

Photocatalytic discolouration of Reactive Black 5 by UV-A LEDs and solar radiation



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ABSTRACT

One of the most important disadvantages of photocatalytic treatments is the high cost associated with the use of UV lamps. In this work, the efficiency of two UV-A LEDs (ultraviolet-a light emitting diodes) photosystems as a low cost alternative to conventional UV lamps was tested. The efficiency of the two UV-A LEDs photosystems was compared to that of the most economical UV source—solar radiation. To this end, the oxidative discolouration of Reactive Black 5 (RB5) aqueous solutions was studied using photocatalysis with different concentrations of TiO₂ (0.5–1 g/L) and H₂O₂ (1.76, 4.41, 8.82 and 17.64 mM), exposed to different radiation sources: UV-A LEDs and solar radiation. The use of H₂O₂ increased the discolouration rate of RB5; however, an excessive dosage reduced the yield of the treatment, and the best results were attained with a concentration of 8.82 mM of H₂O₂. Strong differences were observed between the use of UV-A LEDs (23 W/m²) and solar radiation. In both cases total discolouration was observed, but the discolouration rate was considerably higher with solar radiation. However, the use of a more powerful UV-A LED photo-system (85 W/m²) allowed the achievement of higher discolouration rates ($k=0.284 \text{ min}^{-1}$) than those obtained with solar radiation ($k=0.189 \text{ min}^{-1}$) using only 0.5 g/L of TiO₂. Therefore, UV-A LED radiation is a serious alternative to conventional UV lamps, since they are ecofriendly, have a low operational cost and high energy efficiency.

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1. Introduction

The release of wastewaters into natural environments is very problematic to aquatic life [1] and mutagenic to humans [2]. Although many industries including the paper, cosmetics, and pharmaceutical industries are a source of polluted effluents [3,4], the textile industry is one of the largest consumers of water and generates a high amount of effluents containing a variety of pollutants, of which the dyes and pigments are the most significant. It is estimated that about 15% of the total world production of dyes is released and lost in textile effluents during the dyeing process [5].

Currently, there are more than ten thousand different dyes and pigments available on the market, and several different groups can be distinguished—for example, reactive, direct, vat, sulphur and azo dyes. Approximately 70% of dyes used in textiles industries

contain azo dyes with one or more azo bonds. These dyes are characterized by a strong fragrance and vivid colours, as well as high solubility, stability and, most importantly, a simple dyeing procedure [6]. Azo bonds can break under reducing conditions, resulting in different kinds of amines. Some of these aromatic amines are considered carcinogenic, and for this reason, they are limited by European legislation [7].

In recent years, several research groups have focused on the application of advanced oxidation processes (AOPs) in the treatment of textile wastewater as a serious alternative to conventional technologies [8,9]. AOPs are based on the generation of highly reactive oxygen species (ROS), such as hydroxyl radicals, which are able to destroy organic pollutants and pathogenic germs. Photocatalysis has been studied by several authors in the removal of: dyes [8,10–13]; persistent pollutants as pesticides [14,15]; antibiotics and medicines [16,17]; and microorganisms present in water and wastewater [18,19]. Titanium dioxide (TiO₂) is the most studied semiconductor in photocatalysis, due to its high photo-activity, low cost, chemical and biological stability and innocuousness [20].

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TiO₂ is only activated by UV radiation, which represents only a small fraction of the solar spectrum. For this reason it is necessary to employ UV lamps, which have high operational costs. Recently, several research groups, in an effort to reduce treatment operational costs, have focused on renewable energy sources, such as natural solar radiation in compound parabolic collectors (CPC) [20], or on more efficient UV lamps, such as UV LEDs [21–23]; and in recent years, the application of UV LEDs lamps has been mainly reported with reference to the discoloration of dyes [24,25], and the degradation of organic compounds [26,27].

The intensity (total number of photons) and the band gap of the photocatalyst have direct influence on the absorbed energy of each photon. Thus, the higher energy of the photons, the higher generation of hydroxyl radicals. An increase in the radiation intensity, will lead to an increase in the degradation rate. However, conventional UV lamps, which are mainly mercury lamps, present several problems. These include overheating because of unstable power consumption, short lifetime, low photonic efficiency, and environmentally unfriendly properties [28]. LEDs are a serious alternative to mercury lamps since they have longer lifetimes, lower energy consumption, and higher efficiency. In addition, they do not overheat and are less harmful to the environment [28,29]. Semiconductor LEDs technology is a directional light source with maximum intensity at an angle almost perpendicular to the surface emission. As all emitted photons have approximately the same frequency, the emitted light is monochromatic, and the wavelength depends on the semiconductor material used.

The main objective of this work was to study the efficiency of two different UV-A LED scale-lab photo-systems (365–370 nm) in the discoloration of an azo dye (Reactive Black 5) in combination with TiO₂ and H₂O₂, working in a continuous stirred tank reactor (CSTR) and batch mode. Additionally, TiO₂ and TiO₂/H₂O₂ treatments assisted with solar radiation were carried out in order to compare UV-A LED radiation efficiencies.

2. Materials and methods

2.1. Reagents

The azo dye, Reactive Black 5 (C₂₆H₂₁N₅Na₄O₁₉S₆; colour index 20505; M_w = 991.8 g/mol) was provided by DyStar (Portugal) and used as received, without further purification. UV–vis spectra of RB5 consist of two main characteristic absorption bands. One is in the UV region (310 nm) and another in the visible region (595 nm). The UV band is characterised by two adjacent rings, whereas the visible band is characterised by long conjugated π system linked by two azo groups.

TiO₂ Degussa P-25, was used as photocatalyst. This photocatalyst contains more than 70% anatase with a minor amount of rutile and a small amount of amorphous phase [30], with a surface area of 55 ± 5 m²/g and a mean crystallite size of 30 nm. TiO₂ Degussa P-25 was used in concentrations of 0.5 and 1.0 g/L [31]. Hydrogen peroxide (H₂O₂, Panreac, 30% w/v) was used alone or in combination with TiO₂ in different concentrations (1.76, 4.41, 8.82 and 17.64 mM). Na₂SO₃ (Merck) was used as a reagent grade to quench the hydroxyl radical oxidation.

2.2. Photoreactor and UV-A LED systems

All experiments were carried out in continuous and batch mode in a lab-scale prototype reactor and illuminated with two different UV-A LED photo-systems. The reactor had a volume capacity of 110 mL, and the surface was formed of mirrors. Several factors were considered in the construction of the reactor. These included the

ideal depth of the solution required to obtain an optimal removal of RB5, the optimal distance between the UV-A LEDs system and the liquid in order to avoid shadow zones, and the obtention of a totally stirred reactor.

The first UV-A LED photo-system was composed of a matrix of 96 Indium Gallium Nitride (InGaN) LEDs lamps (Roithner RLS-UV370E), with an illuminated area of 11 × 7 cm². These LEDs had a peak light emission at 375 nm, and the nominal consumption of each LED was 80 mW operating at 20 mA. The total optical power emitted was approximately 100 mW, depending on the root mean square (RMS) current intensity supplied. The system irradiance was measured using a UV enhanced Si-photodetector (ThorLabs PDA155) in a configuration that replicated that used in the photoreactor. In this system, the output optical power was controlled using a pulse width modulation (PWM) circuit and the RMS current intensity was measured with a multimeter (UniVolt DT-64). The experiments were carried out with a RMS current intensity of 240 mA in the first UV-A LED photo-system, corresponding to an UV irradiance of 23 W/m² and a photon flux of 5.53 × 10⁻⁷ Einstein/s.

In addition, a second, more powerful UV-A LED photo-system was developed with 12 InGaN LEDs lamps (Roithner APG2C1-365E LEDs) with a maximum emission wavelength at 365 nm. The nominal consumption of each LED lamp was 1.4 W when the applied current was 350 mA. The output optical power was controlled by maintaining the forward current constant using a power MOSFET in six different current settings. In this second photo-system six different current intensities were used. These current intensities ranged from 58 to 326 mA, corresponding to six different UV irradiance values, varying from 16 to 85 W/m², and the corresponding photon flux ranging from 3.73 × 10⁻⁷ to 2.0 × 10⁻⁶ Einstein/s.

2.3. Experimental procedure

Samples were prepared by dissolving 25 mg/L of RB5 dye in deionised water from a Millipore purification system. Then, the desired amount of TiO₂ (0.5 or 1.0 g/L) was added. Further, in order to increase the catalyst dispersion in the dye solution, an ultrasonic bath (Bandelin Sonorex SUPER PK 106) was used. In the experiments carried out in continuous mode, the RB5 solution was pumped to the photoreactor through a peristaltic pump (Gilson Minipuls 3) with a flow rate of 1 mL/min.

In the TiO₂/H₂O₂ and H₂O₂/UV experiments different concentrations of H₂O₂ were tested (1.76, 4.41, 8.82 and 17.64 mM). The H₂O₂ was directly added to the photoreactor at the beginning of each experiment. Samples of the dye solution were withdrawn at periodic intervals during the course of the reaction, and analysed using a Jasco V-530 UV/VIS (Tokyo, Japan) double-beam spectrophotometer. The colour of the dye solution in the reaction mixture at different times, was obtained by measuring the absorbance at maximum wavelength (λ_{max} = 595 nm) and by computing the concentration from the calibration curve. The H₂O₂ concentration was monitored via Merckoquant peroxide analytical test strips (Test Peroxides, Merck Merckoquant). The temperature and pH of the samples was monitored using a 209 pH Meter from Hanna Instruments. The temperature remained constant around 21 °C, while pH decreased from 5 to 4.5 during the treatment.

Solar photocatalytic experiments were carried out on the roof of the Geociências building at Universidade de Trás-os-Montes e Alto Douro (41°17'10.7"N; 7°44'21.1"W) in Vila Real (Portugal) during the month of July 2014. The average annual value of global solar irradiance in Vila Real (Portugal) is between 4000 and 4500 Wh/m² per day. Fig. S1 (Supplementary material) shows the two UV-A LED photosystem and a diagram of the setup of the solar photocatalytic experiment in continuous mode.

All the experiments were carried out in duplicate and values presented are the average of both results. The observed standard deviation was always less than 5% of the reported value.

In addition, some adsorption tests were carried out in a previous phase of the research. Nevertheless, the adsorbed amount of RB5 in the photocatalyst was considered negligible.

2.4. Statistical analysis

A statistical analysis of the experimental results was performed with Minitab 17 Statistical Software in order to evaluate the influence of the different variables involved in the treatments performed on a response factor (percentage of RB5 discoloration). To do this, a two-level factorial design (2^k) was selected, and the variables considered were TiO₂ concentration (0.5 and 1 g/L), H₂O₂ concentration (1.76 and 17.64 mM), type of radiation (UV-A LED and solar radiation) and reaction mode (continuous and batch mode).

2.5. Electrical energy determination

One of the most important disadvantages of photocatalytic treatments is the high operational cost mainly associated with the electrical energy required by UV radiation. Bolton et al. defined the figures-of-merit electric energy per order (E_{EO}) to use in the first-order kinetic regime of AOPs when the low pollutant concentrations (which apply here) are solved in solution [32].

The above parameter refers to the electric energy in kilowatt hours (kWh) required to reduce the concentration of a pollutant C by one order of magnitude in a unit volume (1000L) of contaminated water. E_{EO} can be calculated as follows (Eqs. (1) and (2)):

$$E_{EO} = \frac{P \times t \times 1000}{V \times \log\left(\frac{C_i}{C_f}\right)} \text{Batchmode} \quad (1)$$

$$E_{EO} = \frac{P}{F \times \log\left(\frac{C_i}{C_f}\right)} \text{Continuousflowmode} \quad (2)$$

where P is the rated power (kW) of the system, V is the volume (L) of water treated in the time t (h), F is the water volume flow rate (m³/h), C_i and C_f are the initial and final concentrations (mol/L) and the factor of 1000 converts g to kg. Higher E_{EO} values correspond to lower removal efficiencies.

3. Results and discussion

3.1. Batch experiments

Fig. 1 shows the RB5 discoloration after the photocatalytic treatment with 0.5 and 1 g/L of TiO₂ with UV-A LEDs and solar radiation. As can be seen, the treatments carried out in the presence of solar radiation produced better results than those performed with the UV-A LED radiation. After 10 min of photocatalytic oxidation with solar radiation, 90–95% of RB5 was discoloured, while, a higher time was required when UV-A LED radiation was used—specifically 60 min with 1 g/L of TiO₂, and 120 min with 0.5 g/L. This large difference is due to the different irradiance exposure of the effluent with the solar radiation and UV-A LEDs.

In addition, the influence of TiO₂ dosage in the final yield of the treatment can also be observed. When photocatalysis was carried out in the presence of UV-A LED radiation, a higher dosage of TiO₂ was required to obtain a faster discoloration of RB5. However, the

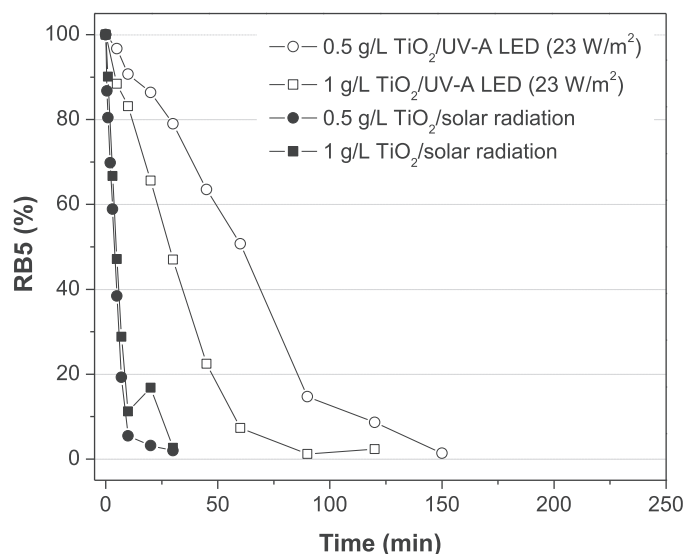


Fig. 1. RB5 discoloration through photocatalysis (0.5 and 1.0 g/L of TiO₂) in batch mode with UV-A LED radiation (open symbols) and solar radiation (closed symbols).

same relationship was not observed in the treatments performed with solar radiation. In this case, a higher dosage of catalyst slightly slowed the discoloration rate of the dye.

Table 1A shows that in almost all of the experiments, the discoloration of dye during the first 30 min of oxidation could be described as a first order reaction kinetics regarding to dye concentration. Table 1 also shows the values of electric energy per order (E_{EO}) for those treatments performed with UV-A LED radiation.

Initial discoloration rate constants were determined from the slope of $\ln(C_0/C)$ vs t (min) plots, where C_0 and C are the dye concentration at zero and t time, respectively. The constant rate (k) of UV-A LED photocatalysis increases two fold when the amount of TiO₂ is doubled (0.010 and 0.0188 min⁻¹ with 0.5 and 1 g/L TiO₂, respectively). As mentioned above, the solar photocatalysis experiments were considerably faster than those carried out with UV-A LED radiation. However, when sunlight was used as a radiation source, a higher dosage of TiO₂ caused a drop in the rate constant (0.3086 and 0.2340 min⁻¹ with 0.5 and 1 g/L TiO₂ respectively). The time necessary to reduce the initial concentration of RB5 to 50%, and the half-life time ($t_{1/2}$) are presented as further details of the discoloration process.

In order to increase the yield and rate of dye discoloration, different dosages of hydrogen peroxide (1.76, 4.41, 8.82 and 17.64 mM) were added to the photocatalytic treatments with UV-A LED (Fig. 2A) and solar radiation (Fig. 2B). As can be seen in both figures, the addition of hydrogen peroxide allowed an increase in the discoloration rate of RB5 dye.

As seen in Table 1A, when 0.5 g/L of TiO₂ was added, the fastest molar ratio TiO₂:H₂O₂ was 3.55 (0.5 g/L of TiO₂:1.764 mM H₂O₂), with a rate constant of 0.0447 min⁻¹—4.5 times faster than the photocatalysis treatment with 0.5 g/L of TiO₂ in the absence of H₂O₂. The rate constant of the RB5 discoloration decreased with increased of H₂O₂ concentration. The optimal ratio varied when 1 g/L of TiO₂ was added. In this case, the same concentration of hydrogen peroxide was required to achieve the fastest yield: molar ratio TiO₂:H₂O₂ (1 g/L of TiO₂:1.764 mM H₂O₂) 7.09, with a rate constant of 0.0728 min⁻¹. Lower ratios (TiO₂:H₂O₂) were required in those treatments carried out in the presence of solar radiation due to the strong influence of radiation in the treatment. Finally, different blank experiments were carried out in order to verify the influence of the variables independently (data not shown). In the

Table 1

First order kinetic rates (k), half-life ($t_{1/2}$) and electric energy per order (E_{EO}) values of photocatalytic experiments assisted by: (a) the first UV-A LED photo-system and solar radiation in batch continuous flow mode; (b) the second UV-A LED photo-system in batch mode.

(A)								
[TiO ₂] g/L	[H ₂ O ₂] mM	UV-A LED (23 W/m ²)				Solar radiation		
		k (min ⁻¹)	R^2	$t_{1/2}$ (min)	E_{EO} (kWh/m/order)	k (min ⁻¹)	R^2	$t_{1/2}$ (min)
Batch mode								
0.5	–	0.01	0.97	69.31	376	0.3086	0.94	2.25
1	–	0.0188	0.96	36.87	199	0.234	0.96	2.96
0.5	1.76	0.0447	0.99	15.51	85	0.429	0.92	1.62
0.5	4.41	0.0173	0.86	40.07	217	0.709	0.89	0.98
0.5	8.82	0.0221	0.99	31.36	162	0.8047	0.98	0.86
0.5	17.64	0.0097	0.99	71.46	3647	0.5435	0.97	1.28
1	1.76	0.0728	0.99	9.52	52	0.7554	0.99	0.92
1	4.41	0.0424	0.96	16.35	81	0.7601	0.94	0.91
1	8.82	0.0696	0.99	9.96	53	0.5732	0.98	1.21
1	17.64	0.0175	0.94	39.61	193	0.7679	0.98	0.90
Continuous mode								
0.5	–	0.0071	0.71	78.77	505	0.3748	0.98	2.57
1	–	0.0163	0.99	47.80	126	0.1687	0.99	5.20
0.5	1.76	0.0353	0.93	24.15	145	0.647	0.98	1.21
0.5	4.41	0.0319	0.98	22.80	104	0.7571	0.99	0.88
0.5	8.82	0.0334	0.98	16.50	90	0.7074	0.97	0.94
0.5	17.64	0.0217	0.94	25.02	92	0.7987	0.98	0.96
1	1.76	0.0638	0.99	13.89	144	0.3998	0.97	2.22
1	4.41	0.0674	0.97	16.39	131	0.7957	0.98	1.15
1	8.82	0.0565	0.99	10.39	129	0.644	0.99	1.09
1	17.64	0.0135	0.83	57.28	122	0.5808	0.97	0.79
(B)								
Irradiance (W/m ²)	0.5 g/L TiO ₂ /UV-A LED							
	k (min ⁻¹)	R^2	$t_{1/2}$ (min)	E_{EO} (kWh/m ³ /order)				
Batch mode								
16	0.0764	0.96	9.07	82				
25	0.1233	0.98	5.62	63				
42	0.1452	0.99	4.77	61				
58	0.1411	0.95	4.91	63				
70	0.1713	0.94	4.05	59				
85	0.1919	0.98	3.61	60				
Continuous mode								
70	0.2317	0.99	2.99	359				

H₂O₂/UV-A LED treatments, radiation did not have any influence over the RB5 dye. Similar conclusions were reached when the effluent was exposed to UV-A LED radiation in absence of other chemicals such as TiO₂ or H₂O₂.

On the other hand, and as shown in Table 1A, with increasing TiO₂ concentration the value of E_{EO} decreases, and so the efficiency of the TiO₂/UV-A LEDs treatment improves. In contrast, because the E_{EO} value increases with increasing H₂O₂ concentration in those treatments combining TiO₂ and H₂O₂, efficiency improves considerably with lowering concentrations of hydrogen peroxide. These results confirm those observed in the kinetic rates of RB5 discolouration.

3.2. Continuous experiments

Fig. 3 shows the RB5 discolouration after the photocatalytic treatments with 0.5 and 1 g/L of TiO₂ with UV-A LEDs and solar radiation, using a flow rate of 1 mL/min. Again, the treatments carried out in the presence of solar radiation produced better results than those performed with UV-A LED radiation. As can be observed in Fig. 3, all the treatments achieved total discolouration of the aqueous solution, except the treatment with 0.5 g/L of TiO₂ irradiated with UV-A LED. This reached a steady state after 270 min at 63% of discolouration.

Kinetic modelling was approached via a first order model, taking into account the fact that the retention time of effluent in

the reactor is almost the same as the reaction time in the batch reactor. In this way, batch and continuous mode experiments could be compared.

Regarding the rate constant observed in Table 1A, the faster treatment carried out with 0.5 g/L of TiO₂ and solar radiation (0.3748 min⁻¹) was 53 times faster than the same treatment assisted with UV-A LED radiation. The increase of TiO₂ concentration to 1 g/L should have increased the RB5 discolouration rate, but this increase was only observed in the presence of UV-A LED radiation. In addition, the experiment using 1 g/L TiO₂ with solar radiation achieved a rate constant of 0.1687 min⁻¹—two times lower than the same treatment with half of the TiO₂ concentration. This effect could be a consequence of the presence of shadow zones due to a high concentration of TiO₂.

The rate constant values obtained in continuous mode were expected to be slower than those of the treatments carried out in batch mode, due to the introduction of new effluent with a flow rate of 1 mL/min. However, comparing rates constants shown in Table 1A and B, this difference was not observed in those treatments carried out with 0.5 g/L of TiO₂, which were slightly faster in continuous mode.

Fig. 4A shows the degradation results of RB5 after the TiO₂/H₂O₂ assisted with UV-A LED radiation treatments with 0.5 and 1 g/L of TiO₂ in continuous mode. As shown in this figure, the discolouration rate of RB5 increases with higher H₂O₂ dosage and 0.5 g/L of TiO₂. However, some authors have reported that an excessive

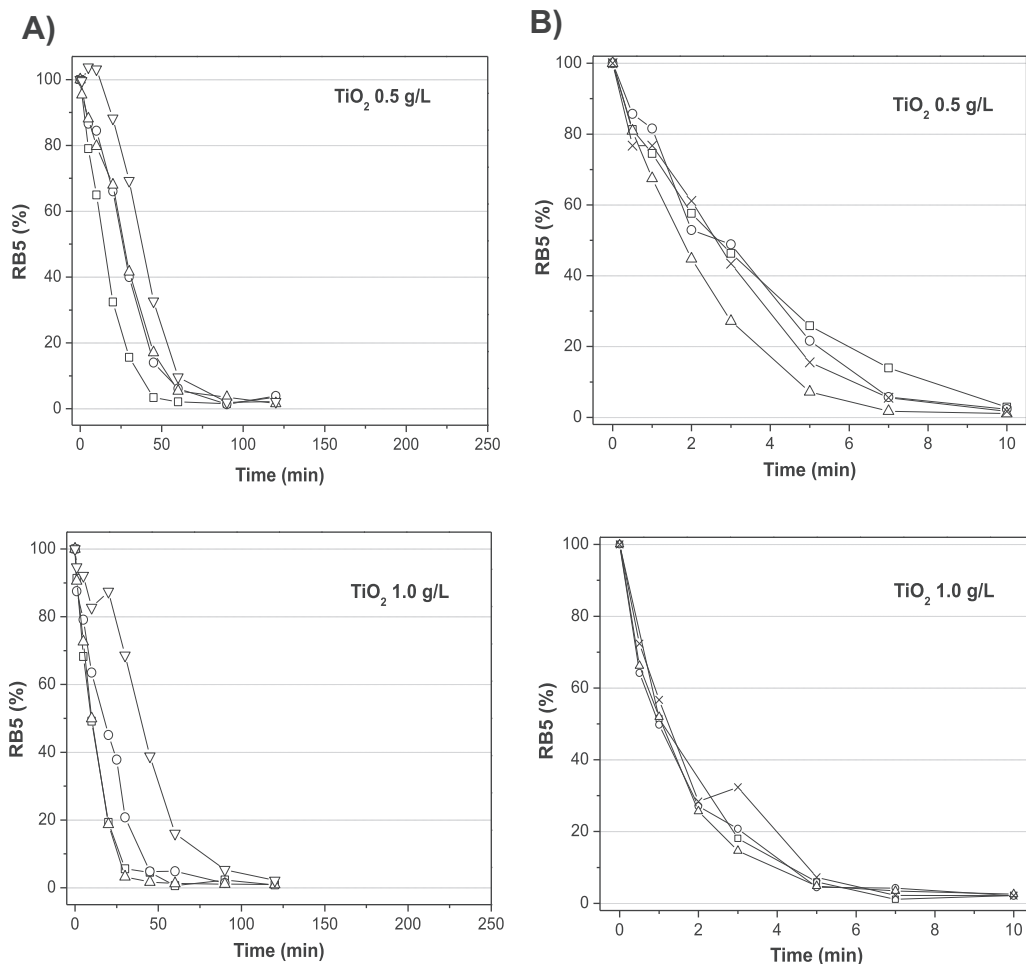


Fig. 2. RB5 discoloration by UV/TiO₂/H₂O₂ in batch mode with: (a) UV-A LED radiation with 0.5 and 1 g/L TiO₂; (b) solar radiation with 0.5 and 1 g/L TiO₂. H₂O₂ concentration: (□) 1.76 mM; (○) 4.41 mM; (△) 8.82 mM; (▽) 17.64 mM.

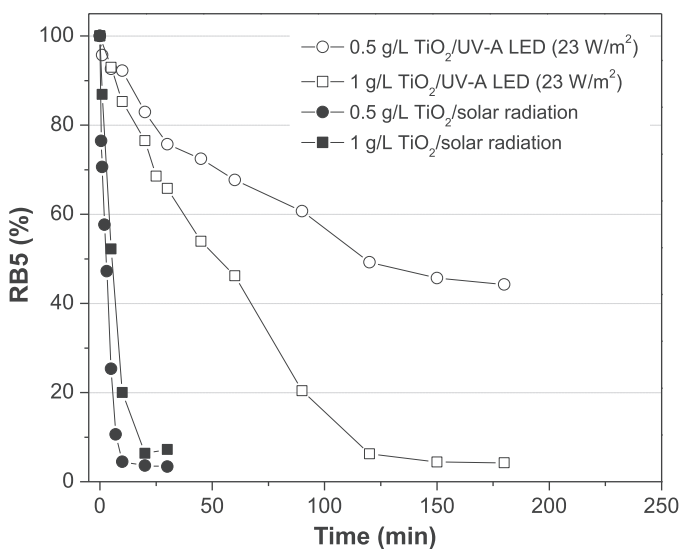


Fig. 3. RB5 discoloration by photocatalysis (0.5 and 1 g/L of TiO₂) in continuous mode with UV-A LED radiation (open symbols) and solar radiation (closed symbols).

dosage of H₂O₂ can generate a contrary effect due to the occurrence of scavenger reactions [33] and the highest used dosage of hydrogen peroxide did not produce the optimum discoloration of RB5. The highest constant rate of discoloration for treatments

with 0.5 g/L of TiO₂ was 0.0334 min⁻¹. This was achieved with 0.5 g/L TiO₂/8.82 mM H₂O₂. However, the highest dosage of hydrogen peroxide (17.64 mM H₂O₂) decreased the rate constant of discoloration to 0.0217 min⁻¹. Values of constant rates can be observed in Table 1A.

With 1 g/L of TiO₂ and different dosages of H₂O₂, the highest concentration of H₂O₂ (17.64 mM) decreased the rate of dye discoloration. This treatment rate, (1 g/L TiO₂/17.64 mM H₂O₂; 0.0135 min⁻¹), is lower than that obtained with a combination of a lower concentration of TiO₂ (0.5 g/L TiO₂/17.64 mM H₂O₂; 0.0217 min⁻¹), and it is even lower than the photocatalytic treatment without hydrogen peroxide (1 g/L TiO₂; 0.0163 min⁻¹).

Fig. 4B shows the degradation results of RB5 after the TiO₂/H₂O₂ assisted with solar radiation treatments with 0.5 and 1 g/L of TiO₂ in continuous mode. This figure shows clearly that the combination of 0.5 g/L of TiO₂ with 8.82 mM of H₂O₂ was (again) the fastest of the studied treatments. 87% of RB5 was discoloured after 2 min of treatment using 8.82 mM of H₂O₂, while only 54% of dye was discoloured when 17.64 mM of H₂O₂ was combined with 0.5 g/L of TiO₂. In all cases, total discoloration of dye was achieved after 10 min of treatment. These results can be cross-checked with rate constants presented in Table 1A. However, small differences between the four treatments studied were observed. Taking into account the rate constants, the fastest treatment was the combination of 17.64 mM H₂O₂ with 0.5 g/L TiO₂ (0.7987 min⁻¹). In the case of 1 g/L of TiO₂, the highest rate of discoloration of aqueous solution of dye was achieved with a dosage of 4.41 mM of

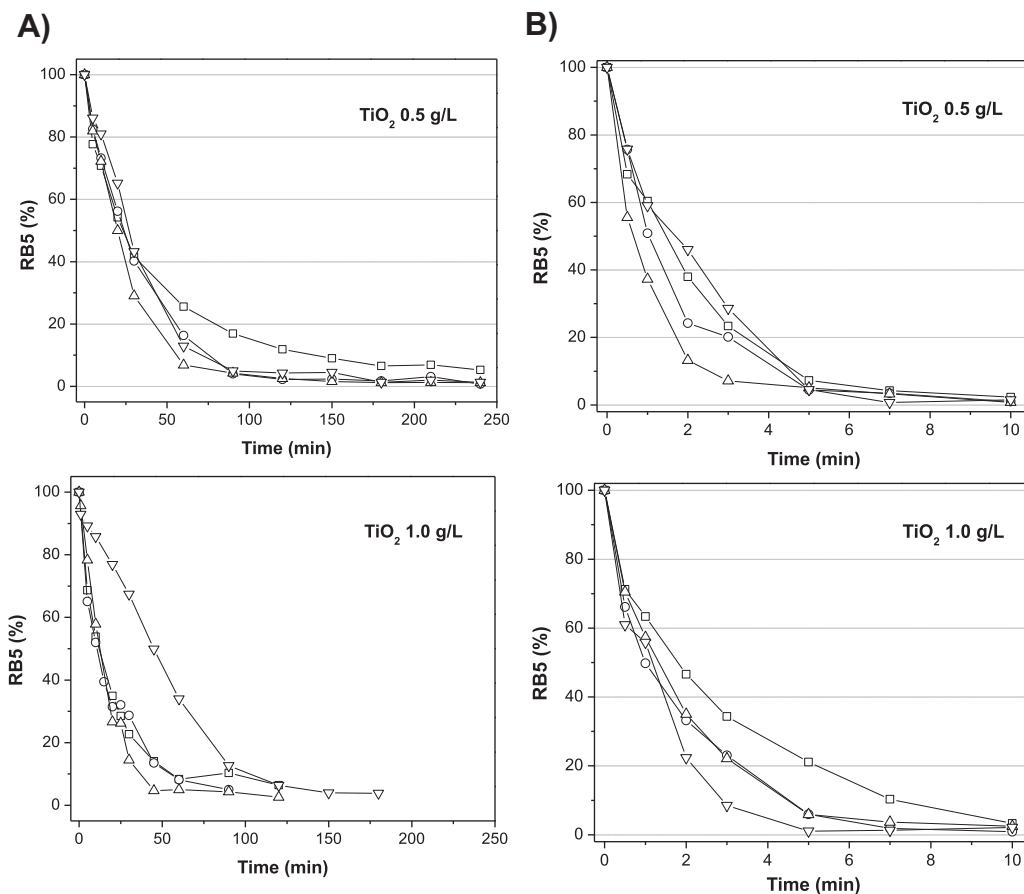


Fig. 4. RB5 discoloration by UV/TiO₂/H₂O₂ in continuous mode with: (a) UV-A LED radiation with 0.5 and 1 g/L TiO₂; (b) solar radiation with 0.5 and 1 g/L TiO₂. H₂O₂ concentration: (□) 1.76 mM; (○) 4.41 mM; (△) 8.82 mM; (▽) 17.64 mM.

H₂O₂ (0.7957 min⁻¹). All rate constants, except that of the treatment 1 g/L TiO₂/4.41 mM H₂O₂ (0.7957 min⁻¹) were lower than those reached with a combination of 0.5 g/L of TiO₂ and hydrogen peroxide (Table 1A). These results obtained with solar radiation are around 10–25 times faster than those observed with UV-A LED radiation. Table 1A also shows the E_{EO} values of treatments in continuous mode. In this reaction mode, the efficiency behaviour of the treatments is totally different from treatments in batch mode. Without H₂O₂, the efficiency of the treatments increases with the increase of concentration of TiO₂. On the other hand, with H₂O₂, the highest efficiency was observed with the lowest concentration of TiO₂ (0.5 g/L) combined with increasing concentrations of H₂O₂, reaching a peak with a concentration of 8.82 mM.

3.3. Statistical analysis

The results obtained were statistically analysed in order to assess the influence of each variable in the treatment. Thus, the effect of the following variables on the discoloration results obtained after 5 min of contact time were studied: TiO₂ concentration (0.5 and 1 g/L), H₂O₂ concentration (1.76 and 17.64 mM), type of radiation (UV-A LED and solar radiation) and reaction mode (continuous and batch mode). Fig. 5A and B portrays the main effects plot and the interaction plot respectively. The main effects plot in Fig. 5A represents the effect of each variable on the response factor. This type of representation shows the contribution to the response factor of changing one of the influential variables chosen for photocatalytic treatments. As can be observed in the figure, the variable with the highest

influence on the treatment is the radiation type, –with solar radiation mainly reaching the higher discoloration yields. As to the rest of variables, the increase of TiO₂ has a slight positive effect on the discoloration of RB5, while the opposite effect is seen with the increase of H₂O₂ concentration. Finally, as shown in the figure, the discoloration results improve slightly in continuous mode compared to batch mode. The results on the response factor (RB5 discoloration) of different interactions among the different variables can be seen in the interaction plot.

3.4. Development of more powerful UV-A LED photo system

Although the first UV-A LED photo-system achieved promising results, it was not considered sufficient to obtain similar results to those obtained with solar photocatalysis. For this reason, a new and more powerful UV-A LED photo-system was developed. Fig. 6 shows the results after the application of 0.5 g/L of TiO₂ with different irradiance dosages (16–85 W/m²) in batch mode. As can be observed in this figure, the rate of dye discoloration increased with increasing irradiance.

Table 1B shows the kinetic parameters obtained after the application of the second UV-A LED photo-system. As shown above, the constant rate increases progressively with increasing irradiance. Thus, photocatalysis assisted with 85 W/m² had a rate discoloration of 0.1919 min⁻¹. A comparison of these kinetic values with those produced by the first UV-A LED photo-system and solar radiation (Table 1A and B), reveals the high efficiency of the second photo-system. All irradiances tested in the second photo-system (from 0.0764 to 0.1919 min⁻¹) exceed the rate discoloration obtained with the first system (0.010 min⁻¹). With

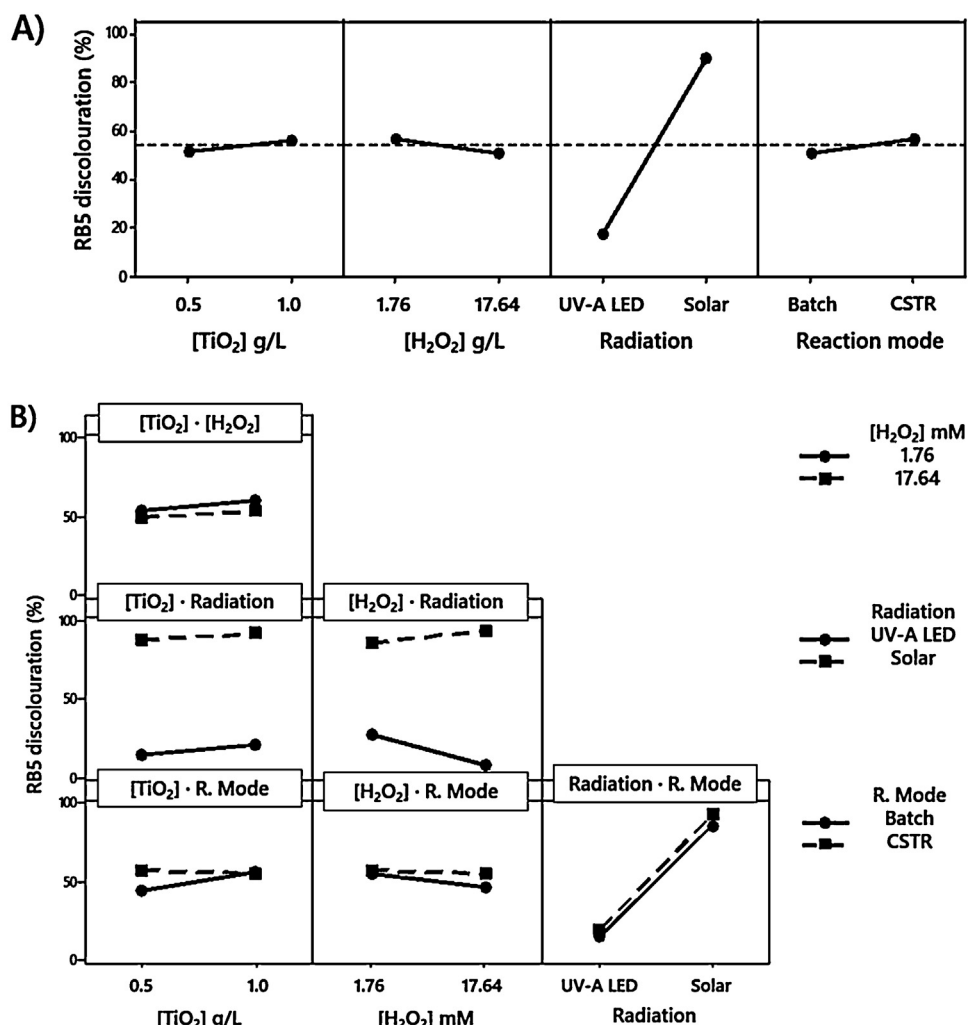


Fig. 5. Statistical analysis of variables: (a) main effects plot; (b) interaction plot.

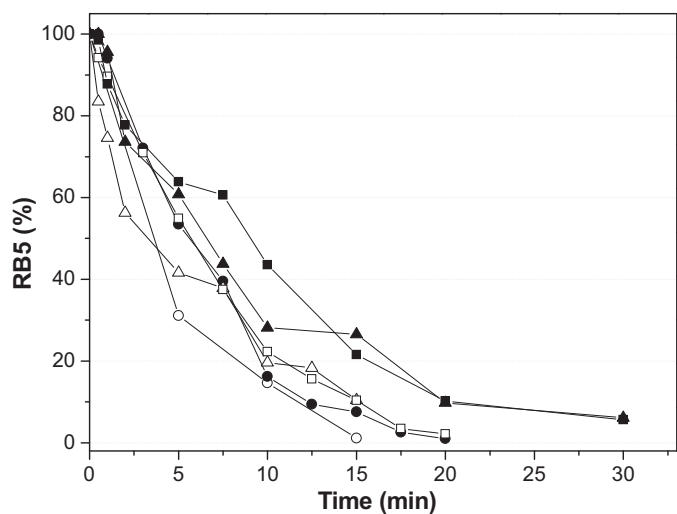


Fig. 6. RB5 discoloration by photocatalysis with 0.5 g/L of TiO₂ assisted with the second UV-A LED photosystem. UV irradiance (W/m²): (■) 16; (▲) 25; (□) 42; (△) 58; (●) 70 and (○) 85.

respect to solar radiation (0.3086 min^{-1}), UV-A LED radiation was already slower; however slight differences were observed between both treatments. In addition, a comparison of the two photo-systems was carried out in continuous mode. Fig. 7 shows the comparison of continuous experiments carried out with 0.5 g/L of TiO₂ with a flow rate of 1 mL/min and 23 and 70 W/m² of irradiance in the first and second photo-system respectively. It is clearly shown, that the second UV-A LED photo-system achieved the total discoloration of the dye in only 20 min, while a maximum discoloration of 63% was attained in the first UV-A LED photo-system after 270 min of treatment, at which time, it reached a steady state.

3.5. Comparison of processes

As observed in the results, the first UV-A LED photo-system was not able to achieve the same yield as solar radiation. Therefore, a more powerful and efficient photo-system was developed. A comparison of E_{EO} values in those treatments performed in both photo-systems (Table 1) shows that the highest E_{EO} value was obtained with the first UV-A LED photo-system ($3647 \text{ kWh/m}^3/\text{order}$). Nevertheless, the E_{EO} values of second UV-A LED system were between 4 and 6 times lower than the first photo-system. These results confirm the low efficiency of the first photo-system,

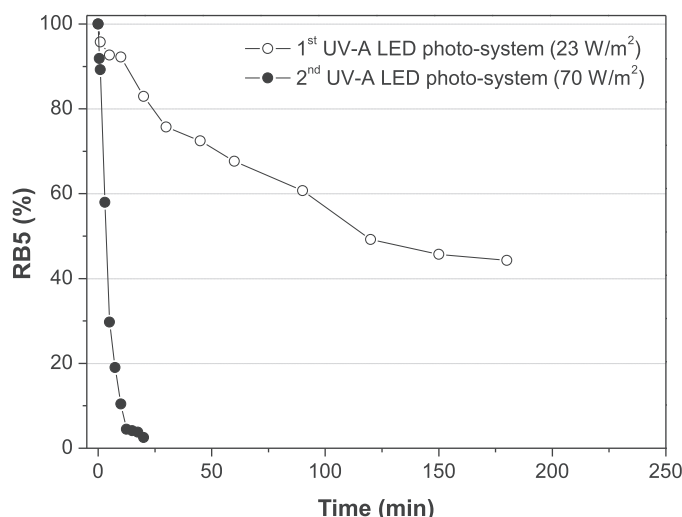


Fig. 7. Comparison of UV-A LED photosystems in the photocatalytic discoloration of RB5 in continuous mode: 0.5 g/L TiO₂; 25 mg/L RB5; F = 1 mL/min.

and show the second system to be much more adequate to perform photocatalytic treatments. Moreover, it was observed that the efficiency of the treatment (E_{EO}) increases slightly with the irradiance. The highest efficiency was observed using 70 W/m² of irradiance (59 kWh/m³/order). These E_{EO} values were compared with those obtained under the same operational conditions (0.5 g/L TiO₂) but using a medium pressure mercury lamp (Heraeus TQ-150). Using the mercury lamp, 20% of RB5 disappeared after 10 min and taking into account Eq. (1), a value of 877 kWh/m³/order was obtained, which demonstrates a lower efficiency than UV-A LED lamps. In addition, the efficiency values of the second UV-A LED photo-system are higher than those reported by other authors in the degradation of different dyes through TiO₂/UV with conventional lamps. These indicate expected higher values of E_{EO} , due to the high electrical cost (0.150 kW) and the slow discoloration of RB5. For instance, Khataee et al., achieved efficiency values in the 71–98 kWh/m³/order in the discoloration of three different dyes (Acid Orange 8, 10 and 12) using 4 g/L of TiO₂/UV-A radiation (365 nm; 15-W UV lamp) [34] and Yu et al., reported the discoloration of 20 mg/L of RB5 by 1 g/L TiO₂/UV-C radiation (15-W UVC lamp; 254 nm; 10 mW/cm²) after 100 min [35].

Finally, the efficiency of both photo-systems was compared in continuous mode using the most efficient irradiance of the second system (70 W/m²) in the treatment with 0.5 g/L of TiO₂. Again, the E_{EO} values indicate that higher efficiency is produced through the use of the second UV-A LED photo-system (359 kWh/m³/order) compared to the first photo-system (505 kWh/m³/order). However, Natarajan et al., reported the discoloration of several dyes (Malachite Green, Methylene Blue and Rhodamine B) in a concentration of 5 mg/L through TiO₂/UV-A LED treatments in continuous mode [28]. The E_{EO} values reported by Natarajan et al., are in the 780–3000 kWh/m³/order range for the different analysed dyes and are considerably higher than the efficiency values of discoloration of 25 mg/L of RB5 with TiO₂/UV-A LED radiation reported in this research work (359 kWh/m³/order).

The efficiency of UV-A LEDs was calculated with the same set of experiments assisted with solar radiation. Solar radiation treatments had discoloration rates between 4 and 72 times faster than those of UV-A LED radiation treatments carried out in the first photo-system (23 W/m²). These values mean that the first UV-A LED photo-system could not match solar radiation in terms of irradiance. However, the second and more powerful UV-A LED photo-system results lead solar radiation yields. At this point, is

also worth highlighting one potential advantage of UV-A LED radiation versus solar radiation—the possibility of continuous usage 24 h per day, 365 days per year, independently of climate conditions and the season of the year.

Regarding the treatments combining TiO₂ and H₂O₂, the addition of a correct concentration of H₂O₂, when compared to TiO₂/UV-A LED process, is better and faster in almost all the situations, as can be seen in Figs. 2 and 4 and through comparing k values and $t_{1/2}$ in Table 1A. In general, an increase in the concentration of hydrogen peroxide enhances the discoloration rate of RB5 dye, although there are some exceptions. For instance, when the treatments were carried out in continuous mode, the degradation rate increased as a function of hydrogen peroxide concentration to some extent. Thus, the fastest degradation rate ($k = 0.0674 \text{ min}^{-1}$) was reached with 4.41 mM of H₂O₂ and 1 g/L of TiO₂, instead of 17.64 mM of H₂O₂ ($k = 0.0135 \text{ min}^{-1}$). In addition, and excess of TiO₂ and H₂O₂ get worse the rate degradation of dye, reaching better results with 0.5 g/L of TiO₂ and 17.64 mM of H₂O₂ ($k = 0.0217 \text{ min}^{-1}$) than the same experiment with 1 g/L of TiO₂ ($k = 0.0135 \text{ min}^{-1}$). These results could be the consequence of scattering and shielding by suspended catalyst [36]. In batch treatments, the behaviour of hydrogen peroxide in combination with TiO₂ and UV-A LED radiation is totally different from that observed in continuous mode. In the latter case, the presence of H₂O₂ also increases the rate of degradation, however the increase of the amount of H₂O₂ in the system does not improve the rate of degradation, and the best results are achieved with the lowest concentration of H₂O₂ (1.76 mM).

Some authors have reported that the addition of hydrogen peroxide to photocatalytic treatment enhances the yield of the treatments, either through the inactivation of microorganisms [37,38] or through the removal of persistent organic micro-pollutants [39]. However, an excess of H₂O₂ is detrimental to the final discoloration rate, and other studies confirm the results obtained from the TiO₂/H₂O₂ treatments performed in this research work. Lanao et al. showed that the TiO₂/H₂O₂ treatment, (0.04 mM H₂O₂, 1 g/L TiO₂ and UV–vis radiation) did not achieve a higher level of inactivation than photocatalysis treatment (1 g/L TiO₂ and UV–vis radiation) in the removal of microorganisms (*Enterococcus* sp.) spiked in fresh water samples [31]. Thus, if there is an excess of hydrogen peroxide, it can also act as a •OH radical scavenger or form peroxocompounds on the TiO₂ surface, thus prejudicing the photocatalytic process [33].

4. Conclusions

After using two UV-A LED photo-systems, the following conclusions can be drawn from TiO₂ and TiO₂/H₂O₂ studies of a model compound of textile wastewater—Reactive Black 5 (RB5) discoloration:

- UV-A LEDs are an attractive alternative to conventional UV lamps, because they are more ecofriendly, have a low operational cost, and high energy efficiency.
- TiO₂/UV-A LED processes lead to complete discoloration of Reactive Black 5 dye with both photo-systems. The degradation rate of the dye increases with the increase of UV irradiance and with the addition of hydrogen peroxide in an adequate dosage. However, an excessive dosage of hydrogen peroxide generates unproductive reactions and scavenger effects, decreasing the degradation rate of the treatment.
- Photocatalysis assisted by the second UV-A LED photo-system was almost as fast as the discoloration of RB5 assisted by solar radiation.
- Thus, this method has the potential to overcome some significant limitations of solar photocatalysis, such as weather

conditions and sunlight exposure time, using a low-cost, relatively eco-friendly photo-system, which, in spite of treatments carried out in continuous mode being slightly slower than the treatments in batch mode, could provide a serious option for industrial wastewater treatment plants.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jece.2015.10.019>.

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