Kinetic Parameters for Gas Phase Photocatalysis: Analytic Versus CFD Approach

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Abstract

Introduction

Among the advanced oxidation processes (AOPs) for removal of volatile organic compounds (VOCs) from air, photocatalytic oxidation (PCO) is considered a very promising technology [1,2]. PCO can achieve mineralization of harmful VOCs to CO2 and H2O using only UV light [3]. A main challenge is to find appropriate kinetic models and parameters that accurately describe the rate of decontamination by PCO coatings under a range of conditions. PCO is a heterogeneous surface process that can best be described as a combined effect of VOC diffusion through the reactor, adsorption-desorption and VOC decomposition at the catalyst surface. The reaction rate for PCO reactions is commonly written as the unimolecular type Langmuir-Hinshelwood (LH) mechanism, which uses two kinetic parameters.

Methodology and use of COMSOL Multiphysics®
Two methods for determining the LH kinetic parameters for a slit-shaped flat bed photocatalytic reactor (Figure 1) were compared: an analytic mass transfer based model adapted from literature and a multiphysics approach using COMSOL Multiphysics®. The mass transfer model is based on the analysis followed by Yang et al. [4] adapted for the geometry of the reactor in our work. In this approach, an 'average total removing factor' is used that combines convective mass transfer and the LH reaction rate coefficient.
COMSOL Multiphysics® simulations were carried out using a laminar flow model. The PCO reaction was included as a reaction on the active surface, expressed in terms of the LH reaction kinetic parameters. For determining the kinetic parameters, an optimization module was used in conjunction with the CFD calculations. Hereby, an objective function was defined and the Nelder-Mead method optimization routine was used for finding the local minimum of the objective function by changing the kinetic parameters within certain constraints.

Results
Despite the differences between both approaches, similar values for the kinetic parameters and similar trends in terms of their UV intensity dependence were found. Using an effectiveness-NTU approach, the analytic mass transfer based method could quantify the relative contributions of the rate limiting steps through a reaction effectiveness parameter. The CFD approach on the other hand could yield the two kinetic parameters that determine the photocatalytic reaction rate

simultaneously. Furthermore, it proved to be more accurate as it accounts for the spatial variation of flow rate, reaction rate and concentrations at the surface of the photocatalyst (Figures 2 and 3).

Conclusions
The main strength of the COMSOL Multiphysics® method lies in its feasibility of accurately calculating the spatial variation of flow rate, reaction rate and concentrations at the reactive surface, which is not accounted for by the analytic mass transfer based approach. Besides, the mass transfer approach requires a substantial dataset in order to derive one single value for both kinetic

Reference

1. A. Di Paola et al., J. Hazard. Mater., 211, 3 - 29 (2012)
2. K. Demeestere et al., Crit. Rev. Env. Sci. Technol., 37, 489 - 538 (2007)
3. O. Carp et al., Prog. Solid State Chem., 32, 33 - 177 (2004)
4. R. Yang et al., J. Air Waste Manage. Assoc., 54, 1516 - 1524 (2004)

Figures used in the abstract

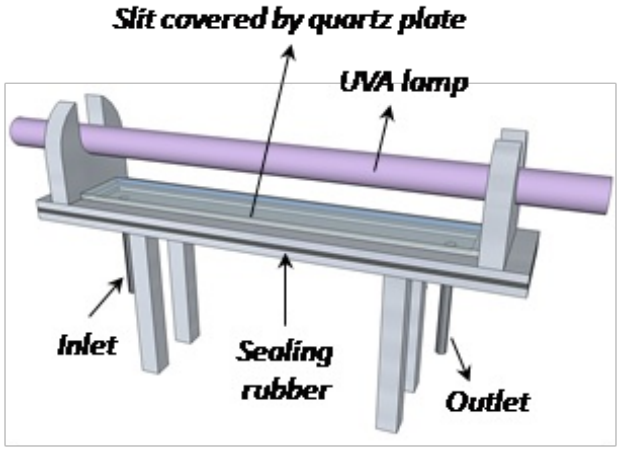

Figure 1: Schematic representation of the flat bed reactor used in this work

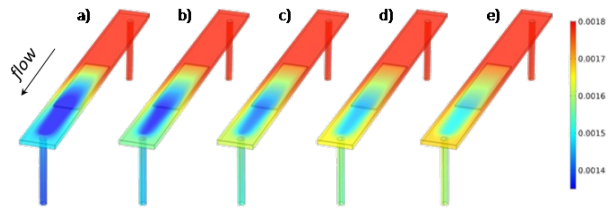

Figure 2: Distributions of acetaldehyde concentrations calculated using CFD simulations in steady state condition. The acetaldehyde inlet concentration was 43 ppmv (0.00179 mol m-3), at an effective total inlet gas flow rate of: a) 300 cm3 min-1, b) 375 cm3 min-1, c) 450 cm3 min-1, d) 525 cm3 min-1 and e) 600 cm3 min-1

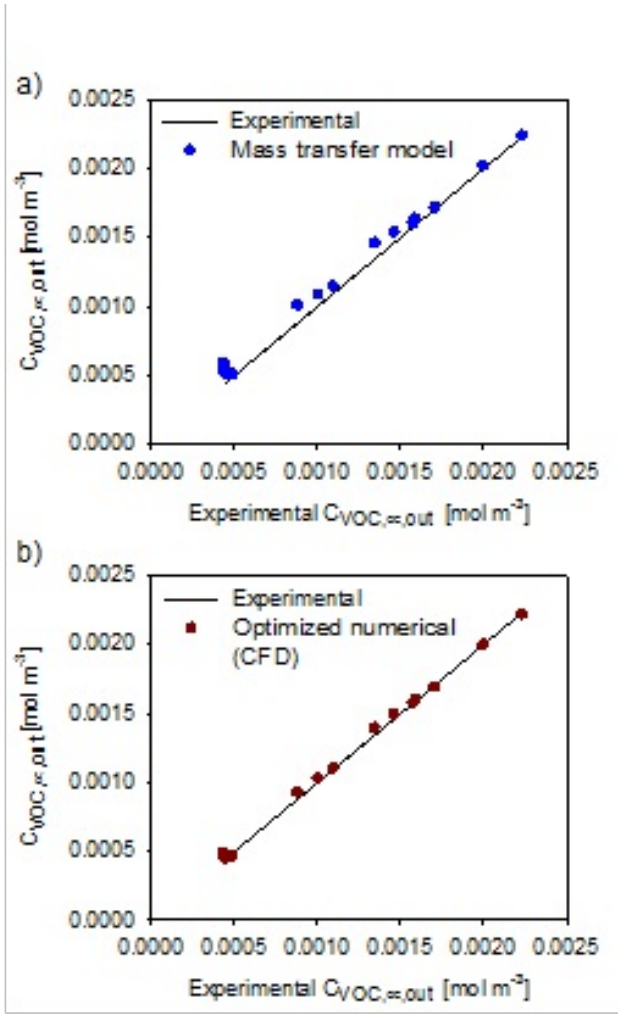

Figure 3: Comparison of the calculated outlet VOC concentrations (data points) with the experimentally determined outlet VOC concentrations (black straight line) using a) the kinetic parameters determined by the analytic mass transfer based model and b) the Comsol method