

Optimized Photocatalytic Degradation of Methylene Blue Using Titaniferous Sand/ZnO Composite: A Sustainable Approach to Wastewater Treatment

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Authors' contributions

This work was carried out in collaboration among all authors. Author EHMD designed the study, performed the statistical analysis, and wrote the first draft of the manuscript. Author MKM managed the information resources. Author MF was commissioned to conduct the analyses of the study. The author BD was responsible for the design of the experimental set-up. All authors have read and approved the final manuscript.

Article Information

DOI: <https://doi.org/10.9734/CSJI/2024/v33i6936>

Open Peer Review History:

This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here:

<https://www.sdiarticle5.com/review-history/127621>

Original Research Article

Received: 01/10/2024

Accepted: 02/12/2024

Published: 07/12/2024

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ABSTRACT

This study explores a novel approach to enhancing photocatalytic efficiency by utilizing an industrial residue, titaniferous sand, in combination with ZnO. The purifying efficiency of this semiconductor mixture was studied for the removal of methylene blue in a fixed-bed reactor. The main objective was to find out with what percentage the titaniferous sand could be incorporated into the ZnO for maximum photocatalytic performance. Box-Behnken Design (BBD) in the Response Surface Methodology (RSM) was used to optimize the operative parameters. The influence of titaniferous sand/ZnO ratio (A:1-2.8), pH (B:4-10) and irradiation time (C:120-480 minutes) on the degradation efficiency of the dye was studied. Initial concentrations of methyl blue and total semiconductor mixture were set at 25 mg/L and 10 g/L, respectively. The ANOVA analysis showed that the photocatalytic process was significantly affected by a positive individual effect of the titaniferous sand/ZnO ratio and the irradiation time. A quadratic polynomial of the second order accurately represented the experimental values with a correlation coefficient R^2 of 0.9921. In addition, this model had a p-value of less than 0.0001 and an F-value of 84.09. Thus, the model used was quite appropriate. Optimal conditions were obtained for a ratio (titaniferous sand/ZnO) of 1.51057, i.e. a titaniferous sand percentage of 66%, a pH of 9.97487 and an irradiation time of 479.765 minutes. Under these conditions, a degradation of 99.4915% was obtained. In addition, the photocatalytic degradation kinetics of methylene blue on the titaniferous sand and ZnO mixture followed the Langmuir-Hinshelwood model and was of the first order with an apparent kinetic constant of 0.402 h^{-1} .

Keywords: *Heterogeneous photocatalysis; methylene blue; titaniferous sand; ZnO; box-behnken design.*

1. INTRODUCTION

While industrialization has contributed economically to the development of countries, it also raises many concerns related to the generation and discharge of large quantities of wastewater. Without any effective treatment of these effluents, various hazardous chemical materials, such as synthetic dyes, can end up in natural water resources [1]. The textile industry, with its intensive use of dyes and chemicals, stands out as a major source of water pollution [2]. Moreover, among all industries, the textile sector is one of the major polluters of surface water. It has been reported that each year, more than 70,000 tons of synthetic dyes are manufactured worldwide and the textile industry consumes more than 10,000 tons [3]. Typically, due to inefficient dyeing techniques, 15–20% of azo dyes, which are not bound to fabrics and fibers, end up in wastewater [4]. The presence of these synthetic dyes in wastewater could lead to significant environmental contamination [5]. Indeed, exposure to some textile dyes, such as azo dyes and their degradation products such as aromatic amines, has been associated with health problems such as skin sensitization, allergic reactions, and even cancer in humans [2]. In addition, these dyes are quite stable and generally resist biodegradation.

The removal of these dyes from the aquatic environment has become a major concern in recent years. Therefore, several treatment techniques have been adopted to address this particular problem, such as coagulation [6,7], flocculation [8], membrane processes [9], chemical oxidation processes [10,11], adsorption [12,13], heterogeneous photocatalysis [14,15] etc. Among all these methods, adsorption has always been the most used process for its ease of implementation and low economic cost. However, it is a non-destructive method and only moves the pollution from one phase to another; which will require additional treatment. Heterogeneous photocatalysis has gained popularity in recent years and is presented as a promising alternative for the treatment of colored effluents. This technique is based on the production of radical entities, which are the most powerful oxidizing species that can be used in the field of water treatment. Hydroxyl radicals can decompose the most toxic and non-biodegradable pollutants into biologically degradable products or mineral compounds [16]. Hydroxyl radicals can be generated by a wide range of semiconductors such as V_2O_5 [17], SnO_2 [18], ZnO [19], TiO_2 [20] etc., by oxidation and reduction reactions initiated by photoinduced positive holes and negative electrons respectively. Titanium dioxide, in its anatase crystallographic form, stands out as the most

studied and widely used semiconductor material due to its exceptional chemical stability, non-toxicity, low cost, and high photosensitivity [20].

In this study, a mixture of titaniferous sand and zinc oxide was used as a new semiconductor material for the removal of methylene blue in aqueous solution by photodegradation. Titaniferous sand, a residue from the zircon industry to be valorized, was composed of several metal dioxides such as TiO₂, ZrO₂, Fe₂O₃, Al₂O₃, MgO and others, whose literature has demonstrated their photocatalytic performances [21]. Moreover, the photocatalytic activity of titaniferous sand as a semi-conductor has been successfully studied for the treatment of pesticide residues [22]. However, for the treatment of colored effluents, titaniferous sand showed a slightly weak performance [23]. For more efficient degradation of dyes, the functionalization of the surface of this material is required. This is possible with the incorporation into the titaniferous sand of ZnO which has photocatalytic properties similar to those of TiO₂ [24]. Furthermore, the use of titaniferous sand and zinc oxide system under ultraviolet radiation for water treatment has not yet gained considerable popularity. The Response Surface methodology according to its Box- Behnken Design was used to study the effect of operating parameters and to optimize the conditions for maximum photocatalytic degradation of the dye. Indeed, the advantage of this statistical method is to reduce the time and effort required to understand the influence of independent variables on the response [25].

2. MATERIALS AND METHODS

2.1 The Pollutant

The pollutant to be treated in this study was methylene blue supplied by Sigma-Aldrich. A 25 mg/L solution, which was used for photodegradation tests, was prepared from the commercial product. The initial pH of the methylene blue solution was adjusted with 0.1 mol/L nitric acid or sodium hydroxide solutions according to the desired pH using a HANNA, HI 223 pH meter.

2.2 Semiconductors

2.2.1 Titaniferous sand

The titaniferous sand used in this study came from a mining industry located in Senegal. It was

metallic black in appearance. The sand had been calcined at 600 °C in a Carbolite -Gero type furnace before undergoing extraction with a molar sulfuric acid solution to remove natural organic matter that could interfere with the analytical parameters. This step was followed by a series of washing with demineralized water and then drying under study at 105 °C. The determination of the physicochemical properties of the titaniferous sand (Table 1) was previously carried out by Ba et al. [23].

An X-ray fluorescence spectrometry characterization was also carried out in previous work by Diop et al. [22], to know the chemical elements composition of the titaniferous sand (Fig. 1) [22]. The results obtained by the different authors had shown that TiO₂ was predominant with a percentage that was estimated at 58%. This was followed by Fe₂O₃ with a percentage of 31.73%. The titaniferous sand also contained other oxides such as Al₂O₃, MnO, SiO₂, ZrO₂, MgO etc. The presence of the latter could thus significantly improve the photocatalytic degradation of pollutants [26].

2.2.2 Zinc dioxide nanoparticles

In this study, zinc oxide, which was combined with titaniferous sand as a semiconductor, was a commercial product of 99% purity and was manufactured by Sigma Aldrich (St. Louis, MO, USA). It was in the form of a white powder with a specific surface area of 55 m²/g and was used without any purification.

2.3 Mathematical and Statistical Procedures

The experiments were performed by the response surface methodology (RSM) according to the Box- Behnken design using 3 levels and 4 center points. The center trials were used to assess the experimental error and reproducibility of the experiments. The number of experiments, (N), to be performed was given by Equation 1.

$$N = 2k(k - 1) + r \quad (\text{Eq1})$$

Where **k** is the number of factors and **r** is the number of repetitions of trials at the center.

The effect of 3 independent factors (Table 2) such as the ratio (titaniferous sand/ZnO) (A:1-2.8), the pH of the solution (B:4-10) and the irradiation time (C:120-480 minutes) on the

photocatalytic degradation efficiency (Y) of methylene blue was studied. Analysis of variance was performed to evaluate the significance of the independent variables and their interactions on the response (Y). The polynomial quadratic model was used to predict the response (Y).

$$Y = b_0 + \sum_{i=1}^n b_i x_i + \left(\sum_{i=1}^n b_{ii} X_i \right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} X_i X_j \quad (\text{Eq2})$$

Where Y is the predicted response, b_0 the constant coefficient, b_i the linear coefficients, b_{ij} the interaction coefficients, b_{ii} the quadratic coefficients and X_i, X_j are the coded values of the operating parameters.

The experimental design, model regression coefficients, analyses of variance, and graphs were determined using Design Expert software version 11.1.2.0 (Stat-Ease Inc., Minneapolis, USA).

2.4 Experimental Design and Analysis Methods

The experiments were carried out in continuous mode in a fixed-bed reactor (Fig. 2). The latter had the shape of a rectangular parallelepiped (Length 31cm; Width 20cm; Height 21cm and a fixed bed surface of 18cm*13cm) designed with plexiglass plates completely repainted in black to trap all the diffuse light. The semiconductor mixture was immobilized on the static bed where the solution to be treated flows. The reactor was pierced on both sides to allow two artificial UV lamps of the PHILIPS PL-L 18W/10/4P 1CT type to be fixed to provide the energy necessary for the activation of the semiconductors. The lamps

were turned on at least 40 minutes before the experiments to ensure constant irradiation. A peristaltic pump (Masterflex, model 7520-47) operating with a minimum flow rate of 0.661 ml/s was used to ensure circulation of the solution to be treated.

As proven in the literature, the initial concentration of the dye should have an inverse relationship with the removal efficiency of the dye [27]. Thus, the influence of the initial concentration of the dye was not studied in this work. Therefore, in all experiments, the concentration of methylene blue was set at 25 mg/L. In addition, in each experiment, the total concentration of semiconductors (titaniferous sand and ZnO) was set at 10 g/L. However, the influence of the ratio (titaniferous sand/ZnO), the initial pH of the solution and the irradiation time was studied. After each experiment, a sample was taken and filtered through a 0.45 μ m HA Millipore membrane for spectrophotometric analysis. The absorbances were measured using a UV-Visible spectrophotometer of the Perkin Elmer Lambda 45 type at a wavelength of 664 nm. From these absorbances, the residual concentrations of the dye solutions were deduced using a calibration curve that was established. Thus, the photocatalytic degradation efficiency (Y in %) of the dye was determined according to equation 3.

$$Y = \frac{C_0 - C_f}{C_0} * 100 \quad (\text{Eq3})$$

Where C_0 is initial dye concentration and C_f is the final dye concentration after photocatalytic degradation.

Table 1. Physicochemical and granulometric parameters of titaniferous sand [23]

Parameters	Values
Absolute density in kg/m ³	4054
Apparent density in kg/m ³	2500
Porosity in %	38.33
External specific surface area in g/m ²	13.4
Average diameter D ₅₀ in mm	0.125
Uniformity coefficient, Cu	1.300
Isoelectric point (pHpzc)	8.75

Table 2. Variables and levels of the Box- Behnken experimental model

Independent variables	Coded symbol	Code levels		
		-1	0	+1
Ratio (Titaniferous sand /ZnO)	A	1.00	1.90	2.80
pH	B	4.00	7.00	10.00
Irradiation time (min)	C	120.00	300.00	480.00

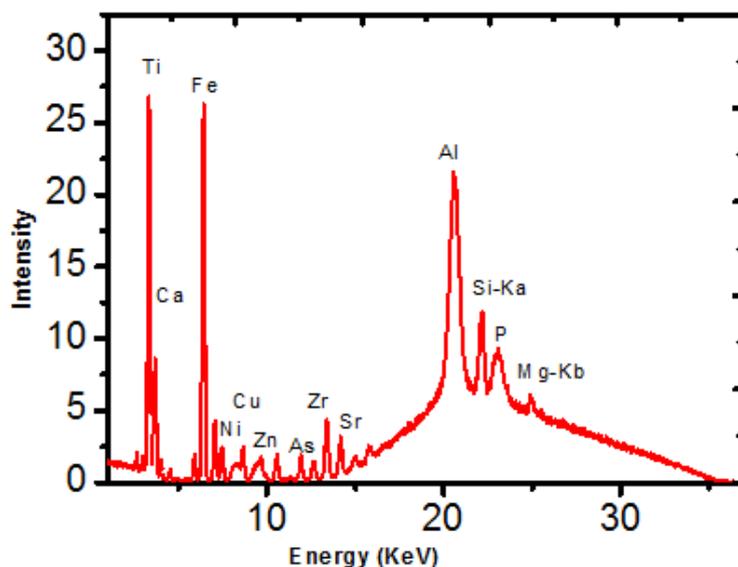


Fig. 1. EDXRF X-ray fluorescence spectrum Niton XLT900s 35KV titanium sand [22]

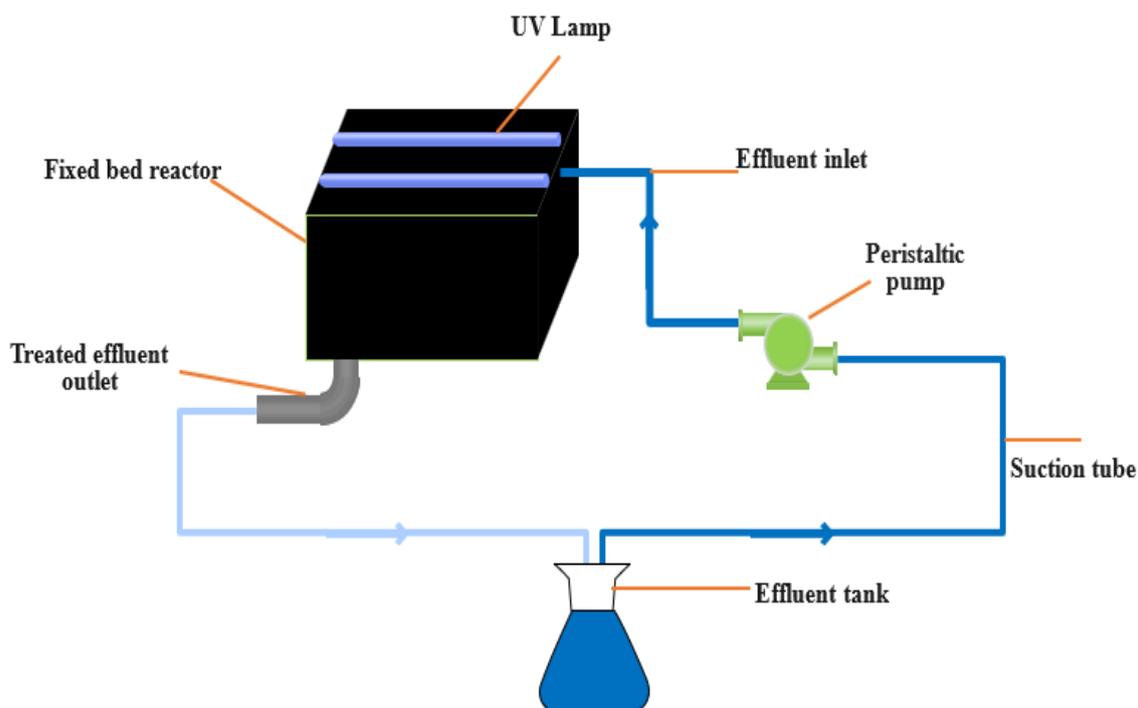


Fig. 2. Device experimental

3. RESULTS AND DISCUSSION

3.1 Experimental Design and Statistical Analysis

The removal of methylene blue was carried out by heterogeneous photocatalysis on a mixture of titaniferous sand and ZnO, under different

conditions according to the Box- Behnken design. This method also allows the generation of mathematical models to predict the process response [28]. On this basis, the quadratic second-order polynomial given by equation 4 was used for the fitting of the experimental values presented in (Table 3) thus inferring the combined effects of the three factors studied.

Y (%) = 90.64227 + 0.469860*A - 2.05182*B + 0.042196*C + 0.107821*AB - 0.007306*AC - 0.000023*BC - 0.092492*A² + 0.130218*B² - 2.31157E- 06*C² (Eq4)

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor.

Table 3. Design matrix and observed response values for the removal of methylene blue by heterogeneous photocatalysis on a mixture of titaniferous sand and ZnO

Std	Run	Factor 1 A: Ratio (Titaniferous sand /ZnO) %	Factor 2 B: pH	Factor 3 C: Irradiation times Minutes	Response Degradation efficiency (Y) %
5	1	1	7	120	87.8397
7	2	1	7	480	99.4599
12	3	1.9	10	480	99.0042
3	4	1	10	300	94.9536
2	5	2.8	4	300	92.4388
11	6	1.9	4	480	98.9873
13	7	1.9	7	300	92.4388
1	8	1	4	300	95.9494
8	9	2.8	7	480	95.2742
9	10	1.9	4	120	88.9451
15	11	1.9	7	300	93.5358
10	12	1.9	10	120	89.0127
6	13	2.8	7	120	88.3881
14	14	1.9	7	300	92.7595
16	15	1.9	7	300	92.827
4	16	2.8	10	300	92.6075

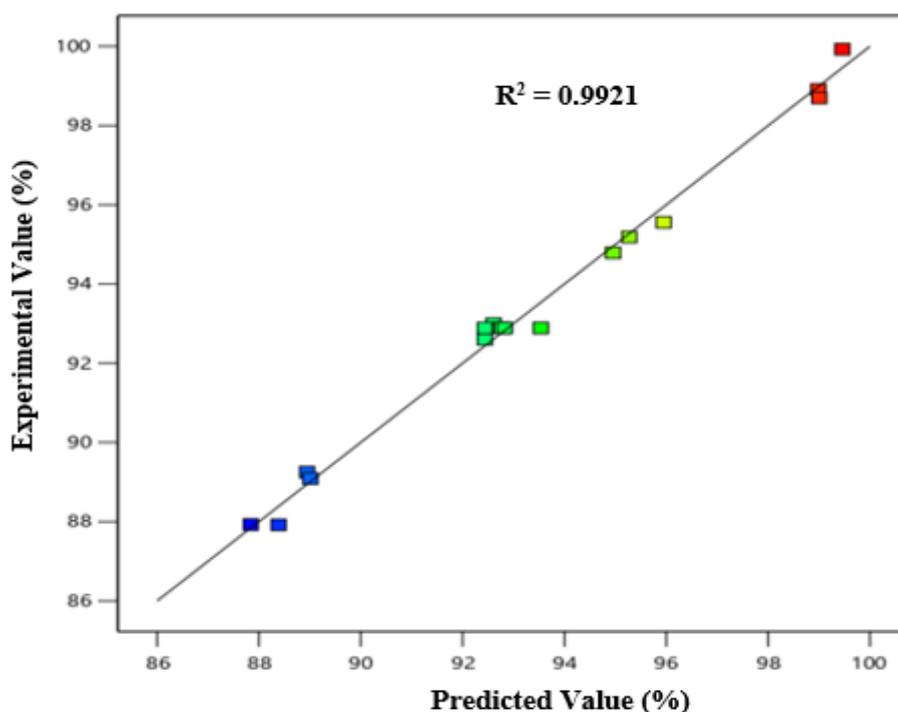


Fig. 3. Predicted response vs. observed response

Table 4. ANOVA of the quadratic model of heterogeneous photocatalysis of BM on titanium sand/ZnO mixture

Source	Sum of Squares	Df	Mean Square	F-value	P-value	
Model	208.48	9	23.16	84.09	< 0.0001	Significant
A- Ratio (Titaniferous sand /ZnO)	11.27	1	11.27	40.90	0.0007	
B-pH	0.0690	1	0.0690	0.2503	0.6347	
C- Irradiation Times	185.67	1	185.67	674.01	< 0.0001	
AB	0.3390	1	0.3390	1.23	0.3098	
AC	5.60	1	5.60	20.34	0.0041	
BC	0.0006	1	0.0006	0.0023	0.9631	
A ²	0.0225	1	0.0225	0.0815	0.7849	
B ²	5.49	1	5.49	19.94	0.0043	
C ²	0.0224	1	0.0224	0.0815	0.7849	
Residual	1.65	6	0.2755			
Lack of Fit	1.01	3	0.3371	1.58	0.3589	Not significant
Pure Error	0.6416	3	0.2139			
Total Horn	210.14	15				
Adjusted R² = 0.9803; Predicted R²=0.9176 ; R²=0.9921						

From (Table 3), the photocatalytic degradation efficiency of methylene blue ranged from 87.8397 to 99.4599%. These results thus demonstrated an almost complete removal of methylene blue by the mixture of titaniferous sand and zinc dioxide as a semiconductor material. These results were somewhat better than those obtained by Iqbal et al. [29] for the removal of methylene blue by photodegradation on ZnO-doped lithium titanate/TiO₂. Indeed, the authors had found a removal efficiency of 95% under optimal conditions. The statistical significance of the data obtained as well as their validity were analyzed and interpreted using an ANOVA (Table 4). The latter makes it possible to determine whether the differences observed between the groups are statistically significant in order to better assess the quality of the chosen model. The results of the ANOVA showed that the model chosen for the response had a *P-value* less than 0.0001 and *F-value* of 84.09, which means that the model was significant. The results also showed a non-significant lack of adjustment (0.3589) of the chosen model, which was desirable [30]. The robustness of the model was also assessed using the fitted correlation coefficient. Indeed, to optimize a response surface, an adequate model fit must be obtained to avoid poor or uncertain results. This is important to ensure the adequacy of the proposed model. (Fig. 3) presents the regression model employed by comparing the experimental and predicted values of the response. A

correlation coefficient of 0.9921 was obtained, which indicates a very acceptable agreement between the experimental and predicted values. Moreover, for the monitored response, the difference between R²-adjusted (0.9803) and R²-predicted (0.9176) was less than 0.20, which confirmed the validity of the quadratic model chosen to explain the monitored response [31]. In view of this statistical analysis, it was concluded that the data fitted well to the quadratic model which gave a convincing estimate of the system response in the experimental range studied.

3.2 Effect of Variables on Methylene Blue Removal

To further explore the effect and interaction between the variables, the three-dimensional (3D) graphs were plotted to analyze the change in response and determine the optimal condition of each factor. (Fig. 4) presented the 3D graphs of the response to the interactions of AB and AC respectively and simultaneously. The results in (Fig. 4a) showed that pH had no significant influence on the dye removal efficiency and regardless of the titaniferous sand/ZnO ratio. This finding was confirmed by ANOVA (Table 4), which indicated that the combined effect of pH (B) and the ratio (titaniferous sand/ZnO) (A) was not significant, thus presenting a *P-value* of 0.3098. The non-significant effect of pH on dye removal would be due to a diffusional

phenomenon and not to an electrostatic phenomenon [32]. Indeed, if the phenomenon were electrostatic, at pHs lower than the pH_{PZC} (isoelectric point) of titaniferous sand (8.75) [23] and ZnO (6.5) [33], there should be a repulsion between the molecules of methylene blue (cationic dye) and the positive charges on the surface of the semiconductors. Which was not obtained.

The titaniferous sand/ZnO ratio had a strong influence on the pollutant degradation efficiency. Indeed, the best yields were obtained for pH values ranging from 4 to 10 and with ratios between 1 (50% in titaniferous sand) and 1.9 (66% in titaniferous sand). However, for titaniferous sand/ZnO ratios greater than 1.9, the pollutant degradation efficiency decreased independently of the pH. This decrease in efficiency beyond a ratio of 1.9 could be attributed to the difference in specific surface areas of the two semiconductors. In addition, the specific surface area of ZnO was more than four times greater than that of titaniferous sand. Thus, as the titaniferous sand/ZnO ratio increased, the total number of active sites decreased and there was less production of hydroxyl radicals. As a result, the removal efficiency decreased. Therefore, the specific surface area of the

semiconductor is a very influential factor in the photocatalysis process [34]. The titaniferous sand, although it was chosen for its high TiO_2 content, did not have the same photocatalytic properties as ZnO. Thus, too much sand reduces the active surface area available for the photocatalytic reaction. Therefore, it would be preferable not to exceed a percentage of 66% of sand in the formulation of the mixture of these two semiconductors (titaniferous sand and ZnO).

In contrast, the combined effect of irradiation time and titaniferous sand/ZnO ratio on the photocatalytic degradation efficiency of the dye was significant with a P-value of 0.0041 (Table 4). From (Fig. 4b), the photocatalytic degradation efficiency increased significantly with irradiation time and at titaniferous sand/ZnO ratios ranging from 1 to 1.9. However, at times shorter than 390 min, the efficiency decreased regardless of the ratio. The best results were obtained with titaniferous sand/ZnO ratios ranging from 1 to 1.9 and at irradiation times ranging from 390 to 480 min. This result could be explained by the fact that a longer irradiation time promotes a more complete and efficient degradation of the dye due to the continuous generation of hydroxyl radicals by the semiconductors. Similar results were obtained by Zhean et al. [35].

Factor Coding: Actual

Degradation efficiency (%)

Design Points:

● Above Surface

○ Below Surface

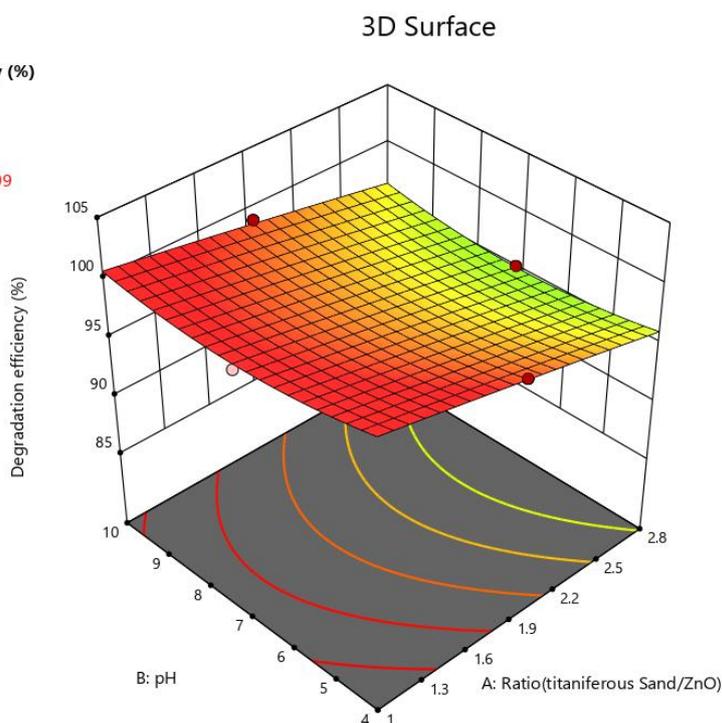
87.8397  99.4599

X1 = A

X2 = B

Actual Factor

C = 480



(a)

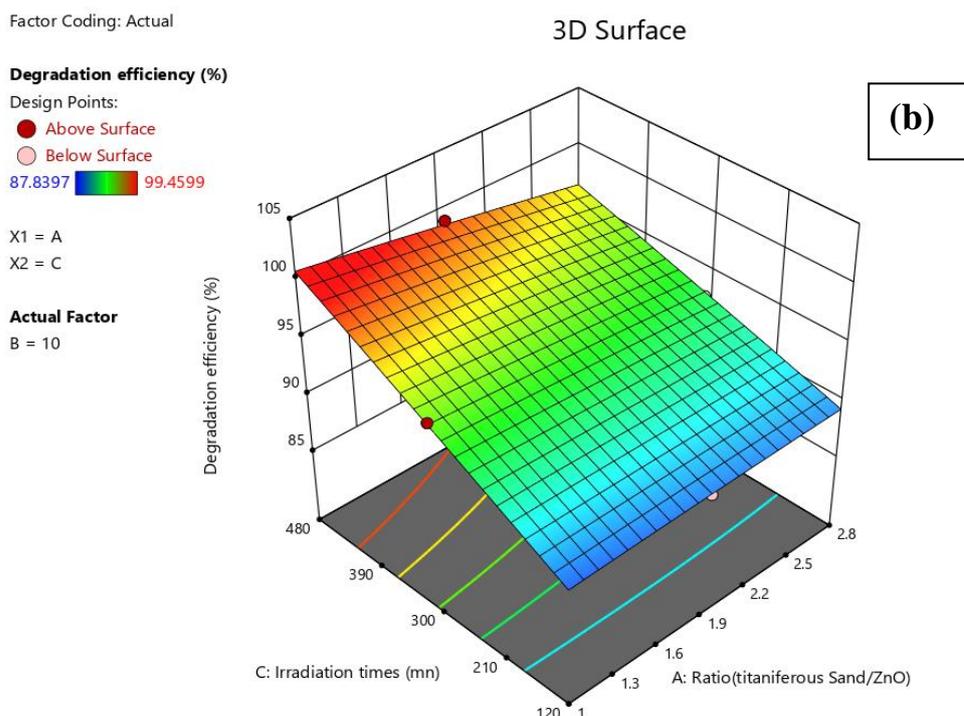


Fig. 4. Three-dimensional plot of the interactions between the ratio (sand/ZnO) and pH (a) and between the ratio (sand/ZnO) and the irradiation time (b) on the removal efficiency of MB by heterogeneous photocatalysis

3.3 Optimal Conditions and Kinetics Study

Desirability allows to identify the optimal combinations of variables to maximize the photocatalytic degradation efficiency of the pollutant. The model suggested the optimal operating conditions shown in (Fig. 5). Under these conditions, the degradation efficiency of the dye should be equal to 99.5606%. A verification experiment was conducted in triplicate with the optimal operating conditions predicted by the model and a degradation efficiency of 99.4915% was obtained. The experimental efficiency was in close agreement with that predicted by the model. This confirms the reliability of the model. Therefore, the approach to optimize the photocatalytic degradation of methyl blue on a mixture of titaniferous sand and ZnO by the Box- Behnken design was successful.

A kinetic study was also carried out, under the optimized conditions, by following the decrease in the dye concentration as a function of the irradiation time (Fig. 6). In addition,

photocatalysis is one of the forms of heterogeneous catalysis involving an electronic transfer process, commonly described by the first-order Langmuir- Hinshelwood (LH) model given by equation (5) [36]:

$$\ln \frac{C_0}{C} = k_{app} \cdot t \quad (\text{Eq5})$$

Where: t is the irradiation time, and k_{app} is the pseudo-first order constant which corresponds to the degradation rate of the photocatalytic system studied.

The plot of $\ln(C_0/C)$ as a function of irradiation time, visible in the inset of (Fig. 6), gave a straight line with a correlation coefficient of 0.9787. The quasi-exponential decrease of the residual dye (Fig. 6) observed during the catalytic degradation kinetics confirms this result [37]. Therefore, we can conclude that the catalytic degradation kinetics of methylene blue on the mixture of titanium sand and ZnO follows the first-order Langmuir- Hinshelwood model with an apparent kinetic constant of 0.4027 h^{-1} . Similar results were obtained by Şahin et al. [38].

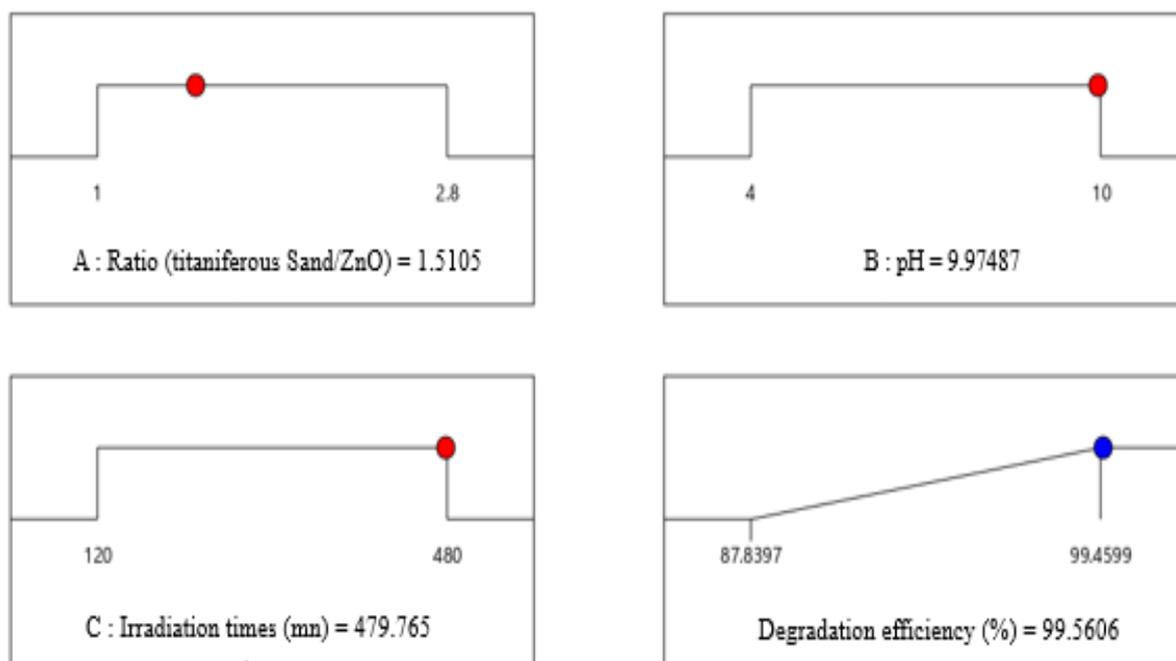


Fig. 5. Optimal conditions predicted by the model for the photocatalytic degradation of Methylene Blue on a mixture of titaniferous sand and ZnO

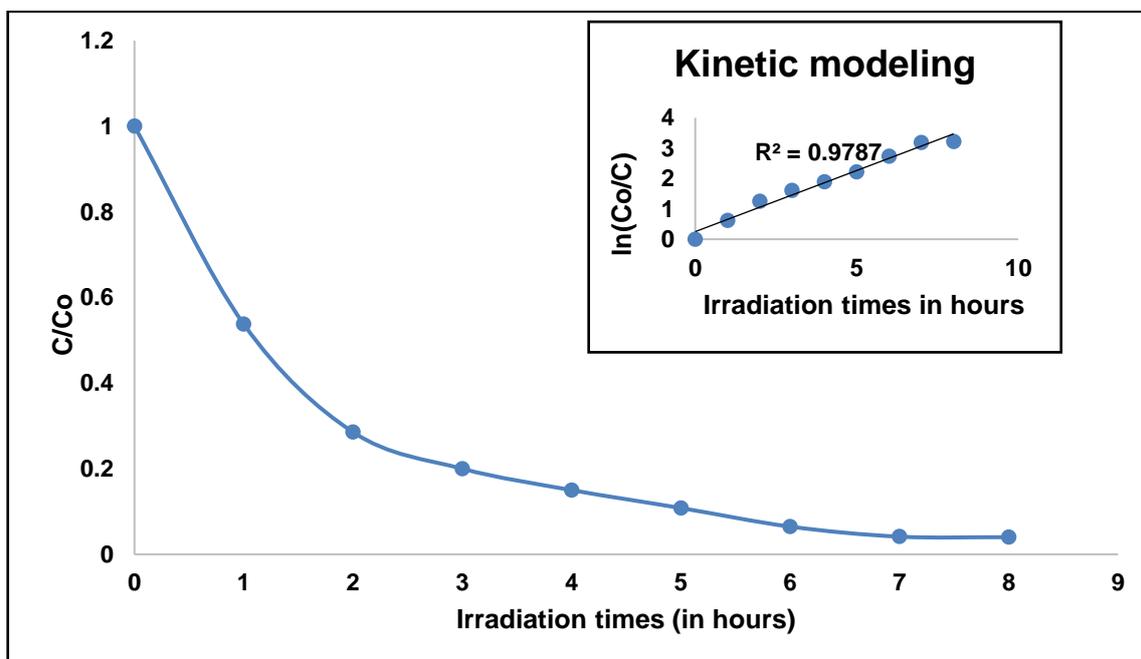


Fig. 6. Kinetic modeling of catalytic degradation of methylene blue on a mixture of titaniferous sand and zinc dioxide

4. CONCLUSION

In this work, a mixture of titaniferous sand and zinc oxide (ZnO) was used as a semiconductor material for the photocatalytic degradation of

methylene blue in aqueous solution. The incorporation of ZnO was justified by the fact that titaniferous sand showed a slightly low photocatalytic activity towards dyes. The study was carried out in a fixed-bed reactor under

artificial irradiation. The Box– Behnken experimental design was applied to optimize the operating conditions. The influence of pH, irradiation time and the ratio (titanium sand/ZnO) on the photocatalytic degradation of the dye was studied. An ANOVA was also performed. The results showed that the irradiation time and the ratio (sand/ZnO) were the main parameters affecting the dye removal with respective P-values of < 0.0001 and 0.0007. The degradation efficiency of the dye was accurately modeled by a quadratic equation with a correlation coefficient R^2 of 0.9921. With the optimal operating conditions predicted by the model as a sand/ZnO ratio of 1.51057, a pH of 9.97487 and an irradiation time of 479.765 minutes, an efficiency of 99.4915% was obtained. While that predicted by the model was 99.5606%. Under these conditions, the photocatalytic degradation kinetics of the dye on the mixture of titaniferous sand and ZnO followed the Langmuir-Hinshelwood. This study not only contributed to sustainable waste management, but also addressed the environmental challenges for effective effluent treatment. The removal of methylene blue from the mixture of titaniferous sand and ZnO was thus successful. However, it would be important to study the influence of light intensity on the rate of degradation of the pollutant, in order to have reasonable mineralization times.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Authors hereby declare that no generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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