

## Evaluation of model parameters for simulating TiO<sub>2</sub> coated UV reactors

J. E. Duran, F. Taghipour and M. Mohseni

### ABSTRACT

A CFD-based model for simulating TiO<sub>2</sub> coated photocatalytic reactors used in drinking water treatment applications was preliminarily evaluated. The model includes aspects of hydrodynamics, mass transfer, UV-radiation field, and surface chemical reactions. Appropriate models for each of the associated physicochemical phenomena were experimentally or analytically examined. Once defined and evaluated, the individual models were integrated into a CFD-based model for simulating photocatalytic reactor performance, which was experimentally evaluated.

**Key words** | CFD, drinking water treatment, photocatalysis, photoreactor, simulation

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### INTRODUCTION

Heterogeneous photocatalysis is a particularly emerging and promising technology for water purification (Adesina 2004; Herrmann 2005). Photocatalytic oxidation processes involve the use of oxygen and nano-structured photocatalyst materials, predominantly titanium dioxide (TiO<sub>2</sub>), activated by ultraviolet (UV) irradiation. The appeal of this technology for drinking water treatment lies mostly in its capability to potentially mineralize the pollutants, in addition to inactivating pathogens including protozoa and viruses. However, despite the many advantages of this technology and the extensive research done in this field, the development of large scale commercial photocatalytic oxidation reactors has not yet been materialized. Lack of proper models and simulation tools for predicting and analyzing the performance of full-scale systems, and therefore lack of adequate scale-up strategies, is among the key factors hindering the development of commercial water treatment systems utilizing this technology (Mukherjee & Ray 1999; Adesina 2004).

Development of models for predicting the behavior of heterogeneous photocatalytic reactors is a complicated task. The complex interactions among transport processes, reaction kinetics, and radiation absorption lead to a strong coupling of physicochemical phenomena (Periyathamby & Ray 1999). To model photocatalytic reactors, the conservation equations of momentum, mass and species, as well as the radiative transfer equation (RTE) should be solved

(Cassano *et al.* 1995; Taghipour & Mohseni 2005). This requires proper definition and incorporation of appropriate turbulence models for the hydrodynamics and mass transfer, ultraviolet (UV) radiation field model, and the intrinsic kinetics of the surface reactions in the photoreactor.

Computational Fluid Dynamics (CFD) has extensively demonstrated to be a very effective tool for the simulation of reacting systems (Kuipers & Van Swaaij 1998). In the field of photocatalysis, Pareek *et al.* (2003) simulated a suspended TiO<sub>2</sub> pilot-scale annular bubble column photocatalytic reactor, solving the RTE with a finite-volume-based discrete ordinate method. The simulated and experimental data showed good agreement indicating the applicability of the developed model in such systems. More recently, Trujillo *et al.* (2007) reported a study on the CFD analysis of the radiation distribution in an immobilized catalyst bubble column, externally illuminated photoreactor. The study showed that gas bubbling considerably increased the fluence rate in the gas-liquid mixture enhancing the absorbed radiation on the TiO<sub>2</sub>-coated plates. Unfortunately, no experimental evaluation was done in the investigation.

CFD has also been successfully used for the simulation of photocatalytic reactors for air treatment. Mohseni and Taghipour (Mohseni & Taghipour 2004; Taghipour & Mohseni 2005) simulated and experimentally evaluated an annular photocatalytic reactors treating chlorinated VOCs. The information obtained could result in reactor design

modification and performance improvement. Castrillón *et al.* (2006) made a flow field investigation in a photocatalytic reactor for air treatment and identified several design issues in the original unit. More recently, Salvado-Estivill *et al.* (2007) presented a methodology for the evaluation of the intrinsic photocatalytic oxidation kinetics of indoor air pollutants. The method proposes the development of a rigorous CFD-based model that allow for deriving kinetic parameters directly from experimental kinetic data. In their article, they exemplified the use of this methodology for the case of the oxidation of trichloroethylene.

In the case of immobilized photocatalytic reactor for water treatment, to the best of our knowledge, there is only one study that reports CFD simulation analysis for this kind of system (Periyathamby & Ray 1999). However, the publication neither offers much information about the CFD model (boundary conditions, radiation model, mesh quality, etc.), nor evaluates the simulation results against experimental data.

Most of the previous studies about CFD simulation of photocatalytic reactors have as common shortcoming the lack of experimental validation of their models. This research has focused on the development of a CFD-based model based entirely on experimental and/or analytical evaluation. The model includes aspects of hydrodynamics, mass transfer, UV radiation field and surface chemical reaction.

## METHODOLOGY

### Individual component evaluations

The development of a successful CFD-based model for simulating TiO<sub>2</sub> coated photoreactors relies on the proper definition of the models representing various phenomena affecting the reactor performance (i.e. hydrodynamics, mass transfer, UV radiation field and surface chemical reaction). In this research, models were individually analyzed and analytically and/or experimentally evaluated for the individual phenomena involved in the photocatalytic reactors. In this way, the proper models can be defined and finally combined into an integral CFD model capable of modeling the performance of immobilized photocatalytic reactors. The commercial CFD package Fluent® (V6.2.16) was used to perform the simulations.

Three different hydrodynamic models (Laminar Model (Lam), Reynolds Stress Model (RSM) and Realizable k-ε Model (R k-ε)) (Fluent-Inc. 2005) were evaluated in terms of their mass transfer modeling capabilities. Mass transfer

experiments were conducted in a differential reactor equipped with 25 mm wide glass slides coated with benzoic acid. Figure 1 shows the schematic of the reactor used, which consisted of a 63-mm-wide aluminium reactor designed to allow water to flow through a 225 mm long passage of 25 mm (width) and 3 mm (height), and over the coated glass plates. The reactor was covered by a clear acrylic plate. The glass slides were coated by dipping them into molten benzoic acid. On contact with the glass slides, the benzoic acid immediately solidified, yielding a uniform layer of the organic acid on the slide. The operation of the system involved injecting a flow of clean water into the reactor causing the dissolution of the slightly soluble acid into the bulk fluid. The average mass transfer coefficients of the system under different hydrodynamic conditions ( $420 < Re < 5,300$ ) and at 25°C were determined by measuring the concentrations of dissolved benzoic acid in the outlet stream once steady state was reached. The concentration of benzoic acid was determined via a UV spectrophotometer (UV-Mini 1240, Shimadzu) at 231 nm. CFD simulations of the studied system were performed utilizing the three different hydrodynamic models and a comparison of modeling prediction of mass transfer with the experimental results was made.

The analysis of radiation field modeling involved solving the RTE using the finite-volume (FV) discrete ordinate (DO) method (included in Fluent) and its comparison against an analytical solution of a simple emission source case. Some of the advantages of the FV-DO method are that it automatically allows the conservation of radiant energy and that the RTE is integrated over both the control angle and the control volume (Pareek & Adesina 2004; Fluent-Inc. 2005). The radiation

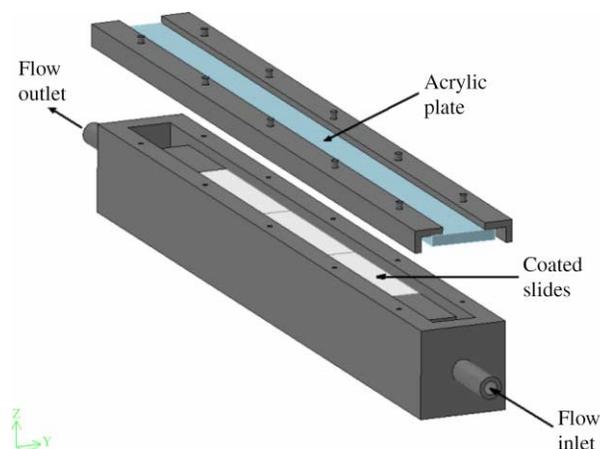


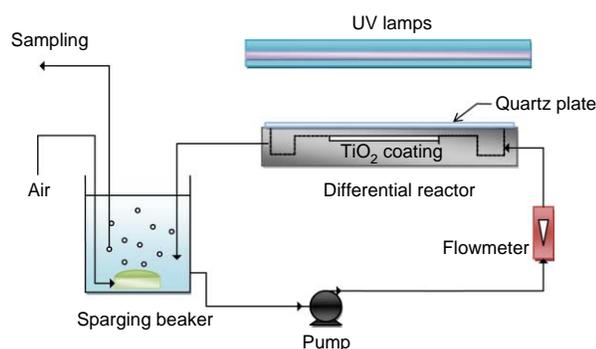
Figure 1 | Schematic of the differential reactor used in the mass transfer experiments.

field generated from an emitting disc (diameter = 10 cm and radiant emittance = 10 W/m<sup>2</sup>) was analytically solved and numerically estimated for points along a perpendicular axis from the center of the disc. The transmitting medium was considered homogeneous, with no scattering or emission, but different absorption coefficients ( $a$ ) were studied. Simulations of the analyzed system were performed and compared with the analytical results.

A first order heterogeneous reaction (not photocatalytic) taking place on the wall of a tubular reactor was simulated, under laminar flow regime, applying the surface reaction model available in Fluent (Fluent-Inc. 2005). The results of the simulation were compared with analytical solution found in the literature (Gill *et al.* 1975).

### Integrated CFD simulation and experimental evaluation

Finally, a CFD model that integrated the hydrodynamics, mass transfer and surface chemical reaction models was evaluated experimentally using the same differential reactor shown in Figure 1. However, for this stage the acrylic plate and the benzoic acid coated glass slides were substituted by a diffused quartz plate and a composite nano-size sol-gel TiO<sub>2</sub> (Keshmiri *et al.* 2004) coated slides, respectively. The reactor was irradiated by two low-pressure monochromatic mercury UV lamps (5.7 W of UV-output at 254 nm) mounted under an aluminium reflector. The lamp center-lines were located 45 mm above the quartz plate and 20 mm away from each other. The differential reactor was set up in a constantly aerated and recirculated reacting system as shown schematically in Figure 2. Formic acid (FA) was chosen as the model pollutant for the degradation studies and its concentration was determined via a Total Organic Carbon (TOC) analyzer (ASI-VCPH TOC, Shimadzu). Experimental runs at different flow rates allowed for



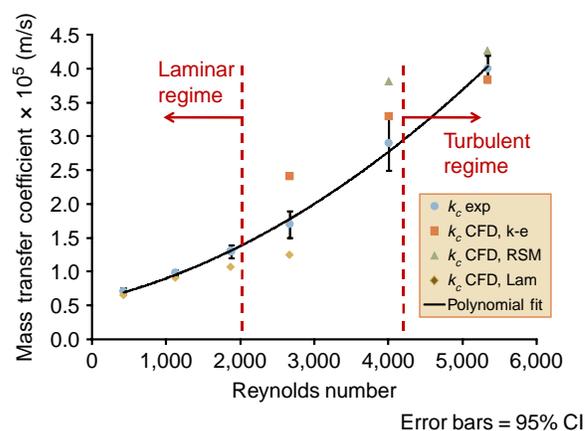
**Figure 2** | Schematic of the recirculated batch reactor used in the photocatalytic degradation studies of formic acid.

determining the intrinsic kinetics of the photocatalytic degradation of FA (at constant UV irradiation and dissolved oxygen concentration). In these runs, the FA concentration (2.5 mM initial concentration) was monitored for a period of three hours, in which a final conversion of at least 50% was achieved. The reaction rate constants for each set of experimental conditions were estimated by fitting the concentration-time data using an optimization method for non-linear parameter estimation in ordinary differential equation models (Gauss-Newton). Also, the results were compared with those of simulation using the integrated CFD model.

## RESULTS AND DISCUSSION

### Evaluation of the hydrodynamic models for mass transfer modeling

The data generated in the experiments performed with the differential reactor equipped with the glass slides coated with benzoic acid were used to calculate the average mass transfer coefficients ( $k_c$ ) of the system. The mass transfer coefficients, presented in Figure 3, were calculated by computing a mass balance over the system. As expected, the experimental average mass transfer coefficients increased with increasing the flow rate over the studied range. It is important to note that the range analyzed covered the hydrodynamic conditions corresponding to the laminar, transition, and turbulent regimes. CFD simulations of the system were carried out using the three studied hydrodynamic models (Lam, R k- $\epsilon$  and RSM) and the results are also presented in Figure 3. Good agreement was obtained for the data with  $Re < 2,000$  or  $> 5,000$ , i.e. those



**Figure 3** | Average mass transfer coefficients ( $k_c$ ) of benzoic acid in the differential reactor: experimental and simulation results.

flows that were either in completely laminar or in completely turbulent regime. These results were expected since the turbulence models studied (RSM and R k- $\epsilon$ ) are applicable only when modeling completely turbulent flows. Since both turbulence models predicted accurately the mass transfer coefficient of the experimental runs under turbulent flow regime, the use of any of them in the integrated CFD simulation tool is supported. In a separate study, further research has been performed utilizing other turbulence models, reactor configurations and geometries, as well as a wider range of flow rates, for obtaining more comprehensive conclusions on the performance of turbulence models for predicting liquid-wall mass transfer (Duran *et al.* 2009b).

### Evaluation of the FV-DO method with the analytical solution of an emitting disc

The fluence rate ( $G$ ) in a point  $P$  located at a distance  $z$  perpendicular to the center of a radiation emitting disc (see Figure 4) can be calculated as follows. By definition, the fluence rate can be computed as (Cassano *et al.* 1995):

$$G = \int_{\Omega=4\pi} I d\Omega = \iint_{\phi, \theta} I \sin \theta d\theta d\phi \quad (1)$$

where  $I$  is the specific intensity,  $\Omega$  is the solid angle, and  $\theta$  and  $\phi$  are spherical coordinates. To calculate the contribution of an infinitesimal element of the disc located at a distance  $\rho$  from point  $P$  to the total fluence rate, this element can be considered as a point source emitter. The intensity coming from a point source emitter in a transmitting and absorbing medium (homogeneous, with no scattering or emission) decays exponentially with the

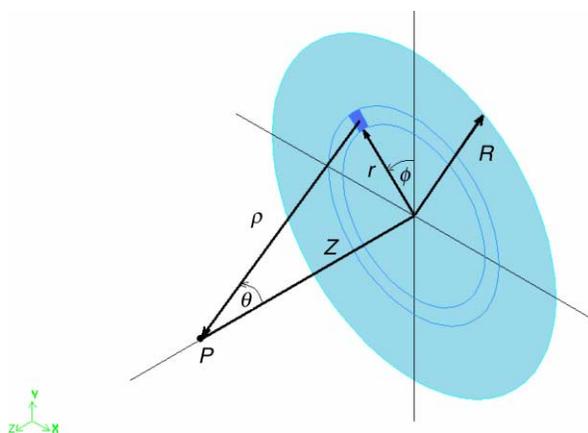


Figure 4 | Geometry of definition for the calculation of the fluence rate in a point located perpendicular to the center of an emitting disc.

distance as:

$$I = I_0 e^{-a\rho} \quad (2)$$

where  $I_0$  is the specific intensity at the source and  $a$  is the absorption coefficient of the medium. Combining Equations (1) and (2), defining the integration limits, and recognizing that  $\rho = z/\cos \theta$ , the following is obtained for the fluence rate:

$$G = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\arctan(R/z)} I_0 e^{-(az/\cos \theta)} \sin \theta d\theta d\phi \quad (3)$$

The solution of Equation (3) is:

$$G = 2\pi I_0 \left[ -e^{-az \sec(\arctan(R/z))} \cos(\arctan(R/z)) - az E_i(-az) E_i(-az \sec(\arctan(R/z))) + e^{-az} + az E_i(-az) \right] \quad (4)$$

where  $E_i$  is the exponential integral function. Using Equation (4), and computing the exponential integral function with a power series, the fluence rate values of the radiation field along the centered perpendicular axis are estimated. Figure 5 presents the results of the analytical solution compared with the simulated fluence rates using the finite-volume DO method available in the CFD software. For the three absorption coefficients of the medium that were analyzed, there was an excellent agreement between the analytical and simulation results, demonstrating the promising potentials of the finite-volume DO method in the CFD-based simulation tool being developed.

### Evaluation of surface reaction model with an exact solution

Gill *et al.* (1975) obtained an exact solution for the concentration profiles in laminar flow reactors with first-order

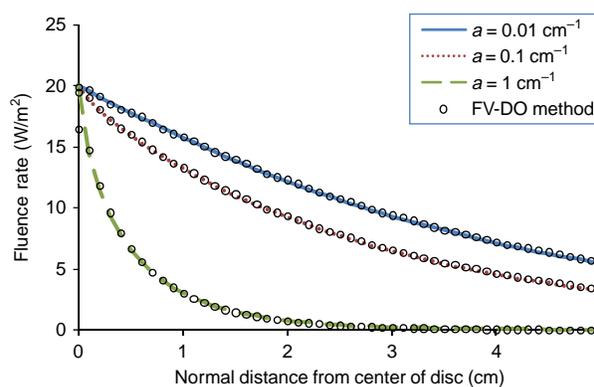
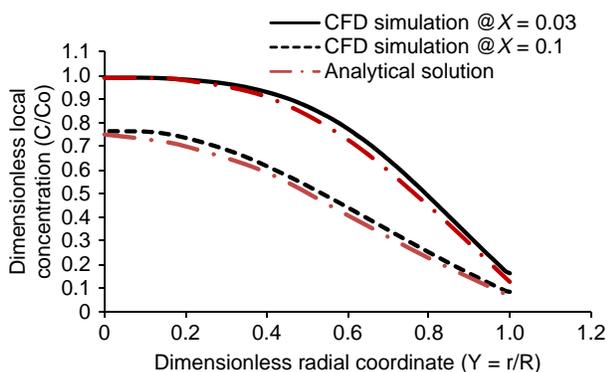


Figure 5 | Fluence rates along the perpendicular axis from the center of an emitting disc in a transmitting medium with different absorption coefficients ( $a$ ).



**Figure 6** | Radial distributions of dimensionless local concentration at dimensionless axial distances  $X = 0.03$  and  $0.1$  with  $\beta = 10$  in a wall tubular reactor.

reactions at the wall. The solution reported by Gill *et al.* (1975) were compared with the results of CFD simulations for the specific case of  $\beta = 10$ ,  $X = 0.03$  and  $X = 0.1$ . These parameters are defined as

$$\beta = \frac{k_s R}{D} \quad (5)$$

$$X = \frac{Dx}{R^2 u_0} \quad (6)$$

where  $k_s$  is the reaction rate constant per unit surface,  $R$  is the radius,  $D$  is the molecular diffusion coefficient,  $x$  is the axial coordinate, and  $u_0$  is the axial velocity at the centerline of the tube. As it can be seen in Figure 6, the exact solution results and the CFD simulations showed excellent agreement.

More research on the evaluation of the surface reaction model under laminar, transitional and turbulent flow regime has been presented elsewhere (Duran *et al.* 2009a).

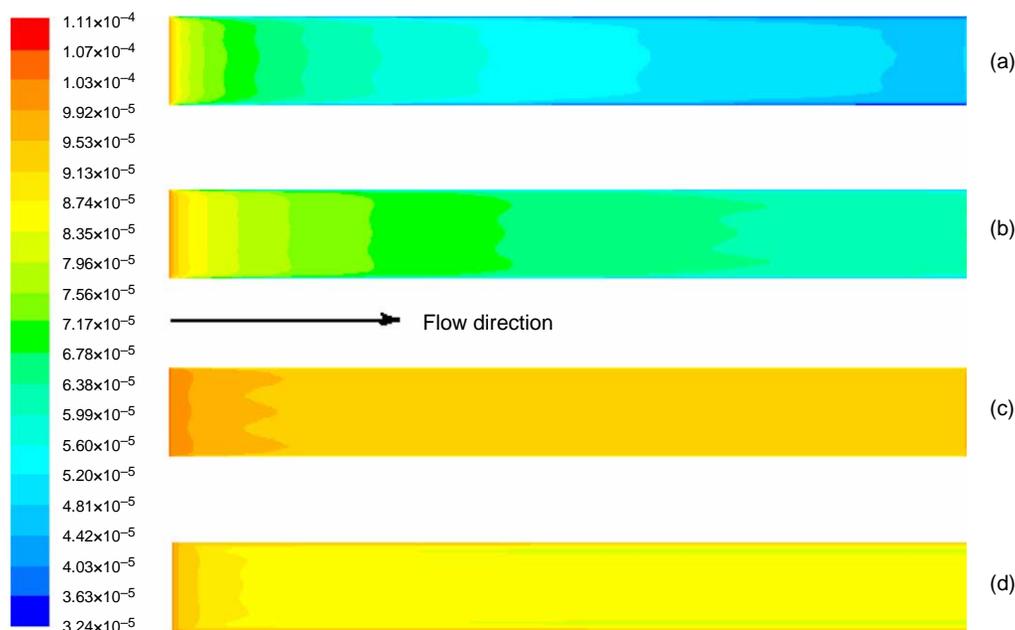
### Evaluation of the integrated CFD model simulating an immobilized photocatalytic reactor

CFD simulations of the UV-radiation field in the system utilized in the experiments demonstrated that the irradiance over the quartz plate (and consequently over the coated slides) is fairly uniform. Figure 7 shows the results obtained using the superficial emission model (Cassano *et al.* 1995) as boundary condition for the tubular lamps. The average value of irradiance computed for the analyzed area was  $107 \text{ W/m}^2$  with deviations no greater than 10%. Based on these results and considering 5% of radiation loss due to reflection in the quartz plate, the irradiance across the whole photocatalytic area was assumed constant at  $102 \text{ W/m}^2$  ( $2.17 \times 10^{-4} \text{ Einstein s}^{-1} \text{ m}^{-2}$ ).

For determining the intrinsic kinetics of the immobilized photocatalytic reaction, it was necessary to make sure that the reaction was not affected by mass transfer limitation. In this sense, several experimental runs using different flow rates were made to find proper operating conditions. It was found that at  $\text{Re} > 2,600$  no mass transfer limitation existed in the system and under those conditions, pseudo-first-order kinetics with an intrinsic surface reaction rate constant of  $8.51 \times 10^{-6} \text{ m/s}$  (equivalent to  $0.17 \text{ min}^{-1}$ ) was determined. This result is in accordance with the literature since photocatalytic reactions of diluted solutions are commonly reported to have pseudo-first-order kinetics (Herrmann 2005). Since the irradiance over the photocatalyst was assumed constant, so as the dissolved oxygen concentration in the solution, the kinetic rate equation of the surface photocatalytic oxidation of FA ( $-r_{\text{FA}}^{\text{p}}$ ) was considered to depend only



**Figure 7** | UV irradiance ( $\text{W/m}^2$ ) computed by the CFD simulation on the quartz plate above the catalyst-coated slides.



**Figure 8** | Contours of the mass fraction of formic acid at the photocatalyst surface as computed with different hydrodynamic models for the system operating at various Re numbers: (a) Laminar model at Re = 422, (b) Laminar model at Re = 1123, (c) R k-ε at Re = 5,337, (d) RSM at Re = 5,337.

on the concentration of FA ( $C_{FA}$ ) according to:

$$-r''_{FA} = 8.51 \times 10^{-6} \text{ m/s} \cdot C_{FA} \quad (7)$$

Utilizing Equation (7) as boundary condition at the photocatalyst coated surface, CFD simulations of the differential reactor operating under the same hydrodynamic conditions of the experimental runs were performed. Figure 8 shows the contours of the mass fraction of formic acid at the photocatalyst surface as computed with different hydrodynamic models. The results present higher concentration decrease of FA along the photocatalyst-coated slides as Re decreases in the system. This behavior can be explained as a result of the longer contact time of the fluid with the photocatalytic surface. Also, three peaks in the transversal profile of FA concentration along the catalyst plates are noticeable in all the simulations performed. These higher concentration regions are consequence of

higher fluid velocity gradients in these zones. This condition was verified through analysis of the velocity field in the system which showed a recirculation zone at the channel entrance that induces these three high velocity gradient regions in the flow distribution.

By knowing the experimental rate constant (apparent or intrinsic) of a first-order reaction taking place in the differential reactor it is possible to estimate the conversion ( $\xi$ ) for one pass in the reactor using:

$$\xi = 1 - e^{-k\tau} \quad (8)$$

where  $k$  is the volumetric reaction rate constant and  $\tau$  is the space time (defined as the volume of reactor coated with catalyst divided by the volumetric feed rate of reactants). In this way, the conversions for one pass for the experimental runs performed were estimated and are reported in Table 1. These values are compared with the corresponding

**Table 1** | One-pass experimental conversion estimations versus CFD-based model predictions

Re	$k$ (min <sup>-1</sup> )	Hydrodynamic model	Experimental conversion of FA (%)	CFD computed conversion of FA (%)	Relative error (%)
422	0.109	Lam	0.580	0.561	3.3
1,123	0.125	Lam	0.251	0.246	2.0
5,337	0.170	R k-ε	0.072	0.063	12.5
5,337	0.170	RSM	0.072	0.066	8.3

conversions per pass computed by the CFD simulations. As reported in Table 1, the relative difference between the results for the case of laminar flow is minimal, whereas in the case of turbulent flow it is in the order of 10% for both turbulence models.

## CONCLUSIONS

- In terms of mass transfer modeling capabilities, the analyzed hydrodynamic models performed well. It was also evident that these models do not perform well simulating fluids under transition flow regime.
- The FV-DO demonstrated promising potentials for being used for simulating radiation distribution in photocatalytic reactors; nevertheless, further evaluations with experimental data are needed.
- The photocatalytic degradation of formic acid followed pseudo-first order kinetics under the operating conditions used in this investigation.
- The CFD simulations of the immobilized photoreactor showed good agreement with analytical and experimental results.
- The approach presented here was demonstrated to be an effective way for integrating a CFD model for simulating immobilized photocatalytic reactors.

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