A brief review on Multiphysics modelling of the various physical and chemical phenomena occurring in active oxidation reactors

A brief review on Multiphysics modelling of the various physical and chemical phenomena occurring in active photocatalytic oxidation reactors

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Abstract

Heterogeneous photocatalysis can be used as an advanced oxidation technology frequently studied for application in photoreactors for air and water treatment. Extensive experimental investigation entails high costs and is also time consuming. Multiphysics modelling, a relatively new numerical method, provides a cost-effective and valuable alternative. By reconstructing the reactor geometry in dedicated software, meshing it and solving for occurring physical and chemical phenomena, Multiphysics models can be used to evaluate the performance of different reactor designs, increase insight into the occurring phenomena and study the influence of operational parameters on reactor performance. Finally, Multiphysics models are also developed for various applications like optimising the operational parameters, creating the ideal reactor design or scaling up a lab-scale reactor to a realistic prototype.

Keywords

- Multiphysics modeling
- Computational Fluid Dynamics
- Photocatalytic oxidation reactor

1 Introduction

Heterogeneous photocatalysis is an advanced oxidation technology frequently studied for applications such as environmental air purification [1] and water treatment [2]. In these fields, a growing number of studies focus on the design, optimisation and scale-up of active photocatalytic oxidation (PCO) reactors, sometimes called photoreactors. Extensive experimental research required for these purposes entails high construction and operation costs and is also time consuming. Moreover, measuring all relevant parameters in real-time and determining all occurring dependencies is challenging. Hence, modelling of PCO reactors and all relevant physical and chemical processes can provide a cost-effective and valuable alternative [3–5]. With the increase of computational power, Computational Fluid Dynamics (CFD) and Multiphysics modelling, a relatively new numerical method, is increasingly used to evaluate the performance of different reactor designs. In addition to process intensification and optimisation, Multiphysics modelling can also increase insight into the occurring phenomena, the influence of operational parameters on reactor performance and provide detailed information on reactant concentration gradients [6–8].

This review focuses on recent articles published on photoreactor modelling for air and water treatment. It includes articles from 2016 until September 2022 with the majority published in the last two years. More specifically, the various physical and chemical phenomena occurring in PCO reactors and how they are modelled will be discussed along with an overview of the applications of Multiphysics photoreactor models in recent literature.

2 Computational Fluid Dynamics and Multiphysics modelling

Computational Fluid Dynamics (CFD) is a method to obtain the dynamics of the fluid flow in a geometry by numerically solving the governing equations, more specifically the Navier-Stokes equations. Nowadays the term CFD is often used in a broader context, targeting not only fluid flow but also other phenomena like transport of pollutants, chemical reactions and physical phenomena like light propagation. A more general and correct term for the simultaneous and coupled simulation of these physical and chemical processes is Multiphysics modelling. Most physical and chemical processes occurring in PCO reactors can be described by partial differential equations (PDE). Multiphysics software is capable of solving PDE's by means of discretization to algebraic equations that can be solved numerically. Commonly used software for PCO reactor modelling include commercial packages provided by e.g. COMSOL, Inc. and ANSYS, Inc., and open-source software like OpenFOAM [9–11]. After building the model, validation is typically realized by comparing the model output with controlled experimental results and/or experimental data found in literature [11–13].

In the following sections, the subsequent steps in setting up a Multiphysics model will be discussed: building the geometry and mesh, and implementing the physical and chemical phenomena.

3 Geometry and mesh

The first step in Multiphysics modelling is to create the model geometry. Here, the shape and dimensions of the reactor are reproduced using dedicated software. For complex geometries, this is often done in 3D. However, if possible, 2D models are used to save computational costs. Even though a 2D model may be less accurate, it is simple, fast and can provide a good approximation [14,15]. Simplifying 3D geometries to 2D is often done when the reactor is axisymmetric, such as the annular reactor in the study by Peralta Muniz Moreira et al. (2021) [10]. If not possible, symmetric geometries may still be simplified by using symmetry planes and modelling only part of the geometry [13,16,17]. In the study by Lira et al. (2022), a combined approach was used by simulating the radiation field in 2D, while modelling the other physics in 3D [11]. The geometry is discretised into mesh elements to solve the governing equations (Figure 1). Critical for modelling fluid flow and surface reactions is a well-defined boundary layer. Here most phenomena such as diffusion, adsorption and desorption will take place. The density of the boundary layer mesh near the surface of the reactor can influence model results greatly. To obtain accurate simulations, the mesh density and quality must be high [18,19]. Nonetheless, mesh refinement must be balanced against the computational cost. When additional refinement affects the solution less than 1 to 5%, mesh independence is achieved. Various parameters like the average velocity or volume flow rate, are used to verify this [16–18]. However, it is important to note that the choice of parameter is critical to ensure adequate mesh independence. Convergence of the mesh for one variable does not guarantee convergence for all phenomena. Hence it is good practice to consider a parameter which is the result of all physical and chemical processes, such as the pollutant concentration at the outlet [11]. Alternatively, multiple parameters accounting for each process separately, such as incident radiation and velocity through a plane, can be considered [18].

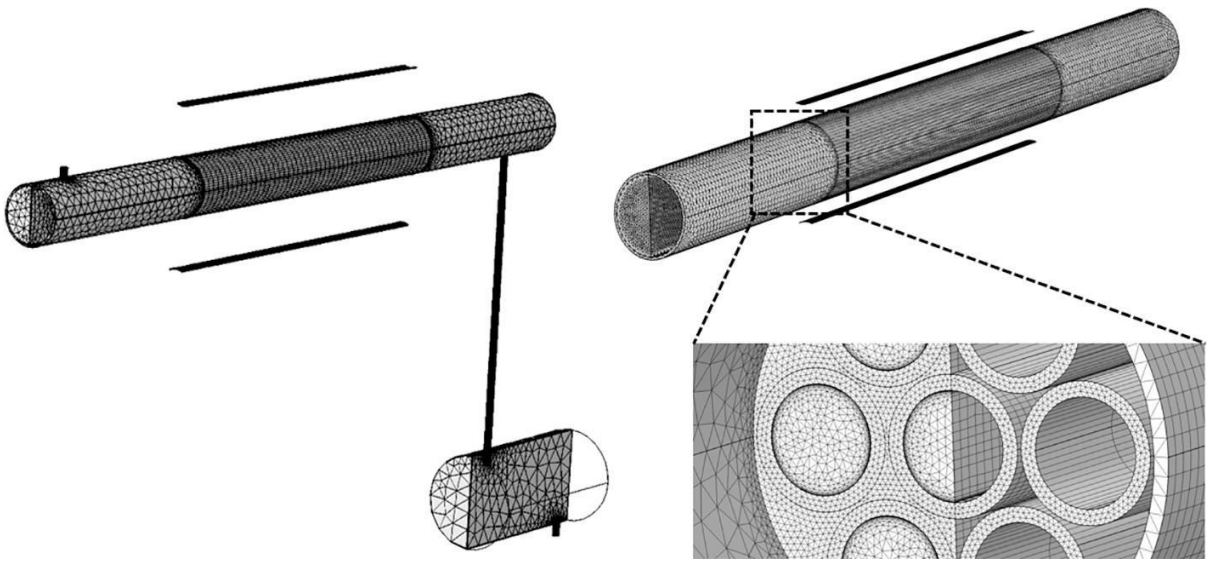

Figure 1: Meshing of a photocatalytic multi-tube reactor (adapted from J. Roegiers et al. [13]*).*

4 Physical and chemical phenomena

4.1 Fluid flow and pollutant transport

Critical for modelling photoreactors is the simulation of fluid flow. Assumptions are made to reduce the complexity of the model and make it less computationally intensive. Generally, the fluid is modelled as an incompressible, Newtonian fluid to reduce computational costs. These assumptions are acceptable considering the commonly used fluid (water or air) and reactor conditions (ambient pressure and temperature). In addition, the fluid flow is often considered stationary [13,20,21]. This is because most researchers are only interested in the stable operation of the photoreactor. The transient behaviour at start-up is often negligible compared to the total reaction time, as demonstrated by Asgharian et al. (2021) [3]. In photoreactors, the Reynolds-averaged Navier-Stokes (RANS) equations are generally used to model the fluid flow. Depending on the reactor geometry, the fluid and the imposed fluid velocity, the established flow is determined to be laminar or turbulent, based on the resulting Reynolds number. Both regimes are frequently encountered in literature [13]. When modelling turbulent flow, a suitable turbulence model like the standard k-ε, realizable k-ε, k-ω or shear-stress transport (SST) k-ω turbulence model should be chosen [16–18,22]. Although the k-ε model is the most robust model, it is not the most suitable in every situation. For example, Malayeri et al. (2020) concluded that the k-ω model is more accurate than the k-ε model in regions with near-laminar flow and for internal flows [17]. Balestrin et al. (2021) evaluated several turbulence models for surface catalytic systems with high and low mass transfer limitations. Additionally, they investigated which turbulent Schmidt (Sct) number was ideal for each turbulence model and checked its applicability for different flow rates by comparing the experimental apparent reaction rate constant with the numerical one. Remarkably, the optimal Sct deviates from the standard Sct values used in commercial CFD codes. They concluded that all studied turbulence models could predict well the mass transfer when the optimal Sct for the applied turbulence model is used. Further, the authors recommend the use of the standard k-ε model with ideal Sct since it had a prediction error of less than 6.5% with a high solution stability and the lowest computational cost [7]. This study shows that even though authors frequently do not elaborate on the used turbulence model, indication of the used Sct is essential.

Once fluid flow is modelled, mass-transport equations for the pollutants are included. Generally, a diluted concentration and thus single-phase flow is assumed. Therefore, the pollutant concentration

can be modelled by solving the convection-diffusion equation coupled to the stationary velocity field with chemical rate expressions added to the transport equations as source terms [13,15]. Some studies do not only consider transport in the bulk phase but also include mass transfer within the porous catalyst coating. For example Luo et al. (2020) developed and validated mathematical models for describing the light propagation, mass transfer and reaction kinetics in the catalyst pores [18]. Even though this enables a more in depth understanding of the PCO processes, the added value depends on the significance of these processes within the pores which is related to the catalyst porosity and thus the type of catalyst and support material.

4.2 Irradiation

UV-light irradiation forms the basis of photocatalytic oxidation, by activating the photocatalyst. Moreover, the incident irradiation on the catalytic surface is one of the critical factors that determine the rate of conversion. It is therefore crucial to consider UV-light irradiance and distribution when developing a PCO model. Modelled UV-light sources be treated as radiation-emitting lines, surface sources or volume sources [18]. The irradiation field is mathematically described by the radiative transfer equation (RTE), which illustrates the light intensity dispersion inside the reactor and is affected by absorption, emission, reflection, and scattering. The RTE can be solved by different methods with the Monte-Carlo (MC), discrete ordinate (DO), or finite volume (FV) approaches the most used ones [19].

Asadollahfardi et al. (2018) compared the DO and MC methods for a photocatalytic wastewater purification reactor by comparison of the simulated data with experimental data. They modelled different TiO_2 loadings in the catalyst layer. Overall, the results computed with the DO method were more consistent with the experimental observations [19]. Since solution of the RTE is computationally intensive, simplifications are made when possible. For example, Lira et al. (2021) proposed a simplification of the RTE for immobilized photoreactors. Since the photocatalytic reaction only takes place at the surface, there is no scattering of light and no radiation absorption in the photocatalyst coating. Hence, the RTE can be simplified to the Beer-Lambert Law [8]. On the other hand, Roegiers et al. (2018) developed a radiation field model by discretizing light into rays that can propagate through the system. The ray trajectory was not resolved with a finite element mesh, unless it interacted with a boundary layer where refraction, reflection or absorption occurred (Figure 2). This way, computational effort was reduced significantly over long-travel light distances compared to methods solving the RTE such as MC, DO or FV [13].

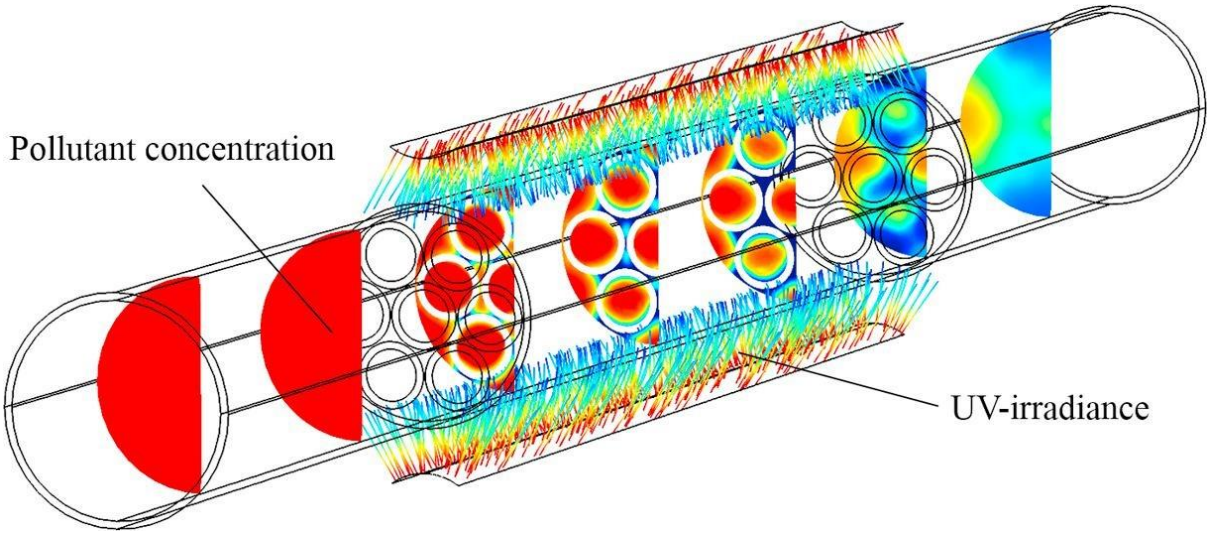

Figure 2: Output of a CFD model that integrates fluid flow and pollutant transport, irradiation and PCO kinetics (adapted from J. Roegiers et al. [13]*).*

4.3 Kinetics

Reaction kinetics provide information on the mechanisms by which reagents are converted to products. In a photoreactor, kinetics are closely related to adsorption/desorption models since they depend on the coverage of pollutants on the catalyst layer. Often, Langmuir-Hinshelwood (LH) kinetics are considered to describe all surface phenomena in a simplified model, excluding water molecules and other compounds like by-products and intermediates [8,23]. LH kinetics are often used as a good approximation for a monolayer adsorption mechanism. Additionally, the model can be easily extended to include more than one kind of adsorbent. However, it treats each adsorbed molecule as an independent entity and thus does not account for intramolecular forces between adsorbents. Furthermore Yusuf et al. (2021) recently developed a CFD model that accounts for multilayer adsorption onto the photocatalytic surface by fitting rate constants for monolayer and multilayer adsorption/desorption to experimental results [24].

In order to apply the developed kinetic model in various situations, the kinetic parameters need to be intrinsic [8,13,17,23]. In the paper of van Walsem et al. (2018) “intrinsic” indicates parameter independence from the radiation field, pollutant concentration and fluid dynamics [23]. Roegiers et al. (2018) considered independence of mass transfer limitations, pollutant concentration and irradiance, but not the influence of relative humidity [13]. While it is generally accepted that the PCO reaction itself is dependent on the light intensity, van Walsem et al. (2016) showed that adsorption and desorption reaction constants are influenced by light as well. By fitting the rate constants to experimental data, they were able to predict a tenfold and hundredfold increase in the adsorption and desorption rate constant upon illumination respectively [25]. Although these investigations yielded interesting results, the majority of numerical CFD models treat the 'dark' adsorption phase separately from the 'light' phase. Future work could focus on shedding light on the exact relationship between adsorption and light intensity.

Although in real environments pollutants are never encountered alone, only little research is done about modelling mixtures of components and their by-products formed by PCO. Nonetheless, Malayeri et al. (2022) developed a 1D kinetic model to estimate the degradation of a binary mixture of VOCs and the generation of by-products. They concluded that determining the removal efficiency based on a single compound cannot accurately predict the removal of VOCs in a mixture since the reaction rates of one compound are influenced by the presence of other compounds. In addition, the

selection of major conversion pathways taken into account into the model are crucial to achieve higher accuracy [26]. This study demonstrates that the complexity of models increases rapidly when approaching reality. Hence it is essential to balance the need for more realistic models and computational demand. A study by Luo et al. (2020) investigated incorporating the formation of hydroxyl and superoxide radicals into the kinetic rate expressions to model the photocatalytic degradation of methylene blue (MB) by H_2O_2. Although the researchers were able to model the transport of intermediates together with reactants and products, the model consistently overestimated the MB breakdown by over 30% [27]. While studies like this highlight the versatility of Multiphysics modelling, precision still needs to be developed further to be able to accurately model all processes in a photocatalytic reaction.

5 Applications

Researchers use Multiphysics models of PCO reactors for various purposes: optimising operational parameters, creating the ideal reactor design or scaling up a lab-scale reactor to a realistic prototype. The study by van Walsem et al. (2019) can be categorised in the latter. Starting from a lab-scale multi-tube reactor concept, they used a modelling approach to evaluate several scaled-up reactors and based on the results, a prototype was built [12]. Whyte et al. (2019) focused on the design by comparing a plate and pleated configuration in a photoreactor. CFD simulations provided insight into the effect on velocity and irradiance distribution [20]. Similarly, Tong et al. (2020) studied the effect of geometric parameters on the photocatalytic performance of a packed bed reactor [28] and Matiazzo et al. (2022) identified the optimal illumination system by investigating 28 LED configurations. Using CFD simulations they balanced the number of required LEDs with the overall photonic efficiency [21]. In some studies, Multiphysics modelling is combined with other techniques. For example, Lira et al. (2022) developed a 3D model of a photocatalytic microreactor and used the model results as input to an artificial neural network combined with a genetic algorithm to predict the conversion of pollutants and determine ideal operating conditions [11]. Finally, Ming et al. (2021) applied Multiphysics modelling to investigate the combination of a solar chimney power plant with photocatalytic methane removal in a prototype-scale model. They analysed the effect of various prototype dimensions on the flow and photocatalytic performance. They believe that the developed model will encourage the development of this new technology [16].

6 Future prospects and conclusions

Multiphysics models are increasingly used to investigate the performance and create insight into the operation of photoreactors. Once a model is validated, it is used to improve the design, optimise the operation and scale-up the reactor. In every step of the modelling process, careful consideration of the adopted assumptions is needed and one has to balance the level of detail and accuracy with the model complexity and computational cost. While the mechanism of fluid flow and radiation transfer has already been well established for photoreactors, more studies should focus on the development of more complex kinetic models which incorporate products and by-product formation and their influence on the overall reaction rate. While LH kinetics are often a good approximation for lab-scale reactors, it needs to be further investigated if the extracted parameters are reliable to be used for upscaling purposes. As of today it is not clear if these parameters are ‘intrinsic’ or model dependent. While photocatalysis appears to be an attractive solution for air and wastewater treatment, commercial applications remain sparse. Because of this, continuous research needs to be done in developing Multiphysics modelling of photoreactors to be able to be a valuable tool in helping photoreactors achieve their potential.

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