Computational modeling of UV photocatalytic reactors: model development, evaluation, and application
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ABSTRACT
A computational model for simulating the performance of immobilized photocatalytic ultraviolet (UV) reactors used for water treatment was developed, experimentally evaluated, and applied to reactor design optimization. This model integrated hydrodynamics, species mass transport, chemical reaction kinetics, and irradiance distribution within the reactor. Among different hydrodynamic models evaluated against experimental data, the laminar, Abe–Kondoh–Nagano, and Reynolds stress turbulence models showed better performance (errors <5%, 12%, and 20%, respectively) in terms of external mass transfer and surface reaction prediction capabilities at different hydrodynamic conditions. A developed finite-volume-based UV lamp emission model was able to predict, with errors of less than 5%, near- and far-field irradiance measurements. Combining all these models, the integrated computational fluid dynamics (CFD)-based model was able to successfully predict the photocatalytic degradation rate of model pollutants (benzoic acid and 2,4-D) in various configurations of annular reactors and UV lamp sizes, over a wide range of hydrodynamic conditions (350 < Re < 11,000). In addition, the integrated model was used in combination with a Taguchi design of experiments method to perform reactor design optimization. Following this approach, a base case annular reactor design was modified to obtain a 50% more efficient design.

Key words | advanced oxidation, CFD modeling, UV photocatalytic reactor, water treatment

NOTATION

\( E_{ex} \) external effectiveness factor
\( f^e \) emission (source) term, W m\(^{-3}\) sr\(^{-1}\)
\( J_i \) diffusive flux of species \( i \), kg s\(^{-1}\) m\(^{-2}\)
\( L \) photon radiance, W m\(^{-2}\) sr\(^{-1}\)
\( m_i \) mass fraction of species \( i \)
\( m'_i \) fluctuating mass fraction of species \( i \)
\( \hat{n} \) unit vector normal to the surface
\( p \) phase function for the in-scattering of photons
\( P \) pressure, Pa
\( r \) position vector, m
\( R^S_i \) surface rate of production/depletion of species \( i \), kg s\(^{-1}\) m\(^{-2}\)
\( \text{Re} \) Reynolds number
\( \text{Re}_\text{w} \) wall-distance-based turbulent Reynolds number
\( s \) propagation direction vector, m
\( s' \) scattering direction vector, m
\( u \) fluctuating flow velocity, m s\(^{-1}\)
\( U \) velocity, m s\(^{-1}\)
\( y^+ \) non-dimensional distance from the wall

GREEK LETTERS

\( \kappa \) absorption coefficient, m\(^{-1}\)
\( \rho \) density, kg m\(^{-3}\)
\( \sigma \) scattering coefficient, m\(^{-1}\)

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\( \tau \) viscous stress tensor, N m\(^{-2}\)  
\( \Omega' \) solid angle about the scattering direction vector \( \vec{s} \), sr

**INTRODUCTION**

The contamination of drinking water with toxic substances has become a major concern worldwide. Beyond the impact of population growth, the contamination of water has been rising as a result of industrial development and agricultural activities. Pesticides (e.g. atrazine, metolachlor, 2,4-D) from agricultural field run-offs and other groundwater contaminants are now frequently found in water resources (Jasim et al. 2006; Na et al. 2006; Pasternak 2006). Also, pharmaceuticals and personal care products have been identified in outflows from sewage treatment plants and surface waters in Canada, Costa Rica, and worldwide (Ternes 1998; Boyd et al. 2003; Spongberg et al. 2011).

In response to the current and projected long-term demand for clean drinking water, significant changes in management and treatment practices are taking place. Federal standards and provincial regulations for surface and ground water sources are becoming more stringent (BC Ministry of Health 2003; Health Canada 2014). Also, an increasing number of new treatment technologies are being developed and evaluated. One such group of technologies is advanced oxidation processes (AOPs) which have many inherent advantages for water treatment (Legrini 2005; de Lasa et al. 2014). A high yield of \(-\text{OH}\) and other reactive species, AOPs can offer significant removal of contaminants; this is in addition to the inactivation of pathogens including protozoa and viruses.

A particularly attractive advanced oxidation technology is heterogeneous photocatalysis. Photocatalytic processes involve the use of nanostructured photocatalyst materials, predominantly titanium dioxide (\( \text{TiO}_2 \)), activated by ultraviolet (UV) irradiation. In the \( \text{TiO}_2 \) particles, the absorbed UV photons generate energetic electron-hole pairs which interact with the surrounding medium-inducing redox reactions that result in the decomposition of the contaminants. More than 1200 different organic pollutants have been reported as degraded using this technology (Adesina 2004). The appeal of this technology lies in its capability to potentially mineralize the pollutants into harmless compounds (carbon dioxide, water, and mineral acids) (Ollis et al. 1991) without producing any other waste streams. In addition, photocatalysis does not require the use of strong oxidizing chemicals of potentially hazardous nature, e.g. \( \text{H}_2\text{O}_2 \) or \( \text{O}_3 \) (Mills et al. 1993), and its operation is under mild conditions near ambient temperature and pressure. However, despite the many advantages of photocatalysis and the extensive laboratory research done in this field, there are still several technical constraints, ranging from catalyst efficiency to reactor design and process optimization, that stymie the development of large-scale photocatalytic oxidation reactors for water treatment. Among others, some of the challenges that need to be addressed are: (i) catalyst improvements for a high photo-efficiency that can utilize wider solar spectra; (ii) catalyst immobilization strategies to provide a cost-effective solid-liquid separation; and (iii) development of proper models, simulation tools and scale-up strategies for adequate reactor design (Li Puma & Yue 1998; Mukherjee & Ray 1999; Adesina 2004; Chong et al. 2010).

Two major configurations of photocatalytic reactors have been employed in photodegradation studies: those with the photocatalyst particles suspended (slurry reactors); and those with the photocatalyst immobilized in layers to a reactor surface (immobilized reactors) (Hoffmann et al. 1995; de Lasa et al. 2005). The slurry reactors are efficient due to the large surface area of catalyst available for the reaction and the efficient mass transfer within such systems; however, the need for a post-process separation of the nanosize semiconductor particles from the fluid adds to the complexity of the overall treatment process and decreases the economic viability and commercialization of slurry reactors. On the other hand, supported catalyst configurations eliminate the need for photocatalyst recovery, but some limitations such as low-surface area-to-volume ratios and significant influence of external mass transfer lessen the efficiency of such treatment systems. Nevertheless, many authors agree that the immobilized photocatalyst configuration is a promising alternative for an efficient reactor scalable to industrial sizes (Dijkstra et al. 2002; McMurray et al. 2004; Mehrotra et al. 2005; Krýša et al. 2006).

Owing to the complexity of the UV reactors and the interaction of many phenomena, the design optimization
of these systems can best be realized through the development of sophisticated models. A number of modeling techniques and approaches have been used to simulate UV photocatalytic reactor performance for water treatment. The modeling of photocatalytic reactors requires the resolution of the momentum and mass-transfer equations, the radiation transfer equation in the fluid phases and across the flow physical boundaries, and the heterogeneous photocatalytic reaction kinetics. The resolution of this set of equations might be a complicated task, not only because of the mathematical complexity of the equations, but also because in many systems they are strongly coupled. Because of this fact, in many of the models reported in the literature (e.g. Cassano & Alfano 2000; Romero et al. 2003; Li Puma et al. 2004), simplifying assumptions in one or more of these equations have needed to be made in order to simplify the mathematical solutions. However, the resolution of the governing equations under hydrodynamic simplification assumptions (e.g. plug-flow, perfectly mixed or fully developed laminar regimes) limits the applicability of the model to those simple systems where those conditions apply. In order to properly predict the behavior of the photoreactor under different operating conditions and scales, the rigorous solution of the hydrodynamics of the system is desired. In this sense, the development of models based on computational fluid dynamics (CFD) provides valuable tools for the design, optimization, and scale-up of photocatalytic reactors.

Several CFD models have been proposed and used for the simulation of photocatalytic reactors. For example, Pareek et al. (2003) and Trujillo et al. (2007) simulated TiO₂ bubble column photocatalytic reactors (with suspended and immobilized photocatalyst, respectively); Taghipour & Mohseni (2005), Castrillón et al. (2006), and Jarandehei & Visscher (2009) used CFD to simulate immobilized photocatalytic reactors for air treatment; Periyathamby & Ray (1999), Sengupta et al. (2001), and Denny et al. (2009) simulated photocatalytic water treatment systems. Unfortunately, many of these models and their components were not adequately evaluated against experimental data.

This article summarizes the development, evaluation, and application of an integrated model for the performance evaluation of immobilized UV photocatalytic reactors (Duran et al. 2009, 2010a, b, 2011a, b). The model integrated hydrodynamics, species mass transport, surface chemical reaction kinetics, and irradiance distribution within the reactor. Each of these aspects was individually analyzed and experimentally evaluated against data generated in our laboratory. As a result of this evaluation, proper turbulence and UV emission models were identified. Moreover, the integrated model was successfully evaluated in prototype photocatalytic reactors degrading model pollutants and was used to perform reactor design optimization.

INTEGRATED MODEL

For the developed model, the photoreactor has the photocatalyst immobilized on its wall; as a result, it was assumed that the fluid was Newtonian, incompressible, isothermal, non-reactive, with constant physical properties, and under turbulent steady-state flow. Under these assumptions and following the Reynolds averaged Navier–Stokes (RANS) turbulence modeling approach (Ranade 2002), the CFD model involves solving the continuity Equation (1), RANS Equation (2) and time-average conservation of species Equation (3), which are expressed as

\[ \nabla \cdot (\mathbf{U}) = 0 \]  
\[ \nabla \cdot (\rho \mathbf{U} \mathbf{U} + \rho \mathbf{m}) = - \nabla P - \nabla \cdot \tau \]  
\[ \nabla \cdot (\rho \mathbf{U} \mathbf{m}_i + \rho \mathbf{u}\mathbf{m}_i) = - \nabla \cdot \mathbf{J}_i \]  

where the overbar indicates a time-averaged value, \( \rho \) is density, \( \mathbf{U} \) is velocity, \( P \) is pressure, \( \tau \) is viscous stress tensor, \( m_i \) is mass fraction of species \( i \), \( \mathbf{J}_i \) is diffusive flux of species \( i \), and \( \mathbf{u} \) and \( m'_i \) are fluctuating flow velocity and mass fraction of species \( i \), respectively. The specification of the apparent stress gradients was made by means of a turbulence model (Wilcox 2006). Since no turbulence model is universally accepted to be superior for all conditions, four hydrodynamic turbulence models were evaluated against experimental results: the widely used standard \( k-\epsilon \) model (S \( k-\epsilon \)) (Lauder & Spalding 1974); the realizible \( k-\epsilon \) model (R \( k-\epsilon \)) (Shih et al. 1995); the Reynolds stress model (RSM) (Lauder et al. 1975); and the low Reynolds number
$k$–$\epsilon$ turbulence model developed by Abe–Kondoh–Nagano (AKN) (Abe et al. 1994). Other turbulence models (e.g. RNG $k$–$\epsilon$ and SST $k$–$\omega$) were also evaluated; however, their results are not shown since their performances were not better than the ones presented here. When modeling laminar flow, similar equations to (1)–(3), but excluding the apparent stress gradients associated with turbulent motion, were solved.

The UV radiation field inside photocatalytic reactors can be computed by solving the general radiative (photon) transfer equation (RTE) (Cassano et al. 1995). For monochromatic radiation, the RTE is defined as

$$\frac{dL(\vec{r}, \vec{s})}{ds} + (\kappa + \sigma)L(\vec{r}, \vec{s}) = f^e(\vec{r}) + \frac{\sigma}{4\pi} \int L(\vec{r}, \vec{s}')p(\vec{s}' \rightarrow \vec{s})d\Omega'$$  \hspace{1cm} (4)

where $L$ is the photon radiance, $\vec{r}$ is the position vector, $\vec{s}$ is the propagation direction vector, $s$ is the path length, $\kappa$ is the absorption coefficient, $\sigma$ is the scattering coefficient, $f^e$ is the emission (source) term, $p$ is the phase function for the in-scattering of photons, and $\Omega'$ is the solid angle about the scattering direction vector $\vec{s}'$. For the immobilized photocatalytic reactors investigated here, this RTE was solved using the finite-volume method (Duran et al. 2010b). The RTE equation was applied to the aqueous phase fluid where $\kappa = \sigma = f^e = p = 0$, and to the UV emitting lamp which was considered part of the computational domain. As part of the boundary conditions definition, all the incident radiation reaching the TiO$_2$-coated walls was assumed to be absorbed; therefore, no radiation was reflected or transmitted. This assumption was valid in our system since low-pressure Hg lamps and thick ($\approx 5$–12 $\mu$m) TiO$_2$-coating layers were used. Low-pressure Hg lamps emit basically monochromatic radiation at 254 nm. For this radiation, the absorption coefficient on TiO$_2$ is reported as $5.1 \times 10^7$ m$^{-1}$ (Mills et al., 1993), implying that 99% of the incident radiation will be absorbed within the first 90 nm of the catalyst layer.

The surface reaction taking place at the photocatalyst-coated walls was considered defining the boundary condition

$$J_i \cdot \vec{n} = R_i^S$$  \hspace{1cm} (5)

where $\vec{n}$ is the unit vector normal to the surface, and $R_i^S$ is the rate of production/depletion of species $i$ arising from the surface. The surface reaction kinetics for each analyzed case was determined in separate studies using a flat plate differential reactor under controlled conditions (Duran et al. 2010a, 2011a, b). The overall reaction was treated as a surface reaction by expressing the overall degradation reaction rate (free of external mass transfer limitation) in per unit area of coated photocatalyst. For the case of photocatalytic reactions, this overall reaction rate is a function of the concentration of the reacting species and UV irradiance at the liquid–catalyst layer interface, and of a series of properties inherent to the photocatalyst layer (i.e. UV absorption coefficient, thickness, tortuosity, porosity, etc.) (Herz 2004; Camera-Roda & Santarelli 2007).

The commercial mesh generator Gambit 2.2.30 was used to create the grid, and CFD code Fluent 6.3.26 was used to perform the simulations. The segregated steady-state solver was used to solve the governing equations. The second-order upwind discretization scheme was employed except for pressure for which the standard scheme was selected. The SIMPLE algorithm was chosen for the pressure–velocity coupling. An angular discretization of 40 divisions was used for solving the RTE. Convergence of the numerical solution was assured by monitoring the scaled residuals to a criterion of at least $10^{-4}$ for the continuity and momentum, and $10^{-6}$ for the concentration and radiation variables. Additionally, the variation of proper magnitudes (e.g. velocity, concentration, and fluence rate) at several points of the computational domain was used as an indicator of convergence. The utilized grids had approximately 1.5 million volume cells and they were verified to give mesh-independent results. A boundary-layer mesh was set up in the region where the surface reaction took place. $y^+$ (non-dimensional distance from the wall) $<0.5$ at the wall adjacent cell and at least 10 cells within the viscosity affected near-wall region ($Re < 200$) were defined.

Taking advantage of the facts that in the studied cases the velocity and radiation fields did not interact, and that the photocatalytic reaction development did not affect these fields, the CFD model was solved in three consecutive steps. First, the equations of conservation of mass and momentum were solved for getting the flow field across the computational domain. Then, the velocity values were kept
frozen’ and the RTE was solved for obtaining the radiation field (when needed). Finally, keeping ‘frozen’ the converged flow and radiation field solutions, the conservation of species equation was solved for computing the species concentration maps within the system. This solving strategy saves computation time and brings stability to the solution.

**EXPERIMENTAL STUDIES**

For this investigation, the annular reactor geometry was utilized as model geometry, taking into account its simplicity and efficiency for photocatalytic applications. This configuration is one of the most commonly found commercial photoreactor geometries in the market. Two frequently used annular UV reactor configurations were studied, with the inlet normal (U-shape) and parallel (L-shape) to the main reactor body. The photocatalyst coatings were made on the internal surface of the outer reactor tube, facing the UV lamps (low-pressure Hg). The photocatalyst utilized in the experiments was a composite sol–gel TiO₂ (Keshmiri et al. 2004) deposited on the desired surfaces (previously sand-blasted to improve adhesion) using a dip-coating technique which produced thick (≈5–12 μm) TiO₂ coatings. A representation of the reactor geometry of parallel inlet design is shown in Figure 1. The actual reactor structures used in the experiments were made of PVC and included a union that allowed for fitting previously sand-blasted glass tubes coated on the inner wall (see Figure 2).

For the studies of external mass transfer (Duran et al. 2009), benzoic acid (Fisher Scientific certified ACS) was coated on the wall and its dissolution into the bulk fluid was monitored over time. Using these data, the average mass transfer coefficients were determined and compared with the CFD-predicted values obtained utilizing different turbulence models. The hydrodynamic models were evaluated in a wide range of hydrodynamic conditions (500 < Re < 11,000) which include laminar, transitional, and turbulent flow within the reactor annulus. Different near-wall models were also considered in the evaluation.

Surface reaction was investigated with the catalytic decomposition of hydrogen peroxide (Fisher Scientific certified ACS) over a Mn/Al oxide coating (Duran et al. 2009a). The reactor was tested within a range of flow rates corresponding to 550 < Re < 11,000 and intrinsic reaction rate constants of 5 × 10⁻⁵ to 1 m/s. The selected range of flow rates and reaction rate constants covered the spectrum of reactor operation from completely surface reaction rate limited to entirely mass transfer limited. Apparent reaction rates obtained experimentally were compared with those obtained using the CFD model.

The radiation field model was evaluated against far- and near-field irradiance measurements for a low-pressure Hg lamp (GPH357T5L/4P, Light Sources, Inc.). For the far-field evaluation, the irradiance was measured at different radial angles from the UV-lamp using a calibrated research radiometer (IL1700, SED240 detector, NS254 filter, International Light). The near-field evaluation was performed using an annular reactor in which both tubes were made of quartz (see Figure 3). This setup allowed measuring the irradiance at specific axial locations around the reactor’s outer wall using a potassium ferrioxalate actinometer that ran inside a
PVC annular jacket. Several lamp emission models, computed utilizing a CFD-based approach, were evaluated against the far- and near-field experimental data (Duran et al. 2010b).

The experimental evaluation of the integrated CFD model was performed using various configurations of annular reactors and UV lamp sizes, over a wide range of hydrodynamic conditions ($350 < Re < 11,000$) (Duran et al. 2011a, b). Benzoic acid and 2,4-D were employed as model pollutants. The concentration of both chemicals was directly analyzed with a Waters 2695 HPLC. Apparent reaction rates obtained experimentally were compared with those obtained using different turbulence models.

The application of the developed CFD-based model in conceptual design of photocatalytic reactors was also explored (Duran et al. 2011b). For this, an optimization design approach which combines CFD modeling and the Taguchi design of experiments method is presented. The effect of different geometrical factors and mass transfer enhancement elements on the pollutant degradation achieved in an annular photocatalytic reactor was examined. The CFD model was experimentally evaluated against degradation data of 2,4-D (model pollutant).

**RESULTS AND DISCUSSION**

Hydrodynamic and mass transfer modeling

In order to correctly predict turbulent fluid flow and mass transfer within a water purification photoreactor, proper turbulence models need to be used. In our research group, Sozzi & Taghipour (2006) performed a detailed CFD simulation of the hydrodynamics of L- and U-shape annular photoreactor configurations, and evaluated the results with the velocity profiles from particle image velocimetry (PIV). Under the evaluated operational conditions, the realizable $k$-$\epsilon$ and the RSM turbulence models displayed the best overall match to the experimental PIV measurements. Even though this investigation brought an important outcome in terms of recommending appropriate turbulence models for computing the fluid velocity field inside annular reactors, further investigation was needed to assess their applicability to mass transfer modeling. Since the wall-liquid mass transfer phenomenon takes place almost completely within the near-wall region, near-wall modeling significantly impacts the validity of numerical solutions.

Different hydrodynamic models including the standard $k$-$\epsilon$ ($S$ $k$-$\epsilon$), realizable $k$-$\epsilon$ ($R$ $k$-$\epsilon$), Reynolds stresses (RSM), and the AKN (a low Reynolds number turbulence model) were evaluated against experimental data in terms of their mass transfer prediction capabilities. When analyzing the CFD hydrodynamics simulations, it was found that all the turbulence models under evaluation, indistinctly of the near-wall region model they utilized, predicted comparable core flow hydrodynamics which were in agreement with previous PIV investigations of similar systems (Sozzi & Taghipour 2006). However, the mass transfer measurements demonstrated that only the laminar, AKN, and RSM models were able to closely predict mass transfer in both annular reactors (see Figure 4). The average prediction errors were estimated as Laminar = 6%, AKN = 16%, RSM = 19%, R $k$-$\epsilon$ = 32%, and S $k$-$\epsilon$ = 35%. The evaluated turbulence models to some
extent underestimated the global mass transfer rates associated with all the flow rates, but more insight on this behavior was obtained when the mass transfer prediction capabilities of the models were analyzed at three individual sections of the reactor (A: inlet, B: middle, C: outlet, as shown in Figure 5(a)). Figure 5(b) shows the experimental and predicted average mass transfer coefficients at sections A, B, and C, obtained for the U-shape reactor operating at a flow rate corresponding to Re = 8000. As can be seen, all the turbulence models underestimated the mass transfer in section A (average model underestimations = 34%), but the agreement between the results in sections B and C was quite close (11% and 7%, respectively). This result suggests that the disagreement found for the overall mass transfer in the reactor is due to the underprediction computed by the turbulence models at section A. One possible reason for this discrepancy is that the turbulence models were not able to capture all the small eddies generated at the inlet, due to the sudden expansion of the flow. However, once the flow redeveloped through sections B and C, turbulence decreased and the models performed better. Over all, the AKN model performed better for transitional and turbulent flow conditions (error < 12%). Low Reynolds number models have been consistently reported to model better near-wall region processes (Wang et al. 1996; Wang & Mujumdar 2005).

Surface reaction modeling

Most of the research carried out to date on modeling the coated-wall tubular and annular reactors has dealt with gaseous systems under laminar flow regime. However, the applications of this reacting system in emerging water purification processes (e.g. photocatalytic degradation of pollutants, residual H₂O₂ decomposition), in membrane reactors, and in some other technologies warrant investigation of proper models for simulating liquid systems operating under either laminar or turbulent flow conditions. Moreover, since the efficiency of coated-wall systems with surface reaction is prone to mass transfer limitation, it is essential that these models perform correctly over the whole spectrum of possible operating conditions: from completely mass transport limited to surface reaction rate limited. The performance of different turbulence and near-wall models in predicting the kinetic
behavior of catalyst-coated annular reactors was examined under different diffusion limiting conditions for the catalyzed decomposition of hydrogen peroxide.

Figure 6 shows the apparent reaction rate constants predicted by CFD for an L-shape annular reactor using different turbulence models. It is clear that increasing mass transfer limitation leads to poorer predictions by CFD with various turbulence models. Nonetheless, AKN performed relatively well (7% error), followed by RSM (9% error), and both $k$-$\epsilon$ models performed similarly for all the conditions analyzed (15% error). Based on the results obtained in the mass transfer studies, it can be derived that the performance of the models is a function of their mass transfer predicting capabilities and ultimately, the degree of mass transfer limitation in the system. A model that predicts mass transfer properly will predict accurately the surface reaction phenomenon regardless of the degree of mass transfer limitation in the system. On the other hand, a model that poorly predicts mass transfer will perform well only in reacting systems that are under surface-reaction limitation (Duran et al. 2010a).

**Radiation field modeling**

Modeling the radiation field in a given photoreactor involves solving the (photon) RTE. Many of the commercially available CFD codes include a finite-volume (FV) method that is capable of solving this equation. However, a key component in the development of a radiation field model is the definition of the lamp emission model (i.e. how UV radiation is emitted by the lamp). Several conceptual and mathematical models have been proposed in the literature (Pareek et al. 2012). Moreover, Imoberdorf et al. (2008) recently proposed a more exhaustive lamp emission model that includes the reflection and refraction effects on/in the quartz envelope, as well as the photon absorption/re-emission phenomena produced by the mercury vapor inside the lamp. Based on this model, Duran et al. (2010b) developed an FV-based UV lamp emission model (ESVERA: extensive source volumetric emission model that incorporates photon reflection, refraction, absorption, and re-emission in the lamp) which is primarily intended to be applied to the CFD simulation of UV photoreactors. Various model predictions were evaluated against far-field (measuring position located away from the lamp) and near-field (measuring position close to the lamp) irradiance measurements.

Figure 7(a) shows the far-field irradiance values measured around a UV lamp using the goniometric method (1 m away), as well as the irradiance predictions obtained using ESVERA and two other widely used extensive source emission models (superficial diffuse emission (ESDE) and volumetric emission (ESVE)). Irradiance predictions based on the ESVE model did not match the experimental data at all (81% error), indicating that ESVE does not model properly the emission pattern of the lamp, and that it should not be utilized for far-field predictions. ESDE predictions had a much closer agreement with the experimental measurements (12% error). The ESDE model considers that radiation is diffusely emitted by the lamp, implying that the real lamp emission must be to some extent similar to that of a lambertian emitter. The ESVERA irradiance predictions fitted the experimental measurements fully (1% error). It was observed that the incorporation of the photon absorption/re-emission process by the mercury vapor inside the lamp into the model adequately reproduced the diffuse radiation emission observed in the experimental measurements.

Figure 7(b) shows the measured irradiances at the reactor outer tube wall together with the model predictions using the ESDE, ESVE, and ESVERA lamp emission models. The
predictions of the models were very close to the experimental values, particularly at the central region (2% error). These results demonstrate that in the region close to the lamp, the radiation emission pattern (isotropic or diffused) has little effect on the irradiance prediction profiles. Owing to the experimental error (~5%), it is not possible to affirm whether one particular model performs better than the others.

Photocatalytic reactor performance modeling

The developed CFD model was evaluated against the performance of prototype photocatalytic reactors of various configurations and lamp sizes, over a wide range of hydrodynamic conditions (350 < Re < 11,000).

Figure 8(a) presents the local surface reaction rate distributions on the photocatalyst surface of a U-shape annular reactor operating at Re = 9000. As expected, the areas combining high-velocity gradients (and therefore, high-mass transfer coefficients) with high-UV irradiance resulted in high-surface reaction rate, whereas low-surface reaction rates were found in the areas having low-mass transport and UV irradiance. In addition, Figure 8(b) shows the corresponding local effectiveness factor ($E_{ex}$) distribution. The magnitude of $E_{ex}$ ranges from 0 to 1, indicating the relative importance of diffusion and reaction limitations. The modeling results indicate that the overall reaction rate in the photocatalytic reactor is largely limited by the rate of mass transport. In such systems, the prediction of the overall reactor performance will be
largely determined by the external mass transfer prediction capabilities of the hydrodynamic models used for the simulations. These results confirm that overall, the pollutant degradation rates in immobilized photocatalytic reactors are strongly limited by external mass transfer. Therefore, identifying areas of low-mass transfer, and finding alternatives for increasing the transport of species toward those photocatalyst-coated areas will increase the degradation rates.

The comparison of modeling and experimental data indicated that the developed CFD model was able to successfully predict the photocatalytic degradation rate of model pollutants (benzoic acid and 2,4-D) in the analyzed reactors (Duran et al. 2011a, b). Overall, among the analyzed turbulence models, the AKN model presented better prediction of the degradation rate in the photocatalytic reactors (prediction errors < 10%). The better performance of the AKN model can be attributed to the better mass transfer prediction capability of this model, due largely to the impact that near-wall region modeling has on interfacial phenomena predictions. The laminar model was also able to accurately predict the performance of the reactors under laminar flow operation (prediction errors < 5%). Figure 9 compares the CFD model predictions using AKN and laminar models with the experimental data obtained for the photocatalytic degradation of benzoic acid and 2,4-D in a L-shape annular reactor.

Design optimization

Since the performance of immobilized photocatalytic reactors is largely limited by the rate of mass transfer of the contaminants to the photocatalyst coating, incorporating external mass transfer promoters into the design of such reactors is desirable. However, in order to be effective, these mass transfer promoters must produce turbulence very close to the wall, exactly where mass transfer limitation is.

Figure 10 presents the CFD simulation of annular reactors with two common promoters (repeated ribs on the internal wall to which mass transfer is desired, and static delta wing mixers placed in the middle of the reactor), compared with a reactor of the same dimensions but plain internal surfaces. The distribution of local mass transfer coefficients in the ribbed surface showed higher values all along the wall (55% higher), whereas the distribution in the reactor with the delta wing mixers was not much different from that of the reactor with a plain surface (1.7% higher). At the entrance, the mass transfer coefficients are particularly high due to the presence of the lamp sleeve holders. Also, in this region the flow is redirected by the lamp sleeve toward the wall producing high-velocity gradients. The better performance of the repeated ribs can be attributed to the fact that they produce turbulence within the near-wall region, while delta wings generate turbulence mainly in the core flow.

The use of repeated ribs on the TiO2-coated wall increased the photocatalytic surface reaction rate by about 50% with only 1% increase in the pressure drop (Duran et al. 2011b). In consequence, repeated ribs appear to be promising enhancement elements to be further considered in immobilized photocatalytic reactor optimization analysis.

The statistical method compared the influence of different reactor design factors (Duran et al. 2011b) and it

![Figure 9](https://iwaponline.com/wqrj/article-pdf/50/1/21/379561/wqrjc0500021.pdf)
indicated that better performance can be obtained using small outer tube diameters, large inner/outer tube diameter ratios, large (rib height)/(hydraulic diameter) ratio, and small (rib pitch)/(rib height) ratios. In addition, it was concluded that the (rib height)/(hydraulic diameter) ratio was the design parameter having the greatest impact (57%) on photoreactor performance.

**CONCLUSIONS**

A CFD model for simulating immobilized photocatalytic reactors used for water detoxification was developed and experimentally evaluated. The experimental results and computational simulations showed that the developed model could predict the benzoic acid and 2,4-D degradation rates in the analyzed photoreactors. The degree of accuracy in the prediction of the photoreactor behavior was limited by the external mass transfer prediction capability of the hydrodynamic models used. Among the analyzed turbulence models, the AKN model presented better performance which can be attributed to the large impact that near-wall region modeling has on interfacial phenomena predictions. ESVERA and diffused emission models predicted fairly well the irradiance distribution around the lamp and inside the photoreactors. The integrated model provided detailed description of the local photoreactor performance and identified the areas where enhancement can be made. The model can be applied to gain a better understanding of the reactor behavior and to design more efficient photocatalytic reactors.

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