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Modeling intrinsic kinetics in immobilized photocatalytic microreactors

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ABSTRACT

The article presents a simple model for immobilized photocatalytic microreactors following a first order reaction rate with either light independency or light dependency described by photon absorption carrier generation semiconductor physics. Experimental data obtained for various residence times, catalyst thicknesses and photon flux densities proved that the model is capable of describing the reactor performance. The extracted reaction rate constant reveals the intrinsic kinetics as both external and internal mass transport are accounted for. The effect of light is also considered by defining a criterion for neglecting light intensity based on film thickness and absorption coefficient. For the first time *k* values on the order of magnitude of 10^1 s^{-1} are reported. In the end, performance parameters are also derived for the light dependent model for which the internal effectiveness factor reveals both mass transfer and light limitations.

1. Introduction

Heterogeneous photocatalysis is a promising technology for environmental remediation. However, commercial products are focused mostly on self-cleaning surfaces and air filtering. Important applications such as removing refractory compounds from wastewater are scarce. In 2007 van Gerven et al. [1] mentioned only 6 examples: Zentox Corporation, Matrix Photocatalytic Inc., Clearwater Industries, Photox Bradford Ltd., Lynntech Inc. and Purifics Environmental Technologies Inc. The invoked reasons are small conversion capacities and inefficient light use, addressing especially the inconsistencies in the definitions of various performance parameters. A progress in optimization requires that individual research efforts can be combined which is possible only if an honest comparison between them can be achieved.

One parameter used frequently when evaluating the conversion capacity of a reactor is the apparent reaction rate constant. Its derivation implies identifying the reaction rate with the conversion $-dc/dt = r$. The kinetic model is usually Langmuir–Hinshelwood $r = kKc/(1 + Kc)$ or a first order reaction $r = kc$ from which the reaction rate constant is obtained [2–10]. The agreement with respect to these basic relations is widespread, as several reviews mention it [11,12].

Heterogeneous reactions involve the diffusion of species to the active catalyst sites. Mass transport becomes important and if omitted can alter the true values of the reaction kinetics. Intrinsic kinetic parameters are of paramount importance. They are required for catalyst screening and necessary when simple engineering tools such as the apparent reaction constant are used for comparing different reactor configurations. The real value for the reaction rate constant allows the evaluation of the mass transfer contribution on the conversion which is a main factor dictating the performance of a reactor. Evidently, comparison complicates further when the gradients in photon absorption become important and kinetics cannot be volume averaged anymore. When both immobilized and dispersed systems are considered, the difference in light dispersion can be bridged only by light dependent intrinsic kinetics.

The standard approach for kinetic investigation is to place the system in the reaction rate limiting regime, so the apparent reaction rate can reach the intrinsic value. The classical method uses a differential reactor which consists of a reaction chamber and a mixing tank, where the reaction volume is much smaller than the total volume. The small conversion per pass allows the simplification of the mass balance to a batch reactor equation. The intrinsic kinetics are determined for flowrate – independent conversions [13–24]. Accepting the reliability of this method to eliminate external mass transport, the question about internal mass transfer remains, which will be present even for thin catalyst layers or for an inevitable degree of aggregation in slurry systems. Ballari et al. [25–27] went on to defining guidelines for canceling mass transfer limitations in

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slurry reactors based on flow rate, catalyst loading and irradiation rates.

Even when concentration gradients are eliminated, the inhomogeneity regarding light distribution has to be carefully considered, especially for slurry systems. Motegh et al. [28] gave guidelines for operating in optically differential mode. Starting from the premise of perfect mixing, a criterion was defined for keeping the gradients in photon absorption rate small enough as to allow the volume-averaging of the reaction rate.

A more thorough method is to model light distribution, fluid dynamics and mass transfer and fit the kinetics to the experimental data. Due to the complexity of large-scale photocatalytic reactors, a lot of assumptions come into play.

The first challenge in a large-scale system is the non-uniform incident flux. To obtain the radiation field distribution, light emission models have to be correlated to the radiation transfer equation (RTE) in order to obtain the local volumetric rate of energy absorption (LVREA) which can be afterwards coupled to the reaction rate. In case of dispersed systems, the radiation transfer equation becomes more complex due to in and out-scattering effects that also depend on the aggregation extent of the particles [29–33].

The next step is to consider the complex hydrodynamics. The most rigorous approach is to perform a CFD simulation which solves the continuity and Navier–Stokes equations and also requires turbulence models. Again, dispersed systems demand the most elaborate models. An Eulerian multi-fluid approach is necessary to connect the fluid velocity field to the solid particle distribution. However, real flow computations are quite challenging. This is why, when possible, approximations are used. In case of small deviations from laminar flow, the axial dispersed model can be considered. For this, the Péclet number (Pe) can be experimentally determined from RTD measurements [34,35]. At the other end of the complexity spectrum, perfect laminar or turbulent flows are the most convenient options.

Once the velocity field is characterized, mass transport can be investigated. The most accepted approximation for slurry reactors is a one phase system with high Pe numbers. Hence, the governing equation represented advection and homogeneous reaction only [36–38].

For immobilized systems it is easier to couple the reaction rate to mass transfer, given the clear definition for the interface. The most realistic transport models for the flow channel take into account both advection and diffusion [39–43]. All these studies neglect the internal mass transport inside the catalyst film. Hence, the reaction rate is set as the boundary condition for the catalyst–fluid interface. A more manageable method is to represent mass transport through the stagnant film model. The mass transfer coefficient can be determined experimentally with the benzoic acid dissolution method [44,45] or can be computed via empirical correlations from Reynolds and Schmidt numbers [46–49].

Microreactors are a special case. The modeling of such systems is straightforward due to their laminar flow and constant photon flux density throughout the entire surface of the reactor. Moreover, for immobilized catalyst, interface scattering due to roughness is neglected. Bulk scattering is not relevant due to absorption. Hence, the RTE simplifies to a Lambert–Beer law.

Very few papers seem to exploit the potential for accurate modeling of microreactors. Most of the articles employ the PFR equation [50–53]. Meng et al. [53] report values for reaction rate constants without providing an equation. It is assumed the same PFR equation is used due to its widespread use. Gorges et al. [50] validate the intrinsic character of k by proving their system is placed in the reaction limiting regime. Lindstrom et al. [54] adopts the same approach of employing Damköhler number to assess mass transfer restrictions. However, for the apparent reaction rate constant they use the highest value in the literature, without computing the one for their system.

Charles et al. [55] used the axially dispersed plug flow model to set up the mass balance in the microreactor. Mass transfer in the radial direction was represented by the stagnant film. Both the axial dispersion and mass transfer coefficients were computed from empirical relations. The kinetic model was initially Langmuir–Hinshelwood, but later on simplified to a first order-like equation. The kinetic coefficients were fitted to the model via iteration.

Nielsen et al. [56] derived a reaction rate expression based on semiconductor physics. The governing equation they set up for the catalyst layer comprised of diffusion and reaction. The gas concentration in the flow channel was considered constant by keeping the conversion under 10%. They also managed to define a continuity equation for the localized excess hole concentration.

The current article draws attention on the simplicity of accurate modeling in the case of microreactors and proposes them as a pertinent choice when attempting to extract kinetic parameters. A complete model for immobilized photocatalytic microreactors is set up for the first time and solved for both light independency and light dependency first order kinetics. Experimental data obtained for various residence times, catalyst thicknesses and photon flux densities proves the model is capable of describing the reactor performance. Furthermore, a criterion is defined based on the absorption coefficient and catalyst thickness to mark the transition toward the regime where the incorporation of photon flux density is required. Performance parameters are also derived for the light dependent model for which the internal effectiveness factor reveals both mass transfer and light limitations.

The potential of the models is not confined to microreactor engineering. Scale-up is straightforward compared to slurry reactors as only channel height and catalyst thickness should be designed for a specific flowrate.

2. Materials and methods

2.1. Microreactor fabrication

The silicon chips cut from 4 in. wafers were cleaned with 65% nitric acid (Merck) for 15 min and rinsed with water and acetone. Following the cleaning, the substrates were covered entirely with a commercial TiO_2 suspension (VP Disp. W 2730 X, Evonik) and spin coated at 3000 rpm angular velocity and 524 rpm/s acceleration. The spin coating time was kept at 1 min. The resulted layer was sintered for 2 h at 500 °C in air. The heating and cooling rates were kept at 2 °C/min.

The standard thickness obtained with the unprocessed dispersion of 30 wt.% solid content was around 1200 nm. Thinner layers were prepared by decreasing the viscosity of the dispersion. 310 nm and 640 nm were obtained by diluting the dispersion with distilled water to 15 and respectively 24% solid content. Thicker films were prepared by multiple coatings with sintering in between. The alteration of photocatalytic activity by repeated sintering was ruled out when the same degradation was observed for layers with one and two sintering cycles. As a general rule, the thickness of the catalyst layer was multiplied by the number of coatings.

Catalytic films of 310, 640, 1200, 2050, 3000 and 4000 nm were used for degradation experiments.

The microreactor was assembled by attaching the TiO_2 coated substrate to a PDMS slab containing the microchannel replicated from a microstructured mold. The PDMS was prepared by blending the polymer base (RTV-615 A, Permacol) with the curing agent