



# Article Amoxicillin Degradation by TiO<sub>2</sub> P25 Solar Heterogeneous Photocatalysis: Influence of pH and Oxidizing Agent H<sub>2</sub>O<sub>2</sub> Addition

Tania L. Alcázar-Medina<sup>1</sup>, Isaías Chairez-Hernández<sup>1</sup>, Ana A. Lemus-Santana<sup>2</sup>, Cynthia M. Núñez-Núñez<sup>3,\*</sup> and José B. Proal-Nájera<sup>1,\*</sup>

- <sup>1</sup> CIIDIR-Unidad Durango, Instituto Politécnico Nacional, Calle Sigma 119, Fracc. 20 de Noviembre II, Durango 34220, Mexico; talcazarm1700@alumno.ipn.mx (T.L.A.-M.); ichairez@hotmail.com (I.C.-H.)
- <sup>2</sup> CICATA-Unidad Legaria, Instituto Politécnico Nacional, Calzada Legaria 694, Delegación Miguel Hidalgo, Ciudad de México 11500, Mexico; adelale@gmail.com
- <sup>3</sup> Ingeniería en Tecnología Ambiental, Universidad Politécnica de Durango, Carretera Durango-México km 9.5, Col. Dolores Hidalgo, Durango 34300, Mexico
- \* Correspondence: cynthia.nunez@unipolidgo.edu.mx (C.M.N.-N.); jproal@ipn.mx (J.B.P.-N.)

**Abstract:** Over the years, there has been an increase in the consumption of drugs, particularly antibiotics. Amoxicillin (AMX) is considered one of the most widely used antibiotics, causing resistance in microorganisms in the ecosystem where it is found. Additionally, it has been cataloged among the drugs under surveillance by the European Commission since 2020. The present work studies the efficiency of AMX degradation by photolysis and heterogeneous solar photocatalysis processes under different reaction pH levels (3.5, 4.15, 7 and 9) and observing the influence of different doses of H<sub>2</sub>O<sub>2</sub> (nil and 4 mM), as an oxidizing agent. TiO<sub>2</sub> P25 was used as photocatalyst, impregnated in glass supports of 0.1 and 1 m<sup>2</sup> in flat plate reactors (FPR). A 2 × 2 × 4 statistical analysis carried out after repeated measurements to determine the relationship between the different parameters involved (process, H<sub>2</sub>O<sub>2</sub> dose, and pH). The kinetics of the AMX degradation reaction showed the best rate constant (K<sub>phC</sub> = 0.10 min<sup>-1</sup>) under acidic medium conditions (pH 4.15), without addition of H<sub>2</sub>O<sub>2</sub>, and by heterogeneous photocatalysis when using a 1 m<sup>2</sup> FPR to achieve 100% COD removal. ANCOVA showed significant differences (p < 0.05) in the use of H<sub>2</sub>O<sub>2</sub> for the first minutes of the reaction and in the different FPR surfaces.

Keywords: advanced oxidation processes; amoxicillin; emergent pollutants; TiO<sub>2</sub>; flat plate reactors

## 1. Introduction

Latin America is one of the main sources of fresh water in the world, producing approximately one third. It is estimated that only 20% of municipal wastewater is treated in most of the countries that comprise this region while in Mexico, less than 50% of wastewater is processed [1]. The entry of different types of drugs into the environment has increased by 1 to 5 million tons per year [2,3], causing concern about adverse environmental impacts related directly to the drugs and their by-products [4]. Due to the high chemical stability of many drugs and the limits of conventional wastewater treatment processes, effluent from treatment plants often contains elevated concentrations of the chemicals and metabolites and thus the wastewater is a source of drug compounds to aquatic ecosystems [2,5,6].

Drugs have been detected in different types of water, such as surface water, groundwater, wastewater, and even drinking water [7], where their concentrations vary from ng/L to mg/L [2,8,9]. However, even in small quantities, they can cause various consequences, not only in the environment where they are found but also in living beings [2]. As a result of this continuous discharge into the environment, aquatic organisms such as fish, are affected, which may accumulate significant amounts of these chemicals, generating alterations such



**Citation:** Alcázar-Medina, T.L.; Chairez-Hernández, I.; Lemus-Santana, A.A.; Núñez-Núñez, C.M.; Proal-Nájera, J.B. Amoxicillin Degradation by TiO<sub>2</sub> P25 Solar Heterogeneous Photocatalysis: Influence of pH and Oxidizing Agent H<sub>2</sub>O<sub>2</sub> Addition. *Appl. Sci.* **2023**, *13*, 7857. https://doi.org/10.3390/ app13137857

Academic Editors: Charles Humphrey and Guy Iverson

Received: 7 June 2023 Revised: 28 June 2023 Accepted: 29 June 2023 Published: 4 July 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). as feminization or masculinization caused by hormones. As fish and birds are intermediaries in the trophic chain, the ingestion of these organisms when contaminated results in the accumulation of these substances in humans, causing in some cases resistance to antibiotics, endocrine disruption, histopathological disorders, and even, if these chemicals manage to cross the placental barrier, serious problems for newborns [8].

Of the main drugs found in aquatic ecosystems are antibiotics. Antibiotics are now used in many different settings including aquaculture and livestock operations for therapeutic and treatment purposes [10,11]. Traces of antibiotics are also found in various natural environments such as aquatic ecosystems [10,11]. Of these, those belonging to the family of  $\beta$ -lactam antibiotics are the ones that appear most frequently, such as penicillin G, cephalosporin and amoxicillin (AMX), which have been found in different concentrations from ng/L to mg/L, both in surface waters and in wastewater [11].

AMX is one of the most widely used antibiotics worldwide due to its broad spectrum elimination of bacteria, both gram-positive and gram-negative. AMX prevents the synthesis of the cell wall of microorganisms is used in both human and veterinary fields [12,13]. However, due to its high demand and its continuous entry into the different wastewaters, detectable concentrations have been reported in different parts of the world. In the case of effluents from wastewater treatment plants, their concentrations vary, the highest being 1.3 mg/L and 1.6 mg/L, both detected in Hong Kong, China [14], and in Italy a magnitude of 0.013 mg/L has been found [15]. For waters used in the pharmaceutical industry, dedicated to the synthesis of this drug, concentrations around 92.2 mg/L have been found in China [16], and in drinking water sources in southeastern Brazil, a maximum concentration of 287.5 ng/L has been reported [17]. Therefore, in August 2020, the European Commission added this drug to the watch list in the field of water policy as it represents a risk both for humans and for aquatic ecosystems [18].

The generation of hydroxyl radicals, a powerful chemical agent, makes advanced oxidation processes (AOPs) an efficient option for the degradation of recalcitrant and emerging compounds [19–21], such as AMX. Among AOPs, heterogeneous photocatalysis, which involves the use of TiO<sub>2</sub> as a catalyst and UV radiation, has been widely studied. The main idea behind photocatalysis is the generation of gaps in electron pairs, which can reach and break molecular bonds [22].

When radiation consisting of photons of wavelength lower or equal to 387 nm reaches the surface of the photocatalyst, an electron–hole pair  $(e^-_{(CB)}, h^+_{(VB)})$  is generated due to the promotion of electrons from valence band (VB) to conduction band (CB) [23], as shown in Equation (1):

$$\text{TiO}_2 + \text{hv} \rightarrow \text{TiO}_2 + e^-_{(CB)} + h^+_{(VB)} \tag{1}$$

In the photocatalytic process, the molecules oxidation is caused mainly by •OH (with a redox potential of 2.8 eV), superoxide ( $O^{2} \cdot -$ ), and hydroperoxide ( $HO_2 \cdot$ ) radicals [24]. The •OH redox potential is higher than that generated by the holes (h<sup>+</sup>) produced in the VB of the photocatalyst (2.53 eV) [25,26]. Reactive species can degrade pollutants until mineralization, thus producing non-toxic substances [27]. Radical •OH is capable of degrading most organic and organometallic pollutants by transforming them into CO<sub>2</sub>, water, and inorganic ions [28]. In the past, recalcitrant substances have been successfully degraded by means of photocatalytic processes [29].

Different types of reactors can be used for wastewater treatment through heterogeneous photocatalysis. They are all based on the use of a semiconductor, which receives UV radiation from either a UV lamp or solar radiation [30]. Flat plate reactors (FPR) using natural solar radiation present several advantages, especially with their low manufacturing and maintenance costs. This type of technology, which works with natural solar radiation, can be applied particularly in countries in the planet's sunbelt given that they receive an average annual solar irradiation of 5.5 kWh/m<sup>2</sup>/day [31].

The objective of the present work was to optimize the degradation of AMX in an aqueous solution by means of photolysis and heterogeneous photocatalysis with the use of sunlight as activation energy, using flat plate reactors (FPR) with surfaces of 0.1 and 1  $m^2$ ,

and TiO<sub>2</sub> P25 as a photocatalyst for the reaction. This work also studied the influence of the addition of  $H_2O_2$  (0 and 4 mM) on the AMX degradation reaction as a function of different pH values (3.5, 4.15, 7, and 9) through a kinetic study and ANOVA.

# 2. Materials and Methods

# 2.1. Chemical Reagents

Trihydrated AMX reagent (Figure 1) was purchased from Tecnofarma (Tecnofarma, San Juan del Río, Qro., Mexico; CAS: 61336-70-7). As an oxidizing agent, 30% H<sub>2</sub>O<sub>2</sub> (Productos Químicos Monterrey, S.A. de C.V. FERMONT, Monterrey, N.L., Mexico; CAS: 7722-84-1) was used. TiO<sub>2</sub> P25 worked as a photocatalyst for photocatalysis experiments (Evonik Industries AG, Essen, NRW, Germany; CAS: 13463-67-7).



Figure 1. The AMX chemical structure.

In order to study pH influence on experiments, the initial pH of the solution was adjusted to different pH magnitudes using 65% nitric acid and 0.1 M sodium hydroxide, both chemicals were Merck brand (Merck, Naucalpan de Juárez, Edomex, Mexico). Also, distilled water (Hycel, Zapopan, Jal., Mexico; CAS: 7732-18-5) was used to prepare all needed solutions.

#### 2.2. Characterization of TiO<sub>2</sub>

XRD was required to characterize the photocatalyst. A D8 Advance (Bruker Corporation, Billerica, MA, USA) was employed to obtain TiO<sub>2</sub> diffraction pattern through 1.5406 Cu-k $\alpha_1$  wavelength. A time-per-point of two seconds, with a range of 2 $\theta$  in the angular range of 20° to 90°, was set. The crystalline phases present in the XRD were identified by comparing them with the PDF-2 2016 database of the International Center for Diffraction Data (ICDD).

Band-gap was calculated by determining at room temperature the absorbance spectrum of the photocatalyst using a UV-visible spectrophotometer with LAMBDA 950 UV/Vis/NIR integration sphere (Perkin Elmer Inc., Waltham, MA, USA). As a last step, the Kubelka–Munk function [32], which allows converting diffuse reflectance into equivalent absorbance spectra, was employed using alumina for reference [33].

#### 2.3. Flat Plate Reactors

Experiments were performed on two FPRs (Figure 2) that use sunlight as a radiation source and are different in size with a contact area of  $0.1 \text{ m}^2$  (reactor 1) and  $1 \text{ m}^2$  (reactor 2). FPRs are both made of an acrylic container supported on a metal base. Inside the acrylic container are frosted glass plates on top of which the sample flows. The constant flow of 127 L/h (reactor 1) and 355 L/h (reactor 2) served as experimental conditions and the latitude of Durango City, Mexico (24°01′37″ N) was considered when setting the reactor inclination (20°), as solar radiation uptake was maximized [30,34].



Figure 2. Flat plate reactors: (a) 1 m<sup>2</sup> reactor surface; (b) 0.1 m<sup>2</sup> reactor surface.

The contaminant solution (AMX) was placed in a collection tank, where a Biopro H-330 submersible pump sent it through a polyvinyl chloride pipe to exit on the superior end of the reactor. Then, the sample flowed over the glass plate and exited the reactor body on the lower part, falling again into the collection tank in order to recirculate [19,30] (Figure 3).



**Figure 3.** Flat plate reactors dimensions; (a)  $1 \text{ m}^2$  surface FPR; (b)  $0.1 \text{ m}^2$  surface FPR; and (c) operational conditions for both reactors, laminar regime Re < 1000, and 20° FPR inclination, which is close to the latitude of Durango City, Mexico (24°01′37″ N).

#### 2.4. Experimental Conditions

The AMX initial concentration of 50 mg/L [11] was prepared by diluting AMX in distilled water and stirring the solution for half an hour. Volume samples of 2 and 3 L were required for reactors 1 and 2, respectively. For photocatalysis experiments, 2 g/m<sup>2</sup> TiO<sub>2</sub> P25 was impregnated on the frosted glass plates by direct spraying [8,23,35].

The influence of pH on contaminant degradation was tested by carrying out the experiments at different initial pH of 3.5, 4.15, 7, and 9; the AMX solution pH was modified by adding, drop by drop, HNO<sub>3</sub> or NaOH solutions. pH was measured with an Orion Star A211 potentiometer (Thermo Fisher Scientific Inc., Waltham, MA, USA).

The influence of  $H_2O_2$  was studied as well. For this purpose, experiments were performed in the absence of  $H_2O_2$  and repeated by adding 4 mM  $H_2O_2$  to the solution just before starting the experiment [36]. Sample recirculation through the reactor lasted for 60 min, with sampling times of 0, 5, 10, 15, 20, 30, 45, and 60 min.

UV-Vis spectrophotometry in a DR 5000TM device (HACH Company, Loveland, CO, USA) served to measure AMX removal in samples, considering the maximum absorption range from 200 to 300 nm [37,38]. As a response variable, Chemical Oxygen Demand (COD) change was measured, using the Hach 2000 method with a DR 2010 spectrophotometer (HACH Company, Loveland, CO, USA).

Control experiments were performed in the absence of radiation at different pH magnitudes to ensure that  $H_2O_2$  presence was not the only factor contributing to AMX degradation.

A meteorological station of the Secretaría de Recursos Naturales y Medio Ambiente provided the radiation, temperature, and humidity data; the station uses a WE300 Solar Radiation Sensor pyranometer (Global Water, Yellow Springs, OH, USA) for measurements. Experiments were conducted on sunny, windless days, from 12:00 to 14:00 h from April to July. The average solar radiation incidence reported was close to 1000 W/m<sup>2</sup>, as shown in Figure 4.



**Figure 4.** Average solar radiation between the months of April and July (2022) in the city of Durango, Mexico.

A 2  $\times$  2  $\times$  4 factorial design with covariates and repeated measures was used to analyze the degradation results for the different FPR areas as described by Equation (2) for a 0.1 m<sup>2</sup> surface FPR and Equation (3) for a 1 m<sup>2</sup> surface FPR:

$$Y_{ijklm} = \mu + P_j + pH_k + H_2O_{2l} + (pH^* H_2O_2)_{kl} + t_m + aRadS + bCOD_0 + \varepsilon_{jklm}$$
(2)

$$Y_{iiklm} = \mu + A_i + P_k + H_2O_{2l} + t_m + aRadS + bCOD_0 + \varepsilon_{iklm}$$
(3)

In Equation (2), the response variable (COD) corresponds to  $Y_{ijklm}$ , the general average of the model is  $\mu$ ,  $P_j$  is the process (photolysis and photocatalysis),  $pH_k$  is the pH (3.5, 4.15, 7, and 9),  $H_2O_2l$  is the  $H_2O_2$  dose (nil and 4 mM),  $t_m$  is the sample time, *a*RadS is the intensity of solar radiation, *b*COD<sub>0</sub> is the initial AMX concentration, and  $\varepsilon_{ijklm}$  represents the error. Due to the fact that it is an open system, the volume of the sample decreased during the reaction, which is why evaporation is considered as a correction factor applied to the dependent variable COD. As well as Equation (3),  $Y_{ijklm}$  is the response variable,  $\mu$  represents the general means of the model,  $A_j$  is the surface area of FPR (0.1 m<sup>2</sup> and 1 m<sup>2</sup>),  $P_k$  is the process and  $H_2O_2l$  is the  $H_2O_2$  dose (0 and 4 mM),  $t_m$  as the sample time, *a*RadS the intensity of solar radiation and *b*COD<sub>0</sub> the initial AMX concentration.

## 2.5. Kinetic Analysis

Kinetic analysis was executed considering a first order reaction (n = 1) [39]. Degradation rate constant was calculated through Equation (4) [23,39–41]:

$$(X)_{t} = (X)_{0} e^{-(K_{phC}) \cdot t}$$
 (4)

In Equation (4), (X)<sub>t</sub> represents the concentration of AMX over time, (X)<sub>0</sub> stands for the initial concentration of AMX in the solution, and  $K_{phC}$  for the photocatalytic rate constant. Half-life time ( $t_{1/2}$ ) was calculated through Equation (5) [42]:

$$t_{1/2} = \frac{\ln(2)}{K_{\rm phC}}$$
 (5)

# 2.6. Statistical Analysis

The effect of the factors considered in the experimental design was determined by an analysis of covariance (ANCOVA), with an  $\alpha$  = 0.05. For the ANCOVA, SAS Studio 9.4 (SAS Institute Inc., Cary, NC, USA) statistical package was used, and previous verification of the Gauss–Markov assumptions was made.

## 3. Results and Discussions

## 3.1. Structural Analysis of TiO<sub>2</sub> P25

This working group published the results of XRD patterns for TiO<sub>2</sub> P25 [26], according to the method of Le Bail et al. [43]. In TiO<sub>2</sub> P25, in addition to anatase, Bragg positions of the anatase phase (JCPDS file 00-021-1272 of the ICDD database), and the rutile phase were found (JCPDS file 01-070-7347 of the ICDD database).

Diffraction data were treated by the Warren–Averbach method [44]. It was possible to calculate crystallite size, average shape, the percentage of each phase, and the tensions caused by structural defects in TiO<sub>2</sub> P25 [26]. With this analysis, it was found that 85.27% of the photocatalyst was anatase and 14.73% was the rutile phase. The crystalline size was 20.97 nm for anatase and 33.96 nm for rutile, both presenting a spherical crystalline form [26].

The Kubelka–Munk method served to handle absorbance spectra from photocatalysts. A graphic representation of  $[F(R)\hbar v]^{1/2}$  against  $\hbar v$  was obtained and allowed determination of the TiO<sub>2</sub> band gap.

Figure 5 shows the graphs of the absorbance spectrum and the band-gap calculation for TiO<sub>2</sub> P25 performed with Origin Pro 2018 software version b9.5.0.193 (OriginLab, Northampton, MA, USA). A TiO<sub>2</sub> P25 band gap of 3.2 eV was determined, being a lower value than that for semiconductors obtained by the sol-gel method with titanium tetrabutoxide (TBT, 3.40 eV) and titanium tetraisopropoxide (TIPT, 3.38 eV) as precursors [30,45]. These results point to easier activation of the photocatalyst TiO<sub>2</sub> P25 when exposed to solar radiation. Concerning band-gap estimation, the following recent references are also an alternative method on how to treat Tauc plot data to extract the band-gap energy [46,47].



**Bandgap TiO<sub>2</sub> Degussa P25** 

**Figure 5.** Band-gap calculation, according to the absorbance spectrum of TiO<sub>2</sub> P25, by means of the graphic representation  $[F(R)\hbar v]^{1/2}$  against  $\hbar v$  of the Kubelka–Munk method.

#### 3.2. Degradation of Amoxicillin by Solar Photolysis

The control experiments (in shade), both for the photolysis and photocatalysis processes on 0.1 and 1 m<sup>2</sup> surface FPR, did not show any degradation under any pH (3.5, 4.15, 7 and 9), with (at 4 mM) and without the addition of  $H_2O_2$ , analyzed by UV-Vis spectrophotometry and COD.

In the treatments by solar photolysis on 0.1 m<sup>2</sup> and 1 m<sup>2</sup> surface FPRs, the results of the experiments carried out at different pH (3.5, 7, and 9), showed no decrease in drug concentration as determined by UV-vis spectrophotometry. No change was noticed by the COD analysis, except in the experiment with pH 4.15 and without the addition of  $H_2O_2$  for both reactors, reflecting a COD reduction of 3–8% at minute 5, to later show no degradation trend.

Kanakaraju et al. in 2015 [48], confirmed that although direct photolysis can slightly help in the degradation of AMX, the effect of pH in the solution plays a very important role, due to increased or decreased formation of hydroxyl radicals depending on solution conditions. In a study carried out by Xu et al. in 2011 [49] the degradation behavior of amoxicillin in solutions of organic matter isolated in a process of solar photolysis, reached 6 to 21% removal for simulated natural waters; however, when interacting with a solution of organic matter in an excited state with the addition of sorbic acid and under deoxygenated conditions, degradation of 48 to 74% was achieved. It is presumed that the degradation obtained by photolysis is due to the energy transferred by the excited state of the organic matter solution, due to the proximity of the formation site of the •OH radicals, as well as the decrease in the pH level of the solution, coinciding with what was previously described by Kanakaraju et al. in 2015 [48].

#### 3.3. Degradation of Amoxicillin by Solar Photocatalysis

For solar photocatalysis with a 0.1 m<sup>2</sup> FPR surface, the analysis showed, for the best-observed experiment, a significant AMX degradation when working with a pH 4.15, without the addition of  $H_2O_2$ , obtaining a percentage of 27% of COD removal, 60 min after

the start of the reaction, and showing, besides, under these same experimental conditions, a 46.9 % decrease in COD, in an extended reaction time of 80 min. In this case, due to the acidic pH of the solution being close to the pH level of maximum stability of the drug, which is around 5 [48,50], there is the possibility of a better performance in the degradation of this drug with the use of a catalyst in the system.

At pH 3.5, 7, and 9, no degradation was observed on this surface  $(0.1 \text{ m}^2)$ . Verma and Haritash in 2020 [13], explain that at a lower magnitude of pH (very acidic), the adsorption of AMX with TiO<sub>2</sub> is affected by the positive charges on their surfaces, where the point of zero charges of TiO<sub>2</sub> (pzc = 6.4), as well as that of amoxicillin, become positive in acidic media, repelling each other. In the case of the removal of AMX with the addition of H<sub>2</sub>O<sub>2</sub>, at these pH values (3.5, 7, and 9), no decrease in the total or partial removal of the contaminant is observed.

The range of solar radiation received during the experiments was close to 1000 W/m<sup>2</sup>, the wavelength ( $\lambda < 387$  nm) was in the UV-A region of the electromagnetic spectrum, and the band-gap energy of the photocatalyst (3.2 eV), provided the necessary activation energy of the photocatalyst (TiO<sub>2</sub> P25); however, due to the size of the reactor surface (0.1 m<sup>2</sup>), the best percentage of COD removal obtained was only 46.9%, as already mentioned.

Plantard et al. in 2012 [51], determined that the speed of the degradation reactions given by the solar photocatalysis process is observed as a set of different operational parameters, such as the intensity of the solar radiation received during the experiments, the concentration of the contaminant and by the reaction surface and the concentration of the catalyst used. Therefore, experiments were carried out using a FPR with a surface area of 1 m<sup>2</sup>, to find out if this factor influenced the degradation of amoxicillin, under the same conditions as in the degradation reaction of the previous experiments.

Figure 6 shows the results obtained by COD for the degradation of AMX by solar photocatalysis, using  $TiO_2$  P25 as the photocatalyst, on a 1 m<sup>2</sup> surface FPR under the reaction conditions mentioned in Section 2.3.



**Figure 6.** COD/COD<sub>0</sub> analysis with respect to time for the degradation of AMX by solar photocatalysis, using TiO<sub>2</sub> P25 as photocatalyst, on 1 m<sup>2</sup> surface FPR, at pH 4.15; the green curve, with the addition of H<sub>2</sub>O<sub>2</sub> (4 mM), and the curve in blue, without the addition of H<sub>2</sub>O<sub>2</sub>.

The results (Figure 6), are similar to what was observed in the experiments carried out with a 0.1 m<sup>2</sup> FPR for solar photocatalysis in that the only reaction conditions that showed significant degradation of AMX were at pH 4.15, not having observed any degradation at pH 3.5, 7 and 9. A possible explanation for such results is AMX speciation: when in aqueous solution, AMX can present different forms according to the solution pH; at pH 4.15, a zwitterionic form is mainly present [52]. This being said, better results were to be expected at this pH, as the AMX molecule is negatively charged while TiO<sub>2</sub>, is positively

charged as the pH is below its isoelectric point, so attraction between AMX and catalyst molecules facilitates interaction ad thus, degradation.

Unlike the results shown for the  $0.1 \text{ m}^2$  FPR, with the  $1 \text{ m}^2$  FPR significant percentages of AMX degradation were obtained, measured as COD at pH 4.15, 65% degradation with the addition of H<sub>2</sub>O<sub>2</sub> (4 mM) to 60 min of reaction and up to 72% when the reaction was extended to 80 min (Figure 6), reaching a final pH of 6.85 for the reaction with the addition of 4 mM H<sub>2</sub>O<sub>2</sub> and a final pH of 5.37 for the reaction without the addition of H<sub>2</sub>O<sub>2</sub>. For experiments without added H<sub>2</sub>O<sub>2</sub>, the degradation of AMX by COD analysis reached 100% after 50 min, with no observable change up to 80 min of reaction (Figure 6). The absence of H<sub>2</sub>O<sub>2</sub> in the reaction gave better results than in its presence, since, despite the fact that H<sub>2</sub>O<sub>2</sub> helps to accelerate the degradation of pollutants through the formation of •OH radicals, in some cases the addition of H<sub>2</sub>O<sub>2</sub> can compete for these radicals, thus reducing the effectiveness of the photocatalytic reaction [16]. Also, as noted above, the solution with a pH of 4.15, which is close to the level of maximum stability of the drug at pH 5 [48,50], showed excellent performance of the TiO<sub>2</sub> P25 catalyst in the removal of AMX.

The use of  $H_2O_2$  as an enhancer in the degradation of different pollutants has been widely studied. The in situ generation of this substance is promoted through the separation of electron<sup>-</sup>/hole pairs<sup>+</sup> [23], where only those e<sup>-</sup> and h<sup>+</sup> that have migrated to the surface and are not recombined participate in surface redox reactions, promoting the formation of  $H_2O_2$  [53,54]. The addition of this oxidation agent in the solution promotes the degradation of the substances under study [54,55]. It has been observed, however, that at high doses of this agent ( $H_2O_2$ ) in the solution, negative effects are produced for the removal of contaminants, as well as slower reaction rates, attributable to the competition between  $H_2O_2$  and other complexes formed during the reaction [54], which compete for union with •OH radicals, favoring their conversion into hydroperoxide radicals ( $HO_2$ ·), and leads to a decrease in the concentration of reactive oxygen species in the solution and therefore to a low rate of degradation [55]. In this study,  $H_2O_2$  was added as degradation enhancer, but it had a detrimental effect on the reaction.

#### 3.4. Chemical Kinetics of Photocatalytic Processes

The results of the chemical kinetics of the degradation of AMX in aqueous solution for the heterogeneous solar photocatalysis process carried out under pH 4.15, show a first order reaction (n = 1) on both 0.1 and 1 m<sup>2</sup> FPR surfaces (Table 1).

FPR Surface	Rad. W/m <sup>2</sup>	H <sub>2</sub> O <sub>2</sub> (mM/L)	COD Degrad. (%)	K <sub>phC</sub> (min <sup>-1</sup> )	t <sub>1/2</sub> (min)
0.1 m <sup>2</sup>	951	0	46.9	0.013	54.02
1 m <sup>2</sup>	956 963	0 4	100 72.0	0.10 0.044	8.59 15.89

**Table 1.** Photocatalytic rate constants (K<sub>phC</sub>) and half-life time ( $t_{1/2}$ ) for AMX degradation in aqueous solution with absence (0 mM) and added (4 mM) H<sub>2</sub>O<sub>2</sub>, at constant pH 4.15 of reaction, for two FPR surfaces (0.1 and 1 m<sup>2</sup>).

Rad: Solar Radiation Intensity; COD Degrad: AMX Degradation by COD analysis, after 80 min reaction.

Table 1 shows the calculation of the photocatalytic rate constant ( $K_{phC}$ ) for AMX degradation, calculated by Equation (4) of Section 2.5, on both 0.1 and 1 m<sup>2</sup> FPR surfaces, with addition (4 mM) and in the absence of H<sub>2</sub>O<sub>2</sub>, under a reaction at pH 4.15. It also shows the % degradation reached by the COD analysis, 80 min after the start of the reaction, and indicates the average radiation of each experiment in W/m<sup>2</sup>. It also gives the half-life of the reagent, calculated in each case using Equation (5), Section 2.5.

As observed in Table 1, AMX degradation in the absence of  $H_2O_2$  shows differences in photocatalytic rate constants for the different 0.1 and 1 m<sup>2</sup> FPR surfaces, agreeing with the indication of Plantard et al. 2012 [51], in that a greater exposed reaction surface  $(\text{FPR}_{1\text{m}}^2 = 10 \text{ FPR}_{0.1\text{m}}^2)$  favors the degradation of AMX under similar reaction parameters, and also favoring the speed of the reaction. The higher the magnitude of K<sub>phC</sub>, the lower the values of  $t_{1/2}$  are obtained (Table 1), and higher percentages of AMX degradation; therefore the solar photocatalysis reaction in 1 m<sup>2</sup> FPR, the experimental magnitude of pH 4.15 and the absence of H<sub>2</sub>O<sub>2</sub>, are the best AMX degradation conditions in this work.

# 3.5. Statistical Analysis on a Reaction Surface of 0.1 $m^2$ FPR

An analysis of covariance (ANCOVA) gave a significance value of p < 0.05, using the data obtained by the COD analysis in the processes for the 0.1 m<sup>2</sup> surface FPR, with COD removal as the dependent variable. As can be seen in Table 2, the results of these statistical tests show there are differences between the processes (photolysis and photocatalysis) at 10 min of the reaction, in terms of drug degradation, which may be due to the formation of by-products [56] and the reaction surface.

Time	Process	pН	$H_2O_2$	$pH^*  H_2O_2$	Radiation	COD <sub>0</sub>		
(min)	<i>p</i> -Value Probab > F							
5	0.1867	0.5454	0.0047	0.7044	0.7547	0.5000		
10	0.0401	0.3551	0.0003	0.1696	0.8077	0.0272		
15	0.1812	0.1629	0.0046	0.4584	0.5753	0.3224		
20	0.8745	0.3401	0.0005	0.3947	0.4950	0.0101		
30	0.3531	0.6367	0.0518	0.0689	0.4506	0.0017		
45	0.3350	0.1959	0.2378	0.3426	0.2546	0.6667		
60	0.8068	0.2376	0.0656	0.3004	0.8335	0.3633		

Table 2. ANCOVA analysis on the reaction surface of 0.1 m<sup>2</sup> FPR.

In the case of the different pH levels (3.5, 4.15, 7, and 9), there was no significant difference for the medium in which the drug is found. Unlike the study conducted by Tanji et al. in 2023 [57] for the degradation of the malachite green dye by means of a composite of mineral nature, using a heterogeneous photocatalytic process, we found significant differences both for the concentration of said material and for the pH level; in this case, the mean was not statistically significant because only one of the processes showed degradation of AMX.

Finally, with the application of different doses of  $H_2O_2$  (nil and 4 mM), it was found that these influenced the treatments in the first 20 min of the reaction, as well as the initial COD concentration, where significant differences appear at 10, 20 and 30 min of the reaction. In 2022, Zaruma et al. [23] observed a similar behavior for the degradation of methylthionine chloride, where significant differences in the use of  $H_2O_2$  were found at 10, 20, 30, and 60 min. However, in the aforementioned study, other factors such as the process and pH levels also showed significant differences throughout the reaction.

Within the ANCOVA, the interaction between the pH levels and  $H_2O_2$  dose was also analyzed, however, no significant differences was found.

A Tukey test was also carried out; the results are shown in Figure 7. The groupings of the means of the different treatments (processes, Figure 7a; pH, Figure 7b; and  $H_2O_2$  dose, Figure 7c) are represented by letters (A and B), where each letter corresponds to a group, with B being the one with the smallest difference between their means. As can be seen, the process (at 10 min) and the different doses of  $H_2O_2$  (5, 10, 15 and 20 min), show two groups, confirming what was previously described by the ANCOVA test.



**Figure 7.** Tukey test of significant differences between the means of the independent variables: (a) process, (b) pH level, and (c) dose of  $H_2O_2$ .

# 3.6. Comparative Statistical Analysis between the FPR Reaction Surfaces (1 $m^2$ and 0.1 $m^2$ )

Once the optimization experiments for the degradation of AMX were carried out, the different reaction surfaces (0.1 m<sup>2</sup> and 1 m<sup>2</sup>) were compared. The processes (photolysis and photocatalysis) were analyzed at pH 4.15, testing both  $H_2O_2$  doses (0 mM and 4 mM) for both FPR surfaces, using ANCOVA and Tukey tests.

In the case of the ANCOVA evaluation (Table 3), it can be observed that the reaction surface influences the degradation of the pollutant during the entire reaction. In the same way, the Tukey test (Figure 8) showed two groups (A and B), confirming that the FPR surface (Figure 8a) played an important role in the removal of AMX. Regarding the means of the processes (Figure 8b), it can only be observed that, in the sampling at 15 min, there is a significant difference.

**Table 3.** Comparative ANCOVA between the different reaction surfaces  $(0.1 \text{ m}^2 \text{ and } 1 \text{ m}^2)$  FPR, the processes (photolysis and photocatalysis), and the H<sub>2</sub>O<sub>2</sub> doses (0 mM and 4 mM) for the degradation of AMX.

Time (min)	Area	Process	$H_2O_2$	Radiation	СоА		
	<i>p</i> -Value Probab > F						
5	0.0391	0.905	0.0109	0.6574	0.4721		
10	0.0352	0.8123	0.0317	0.7009	0.1055		
15	0.0013	0.0267	0.0015	0.0417	0.0097		
20	0.0029	0.182	0.0025	0.975	0.0389		
30	0.0127	0.9033	0.078	0.0843	0.0783		
45	0.0154	0.6841	0.0965	0.9074	0.1384		
60	0.0139	0.3813	0.0851	0.1305	0.166		



**Figure 8.** A comparative test of means by the Tukey model for the degradation of AMX for (**a**) surface FPR, (**b**) process, and (**c**) dose of  $H_2O_2$ .

For  $H_2O_2$  doses (Figure 8c) at pH 4.15, *p* values < 0.05 can be observed, indicating that during the first 20 min of the reaction, the use of  $H_2O_2$  can significantly affect the AMX degradation result, even when the most favorable treatment was observed without the addition of this agent, as in this case, confirming what was previously mentioned on Section 3.5. In 2020, Morones et al. [19] carried out a factorial analysis  $2^3$  with repeated measurements of the degradation of 2,5-dichlorophenol, testing the interaction between advanced oxidation processes (photolysis and photocatalysis), reactor tilt angle, sample flow through the system, and experiment time, as well as radiation and temperature covariates; they found that the interaction between the time of the reaction and the process, as well as the interaction between the time of the reaction, were statistically significant.

#### 4. Conclusions

The band-gap calculation for  $TiO_2$  P25 showed a value of 3.2 eV, lower than the values shown in other  $TiO_2$  semiconductors obtained by the sol-gel method with titanium tetrabutoxide (TBT) and titanium tetraisopropoxide (TIPT) as precursors. This result indicates faster activation of the photocatalysts  $TiO_2$  P25 to the exposure to high radiation emission, in this case, solar energy.

For solar photocatalysis with a 0.1 m<sup>2</sup> FPR surface, the COD analysis showed a significant degradation at a pH of 4.15, without the addition of  $H_2O_2$ , obtaining a percentage of 27% for COD removal, 60 min after the start of the reaction, and 46.9% of the decrease in COD, in an extended reaction time of 80 min.

At pH 3.5, 7, and 9, no degradation by solar photocatalysis was observed, with or without  $H_2O_2$  addition, for both 0.1 and 1 m<sup>2</sup> FPR surfaces.

With the use of 1 m<sup>2</sup> FPR, a significant percentage degradation by COD was obtained at pH 4.15, 65% of COD removal with the addition of  $H_2O_2$  (4 mM) after 60 min of reaction, and up to 72% when the reaction was extended to 80 min. For the experiments without adding  $H_2O_2$ . AMX degradation reached 100% of COD removal after 50 min, with no observable change up to 80 min of reaction.

The results of the chemical kinetics of the AMX degradation in aqueous solution for the heterogeneous solar photocatalysis process, carried out under pH 4.15, without the addition of H<sub>2</sub>O<sub>2</sub>, show first order reaction (n = 1), on both surfaces of 0.1 and 1 m<sup>2</sup> FPR, with magnitudes of K<sub>phC</sub> = 0.013 min<sup>-1</sup> and K<sub>phC</sub> = 0.10 min<sup>-1</sup>, respectively.

A greater exposed reaction surface (FPR 1 m<sup>2</sup> = 10 FPR 0.1 m<sup>2</sup>) favors the degradation of AMX under similar conditions of the reaction parameters, and also favors the reaction rate, defining the solar photocatalysis reaction in for a 1 m<sup>2</sup> FPR, the experimental magnitude of pH 4.15 and the absence (0 mM) of H<sub>2</sub>O<sub>2</sub>, as the best AMX degradation conditions in this work.

The  $H_2O_2$  doses (nil and 4 mM) showed significant differences within the first 20 min of the reaction for the 0.1 m<sup>2</sup> surface FPR, as well as for the 1 m<sup>2</sup> surface by ANCOVA and by a Tukey test.

The FPR surface showed significant differences in the processes, during the entire reaction time (from 0 to 60 min), statistically confirming that a greater reaction surface on FPR favors the degradation of AMX, as well as the speed of the reaction.

Author Contributions: Data curation, T.L.A.-M. and J.B.P.-N.; formal analysis, T.L.A.-M., I.C.-H., A.A.L.-S., C.M.N.-N. and J.B.P.-N.; funding acquisition, J.B.P.-N.; investigation, T.L.A.-M.; methodology, T.L.A.-M., I.C.-H., A.A.L.-S., C.M.N.-N. and J.B.P.-N.; project administration, J.B.P.-N.; resources, J.B.P.-N.; supervision, C.M.N.-N. and J.B.P.-N.; validation, J.B.P.-N.; writing—original draft, T.L.A.-M.; writing—review and editing, C.M.N.-N. and J.B.P.-N. All authors have read and agreed to the published version of the manuscript.

**Funding:** First author wishes to extend their gratitude to the Consejo Nacional de Humanidades, Ciencias y Tecnologías (CONAHCyT) for the scholarship granted to carry out the doctorate. Authors thank Instituto Politécnico Nacional (Project SIP:20221709 and SIP:20230110) for financing this project. The project does not necessarily reflect the views and policies of the funding organizations.

Data Availability Statement: Data is contained within the article.

**Acknowledgments:** The authors wish to acknowledge the Planta de Tratamiento de Aguas Residuales Oriente de Durango, Dgo., México for providing the additional facilities to carry out the research, to the Advanced Materials Research Center (CIMAV-Durango) for the analysis of the samples and to the National Energy Conversion and Storage Laboratory (LNCAE) of CICATA-Legaria, IPN, for allowing us access to its experimental facilities and analysis equipment. Particular thanks go to Manuel Ávila Santos, for his time, great patience and his expertise in the DRX analysis of TiO<sub>2</sub> P25.

Conflicts of Interest: The authors declare no conflict of interest.

## References

- Morin-Crini, N.; Lichtfouse, E.; Liu, G.; Balaram, V.; Ribeiro, A.R.L.; Lu, Z.; Stock, F.; Carmona, E.; Teixeira, M.R.; Picos-Corrales, L.A. Worldwide cases of water pollution by emerging contaminants: A review. *Environ. Chem. Lett.* 2022, 20, 2311–2338. [CrossRef]
- Bavumiragira, J.P.; Yin, H. Fate and transport of pharmaceuticals in water systems: A processes review. *Sci. Total Environ.* 2022, 823, 153635. [CrossRef] [PubMed]
- 3. Khan, S.; Naushad, M.; Govarthanan, M.; Iqbal, J.; Alfadul, S.M. Emerging contaminants of high concern for the environment: Current trends and future research. *Environ. Res.* **2022**, 207, 112609. [CrossRef] [PubMed]
- 4. Oluwole, A.O.; Olatunji, O.S. Photocatalytic degradation of tetracycline in aqueous systems under visible light irridiation using needle-like SnO<sub>2</sub> nanoparticles anchored on exfoliated g-C<sub>3</sub>N<sub>4</sub>. *Environ. Sci. Eur.* **2022**, *34*, 5. [CrossRef]
- Cravo, A.; Silva, S.; Rodrigues, J.; Cardoso, V.V.; Benoliel, M.J.; Correia, C.; Coelho, M.R.; Rosa, M.J.; Almeida, C.M. Understanding the bioaccumulation of pharmaceutical active compounds by clams Ruditapes decussatus exposed to a UWWTP discharge. *Environ. Res.* 2022, 208, 112632. [CrossRef]
- Figuière, R.; Waara, S.; Ahrens, L.; Golovko, O. Risk-based screening for prioritisation of organic micropollutants in Swedish freshwater. J. Hazard. Mater. 2022, 429, 128302. [CrossRef]
- Narayanan, M.; El-Sheekh, M.; Ma, Y.; Pugazhendhi, A.; Natarajan, D.; Kandasamy, G.; Raja, R.; Kumar, R.S.; Kumarasamy, S.; Sathiyan, G. Current status of microbes involved in the degradation of pharmaceutical and personal care products (PPCPs) pollutants in the aquatic ecosystem. *Environ. Pollut.* 2022, 300, 118922. [CrossRef]
- 8. Ojemaye, C.Y.; Petrik, L. Occurrences, levels and risk assessment studies of emerging pollutants (pharmaceuticals, perfluoroalkyl and endocrine disrupting compounds) in fish samples from Kalk Bay harbour, South Africa. *Environ. Pollut.* **2019**, 252, 562–572. [CrossRef]
- 9. Elshikh, M.S.; Huessien, D.; Alkhattaf, F.S.; El-Naggar, R.A.R.; Almaary, K.S. Diclofenac removal from the wastewater using activated sludge and analysis of multidrug resistant bacteria from the sludge. *Environ. Res.* **2022**, *208*, 112723. [CrossRef]
- 10. Alduina, R. Antibiotics and environment. *Antibiotics* **2020**, *9*, 202. [CrossRef]
- Szymańska, U.; Wiergowski, M.; Sołtyszewski, I.; Kuzemko, J.; Wiergowska, G.; Woźniak, M.K. Presence of antibiotics in the aquatic environment in Europe and their analytical monitoring: Recent trends and perspectives. *Microchem. J.* 2019, 147, 729–740. [CrossRef]
- 12. Jalali, S.; Ardjmand, M.; Ramavandi, B.; Nosratinia, F. Removal of amoxicillin from wastewater in the presence of H<sub>2</sub>O<sub>2</sub> using modified zeolite Y-MgO catalyst: An optimization study. *Chemosphere* **2021**, 274, 129844. [CrossRef]
- 13. Verma, M.; Haritash, A. Photocatalytic degradation of Amoxicillin in pharmaceutical wastewater: A potential tool to manage residual antibiotics. *Environ. Technol. Innov.* 2020, 20, 101072. [CrossRef]
- 14. Mutiyar, P.K.; Mittal, A.K. Occurrences and fate of an antibiotic amoxicillin in extended aeration-based sewage treatment plant in Delhi, India: A case study of emerging pollutant. *Desalination Water Treat.* **2013**, *51*, 6158–6164. [CrossRef]
- 15. Trovo, A.G.; Nogueira, R.F.P.; Agüera, A.; Fernandez-Alba, A.R.; Malato, S. Degradation of the antibiotic amoxicillin by photo-Fenton process–chemical and toxicological assessment. *Water Res.* **2011**, *45*, 1394–1402. [CrossRef] [PubMed]
- 16. Karim, A.V.; Shriwastav, A. Degradation of amoxicillin with sono, photo, and sonophotocatalytic oxidation under low-frequency ultrasound and visible light. *Environ. Res.* **2021**, 200, 111515. [CrossRef]
- Monteiro, M.A.; Spisso, B.F.; Ferreira, R.G.; Pereira, M.U.; Grutes, J.V.; De Andradec, B.; d'Avila, L.A. Development and validation of liquid chromatography-tandem mass spectrometry methods for determination of beta-lactams, macrolides, fluoroquinolones, sulfonamides and tetracyclines in surface and drinking water from Rio de Janeiro, Brazil. J. Braz. Chem. Soc. 2018, 29, 801–813. [CrossRef]

- Commission Implementing Decision (EU) 2020/1161 of 4 August 2020 Establishing a Watch List of Substances for Union-Wide Monitoring in the Field of Water Policy Pursuant to Directive 2008/105/EC of the European Parliament and of the Council (Notified under Document Number C(2020) (5205) (Text with EEA Relevance). 2020; pp. 32–35. Available online: https://www.legislation.gov.uk/eudn/2020/1161 (accessed on 1 May 2023).
- Morones-Esquivel, M.; Núñez-Núñez, C.; González-Burciaga, L.; Hernández-Mendoza, J.; Osorio-Revilla, G.; Proal-Nájera, J. Kinetics and statistical approach for 2, 5-dichlorophenol degradation in short reaction time by solar TiO<sub>2</sub>/glass photocatalysis. *Rev. Mex. Ing. Quim.* 2020, 19, 555–568. [CrossRef]
- Núñez-Núñez, C.M.; Osorio-Revilla, G.I.; Villanueva-Fierro, I.; Antileo, C.; Proal-Nájera, J.B. Solar fecal coliform disinfection in a wastewater treatment plant by oxidation processes: Kinetic analysis as a function of solar radiation. *Water* 2020, *12*, 639. [CrossRef]
- López-Ojeda, G.C.; Vargas-Zavala, A.V.; Gutiérrez-Lara, M.; Ramírez-Zamora, R.M.; Durán-Moreno, A. Oxidación fotoelectrocatalítica de fenol y de 4-clorofenol con un soporte de titanio impregnado con TiO<sub>2</sub>. *Rev. Int. Contam. Ambient.* 2011, 27, 75–84.
- González-Burciaga, L.A.; Núñez-Núñez, C.M.; Proal-Nájera, J.B. Challenges of TiO<sub>2</sub> heterogeneous photocatalysis on cytostatic compounds degradation: State of the art. *Environ. Sci. Pollut. Res. Int.* 2022, 29, 42251–42274. [CrossRef]
- 23. Zaruma-Arias, P.E.; Núñez-Núñez, C.M.; González-Burciaga, L.A.; Proal-Nájera, J.B. Solar Heterogenous Photocatalytic Degradation of Methylthionine Chloride on a Flat Plate Reactor: Effect of pH and H<sub>2</sub>O<sub>2</sub> Addition. *Catalysts* **2022**, *12*, 132. [CrossRef]
- 24. Nosaka, Y.; Nosaka, A.Y. Generation and detection of reactive oxygen species in photocatalysis. *Chem. Rev.* **2017**, *117*, *11302–11336*. [CrossRef] [PubMed]
- 25. Wang, J.; Wang, S. Reactive species in advanced oxidation processes: Formation, identification and reaction mechanism. *Chem. Eng. J.* **2020**, *401*, 126158. [CrossRef]
- González-Burciaga, L.A.; Núñez-Núñez, C.M.; Morones-Esquivel, M.M.; Avila-Santos, M.; Lemus-Santana, A.; Proal-Nájera, J.B. Characterization and comparative performance of TiO<sub>2</sub> photocatalysts on 6-mercaptopurine degradation by solar heterogeneous photocatalysis. *Catalysts* 2020, *10*, 118. [CrossRef]
- 27. Sirés, I.; Brillas, E.; Oturan, M.A.; Rodrigo, M.A.; Panizza, M. Electrochemical advanced oxidation processes: Today and tomorrow. A review. *Environ. Sci. Pollut. Res. Int.* 2014, *21*, 8336–8367. [CrossRef] [PubMed]
- 28. Waghmode, T.R.; Kurade, M.B.; Sapkal, R.T.; Bhosale, C.H.; Jeon, B.-H.; Govindwar, S.P. Sequential photocatalysis and biological treatment for the enhanced degradation of the persistent azo dye methyl red. *J. Hazard. Mat.* **2019**, *371*, 115–122. [CrossRef]
- Pantoja-Espinoza, J.; Proal-Nájera, J.; García-Roig, M.; Cháirez-Hernández, I.; Osorio-Revilla, G. Eficiencias comparativas de inactivación de bacterias coliformes en efluentes municipales por fotólisis (UV) y por fotocatálisis (UV/TiO<sub>2</sub>/SiO<sub>2</sub>). Caso: Depuradora de aguas de Salamanca, España. *Rev. Mex. Ing. Quim.* 2015, 14, 119–135.
- Morones Esquivel, M.M.; Pantoja Espinoza, J.C.; Proal Nájera, J.B.; Cháirez Hernández, I.; Gurrola Reyes, J.N.; Ávila Santos, M. Uso de un reactor de placa plana (TiO<sub>2</sub>/vidrio) para la degradación de 2, 5-diclorofenol por fotocatálisis solar. *Rev. Int. Contam. Ambient.* 2017, 33, 605–616. [CrossRef]
- Dean, J.C.; Oblinsky, D.G.; Rafiq, S.; Scholes, G.D. Methylene blue exciton states steer nonradiative relaxation: Ultrafast spectroscopy of methylene blue dimer. J. Phys. Chem. B 2016, 120, 440–454. [CrossRef]
- 32. López, R.; Gómez, R. Band-gap energy estimation from diffuse reflectance measurements on sol–gel and commercial TiO<sub>2</sub>: A comparative study. *J. Solgel. Sci. Technol.* **2012**, *61*, 1–7. [CrossRef]
- Velasco-Arias, D. Obtención de Nanoestructuras Hechas a Base de Bismuto. Cerovalente, Bi<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> y Bi<sub>2</sub>Mo<sub>2</sub>O<sub>9</sub>. Ph.D. Thesis, Faculty of Chemistry, Universidad Nacional Autónoma de México, Mexico City, Mexico, 2013.
- Blanco Gálvez, J. El Reactor Solar Fotocatalítico: Estado del Arte. In *Tecnologías Solares para la Desinfección y Descontaminación del Agua*; Solar Safe Water: Puerto Iguazú, Argentina, 2005; Chapter 17; pp. 277–302.
- Stintzing, A. Solar Photocatalytic Treatment of Textile Wastewater at a Pilot Plant in Menzel Temime/Tunisia. Bachelor's Thesis, Institut f
  ür Thermische Verfahrenstechnik der Technischen Universit
  ät Clausthal, Clausthal-Zellerfeld, Germany, 2003.
- Alcázar-Medina, T.L. Degradación de Amoxicilina en Modelos Acuosos Mediante Fotólisis, Fotocatálisis Solar y Fotocatálisis UV. Master's Thesis, CIIDIR-Durango, Instituto Politécnico Nacional, Mexico City, Mexico, 2019.
- 37. Demirezen, D.A.; Yıldız, Y.Ş.; Yılmaz, D.D. Amoxicillin degradation using green synthesized iron oxide nanoparticles: Kinetics and mechanism analysis. *Environ. Nanotechnol. Monit. Manag.* **2019**, *11*, 100219. [CrossRef]
- Moogooee, M.; Ramezanzadeh, H.; Jasoori, S.; Omidi, Y.; Davaran, S. Synthesis and in vitro studies of cross-linked hydrogel nanoparticles containing amoxicillin. *J. Pharm. Sci.* 2011, 100, 1057–1066. [CrossRef] [PubMed]
- Malato, S.; Fernández-Ibáñez, P.; Maldonado, M.I.; Blanco, J.; Gernjak, W. Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. *Catal. Today* 2009, 147, 1–59. [CrossRef]
- 40. Chen, J.; Cesario, T.C.; Rentzepis, P.M. Effect of pH on methylene blue transient states and kinetics and bacteria photoinactivation. *J. Phys. Chem. A* **2011**, *115*, 2702–2707. [CrossRef]
- Zaruma-Arias, P.; Núñez-Núñez, C.; Villanueva-Fierro, I.; Cháirez-Hernández, I.; Lares-Asseff, I.; Gurrola-Reyes, J.; Proal-Nájera, J. Methylthionine chloride degradation on pilot UV-C reactors: Kinetics of photolytic and heterogeneous photocatalytic reactions. *Rev. Mex. Ing. Quim.* 2021, 20, 649–662. [CrossRef]
- 42. Freudenhammer, H.; Bahnemann, D.; Bousselmi, L.; Geissen, S.-V.; Ghrabi, A.; Saleh, F.; Si-Salah, A.; Siemon, V.; Vogelpohl, A. Detoxification and recycling of wastewater by solar-catalytic treatment. *Water Sci. Technol.* **1997**, *35*, 149–156. [CrossRef]

- Le Bail, A.; Duroy, H.; Fourquet, J.L. Ab-initio structure determination of LiSbWO<sub>6</sub> by X-ray powder diffraction. *Mat. Res. Bull.* 1988, 23, 447–452. [CrossRef]
- 44. Warren, B.E. X-ray Diffraction, 1st ed.; Courier Corporation: North Chelmsford, MA, USA, 1990.
- 45. Sheng, Y.; Liang, L.; Xu, Y.; Wu, D.; Sun, Y. Low-temperature deposition of the high-performance anatase-titania optical films via a modified sol–gel route. *Opt. Mater.* **2008**, *30*, 1310–1315. [CrossRef]
- 46. Jubu, P.; Yam, F.; Igba, V.; Beh, K. Tauc-plot scale and extrapolation effect on bandgap estimation from UV-vis NIR data—A case study of β-Ga<sub>2</sub>O<sub>3</sub>. *J. Solid State Chem.* **2020**, 290, 121576. [CrossRef]
- 47. Jubu, P.R.; Obaseki, O.; Yam, F.; Stephen, S.; Avaa, A.; McAsule, A.; Yusof, Y.; Otor, D. Influence of the secondary absorption and the vertical axis scale of the Tauc's plot on optical bandgap energy. *J. Opt.* **2022**, *24*, 1–10. [CrossRef]
- 48. Kanakaraju, D.; Kockler, J.; Motti, C.A.; Glass, B.D.; Oelgemöller, M. Titanium dioxide/zeolite integrated photocatalytic adsorbents for the degradation of amoxicillin. *Appl. Catal. B Environ.* **2015**, *166*, 45–55. [CrossRef]
- 49. Xu, H.; Cooper, W.J.; Jung, J.; Song, W. Photosensitized degradation of amoxicillin in natural organic matter isolate solutions. *Water Res.* 2011, 45, 632–638. [CrossRef] [PubMed]
- 50. Dou, M.; Wang, J.; Gao, B.; Xu, C.; Yang, F. Photocatalytic difference of amoxicillin and cefotaxime under visible light by mesoporous g-C<sub>3</sub>N<sub>4</sub>: Mechanism, degradation pathway and DFT calculation. *Chem. Eng. J.* **2020**, *383*, 123134. [CrossRef]
- 51. Plantard, G.; Janin, T.; Goetz, V.; Brosillon, S. Solar photocatalysis treatment of phytosanitary refuses: Efficiency of industrial photocatalysts. *Appl. Catal. B Environ.* **2012**, *115*, 38–44. [CrossRef]
- 52. Silva, B.S.; Ribeiro, M.C.B.; Ramos, B.; de Castro Peixoto, A.L. Removal of Amoxicillin from Processing Wastewater by Ozonation and UV-Aided Ozonation: Kinetic and Economic Comparative Study. *Water* **2022**, *14*, 3198. [CrossRef]
- Koltsakidou, A.; Katsiloulis, C.; Evgenidou, E.; Lambropoulou, D. Photolysis and photocatalysis of the non-steroidal antiinflammatory drug Nimesulide under simulated solar irradiation: Kinetic studies, transformation products and toxicity assessment. *Sci. Total Environ.* 2019, 689, 245–257. [CrossRef]
- Chen, Z.; Yao, D.; Chu, C.; Mao, S. Photocatalytic H<sub>2</sub>O<sub>2</sub> production systems: Design strategies and environmental applications. *Chem. Eng. J.* 2022, 451, 138489. [CrossRef]
- Mancuso, A.; Morante, N.; De Carluccio, M.; Sacco, O.; Rizzo, L.; Fontana, M.; Esposito, S.; Vaiano, V.; Sannino, D. Solar driven photocatalysis using iron and chromium doped TiO<sub>2</sub> coupled to moving bed biofilm process for olive mill wastewater treatment. *Chem. Eng. J.* 2022, 450, 138107. [CrossRef]
- 56. Buitrago, J.L.; Sanabria, J.; Gútierrez-Zapata, H.M.; Urbano-Ceron, F.J.; García-Barco, A.; Osorio-Vargas, P.; Rengifo-Herrera, J.A. Photo-Fenton process at natural conditions of pH, iron, ions, and humic acids for degradation of diuron and amoxicillin. *Environ. Sci. Pollut. Res. Int.* 2020, 27, 1608–1624. [CrossRef]
- 57. Tanji, K.; Fahoul, Y.; El Mrabet, I.; Zaitan, H.; Kherbeche, A. Combined Natural Mineral@ZnCoO System for Photocatalytic Degradation of Malachite Green Under Visible Radiation. *Chem. Afr.* **2023**, *6*, 1463–1478. [CrossRef]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.