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Removal of Methylene Blue from Aqueous Solution Using Nano-TiO_2/UV Process: Optimization by Response Surface Methodology

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ABSTRACT

This work describes the photocatalytic removal of methylene blue from aqueous solution by titanium dioxide nanoparticles under ultraviolet irradiation in a batch system. The effect of operational parameters such as irradiation time, nano titanium dioxide dosage, pH and initial methylene blue concentration were analyzed and optimized by response surface methodology in the nano titanium dioxide/ultraviolet irradiation process. As results, the predicted values were best fitted with the experimental data (R^2 = 0.9736). The maximum removal efficiency was in the following conditions: irradiation time of 31.5 min, nano titanium dioxide dosage of 1.19 g L^{-1}, pH of 7.8 and initial methylene blue concentration of 4.5 mg L^{-1}. Under the optimized status, the removal yield was obtained more than 80%. Carrying out the experiment under this optimum condition resulted in the same removal efficiency, which indicated the success and suitability of the central composite design model for the optimization of the process. Prog. Color Colorants Coat. 9 (2016), 135-143 © Institute for Color Science and Technology.

1. Introduction

The textile and paint industries generated dye contaminants that were becoming a main source of environmental pollution. More than fifteen percent of total dye production is discharged in the environment and caused to water pollution [1, 2]. Methylene blue (MB), which was chosen as the model compound in the present study, is a cationic dye and used broadly for dyeing silk, cotton and wool. The risk of the presence of this dye in wastewater may be created from the nausea, burns effect of eye, vomiting and diarrhea [3]. Various methods have been developed for the treatment of textile wastewater, including adsorption [4-6], biological treatment [7-9], ozonation [10-12] and electrochemical treatment [13, 14]. However, these methods have several disadvantages such as large production of sludge, high cost of disposal sludge and high initial capital and maintenance cost. A method that is attracting the attention of many scholars is photocatalytic degradation [15-18]. Photocatalysis by semiconductor is a method that has high performance to control water and air contaminants. The advantages of photodegradation are: (1) usage of near-UV or solar

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light, (2) operation at near room temperature, (3) no addition of other chemicals, and (4) perfect mineralization of the contaminants. One of high potential photocatalysts is titanium dioxide due to its strong oxidizing power, long-term photostability and non-toxicity [19]. The photocatalytic activity of TiO_2 depends on its crystallite size, phase structure, pore structure and specific surface area. Several researches have shown that the nano-TiO_2 P-25 is a superior photocatalytic for water or air decontamination purposes [20-22].

The efficiency of photocatalytic process is dependent on various parameters such as illumination intensity, irradiation time, catalyst dosage, pH and initial concentration of pollutants. In customary methods, the experiments were commonly carried out by changing some studied variables while others were fixed which is time-consuming and costly. Response surface methodology (RSM) is a statistical method to reduce the number of the experiments. Mathematical and statistical techniques are applied in this method to evaluate the effect of the independent parameters on a particular dependent variable. This method gives linear interaction and quadratic effects of the factors and is useful for the optimization of process [23, 24].

In this paper, nano-TiO_2 P-25 was used to photocatalytic removal of MB under ultraviolet irradiation. In order to optimize the value of effective parameters with the minimum number of experiments, central composite design -the most widely used form of RSM- was employed to find improved or optimal process settings in an efficient use of the experimental data.

2. Experimental

2.1. Materials

Nano-TiO_2 (Degussa P-25) was supplied by Degussa, Germany. Surface area and particle size of nanoparticles were about 15-50 m^2g^{-1} and 20 nm, respectively. Methylene blue ($C_{16}H_{18}N_3SCl$, Mw=319.85 $gmol^{-1}$) was purchased from Merck, Germany.

2.2. Photocatalysis experiments

Photocatalytic removal of MB was performed by a batch system with considering the effect of various parameters such as irradiation time, nano-TiO_2 dosage, pH and initial MB concentration. A stock solution was prepared by dissolving the appropriate amount of MB in distilled water and then diluted to the required concentration. The initial pH was adjusted by adding either NaOH or HCl. Batch experiments were done in a beaker contains 250 mL of MB solution and nano-TiO_2 that exposed to UV light (30 W/m^2), and the mixture was stirred on a magnetic stirrer at a speed of 200 rpm. Samples were taken at predetermined time intervals and filtered with 0.22 µm micro filters. The concentration of MB was measured by UV-Vis spectrophotometer (HACH/DR 5000) at maximum wavelength (λ_{max}=660 nm). The removal efficiency of MB, R (%), was calculated by using the equation (1):

$$R\,(\%) = \frac{[MB]_0 - [MB]_t}{[MB]_0} \times 100 \qquad (1)$$

where $[MB]_0$ and $[MB]_t$ are MB concentration at initial and any time, respectively.

2.3. Experimental design

RSM is an important tool to optimize the conditions for wastewater treatment. Such statistical approach reduces the number of runs and provides valuable information on possible interactions between the variables and response. Central composite design (CCD) and Box–Behnken are the most generally chosen methods in RSM technique [25]. RSM based on CCD needs to N experiments ($N=2^k + 2k + c_p$, where k is the factor number and cp is the replicate number of the central point). All factors are evaluated in five levels (-α, -1, 0, +1, +α). Values of α can be obtained by $\alpha=2^{k/4}$. For two, three, and four variables, they are, respectively, 1.41, 1.68, and 2.00 [26]. In the present study, CCD was used to evaluate the photocatalytic process. In order to study the effect of operating parameters, four independent factors were selected: irradiation time (min), nano-TiO_2 dose (gL^{-1}), pH and initial MB concentration (mg L^{-1}). In this research, the k value is equal to four, so $\alpha=2^{4/4}= 2$. The ranges and the levels of the independent variables are given in Table 1. Photocatalytic removal of MB was also investigated by variation in UV light intensity. Nevertheless, decrease of illumination intensity has a negative effect on removal efficiency, due to the reduction of light penetrating to reach the catalyst surface and consequently reduce reactive hydroxyl and superoxide radicals.

A total of 31 experiments were carried out, consists of $2^4=16$ cube points, $2 \times 4=8$ axial points and seven replications at the center point. Obtained data were analyzed using the response surface regression procedure of a statistical analysis system (Minitab software version 17).

3. Results and discussion

3.1. Results of model

The relationship of mathematical between the operational parameters and response can be approximated by the following quadratic equation (2):

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{i\neq j=1}^{k} \beta_{ij} x_i x_j \qquad (2)$$

where y represents the process response and β_0 is the constant. β_i, β_{ii} and β_{ij} are the regression coefficients for primary, quadratic and interaction effects, respectively. x_i and x_j are coded independent variables [26]. The details of the designed experiments along with the results of both experimental and predicted values for removal efficiency are given in Table 2. Consequently, an empirical relationship between the independent variables and response was attained as shown in equation (3):

$$y = -188.74 + 2.44\,x_1 + 240.63\,x_2 + 16.66\,x_3 - 10.16\,x_4 - 0.03\,x_1^2 - 92.86\,x_2^2 - 0.78\,x_3^2 - 1.00\,x_4^2 - 0.12\,x_1 x_2 + 0.02\,x_1 x_3 + 0.04\,x_1 x_4 - 1.85\,x_2 x_3 - 0.16\,x_2 x_4 - 0.34\,x_3 x_4 \qquad (3)$$

The predicted values of removal efficiency of MB obtained using equation (3) are plotted against the corresponding experimental data and shown in Figure 1. Results confirm that the predicted values are closely correlated with experimental results. According to analysis of variance (ANOVA) results (Table 3), the value of correlation coefficient ($R^2=0.9736$) shows that the proposed model predict the performance of the photocatalytic process with high accuracy. Also, it can be seen that the R^2 of 0.9736 is in reasonable agreement with the adjusted R^2 of 0.9504 for the quadratic model and it implies the goodness of fit between model and experimental data. F-value of 294.95 with P-value less than 0.0001 also indicated that the model was statistically significant.

Table 1: Experimental ranges and levels of the operational variables.

Variable	Symbol	Range and level				
		-α (-2)	-1	0	1	+α (+2)
Irradiation time (min)	x_1	10	20	30	40	50
Nano-TiO_2 dosage (g L^{-1})	x_2	0. 4	0. 8	1.2	1.6	2
pH	x_3	1.5	3.5	5.5	7.5	9.5
Initial MB concentration (mg L^{-1})	x_4	2	4	6	8	10

Table 2: The 4-factor CCD matrix with the experimental and predicted responses.

Run	x_1	x_2	x_3	x_4	R (%)	
					Experimental	Predicted
1	20	0.8	3.5	4	40.01	44.3
2	40	0.8	3.5	4	44.95	45.92
3	20	1.6	3.5	4	48.05	47.84
4	40	1.6	3.5	4	50.85	50.54
5	20	0.8	7.5	4	60.89	63.41
6	40	0.8	7.5	4	63.01	63.35
7	20	1.6	7.5	4	58.95	65.5
8	40	1.6	7.5	4	62.5	62.01
9	20	0.8	3.5	8	31.52	31.92
10	40	0.8	3.5	8	40.93	40.21
11	20	1.6	3.5	8	36.93	37.93
12	40	1.6	3.5	8	43.9	48.3
13	20	0.8	7.5	8	43.89	45.54
14	40	0.8	7.5	8	52.02	52.14
15	20	1.6	7.5	8	46.66	52.6
16	40	1.6	7.5	8	50.23	50.28
17	10	1.2	5.5	6	56.73	55.02
18	50	1.2	5.5	6	63.89	68.32
19	30	0.4	5.5	6	14.89	12.72
20	30	2	5.5	6	17.5	17.39
21	30	1.2	1.5	6	60.23	55.43
22	30	1.2	9.5	6	75.01	74.53
23	30	1.2	5.5	2	69.89	68.92
24	30	1.2	5.5	10	51.13	47.82
25	30	1.2	5.5	6	72.56	74.49
26	30	1.2	5.5	6	76.53	74.49
27	30	1.2	5.5	6	73.19	74.49
28	30	1.2	5.5	6	75.01	74.49
29	30	1.2	5.5	6	74.01	74.49
30	30	1.2	5.5	6	73.95	74.49
31	30	1.2	5.5	6	77.19	74.49

Table 3: ANOVA results of the response surface quadratic model.

Source of variations	DF	Sum of squares	Mean square	*F*-value	*P*-value
Regression	14	8490.25	606.45	294.95	0.00
Residual	16	32.9	2.06	-	-
Total	30	8523.15	-	-	-

Note: R^2=0.9736, adjusted R^2=0.9504

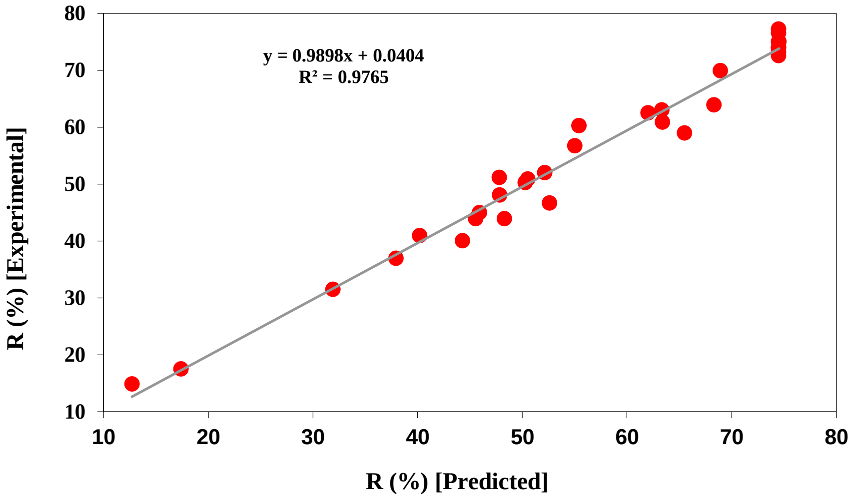

Figure 1: Comparison between experimental and predicted removal efficiency.

3.2. Effect of operational variables

The response surface and counter plots were depicted with two parameters kept constant at their zero level and the other two varying within the experimental ranges. Figure 2 represents the effect of the catalyst dosage and irradiation time on the removal of MB. A trend of increment in the removal efficiency with increasing of nano-TiO_2 dosage was observed from 0.4 to 1.2 g L^{-1}. This is due to increase of available catalytic and adsorption sites on the nano-TiO_2 surface, which are accountable for photocatalytic activity [27]. Further increment in catalyst dosage resulted in a decline in removal efficiency as shown in Figure 2. This reduction had been explained to be due to the overlapping of adsorption sites as a result of overcrowding of catalyst particles above 1.2 g L^{-1}. Also, with increasing of catalyst dosage, scattering effect increases which causes a decline in UV light influence to the solution [28]. Similar result was presented for photocatalytic destruction of methyl orange by nanoparticles of ZnO–SnO_2 [29]. Also from Figure 2, it is clear that irradiation time effect on MB removal is less than the catalyst dosage.

Since pH of dye solution is a key factor on the degradation progress, experiments were conducted at different pH values. Figure 3 shows the response surface and counter plots of the removal efficiency as a function of pH and the irradiation time. This Figure reports the increase in removal efficiency when the pH increases from 1.5 to 9.5. The pH of isoelectric point (pH_{IEP}) for the Degussa P-25 TiO_2 is 6.5 [30]. The surface of TiO_2 carries negative charge at pH values higher than IEP ($pH > 6.5$), so there is an electrostatic adsorption between negative charge surfaces of nano-TiO_2 and cationic dyes in neutral and basic media. On the other hand, for acidic pH values, the nano-TiO_2 surface is positively charged resulting in reduced removal efficiency due to electrostatic repulsion between the positive surface charge of TiO_2 nanoparticles and cationic dyes. Since MB has a cationic configuration, its adsorption is favored in alkaline solution. On the other hand, at alkaline pH values, hydroxyl radicals generated by the photocatalytic process gradually increase and cause destruction of organic compounds such as dye molecules. This observation is consistent with other researches [31, 32].

The effect of the irradiation time and initial MB concentration on the removal efficiency is shown in Figure 4. In this Figure the removal efficiency is decreasing slowly with increasing of initial MB concentration. In fact, by increasing of MB concentration, the amount of light penetrating into the dye solution to reach the catalyst surface is reduced. So, the formation of reactive hydroxyl and superoxide radicals is also simultaneously reduced [33, 34]. Similar results were reported for the photocatalytic degradation of Basic Red 46 dye and leather dye on TiO_2 [35, 36].

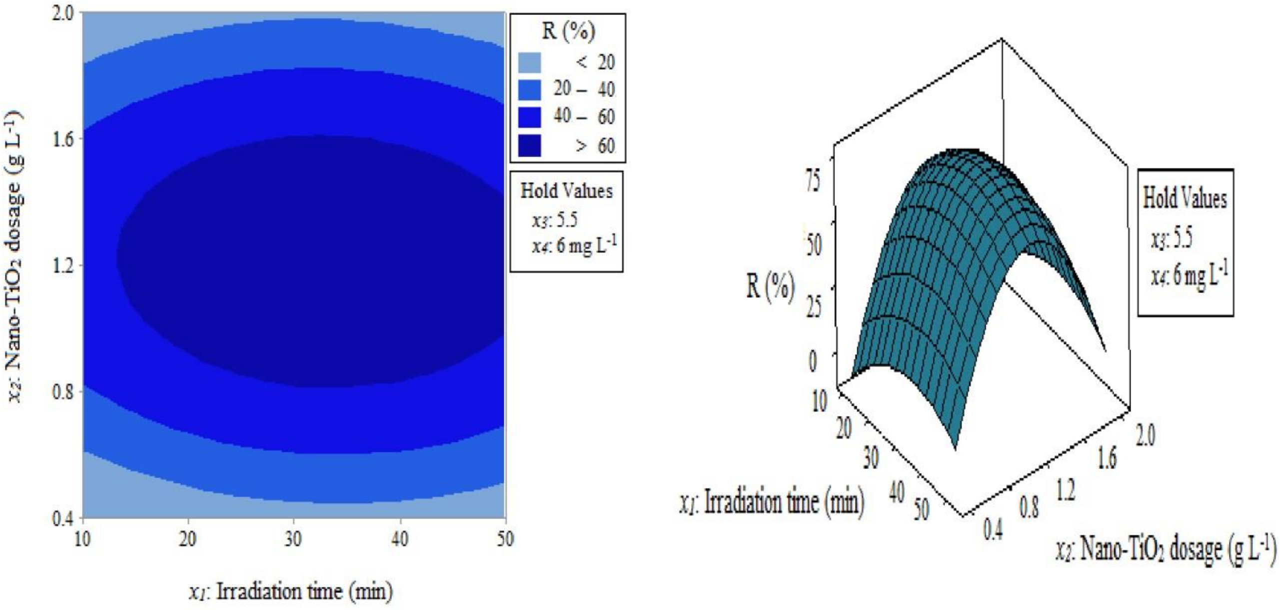

Figure 2: The response surface and contour plots of the removal efficiency of MB as a function of nano-TiO2 dosage and irradiation time.

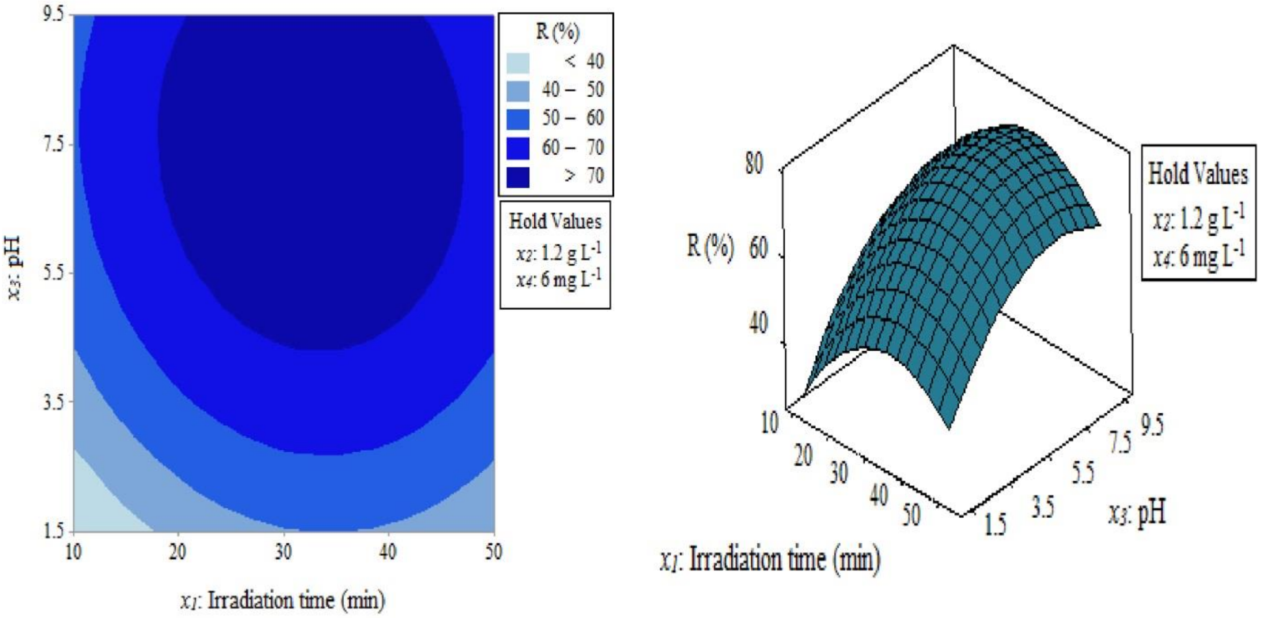

Figure 3: The response surface and contour plots of the removal efficiency of MB as a function of pH and irradiation time.

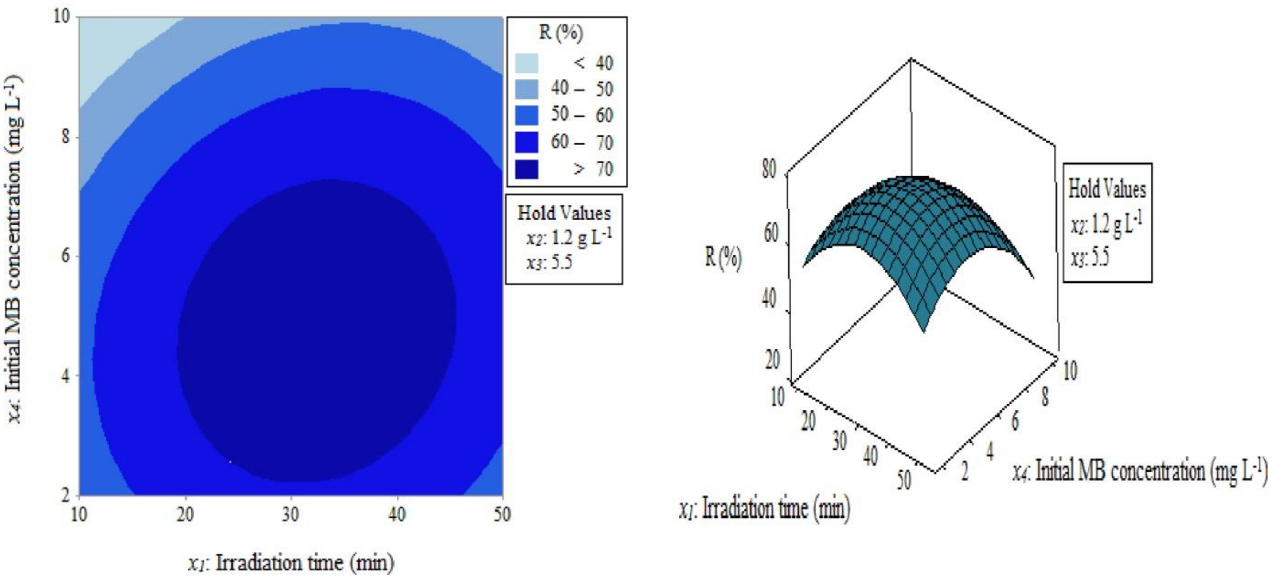

Figure 4: The response surface and contour plots of the removal efficiency of MB as a function of initial MB concentration and irradiation.

3.3. Determination of optimal conditions for operational variables

RSM was used for optimization of the independent variables by the CCD model obtained from experimental data. In order to gain removal efficiency >80%, the optimum values of variables were irradiation time=31.5 min, nano-TiO_2 dosage=1.19 g L^{-1}, pH=7.8 and initial MB concentration=4.5 mg L^{-1}.

Carrying out the experiment under this optimum condition resulted in the same removal efficiency, which indicated the success and suitability of the CCD model for the optimization of the process.

4. Conclusion

The photocatalytic removal behavior of MB by UV/TiO_2 was investigated. RSM was used in this research to optimize the individual and interaction effects of the operational variables. The results confirmed that the anticipated values of removal yield were found to be in good agreement with experimental data with a correlation coefficient (R^2) of 0.9736. Also, the optimum values of the operational variables for the maximum removal yield (>80%) were evaluated and then verified experimentally..

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