

Article

Degradation of Oxytetracycline in Aqueous Solutions: Application of Homogeneous and Heterogeneous Advanced Oxidative Processes

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Abstract: Oxytetracycline is one of the antibiotics most frequently used in the Shrimp Industry during the control of bacterial diseases. These emerging pollutants, which appear in low concentrations, are persistent and alternative treatments and are required for their elimination. The degradation of oxytetracycline was evaluated in an aqueous solution by applying homogeneous (UV/H₂O₂ and photo-Fenton) and heterogeneous (UV/TiO₂/H₂O₂) advanced oxidative processes (AOPs). The studies were carried out using a bench reactor with short-wave ultraviolet lamps (UV-C). We quantified the extent to which the degradation of the drug had been efficient by employing highly efficient liquid chromatography (HPLC) and a PDA detector with a wavelength of 354 nm and a C18 column. The best results were obtained when applying the UV/H₂O₂ treatment, which attained a degradation of 97% under the initial conditions of a dose of 8 µL of H₂O₂ and 120 min of radiation. The pseudo-first order kinetic model proposed by Chan and Chu showed that the experimental results had an adequate fit, with values greater than $R^2 \geq 0.95$. Toxicity tests were applied to verify the effect of AOPs employed, when the drug was present in low concentrations. The test results demonstrated a decrease in the root growth of the species *Lactuca sativa* and *Daucus carota*.

Keywords: antibiotic; degradation; emerging pollutants; kinetic model; toxicity

1. Introduction

Emerging pollutants can generally be said to be of different chemical origins and nature that are released into the environment in low concentrations, but accumulate over time [1,2]. Their presence in the environment is not necessarily new, and these pollutants may have gone unnoticed for decades. This has, therefore, motivated the work currently being carried out in order to study their persistence

and bioaccumulation, which may have a huge ecological impact in addition to adverse effects on health [3,4]. These pollutants can be found in effluents of both industrial and domestic origin, and can contaminate aquifers, subterranean waters and soils. They include pesticides, personal hygiene products and pharmaceutical products [5–7].

Pharmaceutical products, and particularly tetracyclines, are a broad spectrum of antibiotics used in various fields of medicine and veterinary practices throughout the world [8]. One member of this group is oxytetracycline (OTC), vast quantities of which are used by the agricultural industry worldwide owing to its low cost and high efficiency when employed in the cultivation of shrimp larvae [9,10]. This high use has led to the appearance of residues of OTC in aquifers and groundwater and even in the shrimps themselves. Although there are no regulations regarding the minimum amount of this drug in the environment, it may damage ecosystems in several ways, such as inhabiting the growth of aquatic plants, reducing the quality of water as regards to eutrophication, and making bacteria more resistant to these antibiotics [11,12]. It is, therefore, necessary to implement new technologies that will permit their detection and, principally, elimination [13,14].

The conventional processes applied in wastewater treatment plants (WWTP) do not usually work [15–17]. This makes it necessary to apply new tertiary or advanced treatment technologies, such as the use of activated carbon, membrane filtration or advanced oxidization [18,19]. Of the treatments currently used, advanced oxidative processes (AOPs) have proven to be one alternative for the treatment of drugs in aqueous systems. These processes are capable of degrading pollutants by means of the oxidization of organic compounds, from those which are complex to those which are simpler. For example, wastewater treatments with biodiesel [20], volatile organic compounds [21] and the degradation of pharmaceuticals [22,23].

This is done through the use of oxidant agents such as hydrogen peroxide, which is employed to generate hydroxyl radicals, which can also be generated using photochemical reactions by means of the emissions of ultraviolet light [24]. Of all the processes used, those which most stand out are homogeneous advanced oxidative processes, such as Fenton, photo-Fenton or UV/H₂O₂, and heterogeneous photocatalytic processes [25,26].

In this context, several manuscripts report the use of AOPs for OTC degradation in homogeneous and heterogeneous systems. Chee-Hun Han et al. [27] studied the degradation through a homogeneous photo-Fenton process compared to H₂O₂, UV, and UV/H₂O₂ processes, achieving degradation in the order of 95%. Liu et al. [28] applied UV/H₂O₂, focusing on the effect of carbonate and bicarbonate on photochemical degradation, demonstrating that the carbonate radical acts favorably on the degradation of organic compounds such as OTC. Heterogeneous photocatalytic processes emerged as an alternative for drug degradation. Some catalysts containing heavy metals have been used for OTC degradation in these processes [29–32]. However, the use of these metals could generate other types of contaminants (heavy metal contamination). For this reason, TiO₂ has been the most used catalyst, proving its high efficiency and low toxicity [33]. In the works of Pereira et al. [19,34], TiO₂ was applied suspended in aqueous solution under natural and simulated solar radiation conditions, showing good performance in antibiotic degradation, mineralization, biodegradability and low toxicity. Although the use of both processes have been described, at the end of the bibliographic review of this work, the simultaneous study of homogeneous and heterogeneous AOPs for OTC degradation has not been reported. For this reason, the aim of the present work is, therefore, to evaluate the best experimental conditions in which to carry out homogeneous and heterogeneous advanced oxidative processes for the degradation of the OTC found in aqueous solutions.

2. Materials and Methods

2.1. Chemicals and Standards

All chemicals used were of analytical reagent grade. HPLC grade Oxytetracycline hydrochloride (≥95%) was obtained from Sigma-Aldrich (Germany), hydrogen peroxide at 30% (v/v) from Fisher

(USA), extra pure hepta-hydrate iron sulfate at 98.5% from Loba Chemie (India), titanium dioxide 99% from Merck (Germany), ultra water obtained using Brandstead EasyPure II equipment from Thermo Scientific (USA), HPLC grade acetonitrile (Merck) and HPLC grade formic acid (Merck). Standard solutions were prepared using standard OTC at a concentration of $100 \text{ mg}\cdot\text{L}^{-1}$. This solution was then employed to prepare dilutions for concentrations of 2, 4, 6, 8, 10, 12, 14, 16, 18 and $20 \text{ mg}\cdot\text{L}^{-1}$.

2.2. Sample Determination by HPLC

The OTC was quantified and detected by means of High Resolution Liquid Chromatography (HPLC), using a chromatograph UHPLC ACCELA from ThermoFisher Scientific (USA), equipped with a reverse-phase C18 column ($5 \mu\text{m}$; $4.6 \times 100 \text{ mm}$) and a photo-diode matrix detector UV-VIS (PDA). A binary mobile phase was employed composed of acetonitrile and acidified water, with formic acid at pH 2, at a ratio of 20:80, respectively, and with a constant flow of $900 \mu\text{L}\cdot\text{min}^{-1}$. The detection was carried out at a wavelength of 354 nm with an injection volume of $10 \mu\text{L}$ and at a temperature of 25°C in the column and the tray samples.

The methodology used was validated using the parameters of linearity (R^2), coefficient of variation (CV), limit of quantification (LQ), limit of detection (LD), and recovery to guarantee its reliability. All equations and data representing the validation of the analytical method are presented in Appendix A (see Supplementary Materials, Appendices).

2.3. Degradation of OTC using Homogeneous Photocatalysis

The preliminary assays for homogeneous AOPs conditions (photo-Fenton and $\text{UV}/\text{H}_2\text{O}_2$ processes) were carried out under the following conditions: 50 mL of the aqueous solution prepared from the OTC pattern at a concentration of $20 \text{ mg}\cdot\text{L}^{-1}$. The photo-Fenton treatment was carried out by adding $2 \mu\text{L}$ of a solution of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ at a concentration of $1 \text{ mg}\cdot\text{L}^{-1}$ and $2 \mu\text{L}$ of hydrogen peroxide solution at 30%, while $2 \mu\text{L}$ of hydrogen peroxide solution at 30% was used for the $\text{UV}/\text{H}_2\text{O}_2$ system. Both treatments underwent radiation for a period of 120 min.

The influence of the H_2O_2 dose (30% v/v) was evaluated as follows: (i) Single dose using volumes of 2, 4, 6, 8 and $10 \mu\text{L}$ at the start of the operation, and (ii) Fractionated dose of the total volumes 2, 4, 6, 8 and $10 \mu\text{L}$, each divided equally to the times 0, 10 and 20 min (three stages).

2.4. Degradation of OTC using Heterogeneous Photocatalysis

The heterogeneous photocatalysis assays were carried out using a catalyst (TiO_2) impregnated in the walls of a Petri dish, 50 mL of the drug, 120 min of exposure to radiation and $2 \mu\text{L}$ of hydrogen peroxide solution at 30%. The procedure of impregnating the Petri dishes with TiO_2 was carried out by preparing an aqueous suspension (m/v), using 5 g of titanium dioxide, in 250 mL of water, for a period of 30 min. After that, the aqueous solution was removed, leaving a thin impregnated coating on the Petri dishes, which was then dried at $25^\circ\text{C} \pm 2$ for 24 h before use [35].

2.5. Kinetic Study of OTC Degradation

The results obtained after carrying out the homogeneous and heterogeneous AOPs were then used to study the kinetic behavior of the degradation of the OTC at 5, 10, 15, 20, 30, 40, 50, 60, 90 and 120 min. The results obtained at each point (analysis of concentration of equilibrium) were subsequently used as a basis on which to employ the kinetic model described by Chan and Chu [36]. The results indicated that the pseudo-first order [37] could be employed for the degradation process by applying Equation (1).

$$C = C_0 \cdot \left(1 - \frac{t}{\rho + \sigma t} \right) \quad (1)$$

where C is the final concentration of the OTC solution ($\text{mg}\cdot\text{L}^{-1}$) after applying the advanced oxidative process for a determined time (t), C_0 is the initial concentration of the solution containing the drug

($\text{mg}\cdot\text{L}^{-1}$) and the parameters $\frac{1}{\rho}$ and $\frac{1}{\sigma}$ represent the constant of degradation velocity (min^{-1}) and the oxidative capacity of the treatment, respectively. These coefficients were obtained from the linearization of Equation (1), thus obtaining Equation (2).

$$\frac{t}{\left(1 - \frac{C}{C_0}\right)} = \rho + \sigma t \quad (2)$$

2.6. Analysis of Operational Costs of the Bench-Top Photolytic Reactor

The degradation tests were performed with a bench photolytic reactor equipped with lamps emitting three types of radiation UV-C. The reactor was equipped with three UV-C germicidal fluorescent tube lamps with a potential of 30 W, located in parallel on the upper part of the reactor.

A cost analysis for the assembly and operation of the reactor was also carried out. The costs were divided into 3 types: project, materials and operational. In the project costs, expenses with technical drawings were outlined, such as general views and perspectives, in addition to the values associated with the construction of the reactor structure and the installation of lamps and electrical parts. For the material costs, expenses with lamps, electrical ballasts and electrical material such as wires and switches were taken into account, while the operational cost was calculated based on the $\text{kW}\cdot\text{h}$ price of US\$ 0.1. Thus, it was taken into account the operational time of the reactor, in hours, and the power of the lamps and coolers installed.

2.7. Toxicity

The toxicity study was conducted using the method employed by [38,39], using lettuce (*Lactuca sativa*) and carrot (*Daucus carota*) seeds, owing that these seeds are easy to control and quick to germinate. The toxicity study through germination bioassays was developed to evaluate the toxicity of the treatments. For this purpose, the seeds were exposed to different concentrations of aqueous solution (1%, 5%, 10%, 50%, 70% and 100%) for 120 h before and after the application of the different AOPs. Water was used as a negative control while a solution of 3% of boric acid was used as a positive control. Ten seeds of each species were placed in each Petri dish and 2 mL of the aforementioned solutions containing the concentrations and controls were added. All of the assays were carried out at a temperature of 25 ± 1 °C. After five days, the number of seeds that had germinated was evaluated, and the relative growth rate (RGR) and germination index (GI) was calculated using Equations (3) and (4) [40,41].

$$RGR = \frac{RLS}{RLC} \quad (3)$$

$$GI = RGR \cdot \frac{SGS}{SGC} \cdot 100 \quad (4)$$

in which *RLS* is the total root length in the sample; *RLC*, the total root length in the negative control; *SGS*, the number of seeds germinated in the sample; and *SGC*, the number of seeds germinated in the negative control.

3. Results and Discussion

3.1. Determining the OTC and Validating the Method

The spectrum analysis carried out using UHPLC with a PDA detector showed that the levels of OTC had two peaks of maximum absorbance at wavelengths of 276 nm and 354 nm (Figure 1a). The wavelength of 354 nm was selected considering that it is the furthest from the characteristic area of the wavelength of the aromatic rings and closest to the region of the UV-Vis. Other authors have also recommended the use of this wavelength to quantify this drug [42,43].

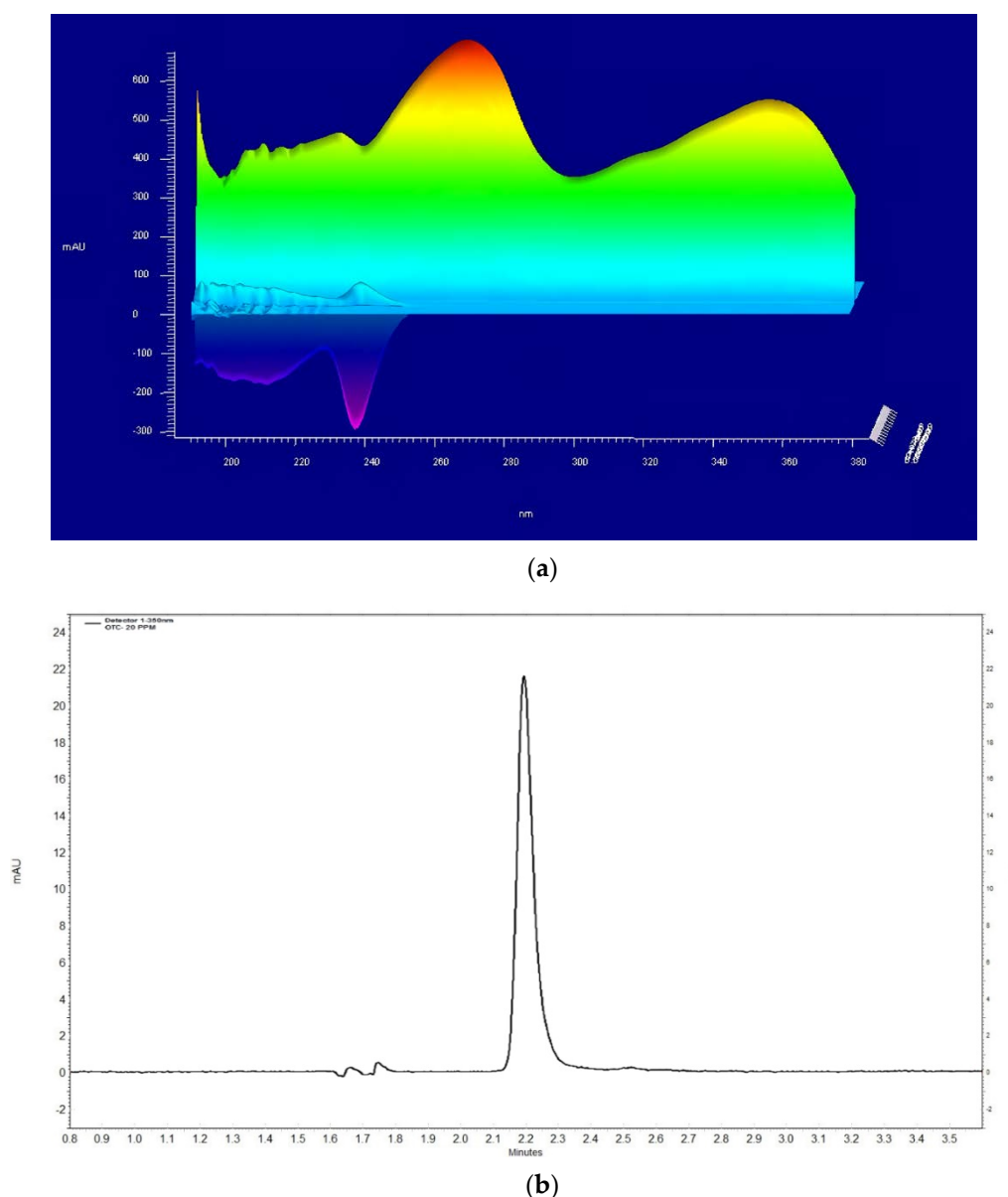


Figure 1. (a) Spectrum of OTC by HPLC/PDA detector; (b) Chromatogram of OTC at 354 nm with retention times of 2.18 min.

The OTC was detected in a range of retention times of 2.18 min (Figure 1b). Other authors have determined longer retention times [19,44], thus indicating that the methodology applied has attained better results (see Supplementary Materials, Appendices).

The analytic curve obtained from the method employed had a correlation coefficient (R^2) of 0.9991 and a straight-line equation of $y = 15334.06x - 1941.46$. The fact that the value of R^2 is over 0.990 indicates that the method is, according to the National Agency for Health Monitoring, linear and acceptable. The coefficients of variance of between 0.69% and 5.53% indicate adequate precision, with values below 20% [39,45]. Quantification limits of $0.435 \text{ mg}\cdot\text{L}^{-1}$ and detection limits of $0.144 \text{ mg}\cdot\text{L}^{-1}$ were also obtained.

3.2. Preliminary Assessment of the Advanced Oxidation Processes

The influence of the H_2O_2 was then studied for the UV/ H_2O_2 process, which indicated that increasing the dose from 2 to 10 μL increases the degradation of the drug from approximately 64.8% to

97% (Figure 2). The percentages of degradation do not vary much among the doses of 6 and 10 μL . By this fact, the dose of 8 μL (96.7%) was selected.

An excess of H_2O_2 may lead to the greater formation of hydroxyl radicals, which may affect the degradation process, since these radicals will react with each other, thus forming hydroperoxides and superoxide radicals, which reduces their oxidization mechanism. However, if the dose of H_2O_2 is too low, then an insufficient number of hydroxyl radicals will be produced, which can cause a decrease in the oxidation reaction rate, thus implying that the drug will degenerate to a lesser extent [46–48].

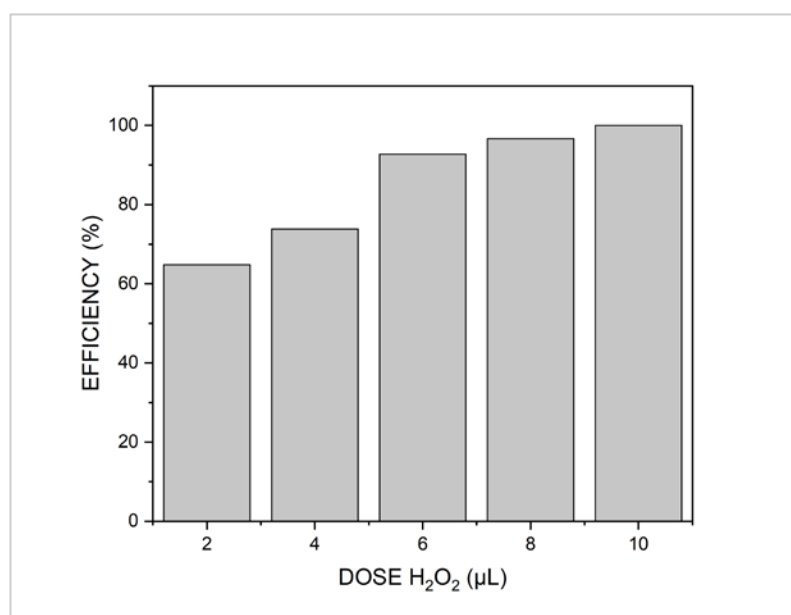


Figure 2. Study of the influence of the concentration of H_2O_2 for the UV/ H_2O_2 AOP. $C_0 = 20 \text{ mg}\cdot\text{L}^{-1}$ of OTC; $t = 120 \text{ min}$, aqueous solution.

Once the most appropriate dose had been selected (8 μL), the influence of the dosage of H_2O_2 added in a single dosage and in fractioned dosages was studied, with the objective of verifying the efficiency of the degradation of the OTC. Other authors have indicated that a fractioned dose provides better results to the degradation process [41]. The present study, however, demonstrates that the single dose of H_2O_2 is more efficient for this drug than a fractioned dose (Figure 3).

Since the single dose contained a greater initial quantity of H_2O_2 in the solution, there was a greater initial generation of hydroxyl radicals. This accelerated the velocity of the reaction, thus leading to greater efficiency as regards to the degradation of the drug, with initial times of 30 min, until a greater degradation was achieved at 120 min, with values of 100%.

The fractioned dosage, meanwhile, produced a slower reaction velocity, and the dose of H_2O_2 was not enough to generate the quantity of hydroxyl radicals required for degeneration. This meant that more time was required to attain the greatest degradation of the drug.

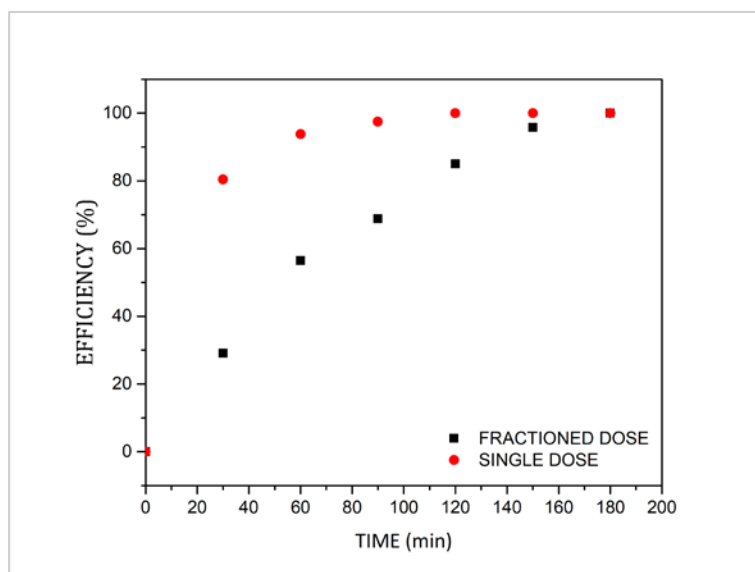


Figure 3. Study of the application of the dose of H_2O_2 in the UV/ H_2O_2 process. $C_0 = 20 \text{ mg}\cdot\text{L}^{-1}$ of OTC; $\text{H}_2\text{O}_2 = 8 \text{ }\mu\text{L}$, $t = 120 \text{ min}$, aqueous solution.

The conditions established in the UV/ H_2O_2 process (dose of H_2O_2 : $8 \text{ }\mu\text{L}$ and exposure time UV: 120 min) were employed to carry out the photo-Fenton process studies. The addition of Fe^{2+} as a catalyst was studied by employing concentrations of $1, 3$ and $5 \text{ mg}\cdot\text{L}^{-1}$. According to the analysis shown in Figure 4, there are no significant variations among the percentages as regards to the efficiency of the process. Considering that Fe^{2+} is a heavy metal with accumulative and toxic properties, the smallest concentration of the catalyst ($1 \text{ mg}\cdot\text{L}^{-1}$) was employed in carrying out the treatment.

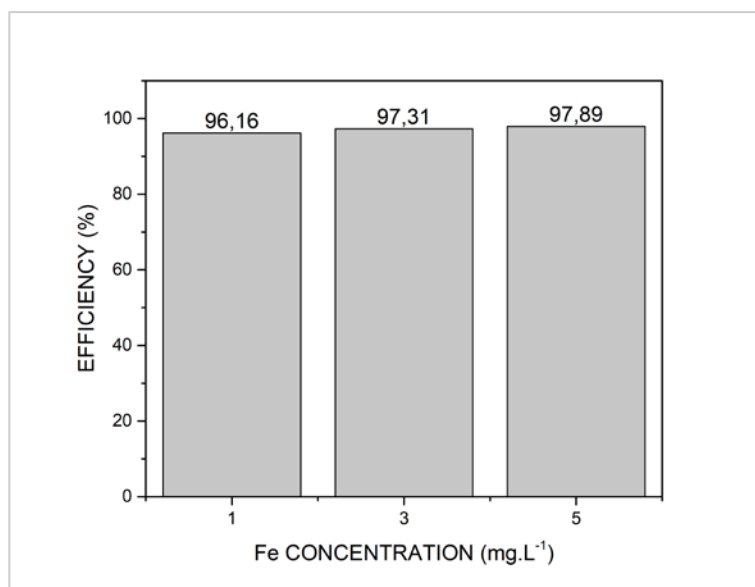


Figure 4. Study of the influence of the concentration of Fe for the photo-Fenton AOP. $C_0 = 20 \text{ mg}\cdot\text{L}^{-1}$ of OTC; $t = 120 \text{ min}$, aqueous solution.

The application of the heterogeneous photocatalysis AOP was carried out by impregnating the Petri dishes with titanium dioxide (TiO_2), as described in Section 2.4. The quantity and dosage of H_2O_2 for the aqueous solution of OTC were analyzed. Positive results were attained, as shown in Figure 5,

and a degradation of 97% of the drug, with a dose of 8 μL of H_2O_2 at the beginning of treatment stage, was obtained.

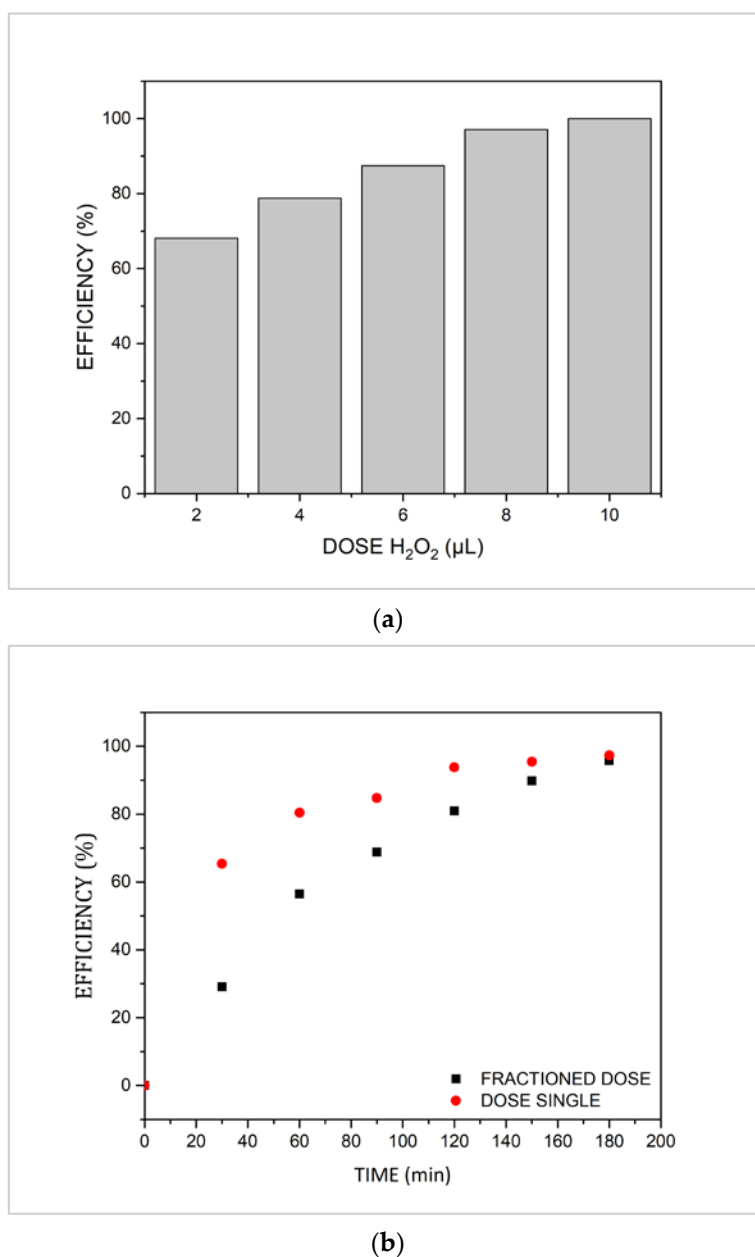


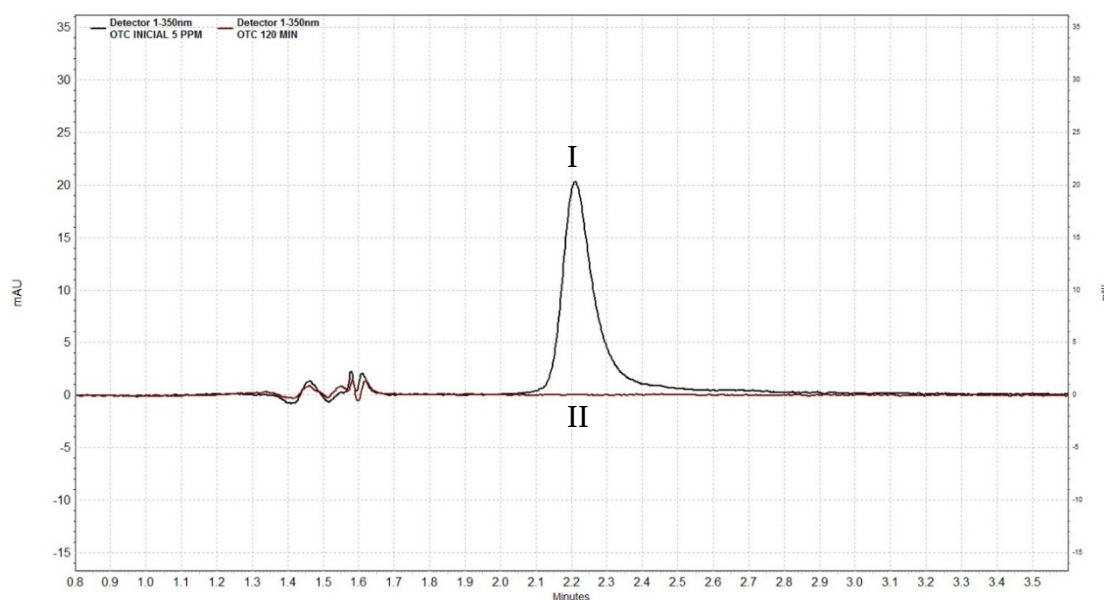
Figure 5. (a) Study of the influence of the concentration of H_2O_2 for the treatment using heterogeneous photocatalysis ($C_0 = 20 \text{ mg}\cdot\text{L}^{-1}$ of OTC; $t = 120 \text{ min}$, aqueous solution); (b) Study of the application of the dose of H_2O_2 for the treatment using heterogeneous photocatalysis ($C_0 = 20 \text{ mg}\cdot\text{L}^{-1}$ of OTC; $\text{H}_2\text{O}_2 = 8 \mu\text{L}$; $t = 120 \text{ min}$, aqueous solution).

This treatment behaves similarly to the advanced oxidative treatments for homogeneous photocatalysis. The conditions for the experimental process were the following: a single dosage of 8 μL of H_2O_2 , $20 \text{ mg}\cdot\text{L}^{-1}$ of a concentration of the drug, using the Petri dishes impregnated with TiO_2 , and an exposure time of 120 min in the bench reactor with UV-C lamps.

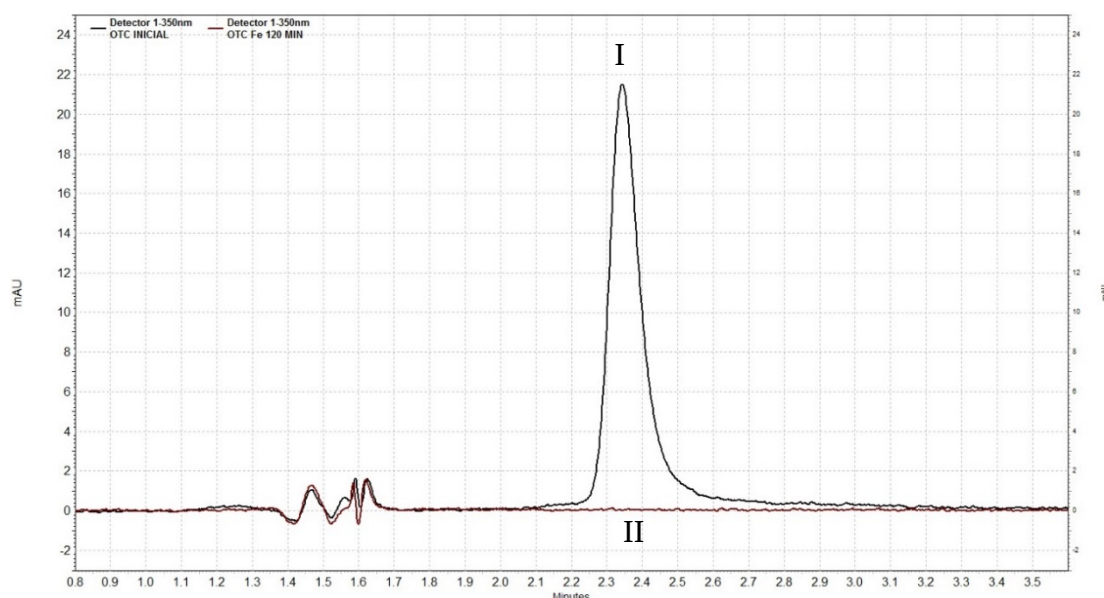
3.3. The Degradation of OTC

The pre-established conditions were then employed to evaluate each of the homogeneous photocatalysis AOPs. The chromatogram in Figure 6a shows the OTC before (I) and after (II)

the UV/H₂O₂ treatment process. Once the period of analysis had passed, the drug was virtually undetectable, as will be noted upon observing the disappearance of the chromatographic peak (II) corresponding to the drug at the end of the treatment, attaining 97.76% degradation. Note also the possible existence of intermediary products that may have formed during the treatment and that it was necessary to verify using a mass spectrometer detector.



(a)



(b)

Figure 6. Chromatograms: (a) UV/H₂O₂ treatment (5 mg·L⁻¹ of concentration, 8 µL of dose of H₂O₂ and radiation exposure of 120 min); (b) photo-Fenton treatment (1 mg·L⁻¹ de Fe, 8 µL de H₂O₂ and radiation exposure of 120 min).

The photo-Fenton treatment behaved similarly to the UV/H₂O₂ process since, as will be noted, the chromatographic peak of the OTC (II) analyzed as regards to the initial concentration of the drug (I), and corresponding to what is shown in Figure 6b, almost disappeared at 120 min. The percentage

of degradation was 97.17%. However, despite attaining percentages of degradation similar to those obtained with the UV/H₂O₂ process, this process has the inconvenience of employing iron as a catalyst.

The heterogeneous photocatalysis was applied by impregnating the Petri dishes with titanium dioxide under the following conditions: 50 mL of aqueous solution; a dose of H₂O₂: 8 µL; time of exposure to UV-C lamps: 120 min. Irradiation with the UV-C light during the heterogeneous treatment with titanium dioxide led to the formation of a large quantity of electrons in the conduction band and positive gaps in the valence band, which reacted with the water absorbed and the OH group to form hydroxyl radicals. An excess in the conduction band leads to the formation of superoxide and hydrogen peroxide, which in turn leads to the formation of more hydroxyl radicals [49].

These radicals can, in appropriate quantities, attain the complete mineralization of organic substances, but the formation of superoxide radicals may produce other reactions that form intermediaries in the process, and even if this process attains 97.22% degradation, peaks may appear. The formation of intermediaries can be observed in Figure 6, in which between 1.3 and 1.7 min there are peaks of low intensity. The formation of these by-products was also verified when using the heterogeneous photocatalysis process, as can be seen in Figure 7.

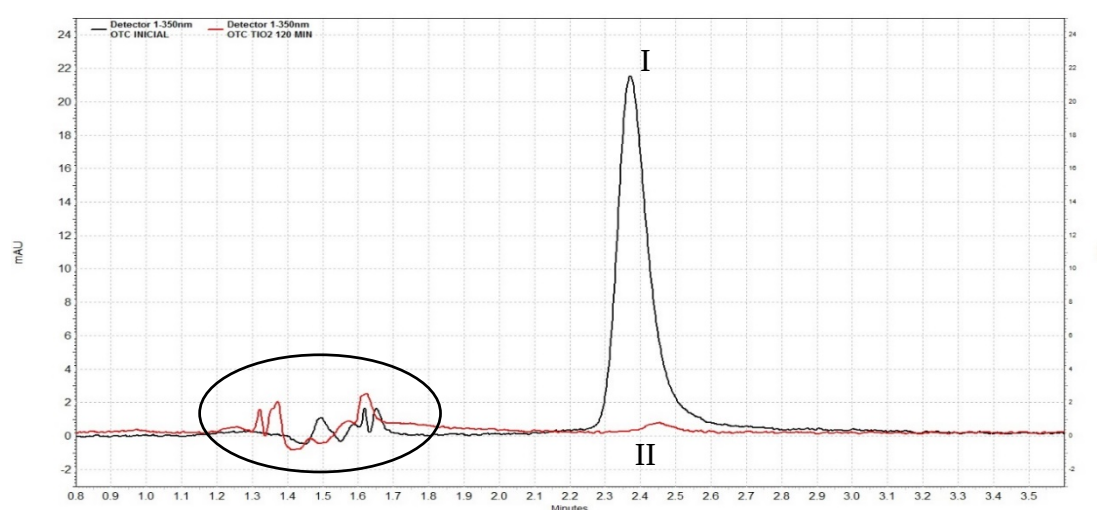


Figure 7. Chromatogram of the oxytetracycline when applying the heterogeneous photocatalysis treatment (8 µL of H₂O₂, 120 minutes of radiation, TiO₂ supported).

When analyzing the chromatogram shown in Figure 7, it is verified that the heterogeneous process led to a greater formation of intermediates than the homogeneous AOP. This fact may be related to a lower availability of hydroxyl radicals available for the degradation of the drug under study.

In [50], Yuan et al. identified sub-products of the photo-degradation of OTC using GC-MS analysis. These sub-products were: 1,4-benzenedicarboxylic acid, 4-oxopentanoic acid, propanedioic acid, hydroximalonic acid, glycerin and butanedioic acid. In their work, meanwhile, Halling-Sørensen et al. [8] indicated that the degradation of tetracyclines by means of photolysis may produce highly stable products, such as anhydrotetracycline, anhydrochlortetracycline or terrinolide.

3.4. Kinetic Study

Influence of the time and the kinetic model on the homogeneous photocatalysis (UV/H₂O₂, photo-Fenton) and heterogeneous photocatalysis (UV/H₂O₂/TiO₂) treatments were evaluated. The study was carried out by varying the exposure times from 5 to 120 min. As is shown in Figure 8a, the UV/H₂O₂ process has an efficiency of approximately 90% in the first 30 min, higher than photo-Fenton treatment, which was 64% and higher than heterogeneous photocatalysis (UV/H₂O₂/TiO₂, which was 70%) in about the same time. All the treatments present an efficiency of 97% after 120 min.

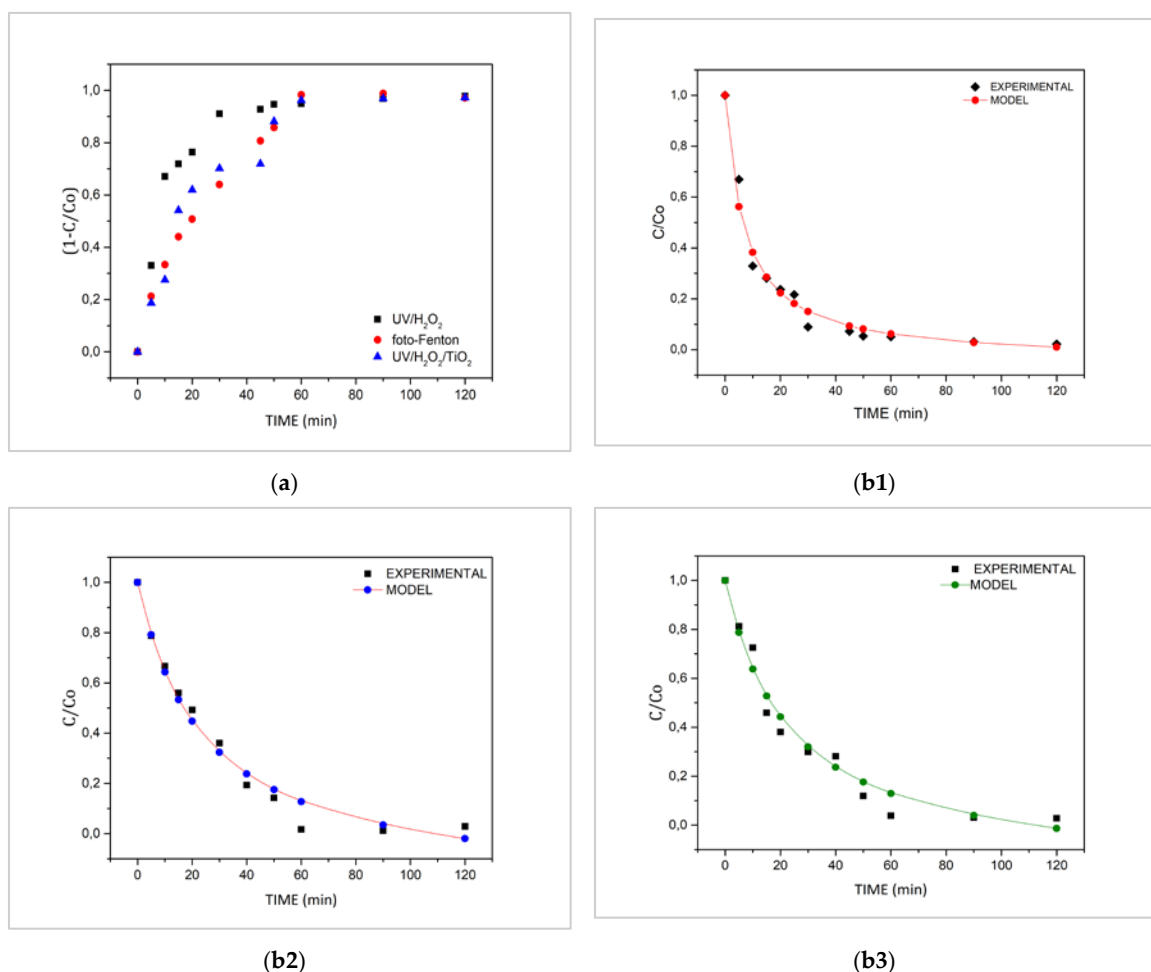


Figure 8. (a) Evolution of the degradation of OTC as a function of time; (b) Adjustment of the model proposed by Chan and Chu; (b1) UV/H₂O₂ process; (b2) Photo-Fenton process; (b3) Heterogeneous photocatalysis.

Similar behavior has been shown by authors such as Reyes et al. [51], who attained an efficiency of 50% after irradiating tetracycline solutions in aqueous suspensions of TiO₂ for 120 min. In their work, Addamo et al. [52] attained an efficiency of 98% in 120 min during the degradation of drugs, while Vogna et al. [53] demonstrated that the UV/H₂O₂ treatment is effective as regards to inducing the degradation of diclofenac, with an efficiency of 39% in 90 min.

In this study, the fit of the kinetic model proposed by Chan and Chu [36] was applied to the experimental data regarding the AOPs employed (Figure 8b). The kinetic model proposed has an adequate fit to the experimental data, as confirmed by the values of $R^2 \geq 0.95$ (Table 1).

Table 1. Parameters of kinetic model of Chan and Chu (2003) for the treatments used in the degradation of OTC.

Treatment	Degradation (%) after 120 min	$1/\rho$ (min ⁻¹)	$1/\sigma$	R^2
UV/H ₂ O ₂	97.76	0.1504	1.0469	0.9975
Photo-Fenton	97.16	0.0526	1.2277	0.9837
Heterogeneous Photocatalysis	97.21	0.0516	1.2112	0.9757

The results depicted in Table 1 show that the highest rate of degradation ($1/\rho$) of the OTC occurred with the UV/H₂O₂ treatment (0.1504 min⁻¹), while both the photo-Fenton (0.0526 min⁻¹)

and heterogeneous photocatalysis (0.0516 min^{-1}) treatments attained lower rates of degradation. This indicates that the UV/H₂O₂ treatment has an advantage over the other two in that it requires less time to attain a greater degradation of the drug. However, the oxidative capacity ($1/\sigma$) in the UV/H₂O₂ is lower (1.0469) than that of the other two treatments—photo-Fenton (1.2277) and heterogeneous photocatalysis (1.2112), and it is interesting to note that the oxidation capacity is more sensitive to the Fe⁺² and TiO₂ concentration in the homogeneous photocatalysis and the heterogeneous treatments, respectively.

3.5. Bench-top Photolytic Reactor—Associated Costs

The costs related to the construction of the photolytic reactor were divided into three types: material costs, projects and operational costs. The material costs involved the expenses to obtain the lamps, the wood structure of the reactor and the utilities (wires, switches and screws, for instance). These costs are detailed in Table 2. The labor cost was fixed in an amount of USD \$80.

Table 2. Material costs for the bench-top photolytic reactor.

Material Costs	Unit Price (USD \$)	Quantity	Total Price (USD \$)
Germicidal Tubular Ultraviolet Lamp (UV-C)—30 W	15.00	3	45.00
Wood to build the reactor	25.00	1	25.00
Tools	5.00	1	5.00
Total material			75.00

Based on Table 2, it can be seen that material and labor costs totaled \$155.00. The operating cost was then determined. For this, it has been taken into consideration the time of use of the reactor in hours, the power of the lamps present and the average price of kW·h in Ecuador, \$0.1. In addition, it was taken as a basis the maximum spending condition of the reactor, with an average of eight hours of use/day and five days a week. In this scenario, a cost of \$0.009/h of operation of the reactor was calculated, with the three lamps in operation and \$1.44/month.

3.6. Study of Toxicity

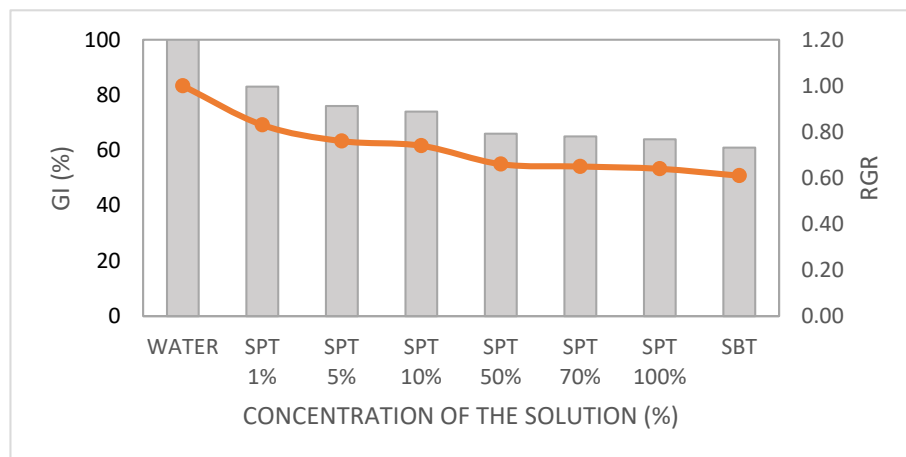
After applying the homogeneous photocatalysis (UV/H₂O₂, photo-Fenton) and heterogeneous photocatalysis (UV/H₂O₂/TiO₂) treatments, the toxicity of the substances formed in the lettuce (*Lactuca sativa*) and carrot (*Daucus carota*) seeds during the process were analyzed. This was done by carrying out assays of germination of the seeds, and two more assays, a negative control (only water) and positive control (3% of boric acid), in which no germination whatsoever occurred. It was found that, in the case of the *Lactuca sativa* species, for all the different concentrations of oxidative treatments analyzed, the results are the same of the negative control; all the seeds germinated. It is, therefore, possible to state that the behavior of the germination for this species is similar in AOP treatments applied and in the presence of only water, thus not seeming to indicate any toxicity. However, fewer seeds of the species *Daucus carota* have germinated, indicating that a greater concentration of treatment solution may produce compounds that inhibit the growth of this species. The germination of the *Daucus carota* seeds was affected to a greater extent than *Lactuca sativa* species, thus indicating that it is less resistant to these treatments.

An analysis of Table 3 indicates that, for the greatest concentration of effluents, the growth of the roots of *Lactuca sativa* and *Daucus carota* seeds is inhibited. This shows that, in spite of the fact that compounds are formed after applying the advanced oxidative treatments, they do not interfere with germination, although they have caused some problems as regards to root growth. The results obtained are shown in Figures 9 and 10 in order to provide a better understanding of the relative growth rate (RGR) and germination index (GI).

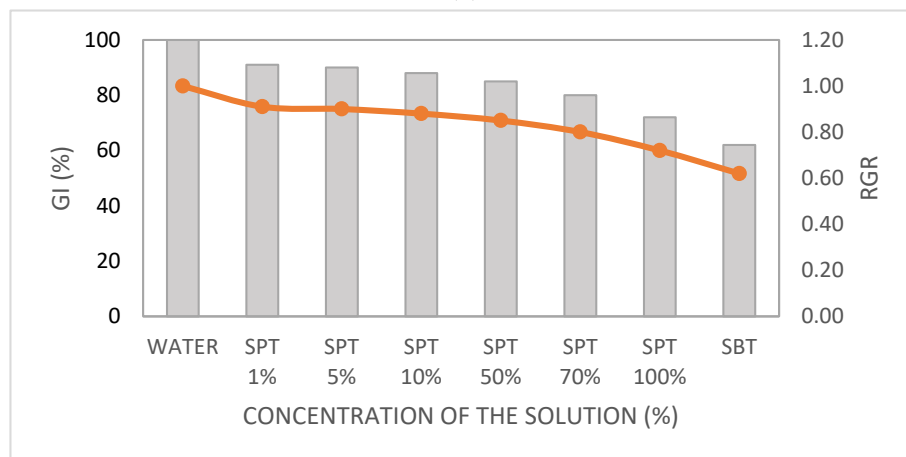
Table 3. Mean length of roots, Relative Growth Rate (RGR) and Germination Index (GI) of lettuce (*Lactuca sativa*) and carrot (*Daucus carota*) seeds according to the concentration of the aqueous OTC solution used for advanced oxidative treatments.

AOP Treatment	UV/H ₂ O ₂				Photo-Fenton				Heterogeneous Photocatalysis			
Species	<i>Lactuca sativa</i>		<i>Daucus carota</i>		<i>Lactuca sativa</i>		<i>Daucus carota</i>		<i>Lactuca sativa</i>		<i>Daucus carota</i>	
Aqueous Solution	* RG ± DP	RGR/GI (%)	* RG ± DP	RGR/GI (%)	* RG ± DP	RGI/GI (%)	* RG ± DP	RGR/GI (%)	* GR ± DP	RGR/GI (%)	* CR ± DP	RGR/GI (%)
Water	4.29 ± 0.33	1/100	2.44 ± 0.15	1/100	4.29 ± 0.33	1/100	2.44 ± 0.15	1/100	4.29 ± 0.33	1/100	2.44 ± 0.15	1/100
SPT 1%	3.54 ± 0.27	0.83/83	2.36 ± 0.20	0.97/87	3.91 ± 0.26	0.91/91	1.24 ± 0.18	0.55/44	3.63 ± 0.27	0.85/85	2.18 ± 0.34	0.89/71
SPT 5%	3.28 ± 0.38	0.76/76	2.31 ± 0.20	0.95/85	3.85 ± 0.57	0.9/90	1.13 ± 0.21	0.46/37	3.32 ± 0.38	0.77/77	1.96 ± 0.25	0.8/64
SPT 10%	3.19 ± 0.58	0.74/74	2.11 ± 0.20	0.87/78	3.76 ± 0.33	0.88/88	1.09 ± 0.19	0.44/31	3.26 ± 0.58	0.76/76	1.89 ± 0.29	0.77/62
SPT 50%	2.84 ± 0.46	0.66/66	2.03 ± 0.41	0.83/67	3.63 ± 0.22	0.85/85	1.03 ± 0.35	0.42/30	3.07 ± 0.46	0.72/72	1.79 ± 0.36	0.73/59
SPT 70%	2.79 ± 0.31	0.65/65	1.5 ± 0.30	0.61/49	3.45 ± 0.19	0.8/80	0.91 ± 0.16	0.41/27	2.66 ± 0.31	0.62/62	1.61 ± 0.47	0.66/46
SPT 100%	2.75 ± 0.22	0.64/64	1.34 ± 0.18	0.55/44	3.07 ± 0.41	0.72/72	0.83 ± 0.23	0.37/26	2.43 ± 0.22	0.57/57	1.34 ± 0.33	0.55/39
SBT	2.6 ± 0.24	0.61/61	1.3 ± 0.42	0.53/37	2.68 ± 0.37	0.62/62	0.68 ± 0.22	0.36/21	1.73 ± 0.24	0.4/40	0.99 ± 0.28	0.4/28

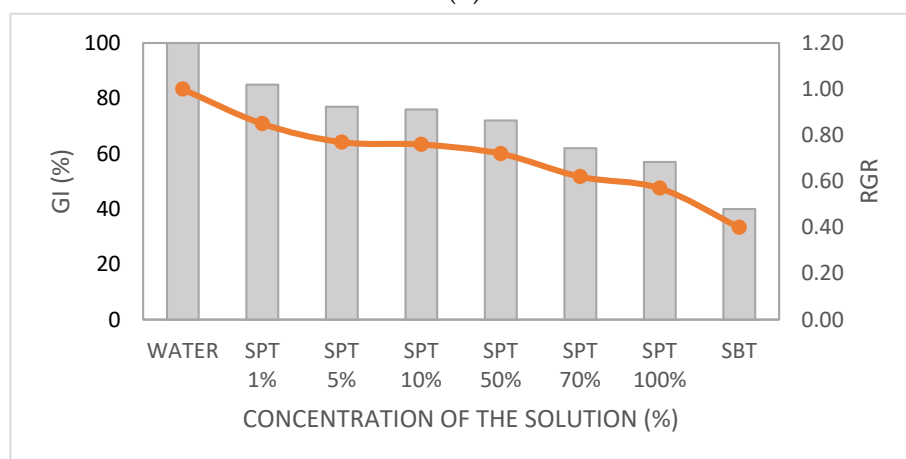
* SBT = solution before the treatment; SPT = solution post-treatment; RG = root growth in cm.



(a)

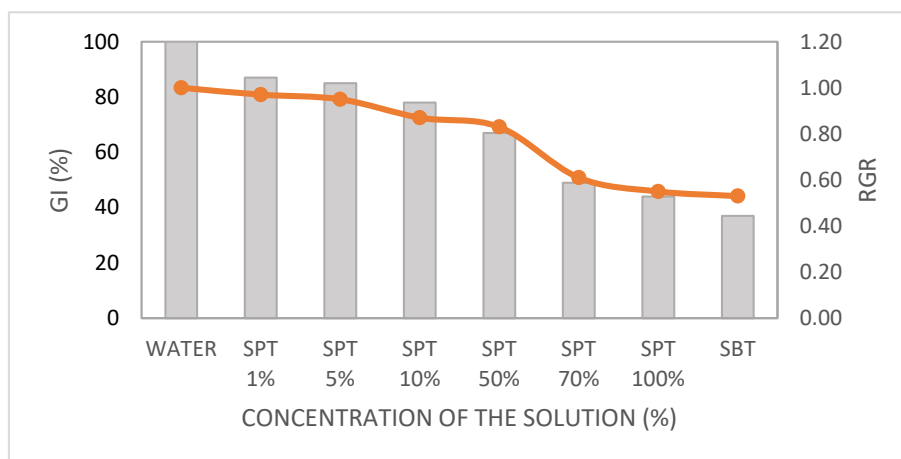


(b)

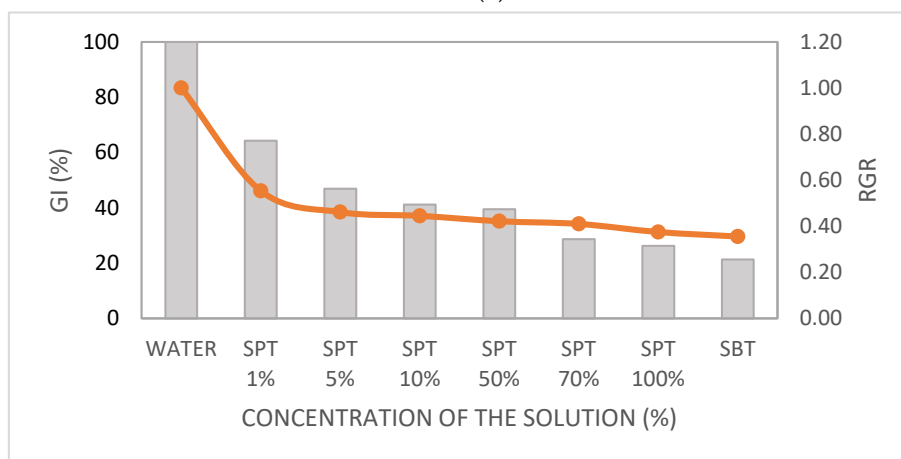


(c)

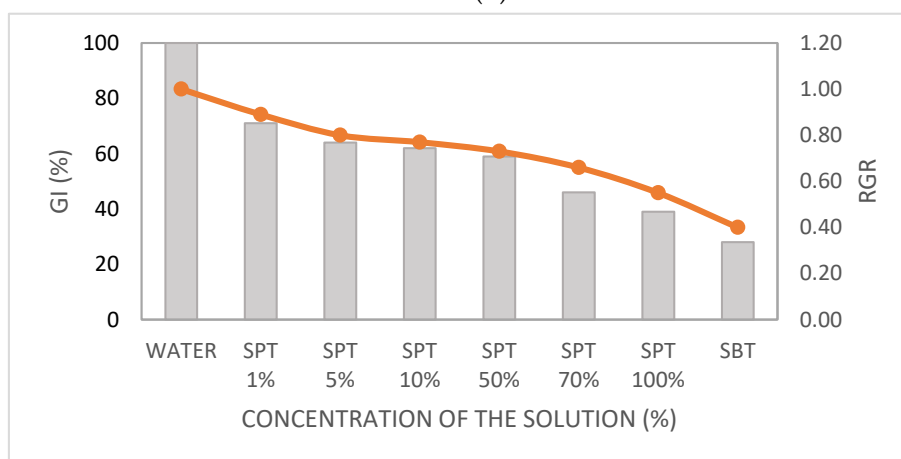
Figure 9. Relative Growth Rate (RGR) and Germination Index (GI) of the lettuce seed (*Lactuca sativa*) for the treatments: (a) UV/H₂O₂; (b) Photo-Fenton; (c) Heterogenic photocatalysis (UV/H₂O₂/TiO₂).



(a)



(b)



(c)

Figure 10. Relative Growth Rate (RGR) and Germination Index (GI) of the carrot seed (*Daucus carota*) for the treatments: (a) UV/H₂O₂; (b) Photo-Fenton; (c) Heterogenic photocatalysis (UV/H₂O₂/TiO₂).

Clearly, there is observed the reduction in the growth of the roots of the species *Lactuca sativa* for all treatments (Figure 9). This reduction is not affected to such a great extent when the concentrations used in the treatments are more diluted. It will be very important to remember that when the effluents are dumped in water bodies, they dissolve, signifying that their behavior will not be as marked as that

of the SPT 50% aqueous solutions and that the root growth will, therefore, be more similar to that of the negative control, as is demonstrated in this experiment.

It is worth highlighting that this will also depend on the type of seed analyzed, since the *Daucus carota* were affected to a greater extent as regards to their root growth (Figure 10). In [37], Napoleão et al. pointed out that, in the case of species such as *Impatiens balsamina*, *Celosia cristata*, and *Americano Hard*, when carrying out a toxicity analysis after applying AOPs, the growth of the species analyzed have been affected.

4. Conclusions

The application of the advanced oxidative processes of homogeneous photocatalysis (UV/H₂O₂ and photo-Fenton) and heterogeneous photocatalysis (TiO₂) to aqueous solution of OTC have obtained a degradation rate of 97%, with the UV/H₂O₂ treatment being the most suitable, since its performance was similar to that of the other treatments, but with the advantage that it was not necessary to use a catalyst to increase the effect of the process. The model kinetics proposed had a good fit to the experimental data, showing that the UV/H₂O₂ treatment required less exposure time but attained higher rates of degradation. The toxicity studies showed that the *Daucus carota* seeds were more sensitive, since the percentage of their inhibition as regards to growth and germination when exposed to the treatments was greater. The *Lactuca sativa* seeds, meanwhile, behaved similarly to the negative controls as regards to the most diluted concentrations of the treatments, thus demonstrating that the advanced oxidative processes applied do not compromise the root growth and germination of this species.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2071-1050/12/21/8807/s1>, Appendix A: Validation of analytical parameters.

Author Contributions: Development of research, obtaining and realization of experimental data, results analysis and writing the manuscript, J.M.G.-M.; development of methods of analysis and experimental methodology, results analysis and validation of methods, L.A.Z.-I.; acquisition of funds, supervision of experimental development and analysis of the final results, L.S.Q.-F.; experimental design direction, interpretation and conceptualization of results, D.C.N.; experimental design direction, acquisition of funds, interpretation and conceptualization of results and analysis of the final results, N.S.O. and J.d.S.V.; conception of the investigation, supervision of experimental data, interpretation of the final results of the investigation, J.M.R.-D. All authors have read and agreed to the published version of the manuscript.

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