APLICATION OF COMPUTATIONAL FLUID DYNAMICS TECHNIQUES TO THE MODELLING AND SIMULATION OF PHOTOCATALYTIC REACTORS FROM INTRINSIC KINETIC PARAMETERS

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Despite the many advantages of photocatalysis for water purification and the extensive laboratory research done in this field, including 13500 papers, reviews and reference work over the last 38 years, photocatalytic technologies for water remediation are not fully industrially developed yet. Tremendous efforts have been devoted to improve photocatalytic efficiency of TiO_2 or to the development on new photocatalytic materials. Materials improvement has been accompanied with extensive research to identify reaction mechanisms and obtain appropriate kinetic models, but there are several challenges preventing the development of this technology to the commercial scale: mass transfer limitations, catalyst deactivation, generation of intermediate products and by-products and especially low quantum efficiency of the process, requiring further developments on the optimization of the materials, the reactors and the light sources.

The modelling of photocatalytic reactors is one of the challenges in the scaling-up process and industrial development of this technology. Rigorous kinetic description of the photocatalytic process requires the explicit inclusion in the model of the photon absorption rate. However, due to the intrinsic nature of photoactivated processes, it is not possible to achieve a uniform light intensity along the whole reactor volume. Therefore, an appropriate knowledge of the irradiance distribution inside the reactor is required through the rigorous resolution of the Radiative Transfer Equation (RTE), especially in heterogeneous media such as TiO_2 suspensions, where is present the simultaneous effect of volumetric absorption and scattering phenomena.

For this purpose, Computational Fluid Dynamics (CFD) has been shown to be a very promising tool in the design, optimization, and scaling-up of photocatalytic systems for different applications, saving time, costs and efforts. Its principal advantage lies on the possibility of coupling the rigorous calculations of the radiative transport equation, in absorbing and scattering media, with the hydrodynamics, radiation transfer, mass transport and chemical reaction rate within the reactor.

Additionally, the determination of intrinsic kinetic parameters in slurry TiO_2 reactors is also hindered by the difficulties in the estimation of the Volumetric Rate of Energy Absorption (VREA) in heterogeneous media. Similarly to thermally activated chemical processes, kinetic experiments in photocatalytic systems require working under chemical reaction kinetic control avoiding mass transfer profiles and differential conversions to simplify the mass balances. However, heterogeneous photoactivated processes also require working under optically differential conditions avoiding radiation profiles. Under these conditions, constant concentration of reactants and VREA along the reactor volume can be assumed for the determination of intrinsic (not averaged) kinetic constants.

This PhD Thesis reports a procedure for the global computational modelling of photocatalytic reactors considering all the phenomena involved in the process: fluid mechanics, radiation transfer, mass transport, and chemical reaction. Intrinsic kinetic parameters experimentally obtained in an optically differential reactor have been used in the CFD modelling of three different photocatalytic slurry reactors using different lighting technologies: i) An annular photoreactor (A-PR) illuminated internally with a tubular fluorescent mercury lamp, ii) A tubular photoreactor (T-PR) illuminated externally with 36 LEDs located in a reflector cylindrical surface and iii) A compound parabolic collector coupled with a tubular photoreactor (CPC-PR), illuminated with a xenon lamp as a solar simulator, and under natural sunlight.

A mechanistic kinetic model was developed for the photocatalytic oxidation of methanol able to reproduce the explicit effect of energy absorption on the reaction rate, and was introduced in the computational model. To carry out the simulations, done with the software ANSYS Fluent v.14.5, the model was solved in three stages: first the flow field (equations of moment and mass conservation) was calculated, then the radiation field and, finally, the conservation of species (including chemical reaction). The fluid dynamics and the radiation balance were solved at steady state, while the photocatalytic reaction was simulated in a transient mode, including the effect of the reservoir tank. This strategy saves calculation time and provides stability to the system.

To consider optically differential conditions with optical thickness below 0.25, the values of absorbed energy have been found to be lower than 150 $W \cdot m^{-3}$. Under these conditions and with methanol in excess, the reaction rate of formaldehyde formation follows a complex dependence with the absorbed energy that can be simplified to a linear dependence for low irradiation conditions, whereas. The intrinsic kinetic parameters were obtained for both kinetic expressions, being the first time that this criterion is applied in slurry reactors, and it is combined with the CFD modelling.

The resolution of the fluid dynamics allowed the determination of the existence of dead and recirculation zones in the annular reactor. It was found that the inlet and outlet tube inclination should be rigorously included in the model, since it has a great impact on the flow field. The velocity field has been satisfactorily validated by obtaining the experimental residence time distribution curve by injection of a tracer. By comparing the resolution of the analytical expression for the calculation of the radial velocity profile in the other reactors, it was determined that in the tubular reactor the fully developed flow is not reached due to its short length, as it is practically reached in the CPC-PR.

The calculation of the radiation incident on each reactor has allowed to identify that the reactor illuminated by LEDs reaches values of radiation much higher than the other reactors studied, and that the effect of the reflection, besides increasing the radiation in the reactor, improves the homogeneity of the radiation, which must be taken into account in reactors illuminated by LEDs. The modelling of non-monochromatic sources, such as the xenon lamp case, or the solar spectrum, should be done by establishing different ranges in the UV of emission and TiO_2 absorption. The knowledge of the irradiance distribution inside the reactor has allowed the establishment of the optimum catalyst concentration for the operation in each reactor.

The kinetic dependence of the A-PR and the CPC-PR on the energy absorbed by the catalyst follows a linear behaviour, leading to very similar reaction rates in both reactors. The smoother radial absorption profiles support the use of the kinetic expression for the limiting case of low absorption, used for the simulation of these reactors. However, in the T-PR, illuminated by high intensity LEDs, the increase in the average volumetric rate of energy absorption does not imply a proportional increase in the methanol degradation rate values. The high absorption values present in different points of the T-PR radius, led to use for the modelling of the photocatalytic reaction of the general expression of the kinetic model.

The simulation of the photocatalytic activity in the different reactors studied led to a very good prediction in all reactors, validated with experimental results in different conditions of catalyst concentrations and lighting intensities, confirming the validity of the kinetic expressions and the obtained parameters. For similar values of absorbed energy, the reaction rates obtained are lower as the radiation absorption gradient in the reactor increases. This factor should be very considered in scaling-up steps, and in general, high optical paths should be avoided, a situation that can be studied in a simple and efficient way through the use of numerical simulation tools. This fact emphasizes the importance of the use of local absorbed energy values at each reactor position, rather than the use of reactor averaged values.

Finally, the computational tool called *solar calculator,* included in Fluent, was used and has proved to be a very interesting tool in the modelling of solar reactors. This is due to its capacity to be integrated into the radiation transport model, allowing the calculation of the solar radiation that would reach the reactor, through the calculation of the solar vector, as a function of the latitude, longitude, time zone, date and weather conditions indicated by the user. The possibility of orienting the model mesh has allowed to reproduce the inclination of the CPC-PR and its south-facing, to maximize the average of annual incident radiation, effect validated numerically by the realized simulations.

In summary, it can be concluded that the proposed methodology for the modelling of photocatalytic reactors in suspension has been very successful in the prediction of very different photocatalytic reactors, with errors below 14%. The success of validations when comparing experimental results and model predictions in different reactors, confirms not only the scientific context of the model, but also its usefulness in engineering applications for the design and optimization of photocatalytic reactors on a large scale, contributing to

overcome some of the limitations that prevent the commercial development of this technology.