Journal of Environmental Chemical Engineering 4 (2016) 109–114

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

# Photocatalytic oxidation of Reactive Black 5 with UV-A LEDs

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ARTICLE INFO

*Article history:*
Received 23 March 2015
Received in revised form 29 October 2015
Accepted 30 October 2015
Available online 4 November 2015

*Keywords:*
Heterogeneous photocatalysis
Titanium dioxide
Light emitting diodes
Reactive Black 5
UV-A

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 ($r$, $2.483 \times 10^{-7}$ mol/L min) and the reaction rate constants ($k$, $7.351 \times 10^{-3}$ $min^{-1}$).

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 $4.8 \times 10^{-6}$ $m^3$/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

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http://dx.doi.org/10.1016/j.jece.2015.10.042
2213-3437/

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 $11 \times 7$ 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

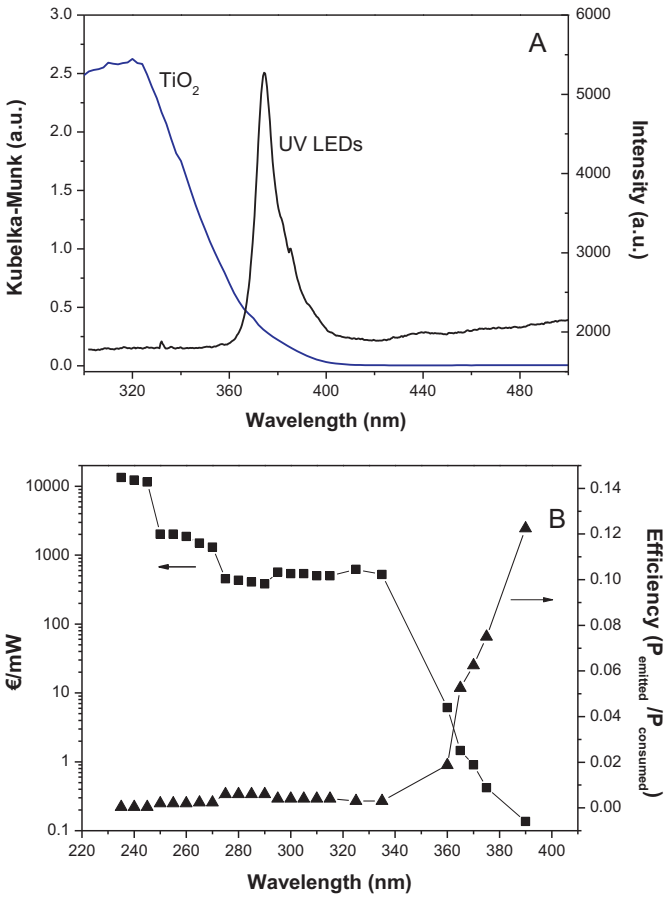


**Fig. 1.** UV-LEDs selection: (A) $TiO_2$ absorption spectra and LEDs maximum emission wavelength (375 nm); (B) €/mW and LEDs power efficiency at different maximum emission wavelengths.

of $7.59 \times 10^{-7}$ 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 $5.0 \pm 0.1$ in the experiments without $TiO_2$, and $4.5 \pm 0.2$ 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