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Relationship Between Degradation Half-life of Methylene Blue and Preparation Conditions of Nano-TiO_2 Based on Response Surface Methodology

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ABSTRACT

TiO_2 powders were prepared by modified sol-gel technique. Methylene Blue (MB), as simulated pollutants, was decomposed by UV and TiO_2. The degradation of MB followed pseudo first order kinetics and half life ($t_{1/2}$) of MB was used to evaluate the degradation speed. Response surface methodology was applied to research the relationship between the half life of MB and preparation conditions. The results showed that half life was increased with the rise of acetyl acetone/tetrabutyltitanate molar ratio and n-hexanol/TX-100 molar ratio, and the rise of water/Triton X-100 molar ratio almost had no effect on half life of MB. The optimized experimental condition was water/Triton X-100 molar ratio of 5.32, n-hexanol/TX-100 molar ratio of 7.97 and acetyl acetone/tetrabutyltitanate molar ratio of 0.44 with half life of 5.34 min of predicted value, and the experimented value of half life was 5.52min, only 3.4% error.

INTRODUCTION

Titanium dioxide (TiO_2) (Lutifi 2015) photo-catalyst is a "star molecules" in recent decades and attracts more attention of scientists around the word because of its great degradation performance without any selectivity for organic substance in environment. In order to improve the photocatalytic activity of TiO_2, nano level TiO_2 with a big specific surface area was prepared to express the great quantum effects and increase the reaction surface. There are many methods to prepare nano level TiO_2, such as hydrothermal synthesis, vapour deposition, physical crushing, vacuum condensation, precipitation, sol-gel (Leyva-Porras 2015), micro-emulsion, and so on. The sol-gel method is used commonly to prepare nano level particles because it is a great advantage to slow up the hydrolysis rate of titanium salt and obtains nano level powders. However, some researchers find that sometimes it is difficult for sol-gel technology to prepare the nano-level particles (Maria 2015). The reason is that sol-gel technology (Bridget 2015) is difficult to control agglomeration of nano level particles and form a big secondary particle size which decrease the photocatalytic activity. The micro-emulsion can provide a surfactant stabilized micro cavities to restrict successfully agglomeration phenomenon and acquire superfine particle. It can be named "cage-like" effect.

Response surface methodology (RSM) (Hyungseok 2015) is reasonable experimental design method to instruct how to do the experiment and obtain the acceptable data. A function relationship between factors and response is fitted by multivariate quadratic regression equation and through the regression equation, the optimal process parameters is obtained. The aim of RSM is to solve the multivariate problem using statistical method (Mohammed 2010). So, RSM is the combination method of mathematical, statistical analysis and experimental design. The mathematical model can accurately describe the relationship between the factor and the response values, which also can choose different operating parameters and predict the experimental results according to the mathematical model. Thus, RSM has a good application in the design of experiments, data analysis and experimental prediction.

In this study, we employed microemulsion mediated sol-gel technique to prepare TiO_2 photocatalyst and control the particle size. The effect of the main operation parameters of the process, such as water/surfactant Triton X-100 (TX-100) molar ratio (w), n-hexanol/TX-100 molar ratio (m) and acetyl acetone/tetrabutyltitanate molar ratio (p), on the half-life ($t_{1/2}$) of the photocatalytic methylene blue degradation activity. The RSM was employed to optimize experimental conditions and establish the relationship between w, m, p and $t_{1/2}$ in TiO_2.

MATERIALS AND METHODS

TiO_2 preparation: At first, a reverse microemulsion was prepared by ultrasonic dissolving Triton X-100 and n-hexanol in n-hexane and by adding a required amount of water with pH value of 9 regulated by methylamine saturated solution (25-30% wt). The water-clear appearance of the mixture indicated the formation of the microemulsion. The water/Triton X-100 molar ratio (w) and n-hexanol/Triton X-100 molar ratio (m) were varied in the range of 3-7 and 4-8, respectively. The Triton X-100/n-hexane molar ratio was set at 0.35. Then, by adding an n-TBT solution of n-hexane into the reverse microemulsion with the water/n-TBT molar ratio of 4, the hydrolysis of n-TBT was carried out at 35°C in a sealed 3-way flask (250 mL) for 90 min, followed by the formation of the sols. In the n-TBT solution, acetyl acetone was employed to regulate the reactivity of n-TBT with an acetyl acetone/n-TBT molar ratio (p) ranged from 0.35 to 0.45. The obtained sols were transferred to rotated solvent-thermal autoclaves and continued to react at 120°C for 90 min. During the solvent-thermal process, the sol was transformed to gels and TiO_2 particles precipitated formed. The TiO_2 particles precipitated were separated in a centrifuge at 12,000 rpm for 2 min and were then washed with acetone to remove organics and surfactants from the particles. The particles were dried at 105°C for 12h and then calcined at 450°C for 4h.

TiO_2 characterization and half time of methylene blue: The crystal phases of TiO_2 nanoparticle was analysed by X-ray diffraction (XRD) on PaNalytical X-ray diffractometer (X'Pert Pro MPD, Dutch). The concentration of methylene blue (λ_{max}=665 nm) in treated wastewater samples was analysed by a UV-2102PC UV-Vis spectrophotometer (UNICO, China). According the a lot of references and our previous research, UV/TiO_2 process was followed first order kinetic, $\ln(C_0/C) = kt$. Here, The k and t are apparent rate constant and reaction time, respectively. The C_0 and C are the initial concentration of methylene blue (MB) and t time, respectively. Half-time of MB is ln2/k which is mines the time at 50% MB degradation rate.

Experimental design of response surface methodology: A standard RSM design (Muhammad 2011) called a Box-Behnken Design (BBD) was applied to develop the experimental design for nano-TiO_2 preparation. There are three main operating conditions that affect half-life($t_{1/2}$), which are water/surfactant Triton X-100 (TX-100) molar ratio (w), n-hexanol/TX-100 molar ratio (m) and acetyl acetone/n-TBT molar ratio (p). Table 1 lists the levels are range of the three independent variables. RSM analysed the experimental data obtained from above procedure by the following second-order polynomial as shown by Eq. 1 (Almeida 2011):

$$Y = \beta_0 + \sum_{i=1}^{n}\beta_i x_i + \sum_{i=1}^{n}\beta_{ii} x_i^{\ 2} + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\beta_{ij} x_i x_j \qquad ...(1)$$

Y is the predicted response ($t_{1/2}$). The x_i and x_j are independent variables. The β_0 is the regression intercept and β_i, β_{ii}, β_{ij} are the regression coefficient. The Design Expert software version 8.06 was used to perform the regression analysis and analysis of variance (ANOVA). Using regression analysis to get the fitted quadratic polynomial equation, and then use the equation to develop the response surfaces and contour plots.

RESULTS AND DISCUSSION

XRD of TiO_2: TiO_2, as a photocatalytic material, has two crystalline structures, anatase and rutile. The surface adsorptive capability of the rutile to organic pollutants is lower than the anatase and the recombination between electron and hole is faster. Therefore, the anatase has a higher photocatalytic activity than the rutile. The results of the crystal structures of TiO_2 samples calcined at 450°C analysed by XRD are shown in Fig. 1. The XRD pattern of the sample calcined at 450°C shows diffraction peaks at 25.32°, 37.82°, 48.05°, 53.94°, 55.14°, 62.72° and 75.06°, which are identified as crystalline anatase.

Evaluation of experimental results: Central composite Box-Behnken experimental design was chosen for finding out the relationship between the response function and variables. Values of the independent variables (w, m, p) as well

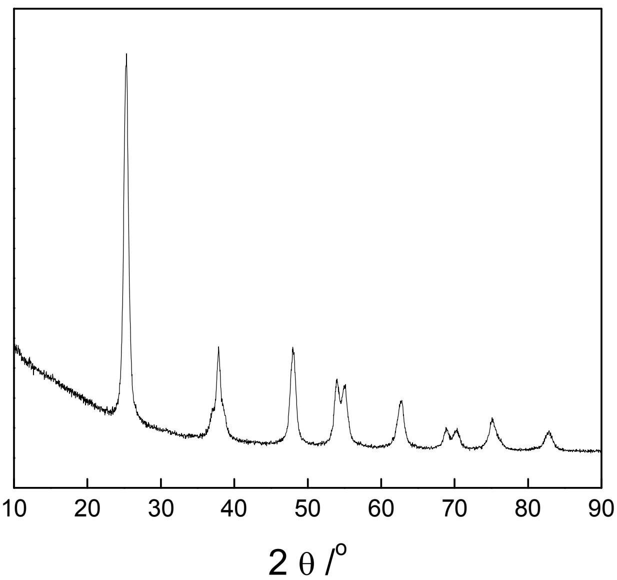

Fig. 1: XRD of TiO_2.

Table 1: Levels of the variables for BBD experimental design.

Variables	Code	Unit	Levels		
			-1	0	1
Water/Triton X-100 molar ratio (w)	A	mol/mol	4.00	5.00	6.00
n-hexanol/TX-100 molar ratio (m)	B	mol/mol	4.00	6.00	8.00
Acetyl acetone/n-TBT molar ratio (p)	C	mol/mol	0.35	0.40	0.45

Table 2: Experimental design matrix and results for process optimization.

Run	wA/(mol/mol)	mB/(mol/mol)	pC/(mol/mol)	Experimental $t_{1/2}$	Predicted $t_{1/2}$
1	4.00	4.00	0.40	7.22	7.40
2	6.00	4.00	0.40	8.06	7.96
3	4.00	8.00	0.40	6.54	6.65
4	6.00	8.00	0.40	6.36	6.19
5	4.00	6.00	0.35	8.45	8.17
6	6.00	6.00	0.35	9.12	9.12
7	4.00	6.00	0.45	7.37	7.37
8	6.00	6.00	0.45	6.24	6.52
9	5.00	4.00	0.35	8.25	8.36
10	5.00	8.00	0.35	7.97	8.15
11	5.00	4.00	0.45	7.88	7.71
12	5.00	8.00	0.45	5.50	5.40
13	5.00	6.00	0.40	7.53	7.35
14	4.00	6.00	0.45	7.37	7.35
15	5.00	6.00	0.40	7.15	7.35
16	5.00	6.00	0.40	7.07	7.35
17	5.00	6.00	0.40	7.62	7.35

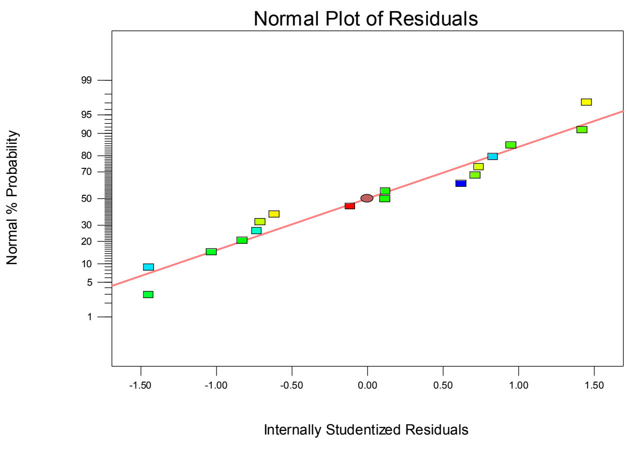

Fig. 2: The actual and predicted plot of $t_{1/2.}$

as their variation limits, and the experimental data obtained for response ($t_{1/2}$) are presented in Table 2. The batch runs were conducted in Box-Behnken experimental design to visualize the effects of independent factors on the response and the results along with the experimental conditions. The experimental results were evaluated and approximating function of half-live ($t_{1/2}$) in Eq. 2.

$$t_{1/2} = -7.35 + 0.025w - 0.63m - 0.85p - 0.26wm - 0.45wp- 0.52mp + 0.046w^2 - 35m^2 + 0.40p^2 \quad ...(2)$$

Analysis of variance (ANOVA): Table 3 shows the analysis of variance (ANOVA) of regression parameters of the predicted response surface quadratic model for half-life ($t_{1/2}$). As can be seen from Table 3, the model F-value of 17.44 and a low probability value (Pr>F<0.05) indicate that the model was significant for half-life($t_{1/2}$). The "Adequate Precision " ratio of the model was 17.37 (Adequate Precision >4), which is an adequate signal for the model. The lack of fit F-statistic was statistically significant as the P values were less than 0.05. A significant lack of fit suggests that there may be some systematic variation unaccounted for in hypothesized model. This may due to the exact replicate values of independent variable in the model that provide an estimate of pure error. The value of correlation coefficient ($R^2 = 0.9573$) obtained in the present study for the $t_{1/2}$ of the degraded methylene blue was higher than 0.80, indicating that only 4.27% of the total dissimilarity might not be explained by the empirical model. In this study B, C and BC are significant model terms. Insignificant model term, which have limited influence, such A, A_2, B_2,C_2, AC and AB, were excluded from the study to improve the model. Based on

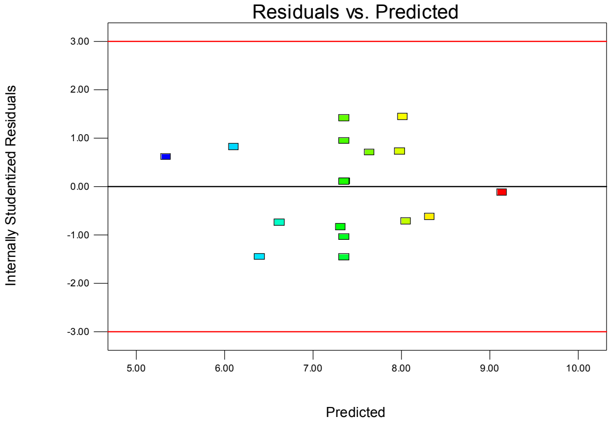

Fig. 3: The predicted $t_{1/2}$ and studentized residuals plot.

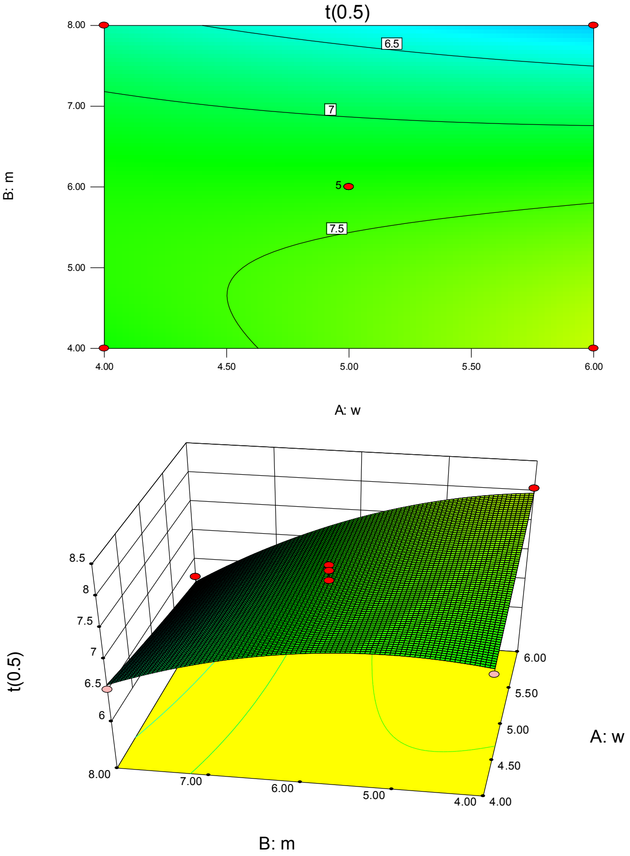

Fig. 4: Contour and 3D map plotted on A and B of $t_{1/2}$.

results, the response surface model constructed in this study for predicting the $t_{1/2}$ of the degrade methylene blue was considered reasonable.

Analysis of RSM: By applying the diagnostic plots provided by the Design Expert 6.0.7 software, such as normal probability plots of the studentized residuals, as well as the

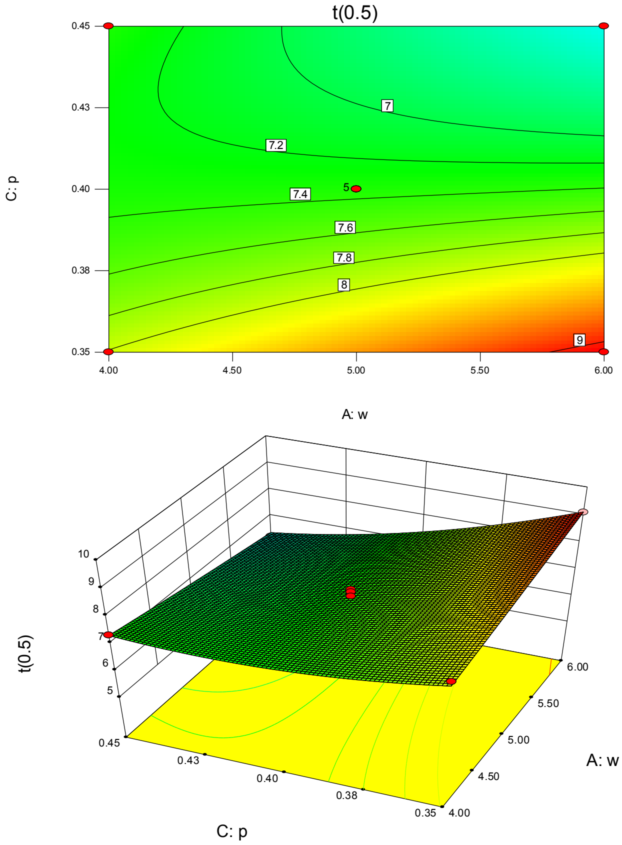

Fig. 5: Contour and 3D map plotted on A and C of $t_{1/2}$.

predicted versus actual value plots, the model adequacy can be judged by Fig. 2, the predicted values of the $t_{1/2}$ of the degrade methylene blue obtained from the model and the actual experimental data were in good agreement.

Fig. 3 shows the plot of residuals for the $t_{1/2}$ of the degrade methylene blue. The plot indicates a random scatter without any obvious patterns and unusual structure. This implies that the model proposed is adequate.

Figs. 4-6 show three-dimensional response surface plot on the effects of $t_{1/2}$ of the degraded methylene blue, which are water/Triton X-100 molar ratio (w) A and n-hexanol/TX-100 molar ratio (m) B on the $t_{1/2}$ of the degraded methylene blue. The 3D surface response and contour plots of the quadratic model were achieved by the Design Expert 6.0.7 software and utilized to assess the interactive relationships between independent variables and the response. As shown in Figs. 4-6, in each plot, one variable was kept constant while the other two were varied within the experimental ranges. The 3D response surface and contour plots were introduced as a function of water/Triton X-100 molar ratio (w) and n-hexanol/TX-10 molar ratio (m), while the acetyl ac-

Table 3: Results for the reduced quadratic model of the variable effects on the response.

Source	Sum of squares	f	Mean square	F-Value	Prob>F	Significant
Model	12.27	9	1.36	17.44	0.0005	Significant
A	5.000E-003	1	5.000E-003	0.064	0.8077	
B	3.18	1	3.18	40.60	0.0004	
C	5.78	1	5.78	73.90	<0.0001	Significant
AB	0.26	1	0.26	3.33	0.1110	
AC	0.81	1	0.81	3.33	0.0147	
BC	1.10	1	1.10	14.10	0.0071	
A^2	8.909E-003	1	8.909E-003	0.11	0.7456	
B^2	0.51	1	0.51	6.56	0.0375	
C^2	0.68	1	0.68	8.66	0.0216	
Residual	0.55	7	0.078			
Lack of Fit	0.32	3	0.11	1.92	0.2673	Non-significant
Pure Error	0.22	4	0.056			

R^2=0.9573, Adj-R^2=0.9024, Adequate Precision (AP)=17.37, CV=3.78%0

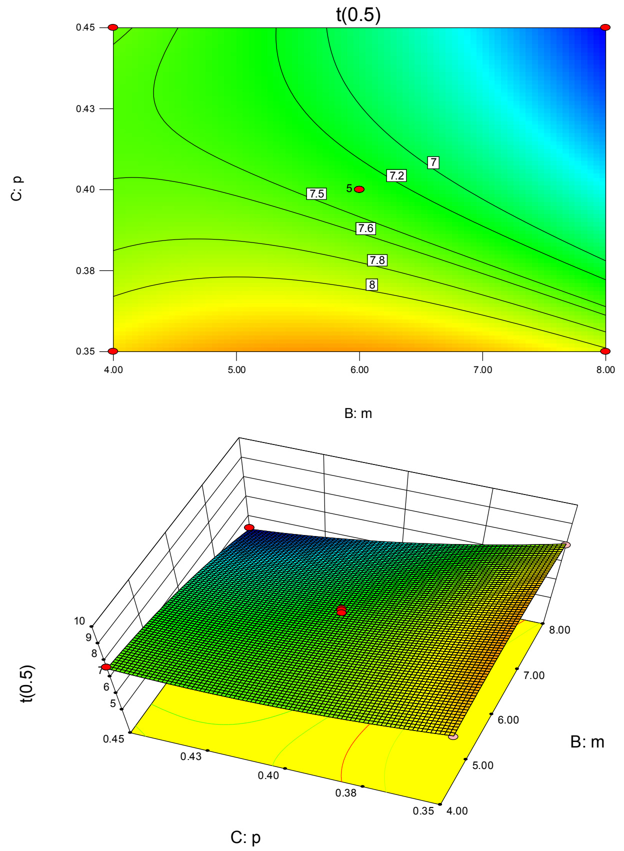

Fig. 6: Contour and 3D map plotted on B and C of $t_{1/2}$.

etone/n-TBT molar ratio (p) was kept constant. The effects of operational variable i.e., w and m on $t_{1/2}$ at constant the acetyl acetone/n-TBT molar ratio (p) was 0.4 are illustrated in Fig. 4. It can be seen that the $t_{1/2}$ decreases with increase in the n-hexanol/TX-10 molar ratio (m) (B) and the $t_{1/2}$ almost unchanged with the water/Triton X-100 molar ratio (w)(A).

As can be seen form Fig. 5 that the effects of operational variable i.e., w and p on $t_{1/2}$ at constant the n-hexanol/TX-10 molar ratio(m) was 6.00. It can be seen that the $t_{1/2}$ decreases with increase in the acetyl acetone/n-TBT molar ratio (p)(C) and the $t_{1/2}$ almost unchanged with the water/Triton X-100 molar ratio (w)(A). Fig. 6. illustrated that effects of operational variable i.e., m and p on $t_{1/2}$ at constant the water/Triton X-100 molar ratio (w) was 5.00. It can be seen that the $t_{1/2}$ decreases with increase in the acetyl acetone/n-TBT molar ratio (p)(C) and the water/Triton X-100 molar ratio(w)(A).

Optimization for prepared TiO_2: To keep all the variables in range of the experimental values, numerical optimization method is used to optimize the desired response of the system. Using this optimized solution, the experimental run for prepared nano-TiO_2 by sol-gel process was conducted according for verification. The optimized experimental condition is water/surfactant Triton X-100 molar ratio (w) of 5.54, n-hexanol/TX-100 molar ratio (m) of 7.97 and acetyl acetone/n-TBT molar ratio (p) of 0.44 with $t_{1/2}$ is 5.52 min and the predicted value is 5.34. The result implies that the experimental value obtained is close to the value calculated from the model and the error rate is only very small, which consequently verifies the model capability.

CONCLUSIONS

Anatase TiO_2 particles were successfully prepared by the hydrolysis of n-TBT in a sol-gel process. Response surface methodology (RSM) was applied to evaluate and optimize preparation parameters influencing half-life ($t_{1/2}$) of the first-order degradation reaction. The optimized experimental condition is water/surfactant Triton X-100 molar ratio (w) of 5.54, n-hexanol/TX-100 molar ratio (m) of 7.97 and acetyl acetone/n-TBT molar ratio (p) of 0.44 with $t_{1/2}$ of 5.52.

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