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Photocatalytic oxidation of Reactive Black 5 with UV-A LEDs

Leonor C. Ferreira[a], Marco S. Lucas[a,b,*], José R. Fernandes[c,d], Pedro B. Tavares[a]

[a] Centro de Química—Vila Real, Departamento de Química, UTAD—Universidade de Trás-os-Montes e Alto Douro, Quinta de Prados, 5000-801 Vila Real, Portugal
[b] Environmental Nanocatalysis & Photoreaction Engineering, Chemical Engineering Department, Loughborough University, Loughborough LE11 3TU, United Kingdom
[c] Departamento de Física, UTAD—Universidade de Trás-os-Montes e Alto Douro, Quinta de Prados, 5000-801 Vila Real, Portugal
[d] INESC-TEC, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal

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ABSTRACT

The effectiveness of UV-A Light emitting diodes (UV-A LEDs) for decolourization of Reactive Black 5 (RB5) solutions in a continuous photoreactor and the effect of different operational parameters on the photocatalytic decolourization of RB5 were investigated in the present work. The operational parameters included catalyst load, initial dye concentration, irradiance and solution flowrate. Photocatalytic experiments were conducted in a self-designed photoreactor with a matrix of 96 UV-A LEDs (375 nm) and Evonik P-25 TiO_2 was used as a photocatalyst. The optimum experimental conditions that allowed the highest decolourization of RB5 (89%) were an irradiance of 40 W/m^2, 1.0 g/L of TiO_2, 50 mg/L of RB5 and a flowrate of 0.8 mL/min.

A continuous stirred tank reactor (CSTR) design equation, subsequently simplified to a pseudo-first order rate equation, was used to analyse the kinetics of the experimental results. From the kinetics it is possible to observe that high TiO_2 concentrations (1.0 g/L) and light irradiances (40 W/m^2) positively affect the reaction rate (r, 2.483×10^{-7} mol/L min) and the reaction rate constants (k, 7.351×10^{-3} min^{-1}).

The figure-of-merit electrical energy per order (E_{EO}) was calculated for the photoreactor, and values of 220 kWh/m^3/order were reached for an electric power consumption of 0.0129 kW and a solution flowrate of 4.8×10^{-6} m^3/h. Results demonstrated that a UV-A LED/TiO_2 process can effectively decolourize RB5 dye solutions within the selected optimum conditions.

1. Introduction

The textile industry is one of the largest polluters worldwide. The industry has a high water consumption and uses an elevated number of compounds, of which dyes and pigments are the most problematic. This results in a large volume of highly toxic and barely biodegradable wastewater [1,2].

The removal of toxic and/or refractory contaminants from water using conventional treatments (e.g. coagulation/flocculation, biological treatment) is difficult and finding new and effective wastewater treatment processes to restore water quality is a major challenge.

In this context, Advanced Oxidation Processes (AOPs) have emerged as a suitable route for mineralization of organic contaminants in water and wastewater [3,4]. Of these, photocatalysis stands out as the most environmentally friendly, with a wide application in the total degradation of organic contaminants into H_2O and CO_2 [5,6].

Furthermore, titanium dioxide (TiO_2) is the most applied photocatalyst in wastewater treatment, since it is inexpensive, chemically stable and its photogenerated holes and electrons are highly oxidizing and reducing, respectively [7,8]. However, due to its large band gap (3.2 eV for anatase), which prevents the use of visible light in photocatalytic reactions, it can only be activated by UV radiation [9]. Currently, conventional UV-driven applications are based on low or medium pressure mercury vapour lamps. However, several drawbacks are associated with these lamps. They include instability upon long-term exposure due to overheating, low photonic efficiency resulting in high energy consumption, short lifetime, and, since mercury is a hazardous pollutant, issues

* Corresponding author at: Environmental Nanocatalysis & Photoreaction Engineering, Chemical Engineering Department, Loughborough University, Loughborough LE11 3TU, United Kingdom.
E-mail addresses: mlucas@utad.pt, m.p.lucas@lboro.ac.uk (M.S. Lucas).

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related to end of life disposal [10,11]. Therefore, a search for alternative, cost-effective and efficient UV radiation sources has been pursued.

Recent advances on the development of light emitting diodes (LEDs) have opened the possibility of employing LEDs as an alternative artificial UV radiation source for photoreactors [12–14]. Potential advantages over traditional UV lamps offered by LEDs include greater efficiency in converting electricity into light (high quantum yields), lower power requirements, compactness and robustness, no warm-up time, potential for long lifetimes, the enabling of the construction of reactors with variable geometries and the avoiding of the use of environmentally hazardous heavy metals (such as mercury) [11,15,16]. Among UV LEDs, several options, which impact on UV-driven efficiency and treatment costs, are available (e.g. different peak emission wavelength, output optical power). Exploring the substitution of common UV lamps with low-cost UV-A LEDs, this work aims to present a low-cost alternative to conventional UV-driven treatment processes.

The objective of this study was to determine the efficiency of currently marketed UV-A LEDs in the photocatalytic degradation of a textile azo dye (Reactive Black 5) in continuous flow through mode. The effect of various parameters such as catalyst loading, initial dye concentration, UV-LEDs irradiance (W/m^2) and dye solution flowrate were investigated. For the first time, UV-A LEDs were used in photocatalytic wastewater treatment using Reactive Black 5 as a key organic pollutant.

2. Materials and methods

2.1. Reagents

The azo dye, Reactive Black 5 ($C_{26}H_{21}N_5O_{19}S_6Na_4$, CI 20505), was kindly provided by DyStar (Portugal) and used as received. UV–vis absorption spectra of Reactive Black 5 in non-hydrolyzed form is illustrated in Fig. S1. Titanium dioxide (TiO_2, P25 Evonik) was used as received. It has an average particle size of 30 nm and a BET specific surface area of 55 m^2/g. The anatase and rutile percentages were 70% and 30%, respectively. RB5 solutions were prepared by dissolving the required quantity of dye in deionized water from a Millipore® purification system. Initial pH of the solution was monitored using a 209 pH meter from Hanna Instruments.

2.2. UV-LEDs photoreactor

The UV-LEDs selection was carried out aiming for a compromise between the price of each UV-LED, the TiO_2 absorption spectra (Fig. 1A) and the LEDs power efficiency (Fig. 1B). LEDs with UV-C wavelength (235–280 nm) present a high cost (€/mW) and a reduced power efficiency (power emitted vs power consumed), compared to UV-A LEDs (Fig. 1B) [17]. Therefore, UV-A LEDs that present a reduced cost and a higher power efficiency were selected.

Experimental assays were carried out in a self-designed photoreactor. The photoreactor was composed of a matrix of 96 Indium Gallium Nitride (InGaN) UV-LEDs (Roithner RLS-UV370E) with a maximum emission $\lambda = 375$ nm (UV-A) (Figs. 1 A and S2). The nominal consumption of each LED lamp is 80 mW operating at 20 mA. Blue light is emitted (Figs. 1 A and S2) and the UV-A LEDs matrix has an illuminated area of 11×7 cm^2 and a total optical power emitted of approximately 100 mW, depending on the root mean square (RMS) current intensity supplied. The system irradiance was measured using an UV enhanced Si-photodetector (ThorLabs PDA155) in a configuration that replicates the one used in the photoreactor. From the measured irradiance the photon flux delivered to the sample can be calculated and for the maximum value of irradiance, the 96 UV-A LEDs matrix presents a photon flux

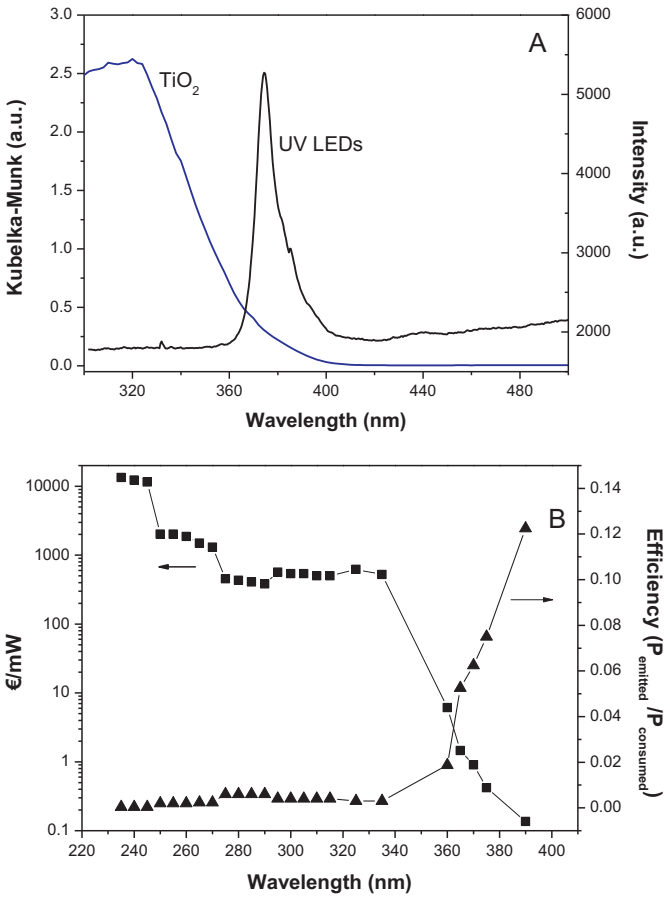

Fig. 1. UV-LEDs selection: (A) TiO_2 absorption spectra and LEDs maximum emission wavelength (375 nm); (B) €/mW and LEDs power efficiency at different maximum emission wavelengths.

of 7.59×10^{-7} Einstein/s. The output optical power is controlled using a pulse width modulation (PWM) circuit and the RMS current intensity was measured with a multimeter (UniVolt DT-64). Fig. S3 shows the UV-A LEDs irradiance (I, W/m^2) as function of current intensity (mA). The reactor was operated in a continuous flow-through mode. The UV-A LEDs photoreactor has a capacity of 100 mL and all its internal surfaces are formed by mirrors. The UV-A LEDs matrix was fixed 5 cm above the RB5/TiO_2 mixture.

2.3. Experimental procedure

RB5 aqueous solutions were prepared in Milli-Q® water with different concentrations (25, 50 and 100 mg/L). Then the desired amount of TiO_2 was added (0, 0.25, 0.5 or 1.0 g/L) and an ultrasonic bath was used (Bandelin Sonorex SUPER PK 106) for 2 min to promote the catalyst dispersion in the suspension.

In a typical experiment, the suspension was loaded to the UV-A LED photoreactor through a peristaltic pump (Gilson Minipuls 3) with a specific flowrate. The photoreactor was fitted with a mixing unit and experiments were performed under well-mixing conditions. The RB5/TiO_2 suspension was equilibrated in the dark for 1 h, before each experiment.

Irradiation of the suspensions started after the adsorption equilibrium between TiO_2 and RB5 was achieved. The experiments were carried out at the natural pH of the solution suspension. The initial pH was 5.0 ± 0.1 in the experiments without TiO_2, and 4.5 ± 0.2 in the experiments with TiO_2. These values remained practically constant during the course of the reaction. Samples of the dye solution were withdrawn at periodic intervals during the

course of the reaction, then analysed in a UV/vis Jasco V-530 spectrophotometer (Tokyo, Japan) at λ_{max} = 595 nm.

The temperature was in the range of 21–22 °C. The concentration of RB5 in the bulk solution prior to irradiation was used as the initial value for the measurements of RB5 dye decolourization. At predetermined times, a 2 mL sample was withdrawn frm the irradiated suspension using a syringe. The catalyst was separated by centrifugation (7500 rpm) from the aqueous solution prior to UV–vis analysis and the concentration of Reactive Black 5 in the solution was determined using a calibration curve of RB5 (concentration vs absorbance) prepared with known concentrations. 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.

The concentration of residual RB5 was calculated by Beer–Lambert law, after dilution when necessary, using the optical density and the molar extinction coefficient observed at the characteristic wavelength and expressed as:

$$\text{Dye decolourization} = \frac{1 - C_{dye,t}}{C_{dye,t=0}} \times 100\%$$

where $C_{dye,\ t}$ and $C_{dye,\ t=0}$ are the concentration of RB5 at reaction time t and 0 min, respectively.

3. Results and discussion

3.1. Effect of TiO_2 and RB5 concentration

First, to study the effect of the amount of catalyst, the RB5 decolourization was evaluated with TiO_2 absent (only UV-A LEDs photolysis). Colour disappearance was almost null. RB5 colour removal was then evaluated under a combination of TiO_2 and UV-A LEDs. Fig. 2 shows the decolourization profile against irradiation time of RB5 solutions with: (A) different amounts of catalyst (0, 0.25, 0.5 and 1.0 g/L of TiO_2) and (B) different dye concentrations (25, 50 and 100 mg/L of RB5). This experiment revealed that the UV-A LEDs maximum wavelength (λ = 375 nm) is unable to break the azo bonds (—N=N—) which are responsible for the dye colour (λ = 595 nm) and present in the RB5 structure (Fig. S1). However, using an irradiance of 40 W/m^2 and a flowrate of 1.5 mL/min, with 0.25, 0.5 and 1.0 g/L of TiO_2, 22, 41 and 64% of decolourization were reached, respectively. These results demonstrate that RB5 cannot be decolourized by UV-A LEDS photolysis alone and that, by increasing the catalyst amount up to 1.0 g/L, it is possible to increase the dye colour removal without any light scattering and/or screening effect which could affect the catalyst activity [10].

Fig. 2B shows the influence of dye concentration in the photocatalytic oxidation. The data obtained reveals that increasing the RB5 concentration diminishes the UV-A LEDs/TiO_2 capacity to decolourize the aqueous solution. The highest decolourization was achieved with 25 mg/L (70%) and the lowest with 100 mg/L of RB5 (only 15%), for a flowrate of 1.5 mL/min. A possible explanation for this behaviour is that as the initial concentration of the dye increases, the path length of photons entering the solution decreases and in low concentration the reverse effect occurs, increasing the quantity of photon absorption by the catalyst in lower concentrations [18,19].

The RB5 decolourization achieved with the UV-A LEDs photocatalytic system can be tracked through the UV–vis spectra at different reaction times (Fig. 3). Before the photocatalytic treatment, the UV–vis spectra of RB5 consists of two main characteristic absorption bands. One in the UV region (λ_{max} = 310 nm) and another in the visible region (λ_{max} = 595 nm). Significant changes are observed throughout the entire spectrum with

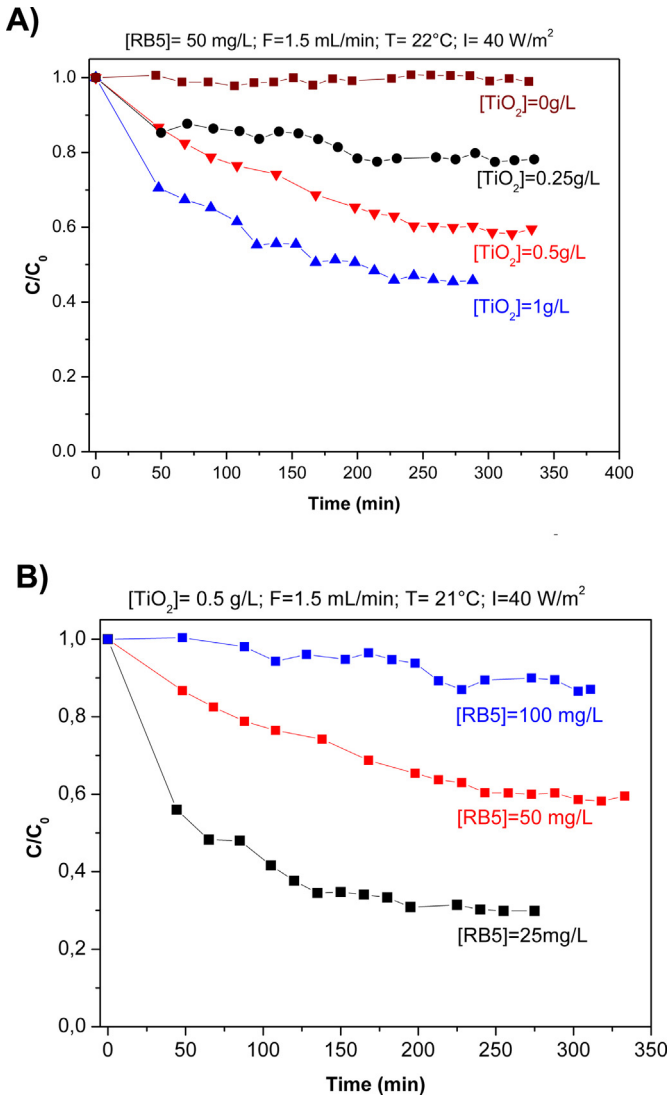

Fig. 2. Influence of (A) TiO_2 and (B) dye concentration in the decolourization of RB5 solutions with the UV-A LEDs photoreactor.

time—especially at λ_{max} = 595 nm. The typical absorption band gradually diminishes as the reaction time increases, which suggests a significant photodegradation of RB5 by UV-A LEDs. The UV band at λ_{max} = 310 nm also vanishes, but at lower rate. This UV band is characteristic of two adjacent aromatic rings, whereas the visible band (λ_{max} = 595 nm) is due to a long conjugated π system linked by two azo groups [20,21]. From UV–vis spectra it is possible to observe that the UV region between λ = 200 and 350 nm shows higher absorption compared to the visible region. Therefore, decolourization occurs faster since it is easier to break the azo bond (opening the N=N bonds) than the aromatic rings.

3.2. Kinetics of RB5 decolourization

To determine the kinetics of RB5 decolourization, the experimental results obtained were analysed using a continuous stirred tank reactor (CSTR) design equation in terms of kinetic investigation, further simplified to a pseudo-first order rate equation with respect to the dye concentration:

$$\frac{dN}{dt} = F_0 - F + V \times r \quad (1)$$

where N number of moles in a reactor, F_0 is the inlet molar flowrate, F is the outlet molar flowrate, V is the reactor volume and r is the reaction rate. This continuous stirred tank reactor system is steady state and the first term will be zero. Rearranging Eq. (1),

$$V = \frac{F_0 - F}{-r} \quad (2)$$

$F_0 = C_0 \times v_0$ (v_0 = volumetric flow rate)

$F = C \times v_0$

Using these constants and rearranging Eq. (2),

$$V = \frac{C_0 \times v_0 \times X}{-r} \quad (3)$$

$-r = k \times C$ and $C = C_0 \times (1 - X)$

$-r = k \times C_0 \times (1 - X)$

Eq. (3) shows the kinetic details obtained from the experimental data.

In the continuous stirred tank reactor, the reacting mixture was well mixed so that the properties of the reacting mixture were uniformly distributed throughout the reactor and also to ensure the properties of the exit stream were the same as the reacting mixture within the reactor.

The influence of RB5 concentration, TiO_2 dosage, flowrate and light irradiance in terms of kinetics is given in Table 1. Although increased concentration and flowrate negatively affect the reaction rate and reaction rate constants, the latter are positively affected by an increase in TiO_2 amounts and light irradiances.

3.3. Irradiance and flowrate influence

Fig. 4 presents the photocatalytic oxidation of RB5 in the UV-LEDs photoreactor under different water flowrates (from 0.8 to 2.2 mL/min) and UV irradiance (36, 40 and 46 W/m^2). These experiments were performed using a 50 mg/L RB5 solution and 1.0 g/L of TiO_2. From the data it is possible to observe that

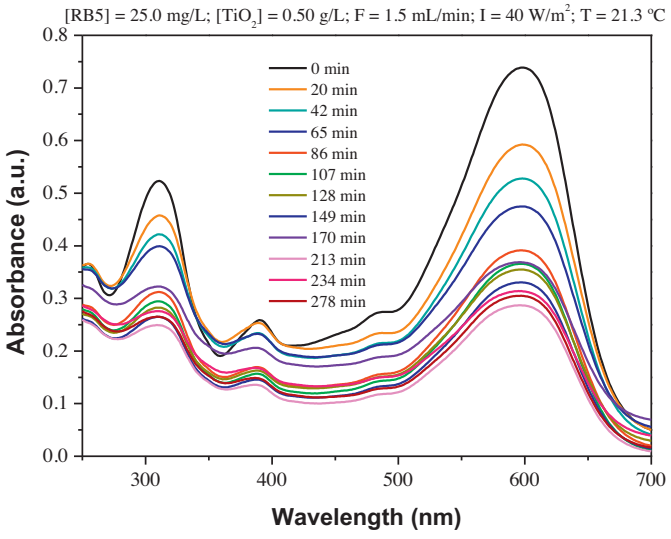

Fig. 3. Reactive Black 5 UV–vis spectra evolution along photocatalytic decolourization.

Table 1
Reaction rate and reaction rate constants calculated for different operational conditions.

Experiments	k (min^{-1})	r (mol/L min)
Effect of RB5 concentration (mg/L) (Fig. 2B)		
25	1.617×10^{-2}	1.957×10^{-7}
50	3.277×10^{-3}	1.355×10^{-7}
100	3.047×10^{-4}	3.011×10^{-8}
Effect of TiO_2 amount (g/L) (Fig. 2A)		
0.25	2.035×10^{-3}	9.031×10^{-8}
0.50	3.277×10^{-3}	1.355×10^{-7}
1.0	7.351×10^{-3}	2.483×10^{-7}
Effect of flowrate (mL/min) (Fig. 4)		
0.8	3.211×10^{-2}	3.227×10^{-7}
1.5	4.974×10^{-3}	1.881×10^{-7}
2.2	4.552×10^{-3}	1.905×10^{-7}
Effect of irradiance (W/m^2) (Figs. 2 A and 4)		
36	4.974×10^{-3}	1.881×10^{-7}
40	7.351×10^{-3}	2.483×10^{-7}

RB5 decolourization is favoured by high irradiances, independently of the dye solution flowrate applied. However, this higher decolourization reveals a lower quantum yield of the system. In a chemical photodegradation process, when a molecule decomposes after absorbing a light quantum, the quantum yield is the number of destroyed molecules divided by the number of photons

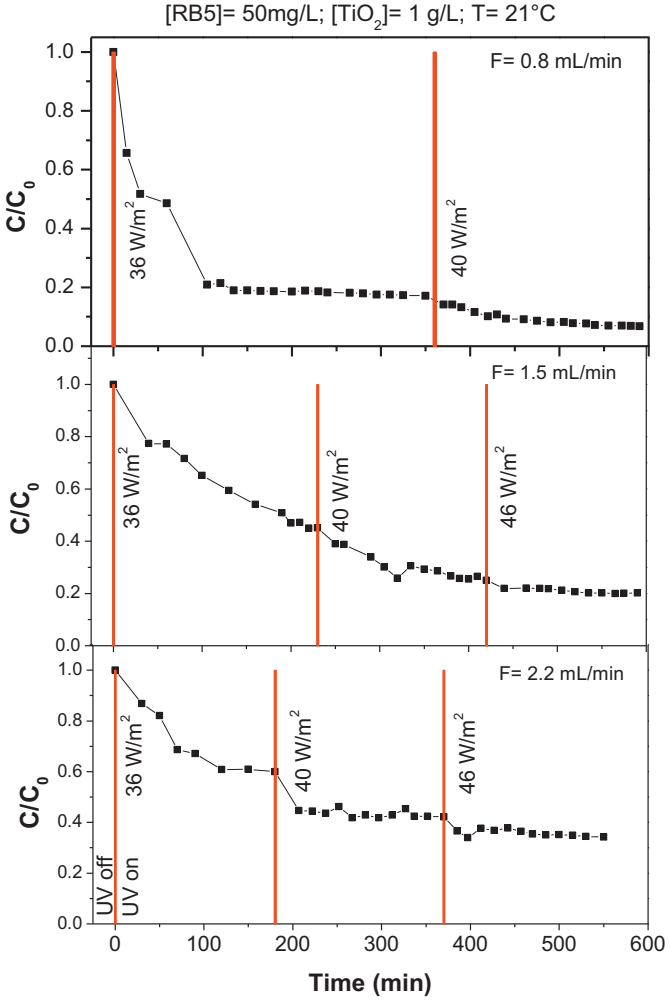

Fig. 4. Influence of irradiance (I) and solution flowrate (F) on RB5 decolourization.

absorbed by the system. In photocatalysis the quantum yield (Φ) can be defined as the ratio of moles of reactant consumed, or product formed, in the bulk phase per Einstein absorbed by the photocatalyst, according to Eq. (4) [22]:

$$\Phi_{\text{photodegradation}} = \frac{k}{2.303 \times I_\lambda \times \varepsilon_\lambda \times l} \quad (4)$$

where $\Phi_{\text{photodegradation}}$ is the photodegradation quantum yield, k (s^{-1}) is the pseudo first order rate constant, I_λ (Einstein L^{-1} s^{-1}) is the light intensity at wavelength λ, ε_λ (cm^{-1} mol dm^{-3}) is the molar absorptivity at wavelength λ, and l is the cell path length (cm).

Regarding the above mentioned equation it is easily verified that an increase in the light intensity (I_λ) will decrease the quantum yield of the photocatalytic process. Thus, high UV intensities rise the number of molecules destroyed but the yield is inferior, since the number of photons applied is significantly higher.

Among the factors taken into account in selecting a method for the degradation of pollutants, one of the most important is economic. Photodegradation of pollutants in aqueous solution is an energy demanding process, electric energy being the major factor of operating cost. The electrical energy efficiency (E_{EO}) is the electric energy in kilowatt hours (kWh) required to degrade a contaminant by one order of magnitude in a unit volume of contaminated water. E_{EO} (kWh/m^3/order) can be calculated according to the following Eq. (5) [23]:

$$E_{EO} = \frac{P}{F \times \log(C_i/C_f)} \quad (5)$$

where P is the electric power consumed by the lamp (kW), F is the dye solution flowrate (m^3/h), C_i and C_f are the initial and final concentrations of the RB5 dye.

Fig. 5 shows that the cheapest UV-A LEDs/TiO_2 treatment is achieved with low flowrates and high electric power. The figure-of-merit E_{EO} reaches values of about 220 kWh/m^3/order, clearly below that obtained with other UV LEDs, Table 2 [24], for an electric power consumption of 0.0129 kW and a solution flowrate of 4.8×10^{-6} m^3/h. Based on the data obtained with an electric power consumption of 0.0142 kW and wastewater flowrate of 9.0×10^{-6} m^3/h, it is possible to surmise that a value nearer to 200 kWh/m^3/order could be achieved. It is worth highlighting that electrical efficiency is higher for the photocatalytic process

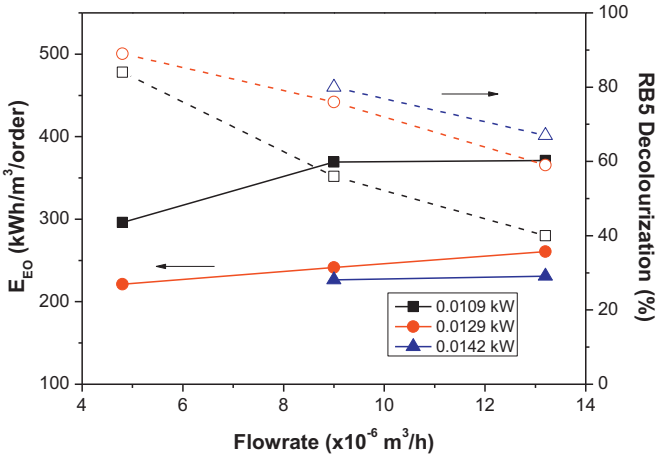

Fig. 5. Power (kW) and wastewater flowrate influence on RB5 decolourization and electric energy per order (E_{EO}).

Table 2
Kinetic constants and E_{EO} values obtained in continuous dye degradation with UV LEDs/TiO_2 [24].

Dye	k (min^{-1})	E_{EO} (kWh/m^3/order)
Malachite green	3.8×10^{-3}	789.47
Methylene blue	1.0×10^{-3}	3000
Rhodamine B	2.0×10^{-3}	1500

compared to the photolytic process (Fig. 2A, 0 g/L TiO_2). The UV-A LEDs photolytic process, with the almost null decolourization of the dye, attains an E_{EO} value of 32,838 kWh/m^3/order. This shows the extreme importance of TiO_2 in the decolourization process. Despite the small overlapping of the TiO_2 absorption curve with the UV-A LEDs maximum emission wavelength (Fig. 1A), this is the key to promoting the generation of HO, and therefore, promoting RB5 oxidation.

4. Conclusions

As a potential alternative to conventional treatments, the photocatalytic oxidation of a textile dye in a continuous stirred tank reactor with UV-A LEDs/TiO_2 was revealed to be an efficient treatment process. An RB5 decolourization of 89% was achieved using an irradiance of 40 W/m^2, 1.0 g/L of TiO_2, 50 mg/L of RB5 and a wastewater flowrate of 0.8 mL/min. In addition, the figure-of-merit electrical energy per order (E_{EO}) was obtained for the photoreactor and values of around 200 kWh/m^3/order were attained.

From the above, it can be seen that UV-A LEDs photocatalysis could be an excellent way to reduce the high cost of UV-driven advanced oxidation processes and make them viable to industrial wastewater treatment plants.

Furthermore, different operational conditions, such as catalyst variation (e.g. N–TiO_2, CNT–TiO_2, graphene–TiO_2), UV-A LEDs maximum emission wavelength, temperature, pH and hydrogen peroxide addition, could be explored in future research.

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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.2015.10.042.

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