

# Heterogeneous Photocatalysis with Wireless UV-A LEDs <sup>†</sup>

Leonor C. Ferreira <sup>1,2</sup>, José R. Fernandes <sup>3</sup> , José A. Peres <sup>1</sup> , Pedro B. Tavares <sup>1</sup>  and Marco S. Lucas <sup>1,\*</sup> 

<sup>1</sup> Centro de Química de Vila Real (CQVR), Departamento de Química, Universidade de Trás-os-Montes e Alto Douro, 5000-801 Vila Real, Portugal; leonor.ferreira@awam.fraunhofer.pt (L.C.F.); jperes@utad.pt (J.A.P.); ptavares@utad.pt (P.B.T.)

<sup>2</sup> Associação Fraunhofer Portugal Research–AWAM, Regia Douro Park, Andrães, 5000-033 Vila Real, Portugal

<sup>3</sup> Centro de Química de Vila Real (CQVR), Departamento de Física, Universidade de Trás-os-Montes e Alto Douro, 5000-801 Vila Real, Portugal; jraf@utad.pt

\* Correspondence: mlucas@utad.pt

<sup>†</sup> Presented at the 4th International Electronic Conference on Applied Sciences, 27 October–10 November 2023; Available online: <https://asec2023.sciforum.net/>.

**Abstract:** Water reuse policies demand high-quality treated water, ensuring no harm to human health and ecosystems. Advanced oxidation processes seem to be one of the most appropriated technologies to achieve the goal of ensuring safe water reuse. In this work, a wireless lab-scale UV-A LED reactor powered by a resonant inductive coupling system was built, maximizing UV photon absorption. The energy inside the photoreactor was supplied through a magnetic field generated by induction coils placed on the external wall. The optimal operating parameters were found to be  $[\text{TiO}_2] = 500 \text{ mg L}^{-1}$  and  $[\text{H}_2\text{O}_2] = 100 \text{ mg L}^{-1}$ , attaining 50% of RB5 removal after 180 min, with  $E_{EO} = 17.6 \text{ kWh m}^{-3} \text{ order}^{-1}$  and  $E_{SAE} = 1.75 \times 10^3 \text{ kWh mol}^{-1} \text{ order}^{-1}$ .

**Keywords:** azo dye; water reuse; advanced oxidation processes; wireless LEDs

## 1. Introduction

Worldwide, 80% of generated wastewater is released without proper treatment. Water scarcity is a reality, and so wastewater is now seen as a valuable resource. In line with this, wastewater treatment and reuse are being implemented globally as a promising solution. Water is an essential resource in all sectors, but agriculture is the sector that places this resource under more pressure, requiring 70% of all the water globally consumed, and also being the sector that most contributes to environmental pollution [1,2]. To minimize water depletion and ensure food for all, the agricultural sector must be of major concern. The majority of industries are not prepared to strive for an efficient treatment, in the best cases being able to treat the wastewater in order to comply with legislation or only to discharge into wastewater treatment plants [1,3].

Advanced oxidation processes (AOPs), generate hydroxyl radicals ( $\text{HO}^\bullet$ ) with an oxidation potential = 2.8 eV, that can react with the several pollutants, oxidizing them to simpler intermediates and potentially to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [4]. These advanced treatments have already proven their efficiency via different processes, such as  $\text{TiO}_2$  heterogeneous photocatalysis [5–8], electrochemical treatments [9,10], photo-Fenton [3,11] and ozonation [12,13]. The combination of AOPs with UV radiation enhances overall system efficiency, in which light emitting diodes (LEDs) are on the rise compared to traditional mercury vapor lamps. Nevertheless, by considering commonly used wired systems, photons are scattered throughout the air path diminishing treatment effectiveness.

In this work, an azo dye (Reactive Black 5) was selected as a model compound to assess the capability of a lab-scale wireless UV-A LED photoreactor to activate  $\text{TiO}_2$  and decolorize the commercial dye. When disposed of without proper treatment in water streams, dyes are found to be stable to light and oxidizing agents, interfering with the



**Citation:** Ferreira, L.C.; Fernandes, J.R.; Peres, J.A.; Tavares, P.B.; Lucas, M.S. Heterogeneous Photocatalysis with Wireless UV-A LEDs. *Eng. Proc.* **2023**, *56*, 175. <https://doi.org/10.3390/ASEC2023-15977>

Academic Editor: Simeone Chianese

Published: 14 November 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

transmission of light in water bodies and inhibiting the photosynthetic activity of aqua biota [14].

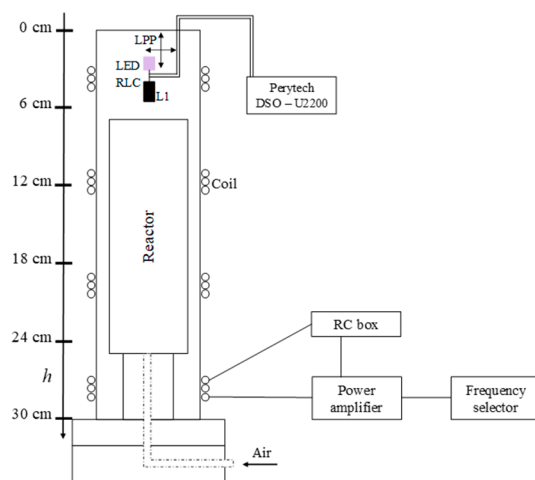
## 2. Material and Methods

### 2.1. Reagents and Analytical Determinations

The Reactive Black 5 (RB5,  $C_{26}H_{21}N_5O_{19}S_6Na_4$ , CI 20505) was provided by DyStar (Porto, Portugal) and used without purification. The UV-vis absorption spectrum of the azo dye is consistent with the non-hydrolyzed form, showing two absorption bands at 310 and 595 nm. The catalyst used was titanium dioxide ( $TiO_2$ , P25 Evonik), comprising 86.5% of anatase and 13.5% of rutile and having a BET specific surface area of  $55\text{ m}^2/\text{g}$ . The hydrogen peroxide ( $H_2O_2$ ) was purchased from Panreac (30% *w/v*) and the Merckoquant peroxide analytical test strips were bought from Merck (Lisboa, Portugal). The sodium hydroxide (NaOH) and sulfuric acid ( $H_2SO_4$ ) were supplied from Sigma (Lisboa, Portugal).

### 2.2. Reactor and the UV-A LED Wireless System

A total of 15 wireless UV-A LEDs (InGaN Roithner RLS-UV365E, Vienna, Austria) were placed inside a lab-scale bubble column reactor (330 mL) (Figure 1) and used in the decolorization of dye (RB5) by  $TiO_2$  photocatalysis. Each LED has a radiant flux of 1 mW and a viewing angle of  $30^\circ$ . Wireless power transfer using a resonant inductive coupling system provided the electrical power to each LED, with the LED emitters placed inside the reactor. The reactor tube was made of polyvinyl chloride with a height of 30 cm and an inside diameter of 7 cm. The system incorporated a bottom-side air injection generated by an aquarium air pump. This wireless LED system and reactor are described in more detail in [3].



**Figure 1.** Lab-scale wireless UV-A LED reactor scheme.

### 2.3. Experimental Procedure

The RB5 solutions ( $10\text{ mg L}^{-1}$ ) were prepared by dissolving the required amount of dye in distilled water and then adding the catalyst ( $200, 400, 500, 600\text{ mg L}^{-1}$ ). In order to enhance the dispersion of the  $TiO_2$  P25, the suspension was placed in an ultrasonic bath (Bandelin Sonorex SUPER PK 106, Algés, Portugal) for 3 min. To reach the adsorption equilibrium the dispersion was placed under continuous stirring in the dark for 30 min before each experiment. The initial pH was measured (Jenway 3510 pH meter) and, when necessary, adjusted with NaOH or  $H_2SO_4$  to the required pH value (between 3 and 8). The experiment started when the UV-A LEDs were turned on. When using  $H_2O_2$  ( $250, 100, 150, 100\text{ mg L}^{-1}$ ), time zero was set at the time both  $H_2O_2$  was added and the UV-A LEDs were turned on. During the experiments the solution was kept in constant aeration (Air pump Ecoair-9800, Porto, Portugal) through the bottom and the temperature was monitored with an analytical thermometer (Ama Spezial  $\pm 0.01^\circ\text{C}$ ), being maintained at

25 °C. Samples were taken at specific times with a syringe and centrifuged twice for 15 min at 6000 rpm to separate the TiO<sub>2</sub> P25 in suspension. The samples were analyzed using an LLG-uniSPEC 2 UV/Vis single spectrophotometer and the absorbance was measured at 595 nm, once it had reached the RB5 maximum absorption wavelength. Additionally, the H<sub>2</sub>O<sub>2</sub> concentration was roughly followed by Merckoquant peroxide analytical test strips. All the experiments were conducted in duplicate, with the represented values being the averages of accepted results. The RB5 removal concentration was calculated with the Beer–Lambert law, using the optical density and the molar extinction coefficient. The obtained data were adjusted to pseudo-first-order kinetics and the kinetics constants were calculated.

### 3. Results and Discussion

Firstly, it is important to highlight that the system and UV-A LEDs were previously characterized in terms of the amplitude of the alternating current (AC) signal, the magnetic field that reaches the LEDs, and the optical irradiance. Very briefly, it was determined that: (i) the maximum magnetic field and optical irradiance were obtained at 26.8 and 27.0 kHz; (ii) the AC signal remains constant independently of the LED position, if below 45 mm from the top; and (iii) the receptor coil (L1 displayed in Figure 1) must always be in the vertical position to ensure LED optical irradiance.

#### 3.1. Oscillation Frequency and the Number of UV-A LEDs

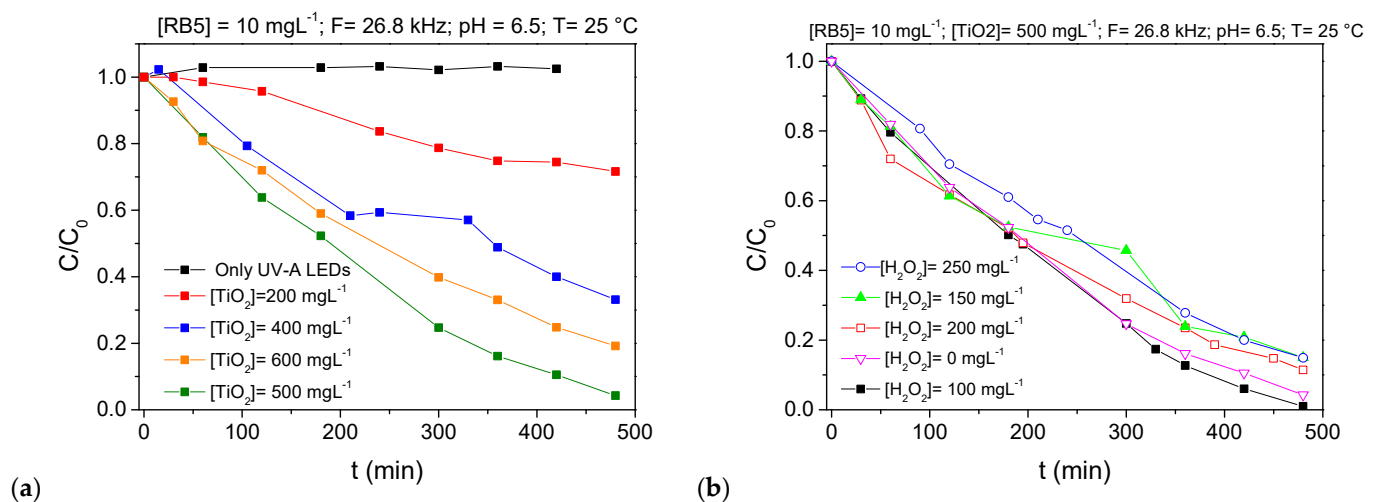
In line with the abovementioned, it was important to verify which oscillation frequency presented the best kinetic results, whether 26.8 or 27 kHz. Experimental data confirmed the assumption previously made (data not shown). The data revealed that of all the working oscillation frequencies (25, 26, 26.5, 26.8, 27, 28, 29, 30, 31 kHz), those between 26.5 and 27 kHz are expected to have the best kinetic results. A better kinetic result was achieved in 26.8 kHz ( $0.00885 \pm 0.00064 \text{ min}^{-1}$ ), followed by 26.5 kHz ( $0.00619 \pm 0.00054 \text{ min}^{-1}$ ), and then 27 kHz ( $0.00590 \pm 0.00028 \text{ min}^{-1}$ ). For this reason, all the following experiments were carried out with an oscillation frequency of 26.8 kHz and the following operating conditions: [RB5] = 10 mg L<sup>-1</sup>; [TiO<sub>2</sub>] = 500 mg L<sup>-1</sup>; pH = 6.5; T = 25 °C.

#### 3.2. Effect of the TiO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and RB5 Concentrations

Initially, two control tests were carried out with UV-A LEDs and only RB5 solution (dark/no UV-A LEDs), showing almost no decolorization. Adsorption experiments revealed the same tendency when exposed to [TiO<sub>2</sub>] = 500 mg L<sup>-1</sup> in the dark.

When assessing TiO<sub>2</sub> dosage, the increase on the amount of TiO<sub>2</sub> promotes a faster decolorization (Figure 2a), except when TiO<sub>2</sub> is increased from 500 ( $k = 6.19 \times 10^{-3}$ ) to 600 mg L<sup>-1</sup> ( $k = 3.35 \times 10^{-3}$ ) (Table 1). The decrease in the pseudo-first-order kinetic value suggests an excess of catalyst in solution, hindering catalyst activation. The catalyst dosage is a critical factor, because if the solution is too opaque, light is unable to pass through it and activate the TiO<sub>2</sub>, decreasing or even inhibiting the photocatalytic process. These results agree with the literature on using TiO<sub>2</sub> powder as catalyst [5].

Regarding the H<sub>2</sub>O<sub>2</sub> concentration (Figure 2b), it is possible to detect a slight increase in the decolorization of RB5 when adding 100 mg L<sup>-1</sup> of H<sub>2</sub>O<sub>2</sub> to the solution, which is attributed to the dissociation of H<sub>2</sub>O<sub>2</sub> and the consequent formation of HO•, O<sub>2</sub>•<sup>-</sup> and HOO•. In contrast, when adding higher concentrations, a negative effect is observed. This may suggest an excess of H<sub>2</sub>O<sub>2</sub> in the solution, which acts as a radical scavenger of HO•, generating radicals with lower reactivity and therefore slowing the kinetic rate [15]. Additionally, it is known that TiO<sub>2</sub> can be dissociated or even adsorbed by H<sub>2</sub>O<sub>2</sub>, generating Ti-peroxo complexes, which present lower photocatalytic activity than TiO<sub>2</sub> [16]. Nevertheless, to the best of our knowledge, it is necessary to further investigate the interaction mechanisms between H<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub>, to better understand the decolorization reactions.

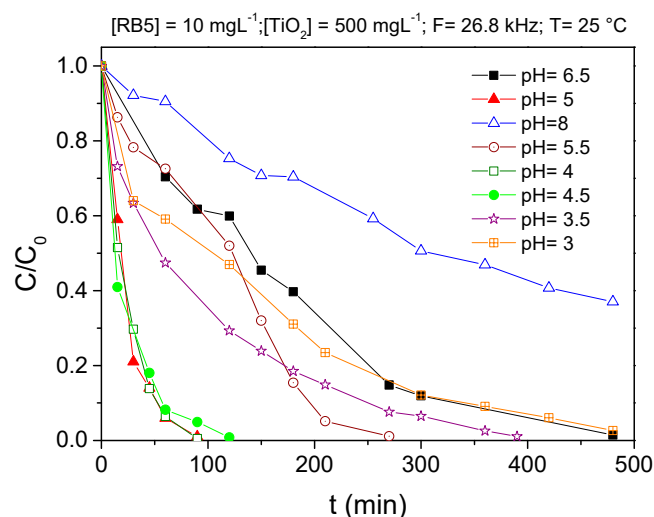


**Figure 2.** RB5 decolorization with different: (a) TiO<sub>2</sub> concentration, (b) H<sub>2</sub>O<sub>2</sub> concentration. Fixed operating conditions: [RB5] = 10 mg L<sup>-1</sup>; pH = 6.5; F = 26.8 kHz; T = 25 °C.

**Table 1.** Calculated pseudo-first-order kinetic rates (*k*), electric energy per order (*E*<sub>EO</sub>) and specific applied energy (*E*<sub>SAE</sub>), for the experiments in Figures 2 and 3.

| Fixed Parameters                                                                                       | Variable                         |     | <i>k</i><br>(min <sup>-1</sup> ) | <i>E</i> <sub>EO</sub><br>(kWh m <sup>-3</sup> order <sup>-1</sup> ) | <i>E</i> <sub>SAE</sub><br>(kWh mol <sup>-1</sup> order <sup>-1</sup> ) |
|--------------------------------------------------------------------------------------------------------|----------------------------------|-----|----------------------------------|----------------------------------------------------------------------|-------------------------------------------------------------------------|
| [RB5] = 10 mg L <sup>-1</sup><br>pH = 6.5<br>T = 25 °C                                                 | [TiO <sub>2</sub> ]              | 0   | 9.17 × 10 <sup>-6</sup>          | 1.52 × 10 <sup>4</sup>                                               | 1.51 × 10 <sup>6</sup>                                                  |
|                                                                                                        |                                  | 200 | 7.78 × 10 <sup>-4</sup>          | 1.79 × 10 <sup>2</sup>                                               | 1.78 × 10 <sup>4</sup>                                                  |
|                                                                                                        |                                  | 400 | 2.19 × 10 <sup>-3</sup>          | 6.38 × 10 <sup>2</sup>                                               | 6.32 × 10 <sup>3</sup>                                                  |
|                                                                                                        |                                  | 500 | 6.19 × 10 <sup>-3</sup>          | 2.26 × 10 <sup>1</sup>                                               | 2.24 × 10 <sup>3</sup>                                                  |
|                                                                                                        |                                  | 600 | 3.35 × 10 <sup>-3</sup>          | 4.17 × 10 <sup>1</sup>                                               | 4.13 × 10 <sup>3</sup>                                                  |
| [RB5] = 10 mg L <sup>-1</sup><br>[TiO <sub>2</sub> ] = 500 mg L <sup>-1</sup><br>pH = 6.5<br>T = 25 °C | [H <sub>2</sub> O <sub>2</sub> ] | 0   | 6.19 × 10 <sup>-3</sup>          | 2.26 × 10 <sup>1</sup>                                               | 2.24 × 10 <sup>3</sup>                                                  |
|                                                                                                        |                                  | 100 | 7.92 × 10 <sup>-3</sup>          | 1.76 × 10 <sup>1</sup>                                               | 1.75 × 10 <sup>3</sup>                                                  |
|                                                                                                        |                                  | 150 | 3.77 × 10 <sup>-3</sup>          | 3.7 × 10 <sup>1</sup>                                                | 3.67 × 10 <sup>3</sup>                                                  |
|                                                                                                        |                                  | 200 | 4.15 × 10 <sup>-3</sup>          | 3.36 × 10 <sup>1</sup>                                               | 3.34 × 10 <sup>3</sup>                                                  |
|                                                                                                        |                                  | 250 | 4.07 × 10 <sup>-3</sup>          | 3.43 × 10 <sup>1</sup>                                               | 3.40 × 10 <sup>3</sup>                                                  |
| [TiO <sub>2</sub> ] = 500 mg L <sup>-1</sup><br>pH = 6.5<br>T = 25 °C                                  | [RB5]                            | 10  | 6.19 × 10 <sup>-3</sup>          | 2.26 × 10 <sup>1</sup>                                               | 2.24 × 10 <sup>3</sup>                                                  |
|                                                                                                        |                                  | 25  | 7.70 × 10 <sup>-4</sup>          | 1.81 × 10 <sup>2</sup>                                               | 1.80 × 10 <sup>4</sup>                                                  |
|                                                                                                        |                                  | 40  | 3.65 × 10 <sup>-4</sup>          | 3.83 × 10 <sup>2</sup>                                               | 3.79 × 10 <sup>4</sup>                                                  |
|                                                                                                        |                                  | 50  | 2.74 × 10 <sup>-4</sup>          | 5.10 × 10 <sup>2</sup>                                               | 5.05 × 10 <sup>4</sup>                                                  |
| [RB5] = 10 mg L <sup>-1</sup><br>[TiO <sub>2</sub> ] = 500 mg L <sup>-1</sup><br>T = 25 °C             | pH                               | 3   | 6.91 × 10 <sup>-3</sup>          | 2.02 × 10 <sup>1</sup>                                               | 2.00 × 10 <sup>3</sup>                                                  |
|                                                                                                        |                                  | 3.5 | 1.02 × 10 <sup>-2</sup>          | 1.38 × 10 <sup>1</sup>                                               | 1.36 × 10 <sup>3</sup>                                                  |
|                                                                                                        |                                  | 4   | 5.74 × 10 <sup>-2</sup>          | 2.43                                                                 | 2.41 × 10 <sup>2</sup>                                                  |
|                                                                                                        |                                  | 4.5 | 3.70 × 10 <sup>-2</sup>          | 3.77                                                                 | 3.74 × 10 <sup>2</sup>                                                  |
|                                                                                                        |                                  | 5   | 5.10 × 10 <sup>-2</sup>          | 2.74                                                                 | 2.72 × 10 <sup>2</sup>                                                  |
|                                                                                                        |                                  | 5.5 | 1.51 × 10 <sup>-2</sup>          | 9.25                                                                 | 9.18 × 10 <sup>2</sup>                                                  |
|                                                                                                        |                                  | 6.5 | 6.19 × 10 <sup>-3</sup>          | 2.26 × 10 <sup>1</sup>                                               | 2.24 × 10 <sup>3</sup>                                                  |
|                                                                                                        |                                  | 8   | 2.10 × 10 <sup>-3</sup>          | 6.65 × 10 <sup>1</sup>                                               | 6.59 × 10 <sup>3</sup>                                                  |

The system behavior under different RB5 concentrations (10, 25, 40 and 50 mg L<sup>-1</sup>) was also evaluated. By increasing the pollutant dosage there is a decrease in the system response, translating into lower kinetic values (Table 1). The RB5 solution presents a strong dark color and, by increasing the concentration, it may hinder the photons path and reduce the illuminated volume, resulting in a reduction in oxidation zones.



**Figure 3.** Effect of pH on RB5 decolorization. Operating conditions:  $[RB5] = 10 \text{ mg L}^{-1}$ ;  $[TiO_2] = 500 \text{ mg L}^{-1}$ ;  $F = 26.8 \text{ kHz}$ ;  $T = 25 \text{ }^{\circ}\text{C}$ .

The literature reports two possible decolorization pathways: (i)  $HO^{\bullet}$  attacks RB5 in the azo form leading to the breakage of  $N=N$ ; or (ii)  $HO^{\bullet}$  attacks RB5 in the hydroazo form leading to the breakage of  $C-N$  bonds. Both configurations are stable in aqueous media [17]. A study conducted with Reactive Red 195 dye using  $TiO_2$ /UV-A revealed that  $N=N$  breakage would be the preferred site for  $HO^{\bullet}$  attack, but in this case, it was not considered the hydroazo tautomer [6]. However, when considering both configurations, theoretical studies concluded that the  $C-N$  bonds are the preferred site for  $HO^{\bullet}$  attack [18,19]. In line with this and from the proposed mechanisms found in the literature for the photodegradation of different dyes, it can be assumed that there is a prevalence of  $C-N$  breakage, and therefore a predominance of stable hydroazo tautomer species in the aqueous solution used in the present study. In this sense, the photodegradation reaction mechanism could be initiated by the nucleophilic attack of the carbon in the aromatic ring connected to the nitrogen ( $C-N$  bond). Since the RB5 configuration is mirrored, there is a double  $N=N$  azo bond in the molecule, and so the linkage with higher atomic charge will be the first one to suffer nucleophilic attack. This attack leads to the formation of the intermediate species hydroazo-OH, with an increase in the adjacent  $C-N$  bond energy. The increased  $C-N$  bond energy favors its breakage, and there is a total separation of this aromatic ring from the main molecule, forming a new intermediate species, which is in an equilibrium state with its tautomer. This chain reaction is readily followed by a second nucleophilic attack to the other carbon adjacent to the  $N=N$  bond, forming once again a hydroazo-OH and all the subsequent steps. In sum, the  $C-N$  bond is more likely to be attacked by  $HO^{\bullet}$  rather than the  $N=N$  bond [17,18].

### 3.3. Influence of pH

The pH value (3, 3.5, 4, 4.5, 5, 5.5, 6.5, 8) of the solution influences the photocatalytic rates, under the following conditions:  $[RB5] = 10 \text{ mg L}^{-1}$ ;  $[TiO_2] = 500 \text{ mg L}^{-1}$ ;  $F = 26.8 \text{ kHz}$ ;  $T = 25 \text{ }^{\circ}\text{C}$  (Figure 3). The pH value affects the  $TiO_2$  surface properties, the hydroxyl radical's generation, and the deprotonation of the dye [20–22]. The RB5 dissociation constants ( $pK_a$ ) were at 3.8 and 6.9.  $TiO_2$  point of zero charge was 6.7, which indicates that under 6.7 its surface is charged positively and above it is negatively charged. For RB5, the same behavior was observed, therefore the best pH to work with should be between 3.8 and 6.7 or between 6.7 and 6.9, in which higher attraction forces are noticed. Moreover, it is known that the  $TiO_2$  zeta potential is pH dependent, having lower values at higher pH values. The higher the value, the more stable the solution will be. pH values of 4, 4.5, and 5 present the fastest pseudo-first-order kinetic value (Table 1); however, the experimental work revealed some

TiO<sub>2</sub>/RB5 agglomeration as we started decreasing the pH from 5.5. For this reason, the experiments were conducted at a natural pH of around 6.5. Additionally, the costs related to reagents were also diminished. Nonetheless, future work should include exploring these pH values and try to achieve a compromise between treatment time, efficiency, reagent, and energy consumption.

### 3.4. Electric Energy Per Order ( $E_{EO}$ ) and Specific Applied Energy ( $E_{SAE}$ )

The amount of electric energy necessary to reduce the RB5 concentration by one order of magnitude in a unit of volume is defined as electric energy per order ( $E_{EO}$ ) and the specific applied energy ( $E_{SAE}$ ) indicates the energy necessary to break 1 mol of the pollutant.  $E_{EO}$  is defined by Equation (1), in which  $P$  is the rated power (kW) of the system,  $V$  is the reactor volume (m<sup>3</sup>) at the time  $t$  (h),  $k_{obs}$  (min<sup>−1</sup>) and  $E_{SAE}$  are defined by Equation (2), where  $C_0$  is the initial pollutant concentration (mol L<sup>−1</sup>).

$$E_{EO} = \frac{38.4 \times 10^{-3} P}{V k_{obs}} \quad (1)$$

$$E_{SAE} = \frac{E_{EO}}{C_0 \times 10^3} \quad (2)$$

Low  $E_{EO}$  values indicate lower electrical treatment costs. In this case,  $E_{EO}$  values will only refer to the UV-A LEDs' nominal electrical consumption. Since the  $E_{EO}$  equation takes into account the pseudo-first-order kinetic constants obtained in each experiment,  $E_{EO}$  values will follow the same tendency [23].  $E_{SAE}$  depends on the  $E_{EO}$  and  $C_0$  values. In line with this, it is possible to analyze both the electrical consumption values and the energy required to decolorize RB5 in Table 1, as follows: (i) [TiO<sub>2</sub>] dosage—increasing the amount of catalyst led to lower  $E_{EO}$  and  $E_{SAE}$  values, except when the TiO<sub>2</sub> concentration was changed to 600 mg L<sup>−1</sup>; (ii) [H<sub>2</sub>O<sub>2</sub>] concentration—the addition of 100 mg L<sup>−1</sup> resulted in a lower electrical consumption when compared to the sample without H<sub>2</sub>O<sub>2</sub> in the media. However, by adding a higher concentration of H<sub>2</sub>O<sub>2</sub> there was not a linear decrease in the electrical values, instead a negative effect on the treatment was noticed. Similarly, the  $E_{SAE}$  values were revealed to require less energy to break the RB5 chromophore groups when adding 100 mg L<sup>−1</sup> of H<sub>2</sub>O<sub>2</sub>; (iii) [RB5] concentration—since absorptivity decreases when increasing the pollutant concentration, it was harder to decolorize the pollutant and therefore electrical values rose with increasing RB5 concentration; and (iv) pH values—pH 4, 4.5, and 5 presented the lowest  $E_{EO}$  and  $E_{SAE}$  values.

Overall, the lowest values were at an acidic pH between 4 and 5. Nevertheless, at the conditions considered optimal ([RB5] = 10 mg L<sup>−1</sup>, [TiO<sub>2</sub>] = 500 mg L<sup>−1</sup>, [H<sub>2</sub>O<sub>2</sub>] = 100 mg L<sup>−1</sup>, pH = 6.5,  $F$  = 26.8 kHz;  $T$  = 25 °C) the  $E_{EO}$  was 17.6 kWh m<sup>−3</sup> order<sup>−1</sup> and  $E_{SAE}$  was  $1.75 \times 10^3$  kWh mol<sup>−1</sup> order<sup>−1</sup>. Despite other papers presenting RB5 decolorization with  $E_{EO}$  value calculations, wireless radiation was not used. Nevertheless, the use of both low-pressure Hg lamps and wired LEDs seems very interesting in terms of electrical consumption, reaching  $E_{EO}$  values of 12 and 60–82 kWh m<sup>−3</sup> order<sup>−1</sup>, respectively [7,8].

## 4. Conclusions

This work reported the decolorization of a dye, Reactive Black 5, by means of TiO<sub>2</sub> photocatalysis assisted by a wireless UV-A LED system.

The best operating parameters were found to be [TiO<sub>2</sub>] = 500 mg L<sup>−1</sup> and [H<sub>2</sub>O<sub>2</sub>] = 100 mg L<sup>−1</sup>, with an electric energy per order ( $E_{EO}$ ) of 17.6 kWh m<sup>−3</sup> order<sup>−1</sup>. The wireless UV-A LED system proved to be efficient in the removal of RB5 with TiO<sub>2</sub> photocatalysis, despite requiring long treatment times. The results showed that the wireless UV-A LED system is efficient in the activation of the catalyst TiO<sub>2</sub> under different conditions, favoring the generation of hydroxyl radicals and promoting RB5 decolorization. Nonetheless, this wireless UV-A system requires further studies to upgrade it and to maximize its efficiency in order to be able to work in more realistic conditions.

**Author Contributions:** Conceptualization, L.C.F. and M.S.L.; methodology, L.C.F. and M.S.L.; validation, L.C.F., J.A.P., J.R.F., P.B.T. and M.S.L.; formal analysis, L.C.F. and M.S.L.; investigation, L.C.F.; resources, L.C.F., J.A.P., J.R.F., P.B.T. and M.S.L.; data curation, L.C.F., P.B.T. and M.S.L.; writing—original draft preparation, L.C.F.; writing—review and editing L.C.F., P.B.T. and M.S.L.; visualization, L.C.F. and M.S.L.; supervision, P.B.T. and M.S.L.; project administration, M.S.L.; funding acquisition, L.C.F. and M.S.L. All authors have read and agreed to the published version of the manuscript.

**Funding:** Financial support was provided by the OBTAIn project (NORTE-01-0145-FEDER-000084) and the project INICIO-Setup of research infrastructure for closed circles of water, nutrients and energy in Portuguese agriculture (NORTE-01-0145-FEDER-072685), both co-financed by the European Regional Development Fund (ERDF) through NORTE 2020.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data are contained within the article.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. Simhayov, R.; Ohana-Levi, N.; Shenker, M.; Netzer, Y. Effect of long-term treated wastewater irrigation on soil sodium levels and table grapevines' health. *Water Manag.* **2023**, *275*, 108002. [CrossRef]
2. Morgera, E.; Webster, E.; Hamley, G.; Sindico, F.; Robbie, J.; Switzer, S.; Berger, T.; Sánchez, P.P.S.; Lennan, M.; Martin-Nagle, R.; et al. *The Right to Water for Food and Agriculture*; Food and Agriculture Organization of the United Nations: Rome, Italy, 2020; ISBN 978-92-5-132301-4. Available online: <https://www.fao.org/3/ca8248en/CA8248EN.pdf> (accessed on 15 March 2023).
3. Ferreira, L.C.; Fernandes, J.R.; Peres, J.A.; Tavares, P.B.; Lucas, M.S. Wireless UV-A LEDs-driven AOP in the treatment of agro-industrial wastewaters. *Environ. Res.* **2021**, *200*, 111430. [CrossRef] [PubMed]
4. Ji, Q.; He, H.; Gao, Z.; Wang, X.; Yang, S.; Sun, C.; Li, S.; Zhang, L. UV/H<sub>2</sub>O<sub>2</sub> oxidation of tri(2-chloroethyl) phosphate: Intermediate products, degradation pathway and toxicity evaluation. *J. Environ. Sci.* **2020**, *98*, 55–61. [CrossRef] [PubMed]
5. Ferreira, L.C.; Fernandes, J.R.; Rodríguez-Chueca, J.; Lucas, M.S.; Tavares, P.B. Photocatalytic degradation of an agro-industrial wastewater model compound using a UV LEDs system: Kinetic study. *J. Environ. Manag.* **2020**, *269*, 110740. [CrossRef] [PubMed]
6. Turkten, N.; Cinar, Z. Photocatalytic decolorization of azo dyes on TiO<sub>2</sub>: Prediction of mechanism via conceptual DFT. *Catal. Today* **2017**, *87*, 169–175. [CrossRef]
7. Lucas, M.S.; Tavares, P.B.; Peres, J.A.; Faria, J.L.; Rocha, M.; Pereira, C.; Freire, C. Photocatalytic degradation of Reactive Black 5 with TiO<sub>2</sub>-coated magnetic nanoparticles. *Catal. Today* **2013**, *209*, 116–121. [CrossRef]
8. Rodríguez-Chueca, J.; Ferreira, L.C.; Fernandes, J.R.; Tavares, P.B.; Lucas, M.S.; Peres, J.A. Photocatalytic discolouration of Reactive Black 5 by UV-A LEDs and solar radiation. *J. Environ. Chem. Eng.* **2015**, *3*, 2948–2956. [CrossRef]
9. Iovino, P.; Chianese, S.; Fenti, A.; Blotevogel, J.; Musmarra, D. An innovative approach for atrazine electrochemical oxidation modelling: Process parameter effect, intermediate formation and kinetic constant assessment. *Chem. Eng. J.* **2023**, *474*, 146022. [CrossRef]
10. Salvestrini, S.; Fenti, A.; Chianese, S.; Iovino, P.; Musmarra, D. Electro-oxidation of humic acids using platinum electrodes: An experimental approach and kinetic modelling. *Water* **2019**, *12*, 2250. [CrossRef]
11. Bello, M.M.; Raman, A.A.A.; Asghar, A. A review on approaches for addressing the limitations of Fenton oxidation for recalcitrant wastewater treatment. *Process Saf. Environ. Prot.* **2019**, *126*, 119–140. [CrossRef]
12. Wang, J.; Chen, H. Catalytic ozonation for water and wastewater treatment: Recent advances and perspective. *Sci. Total Environ.* **2020**, *704*, 135249. [CrossRef] [PubMed]
13. Liu, Z.; Hosseinzadeh, S.; Wardenier, N.; Verheust, Y.; Chys, C.; Hulle, S.V. Combining ozone with UV and H<sub>2</sub>O<sub>2</sub> for the degradation of micropollutants from different origins: Lab-scale analysis and optimization. *Environ. Technol.* **2019**, *40*, 3773–3782. [CrossRef] [PubMed]
14. Al-Tohamy, R.; Ali, S.S.; Li, F.; Okasha, K.M.; Mahmoud, Y.A.G.; Elsamahy, T.; Jiao, H.; Fu, Y.; Sun, J. A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety. *Ecotoxicol. Environ. Saf.* **2022**, *231*, 113160. [CrossRef] [PubMed]
15. Asaithambi, P.; Saravanathamizhan, R.; Matheswaran, M. Comparison of treatment and energy efficiency of advanced oxidation processes for the distillery wastewater. *Int. J. Environ. Sci. Technol.* **2015**, *12*, 2213–2220. [CrossRef]
16. Wang, L.; Wang, Q.; Ren, F.; Wang, Y. An unexpected interaction between a H<sub>2</sub>O<sub>2</sub> molecule and anatase TiO<sub>2</sub> (101) surface. *Appl. Surf. Sci.* **2019**, *493*, 926–932. [CrossRef]
17. Santos, P.B.; Dos Santos, H.F.; Andrade, G.F.S. Photodegradation mechanism of the RB5 dye: A theoretical and spectroscopic study. *J. Photochem. Photobiol. A Chem.* **2021**, *416*, 113315. [CrossRef]
18. Luo, C.; Wang, H.; Dong, W.; Zhang, X. Theoretical investigation on the mechanism of the OH-initiated degradation process of reactive red 2 azo dye. *RSC Adv.* **2017**, *7*, 41799–41811. [CrossRef]

19. Luo, Q.; Yang, X.; Zhao, X.; Wang, D.; Yin, R.; Li, X.; An, J. Facile preparation of well dispersed ZnO/cyclized polyacrylonitrile nanocomposites with highly enhanced visible-light photocatalytic activity. *Appl. Catal. B Environ.* **2017**, *204*, 304–315. [[CrossRef](#)]
20. Dimitrakopoulou, D.; Rethemiotaki, I.; Frontistis, Z.; Xekoukoulotakis, N.P.; Venieri, D.; Mantzavinos, D. Degradation, mineralization and antibiotic inactivation of amoxicillin by UV-A/TiO<sub>2</sub> photocatalysis. *J. Environ. Manag.* **2012**, *98*, 168–174. [[CrossRef](#)]
21. Wu, C.H.; Kuo, C.Y.; Dong, C.D.; Chen, C.W.; Lin, Y.L. Removal of sulfonamides from wastewater in the UV/TiO<sub>2</sub> system: Effects of pH and salinity on photodegradation and mineralization. *Water Sci. Technol.* **2019**, *79*, 349–355. [[CrossRef](#)]
22. Díaz-Flores, P.E.; Guzmán-Álvarez, C.J.; Ovando-Medina, V.M.; Martínez-Gutiérrez, H.; González-Ortega, O. Synthesis of  $\alpha$ -cellulose/magnetite/polypyrrole composite for the removal of reactive black 5 dye from aqueous solutions. *Desalin. Water Treat.* **2019**, *155*, 350–363. [[CrossRef](#)]
23. Bolton, J.R.; Bircher, K.G.; Tumas, W.; Tolman, C.A. Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric-and solar-driven systems (IUPAC Technical Report). *Pure Appl. Chem.* **2001**, *73*, 627–637. [[CrossRef](#)]

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