CHEMICAL ENGINEERING RESEARCH AND DESIGN 92 (2014) 657–662

Contents lists available at ScienceDirect

Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

Mass transfer measurements and modeling in a microchannel photocatalytic reactor

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ABSTRACT

The main objective of this paper was to evaluate the influence of mass transfer on the photocatalytic efficiency at a low flow rate in the order of several mL per hour. Several continuous flow microchannel reactors have been used to study the degradation of salicylic acid (SA) taken as a model pollutant. The photocatalytic degradation of salicylic acid, under UV illumination of 1.5 mW cm^{-2}, was assessed from the outlet concentration measured by liquid chromatography HPLC. It was shown that the degradation of SA by UV was limited by mass transfer. Numerical simulations have allowed establishing a relationship of the Sherwood number valuable for all the microchannel geometries. Computational fluid dynamics with Comsol Multiphysics is useful for predicting the degradation yield for a given geometry of the microreactor. The best representation of the experimental data is obtained by introducing a kinetic law taking into account mass transfer limitation.

Keywords: Photocatalysis; Continuous-flow; Microreactor; Kinetic modeling; Mass transfer; Microstructuration; Simulation

1. Introduction

Traditionally, photochemical reactors have operated in batch mode. This configuration leads to a non-uniform distribution of UV light and a mass transfer limitation due to a slow diffusion. Among the possible solutions for intensification of photocatalytic reactions, there is the use of microreactors (Van Gerven et al., 2007). Microreactors with channel dimensions of a few hundred microns, enable optimum utilization of incident radiation (Georges et al., 2004) and larger surface to volume ratio compared to classic reactors. In the light of these advantages, there have been a number of developments in the area of flow-based photochemical microprocesses (Teekateerawej et al., 2006; Mills et al., 2007; He et al., 2010; Charles et al., 2012; Tsuchiya et al., 2012).

In spite of the many work on heat transfer and pressure drop in microchannels, the mass transfer studies remains very limited. Acosta et al. (1985) investigated experimentally the mass transport in narrow flow gaps with dimensions ranging between 0.2 and 0.5 mm at large Reynolds numbers ($Re = 1300$–$22\,000$). Van Male et al. (2004) explored, numerically and experimentally, the mass transfer in a square microchannel. They reported a Sherwood correlation for the channel heated from topside under laminar plug-flow. To the best of our knowledge, only one study relates the mass transfer determination in a rectangular microchannel (Barlay Ergu et al., 2009). The authors studied experimentally the local mass transfer in a rectangular channel with a hydraulic diameter of 0.208 mm. The Sherwood number correlation was reported with a power of the Reynolds number equal to 0.28.

In line with this reasoning, we report the photocatalytic degradation of SA on deposited catalyst TiO_2 in two microchannel reactors. The main objective of this paper was to evaluate the influence of mass transfer on the photocatalytic efficiency at a low flow rate. For this purpose, we have simulated the degradation reaction, with the objective to establish a relationship of the Sherwood number valid for several geometries and flow rates.

Overall, in this research, photocatalysis degradation of SA in TiO_2/UV system was investigated by (i) finding the conversion yield at each flow rate, (ii) modeling with COMSOL Multiphysics, and (iii) investigating the influence of mass transfer coefficient with the hydrodynamics.

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Received 19 July 2013; Received in revised form 30 August 2013; Accepted 10 October 2013
0263-8762/$ – see front matter
http://dx.doi.org/10.1016/j.cherd.2013.10.011

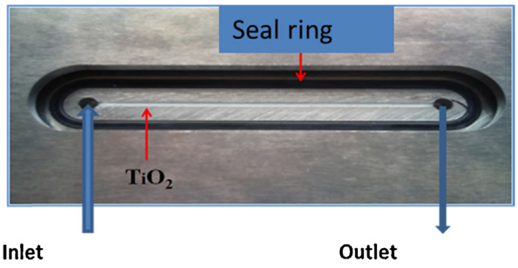

Fig. 1 – Photography of the microreactor with the central microchannel where is deposited the catalyst TiO_2.

2. Materials and methods

Several microchannel reactors have been tested (Corbel et al., 2008, 2011, 2012). They have been fabricated in inox by numerical machine. The top of the reactors was grooved with a microchannel. The micro-channels had a length of 70 mm. Only the results concerning two reactors are presented in this paper. Fig. 1 shows the design of the microreactor.

The two microchannel reactors characteristics are presented in Table 1. Both reactors display the same catalytic surface and roughly the specific surface κ (i.e., the surface area per unit of volume). All of them have a channel length of 70 mm.

The titanium dioxide samples were deposited on the micro-channel reactor (inner surface of the channel) according to the procedure of Furman et al. (2007). An aqueous suspension of TiO_2 Degussa P25 (Evonik) of 4 g/L at pH 3 was poured on the channel and the excess removed. The wetted channel was dried at 70 °C for 1 h. This coating process was repeated several times. After rinsing under running distilled water in order to remove loose particles, the amount of deposit was determined by weighing the dried reactor before and after the deposition. This method leads to a coating thickness of $5 \pm 1\,\mu m$ (determined by profilometry) and a surface load of $2.3 \pm 0.3\,mg/cm^2$. This value is generally required for complete light absorption (Ould-Mame et al., 2000; Zahraa et al., 1999). The photoreactor is a self-constructed microreactor with fluorescent lamp ($\lambda_{max} = 365\,nm$). The microchannel is closed to the UV lamp so that the incident light power is $1.5\,mW\,cm^{-2}$ at the surface of the catalyst, i.e., the level of the bottom of the channel (Fig. 2). The measure was performed with an UV radiometer.

Salicylic acid (SA) solution ($10\,mg\,L^{-1}$) was injected by means of a syringe pump through the microreactor at a constant inlet flow rate between 2.5 and 20 mL/h. During the residence time, SA is adsorbed on TiO_2, which may result in a decrease of the solution concentration. To take into account of this effect, we carried out the photodegradation reaction after flowing SA in the microreactor for 1.5 h in the dark to reach the adsorption equilibrium. During the course of photocatalysis and irradiation, a sample is withdrawn after regular time intervals. The peak area on the chromatograms is converted to SA concentration using a linear calibration curve. It gives the output concentration of salicylic acid and then the conversion yield. For each reaction time, final results were averaged out of at least three independent experiments.

Fig. 2 – Experimental setup equipped with feed control consisting of a syringe pump system.

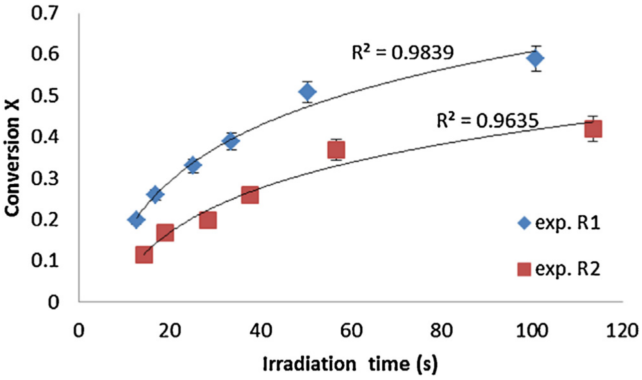

Fig. 3 – Experimental photocatalytic conversion yield of SA in microreactors R1 (depth = 0.5 mm) and R2 (depth = 0.75 mm) as a function of the irradiation time (lines are drawn for readability).

3. Photocatalytic activity

The reactors R1 and R2 have the same catalytic surface. In these experiments, the contact time τ equal to V/Q is adjusted by changing the flow rate Q. In this case, it is possible to compare the efficiency of the two reactors at the same contact time. Fig. 3 illustrates the variation of the conversion yield in the two reactors in function of irradiation time.

The conversion yields show a logarithmic growth with time to reach a constant level. The reactor with the smaller depth has the highest conversion. As they present almost the same catalytic surface S_c, the rate of degradation is improved by lowering the depth of the channel and by increasing the specific area κ. The apparent kinetic depends on the hydrodynamic and the boundary layer. This could be logically explained by a lower limitation by the mass transfer in reactor R1 and this aspect has been confirmed by simulation. A good agreement

Table 1 – Geometric characteristics for two microreactors with a channel length of 70 mm.

R_i	Width w (mm)	Depth h (mm)	Aspect ratio w/h	Volume V (mm^3)	Channel surface S_c(mm^2)	Spec. surface κ (mm^{-1})
R1	2	0.5	4	70.0	210	3.0
R2	1.5	0.75	2	78.7	210	2.7