GENERAL RESEARCH

Decomposition of Acid Dye by TiO$_2$ Thin Films Prepared by the Sol−Gel Method

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Textile plants exhaust a great deal of water and generate a great deal of wastewater with high color contents, high suspended solids, and dissolved organics. To meet increasingly stringent environmental regulations, many technologies are used to remove toxic nonbiodegradable organic matters from the wastewaters. In this study, TiO$_2$ thin films coated on glass bottles for use as photocatalytic reactors to decompose dye in aqueous solutions were prepared by the sol−gel method, followed by coating, drying, and calcination. An experimental design methodology was adopted to screen the most important factors and to search for the optimal preparation conditions. According to the Plackett−Burman design, the alcohol-to-titanium ratio, the acid-to-titanium ratio, and the sol−gel reaction time were found to be the most important variables that might affect the final TiO$_2$ film performance in terms of dye decomposition efficiency. The maximum dye decomposition efficiency was found, by the simplex method, to be 49.2% under 4-W UV illumination for 6 h.

1. Introduction

The textile industry, one of the major industries in Taiwan, exhausts a great deal of water and generates a great deal of wastewater with high color contents, high suspended solids, and dissolved organics. Most dye wastewater treatment processes consist of pretreatment for flow equalization, primary treatment for suspended solids removal and pH neutralization, and secondary treatment for biodegradable organics removal. To meet the increasingly stringent environmental regulations, tertiary treatments such as activated carbon adsorption, chemical oxidation, wet air oxidation, chemical coagulation, activated sludge treatment, and photocatalysis are used to remove the colors and nonbiodegradable organic matters from the wastewaters. Among tertiary treatment technologies, photocatalysis using TiO$_2$ seems quite simple and cost-effective for removing the colors from dye-containing wastewaters. The degradation of organic pollutants using TiO$_2$ suspensions along with UV illumination has proven to be a simple and effective method.[1−4] However, the solid−liquid separation needed for the recovery of the TiO$_2$ particles is sometimes difficult, especially when very fine TiO$_2$ particles are used. Immobilization of the fine TiO$_2$ particles on some suitable substrates is therefore highly desirable to avoid solid−liquid separation problems.

Another approach is to directly form TiO$_2$ thin films on substrates to act as the photocatalyst for pollutant decomposition. Such TiO$_2$ thin films can be prepared by several different methods, including sol−gel processing, physical vapor deposition, chemical vapor deposition, anodic oxidation, sputtering, thermal decomposition, and arc-plasma spraying.[5] The sol−gel method is based on liquid-phase chemical reactions; it uses alkoxides, organic salts, inorganic salts, metal oxides, and other salts to collocate the products that reach the required density and purity. The sol−gel method provides excellent chemical homogeneity and the possibility of deriving unique metastable structures at low reaction temperatures. When the sol−gel method is used, the reactant concentration, temperature, and type of solvent will affect the quality of the final product.

Design of experiments (DOE) has become one of the most popular statistical techniques of the 1990s. Today, the most commonly used DOE methods are full factorial design, fractional factorial design, Taguchi methods, the response surface methodology, Plackett−Burman design, and the simplex method.[6−11] Plackett−Burman statistical experimental design is very useful for screening the most important factors from a large number of candidates. This design does not consider the effects of interactions among the variables and is used to screen the important variables affecting the result. To detect any possible interactions, one must use factorial design. Full factorial designs are useful when the number of factors is relatively limited. For a typical factorial design, it is necessary to determine the number of factors of interest and the number of levels at which each factor is to be studied. The factorial design provides information about the importance of interactions among the effects. This means that, sometimes, the level at which some factors must be set is influenced by their interactions with other factors, so that one can ensure a better expected experimental response. A simplex is defined as the simplest possible *n*-dimensional figure. In one dimension, this is a line; in two dimensions, a triangle; in three dimensions, a tetrahedron; and in more dimensions, a hypertriangle. In using the simplex method, one needs to define a "starting" simplex. Then, one compares the response of each vertex of this simplex. When the worst response is found, this point is linked to the center of the appropriate polygon by a line, a new vertex is sought that is better than the worst response along this line. Then, the original vertex giving the worst response is replaced by this new vertex, and a new simplex is formed. The new vertex is judged by reflection, contraction, and expansion.[10,11,13,14] This

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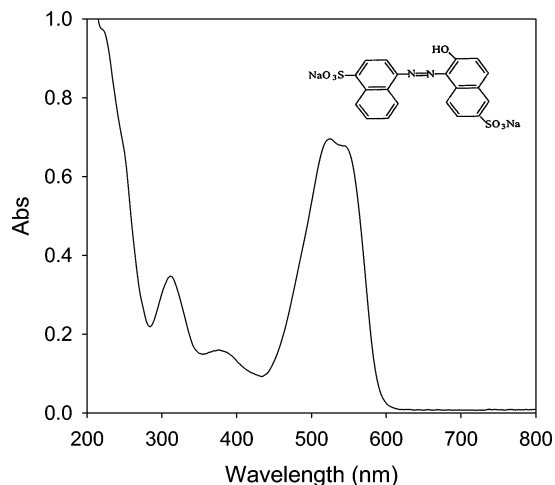
Figure 1. Chemical structure and UV absorbance spectrum of 40 mg/L peach red acid dye solution.

procedure is repeated until the responses of all vertexes are very close to each other, at which point the iteration process comes to an end.

The objective of this study was to use a sol−gel process to prepare a stable gel solution of TiO$_2$ precursor, and then to coat this precursor onto glass bottles, dry the bottles, and finally calcine the coated bottles to obtain TiO$_2$ thin films with photocatalytic activity. Because the preparation of TiO$_2$ thin films on the glass wall involves many steps and many factors that might affect the final TiO$_2$ film performance, the DOE methodology was adopted to identify the optimal preparation conditions. First, the Plackett−Burman design was used to screen several important factors that might influence the final TiO$_2$ film performance. Then, a full factorial design was used to investigate the main effects of the important factors and possible interactions. Finally, the simplex method was used to search for the optimal conditions for preparing the TiO$_2$ films. An acid dye was selected as the model compound for evaluating the relative performances of the prepared TiO$_2$ films under the same reaction conditions.

2. Experimental Section

2.1. Materials. Among many commercially available chemicals, reagent-grade titanium tetraisopropoxide, Ti(OC$_3$H$_7$)$_4$ (assay 95.0%, Wako Pure Chemicals, Osaka, Japan), was chosen as the precursor for the preparation of titanium dioxide thin films by the sol−gel method. Reagent-grade acetic acid (assay 99.0%) and 1-butanol (assay 98.0%) were also purchased from Wako Pure Chemicals for use in the esterification reaction. To compare the performance of the TiO$_2$ films prepared under varying operating conditions, the acid dye peach red, with main ingredient of triphenyalmethane (Taipei First Chemical Company, Taipei, Taiwan), was selected as the model compound for preparing the synthetic wastewater used for the tests in this study. The chemical structure and UV absorbance spectrum of the dye are shown in Figure 1. As shown by Figure 1, the maximum absorbance wavelength (MAWL) of the dye solution is 523 nm. The UV absorbance spectra of dye solutions with different pH values were scanned, and very similar results were obtained. Furthermore, the solution pH before and after photocatalytic reaction remained almost the same, so we did not control the solution pH during the photocatalytic reaction.

2.2. Apparatus. The experimental apparatus is schematically shown in Figure 2. A magnetic hot plate with a stirrer (Mirak S72725, Barnstead Thermolyne, Boston, MA) was used to
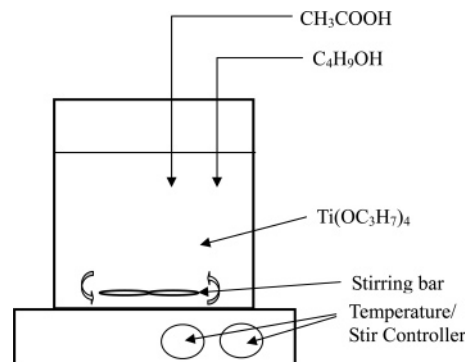

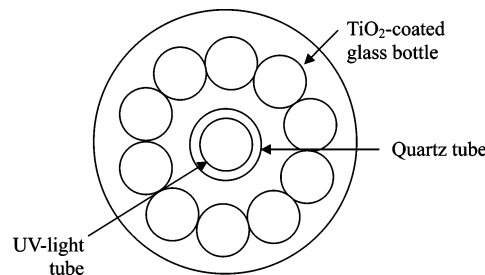**Figure 2.** Experimental apparatus of sol−gel process.

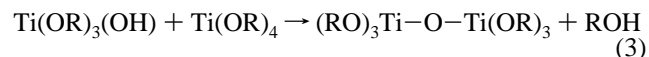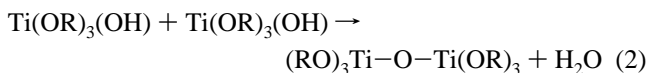**Figure 3.** Irradiation apparatus of photocatalytic reaction.

control the temperature and agitation speed of the sol−gel process. After the photoreactors had been prepared, dye decomposition tests were carried out in an irradiation apparatus as schematically shown in Figure 3. One set of germicidal lamps (model G4T5, 4 W, Sankyo, Tokyo, Japan) with a maximum light intensity at 365 nm was used as the light source. After the sol−gel process, drying and calcination to form the final TiO$_2$ thin films were conducted in a drying oven (RHD-452, Risen, Taiwan). After the drying and calcination process, an ultrasonic cleaner (LC 30H, Elma, Pforzheim, Germany) was used to remove any possible excess reactant or TiO$_2$ powder from the thin films. Finally, a UV/vis spectrophotometer (Jasco V-560, Tokyo, Japan) was used to measure the acid dye absorbance at its MAWL for determining the acid dye concentration before and after the photocatalytic reaction.

2.3. Procedures. In the sol−gel process, titanium dioxide thin film precursor was formed by hydrolysis and condensation described by the following reactions, where R represents C$_3$H$_7$:

Hydrolysis

$$Ti(OR)_4 + H_2O \rightarrow Ti(OR)_3(OH) + ROH \qquad (1)$$

Condensation

$$Ti(OR)_3(OH) + Ti(OR)_3(OH) \rightarrow$$
$$(RO)_3Ti-O-Ti(OR)_3 + H_2O \quad (2)$$

$$Ti(OR)_3(OH) + Ti(OR)_4 \rightarrow (RO)_3Ti-O-Ti(OR)_3 + ROH \qquad (3)$$

In the traditional sol−gel method, water is directly added to titanium alkoxide to cause the hydrolysis reaction. Because titanium tetraisopropoxide hydrolyzes rapidly, in this study, we used water that was slowly generated by the esterification reaction of 1-butanol and acetic acid. Because the acetic acid used in this study exhibits chelating agent characteristics, Ti(OC$_3$H$_7$)$_4$ forms the new precursor Ti(OC$_3$H$_7$)$_{4-x}$(OAc)$_x$ upon addition of acetic acid. This modified precursor can decrease the rate of the hydrolysis reaction and thus prevent sedimenta-

tion, because the acetate functional group is more difficult to hydrolyze than the OH functional group.

Equation 4 is the esterification reaction of 1-butanol and acetic acid, and eq 5 is the reaction of $Ti(OC_3H_7)_4$ with the added acetic acid:

$$C_4H_9OH + AcOH \rightarrow H_2O + AcOC_4H_9 \qquad (4)$$

$$Ti(OC_3H_7)_4 + xAcOH \rightarrow Ti(OC_3H_7)_{4-x}(OAc)_x + xC_4H_9OH \qquad (5)$$

With the water slowly generated by the esterification reaction of C_4H_9OH and CH_3COOH, the hydrolysis reaction occurs. Because of the slow release of water, coarse TiO_2 particles will not form and sediment right away. On the contrary, homogeneous hydrolysis will occur, and a suspension of very tiny TiO_2 particles will form.

In accordance with the above considerations, the procedure used to prepare the TiO_2 thin film reactors was as follows:

(1) Place, in order, $Ti(C_3H_7O)_4$, C_4H_9OH, and CH_3COOH in the sol−gel reactor at the desired mole ratio.

(2) Agitate the clear solution for the desired sol−gel reaction time.

(3) Pour the sol−gel solution into five 25-mL glass bottles for the desired coating time to allow the inside surfaces of the bottles to be coated with the sol−gel solution.

(4) Dry the five coated glass bottles by the desired drying method.

(5) Transfer the five coated glass bottles to a furnace and calcine them at the desired temperature (heating rate = 10 °C/min) for the desired time.

(6) Wash the glass bottles in an ultrasonic chamber to ensure that the TiO_2 films are not stripped off.

(7) Dry the glass bottles in air at room temperature.

The procedure to carry out the dye photocatalytic decomposition is as follows:

(1) Pour 25 mL of 10 ppm dye solution into each glass bottle and put the glass bottles in the photocatalytic reactor chamber as shown in Figure 3.

(2) Start illumination with a 4-W 365-nm UV light for 6 h.

(3) After 6 h of irradiation, analyze the dye solution samples with a UV/vis spectrophotometer at $\lambda_{max} = 523$ nm to determine the residual dye concentrations with a calibration curve based on the Beer−Lambert law.

(4) Calculate the dye decomposition fraction using the equation

$$\eta = \frac{A_0 - A_1}{A_0} \times 100\% \qquad (6)$$

(5) Pour the dye solutions from the glass bottles, wash the bottles, and conduct replicate test runs.

For each set of sol−gel preparation conditions, we used five replicated bottles, with each bottle tested twice as the photo-reactor. For each dye decomposition test run, the best and worst data from the five bottles were not used; only the three middle data were used to calculate the average percentage dye decomposition for that test run. For the same bottle, the average decomposition percentage of the two test runs was used as the response.

2.4. Experimental Design. The first stage of the experimental design was to use the Plackett−Burman design to screen the most significant factors from among the many factors that might influence the performance of the final TiO_2 films prepared by the sol−gel process, followed by coating, drying, and calcina-

Table 1. Operating Conditions of the Plackett−Burman Design

factor	low level (−1)	high level (+1)
mole ratio of alcohol to Ti, X_1	1	4
mole ratio of acid to Ti, X_2	1	4
reaction time, X_3	6 hr	24 hr
coating time, X_4	2 min	5 min
drying method, X_5	air/room temp/6 h	oven/150 °C/1 h
calcination temperature, X_6	400 °C	600 °C
calcination time, X_7	1 h	2 h

Table 2. Orthogonal Array of the Plackett−Burman Design and Experimental Results

no.	X_1	X_2	X_3	X_4	X_5	X_6	X_7	Y	σ^a
1	1	1	1	1	1	1	1	29.14	2.36
2	1	1	−1	1	−1	−1	−1	32.43	0.45
3	1	−1	1	−1	1	−1	−1	11.75	0.75
4	1	−1	−1	−1	−1	1	1	26.72	0.13
5	−1	1	1	−1	−1	1	−1	14.84	0.24
6	−1	1	−1	−1	1	−1	1	22.25	3.76
7	−1	−1	1	1	−1	−1	1	4.90	0.15
8	−1	−1	−1	1	1	1	−1	9.40	0.87

^{a} Standard deviation.

tion. In this study, we selected two levels of each factor to run the tests. The coded high and low levels are set as +1 and −1, respectively, as listed in Table 1. In this series of experiments, seven factors were considered to affect the final TiO_2 film performance. The orthogonal array of the eight test runs in the Plackett−Burman design is shown in Table 2. It is important to note that the order of the runs of the experiments was randomized to get better statistical results. All of the experimental procedures were the same except for the factors varied as shown in Table 2.

After the Plackett−Burman design, we screened three notable factors. Therefore, we performed a series of full factorial experiments consisting of eight test runs. All of the responses, i.e., the dye decomposition fractions, were analyzed to determine the main effects of each factor and the interactions between factors.

After the two series of experimental designs, we identified the factors that had significant effects on the experimental response. The final step we took was to find the optimal operation conditions for obtaining the TiO_2 films leading to the highest dye decomposition fraction by the simplex method.

3. Results and Discussion

3.1. Plackett−Burman Design. To screen the major factors that might affect the performance of the TiO_2 film, the Plackett−Burman design with the following empirical model was used:[10,11]

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4 + a_5X_5 + a_6X_6 + a_7X_7 \qquad (7)$$

where Y is the response, the dye decomposition fraction in this study; a_0 is the grand average of the response; and a_i is the main effect of factor X_i, $i = 1, 2, ..., 7$.

The eight coefficients in eq 7 can be readily calculated by solving eight simultaneous algebraic equations. All of the effects close to the straight line on the normal probability plot are negligible, whereas the significant effects are far from the line.[7] According to the normal probability plot of the main effects, as shown in Figure 4a, the significant effects in this study are the alcohol/Ti ratio, the acid/Ti ratio, and the sol−gel reaction time; the coating time, drying method, calcination temperature, and calcination duration seem to have negligible effects on the
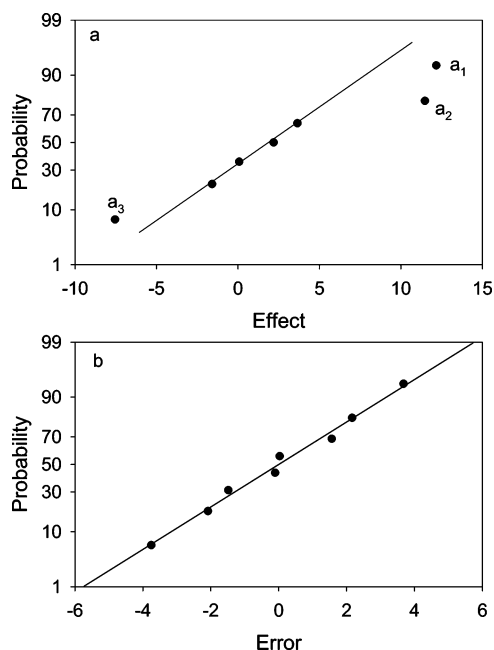
Figure 4. Normal probability plot of the effects and residuals in the Plackett−Burman design.

performance of the final TiO$_2$ film. Therefore, the final empirical model became

$$Y = 18.93 + 6.08X_1 + 5.73X_2 - 3.77X_3 \qquad (8)$$

The difference between the experimental response shown in Table 2 and the predicted response calculated by eq 8 is called the error or residual. Figure 4b shows the normal probability plot of the residuals. As is shown by the good linear correlation with $R^2 = 0.9894$, the selected model, eq 8, fits the experimental response quite well.

3.2. Full Factorial Design. Although the Plackett−Burman design identified the most significant factors affecting the performance of the prepared TiO$_2$ films, no interactions between the factors were considered. To investigate any possible binary and tertiary interactions, a series of 2^3 full factorial designs were carried out. Table 3 lists the experimental conditions and responses of the 2^3 full factorial designs. The empirical model for the 2^3 full factorial designs is

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{12}X_1X_2 + a_{13}X_1X_3 + \\ a_{23}X_2X_3 + a_{123}X_1X_2X_3 \quad (9)$$

Using the method described in Box et al.[7] or the software of Design Expert (Stat-Ease, Minneapolis, MN) to analyze the results, the only negligible coefficient in eq 9 was found to be a_{13}. The final empirical model therefore became

$$Y = 17.50 + 2.70X_1 + 5.88X_2 - 6.45X_3 - 3.20X_1X_2 - \\ 4.96X_2X_3 + 3.04X_1X_2X_3 \quad (10)$$

The analysis of variance summarized in Table 4 suggests that only the 1−3 interaction can be neglected; all three main effects, the 1−2 and 2−3 binary interactions, and even the ternary interaction must be taken into account. In Table 4, the model F value of 103.60 implies the model is significant. There is only a 0.01% chance that a "model F value" this large could occur due to noise. The values of "prob > F" of less than 0.05 indicate the model terms that are significant. The values greater than 0.1 indicate the model terms that are not significant. In this

Table 3. Results of the Full Factorial Design[a,b]

no.	X_1	X_2	X_3	Y	σ
1	−1	−1	−1	3.93	2.28
2	1	−1	−1	22.3	0.17
3	−1	1	−1	38.1	0.62
4	1	1	−1	31.5	0.49
5	−1	−1	1	7.50	0.06
6	1	−1	1	12.7	2.69
7	−1	1	1	9.67	2.99
8	1	1	1	14.3	0.70

[a] Other experimental conditions are as follows: $X_4 = -1$, $X_5 = 1$, $X_6 = -1$, $X_7 = -1$. [b] Runs in bold were used as the starting points for the simplex method.
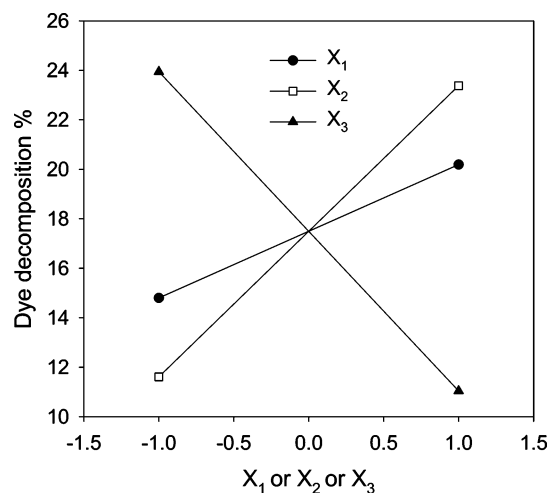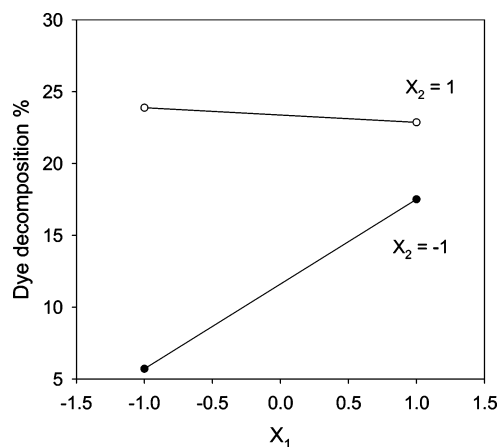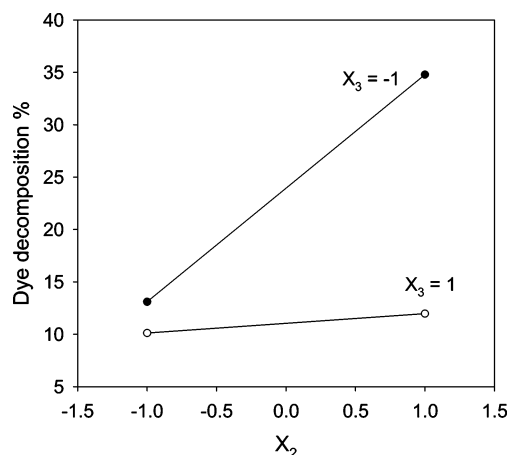

Figure 5. Main effects of X_1, X_2, and X_3.

Table 4. ANOVA for Selected Factorial Design

source	sum of squares	degrees of freedom	mean square	F value	prob > F
model	2042.40	7	291.77	103.60	<0.0001
X_1	116.26	1	116.26	41.28	0.0002
X_2	553.54	1	553.54	196.54	<0.0001
X_3	665.77	1	665.77	236.39	<0.0001
X_1X_2	164.03	1	164.03	58.24	<0.0001
X_1X_3	0.90	1	0.90	0.32	0.5878
X_2X_3	393.72	1	393.72	139.80	<0.0001
$X_1X_2X_3$	148.17	1	148.17	52.61	<0.0001
pure error	22.53	8	2.82		
cor total	2064.93	15			

case, X_1, X_2, X_3, X_1X_2, X_2X_3, and $X_1X_2X_3$ are the significant model terms. The main effects of X_1, X_2, and X_3 are plotted in Figure 5. As shown in Figure 5, the main effects of X_1 and X_2 are positive, whereas the main effect of X_3 is negative. If we consider only these main effects, we might want to keep X_1 and X_2 at their high levels and keep X_3 at its low level to maximize the dye decomposition fraction. However, it is always necessary to examine any possible interactions that are significant. The main effects do not have much meaning if any significant interactions are involved in the process. If we examine the chemistry involved in the sol−gel process, a higher alcohol-to-titanium ratio (X_1) and a higher acid-to-titanium ratio (X_2) certainly facilitate the formation of the TiO$_2$ precursor; but does a lower reaction time (X_3) really help the formation of the TiO$_2$ precursor? From the viewpoint of chemical reaction, a sufficiently long reaction time is probably needed to form the TiO$_2$ precursor. Therefore, we cannot use the main effects alone to interpret the experimental results.

In addition to the main effects, we have to analyze the interactions between X_1 and X_2 and between X_2 and X_3 that are plotted in Figures 6 and 7, respectively. Figure 6 shows that

Figure 6. Interaction between X_1 and X_2.

Figure 7. Interaction between X_2 and X_3.

Table 5. Experimental Design Points and Responses of the Simplex Method

no.	X_1	X_2	X_3	Y	σ	remark
1	−1	1	−1	38.1	0.62	
2	1	1	−1	31.5	0.49	
3	1	−1	−1	22.3	0.17	
4	1	1	1	14.3	0.70	worst
5	−0.33	−0.33	−1.33	30.3	2.63	
6	−1.22	2.11	−1.22	33.2	3.49	
7	−0.48	3.07	−0.81	21.0	0.49	
8	−0.44	2.22	−0.94	36.2	1.14	
9	−2.78	2.56	−1.11	−	−	out of exptl range
10	−1.33	2.56	−1.11	31.3	3.54	
11	−1.11	2.17	−1.08	36.9	4.39	
12	−0.48	1.48	−0.80	25.8	1.70	
13	−1.04	1.95	−1.12	47.0	0.69	
14	−1.65	1.19	−1.19	49.2	0.11	best
15	−1.35	0.60	−1.12	29.0	2.36	
16	−1.29	0.99	−1.11	31.3	4.46	
17	−1.17	1.77	−1.09	22.5	1.65	

the dye decomposition fraction significantly increases with the alcohol-to-titanium ratio (X_1) when the acid-to-titanium ratio (X_2) is at the low level, but it slightly decreases with X_1 when X_2 is at the high level. Therefore, a higher X_1 value does not guarantee a better result; the X_2 level should also be taken into account. Figure 7 shows that the dye decomposition fraction increases with the acid-to-titanium ratio (X_2) regardless of the reaction time; it also shows that a lower reaction time ($X_3 = -1$) leads to TiO$_2$ films that give higher dye decomposition fractions.

3.3. Simplex Method. The results of the above full factorial design reveal that the two- and three-factor interactions are significant and must be taken into account to obtain TiO$_2$ films with desirable performance. The simplex method[10,11,13,14] was therefore used to search for the optimal preparation conditions of the TiO$_2$ films. We chose the four bold runs (runs 2−4 and 8) in Table 3 as the starting points. The new design point in the simplex method was calculated as the reflected point of the worst-response point (run 8 in Table 3): $X_1 = -0.33$, $X_2 = -0.33$, $X_3 = -3$. The reaction time corresponding to $X_3 = -3$ was −12 h, which was unrealistic. We therefore used $X_3 = -1.33$ for the new design point, and the result is shown in Table 5. As is shown in Table 5, the response of the new design point is 30.3%; this means that we are moving in the right direction to optimize the response.

We then used runs 1−3 and 5 to start a new design, and the response of this new design point (run 6) was 33.2%, which was better than those of runs 2, 3, and 5. Again, we calculated the reflected point of run 5 to get the new design point (run 7), but this time, the response of run 7 was 21.0%. This suggested

that we had moved too far; a modified new design point (run 8) was then calculated.[13] With this modification, the response of run 8 became 36.2%, which was greater than those of runs 2, 5, and 6.

In the fourth design, the calculated X_1 value for the new design point (run 9) was −2.78, corresponding to a negative alcohol-to-titanium ratio. A new design point (run 10) was thus selected, and the resultant response was 31.3%, which was worse than those of runs 2, 6, and 8. Therefore, a modified design point (run 11) was used, and the resultant response became 36.9%, which was better than those of runs 2, 6, and 8.

In the fifth design, the response of the new design point (run 12) was 25.8%, which was even lower than the worst (run 6) response of 33.2%. A modified design point (run 13) was therefore used to obtain an improved response of 47.0%.

In the sixth design, the response of the new design point (run 14) was 49.2%, a further improved result. In the seventh design, the response of the new design point (run 15) was 29.0%, which was even lower than the worst (run 11) response of 36.9%. The other two modified design points (runs 16 and 17) did not give any better results. The iteration of the simplex method was thus ended, and the optimal response 49.2% occurred at $X_1 = -1.65$, $X_2 = 1.19$, and $X_3 = -1.19$.

Because the UV light intensity used in this study might not be powerful enough and the reaction time was 6 h only, the optimal dye decomposition fraction was only 49%. In the future, TiO$_2$ thin films should be prepared under the optimal conditions; a longer photocatalysis reaction time and a more powerful UV light source should be used to improve the dye decomposition fraction.

4. Conclusions

TiO$_2$ thin films coated on glass bottles for use as photocatalytic reactors to decompose dye in aqueous solutions were prepared by the sol−gel method, followed by coating, drying, and calcination. Seven preparation parameters, namely, the alcohol-to-titanium ratio, acid-to-titanium ratio, sol−gel reaction time, coating time, method of drying, calcination temperature, and calcination time, were varied in accordance with the Plackett−Burman design matrix first to screen the most significant variables. According to the Plackett−Burman design, the alcohol-to-titanium ratio, acid-to-titanium ratio, and sol−gel reaction time were found to be the most significant variables that might affect the final TiO$_2$ film performance in terms of dye decomposition fraction.

A series of 2^3 full factorial designs were performed, and the results showed that only the interaction between the alcohol-to-titanium ratio and the sol−gel reaction time could be neglected; all of the main effects and other interactions had to be taken into account. The simplex method was therefore adopted to carry out another series of designs leading to an optimal dye decomposition fraction of 49.2% after 6 h of reaction time. The optimal preparation conditions for TiO_2 thin films obtained in this study are as follows: mole ratio of Ti/alcohol/acid = 1: 0.02: 4.29, reaction time = 4.3 h.

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