treated well before discharged into the environment due to the fact that about 15% of azo dyes of the total world production are from the textile wastewater [3]. Hence, it makes degradation of azo dyes in the industry has been appealed around the world [4].

Over the years, many conventional methods are used in order to get an achievement of the treatment of textile wastewater. Those methods are mainly the combinations of physical, chemical and biological processes which interferences could occur in a large scale operation. The drawbacks include secondary pollution would occur when some chemical oxidants are added into the water and their unsatisfied yields are formed due to the recalcitrant characteristics and non-biodegradable by the conventional activated sludge process [5].

Advanced oxidation process (AOP) is a process that able to degrade numerous pollutants such as hazardous compounds into mineral end-product for example CO_2 and inorganic ions. The AOP chemistry consists of hydroxyl radicals (HO^\bullet), which is a non-selective reactive species [6] and has a high standard potential which is 2.8V [7]. Ozonation process is an effective and environment-friendly method that has been proven performed well in the colour removal problem in textile wastewater among all the AOPs [8]. Ozonation does not influence by the addition wastewater volume, sludge, and removed colour and their organic contents will not produce by-products that need to be retreated back. In order to get a plausible overall cost, effluent treatment with addition of catalyst or combination with other methods were suggested due to ozonation process consumed a high cost [9]. Abu Amr and co-workers reported that ozonation process when combined with the usage of persulfate yields higher removal efficiencies for COD, colour and ammoniacal nitrogen ($\text{NH}_3\text{-N}$) as compared to ozone only [10].

There are various available oxidants that can be used in ozonation process, and persulfate is the one of latest and least studied, where still need an improvement [11]. The advantages that make persulfate a promising choice among others are it has a relative stability in subsurface, strong oxidation potential, high reactivity, high aqueous solubility, low cost and favourable end products that treating aromatic organic compounds [12]. Persulfate also has a strong, reactive sulfate radical with a high aqueous solubility and high stability oxidizing agent at room temperature, SO_4^- ($E^\circ = 2.6\text{V}$) that often obtained from peroxydisulfate (PS, $E^\circ = 2.1\text{V}$), compared to hydrogen peroxide (H_2O_2), $E^\circ = 1.77\text{V}$) [13].

There are many factors that influences the oxidative degradation process which are pH of solution, initial concentration of solution, contact time and persulfate dosage. Thus, the process to study each factor will may risk towards time consuming and slow processes [14]. Therefore, 2^4 level factorial experimental designs can be adopted to minimize all the possibilities of the difficulties by screening all the affecting parameters collectively at a time. In this research, the oxidative degradation of methyl orange using 2^4 factorial experimental designs was performed. The design consists of four factors such as initial concentration, pH, persulfate dosage and contact time with two responses, in which the effects and interaction of factors and significances of the model will be analysed based on the responses.

2 Materials and methods

2.1 Reagent

Analytical grade methyl orange (MO) was obtained from Sigma-Aldrich. MO was selected as model due to its common application in industries. Its molecular weight and molecular formula were 327.33 g/mol and $C_{14}H_{14}N_3NaO_3S$ respectively. The appropriate weight of dye will be dissolved into ultrapure water for the preparation of stock solution. Fig. 1 represented the chemical structure of the studied dye.

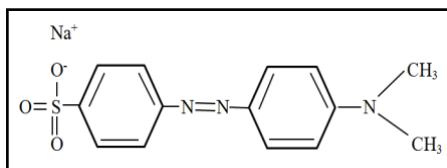


Fig. 1. Chemical structure of methyl orange.

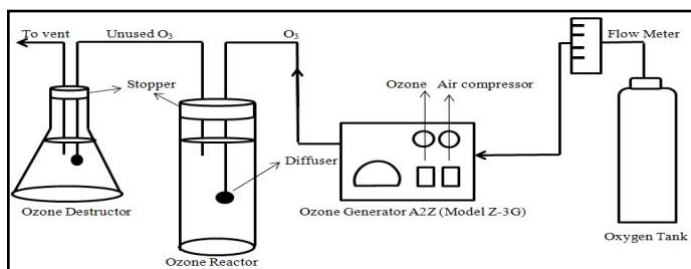


Fig. 2. Schematic diagram of experimental set-up.

2.2 Experimental procedures

In this experiment, ozone gas was generated and constantly flowed through a diffuser to produce fine bubbles into 2L dye sample by using A2Z (model Z-3G) Ozone Generator which continuously supplied with purified O₂. It was equipped with 2L of cylindrical glass reactor connected to 2% of potassium iodide trap which acted as O₃ destructor. Then, 2L sample was prepared with a certain desired condition of initial concentration, pH and persulfate dosage before O₃ entered the reactor based on run that constructed in the Table 2. 2 L/min O₂ flow rate was applied to generate O₃ throughout the experiments. Different ranges of persulfate dosage (20, 60, 100mM), pH (3, 7, 11), initial concentrations (100, 300, 500 mg/L) were conducted at room temperature with different conditions and undergoing various contact time (10, 30, 60 min). Finally, the samples were withdrawn at definite intervals for analyses.

2.3 Analysis methods

UV-Vis spectrophotometer at 461nm was used to analyse the absorbance colour change and concentration of the dye samples. The pH value before and after the treatment were tested by using pH meter (Hannah Instruments H1223). The value of COD was tested with the standard APHA method. HACH DR200 COD reactor and DR2800 spectrophotometer

were used to react and COD readings were taken in terms of mg/L, respectively. The removal efficiency of COD and colour were determined by using Eq. 1.

$$\text{Removal (\%)} = [C_i - C_f / C_i] \times 100 \tag{1}$$

where C_i and C_f were respectively referred to the initial and final colours and COD concentration (mg/L).

2.4 Experimental design

Factorial design of Design-Expert® (Version 7.1.5) Stat-Ease, Inc., USA) was utilized for the statistical analysis and interaction of the experiments. Experimental factors and responses were applied to investigate the relationships between the three independent factors, as presented in Table 1.

For this research, factorial design for experimental data was chosen, because the design allowed the determination of factors with the highest impact on the process. Generally, the design achieved best result in screening and optimization processes [15]. The main advantage was able to analyse the effects of each factor towards the response that varies with different levels and interaction effects of different factors could be verified using design of experiment only compared to one-factor-at a time experiment [16]. Thus, the software will reduced the number of experiments, time, and overall processes costs in order to obtain a good response.

Full factorial design of 2^k runs, where k was the number of variables, was selected for the screening design. The full factorial screening design involved runs at every possible combination at the defined upper and lower limit for each variable, see Table 1.

Table 1. Experimental ranges and levels of independent variables used in the screening.

Level of value	pH (A)	Initial concentration (mg/L) (B)	Contact time (min) (C)	Persulfate dosage (mM) (D)
-1	3	100	10	20
0	7	300	30	60
1	11	500	50	100

3 Results and discussions

3.1 Multiple linear regression and Analysis of Variance (ANOVA)

Table 2 showed that Run 6 (pH 3, 100mg/L, 50min, 100mM) and Run 14 (pH 3, 100mg/L, 50min, 20mM) gave the highest percentages of colour and COD removal, which were 98.59% and 98.52% respectively. However, Run 2 (pH 3,100mg/L, 10min, 100mM) and Run 17 (pH 11, 100mg/L, 50min, 100mM) gave the lowest data for both responses, which were 89.26% and 69.49% for colour removal and 36.84% and 63.13% for COD removal.

ANOVA was performed to determine the significant effect of the main factors and their interactions, which influencing towards both responses. Statistically, a factor that significant for 95% confidence level, the p-value should be less than or equal to 0.05 [17]. Both colour and COD removal MO responses gave the best data of significant p-value. However, COD Removal response showed a non-significant curvature in this study. This was due to the technical problem where the factor B gave a disturbance towards COD removal. All factors were significant where R^2 values were approximately to 1, which were 0.9976 and 0.9924 as stated in Table 3. The fit of the model was further checked by the

coefficient of determination R^2 . R^2 value should be always between 0 and 1. The closer the R^2 value to 1.0, the better the model predicts the response. A high R^2 value described a good agreement of results and shows that a desirable and reasonable agreement with the adjusted [18]. Fig. 3(a) and (b) showed the Pareto charts for colour and COD removal of Methyl Orange. Pareto chart indicated the relative importance of each independent model's parameter and their interactions towards both responses. Table 3 showed the contribution percentage of each factor and interaction between factors.

These screening analyses were necessary to know specifically the percentage of each factor's effect on the colour removal and COD removal. The findings showed that all factors (A, B, C, D) as stated in Table 1 previously acted as influencer in this experiment. Interaction between factors ABCD was the highest amongst all, in which the percentages of contribution for colour and COD removal of MO were 14.4% and 0.87%, respectively, while for factor AB and ABC referred to the best percentages of contribution which were 7.73% and 10.30%. However, factor C and AD gave the least percentage of contribution. Based on Table 3, the model and curvature that had been formed were significant. There indicated that all parameters were significant to be optimized at certain range condition based on the value of ABCD factors for colour and COD removal were 14.44% and 0.87% respectively. As a result, one of the factors must be excluded to be proceeding in optimization stage study to enhance the result for both responses.

3.2 Effect of parameters studied on 2D contour plot on colour and COD removal of methyl orange

3.2.1 Effect of pH on colour and COD removal of MO

Fig.5 a) and c) depicted a 2D contour plot of significant factors for COD removal of MO. Based on the figures, pH had the greatest influence in both colour and COD removal of MO. This was because at pH 3-11, conditions in this experiment were still able to get the highest percentage of colour and COD removal. Colour removal of MO decreased as the pH increased from pH 3 to pH 11 but the COD removal increased as the pH increased from acidic to alkaline condition as shown in Fig.4 a) and b).

Generally, the percentages of colour removal MO in alkaline condition was lower than in acidic condition, due to the fact that under neutral or basic pH conditions, sulfate anion radical can react with H_2O to produce OH^- and HO^\cdot . Therefore, it was likely that more HO^\cdot would be scavenged by sulfate ions at alkali rather than acidic or neutral pH that resulting in the decreased of colour removal. While in an acidic condition, further $SO_4^{\cdot-}$ could be formed due to acid-catalyzation. Under alkaline condition, the formation of bicarbonate and carbonate ions may inhibit oxidation due to carbon dioxide that was formed in the process. Thus, sulfate and hydroxyl radicals decay can be accelerated by reason of their reaction with hydroxyl ions. Under acidic conditions, breakdown of persulfate into sulfate free radicals can be further undergoes acid catalyzed as stated in Eq.2 and Eq.3 [19].

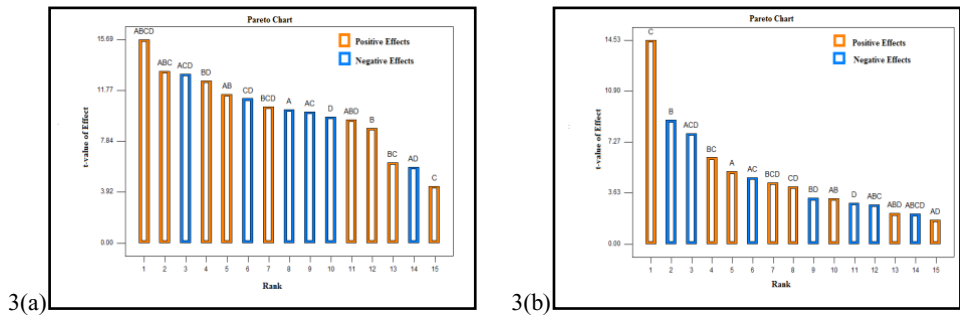


Fig.3. Pareto chart methyl orange (a) colour removal (b) COD removal.

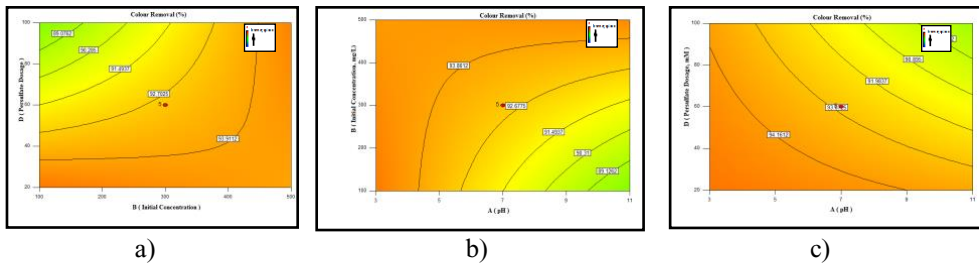


Fig. 4. 2D contour plot of significant factors accordingly (Highest, average, lowest) towards color removal a) BD (9.20%) b) AB (7.73%) c) AD (2.01%).

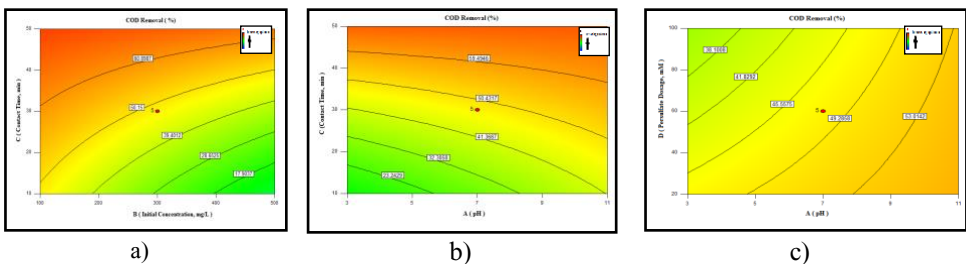


Fig.5. 2D contour plot of significant factors accordingly (Highest, Average, Lowest) towards COD removal a) BC (7.20%) b) AC (4.26 %) c) AD (0.56 %).

Sulfate anion radicals when react with hydroxide anion, or water, will formed hydroxyl radical as referred to Eq.4 and Eq.5 [20]. An increased of pH will significantly enhanced COD removal due to alkaline pH that accelerated COD removal by generating OH^- radicals, which contained electrochemical oxidation potential (EOP) that was stronger than the ozone molecule (2.8/2.08V) [21].

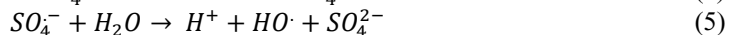


Table 2. Percentage of colour and COD removal.

Run	A	B	C	D	Colour removal (%)	COD removal (%)
1	3	500	50	100	94.73	74.72
2	3	100	10	100	89.26	36.84
3	11	500	10	100	93.06	28.21
4	11	500	50	100	98.19	60.13
5	3	500	10	100	93.36	-54.42
6	3	100	50	100	98.59	80.35
7	7	300	30	60	95.27	39.86
8	3	500	10	20	92.58	24.63
9	11	500	10	20	91.6	30.2
10	7	300	30	60	93.86	51.21
11	7	300	30	60	94.44	51.05
12	11	100	50	20	98.18	80.12
13	7	300	30	60	94.93	47.37
14	3	100	50	20	98.52	62.99
15	11	100	10	20	89.97	45.8
16	11	100	10	100	94.13	62.07
17	11	100	50	100	69.49	63.13
18	7	300	30	60	93.78	40.56
19	3	500	50	20	96.09	51.52
20	11	500	50	20	95.43	70.85
21	3	100	10	20	93.81	49.67

Table 3. Analysis of Variance (ANOVA).

4FI	% Colour removal contribution	% COD removal contribution
A	6.24	5.05
B	4.60	14.75
C	1.13	39.86
D	5.55	1.62
AB	7.73	1.99
AC	6.01	4.26
AD	2.01	0.56
BC	2.27	7.20
BD	9.20	2.03
CD	7.29	3.17
ABC	10.30	1.49
ABD	5.33	0.91
ACD	9.99	11.78
BCD	6.47	3.61
ABCD	14.44	0.87
Model	Significant p-value :0.0002	Significant p-value:0.0018
Curvature	Significant p-value :0.0104	Not Significant p-value:0.5352
R² value	0.9976	0.9924

3.2.2 Effect of initial concentration on colour and COD removal of MO

Strong evidence of initial concentration factor was found when it gave significant effect towards contact time and persulfate dosage factors as shown in Fig.4a) and Fig 5 a). This can be supported with a hypothesis, that the higher initial concentration of MO, the longer their contact time to decolorize it. However, due to the least percentage of colour removal produced at 100mM, the range of persulfate dosage from 20-100mM would give some disturbance if the usage were higher than 60mM. Basically in AOPs, increasing initial concentration of dyes would cause formation of intermediates during the degradation of the primary dye and consequently, may interfere the desirable oxidation [22]. Besides, the contact time for colour removal would be longer at higher initial dye concentration in constant operational conditions in order to get a higher percentage for both responses.

3.2.3 Effect of persulfate dosage on colour and COD removal of MO

The results indicated that at acidic condition than basic condition with medium persulfate dosage at 60mM achieved the highest colour removal of MO as stated in Fig.4(c) and Fig. 5(c). This disturbance would give a negative effect to both colour and COD removal efficiencies at a persulfate dosage that higher than 60mM. Based on [23] indicated that excess SO_4^- would generated at higher persulfate dosage and these excessive may work as scavengers for $S_2O_8^{2-}$. While based on Fig.4. a), persulfate dosage clearly can enhance the efficiency of colour removal for all range of initial concentration.

3.2.4 Effect of contact time on colour and COD removal of MO

As referring to contact time factor, it can be concluded that the longer of time treatment, the higher the percentage of colour removal MO. The result showed that process can enhanced more than 90% colour removal while COD removal will be increased about 80% as well as contact time will be increased. Based on [24] some part of organic products were not oxidized completely in the presence of ozone only, due to carboxylic acids directly attacked by ozone from some dyes. Thus, some of the organic compounds were not completely degraded in this process. As a result, persulfate dosage which higher than 60mM gave least percentage of response and less affected towards contact time factor.

Overall, the response of colour removal was faster compared to removal of COD in oxidative degradation of methyl orange by ozone/persulfate. This was because the colour of MO can be removed once the chromophore in MO molecular, azo bonds (-N=N-) were destructed, that made the speed of removal of chemical oxygen demand slower than the colour removal efficiency [25].

4 Conclusions

The important finding to emerge in this study is preliminary screening oxidative degradation MO using ozone/persulfate by 2⁴ level factorial designs allowed us to determine the importance and suitable range of operational conditions for a better degradation performance. According to this study, the main parameters that influenced the ozonation process were pH and persulfate dosage for colour removal MO while contact time and initial concentration for COD removal response. The interaction between pH, initial concentration, persulfate dosage and contact times is the most important interaction as it has the highest percentage contribution. The excellent correlation between predicted and observed degradation efficiency, R² for colour removal and COD removal of Methyl Orange were R²=0.9976 and R²=0.9924 which ensured to give a good accordance between the model and experimental data which confirmed the validity and practicability of the model.

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