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Influence of radiation and TiO_2 concentration on the hydroxyl radicals generation in a photocatalytic LED reactor. Application to dodecylbenzenesulfonate degradation

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ABSTRACT

One of the main issues associated to the development of photocatalysis is the lack of adequate indexes that allow the comparison of the results obtained in different experimental setup designs. The hydroxyl radicals (•OH) generation rate is a key factor to determine the overall oxidation rate.

In this work, using a Light Emitting Diodes (LEDs) reactor aimed to maximize light efficiency and minimize energy consumption, the •OH generated have been determined as a function of the radiation and catalyst concentration following an indirect method based on the reaction between •OH and dimethyl sulfoxide (DMSO) to produce formaldehyde.

Finally, the methodology has been applied to analyze the degradation kinetics of the anionic surfactant dodecylbenzenesulfonate (DBS), frequently used in shampoo formulations and detergents for washing machines. We propose a method based on the indirect determination of •OH radicals generation rate that allows the assessment and comparison of the kinetics of photocatalytic oxidation of pollutants.

1. Introduction

Increasing water demand and shortage of available water are growing concerns for our society [1]. Since wastewaters constitute one of the largest possible water resources, one attractive option is the possible reuse of onsite wastewater or the effluent of wastewater treatment plants (WWTPs). Conventional water treatments such as chemical oxidation, activated carbon adsorption and biological treatment sometimes seem to be inefficient in degrading some organic compounds [2–4].

Hence, over the last few decades, a group of new technologies called advanced oxidation processes (AOPs) has been widely reported because of their effectiveness in the oxidation of organic compounds. AOPs are processes based on the generation of strongly reactive species such as hydroxyl radicals (•OH) [4–6].

Among these technologies, photocatalysis is an attractive instrument for the removal of organic and inorganic pollutants from water, due to its ambient operating temperature and pressure and absence of secondary pollution. Heterogeneous photocatalysis is a process in which a source of appropriate light and a solid semiconductor material as catalyst are necessary to promote a chemical reaction by means of the generation of electron-hole pairs [6], [7].

Up to now, TiO_2 is the most promising material used as catalyst because it is highly photoreactive, stable with respect to corrosion, inexpensive, nontoxic, biologically and chemically inert and capable of repeated use without considerable loss of catalytic capacity [6–9].

Nevertheless, the inherent difficulty to compare the results obtained in the countless experimental setup designs and configurations represents an important issue in the development of photocatalysis that needs further research [10], [11]. Hence, the quantitative determination of the hydroxyl radicals generated in the photocatalytic processes is essential for a better understanding of the results obtained with this technology. However, their high reactivity and short lifetime complicate their direct determination. Therefore, several indirect detection methods related with the introduction of a probe molecule in the medium have been developed [12–14].

Some kinetic models considering radiation can be found in literature, but most of them are quite complex and consider the geometry of the reactor [15], [16]. Moreover, they include many parameters that sometimes are difficult to quantify.

To develop an efficient and sustainable photocatalytic process several design parameters must be optimized. A key factor is the

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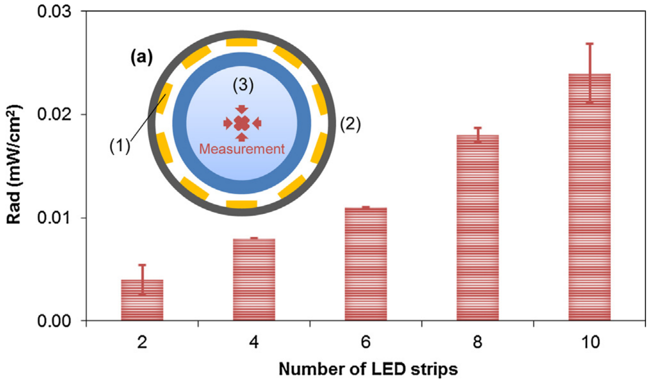

Fig. 1. Radiation distribution in the reactor. (a) Schematic diagram of the transverse section of the LEDs reactor: (1) LEDs strips, (2) PVC case and (3) reaction vessel.

energy efficiency. Most of the previously reported photocatalytic studies were carried out using mercury lamps as ultraviolet light source. However, these lamps showed a lack of reliability, durability and efficiency. Light emitting diodes (LEDs) seem to be a promising light source substitute. The main reason is that they are highly efficient converting electricity into light, with little energy burned off into heat and emitting in a specific wavelength. Furthermore, they are considerably cheaper and their useful life is significantly longer than the mercury lamps [17]. Some researchers suggested the feasibility of using LEDs in photocatalytic applications for the removal of environmental pollutants, such as 4-chlorophenol [17], dimethyl sulfide [18], perchloroethylene [19], o-cresol [20], formaldehyde [21], [22] or dyes [23].

Surfactants comprise a broad group of chemical compounds synthesized to exhibit tensioactive properties that make them useful as a key ingredient of household and industrial detergents and in personal care products. Most surfactants are only partially biodegradable and they can be found in effluents of WWTPs [24]. Dodecylbenzenesulfonate (DBS) is an important anionic surfactant frequently used in shampoo formulations and in detergents for washing machines that can be easily found in water effluents [25], [26]. Previous studies of DBS photocatalytic degradation using TiO_2 showed the viability of the treatment under specific illumination conditions and analyzed the kinetics of the process [27–30]. However, they cannot be compared due to the different light applied and a general model considering light and catalyst influence is still an issue.

The aim of this work is to quantify the $^{\bullet}OH$ generated as function of the light intensity and the catalyst dosage and to correlate this information with the photocatalytic degradation rate of DBS in a LEDs reactor.

Thus, the determination of a new model for the removal of an organic compound as the DBS correlating to the concentration of contaminant, light intensity and catalyst content will be shown. This model will play an important role in the comparison of organic compound removal in different experimental setups and will be essential for an optimal design of the process.

2. Experimental

The LEDs reactor, depicted in Fig. 1, was constructed according to the authors' specifications. 180 LEDs (OSA Opto Light Series 400) were employed as source of light in this work. The emission wavelength was between 375 and 380 nm and the electrical operation conditions were 3.2 V forward voltage and 20 mA forward current for each LED. They were assembled into 10 strips of 18 units providing 0.2 m long illuminating zone and the strips were mounted onto a dark PVC case (height 41.5 cm, diameter 21 cm) arranged uniformly in the angular direction. A Pyrex glass reaction vessel of 1 L of capacity (height 25 cm, diameter 7.4 cm) was inside the case. A magnetic stirring plate (Velp Scientifica) was used to provide proper mixing.

To evaluate the influence of light intensity on the $^{\bullet}OH$ generation and DBS degradation, between 2 and 10 LEDs strips were switched on, which corresponded with values of radiation in a range between 0.004 and 0.024 mW/cm^2. All the catalytic experiments were performed in duplicate at room temperature (25 °C), and dissolved oxygen, pH and temperature were measured in the LEDs reactor with a Crison Multimeter 44.

A PCE-UV34 radiation meter (PCE Instruments), with an irradiance measurement range between 290–390 nm and 0–2 mW/cm^2 and resolution of 0.001 mW/cm^2, was employed to quantify the average radiation intensity. The measurements were carried out in the center of the empty reactor.

2.1. $^{\bullet}OH$ quantification

The method used in this study for the determination of the $^{\bullet}OH$ formation was initially proposed by Tai et al. [13], and is based on the reaction between $^{\bullet}OH$ and dimethyl sulfoxide (DMSO) to produce formaldehyde that reacts with 2,4-dinitrophenylhydrazine (DNPH) to form the corresponding hydrazone (DNPHo). Then, quantification of the $^{\bullet}OH$ generated is carried out through the determination of the formaldehyde concentration when the DNPHo is analyzed by high performance liquid chromatograph (HPLC), assuming that all the $^{\bullet}OH$ are consumed by the DMSO. Therefore, this indirect method allows knowing the rate of $^{\bullet}OH$ generation, as it is the same as the rate of DMSO transformation into formaldehyde.

0.8 L of a 250 mM DMSO solution were mixed with the TiO_2 and kept for 30 min in the dark to reach adsorption equilibrium, then photocatalytic degradation was initiated. At different time intervals, 2 mL of suspension were sampled and filtered through a 0.45 μm syringe filter (Teknokroma). Then 2.5 mL of pH 4.0 H_3PO_4-NaH_2PO_4 buffer solution (Panreac), 0.2 mL of 6 mM DNPH solution dissolved in acetonitrile and 0.3 mL of ultrapure water were added [13]. The mixture was maintained at room temperature for 30 min and analyzed by a Waters 2690 HPLC equipped with a Waters 996 Photodiode Array detector and a XBridge C18 (5 μm, 4,6 × 250 mm) analytical column. With a flow rate of 0.6 mL/min, the mobile phase used was a mixture of methanol (Panreac) and water (60:40 v/v). The detection wavelength was 355 nm.

2.2. DBS degradation

DBS was obtained from Sigma–Aldrich and the TiO_2 catalyst used was Aeroxide P25 provided by Evonik Industries. 0.8 L of a 0.144 mM DBS solution were mixed with the catalyst and kept for 30 min premixing in the dark to reach adsorption equilibrium before the photocatalytic experiments were started. The suspension was sampled at defined time intervals and filtered through a 0.45 μm syringe filter (Teknokroma) prior to analysis. DBS was analyzed at 223 nm by UV spectrophotometry (Shimadzu, UV-1800).

3. Results and discussion

Fig. 1 shows the average radiation detected in the center of the reactor. As expected, a linear relationship between the number of LEDs employed and the applied light intensity is observed.

3.1. Light intensity influence

The reactor design allows working with five combinations of LEDs strips switched on to manipulate light intensity.