

Heterogeneous photocatalysis with wireless UV-A LEDs [†]

L. C. Ferreira^{1,2}, José R. Fernandes¹, J. A. Peres¹, P. B. Tavares¹, M. S. Lucas^{1*}

¹ Centro de Química de Vila Real (CQVR), Departamento de Química, Universidade de Trás-os-Montes e Alto Douro, 5000-801 Vila Real, Portugal. jperes@utad.pt (J.A.P.); ptavares@utad.pt (P.B.T.)

² Associação Fraunhofer Portugal Research – AWAM, Regia Douro Park, Andrães, 5000-033 Vila Real, Portugal. leonor.ferreira@awam.fraunhofer.pt (L.C.F.)

* Correspondence: mlucas@utad.com (M.S.L.);

† Presented at the 4th International Electronic Conference on Applied Sciences, will be held online from 27 October to 10 November 2023.

Abstract: Water reuse policies demand high treated water quality, ensuring no harm to human health and ecosystems. To foresee a safe water reuse, Advanced Oxidation Processes seem to be one of the most appropriated technologies to achieve that goal. In this work, a wireless UV-A LEDs lab-scale reactor powered by a resonant inductive coupling system was built maximizing the UV photon absorption, being the energy inside the photoreactor supplied through a magnetic field generated by induction coils placed on the external wall. The best 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 minutes, 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 the generated wastewater is released without a proper treatment. Water scarcity is a reality and so, wastewaters are now seen as a valuable resource. In this line, 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 put this resource under more pressure, requiring 70% of all the water globally consumed, being also 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 biggest part of industries is not prepared to attain an efficient treatment, being in the best cases only able to treat the wastewater to comply with the legislation to discharge into wastewater treatment plants [1, 3].

Advanced Oxidation Processes (AOPs), generate hydroxyl radicals (HO^\bullet) with an oxidation potential = 2.8 eV, that can react with the several pollutants, oxidizing them to simpler intermediates and potentially to CO_2 and H_2O [4]. These advanced treatments have already proved their efficiency by different processes, such as TiO_2 heterogeneous photocatalysis [5, 6-8], electrochemical treatments [9, 10], photo-Fenton [3, 11] and ozonation [12, 13]. The combination of AOPs with UV radiation enhances the overall system efficiency, in which light emitting diodes (LEDs) are rising comparing to the traditional mercury vapor lamps. Nonetheless, by considering the commonly used wired systems, photons are scattered during the air path diminishing the treatment effectiveness.

In this work, an azo dye (*Reactive Black 5*) was selected as a model compound to assess the capability of a wireless UV-A LEDs lab-scale photoreactor activate TiO_2 and decolorize the commercial dye. When disposed without proper treatment in water streams, dyes are found to be stable to light and oxidizing agents, interfering with the transmission of light in water bodies and inhibiting the photosynthetic activity of aqua biota [14].

Citation: To be added by editorial staff during production.

Academic Editor: Firstname Last-name

Published: date



Copyright: © 2023 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

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 (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 (TiO₂, P25 Evonik), having on its constitution 86.5% of anatase and 13.5% of rutile and a BET specific surface area of 55 m²/g. Hydrogen peroxide (H₂O₂) was purchased from Panreac (30% w/v) and Merckoquant peroxide analytical test strips were bought from Merck. Sodium hydroxide (NaOH) and sulfuric acid (H₂SO₄) were supplied from Sigma.

2.2. Reactor and UV-A LEDs wireless system

15 wireless UV-A LEDs (InGaN Roithner RLS-UV365E) were placed inside a lab-scale bubble column reactor (330 mL) (Figure 1) and used in the decolorization of dye (RB5) by TiO₂ photocatalysis. Each LED has a radiant flux of 1 mW and a viewing angle of 30°. A wireless power transfer using a resonant inductive coupling system provided the electrical power to each LED, being 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 has incorporated a bottom air injection made by an aquarium air pump. This wireless LED system and reactor are described in more detail in [3].

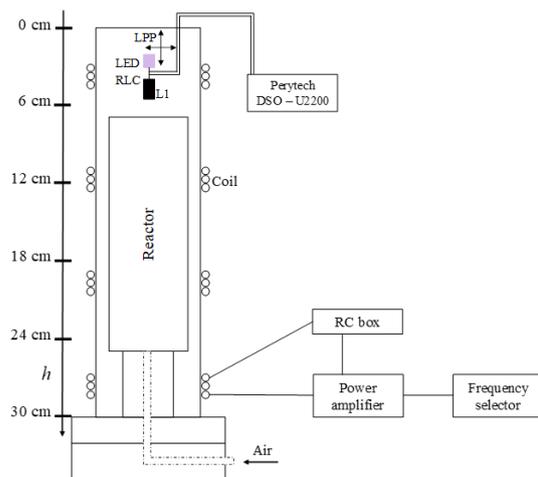


Figure 1. Wireless UV-A LEDs lab-scale reactor scheme.

2.3. Experimental procedure

RB5 solutions (10 mg L⁻¹) were prepared by dissolving the required amount of dye in distilled water and then added the catalyst (200, 400, 500, 600 mg L⁻¹). In order to enhance the dispersion of the TiO₂ P25, the suspension was placed in an ultrasonic bath (Bandelin Sonorex SUPER PK 106) for 3 minutes. To reach the adsorption equilibrium the dispersion was placed in continuous stirring in the dark during 30 minutes, before each experiment. The initial pH was measured (Jenway 3510 pH meter) and, when necessary, adjusted with NaOH or H₂SO₄ to the required pH value (between 3 and 8). The experiment started at the time that the UV-A LEDs were turned on. When using H₂O₂ (250, 100, 150, 100 mg L⁻¹), time zero was set at the time both H₂O₂ was added, and UV-A LEDs were turned on. During the experiments the solution was kept in constant aeration (Air pump Ecoair-9800) through the bottom and the temperature was monitored with an analytical thermometer (Ama Spezial ± 0.01 °C), being at 25 °C. Samples were taken at specific times with a syringe and centrifuged twice for 15 minutes at 6000 rpm to separate the TiO₂ P25 in suspension. The samples were analyzed using a LLG- uniSPEC 2 UV/Vis single spectrophotometer and the absorbance was measured at 595 nm, once it is the RB5 maximum absorption

wavelength. Additionally, the H_2O_2 concentration was roughly followed by Merckoquant peroxide analytical test strips. All the experiments were made in duplicate being the represented values the average of accepted results. The RB5 removal concentration was calculated by Beer–Lambert law using the optical density and the molar extinction coefficient. The obtained data was adjusted to pseudo-first order kinetics and 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 amplitude of the alternate 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 number of UV-A LEDs

In line with the above mentioned, it was important to verify which oscillation frequency presented the best kinetic results, if 26.8 or 27 kHz. Experimental data confirmed the assumption previously made (Data not shown). Data revealed that from all the working oscillation frequencies (25, 26, 26.5, 26.8, 27, 28, 29, 30, 31 kHz) 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 done with 26.8 kHz of oscillation frequency and the following operating conditions: $[\text{RB5}] = 10 \text{ mg L}^{-1}$; $[\text{TiO}_2] = 500 \text{ mg L}^{-1}$; $\text{pH} = 6.5$; $T = 25 \text{ }^\circ\text{C}$.

3.2. Effect of TiO_2 , H_2O_2 and RB5 concentrations

Initially, two control tests were carried out with only 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 $[\text{TiO}_2] = 500 \text{ mg L}^{-1}$ in the dark.

When assessing about TiO_2 dosage, the increase on the amount of TiO_2 promotes a faster decolorization (Figure 2a), except when TiO_2 is increased from 500 ($k = 6.19 \times 10^{-3}$) to 600 mg L^{-1} ($k = 3.35 \times 10^{-3}$). 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 TiO_2 , decreasing or even inhibiting the photocatalytic process. These results agree with the literature, using TiO_2 powder as catalyst [5].

Regarding the H_2O_2 concentration (Figure 2b), it is possible to detect a slightly increase in the decolorization of RB5 when adding 100 mg L^{-1} of H_2O_2 to the solution. Attributed to the dissociation of H_2O_2 and consequent formation of HO^\bullet , $\text{O}_2^{\bullet-}$ and HOO^\bullet [16]. In contrast, when adding higher concentrations, it is observed a negative effect. This may suggest an excess of H_2O_2 in solution which is acting as a radical scavenger of HO^\bullet , generating radicals with lower reactivity and therefore slowing the kinetic rate [15]. Additionally, it is known that TiO_2 can be dissociated or even adsorbed by H_2O_2 generating Tiperoxo complexes, which present lower photocatalytic activity than TiO_2 [16]. Nonetheless, to the best of our knowledge, it is necessary to further investigate the interaction mechanisms between H_2O_2 and TiO_2 , to better understand the decolorization reactions.

It was also evaluated the system behavior under different RB5 concentrations (10, 25, 40 and 50 mg L^{-1}). 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, indicating a reduction of oxidation zones.

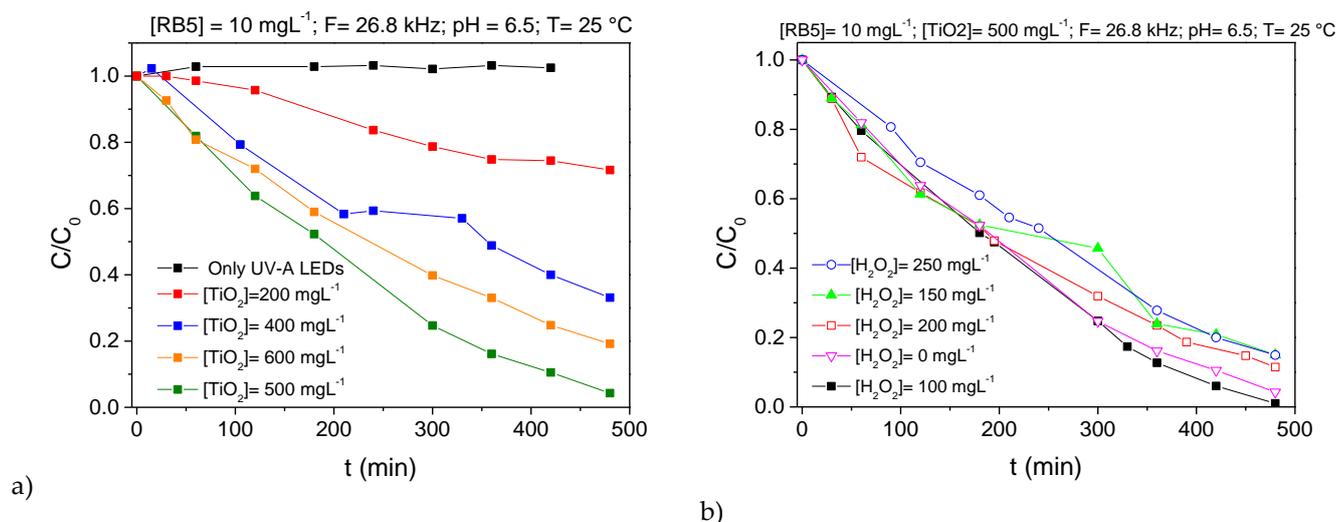


Figure 2. RB5 decolorization with different: **a)** TiO_2 concentration; **b)** H_2O_2 concentration. Fixed operating conditions: $[RB5] = 10 \text{ mg L}^{-1}$; $pH = 6.5$; $F = 26.8 \text{ kHz}$; $T = 25 \text{ }^\circ\text{C}$.

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]. But when considering both configurations, theoretical studies concluded that the $C-N$ bonds are the preferred site for HO^\bullet attack [18, 19]. In this line 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 tautomers 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 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 the nucleophilic attack. This attack leads to the formation of the intermediate specie 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 specie, being 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].

3.2. Influence of pH

The pH value (3, 3.5, 4, 4.5, 5, 5.5, 6.5, 8) of the solution to treat 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]. RB5 dissociation constants (pK_a) are at 3.8 and 6.9. TiO_2 point of zero charge is 6.7, what indicates that under 6.7 its surface is charged positively and above it is negatively charged. For RB5 the same behavior is 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 TiO_2 zeta potential is pH dependent, having lower values at higher pH. The higher the value, more stable the solution will be. pH 4, 4.5 and 5 present the fastest pseudo-first

order kinetic value (Table 1), however, the experimental work revealed some TiO₂/RB5 agglomeration as we started decreasing the pH from 5.5. For this reason, experiments were conducted at around natural pH 6.5. Additionally, costs related to reagents were also diminished. Nonetheless, future work includes exploring these pH values trying to attain a compromise between treatment time, efficiency, reagent and energy consumption.

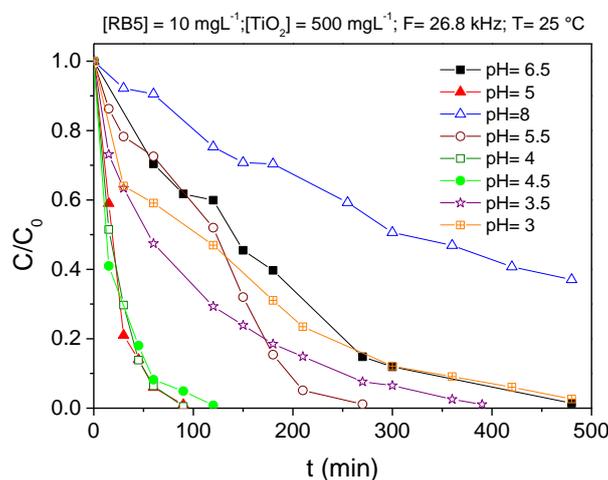


Figure 3. Effect of pH in RB5 decolorization. Operating conditions: [RB5] = 10 mg L⁻¹; [TiO₂] = 500 mg L⁻¹; F = 26.8 kHz; T = 25 °C.

3.2. Electric Energy per order (E_{EO}) and Specific Applied Energy (E_{SAE})

The amount of electric energy necessary to reduce 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 (m³) at the time t (h), k_{obs} (min⁻¹) and E_{SAE} by equation 2, where C_0 is the initial pollutant concentration (mol L⁻¹).

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

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

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 E_{EO} and C_0 values. In this line, it is possible to analyse both the electrical consumption values and the energy required to decolorize RB5 in Table 1, as follows: i) [TiO₂] dosage, increasing the amount of catalyst led to lower E_{EO} and E_{SAE} values, except when TiO₂ concentration to 600 mg L⁻¹; ii) [H₂O₂] concentration, the addition of 100 mg L⁻¹ originated a lower electrical consumption when compared to without H₂O₂ in the media. However, by adding a higher concentration of H₂O₂ there was not a linear decrease in the electrical values, instead it was noticed a negative effect in the treatment. Similarly, the E_{SAE} values revealed to require less energy to break the RB5 chromophor groups when adding 100 mg L⁻¹ of H₂O₂; iii) [RB5] concentration, since absorptivity decreases when increasing the pollutant concentration, it was harder to decolorize the pollutant and therefore electrical values rise by increasing RB5 concentration; iv) pH values, pH 4, 4.5 and 5 presented the lowest E_{EO} and E_{SAE} values.

Table 1. Calculated pseudo first order kinetic rates (k), Electric Energy per order (E_{EO}) and Specific Applied Energy (E_{SAE}), for the experiments in Figures 2 and 3.

Fixed Parameters	Variable	k (min^{-1})	E_{EO} ($\text{kWh m}^{-3} \text{ order}^{-1}$)	E_{SAE} ($\text{kWh mol}^{-1} \text{ order}^{-1}$)
[RB5] = 10 mg L ⁻¹ pH = 6.5 T = 25 °C	[TiO ₂]	0	9.17x10 ⁻⁶	1.52x10 ⁴
		200	7.78x10 ⁻⁴	1.79 x10 ²
		400	2.19x10 ⁻³	6.38 x10 ²
		500	6.19x10 ⁻³	2.26x10 ¹
[RB5] = 10 mg L ⁻¹ [TiO ₂] = 500 mg L ⁻¹ pH = 6.5 T = 25 °C	[H ₂ O ₂]	600	3.35x10 ⁻³	4.17 x10 ¹
		0	6.19x10 ⁻³	2.26 x10 ¹
		100	7.92x10 ⁻³	1.76 x10 ¹
		150	3.77x10 ⁻³	3.7 x10 ¹
[TiO ₂] = 500 mg L ⁻¹ pH = 6.5 T = 25 °C	[RB5]	200	4.15x10 ⁻³	3.36 x10 ¹
		250	4.07x10 ⁻³	3.43 x10 ¹
		10	6.19x10 ⁻³	2.26x10 ¹
		25	7.70x10 ⁻⁴	1.81x10 ²
[RB5] = 10 mg L ⁻¹ [TiO ₂] = 500 mg L ⁻¹ T = 25 °C	pH	40	3.65x10 ⁻⁴	3.83x10 ²
		50	2.74x10 ⁻⁴	5.10x10 ²
		3	6.91x10 ⁻³	2.02 x10 ¹
		3.5	1.02x10 ⁻²	1.38 x10 ¹
		4	5.74x10 ⁻²	2.43
		4.5	3.70x10 ⁻²	3.77
		5	5.10x10 ⁻²	2.74
5.5	1.51x10 ⁻²	9.25		
6.5	6.19x10 ⁻³	2.26x10 ¹		
8	2.10x10 ⁻³	6.65 x10 ¹		

Overall, the lowest values were at acidic pH between 4 and 5. Nonetheless, at the considered optimal conditions ([RB5] = 10 mg L⁻¹, [TiO₂] = 500 mg L⁻¹, [H₂O₂] = 100 mg L⁻¹, pH = 6.5, F = 26.8 kHz; T = 25 °C) the E_{EO} is 17.6 kWh m⁻³ order⁻¹ and E_{SAE} is 1.75x10³ kWh mol⁻¹ order⁻¹. Despite other papers presenting RB5 decolorization with E_{EO} values calculation, it is not used wireless radiation. Nonetheless, 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⁻³ order⁻¹, respectively [7, 8].

4. Conclusions

This work reported the decolorization of a dye, *Reactive Black 5*, by means of TiO₂ photocatalysis assisted by a wireless UV-A LEDs system.

The best operating parameters were found to be [TiO₂] = 500 mg L⁻¹ and [H₂O₂] = 100 mg L⁻¹, with an Electric Energy per Order (E_{EO}) of 17.6 kWh m⁻³ order⁻¹. The wireless UV-A LEDs system proved to be efficient in the removal of RB5 with TiO₂ photocatalysis, despite requiring long treatment times. The results showed that the wireless UV-A LEDs system is efficient in the activation of the catalyst TiO₂ under different conditions, favoring the generation of hydroxyl radicals and promoting the 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., M.S.L.; methodology, L.C.F., M.S.L.; validation, L.C.F., J.A.P., J.R.F., P.B.T., 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., M.S.L.; data curation, L.C.F., P.B.T., M.S.L.; writing—original draft preparation, L.C.F.; writing—review and editing L.C.F., P.B.T., M.S.L.; visualization, L.C.F., M.S.L.; supervision, P.B.T., 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: The financial support was provided by OBTain project (NORTE-01-0145-FEDER-000084) and 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: The data presented in this study is available on request from the corresponding author

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

References

1. Simhayov, R.; Ohana-Levi, N.; Shenker, M.; Netzer, Y. Agric. Effect of long-term treated wastewater irrigation on soil sodium levels and table grapevines' health. *Water Manag.* 2023, 275, 108002. <https://doi.org/10.1016/j.agwat.2022.108002>
2. Morgera, E.; Webster, E.; Hamley, G.; Sindico, F.; Robbie, J.; Switzer, S.; Berger, T.; Sánchez, P.P.S.; Lennan, M.; Martin-Nagle, R.; Tsioumani, E.; Moynihan, R.; Zydek, A. The right to water for food and agriculture. *Food and Agriculture Organization of the United Nations*. Rome. 2020, ISBN 978-92-5-132301-4. <https://www.fao.org/3/ca8248en/CA8248EN.pdf>
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. <https://doi.org/10.1016/j.envres.2021.111430>
4. Ji, Q.; He, H.; Gao, Z.; Wang, X.; Yang, S.; Sun, C.; Li, S.; Zhang, L. UV/H₂O₂ oxidation of tri(2-chloroethyl) phosphate: Intermediate products, degradation pathway and toxicity evaluation. *J. Environ. Sci.* 2020, 98, 55-61. <https://doi.org/10.1016/j.jes.2020.05.015>
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. Manage.* 2020, 269, 110740.
6. Turkten, N.; Cinar, Z. Photocatalytic decolorization of azo dyes on TiO₂: prediction of mechanism via conceptual DFT. *Catal. Today* 2017, 87, 169-175. <https://doi.org/10.1016/j.cattod.2017.01.019>
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 TiO₂-coated magnetic nanoparticles. *Catal. Today*. 2013, 209, 116-121. <https://doi.org/10.1016/j.cattod.2012.10.024>
8. Rodríguez-Chueca, J.; Ferreira, L.C.; Fernandes, J.R.; Tavares, P.B.; Lucas, M.S.; Peres, J. A. Photocatalytic discoloration of Reactive Black 5 by UV-A LEDs and solar radiation. *J. Environ. Chem. Eng.* 2015, 3, 2948-2956. <https://doi.org/10.1016/j.jece.2015.10.019>
9. Iovino, P.; Chianese, S.; Fenti, A.; Blotvogel, 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. <https://doi.org/10.1016/j.cej.2023.146022>
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. <https://doi.org/10.3390/w12082250>
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). <https://doi.org/10.1016/j.psep.2019.03.028>
12. Wang, J.; Chen, H. Catalytic ozonation for water and wastewater treatment: Recent advances and perspective. *Sci. Total Environ.* 2020, 704, 135249. <https://doi.org/10.1016/j.scitotenv.2019.135249>
13. Liu, Z.; Hosseinzadeh, S.; Wardenier, N.; Verheust, Y.; Chys, C.; Hulle, S. V. Combining ozone with UV and H₂O₂ for the degradation of micropollutants from different origins: lab-scale analysis and optimization. *Environ. Technol.* 2019, 40, 3773-3782. <https://doi.org/10.1080/09593330.2018.1491630>
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. <https://doi.org/10.1016/j.ecoenv.2021.113160>
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 (7), 2213-2220. <https://doi.org/10.1007/s13762-014-0589-9>
16. Wang, L.; Wang, Q.; Ren, F.; Wang, Y. An unexpected interaction between a H₂O₂ molecule and anatase TiO₂ (101) surface. *App. Surf. Sci.* 2019, 493, 926-932. <https://doi.org/10.1016/j.apsusc.2019.07.032>
17. Santos, P. B.; Santos, H. F. Dos; Andrade, G. F.S. Photodegradation mechanism of the RB5 dye: A theoretical and spectroscopic study. *J Photochem. Photobiol, A: Chem.* 2021, 416, 113315. <https://doi.org/10.1016/j.jphotochem.2021.113315>
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. <https://doi.org/10.1039/C7RA05727J>
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. *Applied Catal. B, Environ.* 2017, 204, 304-315. <https://doi.org/10.1016/j.apcatb.2016.11.037>

20. Dimitrakopoulou, D.; Rethemiotaki, I.; Frontistis, Z.; Xekoukoulotakis, N.P.; Venieri, D.; Mantzavinos, D. Degradation, mineralization and antibiotic inactivation of amoxicillin by UV-A/TiO₂ photocatalysis. *J. Environ. Manag.* 2012, 98, 168–174. <https://doi.org/10.1016/j.jenvman.2012.01.010>
21. Wu, C.H.; Kuo, C.Y.; Dong, C.D.; Chen, C.W.; Lin, Y.L. Removal of sulfonamides from wastewater in the UV/TiO₂ system: effects of pH and salinity on photodegradation and mineralization. *Water Sci. Technol.* 2019, 79, 349–355. <https://doi.org/10.2166/wst.2019.053>
22. Díaz-Flores, P. E.; Guzmán-Álvarez, C. J.; Ovando-Medina, V. M.; Martínez-Gutiérrez, H.; González-Ortega, O. Synthesis of α -cellulose/magnetite/polypyrrole composite for the removal of reactive black 5 dye from aqueous solutions. *Desalin. Water Treat.* 2019, 155, 350–363. <https://10.5004/dwt.2019.24013>
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. <https://doi.org/10.1351/pac200173040627>

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.