Oxytetracycline Water Contamination Treated with Biocarbon TiO₂ and Solar Photodecomposition

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Abstract

Reliable data of antibiotic use and environmental discharge as veterinary medicine are essential to help countries raise awareness of the appropriate use, control, and correct water release. The first approach is to change the regulatory framework based on consuming information, use policy, and discharge laws. The important research contribution is a novel water treatment process to treat, remove, and reduce antibiotic concentration in discharged water, mainly those used in the animal protein industry. The low particle biochar added during the titanium isopropoxide hydrolysis reduces the titanium dioxide (TiO₂) agglomerates and promotes the adsorption surface process. Such improved catalyst material enhances the solar decomposition efficiency to 93% from original oxytetracycline with better correspondence with the Elovich kinetics, intraparticle diffusion, R-P isotherm, and Langmuir-Hinshelwood model.

Keywords

Oxytetracycline, Solar Photodecomposition, Biocarbon, Elovich, Langmuir-Hinshelwood (L-H)

1. Introduction

Antibiotics save millions of lives by effectively fighting bacteriological diseases. The discovery was in the 1920s, and, over the years, the pathogen bacteria have changed to improve the adaptation and resist these drugs.

Nowadays, animal production use also antibiotics as a growth promoter. In some countries, 80% of total antibiotic use comes from veterinary medicine, ac-

cording to the World Health Organization [1].

The pharmaceuticals production is essential and responsible for life quality and public health improvement, increasing the life expand and therefore perform a significant role in prevention, diagnostic, and treatment in human and veterinary medicine.

Some published environmental studies indicated the main routes and sources of pharmaceuticals pollution the raw sewage discharge and the urban drainage wastewater with their input in the aquatic environment.

The first public report describing the water contamination by surface water antibiotics was performed in England in 1982, with the detection of tetracyclines in a river at concentrations of 1 $\mu g \cdot L^{-1}$ [2].

The oxytetracycline has low metabolism absorption, and about 70% leave the organisms via urine and feces. It has been detected widely in different environmental systems worldwide, such as soil, aquatic systems, and sediments. Its occurrence in the environment may harm the ecosystem and human health through the development of antibiotic-resistant bacteria and pathogens. Such a problem is obtaining increasing global concern and scientific interest in recent years. Several research studies showed that conventional water treatment methods are not efficient in removing such a micropollutant from water [3]. Hence, the investigation of effective treatment technologies for the removal of this contaminant is highly essential. In many countries, animal excreta is the primary source of indirect contamination of surface resources by drug compounds, including antibiotics.

The wastewater applied in animal treatment flows into watercourses, and also the produced manure is discharged in the soil to fertilize agricultural land. The leaching of the over-administered compounds and metabolites can contaminate surface waters and deep waters [4]. Brazil has the world's most significant protein production, and the use of the antibiotic in veterinary medicine is excessive [5] [6]. Their application in sick animals is usually too common, and also is served to healthy animals, as growing supplement. Brazil is also the third-largest user of antibiotics in animal production after China and the USA.

Terramycin is the most widely used veterinary antibiotic, and its active ingredient is oxytetracycline dehydrate, a broad-spectrum antibiotic, and highly active against a large number of microorganisms [7] [8].

Since its discovery in 1953, oxytetracycline has become the most widely used antibiotic base and marketed in rural areas due to its high power of action against the primary bacterial infections affecting animals [9] [10].

There are many water treatment processes to decompose antibiotics in literature, mostly using UV—ultraviolet radiation combined with H_2O_2; others include high pressurized osmosis and ultrafiltration [10] [11]. The use of solar photodecomposition is sustainable, less expensive, and adapted to distant rural areas, mainly in tropical countries.

The titanium dioxide (TiO_2) synthesis using the hydrolysis process is very ef-

fective, but, in many cases, results in powder agglomerates formed during the standard drying process. The use of eucalyptus biocarbon during the TiO_2 formation avoids the formation of the agglomerate and keeps the high surface area [12] [13] [14].

The air collection of eucalyptus biocarbon powder as solid residue in the steel plant promotes the use of biocarbon with the small particle size and high surface area. It is well known as a labor health problem and commonly collected in the air as solid particle dust using air filters in steel plant. In such a production plant, the biocarbon particles are labor health problem to be avoided at any cost [15].

The research project's justification is the development of the biocarbon additive to TiO_2 synthesis for surface area improvement, a tool to prepare and obtain better TiO_2 to apply in solar photodecomposition processes [16]. Some published results indicated that the physical mixture of the solid activated carbon with TiO_2 particles in water suspensions promotes a robust synergistic effect improving the photodecomposition reaction of many pollutants as phenol, chlorophenol, and an herbicide.

Nowadays, the synergistic effect is not confirmed, but the activated carbon performs the role of efficient surface adsorbent, which allows the solid surface adsorption contact improvement for photodecomposition process. The pré-adsorption of the reactants on the TiO_2 surface during the photocatalytic reaction leads to a more efficient electron transfer process [17] [18]. The interaction of TiO_2 surface and absorbent influenced the adsorbent properties as a functional group, orientation of charges, electronic densities, size of molecules, and mostly surface atoms to make a covalent bond with the adsorbent to lower the surface energy are essential to perform better adsorption and consequently an efficient photodecomposition [19] [20].

The solar photodecomposition process usually involves the production of the $HO^{\star}$ and O_2 radicals. In most heterogeneous catalytic processes, the $HO^{\star}$ is widely regarded as the primary active oxidant and is ubiquitous in the use of the TiO_2 as a catalyzer. The improvement of the TiO_2 properties will promote solar photodecomposition efficiency and utilization.

$$TiO_2 + hv \rightarrow e^- + h^+ \tag{1}$$

$$H_2O + h^+ \rightarrow H^+ + OH^* \tag{2}$$

When the solar energy irradiated the micro TiO_2, there is a promotion of the hydroxyl radicals' formation and increases the decomposition kinetics possible, leading to the organic contaminant mineralization. The use of TiO_2 integrated with the fine biocarbon promotes the water treatment efficiency and water quality polishment removing the antibiotics and its by-products in an efficient, low-cost process with renewable energy [7] [21]. The use of TiO_2 biocarbon as an efficient catalyzer for the water treatment process will reduce the pharmaceuticals contamination in surface water resources in a sustainable low-cost way

[22].

Brazil is responsible for the third animal protein production in the world and has high antibiotics consumption in veterinary medicine. The country geographic location indicates high potential of solar photocatalysis use, fully justified concerning the availability of solar energy. Aiming the promotion of the solar decomposition process sustainable, feasible and highly profitable, this research project searches the development of the TiO_2 with biocarbon to improve the solar photodecomposition efficiency promoting the antibiotics decomposition presents in farm effluents, treating the polluted discharge after reach surface water resources.

2. Methods

The use of oxytetracycline in the experiments was due to its extensive production, and use in veterinarian treatment, actually with raw discharge in sewage water and water resources [13] [14].

The synthesis of the TiO_2 used titanium isopropoxide in aqueous solution with the addition of acetic acid and fine eucalyptus biocarbon. The biocarbon also allows the better morphology of the TiO_2 fine particle formation and avoids the agglomeration.

The TiO_2 preparation started with the titanium isopropoxide volume to a beaker filled with distilled water, acetic acid, and the correspondent biocarbon mass from 1 to 0.05 g. The amount was in the range of 1 to 5 mL for 400 mL of final suspension. The mixing process of the suspension was for two hours using a magnetic stirrer, followed by the filtration. The drying process was overnight at 100°C. Previous studies indicate the solid calcination in high temperatures is not favorable due to the reduction of the surface area and porous vacancies.

The photodecomposition process started with the TiO_2 solid addition on initial antibiotic concentration and the installation inside an ultrasonic system for sonication for 5 min after that was the installation in the artificial solar chamber. The experimental procedure starts with temperature control in the range of 26 to 46°C, and pH from 3 to 5. The mixture and installation of the final suspension in solar chamber still in the beginning in dark for 30 min, and after that with the solar radiation application. The control of the pH and temperature parameters allows to keep constant during the process, there was suspension aliquots collection after 30 min of agitation each to perform the total process control with 5 h in total.

The temperature at 40°C and pH 5 were the optimization values of photodecomposition, the determination of the parameters used the Experiment Planning Project with two settings, and three variables. Starting with initial oxytetracycline concentrations (equivalent to those found for environmental contamination in literature), system temperatures, pH, and biocarbon mass added during the TiO_2 formation by hydrolysis. The use of a controlled solar chamber promotes the development of the solar photodecomposition processes in a controlled en-

vironment. An artificial solar lamp simulates solar radiation used, and a lux meter measured the total lumen per square meter in the chamber during the process. The use of the UV-Vis spectrophotometer allows the determination of the oxytetracycline concentrations in the different aliquots using a prepared calibration curve.

3. Results and Discussion

The use of TiO_2 prepared by the hydrolysis with the bio-carbon improves the solar photo-decomposition process. **Figure 1** compares the crystalline structure of the TiO_2 with the TiO_2 prepared with biocarbon addition. The morphology of the biocarbon sample indicates bigger crystallinity, amorphous content, and possibly the surface area enhancement for the TiO_2 with biocarbon [23] [24].

The anatase phase, TiO_2 has a tetragonal structure, the dimensional characteristics of the unit cell parameters with a = b = 0.379 nm and c = 0.951 nm [25]. The peak heights of the biocarbon sample were higher in comparison with synthetic TiO_2, presenting about 44% greater crystallinity, evidence of higher intensity diffraction for the TiO_2 biocarbon.

The solar photodecomposition processes started with an adsorption step when the system was mixed in dark condition for about 30 min. **Figure 2** presents the comparison between the MEV micrography of the pure TiO_2 and the TiO_2 biocarbon. The TiO_2 biocarbon showed high porous and surface area, such characteristic favors the adsorption process. The initial adsorption condition provides better surface contact between the antibiotic and the TiO_2 biocarbon solid surface.
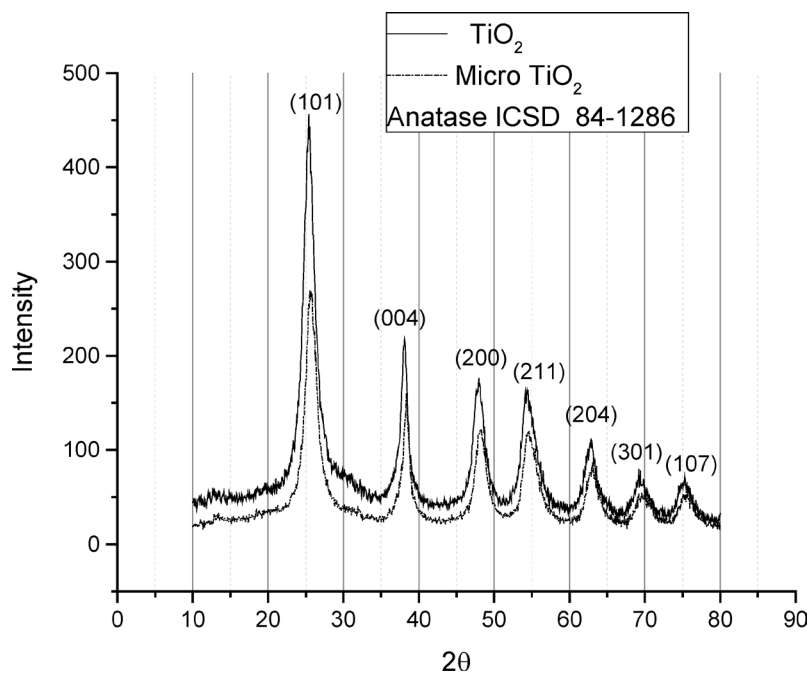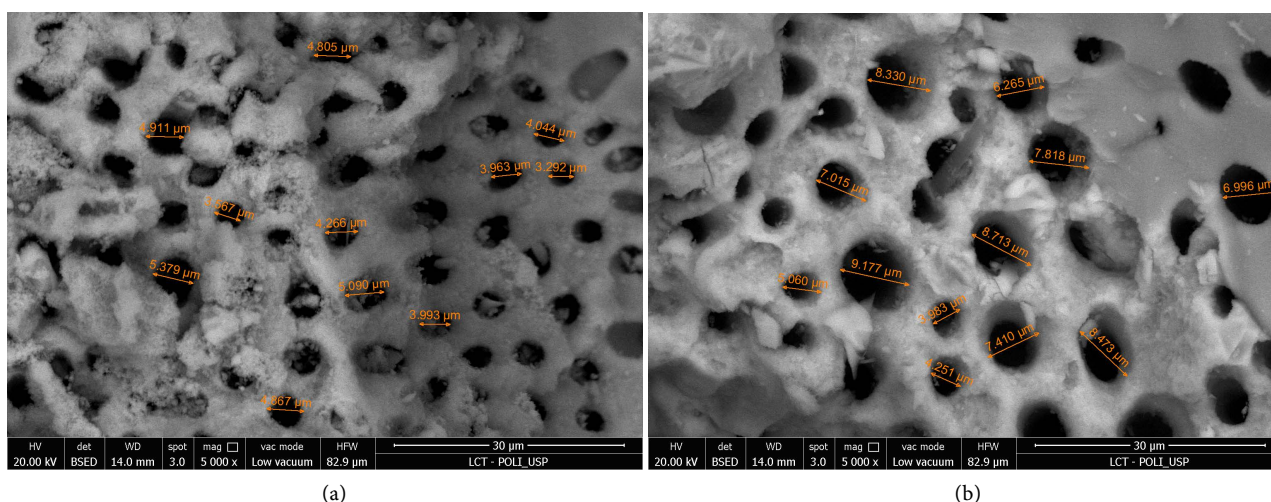

Figure 1. X-ray diffraction patterns for TiO_2 and TiO_2 biocarbon—Anatase with Miller Index [25].

Figure 2. MEV micrography by backscattering electrons BSE: (a) Pure TiO_2 and (b) TiO_2 and Biocarbon.

The MEV analyses in low vacuum allow the surface area comparison with relatively small sample modification. Usually, the treatment of the samples for traditional area measurements as BET implies high drying temperatures. The advice is not to use such treatment in such samples, due to the promotion of sample surface area modifications after measurements.

3.1. Adsorption Calculations

The suspended TiO_2 slurry in the early process stages considered the mass transfer limitation negligible. Usually, the surface adsorption kinetics control the measured reaction rate by the surface adsorption kinetics. Accordingly, the adsorption models are generally used to interpret the kinetic data obtained [23] [26].

The adsorption kinetics studies provide valuable insights about the kinetic models: pseudo-first-order, pseudo-second-order, and Elovic with the determination of adsorption rates using the following equations.

Pseudo-first-order equation:

$$\log(qe - qt) = \log(qe) - \left(\frac{K_1}{2.303}\right)t \tag{3}$$

K_1 is the pseudo-first-order rate (min^{-1}), and qe (mgg^{-1}) is the experimental decomposed mass at t equilibrium. The plotting of the calculated values of $\log(qe - qt)$ for t (time) and the calculation of K_1 used the slope values of the line equation.

Pseudo-second order equation:

$$\frac{t}{qt} = \frac{1}{K_2} + \left(\frac{1}{qe}\right)t \tag{4}$$

where: K_2 (g·mg^{-1}·min^{-1}) is the kinetics decomposition rate, the line equation values of plotted t/qt for t (min), and the calculation predicted decomposition capacity qe (mg·g^{-1}) and the integrated adsorption rate K_2 with the slope and the intercept of the line equation, respectively.

Elovich Equation:

$$qt = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{5}$$

where: α is an initial kinetics flow rate, $min^{-1} \cdot mg \cdot g^{-1}$; β is a degree of TiO_2 biocarbon surface coverage and the activation energy of chemisorption ($g \cdot mg^{-1}$).

The use of the experimental results allows performing the kinetics calculations. Figure 3 and Table 1 presents the decomposition rates with a better correlation with Elovic kinetics.

Table 1 presents the pseudo-first order and pseudo-second-order kinetics constants, and they are less correspondent with the experimental data with R^2 values lower than 0.98. The pseudo-second-order has the limiting step of the chemical contact between the antibiotic and solid surface deposition. The equation is based on the surface contact on the solid-phase and agrees with a chemisorption mechanism being the rate-controlling step.

The successfully interpreted Elovich equation supports the heterogeneous TiO_2 surface contact mechanism responsible for the improvement of the antibiotic decomposition, with a higher removal percentage of 93% removal obtained for 7.5 hours.
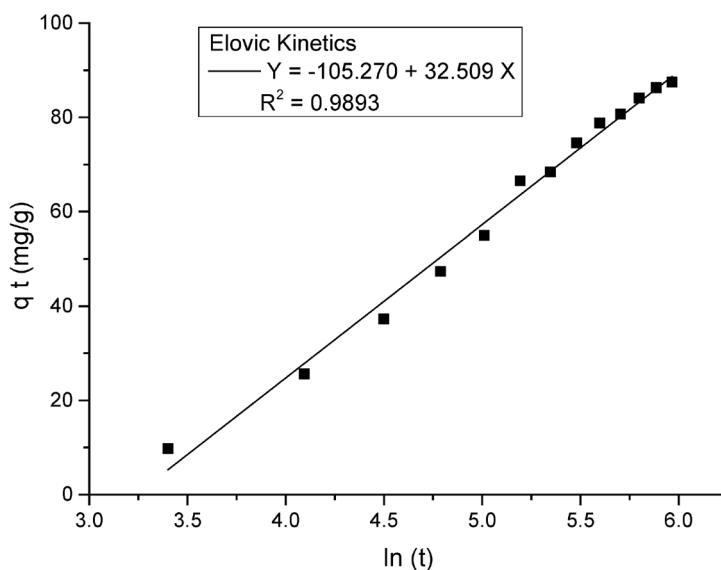

Figure 3. Elovich kinetics calculations.

Table 1. Kinetics and diffusion results of the decomposition with TiO_2.

Kinetics	Decomposition rates	R^2
Pseudo-first order	$K_1 = 0.0113$ (min^{-1})	0.9386
Pseudo-second order	$K_2 = 0.570$ ($g \cdot mg^{-1} \cdot min^{-1}$)	0.9718
Elovich	$\alpha = 1.27$ ($min^{-1} \cdot mg \cdot g^{-1}$) $\beta = 0.03$ $g \cdot mg^{-1}$	0.9893
Interparticle Diffusion	$K_{id} = 5.531$ ($g \cdot mg^{-1} \cdot min^{-1}$)	0.9722

3.2. Intraparticle Diffusion

The calculation of the intraparticle diffusion rate result on K_{id} = 5.531 (g·mg^{-1}·min^{-1}) [27] [28]. In the intraparticle equation, the linear plot intercept values reflect the boundary antibiotic layer effect on surface contact, larger the intercept, the greater the contribution of the surface contact in the rate-limiting step, Figure 4.

Intraparticle equation

$$\log(qt) = \log(K_{id}) + \log(t) \tag{6}$$

If the plot did not pass through the origin is an indication of the intraparticle diffusion was not the only rate-limiting step for the decomposition reaction.

There are the main steps of the decomposition process in heterogeneous photocatalysis. The catalytic reactions involve several physical transport processes that can influence the overall reaction rate) [29]. The photocatalytic process takes place in following specific steps:

1) Reagents diffusion in a boundary layer or film adjacent to the catalyst surface.

2) Diffusion of reagents within the catalyst pores of surface-active sites (intraparticle diffusion).

3) Adsorption of reagents on the catalyst surface.

4) The surface reaction inactive sites followed by desorption.

5) Reaction product diffusion through external surface pores (intraparticle diffusion).

6) Reaction products diffusion through the outer boundary layer until the fluid leaves the catalyst region.

The effective chemical kinetics of the transformation and breakdown of molecules occurs between steps 3 and 4, but the other steps can also influence the process. In general, the slow and complex stage is the limiting step of the total
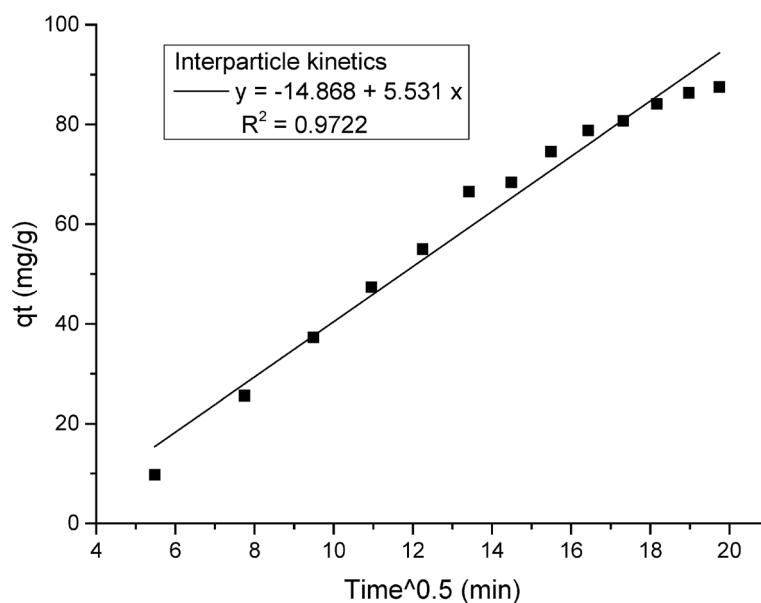

Figure 4. Intraparticle diffusion.

reaction, so it is from this stage that the reaction profile will draw. When the intraparticle diffusion rate decreased, represents the boundary layer effect increased with increasing solution temperature (See Table 1 and Table 2). Table 2 shown the decomposition rate decreasing with temperature, which suggests a chemisorption reaction between the active sites on the TiO_2 surface and the antibiotic molecules.

As decomposition temperature increased, the mobility of the molecules decreased due to chemisorption reaction with active surface sites, reducing the diffusion into the inner surface of the TiO_2, reducing the intraparticle diffusion rate constant with temperature.

On the other hand, the line equation intercept's values indicate that the boundary diffusion or surface contact increased with temperature, suggesting that surface reaction became prominent as the temperature increases. Similar to some reported results, the decreasing intraparticle diffusion rates increase the efficiency of the surface reaction with temperature.

3.3. Isotherm Calculations

The calculation of oxytetracycline adsorption isotherms was varying the initial concentrations in the range of those found for water contamination in literature. The equilibrium data were analyzed using the Langmuir, Freundlich, and Redlich Peterson (R-P) models. The results confirm that the Langmuir isotherm was the most correspondent, presenting the highest Pearson coefficient—R^2. Table 3 showed the parameters of the Langmuir, Freundlich, and R-P adsorption isotherms, respectively.

Using the Langmuir adsorption equilibrium constant was possible to calculate the dimensionless factor (R_L). The value of the R_L parameter, allows the evaluation whether the adsorption of the components in aqueous solution was favorable

Table 2. Intraparticle diffusion results for different temperatures.

Temperature (°C)	K_{id} (g·mg^{-1}·min^{-1})	R^2
38	6.043	0.766
41	5.531	0.9722
43	2.881	0.5287
45	2.620	0.6860
48	4.340	0.9176
50	3.880	0.9527

Table 3. Adsorption isotherm parameters.

Langmuir				Freundlich			R-P		
Q_0 (mg·g^{-1})	b (Lg^{-1})	R_L	R^2	n (gL^{-1})	Kf (mg·g^{-1})	R^2	ar (L·mg^{-1})	Kr (L·mg^{-1})	R^2
104.17	0.87	0.004	0.97	14.08	79.43	−0.37	0.93	0.02	0.91

or not $R_L > 1$ indicates that the process is unfavorable, $R_L = 1$ indicates a linear isotherm, $0 < R_L < 1$ indicates that the process is favorable and $R_L = 0$ indicates that the process is irreversible. The calculated R_L value was between 0 and 1, so the adsorption isotherm was favorable.

In literature, a study using the removal of 4 antibiotics (amoxicillin, ampicillin, cephalexin, and ciprofloxacin) from water using the adsorption process on activated carbon allows the comparison with the results obtained from oxytetracycline [30]. In the research, the isotherms showed a better correlation with the Langmuir model, since Pearson's coefficients for the four antibiotics were above 0.98 [31]. Table 4 showed the Langmuir constants of the following antibiotics: Amoxicillin, ampicillin, cephalexin, ciprofloxacin, and oxytetracycline.

Regarding the Freundlich isotherm, the tests performed with oxytetracycline photodecomposition showed a low R^2 value. Published results indicated the parameter n, of the Freundlich model with values greater than 10, indicating a process not favorable to the interaction model of the adsorbent by the adsorbate [30] [31]. Using tetracyclines and activated carbon, some researchers proved that the Redlich-Peterson isotherm was the isotherm which best described the experimental data. The tests performed with activated carbon to remove paracetamol [32] [33] and some tests with oxytetracycline also demonstrated a correlation with the R-P model, with $R^2 = 0.91$. Table 5 showed the R-P constants presented in the literature of paracetamol, oxytetracycline, and tetracycline. The biocarbon and activated carbon surface and functionality can change considerably according to the constituents as the humic acids, these effects can influence the adsorption efficiency and also isotherms correspondence.

Table 4. Langmuir constants published for different antibiotics and the Oxytetracycline in this study [30] [31].

Model	Antibiotics					
	Parameters	Amoxicillin	Ampicillin	Cephalexin	Ciprofloxacin	Oxytetracycline
Langmuir	q (mg·g^{-1})	50.503	59.171	32.683	62.893	104.17
	b (Lg^{-1})	0.148	0.565	0.232	0.061	0.873
	R^2	0.984	0.983	0.987	0.993	0.965
	R_L	0.119	0.034	0.080	0,2469	0.004

Table 5. R-P constants published in the literature for different pharmaceuticals compounds [28] [33].

Model	Medicine		
	Parameters	Paracetamol	Oxytetracycline	Tetracycline-Coal (35°C)
R-P	kr (L·mg^{-1})	1.752	0.02	0.07
	ar (L·mg^{-1})	1.01	0.93	0.03×10^{-2}
	R^2	0.99	0.91	0.99

3.4. Decomposition Langmuir-Hinshelwood

The Langmuir-Hinshelwood (L-H) kinetic model is mostly applied to describe the photocatalytic mineralization reactions. The model rates of catalyzed reactions to the solid surface covered by the substrate. The unimolecular surface reaction is proportional to the surface coverage [34]. The model proposes as the reactant concentrations increase above a certain level; however, the catalysts become saturated, decreasing the observed rates. The presence of the intermediary compounds also shows a negative effect on the reaction of the parent compounds.

The first simple scenario occurs the TiO_2 solar illumination and the adsorption of the oxidative part with the creation of free hydroxyl radicals. The radicals react with the pollutant, and depending on the compound nature, the process leads to minimal moieties and mineralization. Another possibility is the direct hole oxidation performed by the adsorbed pollutant. The photocatalytic oxidation can be a result of both processes mediated by a hole or also by hydroxyl radicals.

$$-\frac{dC}{dt} = kfKe\frac{C}{(1+KeC)} \tag{7}$$

where: C represents the concentration in solution of the molecule being degraded ($mg \cdot L^{-1}$), kf is the reaction rate constant ($mg \cdot L^{-1} \cdot min^{-1}$), and Ke is the equilibrium constant for the adsorption of the molecule on the catalyst surface at the reaction temperature ($L \cdot mg^{-1}$). The evaluation of term $kfKe$ is global as an apparent rate constant $Kapp$ (min^{-1}).

The simplified L-H equation:

$$\ln\left(\frac{C_0}{C}\right) = kappt \tag{8}$$

Figure 5 shows the photodecomposition efficiency with lower initial concentrations to a certain point when the decomposition curve changes to a higher
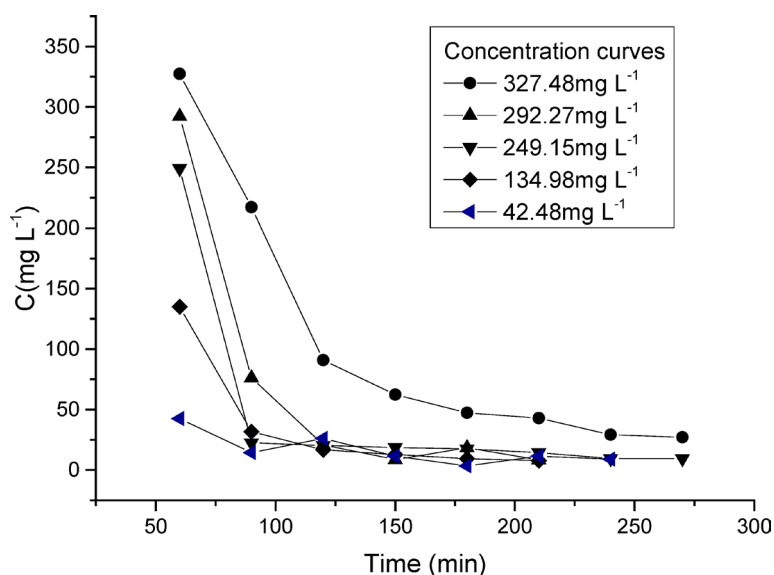

Figure 5. Decay curves for different initial concentrations.
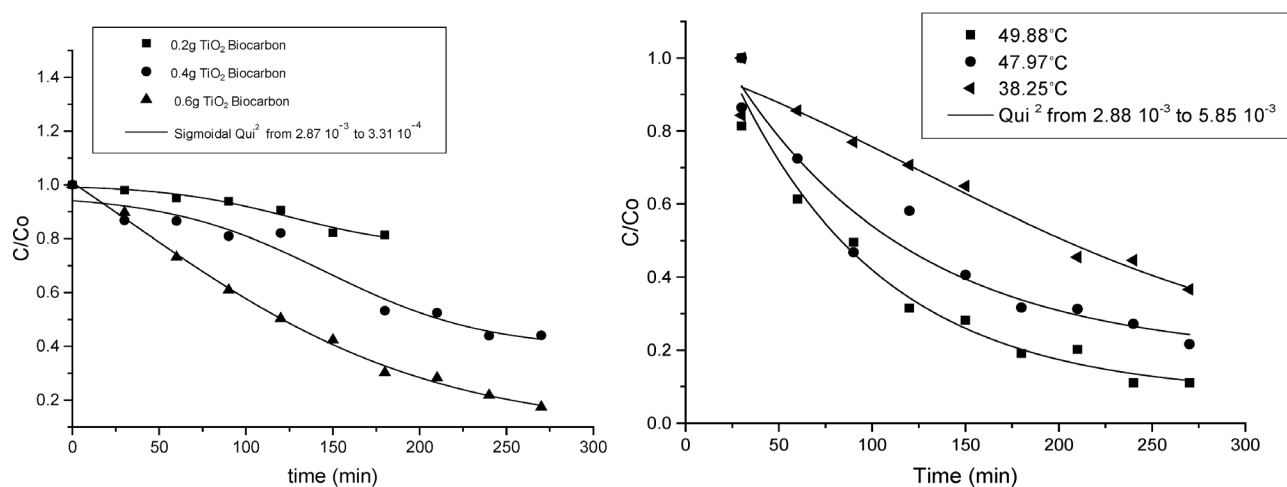
Figure 6. L-H effect of the TiO$_2$ biocarbon mass, and in the right the temperature effect in decomposition efficiency.

equilibrium condition, observed for $Ci = 327.48$ mg·L^{-1}.

Figure 6 shows the decay sigmoidal curves with TiO$_2$ biocarbon content added during the TiO$_2$ hydrolysis and how the decomposition temperature affects the process efficiency.

The results indicate the direct relation between the decomposition efficiency with the initial concentration. The system also shows endothermic behaviors with higher effectiveness in higher temperatures.

The L-H model has many limitations compared to real experiments such as adsorption and desorption processes under the solid catalyst surface, and the initial degradation rate instead of the degradation rate during the whole process. The stable photocatalyst surface is an ideal scenario. In any photodecomposition process, there is much interference of other OH surface groups, bond cleavages, adhesion impurities of the pollutants.

4. Conclusions

- The biocarbon with low particle size addition was efficient, low cost, and renewable material for TiO$_2$ hydrolysis, enhancing the photodecomposition efficiency, with 93% of oxytetracycline decomposition and its by-products. The material led to the better antibiotic removal process allowing the processes parameters optimization as antibiotics initial concentration, agitation time, solar radiation incidence time, TiO$_2$ biocarbon mass, pH, and temperature.
- The Elovic kinetics model presents high correspondence with promising results with chemisorption and the intraparticle diffusion, suggesting that the over-all rate-determining step may be complicated but include the initial adsorption improvement Biocarbon addition.
- The results also show that the predicted equilibrium capacities increase with increasing temperature. The increasing rate of chemisorption-diffusion indicates that both diffusion and chemisorption processes become increasingly important in the rate-determining step as the temperature increases.

- The TiO_2 solar decomposition of antibiotics is so far the best-decomposition processes with low toxic production, capacity effectiveness, better compromise, solution for water treatment, and environment conservation X price.

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Conflicts of Interest

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

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