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# Photocatalytic Elimination of Tetracycline from Wastewater Using Immobilized Titanium Dioxide Coated Glass Under Sunlight

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**ABSTRACT**

The research aimed to investigate the degradation of the tetracycline antibiotic (TC) within wastewater through the application of nanoparticle titanium dioxide ($TiO_2$) supported on glass substrates under solar irradiation. Furthermore, the enhancement of the photocatalytic process utilizing hydrogen peroxide was also examined. Response surface methodology has been employed to evaluate the impact of various operational factors on the efficacy of TC removal. These parameters included the initial concentrations of TC, initial concentrations of hydrogen peroxide, initial concentration of titanium dioxide, contact duration, and pH levels. The results of the investigation indicate that the degradation rate of TC is quantified at 91%, under optimal conditions comprising 75 mg/L of $TiO_2$, a pH of 5, 400 mg/L of $H_2O_2$, and an initial TC concentration of 10 mg/L, exposed to an irradiation duration of 150 minutes. Moreover, the predicted response outcomes generated by the model demonstrate a significant correlation with the empirical data ($R^2 = 0.9$), thereby underscoring the effectiveness of this methodology in producing accurate predictions. A second-order polynomial multiple regression model to assess the performance of immobilized $TiO_2$ in the photocatalytic degradation of antibiotics in wastewater. The model showed a strong fit with the experimental data, indicated by high $R^2$ values ($R^2 = 0.9788$, $R^2adj = 0.9575$, $R^2pred = 0.8657$). The findings highlight the promising potential of using immobilized $TiO_2$ for effective wastewater treatment, particularly for removing antibiotic contaminants, thus suggesting its applicability in environmental remediation efforts.

## 1. INTRODUCTION

Pharmaceuticals present an environmental concern due to their long-lasting presence in the environment, primarily because they are resistant and have very low biodegradability [1, 2]. Pharmaceuticals are commonly used to enhance animal health as well as in agriculture. Antibiotics, in particular, are frequently detected in environments due to their extensive use in veterinary and human medicine [3, 4].

These Pharmaceuticals are found in various water sources, including drinking water and wastewater [5, 6]. At low levels, they can have adverse effects on living organisms and the environment [7]. The continuous release of pharmaceuticals into ecosystems poses a threat to life, like fish, as these products can accumulate in high concentrations within their bodies [8].

Amoxicillin, ciprofloxacin, and tetracycline are among the most commonly used antibiotics to treat infections. Tetracyclines (TCs) represent approximately 29% of the total antibiotic consumption in human and veterinary medicine [8-10]. Following treatment, more than 70% of TC is excreted unchanged into the environment (Figure 1) [11, 12].

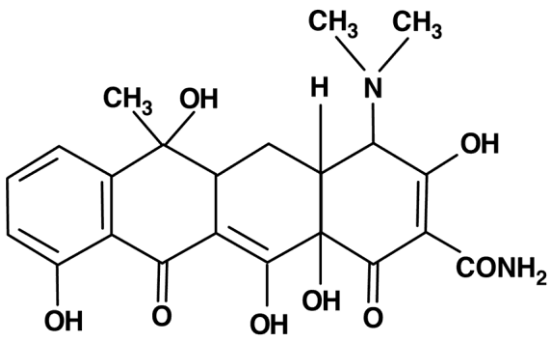


**Figure 1.** Molecular structure of tetracycline

Many traditional wastewater treatment techniques, including biological processes, flocculation, filtration, coagulation, and sedimentation, are often insufficient for the

complete removal of pharmaceutical contaminants [2, 13]. Consequently, advanced oxidation processes (AOPs) such as oxidation, ozonation, Fenton's reagent, and semiconductor catalytic oxidation have attracted considerable interest. These methods are effective at degrading organic pollutants by generating highly reactive species, like hydroxyl radicals, within the treatment environment.

Among AOPs, heterogeneous photocatalysis utilizing titanium dioxide ($TiO_2$) and ZnO as photo-catalysts demonstrates the most promising potential as a destructive technology. Heterogeneous photocatalysis is a technique that deals with environmental contamination because of its ability to oxidize organic materials [3, 14].

Photocatalysts represent a class of materials that promote the breakdown of water and wastewater pollutants, transforming these contaminants into innocuous compounds such as carbon dioxide and water. A photo-catalyst is defined as a material that can initiate a chemical reaction upon being illuminated by light, all the while remaining chemically unaltered. Among the most widely utilized materials for photocatalytic processes is Titanium dioxide ($TiO_2$) and its derivatives, which are extensively applied in the treatment of water and wastewater [15]. $TiO_2$ is characterized by its cost-effectiveness and non-toxic nature, coupled with its significant and consistent photoactivity [16]. Furthermore, $TiO_2$ possesses positively charged holes that exhibit a relative oxidative capability comparable to chlorine, quantified at (2.35) [17]. A principal benefit of $TiO_2$ is its capacity to generate electron-hole pairs in response to light exposure, enabling the production of hydroxyl radicals through the oxidation of water or hydroxide ions. The incorporation of hydrogen peroxide ($H_2O_2$) further augments this mechanism by facilitating the generation of additional •OH radicals through the subsequent reactions: $H_2O_2 + e^- \rightarrow \bullet OH + OH^-$ and $H_2O_2 + h^+ \rightarrow HO_2\bullet + H^+$.

The two main types of photo-reactors used in heterogeneous photo-catalysis: slurry reactors, which utilize a suspended catalyst, and reactors with an immobilized catalyst. Slurry reactors are noted for their efficiency in degrading pollutants due to their larger surface area. However, they face challenges such as catalyst aggregation, the need for separation from effluents, and environmental risks associated with $TiO_2$ contamination [18, 19]. The separation of the catalyst step also makes the process economically impractical [20].

It is necessary for $TiO_2$ to be immobile on inorganic substances that are chemically stable and are resistant to oxidation [21]. Electrodeposition, sol-gel, Chemical spray pyrolysis, hydrothermal synthesis, atomic layer deposition, and chemical vapor deposition are the most commonly employed methods for preparing immobilized catalysts [22]. The sol-gel method provides a suitable and simple way for synthesizing advanced materials and applying them as surface coatings. Various surfaces have been utilized by researchers to support catalysts, including stainless steel [23], glass slides [22], black sand [24], glass spheres, beads [25], Raschig rings [26], ceramic spheres [27], as well as zeolites. In this study, $TiO_2$ was immobilized on a glass substrate. Glass was selected due to its optical transparency, chemical inertness, affordability, and compatibility with sol-gel coating methods. Furthermore, glass enables uniform $TiO_2$ dispersion and efficient light penetration, enhancing photocatalytic activity [22].

The response surface methodology (RSM) includes a set of statistical and mathematical techniques aimed at fitting a polynomial equation to experimental data, hich facilitates the forecasting of a system's behavior while conserving time and resources as operational conditions fluctuate [28]. The conventional optimization approach typically entails the incremental modification of one variable at a time, holding all other parameters constant. However, this traditional methodology is inadequate for capturing the intricate interactions between variables and responses, as highlighted in the investigation by Darvishmotevalli et al. [29].

This study aims to develop a photocatalytic reactor using immobilized titanium dioxide ($TiO_2$) on glass to effectively eliminate tetracycline (TC) from wastewater under natural sunlight. To optimize pollutant removal, the Box-Behnken Design (BBD) is employed to create mathematical models, facilitating a quantitative evaluation of the advanced oxidation process (AOP). The validity and reliability of these models are confirmed through analysis of variance (ANOVA).

## 2. MATERIALS AND METHODS

Tetracycline hydrochloride, a widely used antibiotic, was obtained from Sigma-Aldrich, a reputable supplier based in Munich, Germany. The compound is characterized by a high purity level exceeding 99%, ensuring its suitability for various applications. The chemical structure of tetracycline is illustrated in Figure 1.

To support the $TiO_2$, titanium tetra-isopropoxide (TTIP) was employed. This particular compound contained 95% anatase and 5% rutile, which are essential components for the desired reaction. Additionally, Isopropanol was used as a supporting substance for the $TiO_2$.

In order to facilitate the chemical reactions, hydrogen peroxide $H_2O_2$ with a concentration of 50% w/w was utilized as an oxidizing agent. This particular compound was sourced from Merck, a trusted supplier in the field.

In terms of the supporting material for the $TiO_2$, the glass was selected due to its numerous advantageous properties, such as local availability and low cost. Furthermore, it possesses chemical inertness, mechanical resistance, and is abundant in various particle sizes, making it an ideal choice for supporting the $TiO_2$.

### 2.1 Experimental work and analysis

The implementation of the sol-gel dip-coating methodology was utilized for the direct immobilization of $TiO_2$ onto glass substrates ($TiO_2$/glass) within the framework of the experimental investigation. To facilitate this process, the glass substrates underwent an extensive cleaning procedure involving the use of tap water, which was subsequently followed by rinsing with distilled water, and then dried at a temperature of 120°C for a period of 2 hours. Upon completion of the drying phase, the glass substrates were subjected to sieving to attain grain sizes within the range of 150 to 180 microns, thereby ensuring size uniformity. To establish the requisite molar ratios of TTIP: isopropanol: water (1:25:10, 2:25:10, 3:25:10, 5:25:10), the corresponding components were meticulously combined utilizing a magnetic stirrer. In order to regulate the hydrolysis rate of TTIP and to avert the occurrence of rapid precipitation, the precursor was incrementally introduced into the isopropanol-water solution at a controlled rate of approximately one drop per second while maintaining continuous stirring. This approach

facilitated gradual hydrolysis and promoted the formation of a homogeneous sol formation.

Afterwards, the glass substrate into a composite mixture to achieve a suitable coating. To improve the coating's integrity, the glass was thermally dried in a muffle furnace at 120°C for two hours. Following this, the temperature was increased to 500°C for an additional hour, after which the glass underwent a controlled cooling phase. This method aimed to enhance the quality and durability of the coating on the glass substrate. The calcination procedure is performed in a muffle furnace, where a sample is heated at a controlled rate of 5°C per minute until reaching a target temperature of 500°C. This temperature is held constant for one hour to ensure proper calcination, after which the sample is allowed to cool down gradually to room temperature within the furnace. The process of immobilizing $TiO_2$ on glass involved a secondary coating phase that increased the thickness of the $TiO_2$ film, leading to improved stability and resilience. Following this, any loose $TiO_2$ particles were removed by rinsing the coated glass with distilled water. This careful procedure ensured that the glass was adequately prepared for subsequent applications [30]. The role of silanol (Si–OH) groups on glass surfaces in the sol-gel dip-coating process. These groups facilitate the effective anchoring and dispersion of $TiO_2$ nanoparticles, which helps to minimize aggregation. As a result, the photocatalytic activity of the coated glass is significantly enhanced, showcasing the importance of surface chemistry in optimizing nanomaterial applications.

### 2.2 Procedure and analysis

The specifications and design considerations of a batch-mode reactor intended for photocatalytic degradation experiments under solar irradiation (refer to Figure 2). Constructed from Pyrex glass, the reactor features a cylindrical shape with a diameter of 12 cm and a height of 10 cm, allowing for a total volume capacity of 1 liter. The photocatalytic degradation experiments were conducted in a batch-mode reactor designed for solar irradiation. This particular geometric configuration was deliberately selected to optimize light penetration and mitigate shadowing effects, thereby ensuring uniform exposure of the $TiO_2$-coated glass surfaces to solar radiation. The reactor was treated with silver nitrate to establish a highly reflective surface for solar energy absorption and incorporated a mirror at the base to enhance reflection.

A systematic approach to preparing various concentrations of tetracycline (TC) solutions, specifically 10, 30, 50, 80, and 100 mg/L, with precise pH adjustments made using diluted HCl or NaOH. The solutions were maintained at ambient temperature before adding $TiO_2$/glass at concentrations of 50, 75, and 100 mg/L. The mixture was then stirred magnetically at 200 rpm for 150 minutes to ensure thorough mixing.. To establish the primary adsorption equilibrium, a time interval of 30 minutes was allocated for the interaction between TC and $TiO_2$/glass in the absence of light, followed by the introduction of $H_2O_2$ (200, 400, and 600 mg/L) prior to the activation of the lamp to commence the reaction. Following the reaction phase, a 10 ml sample was extracted at predetermined intervals for catalyst separation and centrifuged at 200 rpm for 15 minutes. The concentration of TC in each sample was quantified at a wavelength of 278 nm utilizing a Perkin–Elmer UV-Vis Spectrophotometer, model 55 OSE. The results were subsequently calculated employing the following equation:

$$\text{Removal percentage} = \frac{Co - Ce}{Co} \times 100 \quad (1)$$

where, $C_o$ and $C_e$ represent the primary and equilibrium drug concentration (mg/L), respectively.

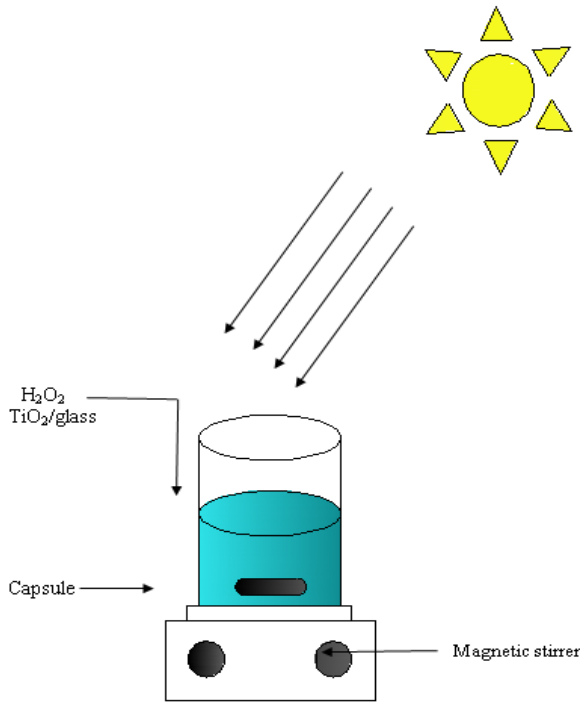


**Figure 2.** Schematic diagram of the batch reactor

### 2.3 Response surface design

The systematic correlation of TC elimination percentages in an adsorption system with various influencing variables is examined. The study employs advanced mathematical statistical methodologies, specifically response surface methodology (RSM), to analyze and model these relationships. By utilizing RSM, the research aims to optimize the adsorption process and enhance the understanding of the factors affecting TC removal efficiency.

The determinants affecting the removal of TC from wastewater were rigorously examined and tracked employing a four-factor, three-level Box–Behnken Design (BBD). The process parameters examined included initial tetracycline concentrations, initial titanium dioxide concentrations, pH levels, contact durations, and initial concentrations of hydrogen peroxide. The response function under consideration was the TC removal ratio, denoted as r1 %.

**Table 1.** Experimental range and levels of independent process parameters for BBD

| Parameters | Units | Symbols | Coded Factor Levels | | |
|---|---|---|---|---|---|
| | | | -1 | 0 | 1 |
| pH | ----- | A | 3 | 5 | 7 |
| TC | mg/L | B | 10 | 50 | 100 |
| $TiO_2$ | mg/L | C | 50 | 75 | 100 |
| $H_2O_2$ | mg/L | D | 200 | 400 | 600 |

The process parameters were standardized into a coding system that represented high levels (1), midpoint levels (0), and low levels (–1). The selected process parameters, along with their respective levels, are detailed in Table 1.

## 3. RESULTS AND DISCUSSION

### 3.1 Response surface and contour plots for the solar photocatalytic TC removal

3.1.1 Initial value of pH

The influence of diverse initial pH levels (specifically, pH levels of 3, 5, and 7) on the efficacy of tetracycline (TC) removal was rigorously examined while ensuring the constancy of all other experimental parameters. These parameters encompassed the concentration of TC (10 mg/L), the concentration of $H_2O_2$ (400 mg/L), and the concentration of $TiO_2$ (75 mg/L). The empirical data acquired from this study were subsequently and systematically charted and visually represented in Figure 3.

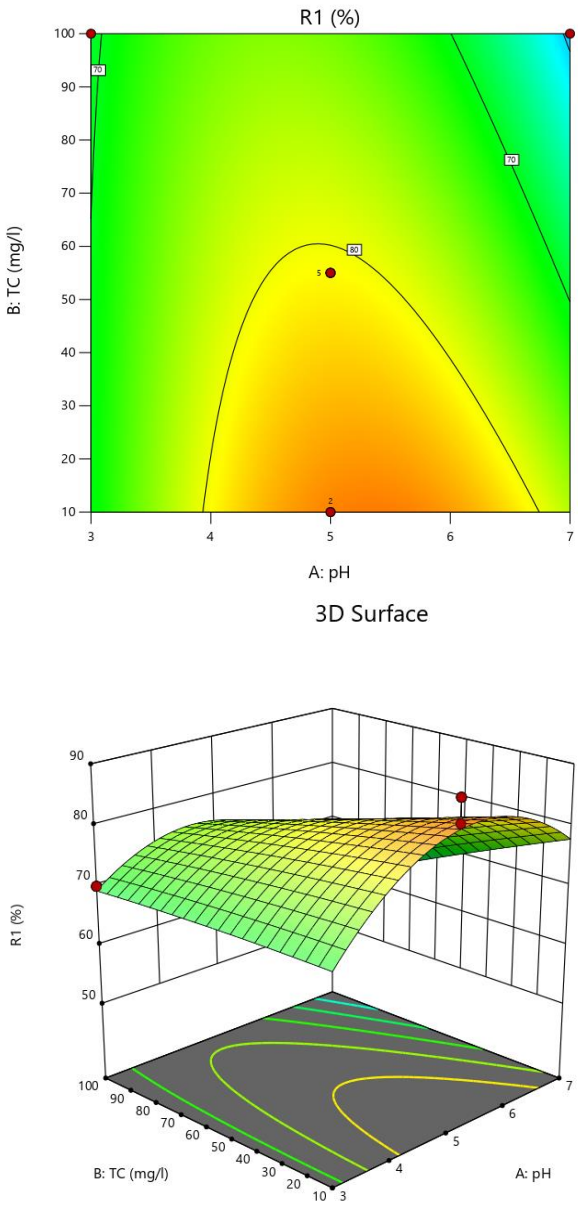


**Figure 3.** 2D and 3D plots of pH on removal efficiency

Upon conducting a thorough analysis of the aforementioned Figure, it becomes apparent that the efficacy of TC removal diminishes when the pH level is excessively low or high. This reduction can be ascribed to the varying ionization states of both the catalyst and the substrate. More specifically, it is significant to highlight that TC possesses a positive charge in acidic conditions, whereas it exhibits a negative charge in alkaline conditions. In contrast, the surface charge of $TiO_2$ shifts from positive to negative. It is pertinent to note that the point of zero charge for $TiO_2$ is documented as 6.8. This information has been sourced from the literature [31]. Moreover, it is imperative to recognize that pH exerts a substantial influence on the electrostatic characteristics of the $TiO_2$ surface during photocatalytic processes. Furthermore, evidence suggests that $TiO_2$ particles are prone to aggregate in aqueous environments, a phenomenon that is modulated by both pH and ionic strength. Specifically, the agglomeration of $TiO_2$ particles is less likely to transpire under acidic conditions in comparison to alkaline conditions.

Moving forward, the increase in the rate of degradation experienced when the pH rises from 3 to 5 can be attributed to two primary factors. Firstly, higher pH levels facilitate the production of hydroxyl radicals to a greater extent, thereby intensifying the degradation process. Secondly, the hydrolysis of the antibiotic TC is also accelerated under such conditions. It is worth mentioning that both TC and $TiO_2$ possess the same charge (specifically, a negative charge) in an alkaline environment as they do in an acidic environment. Consequently, the adsorption process is hindered once again.

Furthermore, the protonation state of TC molecules significantly influences the degradation pathway. At low pH values, TC tends to exist in a fully protonated form, which increases its solubility but may hinder its adsorption on the $TiO_2$ surface due to charge repulsion. At higher pH values, TC exists predominantly in deprotonated (anionic) forms, which may reduce its affinity to the negatively charged $TiO_2$ surface and also alter its susceptibility to hydroxyl radical attack, ultimately affecting degradation efficiency.

These observations are corroborated by the investigation conducted by Tio [31]. Consequently, it can be inferred that the optimal pH level for maximizing TC removal is pH 5. These deductions are in agreement with the results documented by studies [3, 32].

3.1.2 Initial concentration of TC

The research concentrated on investigating the influence of the initial concentration of TC on the efficacy of the photocatalytic process. To thoroughly evaluate this phenomenon, a spectrum of concentrations ranging from 10 to 100 mg/L of TC was examined. The immobilization of $TiO_2$ was held constant at 75 mg/L, while the concentration of hydrogen peroxide was established at 400 mg/L, and the pH was maintained at a consistent level of 5. The results derived from these experimental parameters were subsequently illustrated in Figure 4, offering significant insights into the correlation between the initial concentration of TC and the efficiency of its degradation via photocatalysis. The graph unequivocally indicates a progressive reduction in the efficiency of TC degradation as the initial concentration of TC is elevated from 10 to 100 mg/L. This decrease can be ascribed to the augmented quantity of the antibiotic adsorbed onto the photocatalyst's surface, which arises from the heightened concentration of the antibiotic. As a result, the photoactive sites available on the catalyst surface are diminished, culminating in a reduction in the rate of antibiotic degradation. Furthermore, it was noted that the concentrations of the generated radicals remained stable across all tested samples. Notably, it was observed that samples with lower

concentrations of TC, while possessing an equivalent quantity of hydroxyl radicals, exhibited a greater propensity for removal compared to those samples with a higher concentration of the antibiotic [33, 34].

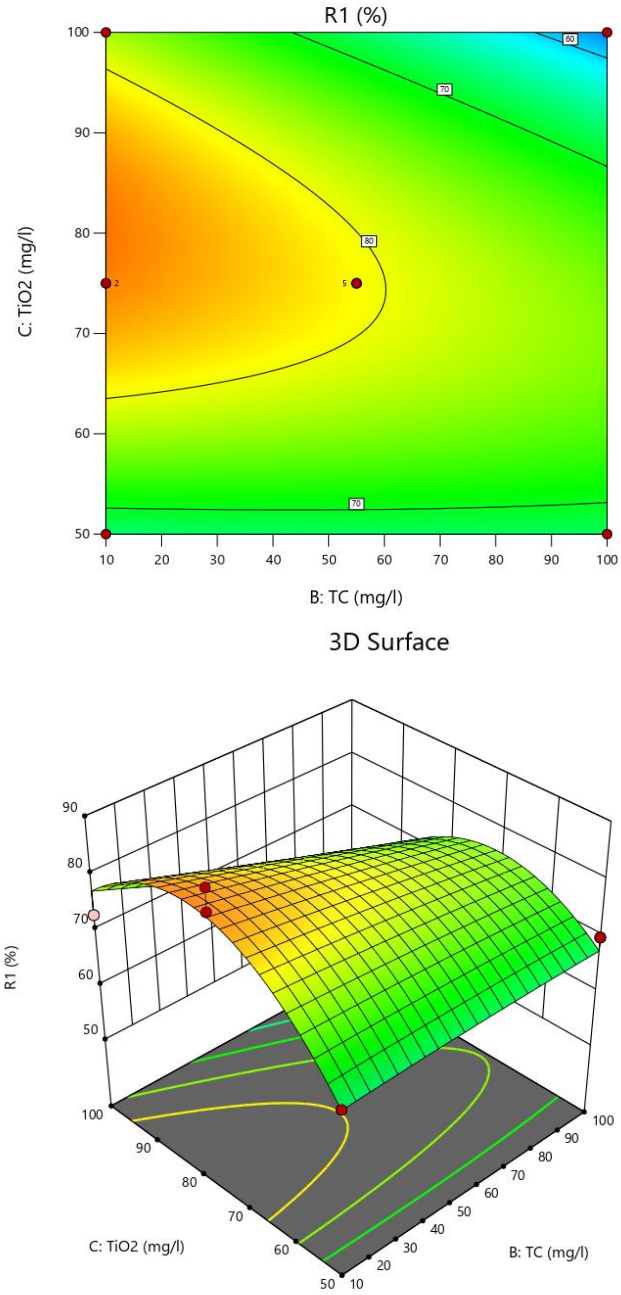


**Figure 4.** 2D and 3D plots of TC concentration on removal efficiency

3.1.3 Effect of the amount of $TiO_2$/glass

The investigation was primarily focused on examining the impact of varying concentrations of $TiO_2$/glass (50, 75, and 100 mg/L) on the removal of TC, while all other experimental parameters were held constant (with TC concentration fixed at 10 mg/L, $H_2O_2$ concentration at 400 mg/L, and a pH value of 5). The results, depicted in Figure 5, indicated that the degradation of TC improved with increasing concentrations of $TiO_2$, peaking at 75 mg/L before showing no further enhancement. Beyond this concentration, the degradation exhibited a decline until reaching 100 mg/L. Nevertheless, the enhancement in antibiotic degradation was not statistically significant when $TiO_2$ concentrations exceeded 100 mg/L. This observed phenomenon may be attributed to reduced light penetration, increased light scattering, or the agglomeration of $TiO_2$/glass [33]. The results suggest that the optimal concentration of $TiO_2$/glass for the degradation of TC in an aqueous environment is 75 mg/L. The observed decline in the mineralization rate at elevated concentrations of $TiO_2$/glass can be attributed to the agglomeration of $TiO_2$ nanoparticles, resulting in a diminished number of active surface sites. Furthermore, this agglomeration leads to enhanced opacity and light scattering of the $TiO_2$ nanoparticles at increased concentrations. As a result, there is a decrease in the quantity of irradiation capable of penetrating the sample [33]. This behavior indicates a strong correlation between the increased film thickness of immobilized $TiO_2$ and the reduction in light penetration depth. As the film becomes thicker, the upper layers of $TiO_2$ can absorb or scatter most of the incoming light, preventing it from reaching the deeper layers where photocatalytic activity is still needed. Such self-shadowing effects diminish the efficiency of the catalyst, even if more $TiO_2$ is present. This qualitative relationship between film thickness and light attenuation was observed experimentally, though it was not quantitatively measured in this study.

It is worth noting that the activation of $TiO_2$ by UV light follows a specific sequence of steps, as outlined by Elmolla and Chaudhuri [3]:

$$TiO_2 + hv \rightarrow TiO_2(e^- + h^+) \quad (2)$$

$$h^+ + H_2O \rightarrow H^+ + {}^*OH \quad (3)$$

$$h^+ + OH^- \rightarrow {}^*OH \quad (4)$$

$$\text{Organics} + {}^*OH \rightarrow \text{Degradation Products} \quad (5)$$

$$e^- + O_2 \rightarrow {}^*O_2^- \quad (6)$$

$$H_2O_2 + e^- \rightarrow {}^*OH + OH^- \quad (7)$$

3.1.4 $H_2O_2$ concentrations

The investigation was conducted to examine the impact of various concentrations of $H_2O_2$ (200, 400, and 600 mg/L) on the removal of TC while keeping other parameters constant. The outcomes of this experiment were graphically represented in Figure 6. The data presented in this figure clearly demonstrate that the efficiency of TC removal witnessed a remarkable increase from 80.96% to 90% when the $H_2O_2$ concentration was raised from 200 to 400 mg/L, respectively. However, it is noteworthy to mention that as the concentration of $H_2O_2$ further increased, the degradation efficiency experienced a decline. The irregular fluctuations observed in this trend can potentially be attributed to the scavenging action of $H_2O_2$, a well-known phenomenon associated with $H_2O_2$ involving advanced oxidation processes (AOPs). It is believed that the local excess of $H_2O_2$ in the system led to the creation of $HO_2^{\bullet}$ (hydroxyperoxyl) radicals, which possess an exceedingly low oxidation potential. This finding is consistent with the equations below, as reported by studies [35-37], respectively:

$$TiO_2(e^-) + H_2O_2 \rightarrow TiO_2 + OH^- + {}^{\bullet}OH \quad (8)$$

$$O^{-2} + H_2O_2 \rightarrow OH^- + {}^{\bullet}OH + O_2 \quad (9)$$

$$H_2O_2 + hv \rightarrow 2OH \quad (10)$$

$$H_2O_2 + \cdot OH \rightarrow HO\cdot_2 + H_2O \quad (11)$$

$$HO\cdot_2 + \cdot OH \rightarrow H_2O + O_2 \quad (12)$$

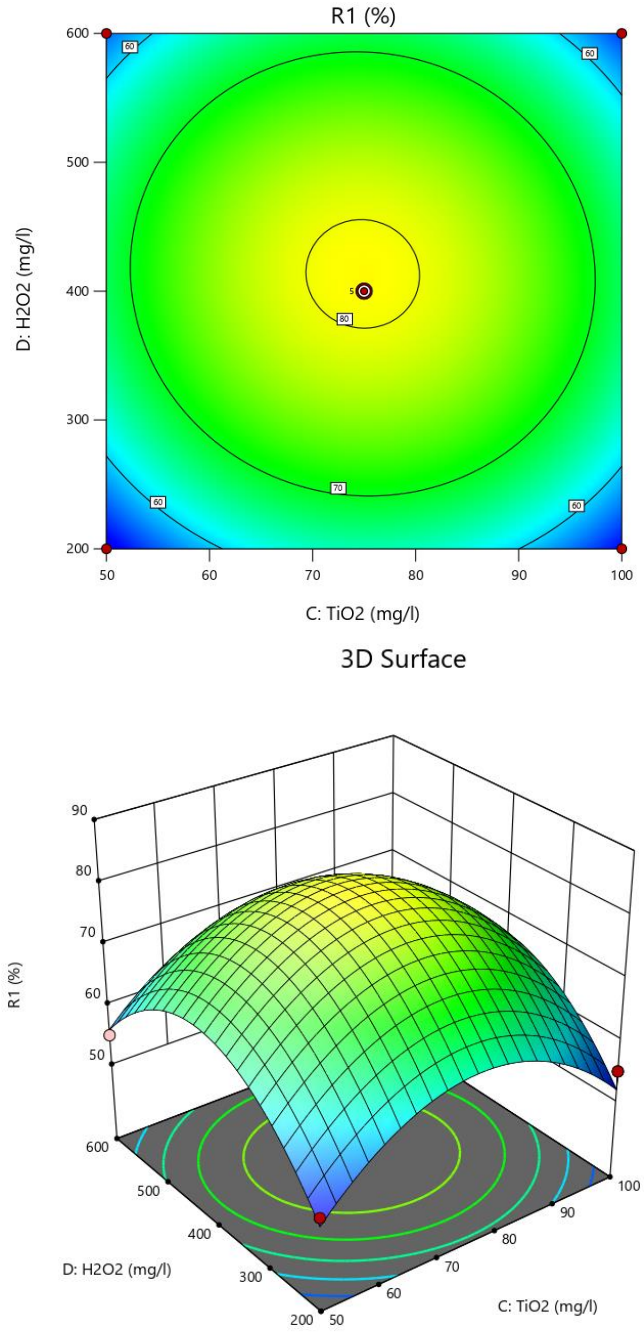


**Figure 5.** 2D and 3D plots of $TiO_2$ levels on removal efficiency

### 3.2 Variance analysis (ANOVA)

The findings derived from the analysis of variance (ANOVA), a statistical method used to compare means, are summarized in Table 2. The analysis of tetracycline (TC) removal demonstrated significant coefficients of determination: $R^2 = 0.9788$, adjusted $R^2$ ($R^2adj$) = 0.9575, and predicted $R^2$ ($R^2pred$) = 0.8657. These values indicate that the independent variables effectively explain the variance in the dependent variable within the regression model. The close alignment of these coefficients suggests a robust relationship between the variables, highlighting the model's effectiveness in capturing their interrelations.

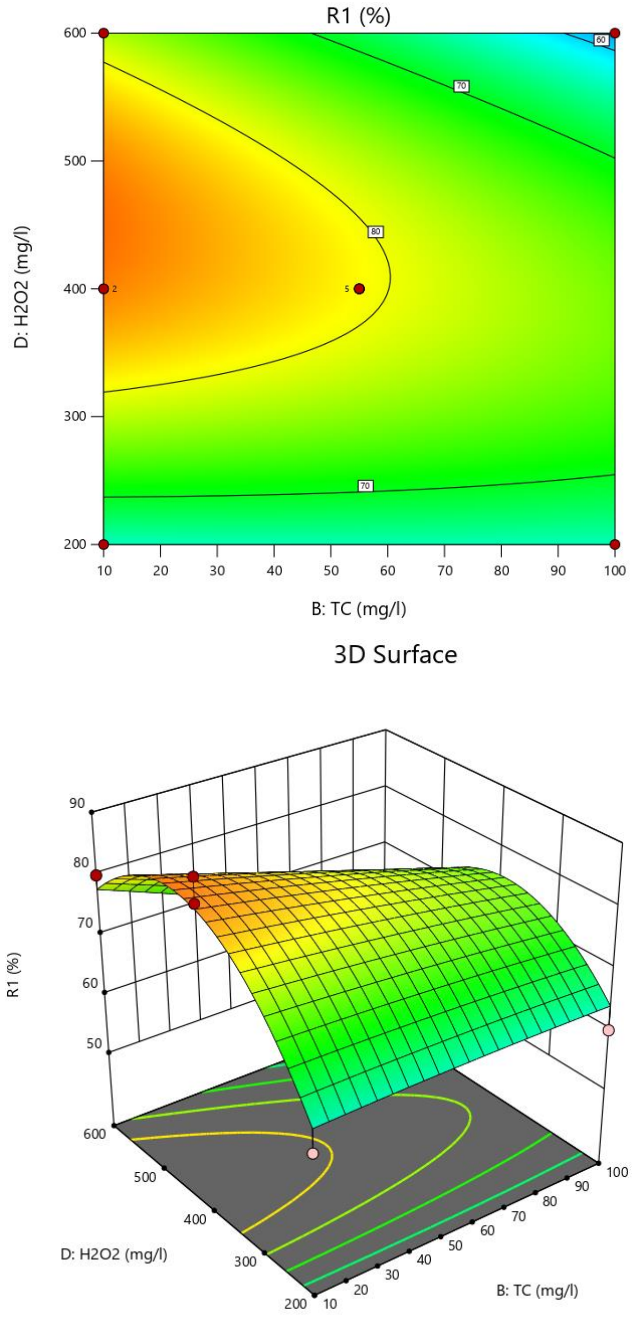


**Figure 6.** 2D and 3D plots of $H_2O_2$ concentration on removal efficiency

To evaluate the significance of the model parameters, both the P-value and F-value were scrutinized. The F-value signifies the ratio of variance between groups to variance within groups, where an elevated value denotes a more substantial association. Conversely, the P-value indicates the likelihood of encountering such an F-value by random chance, with diminished values signifying heightened statistical significance. In the context of this study, the P-value was remarkably low (0.0001), corroborating the substantial significance of the model parameters.

**Table 2.** ANOVA of the response quadratic model for the removal of TC

| Source | Sum of Squares | df | Mean square | F-value | P-value |
|---|---|---|---|---|---|
| Model | 3540.18 | 14 | 252.87 | 46.1 | < 0.0001 |
| A-pH | 3.13 | 1 | 3.13 | 0.5698 | 0.4629 |
| B-TC | 212.3 | 1 | 212.3 | 38.71 | < 0.0001 |
| C-$TiO_2$ | 0.0833 | 1 | 0.0833 | 0.0152 | 0.9037 |
| D-$H_2O_2$ | 33.33 | 1 | 33.33 | 6.08 | 0.0272 |
| AB | 30.63 | 1 | 30.63 | 5.58 | 0.0331 |
| AC | 6.25 | 1 | 6.25 | 1.14 | 0.3038 |
| AD | 0 | 1 | 0 | 0 | 1 |
| BC | 132.25 | 1 | 132.25 | 24.11 | 0.0002 |
| BD | 72.25 | 1 | 72.25 | 13.17 | 0.0027 |
| CD | 2.25 | 1 | 2.25 | 0.4102 | 0.5322 |
| $A^2$ | 667.28 | 1 | 667.28 | 121.66 | < 0.0001 |
| $B^2$ | 4.05 | 1 | 4.05 | 0.7384 | 0.4046 |
| $C^2$ | 1035.2 | 1 | 1035.2 | 188.74 | < 0.0001 |
| $D^2$ | 1370.59 | 1 | 1370.59 | 249.89 | < 0.0001 |
| Residual | 76.79 | 14 | 5.48 | | |
| Lack of Fit | 76.79 | 9 | 8.53 | | |
| Pure Error | 0 | 5 | 0 | | |
| Cor Total | 3616.97 | 28 | | | |

With respect to the model's performance, it was discerned that an escalation in the initial concentration of TC precipitated a diminution in removal efficiency over temporal progression, whereas an augmentation in the catalyst dosage facilitated TC removal. These patterns are in concordance with the model predictions and furnish a lucid elucidation of the experimental data within the evaluated spectrum [38].

Moreover, Table 2 delineates the Adequate Precision ratio, which quantifies the signal-to-noise ratio inherent in the model. The computed value was 19.4593, significantly exceeding the preferred threshold of 4, thereby indicating an adequate signal and affirming the model's reliability and accuracy in delineating the relationship between the variables [29].

## 4. CONCLUSIONS

In the current investigation, response surface methodology (RSM) was employed to optimize and enhance the impact of various experimental factors on the removal efficiency of TC. This was achieved by implementing $TiO_2$ immobilized on sand while utilizing solar irradiation in the photocatalyst process. A remarkably high removal efficiency of TC, amounting to 90%, was successfully attained under the optimal conditions, which included a pH level of 5, the presence of a catalyst $TiO_2$/sand at a concentration of 75 mg/L, an TC concentration of 10 mg/L, as well as an $H_2O_2$ concentration of 400 mg/L, all within a duration of 150 minutes. These conditions were predicted by Box–Behnken design (BBD), and their agreement with the experimental results, which yielded a removal efficiency of 90.12%, was found to be reasonably close. Specifically, the experimental conditions involved a pH level of 5, a TC concentration of 10 mg/L, an $H_2O_2$ concentration of 400 mg/l, and a catalyst $TiO_2$/sand concentration of 75 mg/L, all spanning a time period of 150 minutes. The (ANOVA) analysis revealed the coefficient of determination, denoted as $R^2$, to be equal to 97.88%, while the adjusted $R^2$ ($R^2$adj) and the predicted $R^2$ ($R^2$pred) were calculated as 95.75% and 86.57%, respectively. These results suggest that the third regression model was able to be effectively adjusted to fit the experimental data. This research opens up the possibility of developing modular photocatalytic reactors using immobilized $TiO_2$ on glass for decentralized treatment of farm wastewater, especially in remote areas where traditional treatment facilities are unavailable. However, the use of solar irradiation as an energy source is particularly advantageous in arid and semi-arid regions, where sunlight is abundant and sustainable treatment solutions are required.

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