Nitrogen doping of commercial TiO2 nanoparticles for enhanced photocatalytic degradation of dye under visible light: central composite design approach

A. R. Khataee
M. Zarei
L. Moradkhannenjad
S. Nourie
B. Vahid

Available at: https://works.bepress.com/alirezakhataee/120/

A. R. Khataee¹*, M. Zarei¹, L. Moradkhannejhad¹,², S. Nourie², and B. Vahid¹

¹Research Laboratory of Advanced Water and Wastewater Treatment Processes, Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, 51666-16471, Iran
²Department of Chemistry, Faculty of Science, University of Urmia, Urmia, 57159-159, Iran

In this work, the commercially available anatase TiO₂ powder (Coteix KA-100) was doped with nitrogen to shift the TiO₂ absorption towards the visible region. Nitrogen doped TiO₂ was prepared by manual grinding with urea and annealing at 400 °C for one hour. X-ray diffraction (XRD), diffuse reflectance spectra (DRS), BET and transmission electron microscopy (TEM) were applied to characterize the catalyst properties. Enhanced photocatalytic degradation of C.I. Basic Red 46 (BR46) was observed utilizing N-doped TiO₂ nanoparticles in comparison with undoped ones. Central composite design (CCD) was employed not only for developing a model for prediction of color removal efficiency as a function of the initial BR46 concentration, initial amount of N-doped TiO₂ and reaction time, but also for finding individual and interactive effects of the mentioned parameters. Predicted values of photocatalytic decolorization efficiency were found to be in good agreement with experimental values ($R^2 = 0.916$), which indicated the suitability of the CCD model. Moreover, the results indicated that the color removal efficiency was obviously affected in various operational conditions.


1. INTRODUCTION

Dye pollutants from the textile industry effluents are a significant source of environmental contamination. Indeed, these dyes are toxic and resistant to destruction by biodegradation or physico-chemical treatment methods. Generally, removing of visible dyes (below 1 mg/L) from wastewaters is more essential than other colorless organic substances, because they can influence the water environment considerably.¹,² TiO₂-mediated photocatalysis is one of the advanced oxidation processes method, which has been shown to be potentially advantageous as it may lead to complete mineralization of pollutants to harmless products such as CO₂, water and mineral acids.³⁻⁵ TiO₂ has a band gap of 3.0 eV for the rutile phase and 3.2 eV for the anatase phase, which can absorb UV light (λ < 400 nm) and photo-stimulate redox reactions on its surface producing reactive oxygen species (ROS) such as hydroxyl radical (·OH) and superoxide radical (O₂⁻·).⁶ However, the overall efficiency of TiO₂ under natural sunlight is limited to the UV-driven activity (λ < 400 nm), accounting only to ~4% of the incoming solar energy on the Earth’s surface. From this point of view, TiO₂ based photocatalysts that can operate properly under visible light irradiation like solar spectrum would be ideal for practical and widespread application.⁷⁻⁹ Doping TiO₂ with nitrogen is one of the most effective methods in improving photocatalytic activity of TiO₂ in visible light regions, due to nitrogen can incorporate into the TiO₂ structure as substitution and interstitial.⁶ Nitrogen-doped TiO₂ particles have been produced through different techniques, such as hydrolytic process,¹⁰ mechnanochemical technique,¹¹,¹² magnetron sputtering,¹³ high-temperature treatment of titania under NH₃ flow,¹⁴,¹⁵ sol–gel method,¹⁶ solvothermal process¹⁷ and calcinations of a complex of Ti⁴⁺ with a nitrogen-containing ligand.¹⁸ The elemental nitrogen was mostly derived from ammonium and urea.¹⁹⁻²¹

Central composite design (CCD) is a combination of mathematical and statistical methods which can be applied not only for prediction of the response in various independent variables by developing a mathematical model, but...
also for determination of optimum independent operational parameters to achieve a desired minimum or maximum response. Moreover, the individual and interactive effects of factors on the response can be calculated by CCD. This approach needs less time, materials and experimental work in comparison with conventional one-factor-at-a-time method for modeling and optimization of a process.\textsuperscript{16,17}

The aim of this study was to prepare N-doped TiO\textsubscript{2} nanoparticles by mechanical mixing of urea with commercial TiO\textsubscript{2} nanopowder to shift the TiO\textsubscript{2} absorption towards the visible region. Then, photocatalytic activity of the N-doped catalyst was tested in removal of the dye, C.I. Basic Red 46, as a model pollutant under visible light and compared with undoped TiO\textsubscript{2}. Eventually, central composite design approach was utilized to study the individual and interactive effects of independent operating parameters on the photocatalytic decolorization efficiency by developing a second-order polynomial equation.

2. EXPERIMENTAL AND METHODS

2.1. Materials

The dye, C.I. Basic Red 46, was provided by Sinochem Tianjin Co. (China) and used without further purification. The composition, structure and other characteristics of BR46 are reported in Table I. The investigated Coteix KA-100 TiO\textsubscript{2} (anatase > 99\%) was supplied by Coteix Co. (South Korea). The crystalline mean size and specific surface area were 80 nm and 9.82 m\textsuperscript{2}/g, respectively. These characteristics were proven by TEM, XRD and BET analyses (Figs. 1 and 2). The urea was obtained from Merck Co. (Germany). Distilled water was used throughout the investigation.

Table I. Characteristics of C.I. Basic Red 46.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C\textsubscript{18}H\textsubscript{24}N\textsubscript{6}O\textsubscript{4}S</td>
</tr>
<tr>
<td>Molecular mass (g/mol)</td>
<td>420</td>
</tr>
<tr>
<td>Maximum of absorption</td>
<td>530</td>
</tr>
<tr>
<td>spectrum (nm)</td>
<td></td>
</tr>
<tr>
<td>Other name</td>
<td>Maxilon red GRL</td>
</tr>
<tr>
<td>Chemical class</td>
<td>Cationic monoazo</td>
</tr>
<tr>
<td>Chemical structure</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. TEM image of the used TiO\textsubscript{2}.

2.2. Preparation of Nitrogen-Doped TiO\textsubscript{2} Nanoparticles

The nitrogen-doped TiO\textsubscript{2} nanoparticles were prepared by mechanical mixing of urea with TiO\textsubscript{2} powders in a 4:1 weight ratio. The materials were annealed under air atmosphere for 1 h at 400 °C with a heating rate of 10 °C per minute and cooled at room temperature. The light-yellow powder crushed in an agate mortar into a fine powder before use. Figure 3 shows the flow chart for preparation of N-doped TiO\textsubscript{2} nanoparticles.

2.3. Analytical Procedures

The samples used for TEM observations were prepared by dispersing the TiO\textsubscript{2} powder in ethanol followed by ultrasonic vibration (Sonorex Bandelin Digi Tec, UK) for 15 min, then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon. TEM was carried out on a Zeiss EM 900, Germany. Nitrogen sorption analyses were obtained with a (Micrometrics, Gimmii series) sorptometer using standard continuous procedures.

Fig. 2. XRD pattern of N-doped TiO\textsubscript{2}.
Nitrogen Doping of Commercial TiO\textsubscript{2} Nanoparticles for Enhanced Photocatalytic Degradation of Dye Under Visible Light

Khataee et al.

Fig. 3. Flow chart for the preparation of nitrogen doped TiO\textsubscript{2} nanoparticles by mechanical mixing of urea with TiO\textsubscript{2} powders.

2.4. Photocatalysis Experiments

The dye, C.I. Basic Red 46, was selected as a model cationic mono-azo pollutant to evaluate the photocatalytic activity of the prepared samples under visible light. N-doped TiO\textsubscript{2} nanoparticles (0.4 g) was dispersed into a 100 mL BR46 aqueous solution (5 mg/L) and then irradiated with a 100 W visible light lamp (Nour Co., Iran) equipped with a UV cut-off filter (\(\lambda > 400\) nm) to remove any radiations below 400 nm. The distance between the light and the surface of the dye solution was fixed at 15 cm. The lamp was cooled with flowing air around it, and ambient temperature is maintained during the photocatalytic reaction. Before the irradiation, the suspension was stirred in the dark for 30 min in order to reach the adsorption–desorption equilibrium. Then, the lamp was switched on to initiate the reaction. During irradiation, agitation was maintained to keep the suspension homogeneous, and the suspension was sampled after an appropriate illumination time. The absorbance of the dye in each decolorized sample was determined by a spectrophotometer (UV-Vis Spectrophotometer S2000, England) at \(\lambda_{\text{max}} = 530\) nm, then it was related to the concentration by a calibration curve, which was plotted based on Beer-Lambert’s law. The color removal efficiency (CR\%) at different process time intervals can be obtained by Eq. (1):

\[
CR\% = \left(1 - \frac{C}{C_0}\right) \times 100
\]

where \(C_0\) is initial concentration of BR46 and \(C\) is the concentration of BR46 at a definite time of photocatalytic process.

2.5. Experimental Design

In the present study central composite design, which is a widely used form of response surface methodology (RSM), was employed for modeling and optimization of the photocatalytic degradation process.\textsuperscript{16} In order to evaluate the effect of operating parameters on the photocatalytic degradation efficiency of BR46, three main factors were chosen: initial dye concentration (mg/L) \((X_1)\), initial amount of N-doped TiO\textsubscript{2} nanoparticles (g/L) \((X_2)\) and reaction time (min) \((X_3)\). A total of 20 experiments were employed in this study, including 8 cube points, 6 replications at the center point and 6 axial points. Experimental data were analyzed using Minitab 15 software. For statistical calculations, the independent variables \(X_i\) were coded as \(x_i\) according to the following equation:

\[
x_i = \frac{X_i - X_o}{\delta X}
\]

where \(X_o\) is the value of \(X_i\) at the center point and \(\delta X\) presents the step of change.\textsuperscript{22,23} The experimental ranges and the levels of the independent variables for BR46 removal are demonstrated in Table II.
3. RESULTS AND DISCUSSION

3.1. Central Composite Design Model Development and Validation

The 3-factor CCD matrix and experimental data, which were obtained in the photocatalytic degradation experiments, are presented in Table III. CR% was related to independent variables with a second-order polynomial equation (Eq. (3)):

$$
CR\% = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{23} x_2 x_3 + b_{11} x_1^2 + b_{22} x_2^2 + b_{33} x_3^2
$$

where $b_i$ and $b_k$ are regression coefficients for linear and quadratic effects and $x_i$ is coded amounts of the independent operational variables. Based on the obtained experimental results, the coefficients were estimated and substituted in the above equations:

$$
CR\% = 27.4474 + 5.831 x_1 + 5.044 x_2 - 8.5158 x_3 + 0.6081 x_1x_2 + 0.2140 x_1 x_3 + 1.7620 x_2 x_3 + 0.6971 x_1^2 + 0.5589 x_2^2 + 0.4350 x_3^2
$$

Table III. The 3-factor central composite design matrix and the value of response function (CR %).

<table>
<thead>
<tr>
<th>Run</th>
<th>[BR46], (mg/L)</th>
<th>[TiO2], (g/L)</th>
<th>Time (min)</th>
<th>Experimental</th>
<th>Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>15.70</td>
<td>18.22</td>
</tr>
<tr>
<td>2</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>23.20</td>
<td>19.48</td>
</tr>
<tr>
<td>3</td>
<td>-1</td>
<td>+1</td>
<td>+1</td>
<td>44.77</td>
<td>48.70</td>
</tr>
<tr>
<td>4</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>56.66</td>
<td>51.53</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>28.91</td>
<td>27.45</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>13.08</td>
<td>16.50</td>
</tr>
<tr>
<td>7</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>36.32</td>
<td>38.09</td>
</tr>
<tr>
<td>8</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>35.56</td>
<td>33.65</td>
</tr>
<tr>
<td>9</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>15.80</td>
<td>9.92</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>27.33</td>
<td>27.45</td>
</tr>
<tr>
<td>11</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>28.99</td>
<td>28.94</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>+2</td>
<td>0</td>
<td>38.15</td>
<td>36.68</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>26.38</td>
<td>27.45</td>
</tr>
<tr>
<td>14</td>
<td>+2</td>
<td>0</td>
<td>0</td>
<td>10.37</td>
<td>17.46</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>25.52</td>
<td>27.45</td>
</tr>
<tr>
<td>16</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>27.59</td>
<td>27.45</td>
</tr>
<tr>
<td>17</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>26.99</td>
<td>27.45</td>
</tr>
<tr>
<td>18</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>34.08</td>
<td>36.76</td>
</tr>
<tr>
<td>19</td>
<td>0</td>
<td>0</td>
<td>+2</td>
<td>42.10</td>
<td>41.54</td>
</tr>
<tr>
<td>20</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>25.94</td>
<td>21.30</td>
</tr>
</tbody>
</table>

3.2. CCD Model Validation and Residuals Analysis

The square of correlation coefficient ($R^2$) quantitatively evaluates the correlation between the experimental data and the predicted responses. Experimental results and the predicted values calculated by the models (Eq. (4)) were reported in Table III. The predicted values match the experimental values reasonably with $R^2$ of 0.916. The obtained $R^2$ value suggests good adjustments to the experimental results since this indicates that 91.60% of the variability in the response can be explained by the model.

The adequacy of the model was also evaluated by the residuals (difference between the observed and the predicted response values). Residuals are thought as elements of variation unexplained by the fitted model and hence, it is expected that they occur according to a normal distribution. Normal probability plots are a suitable graphical method for judging the normality of the residuals. The observed residuals are plotted against the expected values, given by a normal distribution (see Fig. 4). The residuals from the analysis should be normally distributed. The normal probability plot of the residuals should roughly follow a straight line. Trends observed in Figure 4, reveal reasonably well-behaved residuals.

3.3. Analysis of Variance

Table IV indicates the results of the quadratic response surface model fitting in the form of analysis of variance (ANOVA). ANOVA is required to test the adequacy of the model. ANOVA subdivides the total variation of the results in two components: variation associated with the model and variation associated with the experimental error, showing whether the variation from the model is significant or not when compared with the ones associated with residual error. This comparison is performed by $F$-value, which is the ratio between the mean square of the model and the residual error. If the model is a good predictor of the experimental results, $F$-value should be greater than the tabulated value of $F$-distribution for a certain number of degrees of freedom in the model at a level of significance $\alpha$. $F$-value obtained, 12.06, is clearly greater than the tabulated $F$ (3.02 at 95% significance) confirming the adequacy of the model. The Student’s $t$ distribution and the corresponding values, along with the parameter estimate, are given in Table V. The $P$-values were used as a tool to check the significance of each coefficient, which in turn, are necessary to understand the pattern of the mutual interactions between the test variables. The larger the magnitude of the Student’s $t$-test and smaller $P$-value, the more significant is the corresponding coefficient.
Fig. 4. Residual plots for photocatalytic destruction efficiency of BR46.

Table IV. Analysis of variance (ANOVA) for fit of decolorization efficiency from central composite design.

<table>
<thead>
<tr>
<th>Source of variations</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Adjusted mean square</th>
<th>( F )-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>2209.68</td>
<td>9</td>
<td>245.520</td>
<td>12.06</td>
</tr>
<tr>
<td>Residuals</td>
<td>203.64</td>
<td>10</td>
<td>20.364</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>2413.31</td>
<td>19</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ R^2 = 0.916. \]

3.4. Effect of Variables as Response Surface and Counter Plots on Photocatalytic Process

In order to gain insight about the effect of variables on photocatalytic decolorization process using N-doped TiO\(_2\) nanoparticles, three dimensional (3D) and contour (2D) plots for the predicted responses were depicted, based on the polynomial function model to analyze the change of the response.

In Figure 7, the response surface and contour plots were developed as a function of initial dye concentration and reaction time while initial amount of N-TiO\(_2\) nanoparticles was kept constant at 0.4 g/L, which was the central level. As can be seen in Figure 7, color removal efficiency decreased with increasing initial dye concentration. This can be attributed to several factors. At high dye concentration, the adsorbed dye molecules may occupy all the active

Fig. 5. DRS spectra of undoped TiO\(_2\) and treated TiO\(_2\) with urea at 400 °C.
sites of TiO$_2$ surface and this leads to decrease in decolorization efficiency. However, the formation of ‘OH and O$_2$$^-$$^-$ on the catalyst surface remains constant for a given light intensity, catalyst amount and duration of irradiation. Hence, the available ‘OH and O$_2$$^-$$^-$ are inadequate for the degradation of the dye at high concentrations. Consequently, the color removal efficiency decreases as the dye concentration increases.$^{27,28}$ In addition an increase in the dye concentration can lead to the generation of more intermediates, which may adsorb on the surface of the catalyst. Slow diffusion of the generated intermediates from the catalyst surface can result in the deactivation of active sites of the photocatalyst and consequently, a reduction in the color removal efficiency.$^{26,27}$ Another reason may be due to the absorption of light by the dye molecules, which is called as inner filtration effect, leading to a less availability of photons for hydroxyl radical generation on the surface of TiO$_2$. $^{29,30}$

The effect of the initial amount of N-TiO$_2$ nanoparticles on the BR46 removal was studied as shown in Figure 8. The experiments were carried out with initial amount of N-TiO$_2$ nanoparticles varying from 0.2 to 0.6 g/L and different initial dye concentrations at constant time of 270 min. As can be seen in the Figure 8, photocatalytic decolorization efficiency increased slightly with an increase in the initial amount of initial N-TiO$_2$. This is reasonable, because as the initial amount of N-TiO$_2$ nanopar-
Nitrogen Doping of Commercial TiO$_2$ Nanoparticles for Enhanced Photocatalytic Degradation of Dye Under Visible Light... 

Fig. 9. The response surface and contour plots of the decolorization efficiency (%) as the function of initial N-TiO$_2$ concentration (mg/L) and reaction time (min).

color particles is enhanced, more ‘OH and O$_2^-$ are available to attack the dye, and the efficiency of degradation reaction improved.$^{1,27}$

To study the interaction effect of initial amount of N-TiO$_2$ nanoparticles and irradiation time on color removal efficiency, the experiments were carried out with irradiation time varying from 90 to 450 min and different initial amount of N-TiO$_2$ nanoparticles with constant initial BR46 concentration of 15 mg/L. The results showed that the color removal efficiency enhanced with an increase in the irradiation time (Fig. 9). The presumed reason is that when the irradiation time is increased, more and more OH and O$_2^-$ are available to attack the dye.

4. CONCLUSIONS

Nitrogen doped TiO$_2$ (N-TiO$_2$) catalyst was successfully synthesized by mechanical mixing of urea with commercial TiO$_2$ nanopowders. The N-doped TiO$_2$ nanoparticles showed higher photocatalytic activity than undoped TiO$_2$ in decolorization of BR46 solution under visible light irradiation. The effect of operational parameters on photocatalytic activity of N-doped TiO$_2$ nanoparticles in decolorization of BR46 solution was studied with central composite design. The results indicated that the color removal efficiency was obviously affected by the initial BR46 concentration, initial amount of N-doped TiO$_2$, and reaction time. Analysis of variance showed a high coefficient of determination value ($R^2 = 0.916$), ensuring a satisfactory adjustment of the second-order regression model with the experimental data.

Acknowledgment: The authors wish to thank University of Tabriz and University of Urmia for all the supports provided.

References and Notes