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Optimal decolorization efficiency of Reactive Red 239 by UV/TiO_2 photocatalytic process coupled with response surface methodology

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Abstract

The decolorization of azo dye by titanium dioxide (TiO_2) with 360 nm ultraviolet (UV) light was studied in a batch reactor. Response surface methodology was applied to optimize four independent parameters, viz. UV light intensity, the concentration of TiO_2, initial pH, and stirring speed, in the photocatalytic degradation process of the dye Reactive Red 239. To obtain the mutual interaction between these four parameters and to optimize these parameters during the process, a 2^4 full-factorial central composite design (CCD) and response surface methodology were employed. The results of our experiments indicate that the concentration of TiO_2 exhibits a significant positive effect on the efficiency of decolorization, whereas initial pH shows a significant negative effect. The optimized condition of the photocatalytic degradation of Reactive Red 239 is as follows: UV light intensity, 16.08 W/m^2; TiO_2 concentration, 3.06 g/l; initial pH, 2.64; stirring speed, 880 rpm. Under this condition, the maximal decolorization efficiency of 99.82% was achieved.

Keywords: Decolorization; Azo dye; Response surface methodology; Photocatalytic; Central composite design

1. Introduction

Different types of dyes have been widely used in many industries such as textile, paint, ink, and cosmetics. A certain amount of them are lost in the process of their manufacturing and utilization, and is considered as one of the major industrial polluters [1,2]. Amongst the 10,000 different types of dyes and pigments available, azo dyes constitute over 50% of all textile dyes used in the industry [3]. Azo dyes are characterized by nitrogen-to-nitrogen double bonds (–N=N–), superior fastness to the applied fabric and high photolytic stability. Due to the stability of modern dyes and the large degree of aromatics present in dye molecules, conventional biological treatment methods are ineffective for decoloring such wastewaters [4]. This had led to the study of other methods for decolorizing textile dye waste streams, including adsorption, chemical coagulation, chlorination, and ozonation. The former two methods do not result in dye degradation, but merely in physical removal of the dye material from the effluent, which still maintains a waste disposal problem [5]. Moreover, new environmental laws may consider the spent adsorbents or sludge as hazardous wastes and require further treatment. The later two methods are effective for decolorization. However, discharge of chlorinated organics into the environment is becoming increasingly undesirable and highly regulated. In addition, since ozone is hazardous, an ozone destruction unit must also be applied in order to prevent unreacted O_3 from escaping from the process and into the atmosphere. Therefore, decolorization of dye effluents using new technologies with more efficiency and less energy used has acquired increasing attention.

In recent years, efforts have been devoted to the study of photochemical processes using semiconductor oxides, such as TiO_2, CdS, or ZnO, in heterogeneous system. As TiO_2

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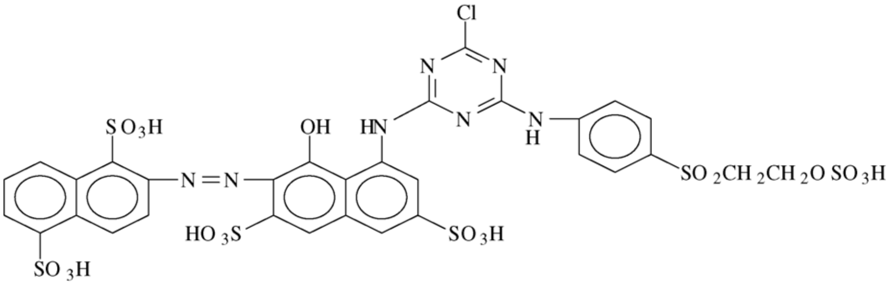

Fig. 1. Molecular structure of Reactive Red 239.

is illuminated by light rays with wavelength below 380 nm, the photons excite valence band electrons across the band gap into the conduction band, leaving holes behind in the valence band. The holes in TiO_2 react with water molecules or hydroxide ions and then produce hydroxyl radicals [6]. Oxygen is usually supplied as electron acceptor to prolong the recombination of electron–hole pairs during photocatalytic oxidation. It has been suggested that the hydroxyl radicals and superoxide radical anions are the primary oxidizing species in the photocatalytic oxidation process. Among many phtocatalysts, TiO_2 has been intensively used in the photodegration of organic dyes in wastewater [7–11]. Thus, applying such a process to textile dye effluent streams might result not only in decolorization, but also in complete degradation of the dyes. In this study, we attempted to obtain the optimal decolorization efficiency of the dye Reactive Red 239 by utilizing the UV/TiO_2 photocatalytic process in cooperated with response surface methodology to optimize four independent parameters, viz. UV light intensity, the concentration of TiO_2, initial pH, and stirring speed. Reactive Red 239 is a well-known mono-azo dye and has been widely used in the dyeing process of textiles industry. Fig. 1 shows the chemical structure of this substance. Several previous investigations have reported that TiO_2 concentration and pH value are important parameters influencing the disappearance of the dye in the photocatalytic degradation process [1,3,12–15]. In this study, the effects of stirring speed for providing a homogenous mixing and the intensity of UV light on the dye degradation process are also considered.

2. Materials and methods

2.1. Reagents

Titanium dioxide powder P-25 with greater than 99.5% purity (average primary particle size: 21 nm, BET surface area: $50 \pm 15\ m^2/g$) used in this study was purchased from Degussa (Germany). Samples of the commercial dye Reactive Red 239 were obtained from Everlight chemical industrial corporation (ECIC, Taipei, Taiwan). In addition, pH was adjusted by both sodium hydroxide and hydrochloric acid as industrial grade, which were purchased from SHOWA (Japan).

2.2. Photoreactors and experimental procedure

A batch photoreactor was set up in this study. For the UV/TiO_2 photocatalytic process, irradiation was performed using a 0.6 W black-light mercury lamp (SANKYO, Japan) with a wavelength of 360 nm, which was placed 21 cm on the top of the batch photoreactor. The light intensity was estimated to be approximately 136 W/m^2 from the light source incident to the top of the Pyrex beaker with the total volume of 500 ml. The UV-irradiated photoreactor was placed on a magnetic stirrer to ensure homogenous mixing during the entire photocatalytic process. The experimental setup is illustrated in Fig. 2.

In each run, 250 ml of 50 ppm aqueous dye solution was mixed with certain amount of titanium dioxide powders. The pH value of the sample was measured with a calibrated pH meter (HANNA, Singapore). As the reaction progressed, a sample solution of 25 ml in volume was taken to separate the photocatalyst by centrifugation (HERMLE, LABORTECHNIK, Germany) at regular time intervals for further analysis.

2.3. Sample analysis

Analytical analysis of Reactive Red 239 in water was performed using a spectrophotometer (UV-1601, Shimadze,

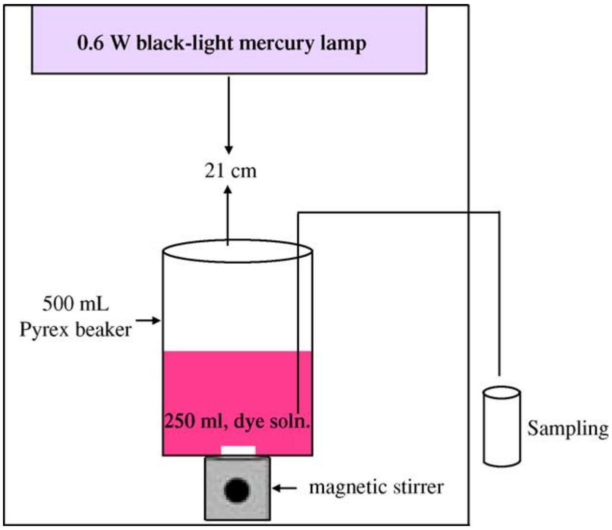

Fig. 2. Experimental setup.

Table 1
Experimental range and levels of the independent test variables

Variables	Ranges and levels				
	−2	−1	0	+1	+2
UV light intensity (X_1) (W/m^2)	13.77	15.27	16.77	18.27	19.77
TiO_2 concentration (X_2) (g/l)	1.96	2.46	2.96	3.46	3.96
Initial pH (X_3)	2	2.74	3.48	4.22	4.96
Stirring speed (X_4)	4.25	5	5.75	6.5	7.25

Japan) coupled with a computer for transmittance data calculation for the American Dye Manufacturers Institute value (ADMI) measurement. The efficiency of decolorization was calculated on the basis of ADMI reduction of solution.

2.4. Experimental design and optimization by response surface methodology

Response surface methodology (RSM) is an experimental technique invented to find the optimal response within the specified ranges of the factors. These designs are capable of fitting a second-order prediction equation for the response. In this study, we adopted a second-order RSM experiment using a five-level full-factorial central composite design (CCD) to optimize the photocatalytic reaction parameters. The parameters chosen in this study are UV light intensity, the concentration of TiO_2, initial pH, and stirring speed. The ranges and the levels of these parameters investigated in this study are given in Table 1. The ranges of these variables were based on the previous experimental results [2,3]. Each parameter in the design was studied at five different levels (−2, −1, 0, 1, 2). All variables were taken at a central coded value considered as zero. An experimental design with more than two levels of each variable was required for exploring the region of the response surface in the vicinity of the optimum [16]. The experimental results of the CCD were fitted with a second-order polynomial equation by a multiple regression technique as follows:

$$\begin{aligned} Y = {} & b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 \\ & + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 \\ & + b_{34}X_3X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2 \end{aligned} \quad (1)$$

where Y is a response variable of decolorization efficiency. The b_i are regression coefficients for linear effects; b_{ik} the regression coefficients for quadratic effects; X_i are coded experimental levels of the variables. The statistical software STATISTICA (Stat-Soft Inc., Tulsa, OK, USA) was used to fit the experimental data to the second-order polynomial equation. The quality of fitting the second-order equation was expressed by the coefficient of determination R^2. The R^2-values provide a measure of how much variability in the observed response values can be explained by the experimental factors and their interactions. The R^2-value is always between 0 and 1. The closer the R^2-value is to 1, the better the model predicts the response [17]. The optimal values of the critical parameters were obtained by solving the regression equation using multi-stage Monte-Carlo optimization method and also by analyzing the response surface contour plots [18].

3. Results and discussion

When fine suspensions of TiO_2 or other suitable semiconductors are irradiated at wavelengths less than 380 nm, it causes electron excitation from the valence band to the conduction band and a vacancy or a hole is left in the valence bond. Such holes have the effect of a positive charge. This, in turn, generates the formation of “holes” on the surface of the semiconductor, which can react with oxygen, water, and hydroxide ion to form hydroxyl radical [19]. Furthermore, superoxide and perhydroxyl radicals are formed from the reaction of excited electrons with oxygen molecules. The highly reactive oxygen species so formed then react with the organic pollutants resulting in their extensive oxidation. Previously, several authors have studied the photocatalytic degradation of various dyes [2,20] and the mechanistic scheme leading to the degradation of the dye is shown below from Eqs. (2) to (9):

$$TiO_2 + h\nu \rightarrow h^+ + e^- \quad (2)$$

$$O_2 + e^- \rightarrow O_2^- \quad (3)$$

$$h^+ + H_2O \rightarrow OH_{ad}{}^\bullet + H^+_{aq} \quad (4)$$

$$h^+ + \text{dye} \rightarrow \text{products} \quad (5)$$

$$OH_{ad}{}^\bullet + \text{dye} \rightarrow \text{products} \quad (6)$$

$$e^- + O_2 \rightarrow O_{2(aq)}{}^- \quad (7)$$

$$e^- + O_2 + H_2O \rightarrow HO_{2(aq)} + OH^+_{(aq)} \quad (8)$$

$$O_2{}^+ + \text{dye} \rightarrow \text{products} \quad (9)$$

RSM is a sequential procedure with an initial objective to lead the experiments rapidly and efficiently along a path of improvement towards the general vicinity of the optimum. Table 1 shows the level and range of four parameters investigated, i.e., UV light intensity, the concentration of TiO_2, initial pH, and stirring speed. All parameters were taken at a central coded value considered as zero and studied at five different levels (−2, −1, 0, 1, 2). In this case, a 2^4 full-factorial design by eight axial points (or called start points) and six replicates at the centre points, resulting in a total number of 30 experiments, was employed to fit the second-order polynomial model. The statistical combinations of the critical parameters along with the maximum observed and predicted decolorization efficiencies are listed in Table 2. These predicted values are very close to the observed ones in all set of experiments. However, the highest decolorization efficiency (99.71%) is only slightly higher than the lowest

Table 2
Full factorial central composite design matrix for four test variables in coded and natural units along with the observed responses

Obs. no.	X_1	X_2	X_3	X_4	UV light Intensity (W/m^2)	Amount of TiO_2 (g/l)	Initial pH	Stirring speed	Decolorization efficiency observed (%)	Decolorization efficiency predicted (%)
1	−1	−1	−1	−1	15.27	2.46	2.74	5	99.53	99.42
2	−1	−1	−1	1	15.27	2.46	2.74	6.5	99.53	99.32
3	−1	−1	1	−1	15.27	2.46	4.22	5	96.12	95.83
4	−1	−1	1	1	15.27	2.46	4.22	6.5	95.87	95.97
5	−1	1	−1	−1	15.27	3.46	2.74	5	99.71	99.94
6	−1	1	−1	1	15.27	3.46	2.74	6.5	99.71	99.73
7	−1	1	1	−1	15.27	3.46	4.22	5	98.50	98.57
8	−1	1	1	1	15.27	3.46	4.22	6.5	98.78	98.61
9	1	−1	−1	−1	18.27	2.46	2.74	5	99.34	99.28
10	1	−1	−1	1	18.27	2.46	2.74	6.5	99.45	99.44
11	1	−1	1	−1	18.27	2.46	4.22	5	96.06	96.10
12	1	−1	1	1	18.27	2.46	4.22	6.5	96.96	96.51
13	1	1	−1	−1	18.27	3.46	2.74	5	99.64	99.60
14	1	1	−1	1	18.27	3.46	2.74	6.5	99.60	99.66
15	1	1	1	−1	18.27	3.46	4.22	5	98.66	98.65
16	1	1	1	1	18.27	3.46	4.22	6.5	98.78	98.95
17	−2	0	0	0	13.77	2.96	3.48	5.75	98.69	98.77
18	2	0	0	0	19.77	2.96	3.48	5.75	98.92	98.97
19	0	−2	0	0	16.77	1.96	3.48	5.75	96.06	96.46
20	0	2	0	0	16.77	3.96	3.48	5.75	99.68	99.42
21	0	0	−2	0	16.77	2.96	2	5.75	99.58	99.54
22	0	0	2	0	16.77	2.96	4.96	5.75	95.08	95.25
23	0	0	0	−2	16.77	2.96	3.48	4.25	99.61	99.60
24	0	0	0	2	16.77	2.96	3.48	7.25	99.65	99.80
25	0	0	0	0	16.77	2.96	3.48	5.75	99.27	99.14
26	0	0	0	0	16.77	2.96	3.48	5.75	99.08	99.14
27	0	0	0	0	16.77	2.96	3.48	5.75	99.15	99.14
28	0	0	0	0	16.77	2.96	3.48	5.75	98.88	99.14
29	0	0	0	0	16.77	2.96	3.48	5.75	99.22	99.14
30	0	0	0	0	16.77	2.96	3.48	5.75	99.29	99.14

Nos. 25–30 represents six replications of the center points; Obs. observation.

one (95.08%). Such insignificant difference may be within the reasonable level of experiment errors. It indicates that the ranges of the tested variables chosen in this work are appropriate for the central composite design. It further implies that the photocatalytic decolorization process is very effective for these tested variables within the ranges. Although it is not clear how applicable of these optimized parameters to industrial practice, the UV/TiO_2 photocatalytic decolorization process coupled with RSM presented in this study still opens a channel in designing large-scale wastewater treatment operation.

Table 3 showed the results of the quadratic response surface model fitting in the form of analysis of variance (ANOVA). ANOVA is required to test the significance and adequacy of the model. The mean squares are obtained by dividing the sum of squares of each of the two sources of variation, the model and the error variance, by the respective degrees of freedom (DF). The Fisher variation ratio, the F-value ($= S_r^2/S_e^2$), which is a statistically valid measure of how well the factors describe the variation in the data about its mean, can be calculated form ANOVA by dividing the mean square due to model variation by that due to error variance. The greater the F-value is from unity, the more certain it is that the factors explain adequately the variation in the data about its mean, and the estimated factor effects are real. The analysis of variance (ANOVA) of the quadratic regression model demonstrates that the model is highly significant, as is evident from the Fisher F-test ($F_{model} = 66.257$) and a

Table 3
Analysis of variance (ANOVA) for the selected quadraticmodel

Sources of variations	Sum of squares	d.f.	Mean square	F-value	Probability P (>F)
Model	54.60295	14	3.9		
Error	0.88292	15	0.0588617	66.257[a]	0.0001[b]
Corrected total	55.48587	29			

$R^2 = 0.98409$; adjusted $R^2 = 0.96924$; MS residual = 0.0588617.

[a] $F_{0.01(14,15)} = S_r^2/S_e^2 = 66.257 \gg F_{0.01(14,15)\text{tabular}} = 3.56$.

[b] $P_{model} > F = 0.0001$.

very low probability value ($P_{\text{model}} > F = 0.0001$). The probability P-value is relatively low, indicating the significance of the model. Moreover, the computed F-value ($F_{0.01(14,15)} = S_r^2/S_e^2 = 66.257$) is much greater than the tabular F-value ($F_{0.01(14,15)\text{tabular}} = 3.56$) at the 1% level, indicating that the treatment differences are highly significant. This fit of the model was further checked by the coefficient of determination R^2. The R^2-values provide a measure of how much variability in the observed response values can be explained by the experimental factors and their interactions. The R^2-value is always between 0 and 1. The closer the R^2-value is to 1, the stronger the model is and the better it predicts the response. When expressed as a percentage, R^2 is interpreted as the percent variability in the response explained by the statistical model. In this study, the value of the determination coefficient ($R^2 = 0.9841$), indicating that 98.41% of the variability in the response could be explained by the model. As well, the adjusted determination coefficient (adjusted $R^2 = 0.9692$) is also very high to advocate for a high significance of the model. These ensured a satisfactory adjustment of the polynomial model to the experimental data. The adjusted R^2 corrects the R^2-value for the sample size and the number of terms in the model. If there are many terms in the model and the sample size is not very large, the adjusted R^2 may be noticeably smaller than the R^2. Here, the adjusted R^2 was very close to the R^2-value.

The application of RSM offers, on the basis of parameter estimate, an empirical relationship between the decolorization efficiency and the test variables under consideration. The response variable and the test variables are related by the following quadratic expression:

$$Y = 99.148 + 0.74X_2 - 1.074X_3 - 0.302X_2^2 - 0.437X_3^2 + 0.138X_4^2 + 0.103X_1X_3 + 0.556X_2X_3 \tag{10}$$

where Y is the response, which is the decolorization efficiency expressed in % and X_1, X_2, X_3, and X_4 are the coded values of UV light intensity, TiO_2 concentration, initial pH, and stirring speed, respectively.

The student t distribution and the corresponding values, along with the parameter estimate, are given in Table 4. The P-values were used as a tool to check the significance of each of the coefficients, which, in turn, are necessary to understand the pattern of the mutual interactions between the test variables. The larger the magnitude of the t-value and smaller the P-value, the more significant is the corresponding coefficient [18]. The parameter estimate and the corresponding P-values (Table 4) suggest that, among the test variables, TiO_2 concentration and initial pH produce the largest effect on decolorization efficiency. Both linear and quadratic relations between TiO_2 concentration and decolorization efficiency and those between initial pH and decolorization efficiency are highly significant ($p < 0.0001$). These observations can be interpreted as a consequence of a proportional relationship between the variables and decolorization efficiency. The mutual between UV light intensity and initial pH ($p = 0.1117$) is significant comparing to those between each other two factors. These results suggest that these interactions of each other two parameters did not improve much in increasing decolorization efficiency.

Table 4
Regression results from the data of central composite design experiments

	Parameter estimate	Standard error coefficient	Computed t-value	P-value
Intercept	99.148	0.0990	1001.025	0.0001
X_1	0.050	0.0495	1.010	0.3287
X_2	0.740	0.0495	14.942	0.0001
X_3	−1.074	0.0495	−21.690	0.0001
X_4	0.050	0.0495	1.010	0.3287
$X_1 \times X_1$	−0.068	0.0463	−1.471	0.1621
$X_2 \times X_2$	−0.302	0.0463	−6.516	0.0001
$X_3 \times X_3$	−0.437	0.0463	−9.431	0.0001
$X_4 \times X_4$	0.138	0.0463	2.982	0.0093
$X_1 \times X_2$	−0.049	0.0607	−0.804	0.4341
$X_1 \times X_3$	0.103	0.0607	1.690	0.1117
$X_1 \times X_4$	0.066	0.0607	1.092	0.2919
$X_2 \times X_3$	0.556	0.0607	9.171	0.0001
$X_2 \times X_4$	−0.025	0.0607	−0.412	0.6860
$X_3 \times X_4$	0.061	0.0607	1.010	0.3286

Response surface plots provide a method to predict the decolorization efficiency for different values of the tested variables and the contours of the plots help in identification of the type of interactions between these variables [16]. Each contour curve represents an infinite number of combinations of two tested variables with the other two maintained at their respective zero level. A circular contour of response surfaces indicates that the interaction between the corresponding variables is negligible. In contrast, an elliptical or saddle nature of the contour plots indicates that the interaction between the corresponding variables is significant. The response surface contour plots for the effect of each pair of variables are shown in Figs. 3–5. Each contour curve represents an infinite number if combinations of two test variables with the other two maintained at their respective zero level. These plots demonstrated

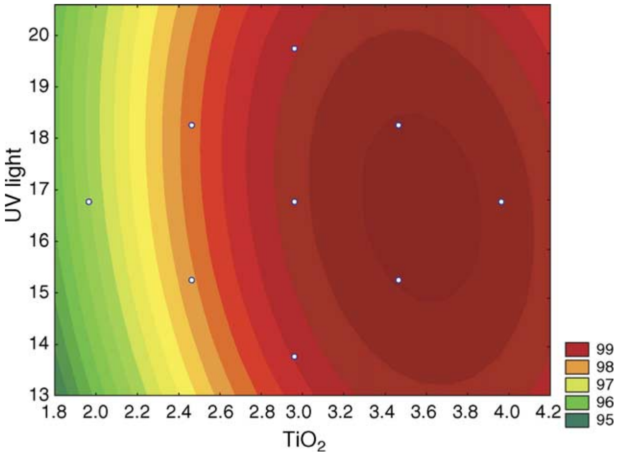

Fig. 3. Contour plot of the decolorization efficiency (%) by the interaction between the UV light intensity and TiO_2 concentration. Other variables were held at zero level.

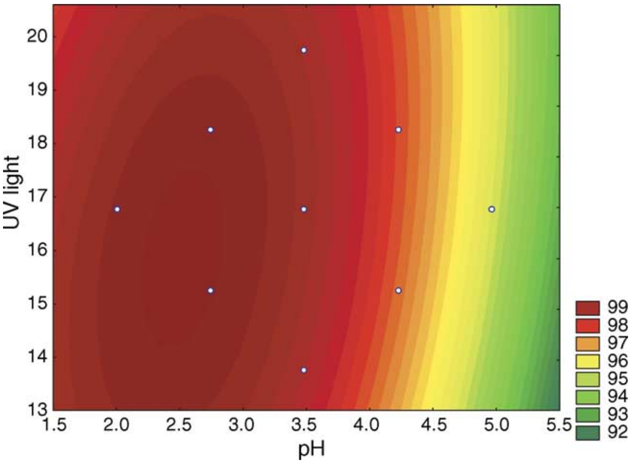

Fig. 4. Contour plot of the decolorization efficiency (%) by the interaction between the UV light intensity and initial pH value. Other variables were held at zero level.

that decolorization efficiency is not dependent of UV light intensity and stirring speed, whereas TiO_2 concentration and initial pH value are very significant affecting the decolorization efficiency.

Fig. 6 is a plot of normal probability of the experimental results. The normal probability plot of the "Studentised" residuals indicates that none of the individual residual exceeded the residual variance (twice the square root of the residual variance) and that an excellent adequacy of the regression model was utilized [21]. It further proves that the experimental values are in good agreement with the predicted values. Table 5 shows the maximal efficiency of decolorization (99.83%) by the critical value of each parameter, which was predicted from the data analysis with the statistical technique. After verifying by a further experimental test with the predicted values, the result indicates that the maximal decolorization efficiency was obtained when the values of each parameter were set as the critical values, which is in good agreement with the value predicted from the regression model. It implies that the strategy to optimize the decolorization conditions and to obtain the maximal decolorization efficiency by RSM for the photocatalytic degradation of the dye Reactive Red 239 in this study is successful.

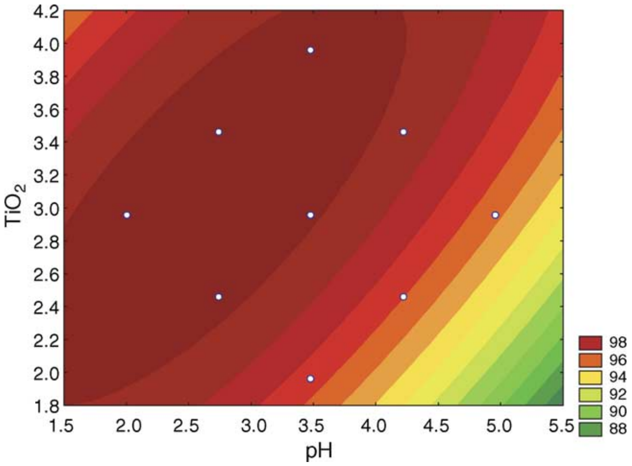

Fig. 5. Contour plot of the decolorization efficiency (%) by the interaction between TiO_2 concentration and initial pH value. Other variables were held at zero level.

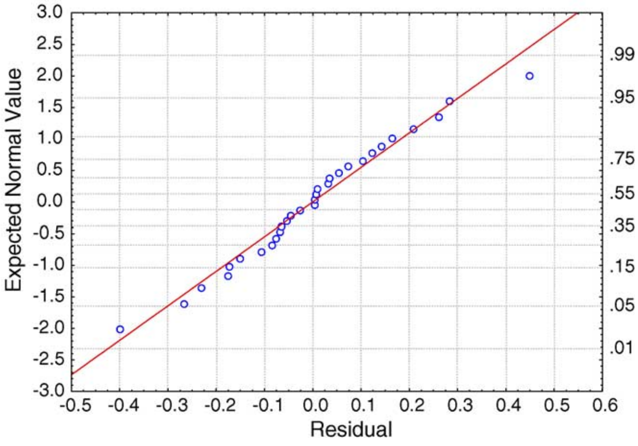

Fig. 6. The normal probability plot of the experimental results.

Table 5
The critical values of variables for the optimal decolorization efficiency

Parameters	Critical values
UV light intensity (W/m^2)	16.08
TiO_2 conc. (g/l)	3.06
Initial pH	2.64
Stirring speed (rpm)	880
Predicted efficiency (%)	99.83
Observed efficiency (%)	99.82

4. Conclusions

Statistical optimization method overcomes the limitations of classic empirical methods and has been proved to be a powerful tool for the optimization of the decolorization efficiency of the dye Reactive Red 239 in this study. The high correlation of the model showed that second-order polynomials could be used to optimize the photocatalytic process condition for maximizing the decolorization efficiency. The optimized parameters for decolorization determined in this study were set as follows: UV light intensity, 16.08 W/m^2; TiO_2 concentration, 3.06 g/l; initial pH value, 2.64; stirring speed, 880 rpm (the scale of 5.9). These values were further validated by actually carrying out the experiment at the optimized values of these parameters. The methodology as a whole has been proved to be adequate for the design and optimization of the photocatalytic decolorization process. Thus, a multi-factorial statistical approach has been testified to be a powerful tool in the development of any photocatalytic process due to its impact on the economy and practicability of the process.

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