

Solar Photocatalysis of a Pesticide in a Tubular Reactor on Titaniferous Sand as a New Semi-Conductor

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How to cite this paper: Diop, E.H.M., Ba, K., Faye, M., Toure, A.O. and Sambe, F.M. (2023) Solar Photocatalysis of a Pesticide in a Tubular Reactor on Titaniferous Sand as a New Semi-Conductor. *Advances in Chemical Engineering and Science*, 13, 119-131.
<https://doi.org/10.4236/aces.2023.132010>

Received: February 6, 2023

Accepted: April 10, 2023

Published: April 13, 2023

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Abstract

This present study comes in addition to overcome the problems of separation of fine particles of TiO₂ in heterogeneous photocatalysis after treatment. It aims to show the potential for using titaniferous sand as a new semiconductor under solar irradiation. The photocatalytic efficiency of this titaniferous sand was tested on a pesticide (Azadirachtin). A tubular photocatalytic reactor with recirculation of the polluting solution was designed for the elimination of the pesticide in an aqueous solution. Before its use as a photocatalyst, the titaniferous sand has undergone a specific treatment that consists of calcination at 600°C followed by extraction of the calcined natural organic materials, which can interfere with the measurement of analytical parameters such as COD. The titaniferous sand was also characterized by X-ray fluorescence spectroscopy (XRF). XRF analyses have shown that TiO₂ is predominant in the titaniferous sand with a percentage that has been estimated at 46.34%. The influence of various experimental parameters such as the flow rate of the polluting solution, the concentration of titaniferous sand, the presence of oxygen and the intensity of the overall rate of sunshine, was studied to optimize the photocatalytic degradation of the pesticide. The results showed that the highest removal rate (70%) was observed under the following conditions: a pH of 6, a titaniferous sand concentration of 150 g/L, a flow rate of 0.3 mL/min, and a sunshine rate of 354 W/m² and in the presence of atmospheric oxygen. Under these experimental conditions, the rate of photodegradation of the pesticide follows the pseudo first order kinetic model of Langmuir Hinshelwood with a coefficient of determination R² of 0.9869 and an apparent rate constant of 0.0029 min⁻¹. The results clearly demonstrated the potential of titaniferous

sand as a photocatalyst sensitive to sunlight for the effective removal of pesticides in the aquatic environment.

Keywords

Solar Energy, Heterogeneous Photocatalysis, Sand Titaniferous, Titanium Dioxide, Pesticide

1. Introduction

In recent decades, increasing industrialization and overuse of available resources by humans have made water pollution one of the global environmental problems [1]. Contamination levels of pollutants in the environment are increasing rapidly due to these repeated anthropogenic, industrial and agricultural activities which amplify and diversify the production of these fractions of pollutants [2]. Pesticides are a group of such environmental pollutants that are widespread in our environment [3]. Classified as persistent organic pollutants, pesticides can remain in aqueous media for a long time and accumulate in biota and/or sediments [4]. The presence of these pesticides in water resources has a negative effect on ecosystems and on humans [5]. Thus, the harmful effect of these pesticides on health and their ecological risks require the development of effective processes capable of eliminating them. However, these pollutants are generally recalcitrant to conventional treatment methods and under these conditions, it is necessary to seek appropriate treatment techniques. Currently, Advanced Oxidation Processes (AOP) are attracting the attention of many researchers as an efficient method capable of degrading a wide range of organic contaminants. OAPs follow a major mechanism that relies on the production of highly active hydroxyl radicals to allow water purification. Among OAPs, heterogeneous photocatalysis under solar irradiation has attracted particular attention to the degradation of pesticides in aquatic environments and is emerging as an effective and sustainable treatment method. Heterogeneous photocatalysis requires a semiconductor or photocatalyst for the removal of pollutants. In recent years, several stable and non-toxic semiconductors like ZnO [6], SnO₂ [7], TiO₂ [8] etc., have been extensively studied. Thus, most of these methods employing these semiconductors, have shown and presented a successful degradation of pesticides under various operating conditions. However, titanium dioxide remains without doubt the most widely used photocatalyst because it has higher oxidation capacities but also long-term photo-stability. It should also be noted that most of the studies of Photocatalysis on TiO₂ have been carried out using the suspension of fine particles of the photocatalyst in the solution to be treated. This operation thus has a limit because the fine particles of TiO₂ complicate the filtration once the solution has been treated [9]. As a result, photocatalytic suspension reactors are not compatible with the production of large-scale installations.

Thus, to overcome the problems of separation of fine TiO₂ particles after

adjustment. The latter was set at 6 because it is the zero charge point pH (PZCpH) of the titaniferous sand [16].

2.2. Titaniferous Sand

The titaniferous sand used as photocatalyst in this study comes from a mining industry based in Senegal. It is metallic black in appearance. To avoid the effect of the presence of Natural Organic Matter (NOM) likely to influence the determination of the analytical parameters, the titaniferous sand was calcined in a Carbolite-Gero type furnace at 600 °C for 2 hours. Then, the calcined (NOM) were extracted using a molar solution of H₂SO₄ and with stirring for 30 min. After decanting for 5 minutes, the supernatant was removed and followed by a series of washes with deionized water. Finally, the sand was put in an oven at 105 °C until completely dry. Its physicochemical and particle size properties are given in **Table 1**.

2.3. Experimental Device and Course of Experiments

The device is shown in **Figure 2**. It consists of two glass tubes 40 cm long and with diameters (2.98/3cm) arranged in parallel. These tubes, provided with plugs with filtering fabrics, each contain a mass of titaniferous sand (M_{STP}) in equal proportions. They are held on a bench making an inclination of 15° with respect

Table 1. Physicochemical and particle size parameters of titaniferous sand.

Physico-chemical and particle size parameters	
Parameters	Values
Absolute density in kg/m ³	4054
Apparent density in kg/m ³	2500
Porosity in %	38.33
External specific surface in g/m ²	13.4
Average diameter D_{50} in mm	0.125
Uniformity coefficient, Cu	1.300
pzcpH_	6

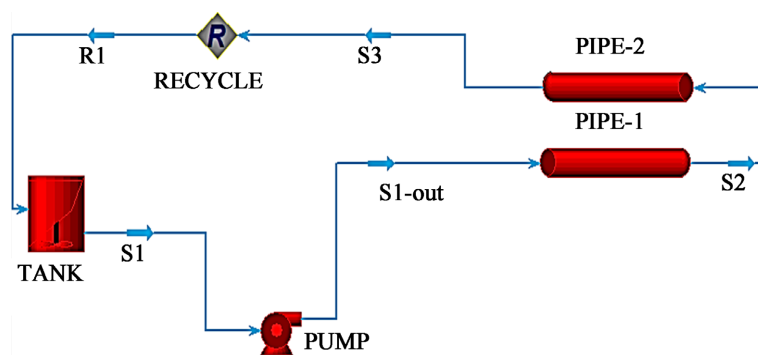


Figure 2. Photocatalytic device with recirculation of the polluting solution.

to the horizontal. The bench is oriented from north to south to obtain good solar irradiation and avoid the shading effect. A ROTARUS-type hydraulic pump ensures the recirculation of the treated pollutant. For each test, the experimental device is exposed to the sun for 8 hours (from 9 a.m. to 5 p.m.). The overall sunshine rate (Φ in w/m^2) of the medium during the treatment was given by a pyranometer. The reduction in pollutant concentration during treatment was monitored by chemical oxygen demand (COD) measurement using a HI83399-02 type COD range integral multi-parameter photometer. All experiments were performed at room temperature and pressure. For all the tests, the volume of the solution (V_s) to be treated was equal to 1.5 L and the initial COD of the solution was set at 200 mg/L. Assuming that the photocatalytic degradation kinetics of the pollutant follows the pseudo-first-order Langmuir-Hinshelwood model, the apparent rate constant was calculated according to Equations (1) and (2). For the pollutant removal yield, it is given by Equation (3).

$$r = -\frac{d\text{DCO}}{dt} = k_{app} \cdot \text{DCO} \quad (1)$$

$$\ln\left(\frac{\text{DCO}_0}{\text{DCO}}\right) = K_{app} t \quad (2)$$

$$\text{Yield}(\%) = \frac{(\text{DCO}_0 - \text{DCO}) * 100}{\text{DCO}_0} \quad (3)$$

COD_0 : Initial chemical oxygen demand of the polluting solution ($\text{mg}\cdot\text{L}^{-1}$);

COD: Residual chemical oxygen demand of the polluting solution ($\text{mg}\cdot\text{L}^{-1}$);

K_{app} : Apparent speed constant in min^{-1} ;

r : Rate of degradation in $\text{mol}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$;

t : Irradiation time in minutes.

3. Results and Discussion

3.1. X-Ray Fluorescence Characterization

Before testing it as a photocatalyst, the titaniferous sand was characterized by X-ray fluorescence spectrometry (XRF), to know its composition in chemical elements. The diffractogram resulting from the analysis is represented by **Figure 3**, whose spectrum shows the different lines of the main elements that make up the titaniferous sand. TiO_2 and Fe_2O_3 whose respective percentages were estimated at 46.34% and 39.71%, are predominant in titaniferous sand. Titanium sand also contains other oxides such as Al_2O_3 , MnO , SiO_2 , ZrO_2 , MgO etc. The presence of the latter could thus significantly improve the photocatalytic degradation of pollutants [17] [18].

3.2. Influence of Recirculation Flow

In continuous or recirculating photocatalytic reactors, the flow rate of the solution to be treated is a very important parameter for assessing the efficiency of the photocatalysis process. Thus, to study this influence, the flow rate of the solution

was varied from 0.3 to 0.6 L/minute. **Figure 4** presents the degradation kinetics obtained at the different recirculation flow rates. During this study, the sunshine values of the environment varied from 119 to 888 w/m².

The results showed that the photocatalytic degradation of the pollutant decreased with increasing solution flow rate. Indeed, the higher the flow rate, the lower the residence time and therefore the shorter the contact time between the catalyst and the molecules of the pollutant. This thus leads to a reduction in the efficiency of degradation of the pollutant. This is how the best abatement rate (54%) was obtained with the lowest flow rate of 0.3 L/minute. In addition, if we refer to the inset of **Figure 4**, the apparent rate kinetic constant is considerably improved at low flow rates. It went from 0.0019 min⁻¹ for the flow rate of 0.3 mL/min to 0.0008 min⁻¹ for 0.6 mL/min. Thus, it was approximately twice as high at 0.3 mL/min as at 0.6 mL/min. Mohammed Redha *et al.* (2020) [19] found similar results. For the following tests, the flow rate was set at 0.3 mL/min.

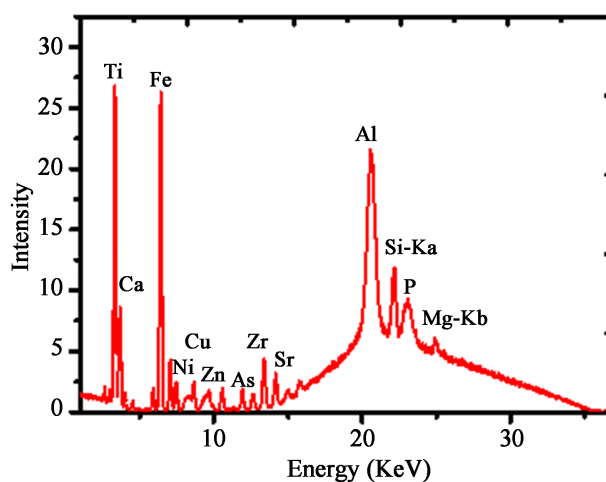


Figure 3. EDXRF X-ray fluorescence spectrum Niton XLT900s titaniferous sand at 35 KV.

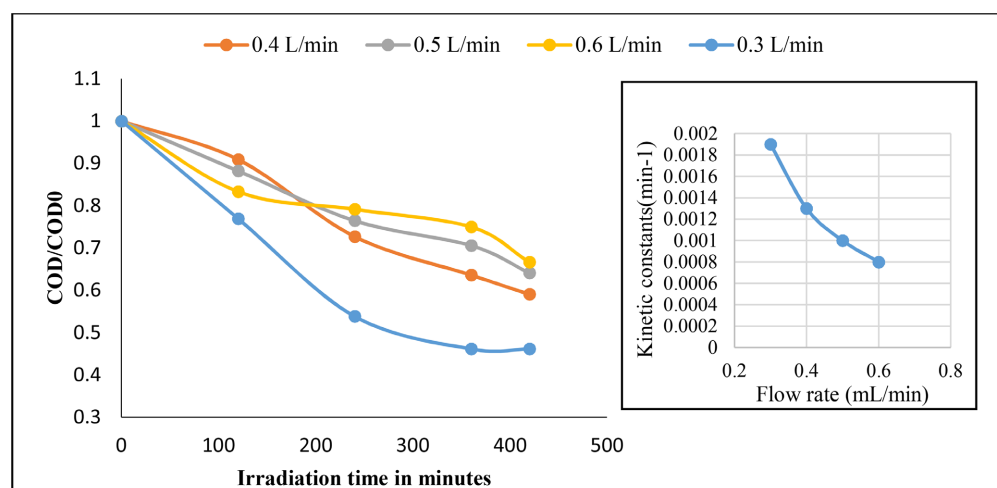


Figure 4. Influence of flow rate on the photocatalytic degradation of azadirachtin ($M_{\text{STF}} = 225$ g; $V_s = 1.5$ L; $\text{COD}_0 = 200$ mg/L; $\text{pH} = 6$).

3.3. Influence of Sand Mass

Still with the aim of optimizing the process, 4 different masses of titaniferous sand were used to study the influence of catalyst concentration on the photocatalytic degradation of azadirachtin. The results obtained during these tests are represented by **Figure 5**.

The analysis of **Figure 5** shows that the variation in the mass of the titaniferous sand has a strong influence on the rate of degradation of azadirachtin. The results showed that the maximum rate of photocatalytic degradation of the pollutant was obtained with the mass of 225 g, *i.e.*, a concentration of 150 g/L in titaniferous sand. This efficiency would be due to the fact that at the maximum concentration, almost all of the molecules of the semiconductor are photoactivated, thus causing an abundant production of hydroxyl radicals. Consequently, the rate of degradation of the pollutant increased considerably at this mass. However, beyond this maximum concentration, the rate of degradation of azadirachtin decreases. Furthermore, from the inset of **Figure 5**, it turns out that the apparent kinetic constant becomes lower and lower for masses of titaniferous sand above the optimum. The apparent kinetic constants change respectively from 0.0023 min^{-1} for $M_{\text{STF}} = 225 \text{ g}$ to 0.0016 min^{-1} for $M_{\text{STF}} = 320 \text{ g}$. In addition, the abatement rate also decreases from 58.5% to 47% when the mass of titaniferous sand increases from 225 g to 320 g. These results could be explained by the fact that the increase in the mass of the catalyst leads to an increase in the turbidity within the reactor and prevents good light penetration. Whereas, the absorption of light fluxes by the catalyst decreases with increasing turbidity. This leads to a decrease in the production of hydroxyl radicals which oxidize organic matter. Similar results were obtained in the work of (Naghizadeh *et al.*, 2023) [20] and (Fadillah, Hidayat, et Saleh 2022) [21].

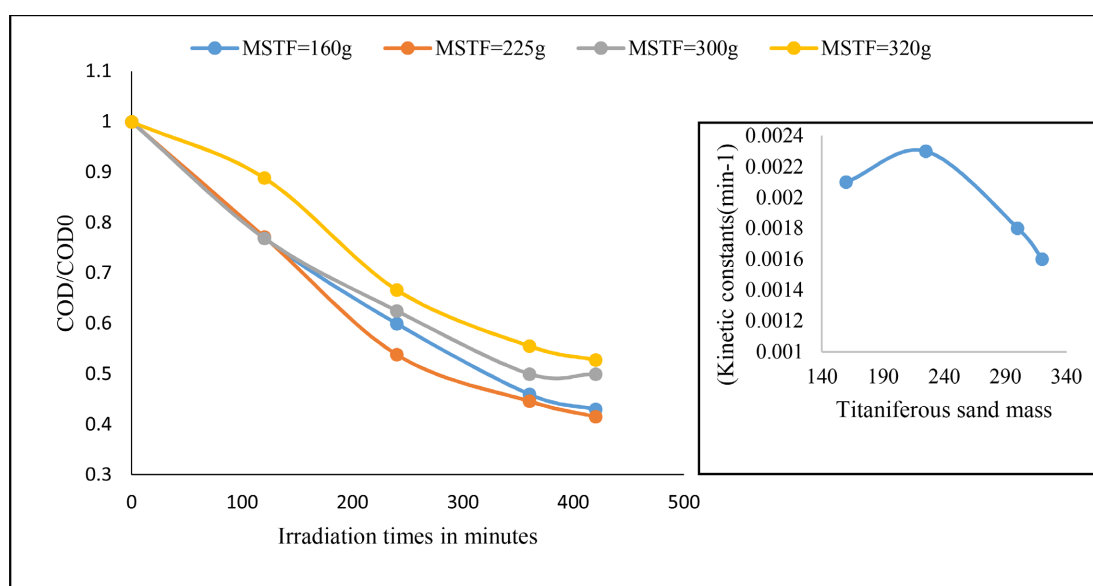


Figure 5. Influence of the mass of titaniferous sand on the photodegradation of azadirachtin (flow = 0.3 L/minute; $V_s = 1.5 \text{ L}$; $\text{COD}_0 = 200 \text{ mg/L}$; $\text{pH} = 6$).

3.4. Influence of Oxygen in the Air

The mineralization of organic compounds by the process of heterogeneous photocatalysis is strongly influenced by the addition of electron acceptors such as oxygen. Thus, to study this influence on the degradation of azadirachtin, a modification was made to the configuration of the reactor. This involves the insertion of a tube open to the atmosphere to continuously supply the reactor with oxygen from the air. These tests were carried out with the optimum concentration of titaniferous sand (150 g/L) ie 225 g and sunshine rates varying from 215 to 915 w/m². The results obtained are illustrated in **Figure 6**.

We found that the degradation rate of azadirachtin is significantly enhanced in the presence of oxygen. Indeed, the COD reduction of the polluting solution went from 58.5% without aeration to 70% with aeration. This can be explained by the fact that the presence of oxygen in the solution limits the risks of hole/electron recombination. Indeed, the oxygen molecules, absorbed on the surface of the photocatalyst, act as very effective traps of electrons from the conduction band, thus totally or partially suppressing the recombination of surface electron-hole pairs [22]. As a result, the formation of hydroxyl radicals ([•]OH) and other reactive species, responsible for the degradation of the pollutant, will be improved. Also, photoelectrons can reduce dissolved oxygen and thus lead to the formation of radical superoxide ions O₂^{•-} according to Equation (4) [23].



The latter will react with water to give HO[•], OH⁻ and O₂ according to the following equations:

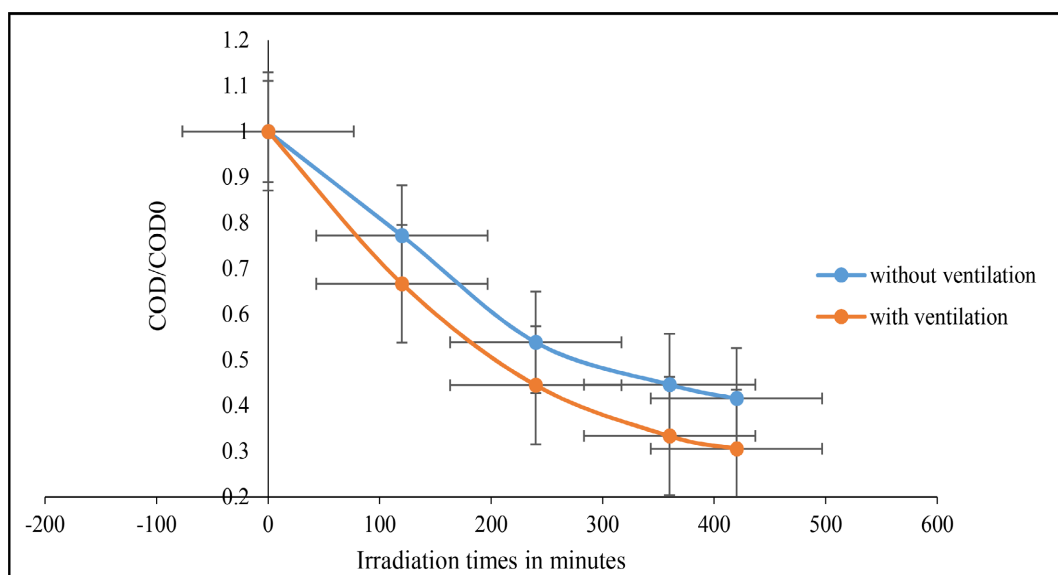


Figure 6. Study of the influence of oxygen in the air on the degradation of azadirachtin ($M_{STP} = 225$ g; flow rate = 0.3 L/minute; $V_s = 1.5$ L; $COD_0 = 200$ mg/L; pH = 6).

Thus, the hydroxyl radicals formed will degrade the pollutants according to Equation (7):



The kinetic modeling of the photocatalytic degradation of azadirachtin under the optimized conditions has been represented by **Figure 7**. Photocatalysis is one of the forms of heterogeneous catalysis involving an electronic transfer process, commonly described by the Langmuir-Hinshelwood model (LH) [24]. The first-order kinetic model of LH assumes that the number of catalytic sites will not be a limiting factor and the rate of degradation of the pollutant is proportional to its concentration [25]. Thereby, the linear correlation between $\text{Ln}(\text{COD}_0/\text{COD})$ and the irradiation time, confirmed the hypothesis that the photocatalytic degradation of the pesticide on the titaniferous sand, follows the LH model well and is of the first order. The values of Langmuir's apparent kinetic constants (k_{app}) and correlation coefficients (R^2) are grouped together in **Table 2**.

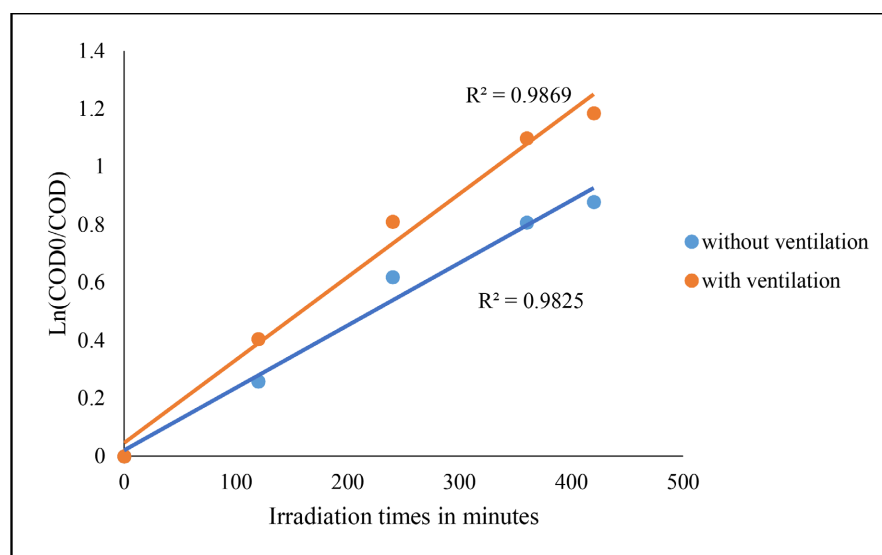


Figure 7. Modeling of the photocatalytic degradation kinetics of azadirachtin on titaniferous sand.

Table 2. Parameters of the Langmuir Hinshelwood linear model applied to the photodegradation of azadirachtin on titaniferous sand under solar irradiation.

Settings	Apparent kinetic constants k_{app} (min^{-1})	R^2
With ventilation	0.0029 ± 0.00015	0.9869
Without ventilation	0.0022 ± 0.00017	0.9825

3.5. Influence of Sunshine on the Degradation of Azadirachtin

The photocatalytic reactions are also influenced by the intensity of the luminous flux received by the catalyst. Light intensity plays a very important role in the photocatalytic degradation reaction as it has a direct effect on the generation of hydroxyl radicals [19]. To demonstrate this effect, we studied the correlation

that exists between the reductions in COD for different values of the global rate of sunshine. This study took place between 9 a.m. and 1 p.m. At time intervals of one hour, the overall level of sunshine in the environment was recorded and the residual COD of the polluting solution was measured. Thus, the figure presents the results obtained.

The evolution of **Figure 8** shows that there is a clear relation of proportionality between the irradiance and the rate of degradation of the pollutant. Generally, the reaction rate is directly proportional to the radiation intensity (W/m^2) and a linear evolution is often observed for low intensities [26]. The results showed that the rate of photocatalytic degradation of the pesticide increases with the intensity of solar radiation. Indeed, the transfer of electrons from the valence band to the conduction band becomes increasingly important, which will increase the number of radical species generated. Thus, for levels of sunshine varying from 154 to 234 W/m^2 , the COD reduction varies linearly with the intensity of the radiation. These results are in agreement with those obtained in the literature [27]. This is due to the low recombination rates between electrons and holes generated. In addition, under these conditions, the formation of electron/hole pairs is predominant. However, we find that for levels of sunshine greater than 354 W/m^2 , the COD reduction of the polluting solution hardly changes. Indeed, when the total amount of incident radiation is high enough, the photocatalyst is almost exclusively activated by incident UV radiation from the sun. In addition, the formation of electron/hole pairs would be in competition with their recombination.

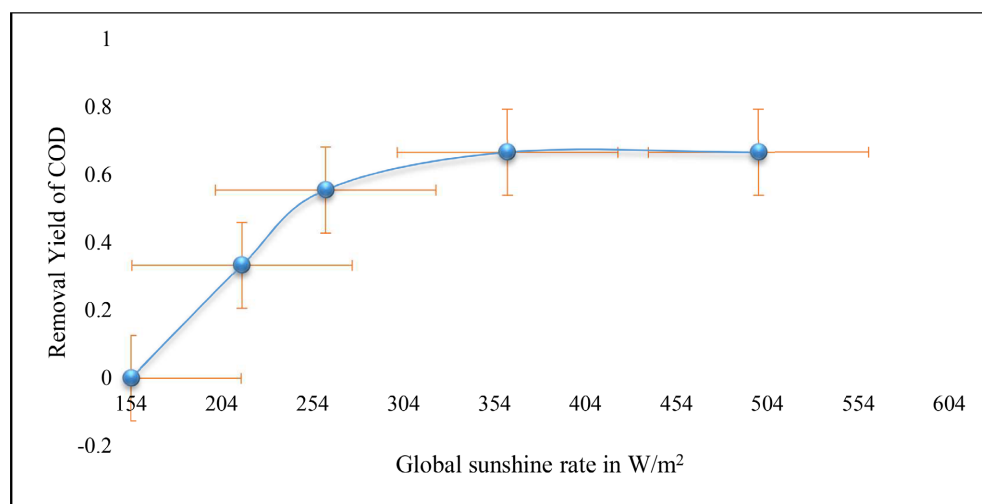


Figure 8. Influence of sunshine intensity on COD reduction (flow = 0.3 L/minute; $M_{\text{STF}} = 225$ g; $V_s = 1.5$ L; $\text{COD}_0 = 200$ mg/L; pH = 6.)

4. Conclusion and Prospects

This study focused on the evaluation of the photocatalytic efficiency of titanium sand for the degradation of a pesticide (Azadirachtin) in the presence of sunlight. The use of solar energy to degrade pollutants by photocatalysis represents

an economical and sustainable alternative. The photodegradation of the pesticide on this new photocatalyst (titanium sand) in a tubular reactor has been successfully applied. The influence of certain operating parameters on the degradation of the pollutant has been studied. The results obtained showed that the optimum pH for the photodegradation of azadirachtin is 6. A titaniferous sand concentration of 150 g/L was retained as the optimum. Studies have also shown that the rate of degradation of azadirachtin is greatly improved for low levels of sunshine, for example between 154 and 234 W/m² and in the presence of oxygen in the air. Under the optimized conditions, a reduction rate of 70% was obtained for an initial concentration of 200 mg/L. Moreover, the degradation kinetics of azadirachtin on titaniferous sand satisfies the Langmuir-Hinshelwood model and is of the first order. These results demonstrated the photocatalytic efficiency of titaniferous sand suggesting that it can be used for the development of new water treatment technologies in the presence of sunlight. This could thus solve the problems posed by the use of photocatalytic systems with conventional powders. However, to improve this study, it would be interesting to dope the titaniferous sand to broaden its absorption spectrum in the visible, which would ensure reasonable degradation times.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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