



Photo-degradation of the methyl blue: Optimization through response surface methodology using rotatable center composite design

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Abstract

Advanced oxidation processes (AOPs) generate *in situ* active hydroxyl radicals which allowed the destruction of polluting agents through mineralization. The suitable experimental design allows adjustment of factor levels to obtain an optimal response in experimental analysis. Rotatable Center Composite design and multivariate analysis were used for the optimization of the removal of methyl blue from aqueous solution, using UV (254 nm) radiation source and hydrogen peroxide as an oxidant. A factorial design (2ⁿ) with repeated central and axial points was used to obtain the best experimental condition to efficiently remove the dye from aqueous solution and initial dye concentration, 50- 150 ppm and hydrogen peroxide 0.05- 5.95 % was used as experimental variables. At optimum level up to 96.5% dye removal was recorded. Dye degradation followed the first order kinetics and dissolved oxygen and pH of the dye aqueous solution were found strongly correlated with the dye degradation.

Keywords: Advanced oxidation process, degradation, methyl blue, response surface methodology

1 Introduction

Methyl blue (C.I. 42780) belongs to triaminotriphenylmethane dyes. Methyl blue and aniline blue are so similar that both dyes are given same color index name "Acid blue 93" (Fig. 1). They are widely used as antiseptic dyes in polychrome staining methods and have applications in histological and microbiological staining solutions [1-2]. Before present study, methyl blue has been used as a model to study the effect of various catalysts on photo-degradation of dyes [3-4].

Wastewater containing dye is very difficult to treat by conventional methods due to their non-biodegradable and complex nature. Various physico-chemical and biological methods have been used in order to degrade the dyes present in wastewater [5-9]. These methods are efficient, however, the major constraints are the secondary pollution problem such as sludge and polluting agent transformation from one phase to another phase. Therefore, attention has to be focused on techniques that lead to the complete degradation of pollutants [10].

The AOPs techniques are attractive alternatives, able to mineralize organic contaminants and destruct the organic pollutants from wastewater rather transferring into solid phase medium. Processes involving the use of UV radiation and H₂O₂ are characterized by the generation of hydroxyl radicals *in situ*, which are short lived, but highly reactive chemical species and react non-selectively with organic matter present in medium. These radicals can oxidize organic compounds producing organic radicals, which are highly reactive and can undergo further oxidation. The possible reactions, which occur during UV/H₂O₂ process, are hydrogen abstraction, electrophilic addition and electron transfer reaction and the final products are H₂O, CO₂ and low molecular weight aliphatic acids and resultantly improve the water quality parameter [11-17].

The UV irradiation in the presence of hydrogen peroxide (H₂O₂) is a very promising AOP technique (200–280 nm) which leads to disassociation of H₂O₂ and resultantly system generates hydroxyl radicals ([•]OH), highly powerful oxidizing species, produce organic radicals (R[•]) and resultantly chain reaction is started [8, 10, 18-19]. Regarding the importance of AOPs, UV/H₂O₂ system was used for degradation of methyl blue and optimized the variable (dye concentration and H₂O₂ percentage) for maximum dye removal. The effect of AOP treatment system on pH and DO was also evaluated and compared with true effluent from textile industry.

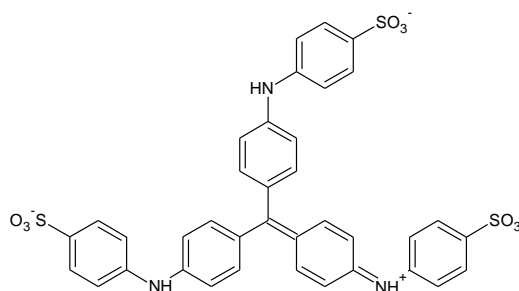


Fig. 1: Structure of methyl blue

2 Material and methods

2.1 Experimental design

Initially a 2^n factorial design with $n=2$ was used with only 4 runs. (-1,-1), (1,-1), (-1,1) and (1,1). However, in this form all of the model parameters (β) could not be estimated. Central Composite design is the best solution, since it gives almost as much information as a multilevel factorial [20]. The number of runs was increased by adding central points and axial points and used for estimating second order surface design Box and Hunter (1957). For axial points, $\alpha=(n_f)^{1/4}$, Where n_f =number of factorial runs. The axiel points used in suggested design were; (0,-1), (-1,0), (1,0), (0,1) So, the distance of axiel points from center is $\alpha=(4)^{1/4}=1$. Generally ($3 \leq n_c \leq 5$) center runs are required to provide stable variance of predicted response. In suggested experiment, 4 axial and 4 central points were added and fitted the second degree model and estimate all of the parameters and second order polynomial equation was obtained from the model (Eq. 1).

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \beta_1 X_1^2 + \beta_2 X_2^2 + \epsilon \quad (1)$$

Where β_0 , β_1 and β_2 are representing the overall average, dye concentration and H_2O_2 percentage, respectively and level (coded and natural) selected for variables (dye concentration and H_2O_2 percentage) are shown in table 1.

Table 1: Experimental matrix of the variables (coded and natural), with corresponding experimental observed and predicted responses to optimize dye degradation.

Run	D (ppm)	H ₂ O ₂ (%)	D removal (%)		DO (mg/L)		pH	
	Level*	Level**	O	P	O	P	O	P
1	50(-1)	0.05(-1)	40	38	4	3.44	6.98	7.22
2	100(0)	0.05(-1)	55	61	4.5	5.71	6.93	6.46
3	150(1)	0.05(-1)	30	26	3.5	2.84	7.05	7.27
4	50(-1)	3(0)	60	68	5	6.29	6.9	6.41
5	100(0)	3(0)	96.5	91.83	9.5	8.6	5.5	5.67
6	150(1)	3(0)	45	57.33	4.3	5.77	6.96	6.5
7	50(-1)	5.95(1)	35	28.66	3.75	3.01	7.02	7.26
8	100(0)	5.95(1)	38	52.66	3.8	5.36	7	6.53
9	150(1)	5.95(1)	27	18.66	3.4	2.57	7.15	7.37
10	100(0)	3(0)	98	91.83	9.4	8.6	5.4	5.67
11	100(0)	3(0)	97	91.83	9.2	8.6	5.37	5.67
12	100(0)	3(0)	96.5	91.83	9.08	8.6	5.47	5.67

*level of dye concentration with natural and coded values, **level of hydrogen peroxide with natural and coded values; natural (coded values), O (observed removal of dye), P (Predicted removal of dye), D (dye concentration) and DO (dissolved oxygen).

2.2 Irradiation process

The model compound (methyl blue) was of analytical grade and purchased from Merck. The radiation source was UV lamp (44 Watt, 254 nm, Pakistan Scientific, Pakistan), protected by a quartz tube. Temperature range of UV system was from 32 °C to 40 °C. The dye solution was projected at the bottom of the reactor (20 cm from the UV source) and irradiated for 45 min. the concentration of dye in solution was measured spectrophotometrically (Cecil, 7200), while DO

and pH values were measured using pH and DO meters (Lovibond). The dye solutions (50-150 mg/L) were prepared immediately before irradiation using deionized water [10].

III. Statistical analysis

The data manipulated using R, Statistical Software (version 2.13) for ANOVA and predicted value, response surface diagrams, model selection and calculation of stationary points. The effect of variable and their interaction were calculated at 95 % confidence interval of mean.

3 Results and discussion

3.1 Degradation

The optimization process was carried out using H_2O_2 /UV photocatalytic system for methyl blue degradation in order to evaluate the effect of the system. Tables 1 shows the coded experimental variables, the order in which the experiments were run and number of experiments. In addition, the corresponding observed and predicted responses for the optimization of methyl blue degradation and treatment effect on pH and DO are also shown in same table 1. Based on the difference between observed and predicted responses, the model determined the experimental error with a 95% confidence interval of mean. After generation of experimental matrices with their respective responses, the experimental variables were combined to construct the three-dimensional surface plots. In these plots the synergism between the experimental variables can be observed, resulting in an optimal zone, where it is possible to identify the values of the variables given by the model for optimal response (dye degradation). The response surface of methyl blue (Fig. 2) indicates that the optimal H_2O_2 concentration for the efficient removal of dye was 3% for 100 ppm of dye concentration. Furthermore, DO was found directly related to the dye degradation, while the pH of the medium decreases by increased degradation. The average ratio of degradation/DO and degradation/pH was found to be 10.19 (increase) and 9.88 (decrease), respectively. The maximum DO value was observed at 96.5 percent degradation and the same medium showed the lowest value of pH (5.67) (Fig. 3-4).

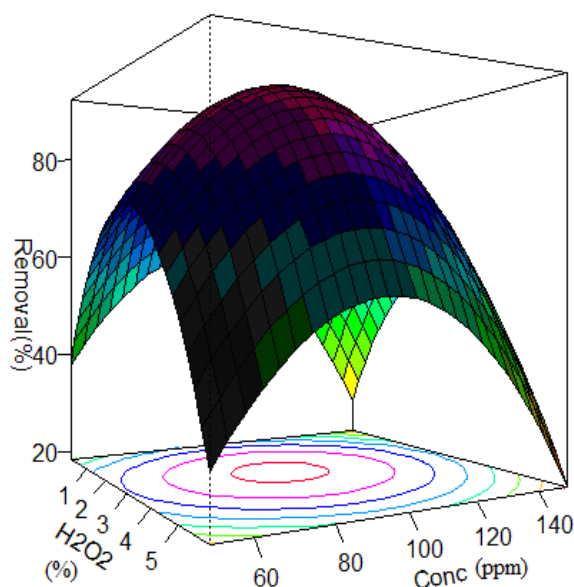


Fig 2: Response surface for the experimental design for dye degradation

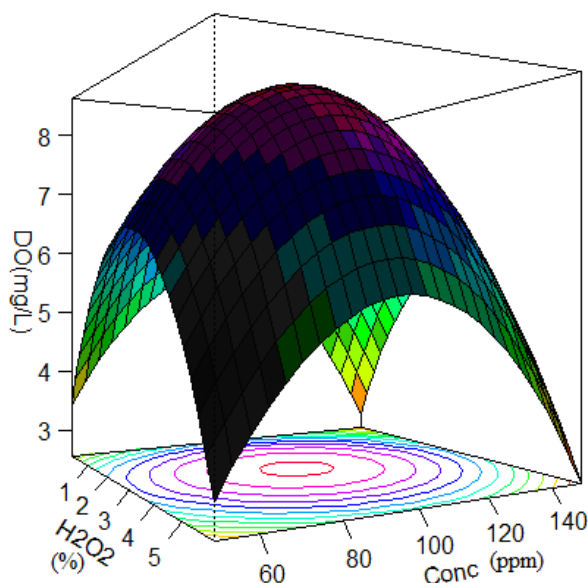


Fig 3: Response surface for the experimental design for dissolved oxygen variation

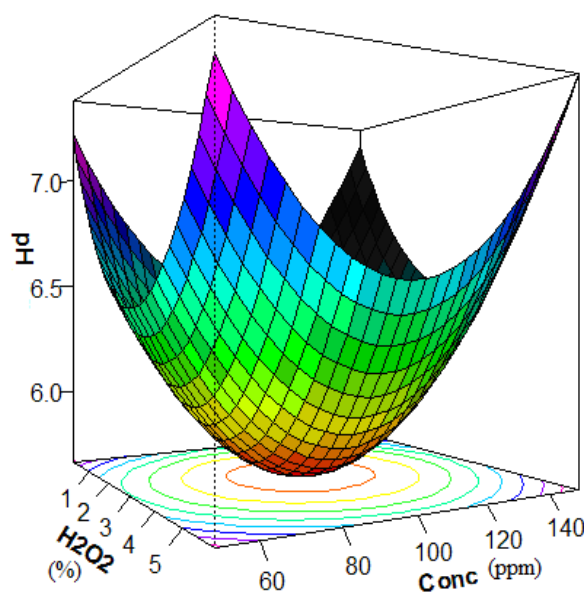


Fig 4: Response surface for the experimental design for pH variation

By solving statistically the experimental matrix, the polynomial modeling equations were developed, each giving rise to the response surface. The model equations were developed so that the importance of the parameters in the mathematical solution was obtained from the experimental design, with respect to the weight of each variable. Thus, an empirical relationship between the response and the variables was expressed by the polynomial equation; response surface for degradation (Eq. 2), Do (Eq. 3) and pH (Eq. 4), respectively, where Y, X_1 and X_2 are representing the response, initial dye concentration and H_2O_2 percentage, respectively.

$$Y (\%) \text{ degradation} = -44.10 (\pm 27.07) + 2.19 (\pm 0.55) X_1 + 22.37 (\pm 6.08) X_2 - 0.011 (\pm 0.002) X_1^2 - 4.02 (\pm 0.7) X_2^2 + \epsilon \quad (2)$$

$$Y (\%) \text{ DO} = -4.06 (\pm 3.48) + 0.19 (0.07) X_1 + 2.02 (0.78) X_2 + 0.001 (0.0003) X_1^2 - 0.35 (0.09) X_2^2 + \epsilon \quad (3)$$

$$Y (\%) \text{ pH} = 9.59 (\pm 1.17) - 0.6 (0.02) X_1 - 0.56 (0.26) X_2 + 0.0003 (0.0001) X_1^2 + 0.09 (0.03) X_2^2 + \epsilon \quad (4)$$

Statistical analyses showed that that the quadratic effects of variables were significant in the response, where the polynomial equation represented the response influenced by combined effect of variables; dye initial concentration and H_2O_2 percentage. Fig. 4 shows the influence of each variable on the response and the correlation coefficient values (percentage) for the statistics, with a 95% confidence interval of mean. In the case of dye degradation and variation in DO, the efficiency of variation was directly influenced by the H_2O_2 concentration, while the change in pH was

influenced by the combined effect of dye initial concentration as well as H₂O₂ percentage. The second degree terms were found non significant for measured parameters and H₂O₂ was found more effective as compared to dye initial concentration (Fig. 5). All models (dye degradation, pH and DO variation) were statistically evaluated as valid, given the values of R² and R² adjusted (adj) as; 0.92 and 0.86 for dye degradation, 0.85 and 0.72 for DO change and 0.80 and 0.63 for pH variation (Table 2). These values of R² and R² adj indicate that the regression model provides a good description of the relationship between the independent variables and the responses because R² represents the fraction of the variation of the response explained by the model and evaluate the statistical validity of the quadratic model with p < 0.001.

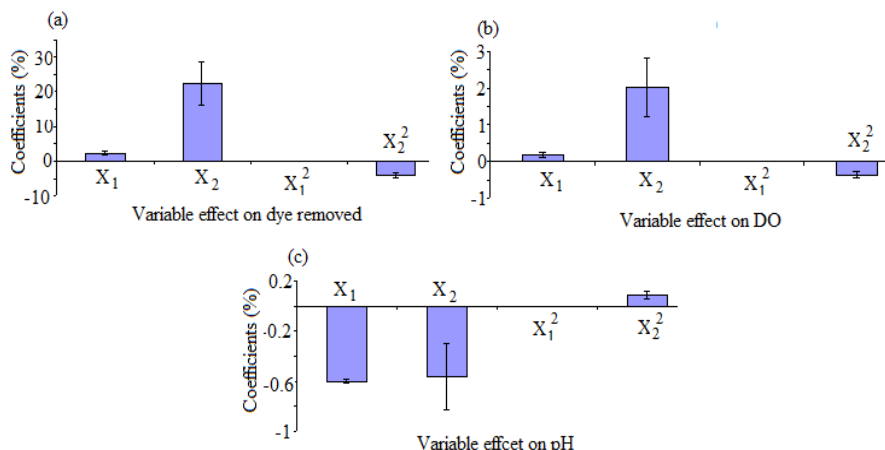


Fig 5: Analysis of the influence of parameters on dye degradation, DO and pH with a 95% confidence interval

ANOVA (Table 2) shows that the fitted model (second order) is not appropriate, since only PQ (Pure Quadratic) was significant. In other words, it is not meaningful if we will not include first order (FO) terms and only include significant PQ terms. So, the model given above was appropriate since we have included FO terms as well as PQ terms. So, we have used RCCD for optimization of variable and to get maximum response (degradation) using UV/H₂O₂ system.

Table 2: Analysis of variance (ANOVA) for response surface model

SOV	DF	SS	MS	F value	P value
Removal (%)					
FO	2	285.7	142.8	1.20	0.36
TWI	1	1.0	1.0	0.008	0.92
PQ	2	8228.0	4114.0	34.74	0.0005*
Residual	6	110.5	118.4		
Lack of fit	3	309.0	236.3	472.66	0.0001
Pure Error	3	1.5	0.5		
DO (mg/L)					
FO	2	0.58	0.29	0.14	0.8
TWI	1	0.006	0.006	0.002	0.9
PQ	2	63.70	31.85	16.26	0.003*
Residual	6	11.74	1.9		
Lack of fit	3	11.64	3.88	107.5	0.001
Pure Error	3	0.1	0.036		
pH					
FO	2	0.01	0.009	0.04	0.95
TWI	1	0.0009	0.0009	0.004	0.95
PQ	2	5.21	2.60	11.70	0.008*
Residual	6	1.33	0.22		
Lack of fit	3	1.32	0.44	121.64	0.001
Pure Error	3	0.1	0.03		

* significant effect, FO = first order, TWI = two way interaction and PQ = pure quadratic,

R2 and R2 adjusted (adj); 0.92 and 0.86 (dye degradation),

R2 and R2 adjusted (adj); 0.85 and 0.72 (DO change)

R2 and R2 adjusted (adj); 0.80 and 0.63 (pH variation)

3.2 Photochemical process and mechanism

The optimal conditions observed for the removal of methyl blue dye from aqueous solution by UV/H₂O₂ system was experimentally verified following the kinetic study of the degradation (Fig. 6). The methyl blue degradation followed the first order kinetics with a rate constant of 0.33 min⁻¹. Chemically, the H₂O₂ activated by UV light during the photolysis process, generated *in situ* hydroxyl radicals (OH[•]), which are a highly reactive species responsible for the oxidation process. Analysis of the kinetics showed a rapid decrease in concentration dye treated photocatalytically, resulting in more than 97% removal after 100 min of treatment. The main mechanism of AOPs function is the generation of highly reactive free radicals. The HO[•] are very effective in destroying organic compound because they are reactive electrophiles that react rapidly and non-selectively with nearly all electron-rich organic compounds with a oxidation potential of 2.33 V and exhibit faster rates of oxidation reactions comparing to conventional oxidants. Once generated, the hydroxyl radicals can attack organic chemicals by radical addition (Eq. 5), hydrogen abstraction (Eq. 6) and electron transfer (Eq. 7) [19, 21-24]. In the following reactions, R is used to describe the dye molecule.



The UV/H₂O₂ process has been widely used for dyes removal and results obtained are in accordance with previous studies. Daneshvar et al [25] reported that the H₂O₂ concentration up to 2 mmol L⁻¹ is effect for dye degradation and Rezaee et al [26] used this process for decolorization of dye and the effects of operating parameters such as H₂O₂ dosage, initial dye concentration, pH and UV dose were evaluated and found that the dye solution was completely decolorized under optimal H₂O₂ dosage (2.5 mmol l⁻¹) and low-pressure mercury UV-C lamps (55 w) in less than 30 min. The decolorization rate increased linearly with UV dosage and nonlinearly with increasing initial H₂O₂ concentration. According to Yeber et al [27] the dye molecule has a strong tendency toward electron, due to presence of electronegative atom in their structures. Due to high electronegativity, these are attacked by hydroxyl radicals through nucleophilic addition, increasing the nitrate and nitrite and other ions in the solution during the oxidation process as a mineralized product. The methyl blue dye has complex molecular structure that contains nitrogen atoms which on photolysis generates nitrites and nitrates ions and might be responsible for enhanced degradation. The AOPs have appeared as interesting techniques for the treatment of organic pollutants [12, 28-30]. Among the most used is the well-known UV/H₂O₂ which allows the generation of highly reactive free hydroxyl radicals from the hydroxide ions of water [31-34]. In this study, it was possible to observe that the hydroxyl radicals generated *in situ* which are responsible for mineralization of methyl blue in the form of nitrate and nitrite ions as well as mineralized carbon. The efficiency of the developed process lies primarily in oxidizing agent strength of the hydroxyl radicals that are formed. On the other hand, the use of multivariate analysis allowed an accurate optimal response and an adequate statistical analysis to obtain the optimal response [7, 20, 35].

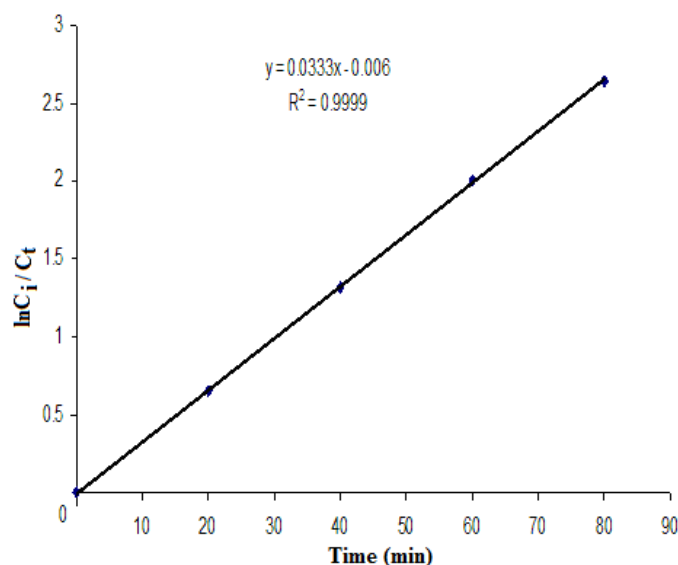


Fig 6: Methyl blue kinetics using the optimized H₂O₂ percentage

4 Conclusions

The advanced oxidation process using the H₂O₂/UV system is an efficient method for degradation of methyl blue. The *in situ* production of hydroxyl radicals cause faster dye reduction with rate constant 0.33 min⁻¹ following first order of kinetics degradation. The variation in pH and DO was found to be dependent on dye degradation. The use of experimental design demonstrates that this is an efficient tool for determining the efficiency of treatments with a statistically reliable analysis.

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