A study on the optimization of photocatalytic removal of enrofloxacin using TiO$_2$ material

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Abstract: Nowadays, antibiotics are used with increasing frequency to meet the needs of human life. The excretion of humans and animals in the livestock industry into the environment generates emerging pollutants with a potential high risk for cancer, antibiotic resistance, and ecological imbalance. Among strategy for antibiotic removal, advanced oxidation processes such as photocatalysis using TiO$_2$ material is a promising technology. This study is aimed to optimize the operational factors for removing enrofloxacin from water using TiO$_2$ photocatalyst under UV-A irradiation. The experiments were designed with 30 experiments and 6 center repetitions to test the effects of initial enrofloxacin concentration, catalyst dosage, reaction time, and solution pH on the treatment performance. An optimal condition was found at the catalytic dosage of 1.081 g/L, the initial enrofloxacin concentration of 21.405 mg/L, pH 5.946, and the reaction time of 120 min. Under these conditions, the enrofloxacin was almost eliminated. It can be concluded that the photocatalysis with TiO$_2$ is fully capable of thoroughly treating enrofloxacin in water.

Keywords: antibiotics, optimization, enrofloxacin, photocatalysis, wastewater treatment

1. Introduction

The advent along with the development and use of antibiotics in life for both humans and animals has significantly reduced mortality and morbidity rates of society and the epidemiology of infectious diseases dangerous such as tuberculosis, gonorrhea, and syphilis. The effect it gives to mankind has an extremely great significance. However, the miracles of these drugs present a potential threat by the emergence, proliferation, and existence of antibiotic resistance. Antibiotics and their products have become one of the new pollutants in the environment for more than two decades. The current reports show that antibiotics are present everywhere in the environment, especially in water, and their concentration is increasing. Antibiotics are released into the environment mainly by human activities in medicine, drug production, animal husbandry, cultivation, and aquaculture [1, 2]. They exist in plant systems that treat wastewater, seawater, surface water, soil, and sediment. Centralized wastewater treatment systems, municipal wastewater treatment plants, and hospitals are hot spots and sources of antibiotic residue emissions into the natural environment. Furthermore, antibiotic excretion products may form compounds that are more toxic than their primary precursors [3, 4].
Enrofloxacin (ENR) is an antibiotic of the fluoroquinolones group with a structural formula of \( \text{C}_{18}\text{H}_{22}\text{FN}_3\text{O}_3 \). It has bactericidal action and has a broad spectrum of inhibition on both gram-positive and negative bacteria. It is commonly used to treat respiratory tract infections and gut bacteria in veterinary medicine [5]. ENR concentrations fluctuate around several dozen ppb in water [6]. Its stable existence in the environment, especially its strong adsorption capacity into the soil, contributes to the impact on the environment, people, and ecosystems even at low concentrations [7]. They are used extensively in high doses but these properties make their detection in wastewater samples limited. A report by Chau et al., 38.2% of surface water samples in the Mekong River contained ENR with an average concentration of 12 ng/L [8].

The conventional treatment methods such as adsorption, membrane filtration, or biological treatment still have many disadvantages in terms of cost and secondary wastes for hard-biodegradable pollutants. Advanced oxidation processes (AOPs) are efficient treatments with the ability to oxidize and mineralize almost all persistent organic compounds including ENR thanks to strong oxidizing radicals [9, 10]. Photocatalysis is one of the AOP methods that are capable of effectively handling low-concentration pollutants when using suitable photocatalysts under irradiation conditions. Semiconductor materials with an appropriate bandgap energy level are often used as photocatalysts. Among them, TiO\(_2\) has been commercialized with commercial products such as P25 and ST01.

Research on treating ENR in water by photocatalysis using TiO\(_2\) material has been conducted by several scientists around the world [11-16]. However, these reports only focus on the synthesis of new materials and evaluate the effect on ENR treatment efficiency when changing individual operating parameters or considering them as constants without a comprehensive assessment of their impact. Design of experiment (DoE) can assess whether the model is in line with reality or not, and at the same time determine the optimal conditions, reducing research time and costs thoroughly. Faced with serious antibiotic residue problems, the use of DoE software is necessary to change conventional research methods (the study of single factors or one factor at a time) to the application of treatment methods. This study aims to evaluate the simultaneous effects of four factors (i.e., pH, catalyst dose, initial ENR concentration, and reaction time) on the ENR treatment efficiency by batch photocatalytic model. First, the effects of the individual factors were investigated. DoE software was then operated to find out the optimal parameters. This study not only provides information to predict and optimize ENR treatment by photocatalytic method using TiO\(_2\) but also a promising option in the treatment of emerging environmental pollutants - antibiotics.

2. Experiments

2.1. Materials
ENR (\( \text{C}_{18}\text{H}_{22}\text{FN}_3\text{O}_3 \)) was imported from Zhejiang Goubang Pharmaceutical Co., Ltd (Zhejiang, China) with over 99% purity. TiO\(_2\) nanomaterials (Degussa P25) manufactured by Merck (Germany) have the combined anatase and rutile crystal structure with particle size from 10 – 30 nm. Other chemicals used in this study were purchased by Country Medicine Reagent Co. (China). Distilled water was distilled from Environmental Analysis Laboratory, Ho Chi Minh City University of Technology (Vietnam).

2.2. Preliminary experiment
The degradation experiment was conducted in a research model (Figure 1), consisting of a 2-L transparent cylindrical tube with a UVA lamp (highest intensity at \( \lambda = 365 \text{ nm} \), 8W, Panasonic, Japan) placed on the magnetic stirrer. In the beginning, ENR concentration was chosen at 50 mg/L and P25 dosage was at 0.5 g/L. The solution pH with a range of 5.0 – 7.5 was adjusted with HCl and NaOH solution. Other parameters were then ranged in 0.25 - 2 g/L of TiO\(_2\), 0 – 150 min of reaction time, and 10 – 50 mg/L of ENR. The water sample was taken every 30 min, centrifuged at 60,000 rpm, and filtered through two layers of filter paper to remove nanoparticles. The residue concentration of ENR after treatment was determined by a UV-Vis spectrophotometer (UV - Vis 6100, Germany) at its characteristic absorption band of 320 nm. All photocatalytic experiments were repeated 3 times to check for repeatability and error.
Figure 1 Schematic diagram of photocatalyst reaction device.

The relationship between the input pollutant concentrations and the treatment efficiency is usually described by the pseudo-first-order kinetics (2). At the same time, the heterogeneous photocatalytic process is often described by the Langmuir-Hinshelwood (L-H) (3) equation. These are two equations widely used to describe the photocatalytic degradation process.

\[
\ln\left(\frac{C_t}{C_0}\right) = -k_{obs} \times t \tag{2}
\]

\[
\frac{1}{k_{obs}} = \frac{1}{K_C} \times K_{L-H} + \frac{C_0}{K_C} \tag{3}
\]

Where \(k_{obs}\) is the degradation rate constant ENR (1/min) in linear first-order and \(C_0\) is the initial concentration of ENR (mg/L). \(K_C\) refers to the surface reaction rate constant (mg/L.min) and \(K_{L-H}\) represents the adsorption equilibrium constant according to the L-H model (L/mg).

2.3. Design of experiment

After preliminary experiments to investigate the individual effects of factors (i.e., pH, ENR concentration, a dose of TiO₂, and reaction time), optimization experiments were conducted to find the optimal conditions with the help of a DoE software (Design Expert 11, Stat-Ease Inc.). Factors of pH, ENR concentration, a dose of TiO₂, and reaction time are the independent variables while ENR treating performance is the response variable. The scope and degree of independence of the variables are described in Table 1.
Table 1 Experimental range and level of independence variables for ENR degradation

| Independent variables (encode) | Unit | Range and level |
|-------------------------------|------|-----------------|
| TiO₂ dose (x₁)                | g/L  | -α -1 0 +1 +α   |
| ENR initial concentration (x₂) | mg/L | 15 20 30 40 45  |
| pH (x₃)                       | -    | 5.5 5.5 6 6.5 6.75 |
| Reaction time (x₄)            | min  | 75 90 120 150 165 |

In this study, 30 experiments were performed. All the experiments were performed at 5 levels (-α, -1, 0, +1, + α). They include 16 fully planned experiments, 6 repeated experiments at the center to evaluate errors, and 8 additional experiments a distance α from the center. An empirical quadratic model for the four parameters is represented in the form of Equation 4:

\[ Y = \beta_0 + \sum_{i=1}^{4} \beta_i X_i + \sum_{i=1}^{4} \beta_{ii} X_i^2 + \sum_{i=1}^{4} \sum_{j=i+1}^{4} \beta_{ij} X_i X_j \]  

Where Y is the performance of the ENR treatment over time and \( \beta_0 \) is the zero-order regression coefficient. \( X_i \) is the ith degree of variation affecting the target function Y and \( \beta_i \) is the first order regression coefficient describing the effect of the factor \( X_i \) with Y. \( \beta_{ii} \) is the interactive regression coefficient describing the effect of factor \( X_i \) with Y and \( \beta_{ij} \) is the interaction regression coefficient describing the simultaneous effects of factors \( X_i \) and \( X_j \) with Y.

2.4. Statistical analysis
The model and regression equation were checked for the relevance of the experiment by analyzing the variance (ANOVA) of the model and the lack of conformity (Lack of fit). If the \( p_{value} < 0.05 \) and the Lack of fit coefficient > 0.05, the new model is suitable. The larger the Lack of fit value, the greater the suitability of the model. Finally, the analysis at the optimization point with the pH conditions, initial ENR concentration, TiO₂ dose, reaction time was performed and the results were compared with predicted results to check the accuracy of the predicted model.

3. Results and discussion
3.1. Preliminary studies
To investigate the effect of pH on the process of removing ENR by P25, the pH value was changed in the range of 5 - 7.5. The initial ENR concentration and P25 were 50 mg/L and 0.5 g/L, respectively. After 150 min of irradiation, the experimental results from adjusted pH condition are displayed in Figure 2, where there results from original pH (pH 6.53) is also provided for comparison purpose. Generally, ENR was more effectively treated under the weak acid conditions than under the neutral and weak alkaline levels. The best pH value for the photocatalytic decomposition of ENR is 6. After 150 min of UVA irradiation, the ENR removal efficiency was up to 82.54% at pH 6, while decreasing to two margins at the same time, pH 5 and 7.5. However, performance drops more rapidly in weakly acidic condition and more slowly in alkaline condition. The effect of solution pH on treatment efficiency is a complex process, it involves the ionization state of the catalytic material surface, the formation of free radicals, and heterogeneous reactions in the system. Accordingly, at pH < 6, the catalytic surface of P25 is positively charged. ENR usually present as cations below pKa₁ and anions above pKₐ₂. Here, it is not clear that the ENR removal effect is based on both the ionization state of the catalyst and the substrate since they both exist in the form of cations and anions under acidic or alkaline conditions. The highest ENR removal efficiency at pH 6 can be explained by adsorption onto the surface of the TiO₂ nanoparticles or the negatively charged post-mineralization products of ENR, resulting in an electrostatic interaction between them.
Figure 2 Effect of pH on the degradation rate of ENR

At pH 6, the dose of TiO$_2$ was adjusted ranging from 0.25 – 2 g/L to investigate its effect on the ENR treatment. The ENR removal efficiency is illustrated in Figure 3 for 150 min of irradiation. Overall, the treatment efficiency increased with an increasing dose of TiO$_2$ in the solution, from 38.37% to 86.74% with an increasing dosage from 0.25 to 1 g/L. Then it began to decrease to 74.03% as the dose of TiO$_2$ continued to increase from 1 to 2 g/L. This is likely due to the high concentration of the catalyst that increases light scattering, hindering light exposure to the pollutants [17]. At the same time, high concentrations lead to an increase in the combination and deposition of TiO$_2$ particles [18, 19], so the treatment efficiency was reduced. Often, testing to find the right dose of catalyst is an important step in avoiding excess or insufficient material to handle contaminants. In this study, the dose of the catalyst was selected at 1 g/L for the next step. Obviously, at a dosage of 1 g/L, ENR treatment efficiency is the highest value and it was stable over time. At the same time, this value is relatively appropriate in the case of real wastewater. The concentration of ENR found in practice is often very low, but the impact of other parameters may be significant. Therefore, the appropriate dosage of TiO$_2$ is 1 g/L when applying this method in practice. For real wastewater, the dose of the catalyst should be increased because of the influence of many other factors such as the presence of other organic substances, anions (e.g., chloride, sulfate, phosphate), and turbidity that reduce the light density in the wastewater.

Figure 3 Effect of dosage TiO$_2$ on the degradation rate of ENR
The results obtained from the kinetic models are provided in Table 2 and Figure 4. The correlation coefficient ($R^2$) for the regression line was 0.9539. Thus, the kinetics of the ENR removal reaction follows the L–H model. The increase in ENR initial concentration leads to increased photon absorption. The number of photons used by TiO$_2$ is reduced, resulting in a lack of photons on the TiO$_2$ active surface. At the same time, the high concentration of ENR occupies a larger number of TiO$_2$ positions, which prevents the formation of free oxidizing radicals and results in a reduced treatment efficiency [11]. The degradation rates are different for each different ENR concentration. However, the correlation coefficient $R^2$ of the first-order linear equations are all high for all investigated concentration ranges, proving the reliability of this equation.

### Table 2 Pseudo-first-order linear and the $k_{obs}$ values for the different initial concentrations of ENR.

| $C_0$ (mg/L) | $k_{obs}$ (1.min$^{-1}$) | $R^2$ | Straight - line equation |
|--------------|-------------------------|-------|--------------------------|
| 10           | 0.0336                  | 0.925 | $Y = 0.0336x + 0.5077$   |
| 20           | 0.0213                  | 0.9449| $Y = 0.0213x + 1.3827$   |
| 30           | 0.0249                  | 0.982 | $Y = 0.0249x + 1.0318$   |
| 40           | 0.0109                  | 0.9832| $Y = 0.0109x + 1.1202$   |
| 50           | 0.0088                  | 0.9753| $Y = 0.0088x + 0.9639$   |

**Figure 4** Variation of reciprocal of constant rate versus different initial concentrations of ENR.

### 3.2. Model fitting and statistical analysis

The preliminary assessment studies of every single factor provide information to choose central values for optimizing the model in the next research period. A goal design with 30 experiments with 6 concentric iterations to test the effect of factors (i.e., initial ENR concentration, catalyst dose, pH, and the reaction time) under UV irradiation. The experimental center values given are based on conclusions from the previous evaluation of each specific parameter. Experimental results are described in Table 3.
### Table 3 Experimental results

| STT | Catalyst dose \((X_1)\) | Initial ENR concentration \((X_2)\) | \(C_0\) (mg/L) | pH \((X_3)\) | Reaction time \((X_4)\) | Efficiency (Y) |
|-----|-----------------|-----------------|-------------|--------|-----------------|---------------|
| 1   | 1               | 30              | 6           | -      | 165             | 99.89         |
| 2   | 1               | 30              | 6           | -      | 120             | 99.45         |
| 3   | 1               | 30              | 6           | -      | 120             | 99.76         |
| 4   | 1.5             | 20              | 5.5         | -      | 150             | 99.98         |
| 5   | 1.5             | 20              | 6.5         | -      | 90              | 98.99         |
| 6   | 1               | 45              | 6           | -      | 120             | 98.52         |
| 7   | 1.5             | 20              | 5.5         | -      | 90              | 99.91         |
| 8   | 1               | 15              | 6           | -      | 120             | 99.75         |
| 9   | 1.5             | 40              | 6.5         | -      | 150             | 98.74         |
| 10  | 1.5             | 40              | 5.5         | -      | 150             | 99.67         |
| 11  | 0.5             | 20              | 5.5         | -      | 150             | 99.49         |
| 12  | 1               | 30              | 6           | -      | 75              | 99.30         |
| 13  | 0.5             | 20              | 5.5         | -      | 90              | 99.26         |
| 14  | 1.5             | 20              | 6.5         | -      | 150             | 100.00        |
| 15  | 1               | 30              | 6           | -      | 120             | 99.72         |
| 16  | 0.5             | 20              | 6.5         | -      | 90              | 98.30         |
| 17  | 1.5             | 40              | 6.5         | -      | 90              | 98.49         |
| 18  | 1               | 30              | 6           | -      | 120             | 99.79         |
| 19  | 0.5             | 20              | 6.5         | -      | 150             | 99.24         |
| 20  | 1               | 30              | 6           | -      | 120             | 99.59         |
| 21  | 1               | 30              | 6.75        | -      | 120             | 96.27         |
| 22  | 0.5             | 40              | 6.5         | -      | 150             | 95.39         |
| 23  | 0.5             | 40              | 5.5         | -      | 90              | 97.56         |
| 24  | 0.25            | 30              | 6           | -      | 120             | 90.89         |
| 25  | 0.5             | 40              | 6.5         | -      | 90              | 95.19         |
| 26  | 1               | 30              | 5.25        | -      | 120             | 99.93         |
| 27  | 1               | 30              | 6           | -      | 120             | 99.77         |
| 28  | 1.75            | 30              | 6           | -      | 120             | 99.44         |
The empirical quadratic polynomial model is more consistent with reality. Therefore, the factors affecting the objective function is showed.

Table 4 ANOVA analysis results for quadratic model multivariate

| Source          | Sum of squares | df. | Mean squares | F values | P values |
|-----------------|----------------|-----|--------------|----------|----------|
| Model           | 85.73          | 14  | 6.12         | 3.74     | 0.008    |
| Residual        | 24.54          | 15  | 1.64         | -        | -        |
| Lack of fit     | 24.45          | 10  | 2.45         | 138.71   | <0.0001  |
| Pure error      | 0.0881         | 5   | 0.0176       | -        | -        |
| Total           | 110.27         | 29  | -            | -        | -        |

\[ R^2 = 0.7775 \]

To provide more insight into the ENR decomposition with TiO2 the experiments have been randomized, a quadratic multivariate equation includes variables of catalytic dose \(x_1\); initial ENR concentration \(x_2\); pH \(x_3\), and reaction time \(x_4\) is formed. The empirical quadratic polynomial equation is expressed as follows:

\[ Y = 99.23 + 1.24x_1 - 0.691x_2 - 0.7240x_3 + 0.2188x_4 + 0.4615x_1x_2 + 0.2278x_1x_3 - 0.0387x_1x_4 - 0.3197x_2x_3 - 0.0558x_2x_4 + 0.0755x_3x_4 - 1.46x_1^2 + 0.2991x_2^2 - 0.1603x_3^2 + 0.5027x_4^2 \]

In which, the values of the variable of \(x_1\), \(x_2\), and \(x_3\) are significant because of \(p < 0.05\). The case of \(p > 0.05\) means that the model variables have a negligible effect on ENR removal efficiency. In this case, for the period of 65 to 175 minutes of irradiation, it had no significant effect on the ENR removal efficiency. Therefore, the factors affecting the objective function is showed in the other of \(x_1 > x_3 > x_2\). The \(p\) value of the monomial coefficients of the regression model for \(x_1\), \(x_2\), \(x_3\), and \(x_4\) were 0.0005, 0.0272, 0.0216, and 0.0015, respectively (Table 5).

Table 5 Coefficient of the regression model and their significance

| Factor | Coefficient estimate | Degree of freedom | Standard error | F value | 95% CI Low | 95% CI High | p value |
|--------|----------------------|-------------------|----------------|---------|------------|------------|---------|
| Intercept | 99.23               | 1                 | 0.4727         | -       | 98.22      | 100.24     | -       |
| \(x_1\)  | 1.24                 | 1                 | 0.2825         | 19.19   | 0.6353     | 1.84       | 0.0005  |
| \(x_2\)  | -0.691               | 1                 | 0.2825         | 5.98    | -1.29      | -0.0889    | 0.0272  |
| \(x_3\)  | -0.7240              | 1                 | 0.2825         | 6.57    | -1.33      | -0.1219    | 0.0216  |
| $x_4$ | 0.2188 | 1 | 0.2825 | 0.599 | -0.3833 | 0.8209 | 0.4507 |
|-------|--------|---|--------|------|---------|-------|-------|
| $x_1x_2$ | 0.4615 | 1 | 0.3198 | 2.08 | -0.22 | 1.14 | 0.1695 |
| $x_1x_3$ | 0.2278 | 1 | 0.3198 | 0.5076 | -0.4537 | 0.9094 | 0.4871 |
| $x_1x_4$ | -0.0387 | 1 | 0.3198 | 0.0147 | -0.7203 | 0.6428 | 0.9052 |
| $x_2x_3$ | -0.3197 | 1 | 0.3198 | 0.9997 | -1.00 | 0.3618 | 0.3332 |
| $x_2x_4$ | -0.0558 | 1 | 0.3198 | 0.0305 | -0.7374 | 0.6258 | 0.8638 |
| $x_3x_4$ | -0.0755 | 1 | 0.3198 | 0.0557 | -0.6061 | 0.7571 | 0.8165 |
| $x_1^2$ | -1.46 | 1 | 0.3792 | 14.91 | -2.27 | -0.6561 | 0.0015 |
| $x_2^2$ | 0.2991 | 1 | 0.3792 | 0.6223 | -0.5091 | 1.11 | 0.4425 |
| $x_3^2$ | -0.1603 | 1 | 0.3792 | 0.1786 | -0.9685 | 0.6480 | 0.6786 |
| $x_4^2$ | 0.5027 | 1 | 0.3792 | 1.76 | -0.3056 | 1.31 | 0.2048 |

3.3. Response surface analysis

The three-dimensional surface graph model and contour plot describe the response of the independent factors to the output dependent variable through the regression equation. These two graphs generally evaluate the model’s best approach concerning each pair of independent variables affecting the target function. Interaction results between 4 independent variables and the dependent variable are shown in Figure 4. Accordingly, the influence of each pair of independent variables on the dependent objective function is painted in detail through each chart. When changing the values of the independent variables then the target function changes, specifically in each chart form. The catalyst concentration had the largest impact on the ENR treatment efficiency because the significance of the variance analyzed by ANOVA confirmed that the quadratic function is shown in this surface response diagram. It is similar to the reaction time variable. Besides, factors such as pH and pollutant concentration also describe a good response when compared with the study of the individual background factor survey. Specifically, Figure 5a shows the simultaneous effects of the TiO$_2$ dose and the initial ENR concentration. It can be seen that while TiO$_2$ dosage ranges from 0.9 - 1.4 g/L, ENR treatment reached the highest efficiency when the initial ENR concentration was in the range of 20 - 23 mg/L. Similarly, when considering the correlation between TiO$_2$ dose and pH to ENR treatment efficiency, ANOVA analysis results confirmed that the dose of TiO$_2$ had the greatest impact on ENR treatment efficiency. Combined with pH, these two factors drastically impact treatment efficiency. When increasing the pH value in range of 5.5 - 6.3 and TiO$_2$ dosage in range of 0.8 - 1.2 g/L, the treatment efficiency increased, then decreased when continuing to increase TiO$_2$ dosage in range of 1.2 - 1.5 g/L no matter what initial pH value. Increasing the dose of TiO$_2$ beyond the optimal value decreased the treatment efficiency even though the pH was still within the optimal value. This result is consistent with the experimental results. The simultaneous effects of TiO$_2$ dose and UVA irradiation time on the ENR removal efficiency are also described in Figure 5c. In the period from 75 to 165 minutes, the irradiation time did not significantly affect the ENR treatment efficiency. Hence, time-factor surface response plots are represented by lines, as can figure 5c, 5e, and 5f. However, the independent variables such as pH, initial ENR concentration, and catalytic dose influence treatment performance. When the values of those parameters are changed, the response chart types will change accordingly. In the Figure 5e and 5f response plots, the time factor response curves are straight, but the initial changes in pH and ENR concentration lead to performance as it changes accordingly. Through these surface response graphs, one can evaluate the impact of each factor independently on the target
function and provide optimal values for each pair of variables to achieve the optimal value for the research model.
Figure 5 Effects of pH, catalyst concentration (TiO<sub>2</sub> concentration) and ENR initial concentration on the degradation rate of ENR: (1) ENR initial concentration of 30 mg/L, (2) TiO<sub>2</sub> dosage of 1 g/L, and (3) pH 6.

3.4 Optimization and verification of the results

The goal of optimization is to find the optimal value of the variables affecting the model through experimental design and analysis. Previous studies mainly focused on the highest treatment efficiency, but rarely looked at the entire process due to the influence of single factors. This study
looks at all aspects of the impact of operating factors on ENR treatment efficiency. DoE software further filters out non-influencing parameters and finds a higher degree of model fit. ENR treatment efficiency is still the target function for research. After treatment, the pH should reach a neutral value to ensure the discharge into the environment. Pollutant concentrations must be of the lowest value because the ENR concentration in wastewater is only a few dozen ppb. The dose of TiO$_2$ is sufficient to treat the ENR without too much-increasing treatment costs. All the above constraints are combined to determine the optimal value for the model. The quadratic multivariate regression is written as follows:

$$Y = 99.6 + 1.24x_1 - 0.691x_2 - 1.36x_1^2$$  \( (6) \)

The optimal conditions found for this research model are 1.081 gTiO$_2$/L, $C_0$ (ENR) = 21.405 mg/L, pH = 5.946, and 120 min of irradiation time. After six repetitive experiments based on the optimal parameters for the model, the treatment efficiency is from 95 - 100%, the possibility of error due to interference is within the given range allowed (< 5%). This result confirmed once again the ENR treatment efficiency by the photocatalytic method using TiO$_2$ material as well as the appropriateness of the model in practice. However, in some cases, the independent variable without meaning is considered and kept to ensure the model system.

4. Conclusion

The photocatalytic treatment of ENR using TiO$_2$ material has been conducted in the study. It was focusing on the influence of some parameters such as pH, TiO$_2$ dosage, and ENR initial concentration. The multivariate experiment design was used thanks to Design Expert 11 software, to construct a multivariate quadratic equation describing the dependence of treatment performance on independent variables and assessed the importance of each variable. Optimal values of parameters under related bound conditions were at 1.08 gTiO$_2$/L, pH = 5.95, initial ENR concentration of 21.4 mg/L, and 120 min of irradiation time. Under optimal conditions, ENR treatment efficiency reaches almost 100%. The results of this study also show that the surface response analysis method is a useful tool to optimize the ENR treatment conditions and maybe other pollutants by the photocatalytic method using TiO$_2$ material.

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