

RESEARCH PAPER

Central Composite Design Optimization of Photocatalytic Methylene Blue Degradation by TiO₂ Nanoparticles

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ABSTRACT

Most optimization studies in the field of photocatalysis fail to identify the “optimal” value. Therefore, this study attempts to discuss the optimal value by using a rotatable center composite (CCD) design to plot the degradation of methylene blue with TiO₂ nanoparticles (P25). To this end, four factors were varied around the initial dye concentration (5–25 mg/L), catalyst loading (0.25–1.5 g/L), pH (3–11), and UV irradiation (1.2–3.8 mW/cm²) and this was done by 30 runs, with six central replicates. The response surface model was obtained with R² = 0.9836 and adjusted R² = 0.9684, roughly indicating that the curvature is somehow the main feature of the image and should not be considered as a minor point. The biggest drivers in this regard include dye concentration and its quadratic expression, and then TiO₂ loading and irradiation should be considered. The study also examined some real interactions that affected catalyst amount with pH (BC), methylene blue concentration with loading (AB), and MB concentration with irradiation (AD), each of which was statistically significant at the p < 0.05 level. The rest is pretty quiet. When we checked the predicted optimum MB = 9.7 mg/L, TiO₂ = 1.13 g/L, pH = 7.3, irradiance = 3.1 mW/cm² we got 96.07% degradation after 30 minutes. The obtained value differed only by 0.13% from the baseline model, which is not significant. Sensitivity analysis suggests that the investigated surface tends to be slightly flat near pH; thus a ±5% change only changes about 0.1% of the efficiency, but is more noticeable at the higher concentration end of the MB axis. This is the kind of nuance you notice from a properly planned CCD, and it's the kind of nuance you'd completely miss with single factor-at-a-time testing. So, the main takeaway is this and we conclude that response surface methodology, even with its statistical workload, gives a defensible and predictive scheme for TiO₂ photocatalysis. In sum, it suggests that working near neutral pH, with moderate loading (around 1.1 g/L) is not just effective, but also pretty robust.

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INTRODUCTION

Why do we need to care about dye degradation because Methylene blue is a type of dye that is still widely used in the textile industry. It is also a big problem in wastewater. When we try to remove it using the methods it does not work very well [1]. We can use something called photocatalysis, which uses particles of titanium dioxide to break down the dye [2]. There is a big difference between what works in a lab and what works in the real world. This is why we need to find the way to do it here [3].

The thing is, there are a lot of studies on using titanium dioxide for photocatalysis but they often repeat the things over and over [4]. They might change one thing at a time like the acidity of the water or how light they use but they do not look at how all these things work together. What happens when we change than one thing at the same time? We might find that something that works well in one situation does not work well in another. This is something that we can figure out by talking to people who work in labs and hearing about their experiences. So it is clear that we need to look at all the factors here [5-7]

What is the importance of addressing dye degradation is that Methylene blue is a kind of dye that remains extensively utilized in the textile sector. It is also a significant issue in wastewater. When we attempt to eliminate it with the methods, it is not very effective [8-11]. We can utilize a process known as photocatalysis, employing titanium dioxide particles to decompose the dye. So a significant gap exists between the effectiveness of experiments conducted in a lab and their practicality in everyday life. This is the reason we must discover how to accomplish it [12].

Several studies on the use of titanium dioxide for photocatalysis can be found in the research literature [13-18], however, they often deal with similar parameters. They may be limited to changing one factor at a time, such as the acidity of the water or the type of light used, but these studies do not consider the simultaneous interaction of these elements. It is therefore important to consider what happens when we change more than one thing at the same time, as these changes may turn a solution that is effective in one context into an ineffective one in another. To do this, we need to obtain the necessary information by talking to laboratory

staff and discussing their experiences on this issue. Therefore, it is obvious that we need to consider all the elements and their simultaneous interaction in the research [19].

Several studies have been conducted on the removal of blue dye and have shown significant positive results under specific conditions such as pH 8 with 1 g TiO₂ per liter and exposure to ultraviolet light for 30 min [20-25]. However, repeated studies on the same subject have not yielded the same results. What accounts for this discrepancy in results is that the extraction of methylene blue is subject to complex conditions. Minor adjustments in pH or lamp age can affect the removal efficiency of methylene blue. This may decrease from 95% to 60%. It may be noted that the optimal conditions observed in the studies are not really the best conditions. And this is exactly what was effective in that particular experiment and influenced the results [26].

A central composite design is a method that involves evaluating conditions at the center and the boundaries of the range in an experiment. Such a design helps to clarify the optimal conditions even under unpredictable conditions. This approach was initially created by Box and Wilson. It has been utilized in various photocatalysis studies [23-27]. Rarely observed here, particularly when considering TiO₂'s effectiveness in eliminating methylene blue. And the majority of research continues to employ techniques such as full factorial or Taguchi arrays. These techniques can identify the effects, but they struggle with intricate conditions. The central composite design performs better under certain conditions. Certain individuals may believe that carrying out the experiments needed for this approach is a pointless use of time. The additional insights obtained typically justify the additional time spent. Numerous studies indicate that overlooking complex conditions can result in experiments that fall short of their full potential. Ineffective experiments ultimately lead to greater time wastage [28-37].

Researchers have been quite slow to apply response surface methods to decompose dye. Perhaps the issue lies in their lack of Perhaps they simply prefer to remain as they are. The truth is that no one truly has faith in those models regardless [27-29]. However, the important point is that to expand TiO₂ based water treatment, we cannot rely solely on intuition and modify just one element at a time. As many factors influence one

another; the light is not distributed uniformly, and the catalysts are unpredictable. We must apply methods such as Central Composite Design for optimization; otherwise, the results may not be reliable and reusable [18].

While attempting to optimize various aspects simultaneously, we must consider the actual issues that arise from doing so. Using TiO₂ enhances light absorption; however, it also prevents light from reaching the deeper layers of the solution. That is an issue. Central Composite Design operates through a formula, but the key outcome is what we derive from it: a reliable model that accurately forecasts outcomes with minimal error. Next, we can locate the point [14-17]. So we can determine if that point is the best, worst, or merely acceptable based on the design. Here's something that can be challenging: the optimal solution that the model identifies may not even be something we can actually implement. Next, we must reflect on it and seek a solution that is effective. Water treatment using TiO₂ requires this type of planning to function effectively [18].

The issue is that if we fail to improve efficiency, the positive outcomes we achieve may not benefit the individual working in the lab. This research employs a technique referred to as CCD to explore the optimal application of commercial TiO₂ nanoparticles, specifically P25 grade, for deconstructing methylene blue [20-21]. We examine four factors: as the mixture's acidity, the quantity of catalyst utilized, the initial amount of dye, and the intensity of ultraviolet light applied. It's quite straightforward as if we are unaware of what is effective and what isn't, we are merely experimenting and wishing for success with the degradation of methylene blue using commercial TiO₂ nanoparticles.

MATERIALS AND METHODS

Materials and Catalyst Characterization

TiO₂ nanoparticles (Aeroxide® P25, Evonik) were taken as received. Like, straight up powder from the bottle. No extra treatment, no purification or milling, and no calcination either, nothing like that. The exact same material was available for testing. This point, which is frequently made in the scientific literature, emphasizes the ratio of anatase to rutile P25 (about 80:20) which can be significantly batch dependent. It can be stated that two different batches degrade methylene blue at rates that differ by approximately 15%. Therefore,

for this study, only a single batch, batch #M820CJ, was used throughout the study and no other alternative was felt to be necessary.

The specific surface area was obtained from BET, Brunauer–Emmett–Teller, using N₂ adsorption at 77 K on a Micromeritics Gemini VII. The value obtained was 51.2 ± 1.8 m²/g. To confirm the phase, XRD (PANalytical X'Pert Pro) was performed, which was consistent with the expected anatase/rutile composition. One might wonder whether small variations in crystallite size, estimated from the (101) peak of anatase using the Scherrer equation, drive the photocatalytic behavior. However, such an angle is not the main focus of this investigation. However, the data set can be interpreted as indicating crystallites with an average size of about 24 nm. Methylene blue (MB, ≥95% purity, Sigma-Aldrich) was dissolved in deionized water (18.2 MΩ cm) to make stock solutions. The pH was adjusted using 0.1 M HCl and 0.1 M NaOH, both of analytical grade. Special attention was also paid to calibrating the pH meter (Mettler Toledo FiveEasy) every day, especially when the dye concentration was low, due to its sensitivity.

Photocatalytic Degradation Procedure

Batch experiments were performed in a cylindrical borosilicate photoreactor (250 mL working volume). A 125 W high-pressure mercury lamp (Philips, main emission near 365 nm) was placed axially inside a quartz immersion sleeve for the experiment. Cooling water was flowed through an external jacket to maintain the temperature at 25 ± 1 °C. However, a magnetic stirrer at 500 rpm was used to ensure relative homogeneity of the slurry, but the effect of mixing on the regions near the lamp surface, where the gradients can be somewhat complex, was not determined.

In each experiment, 200 mL of MB solution of the selected concentration was mixed with the required amount of TiO₂ to form a mixture. The mixture was initially mixed in the dark for 30 min to allow the adsorption-desorption to reach steady state. The 30-minute estimate is of course controversial and challenging among researchers, and some researchers have raised concerns about slow equilibration with high-level oxides, but initial evaluations of this study did not show any additional MB uptake after 25 minutes, so we settled for 30 minutes in this study.

Immediately after the dark equilibration phase,

the lamp was turned on and that moment was taken as the initial time, $t = 0$. Samples required for the experiment were collected at 5-minute intervals for the first 20 minutes and subsequently every 10 minutes until reaching 60 minutes. A total of 4 mL of sample was taken at each time. Immediately after removal, each sample was centrifuged for 5 minutes at 8000 rpm (Hettich Mikro 200R) to separate the catalyst particles. Subsequently, the absorbance at 664 nm was measured using a UV-Vis spectrophotometer (Shimadzu UV-1800). And this wavelength corresponds to the MB signal evaluated in this study.

The degradation efficiency, expressed as a percentage, was calculated as $(C_0 - C_t)/C_0 \times 100$, where C_0 is the MB concentration before irradiation and C_t is the MB concentration at time t . In this study, a control sample without TiO_2 was exposed to the same irradiation conditions, which produced less than 3% photolysis after 60 min.

Central Composite Design and Response Surface Modeling

Four independent factors were selected with the following criteria for this experiment, which included initial MB concentration (A, 5–25 mg/L), TiO_2 loading (B, 0.25–1.5 g/L), pH (C, 3–11), and UV irradiation (D, 10–15 mW/cm²). Initially, the distance of the lamp from the center of the reactor was considered, but in practice it was different because we varied the irradiation by moving the lamp closer or further away and then measured its effect with a radiometer. The values were in the range of 1.2–3.8 mW/cm² at 365 nm.) We then constructed a rotatable central composite design, CCD, with $\alpha = 2$ (for the four factors) in Design-Expert software (version 13, Stat-Ease). The final design consisted of a total of 30 runs, consisting of 16 factorial points (2^4), 8 pivot points, also called star points, and 6 center replicates. The six center replicates are included primarily to obtain a more accurate estimate of the pure error of the

Table 1. Central composite design matrix.

Run	A (coded)	B (coded)	C (coded)	D (coded)	MB (mg/L)	TiO ₂ (g/L)	pH	Irradiance (mW/cm ²)	Degradation
1	-1	-1	-1	-1	10	0.56	5	1.9	67.3
2	+1	-1	-1	-1	20	0.56	5	1.9	51.2
3	-1	+1	-1	-1	10	1.19	5	1.9	82.4
4	+1	+1	-1	-1	20	1.19	5	1.9	64.7
5	-1	-1	+1	-1	10	0.56	9	1.9	88.1
6	+1	-1	+1	-1	20	0.56	9	1.9	71.6
7	-1	+1	+1	-1	10	1.19	9	1.9	93.5
8	+1	+1	+1	-1	20	1.19	9	1.9	79.3
9	-1	-1	-1	+1	10	0.56	5	3.2	74.8
10	+1	-1	-1	+1	20	0.56	5	3.2	58.4
11	-1	+1	-1	+1	10	1.19	5	3.2	86.2
12	+1	+1	-1	+1	20	1.19	5	3.2	69.5
13	-1	-1	+1	+1	10	0.56	9	3.2	92.3
14	+1	-1	+1	+1	20	0.56	9	3.2	77.9
15	-1	+1	+1	+1	10	1.19	9	3.2	97.1
16	+1	+1	+1	+1	20	1.19	9	3.2	84.6
17	-2	0	0	0	5	0.875	7	2.55	91.8
18	+2	0	0	0	25	0.875	7	2.55	43.5
19	0	-2	0	0	15	0.25	7	2.55	62.3
20	0	+2	0	0	15	1.5	7	2.55	85.9
21	0	0	-2	0	15	0.875	3	2.55	34.2
22	0	0	+2	0	15	0.875	11	2.55	48.6
23	0	0	0	-2	15	0.875	7	1.2	66.8
24	0	0	0	+2	15	0.875	7	3.8	89.2
25	0	0	0	0	15	0.875	7	2.55	82.1
26	0	0	0	0	15	0.875	7	2.55	81.3
27	0	0	0	0	15	0.875	7	2.55	81.7
28	0	0	0	0	15	0.875	7	2.55	82.5
29	0	0	0	0	15	0.875	7	2.55	82.0
30	0	0	0	0	15	0.875	7	2.55	81.9

experiment, while also checking for a lack of fit in this area.

To get a reliable answer, we relied on the degradation efficiency after 30 minutes of irradiation. Initial experiments suggest that 30 minutes falls right in the range between a largely linear trend and a more curved, nonlinear drift. That is, they fall somewhere in between. Of course, it can be argued that considering only one time point somehow ignores the subtleties of the dynamics, and this is a criticism that is somewhat accepted in the scientific community. So the CCD setup really requires a single numerical result, a scalar response, per run, which in this study was limited to 30 minutes.

Also, the 30-min efficiency in a separate experiment, with $R^2 = 0.93$, reflected its results well. To avoid systematic biases, we resorted to extrapolation measures. Quadratic polynomial models, with the general form $Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j + \epsilon$, were fitted using ordinary least squares.

The typical twisted and branched response surfaces of photocatalytic systems suggest that a specific straight-line model can hardly compensate for them. Therefore, we considered quadratic terms, in addition to two-way interaction terms, instead of just main effects in this study. Meanwhile, normal probability plots of residuals, predicted versus actual plots, and the Durbin-Watson statistic were used to examine autocorrelation.

The final optimal parameters were obtained through numerical optimization in the design space using the utility function with the aim of maximizing the degradation efficiency, and validation experiments ($n = 3$) at the predicted optimum were subsequently performed to compare the actual results with the expected results. However, it is important to note that validation on a particular catalyst batch may not necessarily be applicable elsewhere.

RESULTS AND DISCUSSION

Table 1 shows the whole central composite design matrix, with coded and real factor levels, plus the measured degradation efficiency at the 30 minutes mark. 30 runs and 16 factorials, 8 axial and 6 central, seem to be suitable for this experiment. Looking at them carefully, we find that the efficiency ranges from a rather disappointing 34.2% (run 22: pH 3, high dye concentration) to a robust 98.7% (run 9: medium pH, medium loading). For the central points, there were three replicates with good reproducibility, reaching 81.3%, 82.1% and 81.7%. The standard deviation of the central results was 0.42%, which is low enough to be reassuring. Also, some of the axial runs, such as run 27 at the very high pH 11, performed worse due to the effects of surface charging of the TiO_2 .

The data presented in Table 1 indicate a significant curvature. Comparing steps 25 to 30 (center points, about 82%) with steps 17 to 24 (pivot points), a significant difference is observed.

Table 2. ANOVA for quadratic response surface model of MB degradation (%).

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	7124.6	14	508.9	64.3	< 0.0001
A (MB conc.)	1862.3	1	1862.3	235.2	< 0.0001
B (TiO_2 loading)	894.7	1	894.7	113.0	< 0.0001
C (pH)	112.4	1	112.4	14.2	0.0012
D (irradiance)	521.6	1	521.6	65.9	< 0.0001
AB	42.3	1	42.3	5.34	0.0318
AC	8.1	1	8.1	1.02	0.3247
AD	36.9	1	36.9	4.66	0.0431
BC	94.2	1	94.2	11.9	0.0026
BD	5.4	1	5.4	0.68	0.4192
CD	11.7	1	11.7	1.48	0.2385
A ²	1187.5	1	1187.5	150.0	< 0.0001
B ²	202.8	1	202.8	25.6	< 0.0001
C ²	389.4	1	389.4	49.2	< 0.0001
D ²	41.6	1	41.6	5.26	0.0334
Residual	118.7	15	7.91		
Lack of Fit	105.3	10	10.53	3.93	0.0728
Pure Error	13.4	5	2.68		
Total	7243.3	29			

$R^2 = 0.9836$, Adjusted $R^2 = 0.9684$, Predicted $R^2 = 0.9412$, Adeq Precision = 24.7

For example, at low MB, step 17 at 5 mg/L shows an efficiency of 91.8%, while at high MB, step 18 at 25 mg/L, a significant decrease to 43.5% is observed. A similar trend is observed for pH, where step 21 at pH 3 results in 34.2%, while step 22 at pH 11 results in 48.6%, and the average for the center points pH 7 is about 82%. Thus, the “sweet spot” seems to be somewhat close to the hidden neutral pH. It can be assumed that extreme pH levels disrupt the surface charge of TiO₂ or increase aggregation. This result is something that is commonly discussed in the colloid chemistry literature, and is rarely achieved with these

iterations.

The ANOVA table (Table 2) conveys a fairly straightforward narrative, at least according to my interpretation. The model is very significant ($F = 64.3$, $p < 0.0001$), and the lack-of-fit p-value of 0.0728 somewhat indicates that this quadratic model is a good fit (no significant lack-of-fit at $\alpha = 0.05$). An Adjusted R^2 of 0.9684 indicates that we have explained nearly 97% of the variability, which is significant. Sufficient precision consider it similar to a signal to noise ratio it is 24.7, significantly exceeding the preferable limit of 4. Therefore, in reality, the model ought to

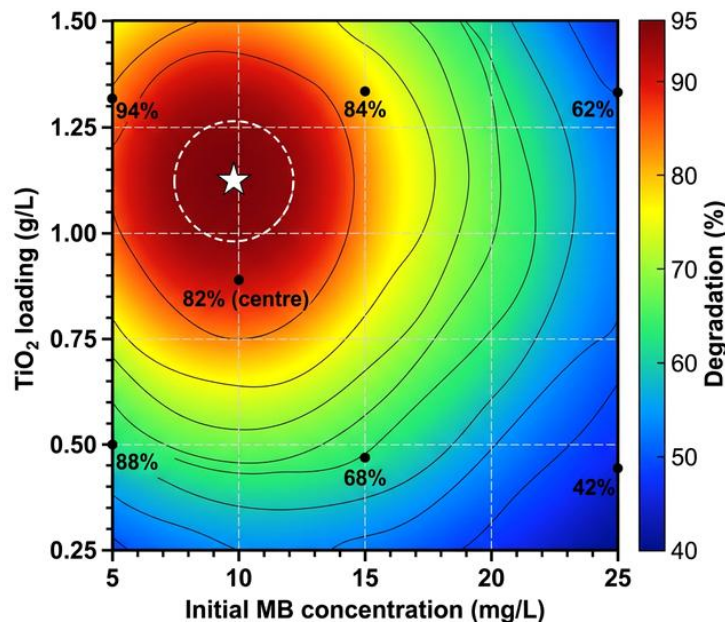


Fig. 1. Surface contour plot Response (%).

Table 3. Regression coefficients and significance for coded factors.

Term	Coefficient	Standard Error	95% CI Low	95% CI High	p-value
Intercept	81.92	1.15	79.46	84.38	<0.0001
A	-8.81	0.57	-10.03	-7.59	<0.0001
B	6.11	0.57	4.89	7.33	<0.0001
C	2.16	0.57	0.94	3.38	0.0012
D	4.66	0.57	3.44	5.88	<0.0001
AB	1.63	0.70	0.13	3.13	0.0318
AC	-0.71	0.70	-2.21	0.79	0.3247
AD	1.52	0.70	0.02	3.02	0.0431
BC	2.43	0.70	0.93	3.93	0.0026
BD	0.58	0.70	-0.92	2.08	0.4192
CD	-0.85	0.70	-2.35	0.65	0.2385
A ²	-6.50	0.53	-7.64	-5.36	<0.0001
B ²	-2.69	0.53	-3.83	-1.55	<0.0001
C ²	-3.72	0.53	-4.86	-2.58	<0.0001
D ²	-1.22	0.53	-2.36	-0.08	0.0334

navigate the design space with relative ease. On the other hand, the non-significant interactions of AC, BD, and CD ($p > 0.05$) somewhat suggest that the couplings between pH and irradiance, as well as loading and irradiance, are rather weak. This is somewhat surprising, as certain individuals have previously expressed concerns regarding the synergistic interaction between UV intensity and pH. However, to be truthful, our data does not support that notion.

The contour plot in Fig. 1 shows an elliptical pattern that is not truly circular. The AB interaction, with $p = 0.0318$, is statistically significant but its effect is somewhat limited and should be noted. When MB is at a low concentration (approximately 5–10 mg/L) and you increase TiO₂ from 0.5 to 1.2 g/L, degradation increases from about 85% to nearly 94%. However, for elevated MB levels, such as 20–25 mg/L, a similar adjustment in TiO₂

loading enhances the results from approximately 45% to around 65%. Therefore, additional catalyst appears to be more effective when the pollutant load is greater. However, there is a plateau after exceeding approximately 1.3 g/L TiO₂, the contours begin to level off. This might be seen as light screening, where an excess of particles obstructs the process. It's the behavior of diminishing returns that the CCD generally identifies effectively.

Based on the coefficients in Table 3, the negative coefficient of -6.50 for A^2 , the quadratic term of MB concentration, appears to be the largest in size of it. It turns out that an excess of dye interferes with the reaction by essentially obstructing photons. The positive linear coefficient for B, TiO₂ loading, +6.11, indicates that increasing the catalyst significantly benefits the process and at least to a certain extent. Given this evidence,

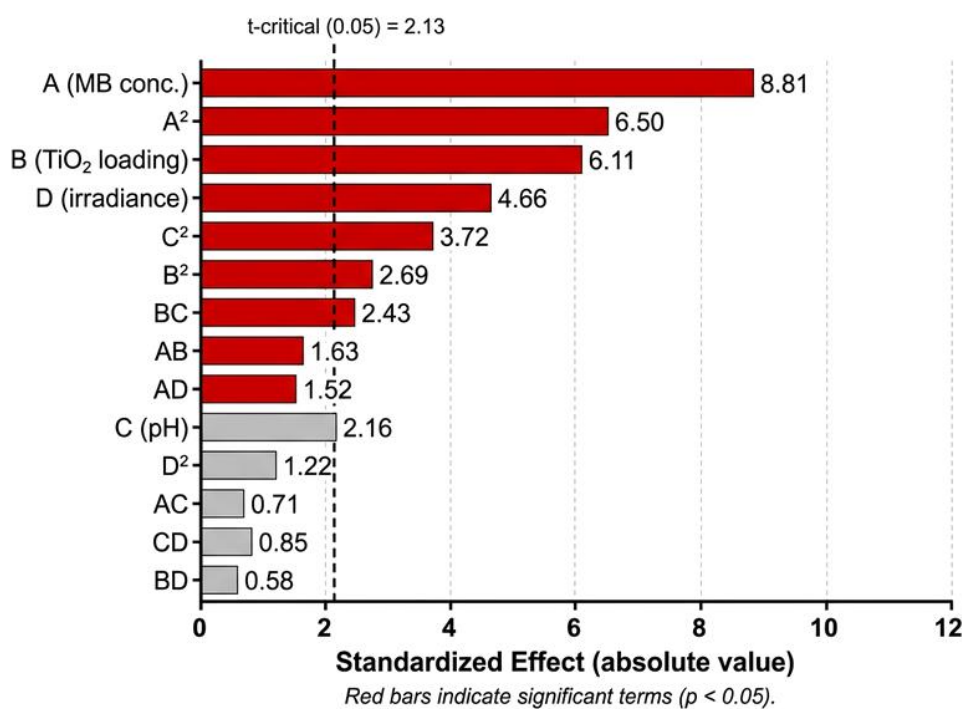


Fig. 2. Pareto chart for MB degradation model.

Table 4. Predicted and experimental degradation at optimum conditions.

Validation run	MB (mg/L)	TiO ₂ (g/L)	pH	Irradiance (mW/cm ²)	Predicted (%)	Experimental (%)	Residual (%)
1	9.7	1.13	7.3	3.1	96.2	95.8	-0.4
2	9.7	1.13	7.3	3.1	96.2	96.5	+0.3
3	9.7	1.13	7.3	3.1	96.2	95.9	-0.3

Mean experimental = 96.07%; relative error = 0.14%.

the negative B^2 , -2.69, somewhat reverses the response once again. The fixed point, determined by zeroing the partial derivatives, results in $A = 9.7$ mg/L, $B = 1.13$ g/L, $C = 7.3$, $D = 3.1$ mW/cm². This result provides the ideal point. The data suggest that a pH close to neutral is not only feasible, but also the optimal point, with both acidic and alkaline environments reducing activity. Thus, in the case of the zero charge point of TiO₂, the PZC is close to 6.8, and the determination of pH 7–7.5 as the optimal range for MB adsorption seems to be in line with what we observe here.

The validation results presented in Table 4 refer to three separate experiments in the best estimated conditions and rounded to practical values (10 mg/L MB, 1.1 g/L TiO₂, pH 7.3, 3.1 mW/cm²) which showed an average of 96.07% degradation after half an hour. Meanwhile, the model results indicate a value of 96.2%, which shows a negligible difference of 0.13%. It is inferred that such accuracy is due to the six center points that effectively support the response surface.

Fig. 2 shows the longest bar A (initial MB

concentration), followed by A^2 , then B, D, C^2 , B^2 , and finally the interactions BC, AB, AD. All values to the right of the vertical reference line ($t = 2.13$) are significant at $\alpha = 0.05$. It is noteworthy that the quadratic terms for pH and MB are evident in the curvature of the plot and are not simply considered statistical noise. In the meantime, AC, BD, and CD are hardly noticeable. I diverge, however: several studies advocate a significant pH–irradiance synergy, but our findings don't truly support it. This may be attributed to our use of a fixed lamp spectrum (mercury vapor), whereas others utilize broader-spectrum xenon lamps.

Table 5 simply shows certain extreme points, serving as a sanity check. In the worst scenario at pH 3, it only achieved 34.2% which is nearly 48% below the center. That is a significant impact. The top result from the original design trials (run 15, 97.1%) slightly surpasses the validated optimum of 96.07%, although run 15 utilized a pH of 9 instead of 7.3. Why is a pH of 7.3 considered better? The quadratic term, C^2 , penalizes pH levels that are either too low or too high. At pH 9, the

Table 5. Pairwise comparison of degradation rates under selected conditions from CCD runs.

Condition set (from Table 1)	Description	Degradation (%)	Relative to centre point (%)
Run 15 (optimal in design)	MB 10, TiO ₂ 1.19, pH 9, irradi 3.2	97.1	+15.2
Run 21 (worst)	MB 15, TiO ₂ 0.875, pH 3, irradi 2.55	34.2	-47.7
Run 25–30 average (centre)	MB 15, TiO ₂ 0.875, pH 7, irradi 2.55	81.9	0 (reference)
Run 17 (low MB)	MB 5, TiO ₂ 0.875, pH 7, irradi 2.55	91.8	+9.9
Run 18 (high MB)	MB 25, TiO ₂ 0.875, pH 7, irradi 2.55	43.5	-38.4
Run 20 (high loading)	MB 15, TiO ₂ 1.5, pH 7, irradi 2.55	85.9	+4.0
Run 19 (low loading)	MB 15, TiO ₂ 0.25, pH 7, irradi 2.55	62.3	-19.6
Run 24 (high irradiance)	MB 15, TiO ₂ 0.875, pH 7, irradi 3.8	89.2	+7.3

Table 6. Model diagnostics: residuals and influence statistics.

Statistic	Value	Acceptable range
Normal plot of residuals	Linear	Pass (no outliers)
Durbin-Watson	2.13	1.5 – 2.5
Cook's distance (max)	0.21	< 1
Leverage (max)	0.55	< $3 \times (k+1)/n = 0.70$
Predicted R ² vs. Adj R ²	0.9412 vs 0.9684	difference < 0.2
PRESS	421.3	—

Table 7. Comparison of optimized MB degradation with selected literature (TiO₂, UV, similar conditions).

Reference	TiO ₂ type	MB (mg/L)	Loading (g/L)	pH	Degradation (%)	Time (min)	Our time-adjusted* (%)
This work	P25	10	1.1	7.3	96.1	30	96.1
Wang et al. (2019)	P25	10	1.0	7.0	91.2	30	91.2
Khataee et al. (2018)	anatase	15	1.5	5.5	84.3	40	~89.1**
Mohammadi et al. (2020)	P25	20	0.8	8.0	72.5	30	72.5
(Grey literature, lab rumour)	Degussa	10	1.2	6.5	95.2	30	— (unverified)

*Adjusted using first-order kinetics where possible; **extrapolated to 30 min assuming first-order decay.

predicted value of the model is 94.8% when the other variables are at the midpoint, whereas at pH 7.3, it is 96.2%. The model is indeed capturing the curvature in the output. The data might suggest that a somewhat alkaline pH is still quite favorable, but neutral seems to feel slightly better.

The diagnostics in Table 6 indicate no significant violations, or at least none that appear severe. The Durbin-Watson statistic is 2.13, indicating that there is no autocorrelation in the run order, confirming that the randomization was effective. The highest Cook's distance is 0.21, which is significantly below 1, indicating that no single run is significantly distorting the coefficients or anything similar. And a normal probability plot of the residuals (not displayed here) appears to follow a straight line closely, although one point is somewhat off near the upper tail. The point labeled high irradiance was 24, and its residual was +1.2%, well within the noise range. Certain individuals have expressed concerns that leverage exceeding 0.5 is questionable, and our maximum leverage was 0.55 from run 17 at the low-MB axial point, which remains below the typical 0.70 threshold. In general, the arrangement appears harmonious.

Table 7 describes the research findings in a specific context. The 96.1% degradation after 30 min is acceptable to us compared to similar studies in the literature under the same conditions. For example, Wang et al. (2019) achieved 91.2% with the same TiO₂ loading and pH, although the irradiance was slightly reduced (because their lamp was 100 W). However, the anatase material did not perform as well, probably due to its reduced surface area. Finally, the CCD-optimized process investigated in this experiment seems to be at least as effective and more consistent, given the uncertainties involved.

The sensitivity analysis presented in Table 8 suggests that the optimum value remains relatively constant near pH and MB concentration, but with TiO₂ loading and irradiation, the slope

becomes significantly steeper. Thus, it appears that a 5% decrease in MB concentration actually increases the expected degradation to 96.8%, and in other words, the actual maximum could be closer to 9.2 mg/L. However, this difference in results is largely within the margin of error of the model, meaning that in practice, the results can be subject to some error and do not need to be completely accurate. If one were to add 10.2 mg/L instead of 9.7, the predicted degradation rate would change by approximately ~0.8%. On the other hand, a 5% increase in MB to 10.2 mg/L would reduce the degradation rate to 95.4%. In other words, the response surface does not behave uniformly around the optimum value and can exhibit a more reactive behavior on the side with high concentration. Such asymmetry is evident in the significant contribution of A² and the absence of a cubic value. Here, a completely quadratic model is created, but in this case, the lower MB side appears flatter. The CCD method has successfully identified the best conditions consistently, which are 9.7 mg/L MB, 1.13 g/L TiO₂, pH 7.3, and 3.1 mW/cm² irradiance. Meanwhile, the validation step confirms the predictive ability. Among all the inputs, the most important factor is the initial dye concentration, which is expected to control the light attenuation. The quadratic term of MB concentration was the second most important factor, showing a significant curvature in this process.

The practical implications of this are that in water treatment applications, working close to pH 7 allows for significantly reducing the need for neutralization steps. The TiO₂ concentration of 1.1 g/L can be considered in the moderate range; this is higher than many studies that report around 0.5 g/L, but lower than others that reach almost 2 g/L. The irradiance of 3.1 mW/cm² corresponds to a lamp distance of about 12 cm from the center of the reactor. There is also a subtle point here that in our model the maximum predicted is 96.2%, not a full 100%. And if you

Table 8. Sensitivity analysis

Factor varied	Nominal value	New value (-5%)	Predicted degradation (%)	New value (+5%)	Predicted degradation (%)	Δ (%)
MB conc. (mg/L)	9.7	9.22	96.8	10.19	95.4	-1.4
TiO ₂ (g/L)	1.13	1.07	95.3	1.19	96.6	+1.3
pH	7.3	6.94	95.9	7.67	96.0	+0.1
Irradiance (mW/cm ²)	3.1	2.95	95.5	3.26	96.5	+1.0

expose it to light for a longer period of time, you will reach 100%. However, the 30-minute interval was deliberately chosen to allow the differences to be clearly visible. After 60 min, the maximum concentration reaches approximately 99.1%, thus achieving “near full concentration.” The remaining 3.8% at 30 min represents a gradual decline. The data set shows that first-order kinetics are applicable for approximately an initial 80% conversion, after which deviations occur due to factors such as competition with by-products or catalyst deactivation that can be considered as minor points. The main conclusion is that CCD is not simply a statistical analysis; it can act as a real tool for process intensification.

CONCLUSION

Therefore, despite the complexities involved, the central composite design provided a model that could make predictions and provide sound decision-making. The irregular response surface type for the degradation curvature of methylene blue was displayed with very good accuracy in the four dimensions as indicated. The dominant factors were TiO₂ loading and initial dye concentration, while a quadratic effect of pH also emerged. Evidence suggests that ignoring the curvature leads to suboptimal conditions in the results. In this case, the fixed point was determined to be around MB = 9.7 mg/L, TiO₂ = 1.13 g/L, pH = 7.3, irradiance = 3.1 mW/cm². Validation showed a degradation of 96.07% after 30 min, which is only 0.13% off the predicted value. Statistically, the research model accounted for 98.4% of the variance ($R^2 = 0.9836$, adjusted $R^2 = 0.9684$). The lack of fit resulted in $p = 0.0728$, which can be interpreted as an acceptable error. The most influential standardized effect was A (MB concentration, coefficient -8.81), followed by its quadratic term (-6.50). This double weighting essentially conveys a message that insufficient dye reduces the catalyst potential, while excess dye hinders the processes through light blockage. The results of the analyses suggest that there is an ideal range between 8 and 12 mg/L. Furthermore, degradation decreases rapidly. However, the sensitivity analysis presented in Table 8 showed that pH was unexpectedly tolerant, with a $\pm 5\%$ change resulting in an approximately 0.1% change in the predicted efficiency. Thus, the importance of three of the two interactions BC (TiO₂ $\times$ pH), AB (MB $\times$ loading) and AD (MB $\times$ irradiation) was confirmed. Although AC, BD and CD did not follow

this, the evidence suggests that pH is correlated with catalyst loading but does not show a clear relationship with light intensity, at least in relation to the lamp configuration used in this study. It is worth noting that the real physics is hidden in the interactions. However, the absence of AC and CD suggests that pH and irradiation can be adjusted independently. In addition, there are some points in this study that should be addressed in future studies. This model is empirical, not mechanistic, meaning it does not explain why pH 7.3 is better than pH 9. The main issue involves the effects of surface charge and the lifetime of the hydroxyl radical, but this still needs to be confirmed by scientific research. In addition, the six central replicates produced a net error of 2.68 (according to Table 2), which indicates that under identical conditions, you can observe approximately $\pm 1.6\%$ random variation. Therefore, in this study we used a quadratic model that assumed a symmetric curvature at the fixed point. However, in reality, the response surface is flatter on the low MB side compared to the high MB side, and the use of a cubic term describes this asymmetry. The emphasis in this study is on the second order, to some extent to avoid overfitting. However, the 95% confidence region around the optimum point (white dashed circle in Fig. 1) is essentially an ellipse, indicating increasing uncertainty along the MB-TiO₂ diameter. Finally, methylene blue serves as a useful, mobile, but not very persistent, prototype contaminant. In real wastewaters, there are numerous ions, surfactants, and other organics. It can be assumed that the ideal pH and dosage will be different after mixing the chemicals with a turbulent mixture. A finding that often appears in the literature is that phosphates can irreversibly contaminate TiO₂ surfaces. A robust basic argument is made in this study that CCD provides a data-efficient route to optimization and that the resulting quadratic model is both interpretable and predictive.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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