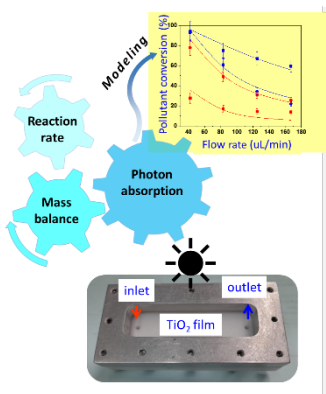


# Kinetic Expressions Including Radiation Absorption Effects to Estimate the Photocatalytic Degradation of Pharmaceutical Mixtures

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In this work a kinetic study of the photocatalytic degradation of mixtures of pharmaceuticals is presented. Experiments were carried out in a microreactor under simulated sunlight. TiO<sub>2</sub> Aeroxide P25, immobilized on a glass plate, was employed as catalyst. The Langmuir-Hinshelwood model was adopted to represent the system kinetics, including explicitly the effect of the radiation absorption. Thus, the kinetic parameters obtained are independent of the reactor configuration and the irradiation conditions. Experimental assays were performed by varying the flow rate and the incident radiation level. Intrinsic kinetic parameters were computed by fitting the model results with experimental data. Good agreement was obtained between model predictions and experiments, with an error of 10.6 % in the estimations of the pollutants concentrations in the mixtures.

## Introduction

Various mixtures of pharmaceuticals can be found in surface waters that receive discharges from human and animal waste, posing a severe threat to the environment. Heterogeneous photocatalysis with titanium dioxide (TiO<sub>2</sub>) is a promising technology for the degradation of this type of pollutants that cannot be removed by conventional water treatment methods. Kinetic modeling with intrinsic parameters, i.e. independent of the irradiation conditions and reactor geometry, is essential to scale-up the photocatalytic process, and microreactors provide an excellent platform for kinetic studies [1]. In this work, we develop a kinetic model with intrinsic parameters that predicts the degradation of mixtures of two pharmaceutical compounds, tetracycline (TC) and clofibric acid (CA), in a continuous flow, planar microreactor with the catalyst immobilized as a thin film on the window of the reaction chamber.

## Material and Methods

The microreactor employed is shown in Fig. 1. A borosilicate glass plate served both as window, to allow the entrance of radiation, and as support, to immobilize the photocatalyst as a film on the inner side (in contact with the fluid of the reaction chamber). The reactor volume is  $V_R = 209 \mu\text{L}$  ( $5.8 \text{ cm} \times 2 \text{ cm} \times 180 \mu\text{m}$ ). The reaction chamber was designed to achieve uniform fields of both fluid velocity and radiation throughout the flow domain, as well as negligible diffusive limitations in the solid and fluid phases. The catalyst TiO<sub>2</sub> Aeroxide P25 was immobilized over the surface of the glass by the dip-coating technique employing a suspension of 150 g/L of TiO<sub>2</sub> [2]. The thickness of the resulting film, estimated from SEM images (SEM Dual Beam Zeiss Cross Beam 350), was  $2.5 \pm 0.3 \mu\text{m}$ .

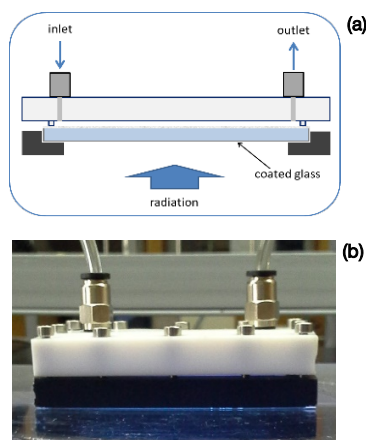


Figure 1. (a) Scheme and (b) Photograph of the photocatalytic microreactor.

Photocatalytic experiments were carried out employing single component solutions and binary mixtures of TC and CA. The inlet concentration of each compound was 20 mg/L. The solutions were injected into the reactor by a syringe pump (APEMA PC11UBT), and illumination was provided by a solar simulator (Oriel, model 9600). Assays were performed under different flow rates ( $Q$ ), in the range 42-167  $\mu\text{L}/\text{min}$ , and three different levels of irradiation: 763  $\mu\text{W}/\text{cm}^2$ , 656  $\mu\text{W}/\text{cm}^2$ , and 533  $\mu\text{W}/\text{cm}^2$  between 300 and 400 nm, corresponding to the distances reactor-solar simulator of 6 cm, 8 cm, and 12 cm, respectively. The concentrations of the pollutants, at the inlet and outlet of the microreactor, were determined by HPLC (Waters). The mobile phase was a solution of 70/30% (v/v) CH<sub>3</sub>CN/H<sub>3</sub>PO<sub>4</sub> 0.2%.

## Results and Discussion

The microreactor works in the operating zone where: (i) the characteristic diffusion time is shorter than residence and kinetic times, and (ii) the photoreaction occurs in the reaction-limited condition. Also, the reactant concentration changes mainly along the flux direction and the concentration gradient can be reduced to a 1D field [2]. Thus, the mass balance for reactant  $i$  results:

$$\frac{dC_i}{dx} = -\frac{wh A_{cat}}{Q} r_i^s$$

where  $C_i$  is the concentration of compound  $i$ ,  $x$  is the spatial coordinate in the flow direction,  $w$  and  $h$  are the reaction chamber width and height, respectively,  $A_{cat}$  is the irradiated photocatalytic area, and  $r_i^s$  is the surface reaction rate.

In heterogeneous photocatalysis, the Langmuir-Hinshelwood (L-H) model is frequently used to represent the reaction rate:

$$r_i = -\frac{k_{i,app} K_i C_i}{1 + \sum_{i=1}^n K_i C_i}$$

where  $k_{i,app}$  is the apparent first order kinetic constant, and  $K_i$  is an equilibrium adsorption constant. The term  $\sum_{i=1}^n K_i C_i$  takes into account the competitive effect of other compounds or stable reaction intermediates.

In this work, the L-H model was assumed to represent the degradation rates of TC and CA. Also, to turn  $k_{i,app}$  independent of the irradiation condition, the influence of the radiation absorption is uncoupled as follow:  $k_{i,app} = k_i (e^{a,s})^m$ , where  $e^{a,s}$  is the surface rate of photon absorption and  $m$  is the order dependence of the reaction rate on the photon absorption rate. Based on previous experiments, square root dependence was adopted ( $m=0.5$ ) [3]. Taking into account both assumptions, the mass balance for compound  $i$  can be written as:

$$\frac{dC_i}{dx} = -\frac{wh A_{cat} k_i K_i (e^{a,s})^{0.5} C_i}{Q V_R (1 + \sum_{i=1}^n K_i C_i)}$$

The absorbed radiation by the TiO<sub>2</sub> film ( $e^{a,s}$ ) was calculated by a radiation balance in terms of the local net radiation fluxes [3]. Numerical integration of the mass balances of both pollutants was carried out by the Runge-Kutta method. The values of the kinetic parameters  $k_i$  and  $K_i$ , adjusted with a nonlinear least-squares solver (MATLAB subroutine *lsqnonlin*), are shown in **Table 1**.

## Conclusions

In this work, intrinsic kinetic parameters of the photocatalytic degradation of single component solutions and mixtures of pharmaceuticals were obtained. These parameters are independent of the irradiation conditions and they are useful to design and scale-up reactors of different configurations.

## Acknowledgments

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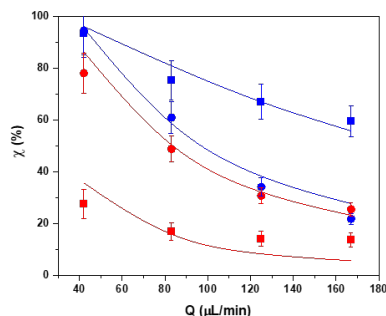
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**Table 1.** Kinetic parameters

Compound	$i$	$k_i$ [ $\mu\text{M cm/min}$ ] ( $\text{Eins/s cm}^2$ ) <sup>-0.5</sup>	$K_i$ [ $\mu\text{M}^{-1}$ ]
TC	1	$1.10 \times 10^4$	0.42
CA	2	$2.04 \times 10^4$	0.05

**Fig. 2** presents experimental data and simulation results of TC and CA conversion ( $\chi = 1 - C_{outlet}/C_{inlet}$ ) as a function of the flow rate in single and binary solutions, for the irradiation level of 656  $\mu\text{W}/\text{cm}^2$ . Similar behavior was observed under the other irradiation levels tested.



**Figure 2.** % Conversion of TC and CA at different flow rates. Symbols represent experimental data and solid lines represent simulation results. TC: Circles. CA: Squares. Blue: single component. Red: binary mixtures.

Conversion of both pollutants decreases when increasing the flow rate, as a result of the reduction of the residence time. In the case of mixtures, degradation of TC is slightly affected by the presence of CA, but the degradation rate of CA decreases significantly in the presence of TC. This competitive behavior is accurately represented by the proposed model, as evidenced in the values of  $K_i$ . A possible explanation is the higher adsorption of TC over TiO<sub>2</sub>, leaving less active sites available on the catalytic film for CA adsorption and degradation [4].

Good agreement was obtained between model predictions and experimental results under all the conditions evaluated. The percentage root mean square error (RMSE) in the estimations of both pollutants concentrations in the mixtures was 10.6 %.