


# Yeast-TiO<sub>2</sub> Biotemplate for Oxytetracycline Solar Photodecomposition

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## Abstract

The detection of the pharmaceutical compounds used in human and veterinary medicine is in several environmental matrices (surface waters, effluents, groundwater, soils, and sediments), and such presence promotes the resistance bacteria development, making them ineffective in some diseases treatment. The research project promotes the TiO<sub>2</sub> synthesis using yeast culture as biotemplate, the step followed by the microstructure characterization with surface area enhancement; such properties are responsible for the improvement of solar photodecomposition processes of the veterinary antibiotic oxytetracycline. In such simple and standard process conditions the system reaches about 84% of removal percentage with a better agreement with the pseudo-first-order with the Pearson coefficient in the range from 0.82 to 0.94 and  $K_1 = 0.035 \text{ M}^{-1}\cdot\text{s}^{-1}$ . The degradation rate constant increased with the increasing initial Yeast-TiO<sub>2</sub> dosage until the maximum mass of 0.1 g or with the decreasing of initial oxytetracycline concentration. The solar light used as a sustainable irradiation source is abundant and low cost in tropical countries, perfect to be applied in water treatment to decompose the pharmaceuticals pollutants, as the veterinarian antibiotics. The study demonstrates that solar photodecomposition is an efficient treatment technology for the removal of antibiotics from polluted water and provides insightful information on the potential practical application of this technology to treat contaminated water, possibly also in rural, distant areas.

## Keywords

Oxytetracycline, Photodecomposition, Bio Template, Yeast, Solar

## 1. Introduction

Brazil still has much to explore in solar energy and also in solar photodecompo-

sition applied to water treatment, to develop and apply an efficient solar photodecomposition process. One way to improve the treatment process is the photocatalyst optimization; a promising photocatalyst is titanium dioxide, mostly as anatase crystalline form, which has high stability, abundance, performance and low cost [1] [2]. Improving the photodecomposition process requires increasing the surface area between the catalyzer and the contaminant solution matrix. The use of biotemplates combined with homogeneous titanium oxide/hydroxide precipitation promotes the ordered microstructure formation with high surface area and greater efficiency in the decomposition of drugs and stable organic compounds, such as antibiotics. The porous structure of the yeast culture serves as a substrate for precipitated titanium hydroxide, and after calcination, TiO<sub>2</sub> preparation [2] [3].

The biotemplates are the process in which biological systems direct the synthesis of inorganic structures from organic templates, which is an example of nanomaterials self-assembly in nature. Its products include yeast shells, rice leaves, and vertebrates' bones. The conventional inorganic synthesis techniques provide limited control over inorganic nanomaterials architecture. The templating field of research emerged in the last two decades as a new paradigm for inorganic nanomaterials assembly designing novel nanostructures in which inorganic nanomaterials synthesis directed from an underlying biomolecular template [3].

The spherical titania microparticles were prepared using the bio-templating method with wet yeast cells culture and the titania shells were formed on the yeast cells via the sol-gel method with isopropoxy titanate. The addition of the acetic acid stabilizes the isopropoxy and catalyzes the hydrolysis, with the synthesis of the titania microparticles are successfully synthesized with well-defined yeast cell morphologies. The diameter of the obtained particles was approximately 1.3  $\mu\text{m}$ , and usually, the TiO<sub>2</sub> crystal structure is anatase. Such a process results in a catalyst with 41.5 m<sup>2</sup>/g specific surface area and average pore diameter of 9.6 nm.

Published studies present the significant advantage of the wet yeast culture method in comparison with dry cultured cells and powdered templates with biological cells. Microscopic images of the yeast cells revealed the spherical morphology with approximately the diameter of the 2.0 to 3.0  $\mu\text{m}$ , the precursor of the Yeast-TiO<sub>2</sub> had a diameter of the same size as the yeast cells. Precipitated TiO<sub>2</sub> particles coated the cell's surface and the cell's gap through just a few yeast aggregations participating in the coating structure. Such effect indicated the production of spherical structures by directly coating shells on the yeast surface, followed by calcination. The resultant solid showed an average diameter of 1.5 - 2.5  $\mu\text{m}$  and the pore thickness between 0.2 to 0.7  $\mu\text{m}$ ; such properties are essential for catalyzer use in antibiotics solar photodecomposition [2] [3].

Veterinary antibiotics have high relevance in livestock exportation in Brazilian and many other countries, besides supplying the domestic market, providing food like meat, milk, and eggs, the basis of the human diet. Despite those positive aspects, if considered the animal excreta deposition, it is also considered the

primary source of indirect contamination of surface water resources by pharmaceuticals and specific antibiotics as the animal effluent flows into water-courses and the manure used to fertilize agricultural land. Such contaminated fertilizer, when dispersed in soils, the pharmaceuticals over-administered compounds, and metabolites leached, contaminating surface waters, deep waters, and soils [4].

The current world scenario shows that Brazil, among the countries that produce and export animal protein the most. In 2016, shipments exportation of agricultural products accounted for 48% of the country's export earnings, which totaled the US \$ 185.2 billion. In the same year, the second-largest cattle herd in the world was in the Brazilian territory (219 million head), corresponding to 22.1% of the world herd. The first place belonged to India, with a herd of 302 million head of cattle [5]. Such herd of animals allowed Brazil to occupy the second position in the world production of red meat.

The world average of veterinary antibacterial use in cattle is 45 mg/kg per body weight, while poultry use, on average, 148 mg/kg per body weight and pigs 172 mg/kg per body weight. These averages include therapeutic use to treat diseases and the use of these substances as growth promoters. Brazil is the third-largest user of antibiotics in animal production, behind only China and the USA. By 2030, is estimated the veterinary antibiotics consumption should increase by 50%, approaching 9 million tons/year, the US will continue second, with just over 10 million tons/year, with the estimation that China will double the current use, exceeding 30 million tons/year [6]. Due to this high volume of produced animal protein, a large number of resources are needed, among them the cattle feed, labor, veterinarians, and medicines to treat the diseases that affect the animals. An alarming problem in such a considerable scenario is a large number of antibiotics used, and such drugs will end up in the environment, either by animal droppings or by improper disposal of medicines.

The first report of antibiotics surfaces water contamination was published in England in 1982 when was detected macrolides, tetracyclines, and sulfonamides in a water river at concentrations of  $1 \mu\text{g}\cdot\text{L}^{-1}$  [7] [8]. Over the years, such antibiotic water contamination promotes the bacteria adaptation to resist these drugs. On many occasions, the WHO organization warned about the decreasing number of effective antibiotics is in the world. "The inadequate and excessive use of antibiotics is a major cause of higher antimicrobial resistance," said Suzanne Hill, WHO Director of Medicines and Essential Health Products, in a statement. "Without effective antibiotics, we will lose our ability to treat simple infections like pneumonia." The results presented in the WHO report confirm the need for urgent action to reduce antibiotic discharge in the environment, to promote the enforcement of prescription policies, and to reduce unnecessary antibiotic use, not only in humans but also in veterinary medicine [9] [10]. Also, the reliable data on antibiotic use in livestock are essential to help countries raise awareness of the appropriate use of antimicrobials, and the need for policy and regulatory changes to improve their use and control, as well as veterinary use.

A report on bacterial resistance by the British government found that by 2050 more people could die from superbug infections already immune to existing antibiotics than from cancer (8.2 million deaths) or traffic accidents (1.2 million). This prediction, if confirmed, must be attributed to the indiscriminate use of medicines in both human and veterinary medicine. [11] [12] [13]. The transference of drug concentrations to the soil by the application of animal manure may favor the selection of resistant microorganism populations even in more remote regions. Waste can also be absorbed and accumulated in plant tissues, causing risks in the harvest and consumption of plant foods.

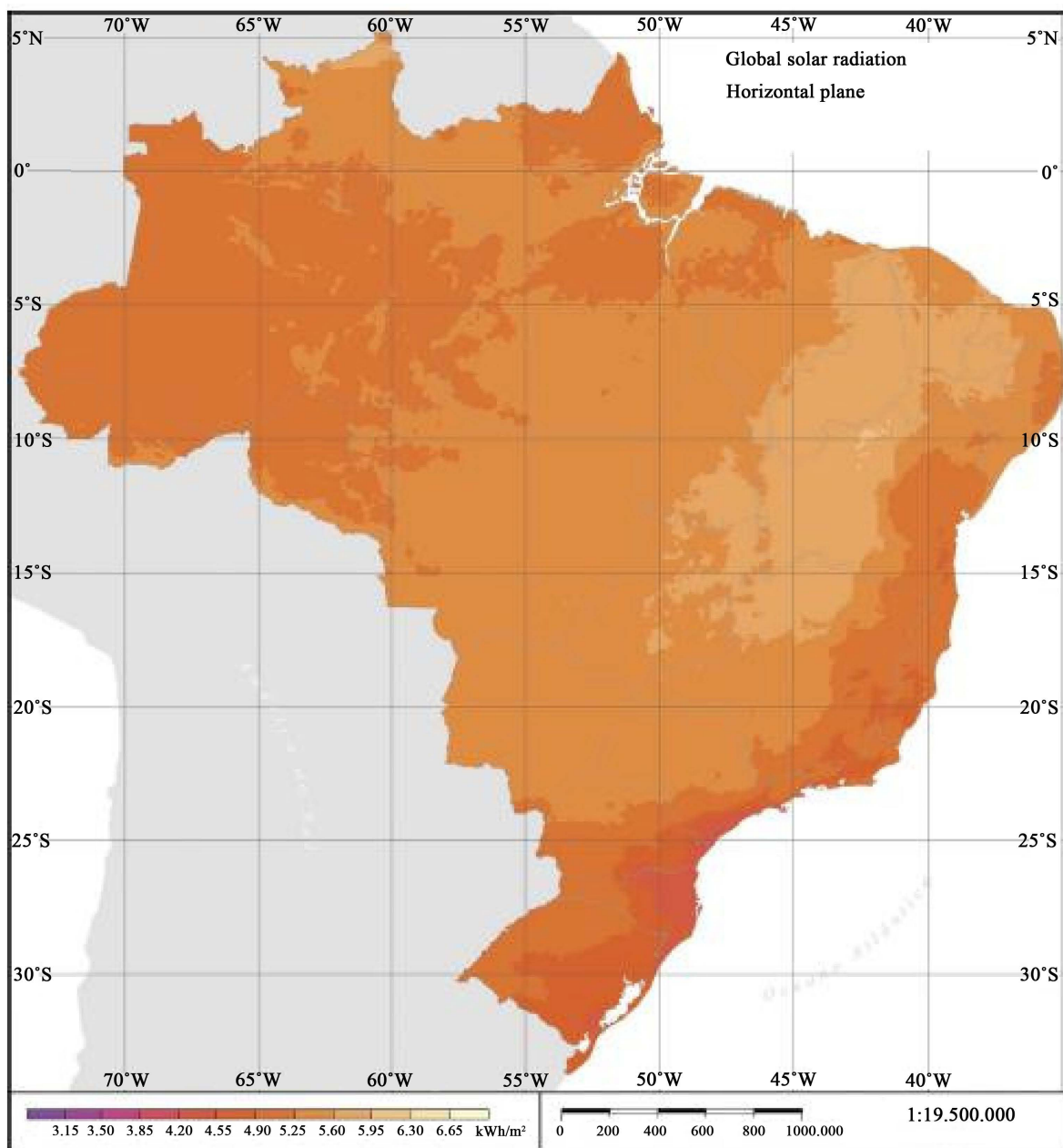
In Brazil, there are no established limits for the presence of antibiotics in the environment (soil, animal manure, groundwater, surface water, drinking water, and sediment [14] [15] [16]). Thus, because of the growing concern about surface water quality issues, the development of ecologically sound and economically viable technologies for water treatment and removal of effluent drugs is essential. In literature, several studies are describing the antibiotics decomposition, and one method widely used is solar photodecomposition, which is a method used for the treatment and decomposition of pharmaceuticals and organic pollutants, **Table 1**.

**Table 1.** Publications of antibiotics photodecomposition processes.

| Antibiotics      | Photodecomposition Process |                                       |                              |   |   |
|------------------|----------------------------|---------------------------------------|------------------------------|---|---|
|                  | Ci (mg·L <sup>-1</sup> )   | Matrix                                | Process                      | Process Parameters  | Results   |
| Amoxicillin      | 42                         | WWTP Effluent                         | Photo-Fenton                 | Solar radiation at 365 nm, 1.0 - 2.0 mM H <sub>2</sub> O <sub>2</sub> 0.20 mM Iron oxalate or Fe(NO <sub>3</sub> ) <sub>3</sub> pH = 2.5                                    | Total degradation obtained after 10 min of irradiation  |
| Amoxicillin      | 1 to 100                   | Distilled water                       | Heterogeneous photocatalysis | pH = 3 - 9, and solar radiation at 365 nm 0.1 - 0.7 g·L <sup>-1</sup> TiO <sub>2</sub> or TiO <sub>2</sub> doped with C and Fe  | Maximum degradation was obtained at neutral pH and with TiO <sub>2</sub> doped with C and Fe 37% of C (85% removal).  |
| Lincomycin       | 25                         | Distilled and residual water          | Foto-Fenton                  | Radiação solar (λ <sub>max</sub> = 365 nm) pH = 2.5 0.20 mM Ferric oxalate, FeSO <sub>4</sub> , Fe(NO <sub>3</sub> ) <sub>3</sub> 1.0 - 10 mM H <sub>2</sub> O <sub>2</sub> | After 8 min of irradiation, complete removal with oxalate. After 20 min total removal with Fe (NO <sub>3</sub> ) <sub>3</sub>   |
| Tetracycline     | 24                         | WWTP, river water and deionized water | Foto-Fenton                  | UV light and sunlight (15 W) 1 - 10 mM H <sub>2</sub> O <sub>2</sub> 0.20 mM ferric oxalate or Fe (NO <sub>3</sub> ) <sub>3</sub> at pH = 2.5                               | Total degradation after 1 min, the artificial light favored by the use of Fe(NO <sub>3</sub> ) <sub>3</sub> , the sunlight by ferric oxalate  |
| Tetracycline     | 40                         | Deionized water                       | Heterogeneous photocatalysis | Heterogeneous photocatalysis at 254 nm and sunlight at 365, 300 - 400 nm  | Degradation by radiation TiO <sub>2</sub> and after 120 min with UV 254 nm: 100% degradation, 90% mineralization, simulated sunlight: 100% degradation, 70% mineralization, at 365 nm |
| Sulfamethoxazole | 10                         | Distilled water, and Seawater         | Photolysis                   | Artificial UV Solar radiation (λ < 290 nm)  | The degradation of 98% of antibiotic presence was in distilled water after 30 h of irradiation.   |

Source: Adapted from Homem, [10] [19].

The solar photodecomposition is an efficient, low-cost method for treating water polluted by drug compounds. The process is still very little explored in Brazil, despite such favorable solar insolation conditions during all seasons. **Figure 1** shows the solar radiation map of Brazil in the horizontal plane [17] [18]. The spatial resolution of the data used to generate the map was 1 km × 1 km. The map grayscale defines the local average daily solar radiation. The most intense shade indicates the average annual daily radiation as 5.0 KWh/m<sup>2</sup>, and there are places where we can find the daily average reaching 5.8 KWh/m<sup>2</sup>, the highest values on the scale.



**Figure 1.** Left: Brazilian Daily, annual average solar radiation chart. Right: Annual average sunshine hours chart. Adapted from Tiba, 2002 [11].

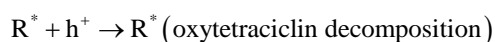
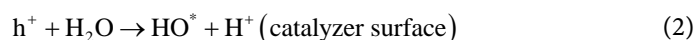
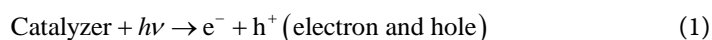
Solar energy has high potential to meet the demands for the wastewater treatment processes of irradiated POAs, and the prospects are more attractive to countries with high insolation rates, such as Brazil, with solar energy available throughout the year also in distant rural areas, **Figure 1**. The global solar radiation values occurring in any region of Brazilian territory (1500 - 2500 Wh/m<sup>2</sup>) are higher than in most European countries, such as Germany (900 - 1250 Wh/m<sup>2</sup>), France (900 - 1650 Wh/m<sup>2</sup>) and Spain (1200 - 1850 Wh/m<sup>2</sup>), with wide dissemination of the solar projects [19] [20].

The photodecomposition is an essential process of water and wastewater treatment due to the generation of hydroxyl radicals which break the chemical bonds of organic molecules until complete mineralization. The current environmental and economic situation promotes the development of efficient water treatment, with environmental sustainability, economically viable, and able to mitigate the dangers of pharmaceutical contaminants released into the environment without any treatment, especially in remote rural areas.

The use of Advanced Oxidative Processes—POAs in water treatment plants become more attractive with the use of UV and solar radiation, due to high removal efficiency in different aqueous matrices, **Table 1**. However, the calculation of the ecological footprint and the economic evaluation of the UV artificial treatment indicated considered electricity consumption and costs, and such evidence highlights the need to find and use solar renewable, sustainable, and clean energy sources [21] [22].

The eco-friendly solar photodecomposition involves the generation and consumption of a highly oxidizing and non-selective chemical species, the hydroxyl radical •OH and O<sub>2</sub><sup>\*</sup>.

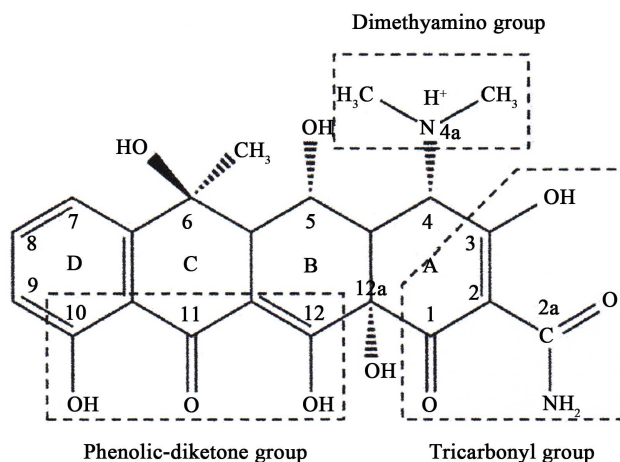
Catalytic reactions with radicals generation:



The photodecomposition processes use incident radiation in the ultraviolet range or visible spectrum on the semiconductor surface. Some semiconductors are photocatalysts and accelerate the photodecomposition through the difference between the filled valence band and the empty conduction band [23] [24], **Figure 2**.

Photocatalytic Oxytetracycline reactions:

Published results indicate the oxytetracycline decomposition process starting with the hydroxylation process from the dimethylamino group in ring A, followed by the demethylation of the phenolic diketone group by the abstraction of the alpha hydrogen resulting in the enol group at C7 and C8. The decarbonylation of the first enolicacetylacetone moiety in ring A due to the bond energy of the C12 to C1 is less strong. Finally, there is the dehydration process refers to the H<sub>2</sub>O



**Figure 2.** Oxytetracycline chemical structure. The dash frames are the three acid decomposition moieties. Adapted from Jin *et al.*, 2016 [16].

an elimination of ring C. The decomposition product was similar to those found in enolic acetone thermal decomposition [15] [16] [17].

Solar radiation photolysis processes have proven to be efficient in treating natural waters contaminated with antibiotics [23] [24]. The mass and surface area of the catalyst employed in heterogeneous catalysis processes dramatically influences the process efficiency. The dependence on other processes parameters was also studied, such as the wavelength and intensity of irradiation, pH, and matrix type. The use of solar radiation is an advantage as it significantly reduces the total costs of treatment, mostly in distant rural areas [1] [25].

The detection of drugs used in human and veterinary medicine was in several matrices (surface waters, effluents, groundwater, soils, and sediments). The antibiotics present in the environment promotes the increased resistance of bacteria and making them ineffective in treating some diseases. Thus, the problem goes beyond the environmental issue, also becoming a public health problem. The project proposition has as main objectives: 1) Optimization of the Yeast-TiO<sub>2</sub> synthesis started with yeast template formation and characterization. 2) The solar photodecomposition improvement using the veterinary antibiotic oxytetracycline and Yeast-TiO<sub>2</sub>. 3) Perform the calculations of the kinetic parameters of the oxytetracycline solar photodecomposition.

## 2. Materials and Methods

The biotemplates are abundant, renewable, and efficient. They have a higher standard of environmental compatibility, and they act as a dispersant and reducing agent, thereby their presence controls the particle size, surface area, and porosity of the TiO<sub>2</sub>, improving light-harvesting and photocatalytic activity. Nowadays, it is common the application of plenty of biotemplates for the synthesis of TiO<sub>2</sub> and the yeast bakers is more common due to their ubiquitous and be a unicellular eukaryotic microorganism. The science investigation uses yeast biotemplate in fundamental processes of cellular gene structure, protein function,

and the synthesis of inorganic materials due to its low pH tolerance, high inhibitor concentrations, and its ability to grow anaerobically. Recently by biomimetic mineralization, yeast cells with magnetic mineral shells have been obtained, which helps yeast cells to have a longer life and new properties.

The Yeast-TiO<sub>2</sub> synthesis results in a biocatalytic route and the controlled hierarchical pores as observed using biotemplates as green leaves, bamboo inner membrane, and eggshell. The hierarchical mesoporous titanium dioxide is highly regulated and exhibit excellent photocatalytic activity and rapid mass transportability. Some authors pointed out the synergy effect of both structure and element-introduced improvements for the catalytic activity of TiO<sub>2</sub> based on cell biotemplate. The valuation, as a promising precursor for titanium dioxide applications in the biosensor, solar cells, photoelectrical devices, and TiO<sub>2</sub> film, showed a uniform morphology of particles with an average particle size of 20 nm. The Yeast-TiO<sub>2</sub>UV-V is behavior also confirmed a reduction in the band gap after the introduction of biotemplates.

The preparation of yeast culture using lyophilized *Saccharomyces Cerevisiae* dissolved in 50 mL of deionized water with the addition of dissolved sugar cane molasses to complete 200 mL of total water volume. After the preparation, heat the mixture at 30°C for 1h for yeast cultivation. The filtration of the slurry separated the solid, and it is dried at 100°C overnight. The titanium oxide preparation started with the 100 mL of water, the addition of 5 mL of acetic acid PA, and 5 mL of titanium isopropoxide 99%, the addition of deionized water complete the total volume of 200 mL. A magnetic mixer agitated the slurry for two h followed by the prepared yeast addition. The agitation of the final suspension was for 2 h when stayed for sedimentation overnight. After the supernatant discharge, the solid dried for 24 h in an oven at 100°C.

The oxytetracycline election for solar photodecomposition experiments was due to its most commonly prescribed veterinary medicine, and its use to control and prevent postoperative and postpartum infections. The antibiotic for veterinary use was licensed at the Ministry of Agriculture and manufactured in Spain and Brazil. More than 70% of the oxytetracycline intake is excreted through feces into the environment due to the reduced body absorption efficiency [14]. Some researchers considered such behavior essential to be more effective in urinary treatment.

The photodecomposition process followed the Yeast-TiO<sub>2</sub> preparation, using a 400 mL becker the reaction beginning with the Yeast-TiO<sub>2</sub> mass addition to oxytetracycline solution. The sonication of the resultant slurry for 5 minutes and the heating system turned on to adjust the slurry to the desired process temperature. After that, the slurry went to the solar chamber at 10 cm distant from the artificial solar lamp and mixed in the dark for 30 min using a magnetic stirrer. The control of the process started with the first aliquot collection, the slurry transference to the quartz becker to perform the photodecomposition process, and the use of an ice cover (to avoid the water evaporation and loss during the process). The process control continues with the continuous system agitation



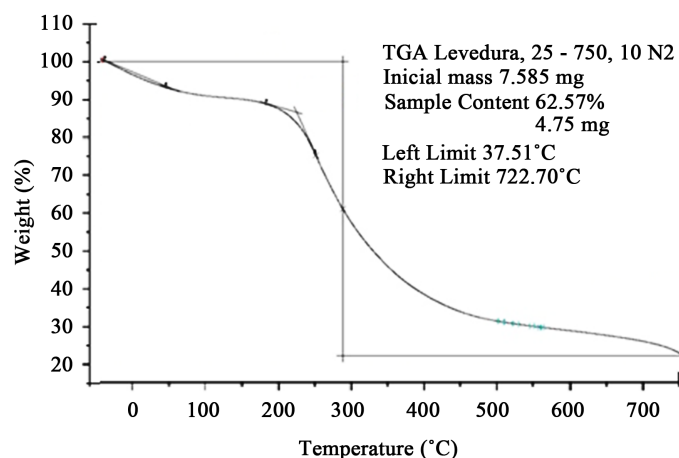
and the collection of the slurry aliquots 30 min each until a total of 3 h. The measurement of collected aliquots was after sedimentations for antibiotic quantification and to evaluate the process efficiency.

The optimization parameters of the process were: Yeast-TiO<sub>2</sub> mass, initial oxytetracycline concentration, artificial solar radiation time, and agitation time. The total shaking interval was 3 hours, with the collection of the suspension aliquots for analysis and determination of antibiotic concentrations. The measurements of the supernatant antibiotic concentration using the spectrophotometer UV-Vis Varian Cary 1E allows calculating the photodecomposition efficiency and kinetic parameters.

### 3. Results and Discussion

The synthetic Yeast-TiO<sub>2</sub> characterization started with differential thermal analysis measurements (TGA), followed by electron scanning microscopy (MEV) and BET results. **Figure 3** shows the thermal analysis results of the Yeast-TiO<sub>2</sub> prepared using the yeast template. The results indicate the drying temperature at 150 °C and the phase transition at 325 °C with a total weight loss of 62.7%. The BET results confirm the phase change after the calcination at 500 °C for 3 h. The BET sample preparation includes degasification Micromeritics-VacPrep 061 procedure at 150 °C with a vacuum of 95 mTorr, and the analysis conditions were nitrogen at 77 K with P/Po of 0.05 to 0.20 and equilibrium time of 5 seconds. The measurements of the BET present a specific surface area reduction after calculations from 134.3 to 98.5 m<sup>2</sup>·g<sup>-1</sup>.

The chemical analysis performed by X-Ray Fluorescence indicate the TiO<sub>2</sub> as the main chemical constituent for Yeast-TiO<sub>2</sub> material, the use of the yeast culture as template added some external chemical contamination on precipitated TiO<sub>2</sub> with potassium phosphate. The microstructure analysis **Figure 4(A)** with 1000× of magnification obtained by electron scanning microscopy indicates the dried yeast template as a structured building formed and organized by yeast colony. **Figure 4(B)** the micrography with 5000× of structured details.



**Figure 3.** The analysis of the yeast-TiO<sub>2</sub>.

**Figure 4** presents the Yeast-TiO<sub>2</sub> samples with high surface area and high porous dimensions. Such microstructure is responsible for the surface area enhancement, confirmed by BET results.

The kinetic study of the solar photodecomposition process aims to determine the chemical reactions rate and the influence factors. The equations of pseudo-first-order, pseudo-second-order, and intraparticle allow the determination of photodecomposition rates, the kinetic model with better fits with the experimental results [24].

Pseudo-first order equation:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t \quad (4)$$

The pseudo-first-order calculation represents a logarithm of the reactant species by the reaction time; higher  $K_1$  indicates fast reagent consumption and short reaction time. Typically, photodecomposition experimental results indicate a lower correlation with pseudo-first-order. Although many studies indicate a kinetic change of the better correspondence model accordingly with the reaction pH values changing from pseudo-first-order in acid and neutral conditions to pseudo-second-order with  $K_2$  values at higher alkaline levels [24] [26].

Pseudo-second order equation:

$$\frac{t}{q_t} = \frac{1}{K_2} + \frac{1}{q_e}t \quad (5)$$

where:  $K_2$  (g·mg<sup>-1</sup>·min<sup>-1</sup>) is a kinetic adsorption rate and the graph  $t/q_t$  for  $t$ (min), and the calculation predicted the adsorption capacity  $q_e$  (mg·g<sup>-1</sup>) and an integrated rate adsorption  $K_2$  with the intercept of the line equation.

Intraparticle equation:

$$\log(q_t) = \log(K_{id}) + \log(t) \quad (6)$$

where:  $K_{id}$  (g·mg<sup>-1</sup>·min<sup>-1</sup>) is a kinetic adsorption rate, the graph  $\log(q_t)$  for  $\log(t)$ , and the calculation of an integrated rate adsorption  $K_{id}$  with the intercept of the line equation [1] [27].

The results indicate 0.10 g of Yeast-TiO<sub>2</sub> as better mass value. More than this, the remained suspended solids start to disturb the solar incidence of antibiotic solutions [18]. The value of 3 showed better efficiency in the oxytetracycline mixture for 30 min first in the dark and after that in the solar chamber with the collection of different aliquots. The optimized process obtained 74% of removal percentage in 270 min of agitation time.

The results indicate the better agreement with the pseudo-first-order with direct correspondence with the reactant oxytetracycline consumption, and the Pearson coefficient was in the range of 0.82 to 0.94 with higher removal efficiency for lower initial solutions with  $K_1 = 0.035 \text{ M}^{-1}\cdot\text{s}^{-1}$  **Table 2. Table 3** allows the comparison between the experimental results and published references for oxytetracycline photodecomposition [27] [28] the  $K_1$  values are lower than expected,  $t$  the improvement of the TiO<sub>2</sub><sup>-</sup>. Yeast synthesis will overcome such dif-

facilities. Usually, the decomposition mechanism is dependent on the process parameters as pH values; in this experiment in an acid environment, the pseudo-first-order seems to be more favorable.

The initial solid catalyzer Yeast-TiO<sub>2</sub> dosage is an essential parameter in the destruction process of organic pollutants. It may affect the degradation efficiency of target contaminants, and the solar photodecomposition rate appeared to be proportional to the initial oxytetracycline concentration, **Figure 4**.

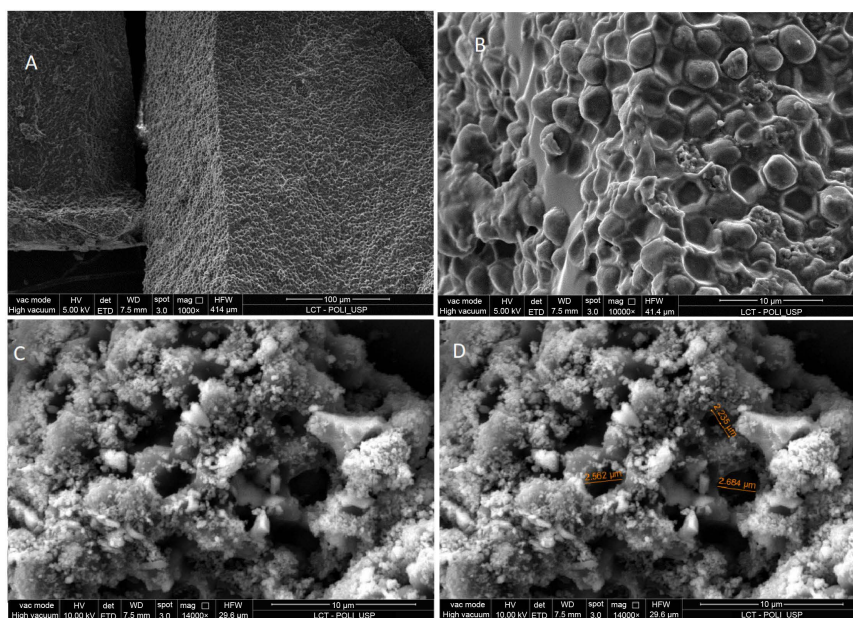
The destruction of oxytetracycline with different initial concentrations showed in **Table 2**, **Figure 5**, and the  $K_1$  values decreased with increasing the initial

**Table 2.** Pseudo first order, pseudo-second-order, and interparticle kinetics for Yeast-TiO<sub>2</sub> solar photodecomposition.

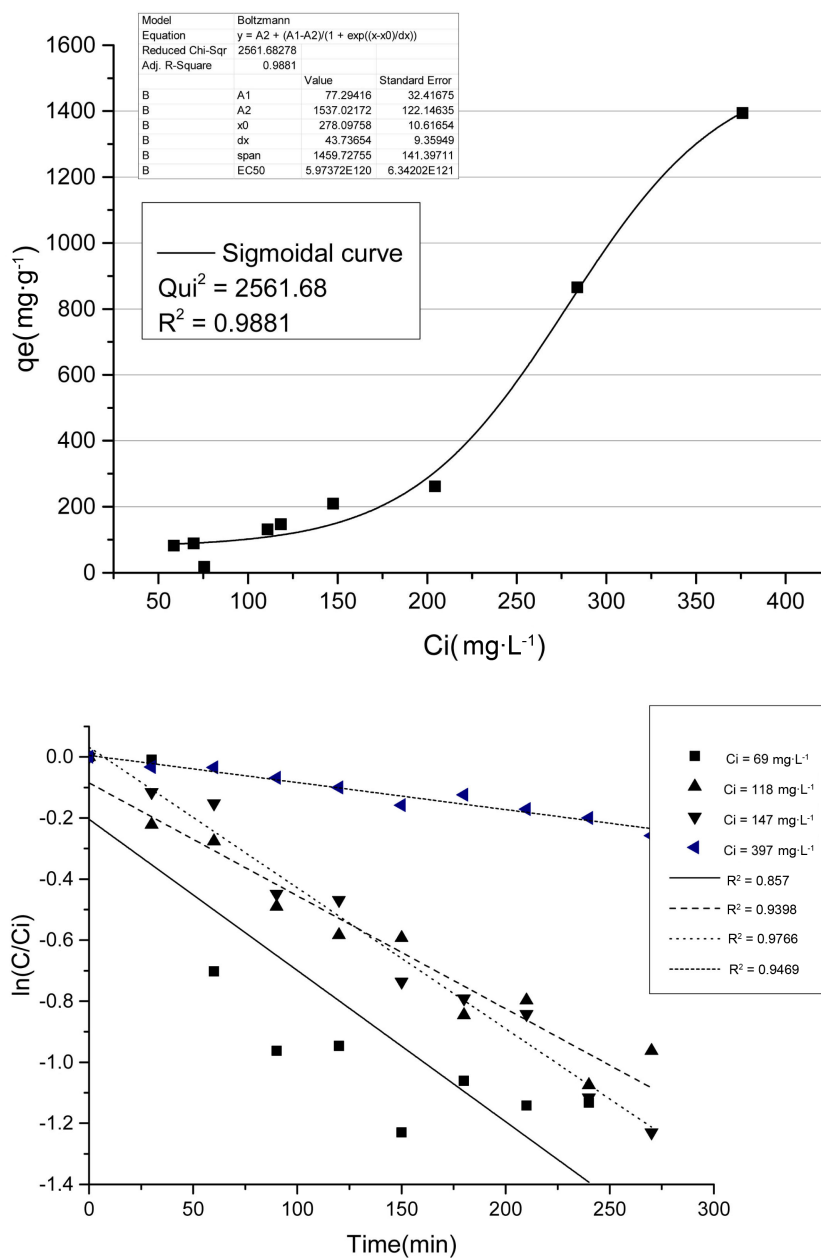
| Ci (mg·L <sup>-1</sup> ) | $K_1$ (M <sup>-1</sup> ·s <sup>-1</sup> ) | $R^2$ | $K_2$ (min <sup>-1</sup> ) | $R^2$ | $K_{id}$ (mg·g <sup>-1</sup> ·h <sup>-1/2</sup> ) | $R^2$ |
|--------------------------|---|-------|----------------------------|-------|---|-------|
| 69.77                    | 0.035                                     | 0.82  | 0.094                      | 0.10  | 18.75   | 0.26  |
| 118.31                   | 0.011                                     | 0.89  | 1.564                      | 0.90  | 20.38   | 0.35  |
| 147.48                   | 0.013                                     | 0.94  | 1.004                      | 0.02  | 23.05   | 0.47  |
| 397.06                   | 0.006                                     | 0.89  | 0.610                      | -0.14 | 20.58   | 0.33  |

**Table 3.** Published results related with oxytetracycline photodecomposition kinetics.

| Kinetic constants  | Reference  |
|--|------------|
| $K_{id} = 0.12 - 0.53$ (mg·g <sup>-1</sup> ·h <sup>-1/2</sup> )  | Zhang [15] |
| $K_2 = 6.0 \times 10^{-4}$ (min <sup>-1</sup> ) at pH 9.2  | Jin [16]   |
| $K_1 =$ at pH 5.5 - 8.5 and SO <sub>4</sub> <sup>2-</sup> = $4.3 \times 10^6$ M <sup>-1</sup> ·s <sup>-1</sup> | Liu [17]   |



**Figure 4.** SEM micrography for yeast template, (A) 1000× magnification; (B) 5000× magnification; and (C) Dried Yeast-TiO<sub>2</sub> a general overview and (D) the measurements of the porous diameters from 2.24 μm to 2.68 μm.



**Figure 5.** The solar photodecomposition efficiency and the initial oxytetracycline concentration.

antibiotic concentration [28] [29]. A possible explanation is for higher concentration; the byproducts also increased and could compete with the original antibiotic molecules for reactive radicals. Other researches observations indicate similar results for oxytetracycline with  $\text{SO}_4^-$  and UV irradiation when the degradation rate was decreasing with the increase in the initial concentration of the target compound [27] [28].

#### 4. Conclusion

The  $\text{TiO}_2$  synthesis using yeast culture as biotemplate followed by the micro-

structure characterization with surface area stability and enhancement, promotes the efficiency improvement of solar photodecomposition processes of the veterinary antibiotic oxytetracycline. In optimal process parameters, the system reaches about 84% of oxytetracycline removal percentage with a better agreement with pseudo-first-order kinetics with  $K_1 = 0.035 \text{ M}^{-1}\cdot\text{s}^{-1}$ . The degradation rate constant increased with the decreasing of initial oxytetracycline concentration and the increasing of the initial Yeast-TiO<sub>2</sub> dosage until 0.1 g using the Langmuir  $\pm$  Hinshelwood model; the continuous TiO<sub>2</sub>-Yeast mass reduces the solar irradiance. The use of a solar sustainable irradiation source needs more research targeting the efficiency enhancement of the abundant and low-cost treatment to be applied to avoid the polluted water discharge in the environment. The process removes and decomposes the pharmaceutical pollutants as oxytetracycline providing new approach and insightful information on the potential practical application of this green technology to treat contaminated water, including in rural, distant areas.

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### Conflicts of Interest

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

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