COMPUTATIONAL MODELLING of a PHOTOCATALYTIC UV-LED REACTOR with INTERNAL MASS and PHOTON TRANSFER CONSIDERATION

M. Enis Leblebici¹, Jan Rongé², Johan A. Martens², Georgios D. Stefanidis¹, Tom Van Gerven¹

¹Process Engineering for Sustainable Systems (ProcESS), Department of Chemical Engineering, KU Leuven, Belgium

²Centre for Surface Chemistry and Catalysis (COK), Department of Microbial and Molecular Systems, KU Leuven, Belgium

Abstract

Photocatalytic breakdown of organic pollutants was modelled and experimentally validated using phenol as probe molecule and UV-LEDs as the radiation source. A nanocrystalline TiO₂ film was immobilized in a quartz continuous parallel plate reactor and illuminated by an array of 88 LEDs, each emitting 375 nm radiation. The degradation of phenol in steady state conditions was recorded for different irradiances and a pseudo first order reaction rate constant was obtained for this process. The rate constant was found to be of the order of 10^{-4} s^{-1} . A Computational Fluid Dynamics (CFD) coupled with reaction model for the studied reactor was developed. The model considers the catalyst coating as a porous medium instead of a surface. It accounts for the mass transfer and light penetration within the immobilized catalyst. The model has one degree of freedom which was validated for different light intensities and flow rates. The degree of freedom in the model can be defined as “rate of free radical generation” and the unit is $\text{mol.L}^{-1}.\text{s}^{-1}$. This variable was experimentally coupled by a linear relation to the irradiance on the catalyst coating. Photonic efficiency of the system was also investigated. A photonic efficiency range of 0.44% to 1.4% was obtained at light intensities of 2000 and 200 $\mu\text{W.cm}^{-2}$, respectively. The model and the data obtained are scalable and applicable to different reactors. Comparison of photonic efficiencies obtained, show that the immobilized TiO₂ reactor has similar efficiency to referred works which considered slurry reactors.

1.0 Introduction

Degradation of aqueous organic pollutants is studied within the scope of this work. Phenol was chosen as the probe molecule due to the availability of comparable data in literature. Furthermore, phenol is an abundant pollutant in the effluents of various industries including producers

of paper, pharmaceuticals, and plastic raw materials [1]. Phenol elimination using a semiconductor catalyst, namely TiO_2 , has been previously studied and reported in detail [2–4]. Kinetic data and operating parameter optimization for this process are widely available for batch, slurry reactors [5] as well as continuous thin film reactors [2].

The majority of the studies conducted on photocatalytic degradation of organic compounds use mercury lamps as light sources [2,4,6]. This work focuses on the performance of LEDs which emit near UV radiation (375 nm). LEDs have much narrower emission spectra compared to the mercury vapour lamps which eliminate any unnecessary irradiation which cannot be absorbed by the catalyst surface. Moreover, the light output efficiency of LEDs is known to be significantly higher than that of mercury vapour lamps [7,8]. LEDs as light sources for degradation of pollutants started to attract attention as well [9–11].

Photocatalytic processes are initiated by exciting valence band electrons of the TiO_2 semiconductor to the conduction band by absorbing photons of above-band gap energy, corresponding to UV light [12]. Visible light is transmitted or scattered, evidenced by the white appearance of TiO_2 . Electron-hole pairs generated by UV absorption are unstable with lifetimes in the order of picoseconds to nanoseconds before they recombine [13]. It is usually assumed that the predominant first step in titania photocatalysis consists of the generation of hydroxyl radicals and H^+ ions from adsorbed water as shown in Equation 1 [10].

The reduction step on the other hand, targets the molecular oxygen which is present in the medium to yield the superoxide radical [10]

The $\text{OH}^{\bullet}$ and $\text{O}_2^{\bullet-}$ radicals are also very unstable in this state and they return back to stable forms within nanosecond time scales [12,13]. However, if they interact with an organic molecule during their lifetime, such as phenol in this case, they trigger the degradation of the organic molecule.

Adsorption of water on the catalyst surface and subsequent oxidation of the adsorbed water are fast and do not limit the degradation process. Water adsorption in aqueous media is fast due to the excessive concentration of water. Oxidation of water (Equation 1) as well as reduction of oxygen (Equation 2), which involve a single electron transfer, are also non-limiting steps [13]. Excitation of phenol molecules by radicals is also known to be a fast step with second order reaction rate constant of $0.841 \times 10^{10} \text{ mol.L}^{-1}.\text{s}^{-1}$ at 21 °C [14]. Therefore, the rate-limiting step of the process is expected to be

either the external mass transfer rate of the organic molecule (phenol) from the bulk flow to the catalyst surface, or the internal mass transfer rate of phenol inside the catalyst volume.

The photocatalysis of various molecules including phenol is popularly modelled using Langmuir – Hinshelwood (LH) kinetics [2,9] which can be described as;

$$-\frac{dc}{dt} = \frac{kKc}{1 + Kc} \quad (3)$$

where k ($\text{mmol.L}^{-1}.\text{s}^{-1}$) is the reaction rate constant, K (L.mmol^{-1}) is the adsorption equilibrium constant and c (mmol.L^{-1}) is the concentration of the organic molecule to be degraded. This equation was often modified with a light irradiance intensity term for photocatalytic applications and fitted to the experimental results by varying the constants. Detailed studies have also been made to analytically model the effect of photon absorption and reactant concentration on the surface of a catalyst particle and in a reactor segment [15,16]. This approach has the advantage of fine-tuning the model for the specific reactor and operating parameters which increases the precision. Furthermore, these models do not require high performance computational hardware and solvers.

The disadvantage of this way of modelling the system is the lack of flexibility. The LH model is independent of the reactor geometry and hydrodynamics. It needs to be re-fitted to different reactor geometries, flow characteristics and different zones of a non-ideal reactor. Moreover, many studies have not used the detailed analytical models but instead modified the LH equation with one light intensity term [2,9,11].

Wang et al. [9] developed a computational model using LH kinetics. They modelled the flow within the reactor using a computational fluid dynamics (CFD) tool and coupled the obtained velocity field to the surface reaction using LH kinetics for a gas phase reaction. This was one step ahead of the empirical modelling done by only fitting the LH kinetics to the reactor output with an additional fitting parameter.

However, this improved strategy is assuming that the reaction takes place in a control volume adjacent to the catalyst coating surface which is in fact not the case. The catalyst coating is not an impenetrable surface but a porous medium [17] as shown in Figure 1. The degradation reaction does not only occur at the surface of the coating but mainly on the much larger surface area within the pores of the catalyst. This could result in internal mass transfer limitations which are an important parameter to model the reaction kinetics [17]. This strategy was not used for photocatalytic degradation models before.

Figure 1. Mass transfer in a parallel plate reactor.

The model demonstrated in this work aims to take a further step from the previous CFD models by modelling the catalyst coating as a porous medium instead of a surface using Fick's law for diffusion and the Brinkman equation for convection, which was shown to model flow-through porous media for diluted species successfully [18]. Overall, the model is flexible to fit different flow rates and reactor designs and has been applied to verify the relative importance of internal and external mass transfer for the degradation process.

To validate the model, an array of UV – LEDs was constructed and the radiation field at different positions of the surface of the coating was measured. The developed model has only one degree of freedom which is varied by a linear equation coupling the variable to light intensity. This degree of freedom is the radical generation rate within the catalyst coating. The model was then tested at light irradiances varying from 186 to 2030 $\mu\text{W}\cdot\text{cm}^{-2}$, and flow rates varying from 0.4 to 3.5 $\text{mL}\cdot\text{s}^{-1}$.

2.0 Materials & methods

2.1 Reactor and experimental setup

A circular quartz flow cell of 131 mm diameter is used. The distance between the parallel plates is kept at 3 mm by the aid of spacers. The reactor has one inlet and one outlet, each with 3 mm diameter. Reactor was equipped with a distributor with 6 openings each having a diameter of 1.6 mm each to be able to apply the plug flow reactor (PFR) model to single pass conversion results. Figure 2 shows a dynamic sequence of the tracer experiment, using 1000 ppm methylene blue, allowing the visualization of the flow patterns in the reactor. Tracer experiment shows a good correlation with the PFR model.

Figure 2. Tracer experiment showing the flow pattern in the used parallel plate reactor at different time intervals. Flow rate is $1.55 \text{ mL}\cdot\text{s}^{-1}$.

The reactor was coupled in a closed loop to a magnetically stirred jacketed vessel of 300 mL, which was connected to a thermostatic bath (Julabo F12 ED), keeping its temperature constant at 25°C in all the experiments. The solution in the jacketed vessel was looped through a peristaltic pump (Ismatec VC MS/CA8) (Figure 3). The pH of the reaction medium was kept constant at 4.8 using a Metrohm Titriprocessor 686 autotitrator which will be referred to as pH controller from this point.

Figure 3. (a) Schematic view of the experimental setup. (b) Exploded view of the circular reactor.

2.2 LEDs and irradiance measuring devices

The LEDs used in the array are XSL 375 TF models from Roithner Laser, Austria. These LEDs do not possess a focusing lens and their viewing angle is of 120° . This wide angle was selected in order to

provide a relatively uniform irradiance throughout the catalyst surface. The LEDs were mounted on a circuit board, making sure that there are 11 branches in parallel with 8 LEDs in each branch in series. The LEDs were driven by a 30V DC power source with current limiter. All the power control performed in the experiments was done by varying the current. Modulation of pulse width was not used.

Irradiance measurements were done using Ocean Optics QE65 spectrometer. The irradiance at the surface of the catalyst coating was measured by separating the parallel plates of the reactor, taking one plate and placing the tip of the optical fibre 3 mm away from the face of it. The 3 mm distance is where the catalyst surface will be when the reactor is assembled. The LEDs were lit from the other side of the plate at 100% power. Spectrum was recorded and the measurement was repeated at 4 different points on the plate.

Resulting absolute irradiance was $2030 \pm 50 \mu\text{W}\cdot\text{cm}^{-2}$ at full power. Since the irradiance deviation between the measurements was 2.5% of the total value, it was concluded that the radiation field is uniform

The light penetration measurements were made by measuring through coated and uncoated plates. The difference in measurements was normalized to the uncoated measurement. Measurements through the coating revealed that the light intensity decreases to $23\% \pm 6\%$ of the intensity in the uncoated measurement.

Spectra measured at different power inputs are shown in Figure 4a. The power input versus the absolute irradiance output graph is shown in Figure 4b. 100% power output corresponds to 3mW for each LED.

Figure 4. Spectra of the LEDs measured from the catalyst surface at different power output (a). Irradiance versus power output (b).

2.3 Preparation and characterization of TiO₂ coating

For preparation of the TiO₂ coatings, 10 g of Degussa P25 (Evonik) was dispersed in 200 g pure ethanol containing 10 g P123 triblock copolymer (BASF) and 5 mL of a 0.1 (mol.L⁻¹) HCl solution. The suspension was stirred overnight. The substrates were dip-coated in the suspension for 5 min and air-dried for 24 h. They were then calcined for 5 h at 350 °C, with a ramping rate of 1 °C min⁻¹, to remove the P123 mesostructuring agent.

HR-SEM images (Figure 5) of the films were obtained with a Nova NanoSEM 450 (FEI, Hillsboro, OR). Samples were mounted on aluminum stubs using carbon tape and observed. Film thickness was determined to be $2.9 \pm 0.8 \mu\text{m}$ using a Mitutoyo Digimatic Indicator. The high variance in the coating thickness (27%) was assumed to have no effect on the results since, as shown by Vezzoli et al. [2], at thickness above 2 μm , the reaction rate is not enhanced by a thicker coating. In this case even the lowest measured thickness is over 2 μm . Film porosity (ε_p) was obtained through nitrogen adsorption. After calcination, films were scraped from the substrate and the obtained powder was inserted in a sample holder. Nitrogen adsorption isotherms were recorded on a Micromeritics Tristar 3000 apparatus at 77 K. Total mesopore volume was $0.257 \text{ cm}^3 \text{ g}^{-1}$, which corresponds with a porosity of 52.5 %. Permeability (π) was estimated using the empirical Rumpf-Gupte relationship [19]:

$$\pi = \frac{\varepsilon_p^{5.5} \bar{D}^2}{5.6} \quad (4)$$

For the surface average pore diameter ($\bar{D}$), 116 nm was used. Permeability was calculated to be $6.94 \times 10^{-17} \text{ m}^2$.

Figure 5. HR-SEM image of porous TiO₂ film after calcination.

2.4 Experimental procedure

The reaction mixture was prepared following a previously optimized formulation by Jamali et al. [10] A 1000 ppm stock solution (ChemLab, Belgium) was diluted to 100 ppm by adding water and 8.6 ml of 35% (w/w) H₂O₂ solution (Riedel de Hën, Germany). All dilutions are made using ultrapure water

(18.2 MΩ.cm). The pH was kept constant to 4.8 by the addition of 1M HCl and NaOH solutions (VWR). The prepared solution is poured in the jacketed vessel and started to loop through the reactor without irradiation to obtain material and thermal equilibrium. After 15 minutes of looping the system in the dark, LED array was turned on and an initial sample was taken. The rest of sampling was done after 10, 20, 40, 60, 90, 120, 180 and 240 min. Each sample is approximately 0.5 ml, therefore the total volume change due to sampling is 4.5 ml which is 1.5% of the total solution in the loop. This volume change was considered insignificant and was not corrected. The samples were kept at +4°C until analysis.

The phenol content of samples was analysed using HPLC (Agilent 1200 DAD). Detection wavelength was 210 nm. Samples are separated through reversed phase chromatography using a C18 Zorbax Eclipse DBD column which is 150 mm long with 4.6 mm diameter and with a pore size of 5 μm. Column is temperature controlled at 40°C. Mobile phase consists of 40 vol.% acetonitrile and 60 vol.% water (Sartorius Arium 611DI) fed at a flowrate of 1 mL.min⁻¹. Injection volume is 20 μL.

The decrease of phenol concentration with time is converted to reaction rate using the differential reactor approximation which can be given as;

$$\frac{dc}{dt} = -R \frac{V_r}{V_{total}} \quad (5)$$

Where R is the reaction rate, V_r is the volume of the reactor and V_{total} is the total volume of the solution in loop. This approximation can be used for this system since the single pass conversion was less than 5% at the investigated flow rates [2]. This low conversion introduced a high error range to the measurement of concentration difference between the reactor's inlet and outlet streams (which was less than 2 ppm for moderate to high flowrates), making differential reactor approximation overall more accurate than using the single pass conversion to calculate apparent reaction rate. The pseudo first order reaction rate constant was calculated using the measured reaction rate assuming the concentration stays constant in the reactor.

3.0 Computational model

3.1 Model equations

The numerical model of the flow through the parallel plate reactor involves the solution of the convection-diffusion equation:

$$\frac{\partial c_p}{\partial t} = \nabla \cdot (D_p \nabla c_p) - \nabla \cdot (\vec{u} c_p) \quad (6a)$$

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (D_i \nabla c_i) - \nabla \cdot (\vec{u} c_i) + R_i \quad (6b)$$

where Equation 6a is solved in the free flowing domain where no reaction occurs and Equation 6b is solved in the porous domain. c is the concentration (mol.m^{-3}), D is the diffusivity ($\text{m}^2.\text{s}^{-1}$) of the species p (phenol) and i (phenol and generated radical) while $\vec{u}$ is the velocity field (m.s^{-1}), t is the time (s) and R_i is the reaction rate ($\text{mol.m}^{-3}.\text{s}^{-1}$) within the porous medium given by

$$R_{rad} = \alpha (r_{gen} - r_{rec}) \quad (7)$$

$$R_{phenol} = -r_{deg} \quad (8)$$

for radicals and dissolved phenol species, respectively. In Equation 7, α is the light intensity coefficient (dimensionless) which varies linearly between 1 – 0.23 depending on the distance from the irradiated surface of the catalyst coating. The α parameter is 1 at the irradiated surface and 0.23 at the interface between coating and reactor wall and varies linearly across the coating. These boundary conditions were established by the light penetration measurements explained in Section 2.2.

r_{gen} is the rate of generation of radicals, r_{rec} is the recombination reaction rate and r_{deg} is the degradation reaction rate which consumes the phenol. In this work r_{rec} was not taken into account so $R_{rad} = \alpha \times r_{gen}$ was assumed. This assumption was made since the radical generation data available in the literature [20] are obtained by a method that uses probe molecules. The reported net generation rate therefore already equals R_{rad} so r_{rec} is implicitly taken into account. The R terms were introduced in the model as volume reactions instead of surface reactions even though the illumination is supplied only to the catalyst surface. This was done since it is known that both light and reagents penetrate the porous coating. Although in nanoscale the reaction takes place only at the surface of the catalyst crystals, within the scope of this work the coating is modelled as a homogeneous domain where the reactions take place.

r_{gen} ($\text{mol.L}^{-1}.\text{s}^{-1}$) is the degree of freedom in this model and its value can be varied to fit the conversion to experimental results. However, as an initial value we have chosen the radical generation rate measured by Xiang et al. [20] which is $5.88 \times 10^{-6} \text{ mol.L}^{-1}.\text{h}^{-1}$ for P25 TiO_2 catalyst irradiated with

a Xenon lamp light source at $5000\mu\text{W}/\text{cm}^2$. Since the spectrum of the irradiance measurement was not given, it is not clear if all the light intensity measured is in UV range or not. Furthermore, the measurement in the reference work was done using a slurry reactor. For these reasons, a deviation was foreseen. This value for r_{gen} was varied to 100%, 90%, 70%, 50% and 10% of the initial value. This variation of r_{gen} was replicated with the experimental setup varying the current driving the LED array to the same percentages of the maximum current (25 mA for each LED) so that the impact of irradiance on the modelled and experimental results could be observed. Relation of r_{gen} and irradiance was assumed to be linear which was proven further in the paper.

The r_{deg} variable is the rate of the phenol decomposition reaction which can be given as:

$$r_{deg} = 0.841 \times 10^{10} \times c_{phenol} \times c_{rad} \quad (10)$$

Where, the reaction rate constant is taken from literature by Bonin et al. [14].

The model does not consider the subsequent steps in the mechanism of phenol degradation and assumes that the phenol molecule is degraded once it reacts with the radical. This assumption was made since the degradation mechanism starts with a reaction of equimolar quantities of phenol and radicals [21]. Although the radicals can enter the mechanism in later steps too, the production and degradation of intermediates produced afterwards do not affect the analytical method used in this work and are not detected.

The velocity field in the free medium is calculated via the Navier-Stokes equations which can be given as:

$$\rho \frac{\delta \vec{u}}{\delta t} + \nabla \cdot \left[-\eta \left(\nabla \vec{u} + (\nabla \vec{u})^T \right) + pI \right] = -\rho (\vec{u} \cdot \nabla) \vec{u} \quad (11)$$

$$\nabla \cdot \vec{u} = 0$$

where ρ is the fluid density ($\text{kg} \cdot \text{m}^{-3}$), η is the dynamic viscosity ($\text{Pa} \cdot \text{s}$) and p refers to the pressure (bar).

The velocity field in the porous medium is calculated by solving the Brinkman equation which can be given as:

$$\frac{\rho}{\varepsilon_p} \frac{\delta \vec{u}}{\delta t} + \nabla \cdot \left[-\frac{\eta}{\varepsilon_p} \left(\nabla \vec{u} + (\nabla \vec{u})^T \right) + pI \right] = -\frac{\eta}{\pi} \vec{u} \quad (12)$$

$$\nabla \cdot \vec{u} = 0$$

where π refers to the permeability (m^2) and ε_p denotes the porosity of the porous medium (dimensionless). It can be seen that the modifications compared to Navier-Stokes divide the kinematic viscosity and the density of the fluid with a term smaller than 1. This increases the impact of viscosity and density making it much more resistant to flow which decreases the convection term in the mass transfer equation mimicking the mass transfer limitation case for porous media.

3.2 Modelling with COMSOL Multiphysics

The model was developed using COMSOL Multiphysics 4.4 software. The used modules are the Chemical Reaction Engineering and the root Multiphysics module. The internal geometry of reactor was constructed directly in the Geometry node. Then it was divided in half using a Boolean operation to save computational resources. The lateral face was set as a symmetry boundary condition as shown in Figure 6. There are two domains in the model. The porous domain is where the reaction occurs; therefore the reaction term in Equation 6 is only active in this domain and is equal to zero in the free domain. The velocity field in the porous domain is defined by Equation 12 and in the free domain by Equation 11.

Figure 6. Domains and boundary conditions in model.

Other boundary conditions are constant velocity at the inlet and uniform and constant pressure at the outlet.

To calculate α for every position in the coating, a wall distance function which is readily available in the software was utilized. This function creates the variable G (m^{-1}) which decreases with the increasing distance of any given point in a domain. In this case, the interface of reaction medium with

the catalyst coating was taken as the reference wall and a step function was defined to vary α as G decreases.

Both 3-D domains were discretized into 200 000 tetrahedral cells using the custom mesh generation method. 60 000 of these generated cells were in the porous domain with a total volume of 16 μL which were created using sweep function. The rest of the cells were created using the free tetrahedral function.

Mesh independence of the model was confirmed by refining the free domain first, until the output concentration is affected less than 0.5% by a further refinement step. After optimizing the mesh refinement in the free domain, the porous domain was refined until a further refinement affects the output concentration by less than 0.1%.

The velocity field in the domains was solved in steady state simulation using the MUMPS solver with convergence criterion of 10^{-5} . Then the obtained velocity fields in both of the domains were coupled to the convection and diffusion equation (Equation 6) in a time dependent step to obtain the concentration of phenol at the outlet of the reactor. The initial condition for the reactor volume is 100 ppm phenol in all the domains. The outlet concentration of phenol was recorded using a boundary probe at the outlet. The solver used was also MUMPS with a convergence criterion of 10^{-5} . The time steps were controlled by a second degree backward differentiation formula. The maximum time step boundary was defined as the time for the fluid at the inlet of the reactor to proceed 1 cm in the direction of the outlet, and is given by:

$$\Delta t = \frac{0.01}{Q/A_{in}} \quad (13)$$

Where Δt is the maximum time step, Q is the flowrate ($\text{m}^3 \cdot \text{s}^{-1}$) and A_{in} is the area of the reactor inlet opening (m^2).

A flow time equal to 5 passage times was simulated to make sure the outlet concentration was stable which was monitored by a boundary probe at the outlet.

Then the reaction rate and rate constant were calculated using the PFR model using the stable outlet value which can be given as follows:

$$k = \frac{\left(-\ln \frac{c_{out}}{c_{in}} \right)}{\tau} \quad (14)$$

Where k is the apparent reaction rate (s^{-1}) and τ is the passage time (s). The constants used in the simulation are summarized in Table 1.

Table 1. Constants used in the numerical model.

Physical Constants		
Name	Symbol	Value
Porosity	ε_p	0.525
Permeability	π	$6.94 \times 10^{-17} \text{ m}^2$
Degradation reaction (Eq. 9) rate constant	k_{deg}	$0.841 \times 10^{10} \text{ L.s}^{-1}.\text{mol}^{-1}$
Fluid density and dynamic viscosity	ρ, η	Reaction mixture was assumed to be pure water at 20 °C. Software material library values were used. $\rho = 998.21 \text{ (kg.m}^{-3}\text{)}$ $\eta = 1.002 \times 10^{-3} \text{ (Pa.s)}$
Diffusivity of phenol	D	$1.013 \times 10^{-9} \text{ (m}^2.\text{s}^{-1}\text{)}$ [22]
Discretization Constants		
Name	Value	
Free domain tetrahedron edge size	1.2 mm	
Porous domain tetrahedron edge size	1.2 mm	
Porous domain sweep step size	$3 \times 10^{-4} \text{ mm}$	

4.0 Results & discussion

4.1 Model validation

Firstly, the effect of irradiance on the apparent first order reaction rate was investigated at 1.5 ml/s constant flowrate. Results of 2030, 1185 and 186 μWcm^{-2} irradiance are shown in Figure 7a. These values correspond to 100 %, 50 % and 10 % power output, respectively. The 70 % and 80 % were not shown in Figure 7a for better visualisation of the results. The corresponding apparent first order reaction rates are shown in Figure 7b.

Figure 7. (a) Normalized phenol concentration in the reaction medium vs. time for different irradiances (100 %, 50 % and 10 % power output). (b) Experimental apparent first order rate constants vs. irradiance. Error bars are standard deviations based on seven measurements.

In their modelling work, Wang et al. observe a first order relation of the reaction rate to the irradiance on the catalyst surface until $1000 \mu W \cdot cm^{-2}$ [9,23]. When the irradiance is higher than this value, they observe a half order relation. In Figure 7b, it is shown that the reaction rate is observed to be related to the irradiance with a power law too. Furthermore, the irradiance has a power of 0.64 while Wang et al. had observed 0.5 which is close to each other considering the two systems are not even exhibiting the same phase.

The results show that increasing the irradiance speeds up the degradation. However, the enhancement in degradation rate is less in higher intensities than in low intensities, thus decreasing the $\frac{dk}{dI}$ slope. This can be due to the increase in electron hole recombination rate at higher irradiance levels. In addition to the increased recombination, the diffusion may not be transferring enough phenol to maintain the directly proportional increase in reaction rate. This can be the reason for the linear relation of k to I observed in several previous works which use the same catalyst but in slurry form [3,24]. This shows that the internal mass transfer of the coating as well as light penetration should indeed be accounted for when modelling such a system.

When the model was run with the r_{gen} values extracted from literature, model overshoot the experimental reaction rate constants as shown in Figure 8. The overshooting of the model was expected due to the higher irradiance and higher mass transfer in the slurry reactor used in the reference work [20].

Figure 8. Experimental reaction rate constants and first model estimations vs. different LED lamp loads.

However, even taken from a different setup, the average deviation of the model with this initial parameter was 92%. When the r_{gen} parameter was decreased to $7.486 \times 10^{-10} \text{ mol.L}^{-1}.\text{s}^{-1}$ and the simulations were rerun, clear correlation was observed throughout the considered irradiance range as shown in Figure 9.

Figure 9. Calculated and measured reaction rate constants vs. irradiance

While fitting the model, the assumed linear relation between the r_{gen} parameter and irradiance was validated as shown in Figure 10.

Figure 10. r_{gen} parameter vs. irradiance.

By utilizing this relation, the demonstrated model can be applied to different reactors using similar photocatalyst and coating method if the radiation field at the surface of the catalyst coating is known. The degree of freedom is now bounded to the irradiance value.

Once the model was validated for different irradiance values, validation for different flow rates was performed. Similar to the observations of Vezzoli et al. [2] no significant change in the apparent reaction rate was observed in the experimental measurements performed between 0.4 and 3.1 mL.s⁻¹ as shown in Figure 11. Since the reactor is circular the hydrodynamic diameter as well as the average fluid velocity was varying in the reactor. Reynolds number (Re) was calculated to be varying between 13 and 64 at the centre of the reactor with varying flowrate. There was no turbulent regime at any point in the reactor within the given boundary of flowrates. No higher flow rate values were used due to excessive computational time (> 1 week) needed to run the model. When a flow rate lower than 0.4 mL.s⁻¹ is used, the single pass conversion of the reactor was over 5% which would be so high that it would introduce a large error to differential reactor approximation used.

Furthermore, the differential reactor approximation introduces a higher error to lower flow rates and this error range decreases as the flow rate increases. This does not affect the error bars since the analytical methods are the same for all flow rates. Model results do not suffer from this error as they are calculated directly from outlet concentration. This difference in errors can result in the deviation observed in Figure 11.

Figure 11. Measured and calculated reaction rate constants at different flow rates. Dashed and dotted lines represent +10% and -10% deviation boundaries from the model respectively. Error bars show deviation of 3 measurements at different times.

Only 2.5% increase in apparent reaction rate constants was observed for 5-fold increase in Re . This is due to the internal mass transfer limitations of the catalyst coating. If the photocatalytic degradation reaction was only a surface reaction, then only the external mass transfer mechanisms would limit the transport of substrate molecules to the catalyst surface. Then, the mass transfer should have increased dramatically with increasing Re since the relative velocity between the liquid and solid surface would increase which would enhance the surface renewal. This would result in an increase in the overall reaction rate and thus in the apparent reaction rate constant, which is not observed. This is the reason the proposed model in this work is considering the coating as a porous medium instead of a surface in contrast to models using only LH kinetics working on surfaces to model the reaction.

Modelling the hydrodynamics and diffusion in the reactor as well as the coating enables the concentration gradient to be calculated throughout the reactor as shown in Figure 12a. The variation of the dimensionless α parameter can be seen across the catalyst coating in Figure 12b.

Figure 12. (a) Concentration contour plot of axial z - y plane of the reactor. (b) Contour plot of the α parameter. Zoomed to observe concentration gradient in coating.

As expected from the relation of reaction rate constant and flow rate, the concentration profile along the z axis within the free domain is uniform. However within the coating, along the $2.9\mu\text{m}$ thickness, a concentration gradient from 1 to 0.1 mol.m^{-3} can be observed. This result is also backed by the findings of Vezzoli et al. on the effect of coating thickness [2]. A thicker coating will not affect the reaction rate since both light and phenol molecules to be degraded cannot reach deep enough in the coating to affect the reaction rate.

This shows that a thicker coating does not necessarily mean a higher reaction rate. Instead of applying a thick catalyst coating, multiple plates with thinner coatings can be stacked for higher performance.

4.2 Photonic efficiency

The photonic efficiency of the degradation reaction using UV-LEDs was recently investigated for different slurry reactors. Chen et al. [25] report a 1% photonic efficiency at $670\text{ }\mu\text{W/cm}^2$ and Jamali et al. [10] report a photonic efficiency range of 0.4% to 0.8% at maximum $1000\text{ }\mu\text{W/cm}^2$ with a single LED similar to the ones used in this work.

The photonic efficiency is calculated by ;

$$\varepsilon = z \frac{R}{\Phi} * 100 \quad (14)$$

Where ε is dimensionless photonic efficiency, R is the reaction rate ($\text{mol.L}^{-1}.\text{s}^{-1}$), z is the amount of electrons transferred per molecule to be degraded (1 for this case) and Φ is the photon flux ($\text{mol.L}^{-1}.\text{s}^{-1}$) which is calculated automatically by the same spectrometer used for irradiance measurements. The photonic efficiencies in this work are given in Figure 13.

Figure 13. Photonic efficiency vs. irradiance.

Despite the usual mass transfer limitations in reactors applying immobilized catalyst, the photonic efficiency of the parallel plate UV LED reactor with immobilized catalyst which was investigated here, gave similar results to the referred slurry reactors [10]. This phenomenon may be due to an

increase in illumination efficiency which compensates for the decrease in mass transfer with immobilization. This facilitates the scale-up and proves that the LED powered TiO₂ coated reactor is a promising technology for photocatalytic advanced oxidation processes.

5.0 Conclusions

A new numerical model for photocatalytic degradation reactions was introduced. This model considers the immobilized catalyst coating as a porous medium rather than as a surface. Results obtained also show that the sharpest concentration gradient in the reactor is along the thickness of the coating which was not considered in the models before. This is due to the internal mass transfer limitations of the coating.

The importance of modelling internal mass and photon transfer limitations for photocatalytic degradation reactors with immobilized catalyst coating was now for the first time addressed with an appropriate model. The introduced model has only one degree of freedom which is related to the irradiance with a linear equation. Keeping the pH, light wavelength, temperature, substrate molecule and catalyst coating constant, the model can predict the reactor performance independent of the geometry as long as the radiation field is known. Furthermore, it can be used to scale-up different systems by using laboratory scale kinetic data.

We consider the proposed model to be one step further than the existing ones using LH kinetics. By changing the case from “parallel plates with surface reaction” to “flow through free and porous media with volume reaction” we have improved the empirical models to a more flexible model. This may facilitate the more efficient degradation reactor designs which will be needed to overcome effluent treatment problems without carbon emission.

Acknowledgements

This work was supported by the KU Leuven funded AOPtimize platform (IOFKP/10/006). JAM acknowledges long-term structural funding by the Flemish government (Methusalem). JR acknowledges the Research Foundation – Flanders (FWO) for a PhD fellowship. We would like to thank Dr. Nikki Janssens (Centre for Surface Chemistry and Catalysis (COK), Department of Microbial and Molecular Systems, KU Leuven, Belgium) for her help in reactor coatings Dr. Sreeprasanth Pulinthanathu Sree (Centre for Surface Chemistry and Catalysis (COK), Department of Microbial and Molecular Systems, KU Leuven, Belgium) for his help with film characterisation, Kenneth Simoens and Kristel Bernaerts (Chemical and Biochemical Process Technology and Control Section (BioTeC), Department of Chemical Engineering, KU Leuven, Belgium) for analytical

determination of phenol and Tycho van Noorden (Comsol BV, the Netherlands) for his help on the model.

References

- [1] J. Michałowicz, W. Duda, Phenols – Sources and Toxicity, *Polish J. Environ. Stud.* 16 (2006) 347–362.
- [2] M. Vezzoli, W.N. Martens, J.M. Bell, Investigation of phenol degradation: True reaction kinetics on fixed film titanium dioxide photocatalyst, *Appl. Catal. A Gen.* 404 (2011) 155–163.
- [3] C.-H. Chiou, C.-Y. Wu, R.-S. Juang, Influence of operating parameters on photocatalytic degradation of phenol in UV/TiO₂ process, *Chem. Eng. J.* 139 (2008) 322–329.
- [4] V. Goetz, J.P. Cambon, D. Sacco, G. Plantard, Modeling aqueous heterogeneous photocatalytic degradation of organic pollutants with immobilized TiO₂, *Chem. Eng. Process. Process Intensif.* 48 (2009) 532–537.
- [5] S. Ahmed, M.G. Rasul, W.N. Martens, R. Brown, M. a. Hashib, Heterogeneous photocatalytic degradation of phenols in wastewater: A review on current status and developments, *Desalination*. 261 (2010) 3–18.
- [6] S.J. Royae, M. Sohrabi, F. Soleymani, Performance of a photo-impinging streams reactor for the phenol degradation process, *J. Chem. Technol. Biotechnol.* 86 (2011) 205–212.
- [7] E. Rosenthal, F. Barringer, Green Promise Seen in Switch to LED Lighting, *New York Times*. (2009).
- [8] P. Principi, R. Fioretti, A comparative life cycle assessment of luminaires for general lighting for the of fi ce e compact fl uorescent (CFL) vs Light Emitting Diode (LED) e a case study, *J. Clean. Prod.* (2014).
- [9] Z. Wang, J. Liu, Y. Dai, W. Dong, S. Zhang, J. Chen, CFD modeling of a UV-LED photocatalytic odor abatement process in a continuous reactor., *J. Hazard. Mater.* 215-216 (2012) 25–31.
- [10] A. Jamali, R. Vanraes, P. Hanselaer, T. Van Gerven, A batch LED reactor for the photocatalytic degradation of phenol, *Chem. Eng. Process. Process Intensif.* 71 (2013) 43–50.
- [11] W.-M. Hou, Y. Ku, Photocatalytic decomposition of gaseous isopropanol in a tubular optical fiber reactor under periodic UV-LED illumination, *J. Mol. Catal. A Chem.* 374-375 (2013) 7–11.
- [12] A. Mills, S. Le Hunte, An overview of semiconductor photocatalysis, *J. Photochem. Photobiol. A Chem.* 108 (1997) 1–35.
- [13] O. Carp, Photoinduced reactivity of titanium dioxide, *Prog. Solid State Chem.* 32 (2004) 33–177.

Postprint of Leblebici M.E., Rongé J., Martens J.A., Stefanidis G.D., Van Gerven T. (2015). Computational modelling of a photocatalytic UV-LED reactor with internal mass and photon transfer consideration. *Chemical Engineering Journal*, 264, 962-970.

- [14] J. Bonin, I. Janik, D. Janik, D.M. Bartels, Reaction of the hydroxyl radical with phenol in water up to supercritical conditions., *J. Phys. Chem. A*. 111 (2007) 1869–78.
- [15] O.M. Alfano, I. Cabrera, A.E. Cassano, Photocatalytic Reactions Involving Hydroxyl Radical Attack I . Reaction Kinetics Formulation with Explicit Photon Absorption Effects, 379 (1997) 370–379.
- [16] M. Motegh, J. Cen, P.W. Appel, J.R. van Ommen, M.T. Kreutzer, Photocatalytic-reactor efficiencies and simplified expressions to assess their relevance in kinetic experiments, *Chem. Eng. J.* 207-208 (2012) 607–615.
- [17] D. Chen, F. Li, A.K. Ray, External and internal mass transfer effect on photocatalytic degradation, *Catal. Today*. 66 (2001) 475–485.
- [18] L. Durlofsky, J.F. Brady, Analysis of the Brinkman equation as a model for flow in porous media, *Phys. Fluids*. 30 (1987).
- [19] H.C.H. Rumpf, A.R. Gupte, Einflüsse der Porosität und Korngrößenverteilung im Widerstandsgesetz der Porenströmung, *Chemie Ing. Tech.* 43 (1971) 367–375.
- [20] Q. Xiang, J. Yu, P.K. Wong, Quantitative characterization of hydroxyl radicals produced by various photocatalysts., *J. Colloid Interface Sci.* 357 (2011) 163–7.
- [21] A. Sobczyński, Ł. Duczmal, W. Zmudziński, Phenol destruction by photocatalysis on TiO₂: an attempt to solve the reaction mechanism, *J. Mol. Catal. A Chem.* 213 (2004) 225–230.
- [22] A. Plugatyr, I.M. Svishchev, Molecular Diffusivity of Phenol in Sub- and Supercritical Water: Application of the Split-Flow Taylor Dispersion Technique, *J. Phys. Chem. B*. 115 (2011) 2555–2562.
- [23] Z. Wang, J. Liu, Y. Dai, W. Dong, S. Zhang, J. Chen, Dimethyl Sulfide Photocatalytic Degradation in a Light-Emitting-Diode Continuous Reactor: Kinetic and Mechanistic Study, *Ind. Eng. Chem. Res.* 50 (2011) 7977–7984.
- [24] A.P. Toor, A. Verma, C.K. Jotshi, P.K. Bajpai, V. Singh, Photocatalytic degradation of Direct Yellow 12 dye using UV/TiO₂ in a shallow pond slurry reactor, *Dye. Pigment.* 68 (2006) 53–60.
- [25] H.-W. Chen, Y. Ku, A. Irawan, Photodecomposition of o-cresol by UV-LED/TiO₂ process with controlled periodic illumination., *Chemosphere*. 69 (2007) 184–90.