Kinetics and Efficiency Analysis of the Photocatalytic Degradation of Two Phamaceuticals in a UV-LED reactor

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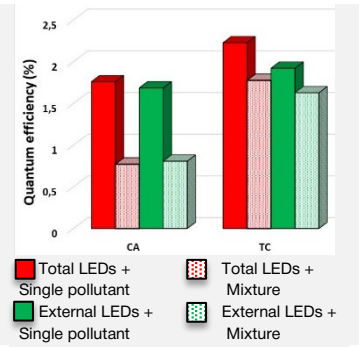

In the present work, the photocatalytic degradation of clofibric acid (CA) and tetracycline (TC) was studied using an annullar, packed-bed reactor filled with TiO_2-coated glass rings, irradiated internally and externally by UV LEDs. The performance of single pollutants solutions and binary mixtures under different irradiation conditions was evaluated. The quantum efficiency parameter was also estimated. It was found that the presence of TC significantly decreased the degradation of CA, whereas CA did not affect TC degradation. Illumination with total LEDs provided higher photon absorption rates and reaction rates than illumination with only external LEDs but the quantum efficiency of each compound was practically not affected by the irradiation condition.

Introduction

The presence of antibiotics and other pharmaceutically active compounds in the water environment is a matter of great concern. Conventional wastewater treatment plants cannot fully remove this type of pollutants and, as a result, they negatively impact aquatic ecosystems and drinking water sources. To address this issue, research is being conducted to develop effective methods to remove pharmaceuticals from the environment. Heterogeneous photocatalysis with TiO_2 is a sustainable technology that can effectively eliminate a wide variety of pharmaceutical compounds from water [1].

The main objective of this study was to investigate the photocatalytic degradation of pharmaceutical compounds, individually and in binary mixtures, in an annular reactor filled with TiO_2-coated glass rings and irradiated with UV-LEDs lamps. The antibiotic *tetracycline* (TC) and the blood lipid regulator *clofibric acid* (CA) were chosen as model compounds.

Material and Methods

Experiments were carried out in an annular reactor made of borosilicate glass, with 4.0 cm of height, 6.5 cm of inner diameter, and 10.5 cm of outer diameter. The reactor was irradiated internally and externally by a total of 40 UV-LEDs (Roithner XSL-375-TF-R2) with maximum emission at 375 nm. The internal UV-LED array consisted of two parallel strips of 6 LEDs each, and the external array was composed by two parallel strips of 14 LEDs each.

The reactor annulus was filled with a total of 900 TiO_2-coated glass rings of 0.5 cm of diameter by 0.5 cm of length. TiO_2 Aeroxide P25 was immobilized over the surface of the rings by the dip-coating technique employing a suspension of 150 g/L [2]. This procedure was repeated 3 times. The final thickness of the TiO_2 coating, calculated by SEM, was 3 µm. The total catalytic area was 1773.1 cm^2.

Experiments were carried out employing single component solutions and binary mixtures of CA and TC at initial concentrations of 20 mg/L and 30 mg/L, respectively, under external irradiation (only external LEDs on) and total irradiation (internal and external LEDs on). The pH of the initial solutions was pH=5 (natural pH). The pollutants concentration were measured by HPLC.

The performance of the reactor was evaluated by means of the quantum efficiency parameter (η_{Rxn}), which relates the photocatalytic reaction rate with the radiation absorption rate:

$$\eta_{i,Rxn} = \frac{\langle r_i^s(x,t_0)\rangle_A}{\langle e^{a,s}(x)\rangle_A}$$

where $\langle r_i^s(x,t_0)\rangle_A$ is the initial surface reaction rate of compound *i* (*i*=CA or TC) averaged over the catalytic area *A*, and $\langle e^{a,s}(x)\rangle_A$ is the local surface rate of photon absorption averaged over *A*.

The initial reaction rate of each pollutant was calculated from experiments. The photon absorption rate was obtained by solving a 3D radiation model in the reactor with the Monte Carlo (MC) method **[3]**.

Results and Discussion

Figure 1 presents the distribution of the radiation absorbed by the catalyst inside the reactor, calculated by MC simulations. External illumination was clearly insufficient to activate most of the catalyst. As expected, this situation was improved by irradiating the reactor from both sides. **Figure 2** shows the degradation of CA and TC under different experimental conditions. The photocatalytic treatment was able to reduce the concentration of both pollutants in single solutions and binary

mixtures but different behaviour of each compound was observed.

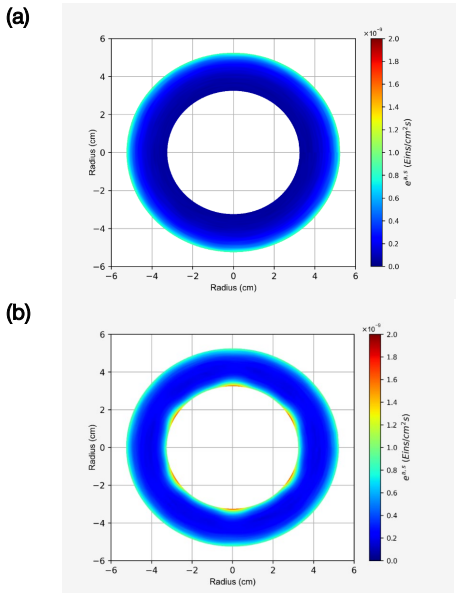

Figure 1. Horizontal cross section radiation profiles. (a) External LEDs (b) Total LEDs.

Table 1 presents the corresponding values of initial reaction rate, photon absorption rate, and quantum efficiency. Under all experimental conditions, the degradation of TC was faster than that of CA. Also, the degradation of CA was significantly affected by the presence of TC, whereas similar TC degradation rates were found in single solutions and mixtures, indicating that CA did not have a major effect on the TC degradation. This observation could be explained by the higher adsorption capacity of TC over TiO_2, hindering the degradation mechanism of CA when TC is present [4]. Regarding the irradiation level, total LEDs provided higher photon absorption rates and reaction rates. Nevertheless, the quantum efficiency of each compound was practically not affected by the irradiation condition. This result indicates that the increase in the reaction rate is proportional to the increase in the photon absortion rate.

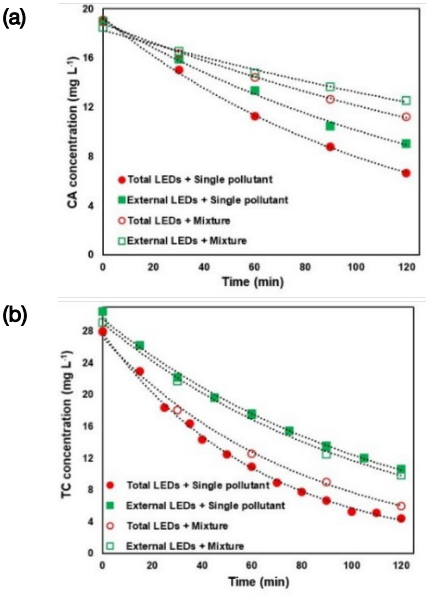

Figure 2. Degradation of pollutants in single and binary solutions. (a) CA (b) TC. Symbols: experimental data. Dotted line: exponential fitting.

Table 1. Photon absorption rate, reaction rate and quantum efficiencies for CA and TC in single solutions and binary mixtures.

Irradiation condition	$\langle e^{a,s}(x)\rangle_A \times 10^{10}$ $(Eins\ cm^{-2}s^{-1})$	i	Single solution		Binary mixture	
			$\langle r_x^s(x,t_0)\rangle_A \times 10^{12}$ $(mol\ cm^{-2}s^{-1})$	η_{Rxn} (%)	$\langle r_x^s(x,t_0)\rangle_A \times 10^{12}$ $(mol\ cm^{-2}s^{-1})$	η_{Rxn} (%)
External	1.79	CA	3.00	1.68 ± 0.03	1.64	0.92 ± 0.03
		TC	3.48	1.98 ± 0.04	3.32	1.85 ± 0.04
Total	2.57	CA	4.40	1.71 ± 0.02	2.24	0.87 ± 0.01
		TC	5.68	2.19 ± 0.03	4.69	1.82 ± 0.05

Conclusions

The photocatalytic degradation of two pharmaceuticals was investigated. The hindering effect of TC in the degradation of CA was significant. On the other hand, CA practically did not affect the degradation of TC. Total LEDs provided more uniform distribution of the absorbed radiation inside the reactor and higher reaction rates but the quantum efficiency was practically not affected by the irradiation condition. Rational reactor design, modeling, and kinetic analysis are useful tools towards the application of photocatalysis in real wastewater treatment facilities.

Acknowledgments

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