

Guillaume Charles, Thibault Roques-Carmes*, Nidhal Becheikh, Laurent Falk and Serge Corbel

Impact of the design and the materials of rectangular microchannel reactors on the photocatalytic decomposition of organic pollutant

Abstract: The objective of this article is to find the optimal design of rectangular microchannel reactors, in terms of reactor dimensions and materials, in order to increase the photocatalytic activity. Microchannel reactors with immobilized titanium dioxide (TiO_2) as photocatalyst have been designed, fabricated, and tested. The photocatalytic degradation of salicylic acid is investigated as a function of microchannel size, materials that constitute the reactor, contaminant concentration and flow rate. All the reactors exhibit the same behavior. Higher degradation is observed for low pollutant concentrations and flow rates. The nature of the constituent element of the reactor has practically no influence on the photocatalytic process. The degradation performance is affected by the microchannel dimensions. The reactor with the largest channel width and length, and the lowest channel height displays the highest photocatalytic activity. For an optimal design of the rectangular microchannel reactors a relation between the degradation ratio X and the dimensions of the microchannel is reported. A linear relationship between X and wL/h^2 (L : length, w : width, h : height of the channel) is found experimentally. The product wL emphasizes the uniform irradiance over the entire catalyst surface and confirms that the bottom of the channel covered with TiO_2 is photoactivated. The term in $1/h^2$ is necessary to take into account the mass transfer limitation.

Keywords: aluminum; microchannel reactor; photocatalysis; stereolithography; titanium dioxide.

*Corresponding author: Thibault Roques-Carmes, Laboratoire Réactions et Génie des Procédés, UPR 3349 CNRS, Université de Lorraine, 1 rue Grandville, BP 20451, 54001 Nancy Cedex, France, e-mail: thibault.roques-carmes@ensic.inpl-nancy.fr

Guillaume Charles: Laboratoire Réactions et Génie des Procédés, UPR 3349 CNRS, Université de Lorraine, 1 rue Grandville, BP 20451, 54001 Nancy Cedex, France

Nidhal Becheikh: Laboratoire Réactions et Génie des Procédés, UPR 3349 CNRS, Université de Lorraine, 1 rue Grandville, BP 20451, 54001 Nancy Cedex, France

Laurent Falk: Laboratoire Réactions et Génie des Procédés, UPR 3349 CNRS, Université de Lorraine, 1 rue Grandville, BP 20451, 54001 Nancy Cedex, France

Serge Corbel: Laboratoire Réactions et Génie des Procédés, UPR 3349 CNRS, Université de Lorraine, 1 rue Grandville, BP 20451, 54001 Nancy Cedex, France

List of abbreviations

a	proportionality factor
A_{cat}	total catalyst surface (mm^2)
C_{in}	salicylic acid concentration at the inlet of the reactor (mg/l)
C_{out}	salicylic acid concentration at the outlet of the reactor (mg/l)
$C_{\text{out}}(\text{dark adsorption})$	lowest concentration during the dark adsorption period (mg/l)
$C_{\text{out}}(\text{dark})$	concentration at the plateau in absence of irradiation (mg/l)
$C_{\text{out}}(\text{UV})$	concentration at the plateau in presence of irradiation (mg/l)
$E_{X/Y}$	elasticity of the degradation with respect to key operating parameters
h	microchannel height (mm)
I	incident light energy density at the surface of the catalyst (mW/cm^2)
L	microchannel length (mm)
Q	volumetric flow rate (ml/h)
Re	Reynolds number
R_a	adsorption efficiency of the photocatalyst
w	microchannel width (mm)
X	degradation ratio of salicylic acid

Greek letter

κ	specific catalyst surface area per volume unit of liquid treated inside the reactor (m^{-3})
----------	---

Acronyms

R	polymeric microchannel reactor fabricated by stereolithography
Aluminum	aluminum microchannel reactor
Polycarbonate	polycarbonate microchannel reactor

1 Introduction

Photocatalysis is a potential technology for the destruction of organic contaminants in water, such as aromatic compounds, which present a potential hazard to the environment [1–3]. The mineralization of remaining traces of organic contaminants in water together with the removal of microorganisms make photocatalysis a very suitable technique for the treatment of waste water but also a valuable alternative to conventional drinking water treatment and for the production of ultrapure water for pharmaceutical applications [4].

Titanium dioxide (TiO_2) is the most commonly used semiconductor photocatalyst because it is highly photoactive, photostable, biologically and chemically inert, and relatively inexpensive. The photochemical technology using TiO_2 photocatalyst for the water treatment process is known as a clean method. Regarding economical and practical reasons, it becomes clear that the most useful form of titania photocatalyst is that of a film or coating on a convenient support [5, 6]. However, immobilized systems have the problem that they are difficult to scale-up, have low interfacial surface areas and mass transfer limitations may occur [7, 8].

In this context, microstructured reactors might prove advantageous because they inherently possess large surface-to-volume ratios (i.e., maximized reagent/catalyst contact) and thus compensate for the disadvantages associated with the immobilization of the photocatalyst [9]. Features unique to microreactors include laminar flow, short molecular diffusion distances, large specific interfacial areas and excellent heat transfer characteristics [10]. However, microreactors have only very recently been investigated in performing photocatalytic reactions [9–18]. For photochemical reactions in particular, microreactors exhibit higher spatial illumination homogeneity and better light penetration through the entire reactor depth in comparison to large-scale reactors [11]. In addition to the miniaturization of the reaction system itself, light emitting sources on the micro- or even nanoscale near the catalyst are necessary to achieve uniform and maximized illumination [11, 18]. For instance, Gorges et al. [9] used an array of 11 UV-A LEDs mounted on a printed circuit board to uniformly illuminate 19 microchannels with a cross-section of approximately $300\ \mu\text{m} \times 200\ \mu\text{m}$.

However, to avoid the difficult fabrication of micro- or nanoreactors and the prohibitive cost of the light sources on the micro- or nanoscale, we propose to introduce rectangular microchannel reactors with typical characteristic dimensions between $500\ \mu\text{m}$ and $2\ \text{mm}$. The size of the

channel is more adapted to future industrial implementation and more particularly for the numbering-up of these devices in order to cope with large volumetric flow rates. Unfortunately, this particular configuration leads to mass transfer limitation (of the pollutant from the solution to the catalyst surface) and axial dispersion under laminar flow [19, 20]. In a previous study, we demonstrated the potentiality of these types of microchannel reactors for the determination of the kinetic constants during a photocatalytic reaction [19]. It becomes now important to evaluate in detail the photocatalytic performances of these microchannel reactors.

The design of an effective photocatalytic microreactor can be obtained by an appropriate optimization of the dimensions and shapes of the reactor geometry in order to: (i) ensure a homogeneous and sufficient irradiation on the whole photocatalyst surface; (ii) achieve the highest contact of the reactant to the surface of the photocatalyst, i.e., large surface-to-volume ratio; and (iii) increase the pollutant mass transfer from the solution to the catalyst surface, i.e., high mass transfer coefficient k_a . In spite of many works on photocatalytic microreactors, the studies dealing with the influence of the microchannel size on the photocatalytic activity are very limited. It then becomes necessary to provide a large amount of experimental data in order to measure the effect of the dimensions of the reactor on the photocatalytic performances. In addition, it is now well established that the supporting material of the catalyst can play a major role in photocatalytic properties [21]. In the case of large-scale reactors, several materials have already been investigated as supports for TiO_2 such as glass, quartz, glass fibers, wool, and steel [22, 23]. Regarding microreactors, much of the previous work was limited to a small number of reactors used as supporting materials such as ceramic [9, 17], silicon wafer, and glass [11, 12]. Studies involving new materials, more particularly polymeric and metallic substrates, would be expected to be highly revealing. In line with this reasoning, microreactors fabricated with different materials are tested. We have identified epoxy polymer, polycarbonate, and aluminum as valuable materials for photocatalytic microdevices.

In this paper, rectangular microchannel reactors with immobilized TiO_2 as photocatalyst are designed, constructed, and tested. This study focuses on the photocatalytic degradation of a model component, salicylic acid, because it is easily degraded. The microchannel sizes, materials that constitute the reactor, contaminant concentration and flow rate are varied. For an optimal design of the microchannel reactors, a relation between the degradation ratio and the dimensions of the microchannel is presented. The described results provide useful

guidelines for the design of photocatalytic microreactors in the presence of mass transfer limitation.

2 Materials and methods

2.1 Fabrication of photocatalytic microchannel reactors

We manufactured rectangular microchannel reactors in which TiO_2 was deposited as the photocatalyst. The microchannel reactors were fabricated with different materials. The epoxy polymer (“R”) microchannel reactors were fabricated by stereolithography, whereas the aluminum (“Aluminum”) and polycarbonate (“Polycarbonate”) microchannel reactors were manufactured using a mechanical machining technique.

The polymeric rectangular microchannel reactors with different dimensions were fabricated in epoxy resin by a home-made stereolithography apparatus using a UV Nd-YAG laser [24–26]. The stereolithography technique is based on the process of photopolymerization, in which a liquid resin is converted to a solid polymer on exposure to laser radiation. The models are produced by curing successive layers of resin material until a three-dimensional object is formed. Figure 1A depicts a photographic view of the polymeric microreactor.

Photocatalytic degradation was also measured on home-made aluminum and polycarbonate rectangular microchannel reactors. The raw material of the reactors consisted of a thick rectangular sheet of aluminum or polycarbonate. The top of the reactors was mechanically grooved with a rectangular microchannel. The microchannels had a width of 1 mm, a height of 0.5 mm and a length of 70 mm.

The TiO_2 samples were deposited on the microchannel reactors (inner surface of the channel) according to the procedure of Furman et al. [27]. 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 50°C for 1 h. This coating process was repeated several times depending on the nature of the material which constitutes the reactor: 15 times for aluminum reactor, 20 times for epoxy polymeric reactors and 23 times for polycarbonate reactor. 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 resulted in a coating thickness of $5 \pm 1 \mu\text{m}$ (determined by profilometry) and a surface load of $2.8 \pm 0.3 \text{ mg/cm}^2$ regardless of

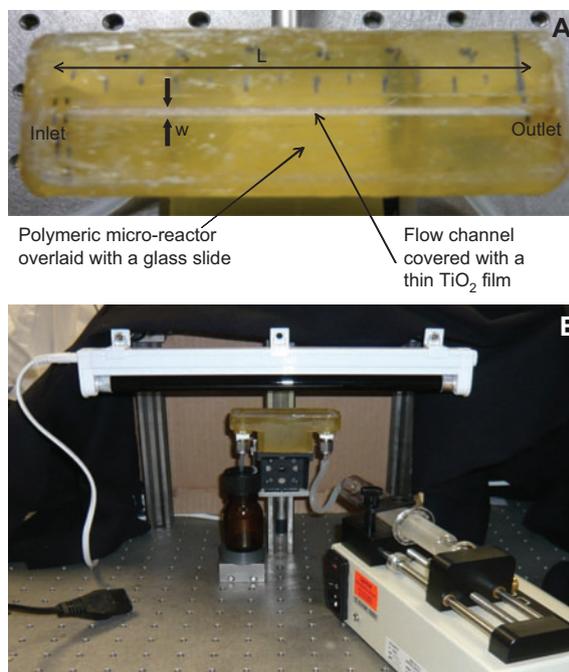


Figure 1 (A) Photographic view of the polymeric microchannel reactor fabricated in epoxy resin by stereolithography. (B) Experimental setup for photocatalytic reactions with a microchannel reactor.

the microchannel nature and dimensions (Table 1). The latter value is significantly above the minimal load generally required for complete light absorption [3, 28, 29]. This experimental procedure enabled to control the mass of the coated catalyst and to obtain a uniform layer on the entire surface of the channel. Note that only the two side walls and the bottom of the channel were covered with the photocatalyst. Following the deposition of the catalyst, the microreactor was sealed with a glass top plate using an epoxy glue.

The total catalyst surface A_{cat} is obtained using:

$$A_{\text{cat}} = L(w + 2h) \quad (1)$$

where L denotes the channel length, w the channel width and h the channel height.

Ray and Beenackers [7] identified the illuminated specific surface area (κ) of a photocatalyst within the reactor that is in contact with the reaction liquid as an important design parameter for the construction of photocatalytic reactors. κ is calculated using the following formula:

$$\kappa = \frac{2h+w}{wh} \quad (2)$$

The characteristics of the rectangular microchannel reactors with different dimensions are shown in Table 1. It appears that the κ values for our microchannel reactors

	Width w (mm)	Height h (mm)	Length L (mm)	κ (m ⁻¹)	A_{cat} (mm ²)	Amount of TiO ₂ deposited on the channel walls (mg/cm ²)
R1	1	0.5	70	4000	140	2.8
R1.5	1.5	0.5	70	3333	175	2.9
R2	2	0.5	70	3000	210	2.5
R0.75	1.5	0.75	70	2670	210	3.0
R4	2	1	70	2000	280	2.6
Polycarbonate	1	0.5	70	4000	140	2.7
Aluminum	1	0.5	70	4000	140	2.9

Table 1 Geometrical characteristics of the rectangular polymeric (“R”), aluminum (“Aluminum”), and polycarbonate (“Polycarbonate”) microchannel reactors.

κ refers to the specific catalyst surface area per volume unit of liquid treated inside the reactor and A_{cat} to the total catalyst surface.

surpass the values for other macroreactor types ($\kappa=27$ m⁻¹ for external type annular reactor and $\kappa=133$ m⁻¹ for immersion type reactor) due to the large surface-to-volume ratio inherent to any microstructured reactor [11].

2.2 Photocatalytic reaction system

The experimental setup used for the photocatalytic tests is shown in Figure 1B. An aqueous solution of salicylic acid was introduced into the microchannel reactor with a syringe pump (KdScientific, KDS-100-Ce, Holliston, USA). All the reaction experiments were performed at room temperature ($21 \pm 0.5^\circ\text{C}$). The flow regime inside the microreactor channels was laminar because the Reynolds numbers ($Re=0.8-7.0$) were smaller than the critical Re . A flexible tube at the outlet of the reactor enabled to collect the irradiated solution samples. The microchannel reactors operated under continuous flow operation as plug-flow reactor.

A UV fluorescent lamp (Oaric Halolite, Gurgaon, Haryana, India, light power 8 W) was positioned outside the reactor (Figure 1B). It was located at 1 cm above the reactor and parallel to the central axis of the channel. The incident light power was recorded by an ultraviolet radiometer (WinCamD-UCM, DataRay Inc., Boulder Creek, CA, USA) and indicated a spectral response centered at 365 nm with a half-bandwidth of 12 nm. The incident light energy density at the surface of the catalyst was $I=1.5$ mW/cm².

To characterize the photocatalytic performance of the microchannel reactors, the degradation of salicylic acid, a widely employed compound for the testing of photocatalytic systems, was investigated [19, 25, 28, 29]. The photocatalytic process was followed by monitoring the disappearance of salicylic acid. Solutions of salicylic acid were prepared with Milli-Q water. Prior to each photocatalytic experiment, the aqueous salicylic acid solution was

magnetically stirred under oxygen for 30 min. During this pretreatment, air was bubbled into the suspension. After the pretreatment, the salicylic acid solution was injected in the syringe to proceed to photocatalytic degradation. The photocatalytic experiments were performed at pH 6. The salicylic acid concentration after photoreaction at the outlet of the reactor (C_{out}) was measured by high performance liquid chromatography (HPLC). The HPLC system was equipped with a variable Shimadzu SPD-20A UV-Vis detector, a Rheodyne Model 7725 injector, a loop size of 20 μl and a Shimadzu LC-20AT pump. Chromatograms were registered with standard reversed-phase HPLC using a Lichrosorb RP-18 column (250 mm \times 4.6 mm, i.e., particle size 5 μm , Supelco-Inc). The eluent was a mixture of 70% (v/v) methanol and 30% (v/v) water containing 0.1% (v/v) of phosphoric acid. The flow rate was 1 ml/min and the detection wavelength was 295 nm.

Prior to the photocatalytic experiment, the experimental system was operated for several hours using distilled water to remove any organic and inorganic impurities adsorbed on the surface of the catalyst as well as any TiO₂ coating particles that were not strongly attached to the surface of the microchannel reactor.

3 Results and discussion

3.1 Influence of the materials that constitute the reactor

3.1.1 Transient regime

To obtain relevant information about the photocatalytic process, it is necessary to carry out experiments where the system operates under continuous flow operation in

transient regime. For this purpose, the aqueous salicylic acid solution is injected continuously in the microchannel reactor in the absence or in the presence of illumination. The outlet salicylic acid concentrations (C_{out}) are collected at appropriate times. An example of a typical experiment is given in Figure 2A. At time $t=0$, the solution is introduced into the reactor, at a given flow rate, in the absence of UV irradiation. The outlet concentration decreases with time. The diminution of the concentration is attributed to the adsorption of the salicylic acid molecules on the TiO_2 surface. After a given adsorption time (typically 6–10 min)

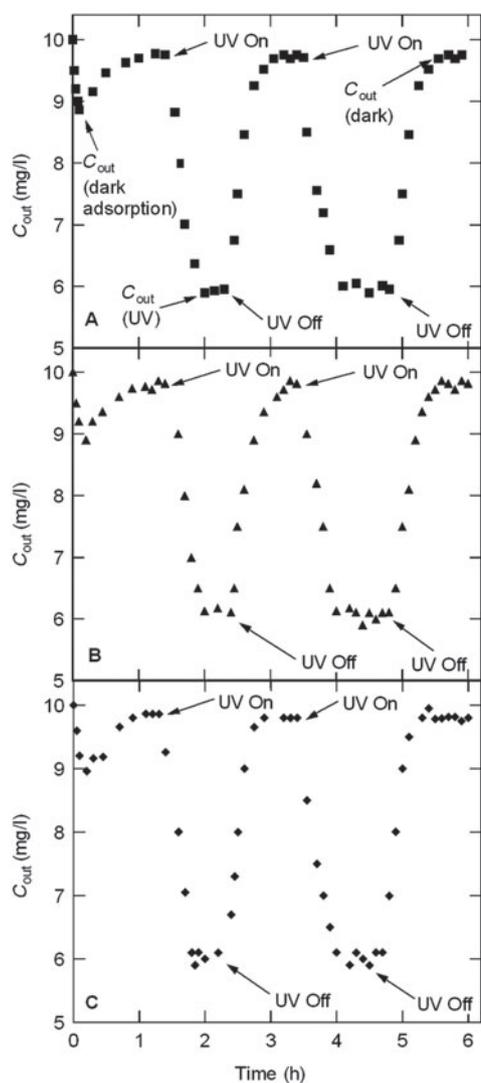


Figure 2 Dark-photocatalytic experiments. The system operates under continuous flow operation in transient regime for: (A) polymeric, (B) aluminum, and (C) polycarbonate microchannel reactors. At $t=0$, the aqueous salicylic acid solution is introduced into the reactor in the absence of UV irradiation. At $t=1.4$ h, a photocatalytic experiment is started by switching on the UV lamp (“UV On”). At $t=2.3$ h, the irradiation is stopped (“UV Off”). Geometrical characteristics of the reactors: $w=1$ mm, $h=0.5$ mm, and $L=70$ mm. Experimental conditions: $Q=5$ ml/h, $C_{in}=10$ mg/l, and $I=1.5$ mW/cm².

C_{out} reaches a minimum value given as C_{out} (dark adsorption)=8.86 mg/l. Then, an increase in concentration is observed. The curve consists of a steep part followed by a leveling off to a plateau value for which the concentration becomes constant and equals C_{out} (dark)=9.77 mg/l. This behavior can be readily explained. When all pollutant molecules are adsorbed on TiO_2 , the addition of higher quantities of salicylic acid would have no effect on the adsorption because the pollutant molecules are in excess in comparison with the amount of active centers of the catalyst. Consequently, no further adsorption occurs and C_{out} increases up to a plateau value. It must be emphasized, however, that the concentration at the plateau [C_{out} (dark)=9.77 mg/l] does not exactly merge with the inlet concentration ($C_{in}=10$ mg/l). Nevertheless, the slight difference in the concentrations is approximately 0.23 mg/l, which is actually within the limit of the measurement confidence [19]. Then, at $t=1.4$ h, a photocatalytic experiment is started by switching on the UV lamp (“UV On”). A decrease in concentration with time is reported. This corresponds to photocatalytic degradation of the pollutant. With time, the photocatalytic rate decreases and the concentration reaches a plateau value which is around C_{out} (UV)=5.93 mg/l. The salicylic acid concentration remains constant indicating that equilibrium has been reached. The concentration at the plateau in the presence of UV light [C_{out} (UV)=5.93 mg/l] is significantly smaller than that obtained during the dark adsorption [C_{out} (dark adsorption)=8.86 mg/l]. Then, at $t=2.3$ h, the irradiation is stopped (“UV off”). Again an increase in the concentration is observed up to a plateau value close to C_{out} (dark)=9.75 mg/l. Photodegradation becomes negligible in the absence of UV light and the pollutants present in the reactor are not degraded. To confirm this behavior, blank experiments are also performed with uncoated microchannel reactors under UV light irradiation. The results, not reported, show no observable change in the outlet concentration of salicylic acid. A significant disappearance of the pollutant could only be observed with the simultaneous presence of titania and UV light. This establishes that the system works in a pure photocatalytic regime.

The dark-photocatalytic process can be repeated many times. If, after the dark period, at $t=3.4$ h, the UV lamp is switched back to the photocatalytic regime (“UV on”), the same equilibrium concentration is found [C_{out} (UV)=6.01 mg/l] and the same dark plateau is reached [C_{out} (dark)=9.74 mg/l] after a second cycle. This is a clear evidence of a reversible mechanism.

In the first decreasing part of the curve ($t<10$ min), we identify the dark adsorption period. The minimum value of C_{out} , defined as C_{out} (dark adsorption), refers to the equilibrium salicylic concentration remaining in the reactor

(nonadsorbed). The extent of adsorption of the pollutant on the photocatalyst is determined by the difference in the concentration of salicylic acid between the inlet and the outlet of the reactor after reaching the adsorption/desorption equilibrium. The adsorption efficiency of the photocatalyst is given by:

$$R_a = \left(\frac{C_{in} - C_{out}(\text{dark adsorption})}{C_{in}} \right) \times 100 \quad (3)$$

where C_{in} denotes the salicylic acid concentration at the inlet of the reactor.

A second set of dark-photocatalytic measurements in transient regime is performed using aluminum (Figure 2B) and polycarbonate (Figure 2C) microchannel reactors. The data clearly show the same trend as above for the polymeric microchannel reactor and moreover, very similar outlet concentrations, in terms of dark adsorption [C_{out} (dark adsorption)], photocatalytic degradation [C_{out} (UV)] and dark experiment [C_{out} (dark)]. The adsorption efficiencies R_a are equal to 12.86%, 12.41%, and 11.73% for polymeric, aluminum, and polycarbonate microchannel reactors, respectively. The slight difference in the adsorption efficiencies is approximately 1%, which is actually within the margin of error of these measurements. Consequently, the adsorbed quantities are analogous for the three microchannel reactors. It can be deduced that the three supported catalysts have very similar characteristics concerning the surface of titania exposed per unit area of microchannel support. As expected, the nature of the material which composes the microchannel reactor does not modify the developed surface of TiO_2 .

In addition, by recording the concentration at the plateau in the presence of irradiation [C_{out} (UV)] one obtains the outlet salicylic acid concentration when the microchannel reactor operated under permanent regime. The experimental degradation ratio of salicylic acid during its contact with the catalyst, in the permanent regime, is defined by:

$$X = \frac{C_{in} - C_{out}(UV)}{C_{in}} \quad (4)$$

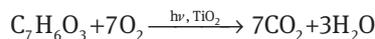
where C_{in} denotes the salicylic acid concentration at the inlet of the reactor.

At the start of every experiment, introduction of the reactant into the system is now performed under light irradiation. Before samples are taken, the solution is passed through the reactor, under light irradiation, for at least 1 h to ensure that steady-state conditions have been reached (permanent regime). The obtained value of the outlet concentration C_{out} (UV) is used to estimate the degrada-

tion ratio of salicylic acid using Eq. (4). Every experiment is repeated at least three times, and the data presented below are the averages of the repeated results. Data are considered acceptable only if for three repetitions, the data for each point differ by <5%.

3.1.2 Permanent regime

The complete photocatalytic degradation of salicylic acid can be summarized as:



Guinea et al. [30] described 2,3-dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid, and maleic acid to be the major intermediates for the photocatalytic degradation of salicylic acid. However, in our experiments with the microchannel reactors, we could not detect any of these substances with the employed HPLC method.

Figure 3 depicts the influence of the flow rate on the degradation ratio of salicylic acid in the polymeric, aluminum, and polycarbonate microchannel reactors. The photocatalytic activity of the microchannel reactors is again confirmed from the degradation of salicylic acid. These results clearly establish the successful integration of the photoreactive TiO_2 into all the microchannel systems regardless of the material that constitutes the reactor. All the curves merge into a unique master curve. The degradation decreases with the flow rate, which can be attributed to the reduction of the residence time of the reactants in the microchannels. It is striking that the degradation performances are not affected by the nature of the materials which compose the

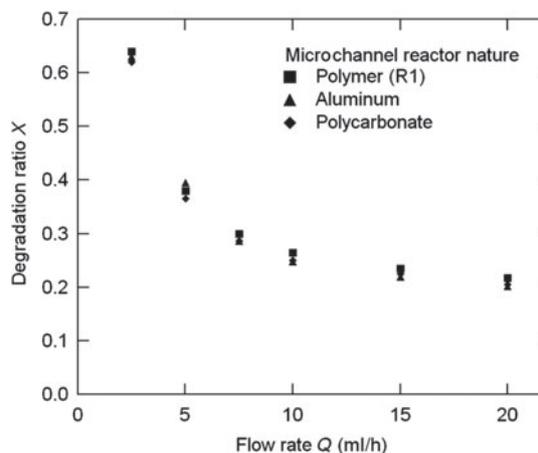


Figure 3 Degradation of salicylic acid in the polymeric, aluminum, and polycarbonate microchannel reactors as a function of the flow rate. Geometrical characteristics of the reactors: $w=1$ mm, $h=0.5$ mm, and $L=70$ mm. Experimental conditions: $C_{in}=10$ mg/l and $I=1.5$ mW/cm².

microchannel reactors because all the curves collapse to a single curve. Recall that the three reactors display very similar characteristics concerning the surface of titania exposed per unit area of microchannel support because the adsorbed quantity of pollutant (R_a) is the same for the three systems (see section 3.1.1). Indeed, if the difference in the degradation ratios between the reactors is significant, this would suggest that the pure photochemical performance (photo-induced nature of the activation of the process with the participation of photo-induced electrical charges such as electrons and holes) is mainly determined by the catalyst support (reactor) nature. This is not the case in the present study. The catalyst deposition procedure leads to a uniform layer of TiO_2 with a thickness of $5 \pm 1 \mu\text{m}$ on the entire surface of the channel. This corresponds to a titania surface load of 2.8 mg/cm^2 which is above the minimal load required for complete light absorption. This confirms that we deal with a TiO_2 film which is sufficiently thick to mask the possible action of the support. For instance, the surface electronic effect induced by aluminum (the presence of metal helps the electron-hole separation by attracting photoelectrons and promotes the formation of supplementary hydroxyl radicals), which generally enhances photoactivity [31, 32], cannot be efficient in the present case because the metal/ TiO_2 contact occurs at the bottom of the reactor whereas the photocatalytic reaction happens at the top of the TiO_2 film far from the metal. In addition, as a result of the deep TiO_2 layer, the penetration depth of the photons is very low and the catalyst particles close to the metallic support could not be photoactivated. Because the improvement in the photocatalytic properties induced by aluminum and polycarbonate supports is not obvious, the other experiments are performed using polymeric microchannel reactors fabricated using stereolithography because it authorizes the fabrication of complex forms with a great flexibility [24, 26].

3.2 Influence of the reactor dimensions

Figure 4 displays the degradation ratio of salicylic acid in the polymeric microchannel reactors as a function of the inlet concentration for different flow rates and reactor dimensions. All the reactors show the same trend. As previously observed, higher degradation is reported for lower flow rates. Furthermore, degradation decreases with inlet concentration. The degradation ratio is closely linked to the salicylic acid adsorbed amount because the photocatalytic reaction occurs on the surface of the catalyst. An inlet concentration of 4 mg/l seems sufficient to saturate the catalyst surface (all catalytic sites of the catalyst surface are occupied) due to the low total catalyst surface

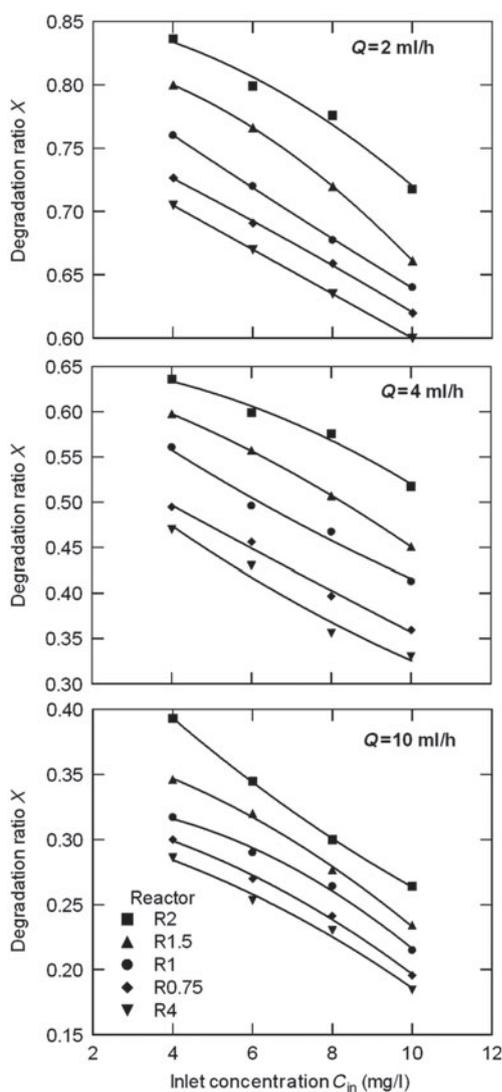


Figure 4 Degradation of salicylic acid in the polymeric microchannel reactors with different dimensions as a function of the inlet concentration at different flow rates (Q). The lines are drawn to guide the eye. Geometrical characteristics of the reactors: $\kappa=3000 \text{ m}^{-1}$ and $A_{\text{cat}}=210 \text{ mm}^2$ for R2, $\kappa=3333 \text{ m}^{-1}$ and $A_{\text{cat}}=175 \text{ mm}^2$ for R1.5, $\kappa=4000 \text{ m}^{-1}$ and $A_{\text{cat}}=140 \text{ mm}^2$ for R1, $\kappa=2670 \text{ m}^{-1}$ and $A_{\text{cat}}=210 \text{ mm}^2$ for R0.75, $\kappa=2000 \text{ m}^{-1}$ and $A_{\text{cat}}=280 \text{ mm}^2$ for R4. κ corresponds to the specific catalyst surface area per volume unit of liquid treated inside the reactor and A_{cat} to the total catalyst surface.

($A_{\text{cat}}=140\text{--}210 \text{ mm}^2$). A further increase in salicylic acid concentration does not affect the actual catalyst surface concentration and therefore results in the diminution of the degradation ratio at higher inlet concentrations.

Degradation performances are also affected by microchannel size. Under the same experimental conditions, the highest photocatalytic degradation is obtained in the reactor R2 which possesses the largest channel width and the lowest channel height among the reactors studied. In addition, the degradation ratio cannot be directly

related to the total catalyst surface (A_{cat}) and also to the specific catalyst surface area (κ). For instance, there is a large difference in the degradation ratio between the microchannel reactors R2 and R0.75 while they display the same catalyst surface. In the same way, degradation is relatively low for reactor R1 while it gets the highest specific catalyst surface area. Note that, usually, a larger surface area should be an advantage in using the photocatalyst [1, 7]. This is not the case in the present study. We are aware, however, that the residence time in the reactors can affect photocatalytic performances. For a flow rate of 2 ml/h, residence times are equal to 63, 94, 126, 141, and 252 s, for reactors R1, R1.5, R2, R0.75, and R4, respectively. The values of the residence time are unable to fully explain the photocatalytic behavior because the highest residence time is reported for reactor R4 while it displays the lowest photocatalytic activity. In addition, there is a large difference in the degradation ratio between the microchannel reactors R2 and R0.75 while they possess approximately the same residence time. To summarize, the effect of the reactor dimensions appears and the different sizes of the channel are responsible for the differences of activity observed.

All previous experiments were performed with reactors having a constant microchannel length ($L=70$ mm). Additional series of measurements are made to test the effect of the channel length. Experiments are then performed with microchannel reactors with different lengths. The reactors used are similar in width and height to R0.75 ($w=1.5$ mm and $h=0.75$ mm) and R4 ($w=2$ mm and $h=1$ mm). In Figure 5 the evolution of the degradation ratio as

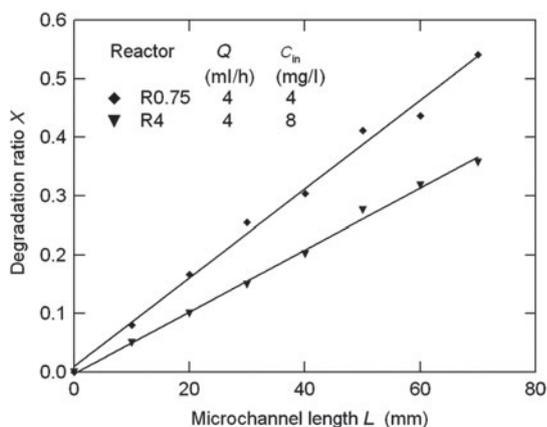


Figure 5 Degradation ratio (X) of salicylic acid as a function of the microchannel length (L) for different inlet concentrations (C_{in}) and polymeric reactors. The reactors used are similar in width and height to R0.75 ($w=1.5$ mm and $h=0.75$ mm) and R4 ($w=2$ mm and $h=1$ mm). The lines represent the best linear fits given by $X=0.0076 L + 0.0097$ ($R^2=0.992$) for R0.75, and $X=0.0053 L - 0.0026$ ($R^2=0.996$) for R4.

a function of the channel length is reported for a variety of experimental conditions. For the different reactors, a similar evolution can be observed. Degradation increases with the microchannel length, which is explained by the rise of the residence time of the reactants in the reactor. The degradation ratio X follows a linear increase as a function of the microchannel length L . The slopes of the curves are 0.0053 and 0.0076 mm^{-1} for R4 and R0.75, respectively. These slopes depend on both the inlet concentration and the reactor dimensions (channel width and height).

For an optimal design of the microchannel reactors, it is important to obtain a relation between the degradation ratio X and the geometrical dimensions of the channel (w , h , and L) in order to reproduce the experimental results, i.e., $X(\text{R2}) > X(\text{R1.5}) > X(\text{R1}) > X(\text{R0.75}) > X(\text{R4})$. It was previously observed that X increases with the channel width w and length L (Figures 4 and 5) while it decreases with the channel height h (Figure 4). For this reason, a dimensionless geometrical parameter, which reads as wL/h^2 , is introduced. The product wL highlights the uniform light irradiation over the entire catalyst surface. It is then considered that the bottom of the channel covered with TiO_2 can be photoactivated. The actual illuminated catalyst surface becomes equal to wL . In addition, the term in $1/h^2$ is necessary to take into account the diffusion of salicylic acid from the solution to the actual illuminated catalyst surface (mass transfer limitation). In a precedent study, we demonstrated that some external mass transfer limitation occurs in our experimental system [19]. For the special case of microchannel reactors, Commenge et al. [33] showed that in the case of heterogeneous reactions limited by mass transfer, the characteristic time for the operation (diffusion limited) varies with the square of the channel height (h^2).

For a constant value of the flow rate and the inlet salicylic acid concentration, the degradation ratio can be reported as a function of wL/h^2 . Each experimental point corresponds to a given microchannel reactor. In Figure 6, the degradation ratios from the data of Figure 4 (reactors R2, R1.5, R1, R0.75, and R4) are plotted against the dimensionless geometrical ratio wL/h^2 , for several flow rates Q and inlet concentrations C_{in} . In all cases, a similar evolution can be observed. For a fixed value of Q and C_{in} , the data points fall on a single line indicating that X increases linearly with wL/h^2 . Based on 12 sets of experimental data the following equation is obtained to correlate the degradation ratio in terms of length, width, and height of the microchannel. The equation can be written as:

$$X = a \frac{wL}{h^2} \quad (5)$$

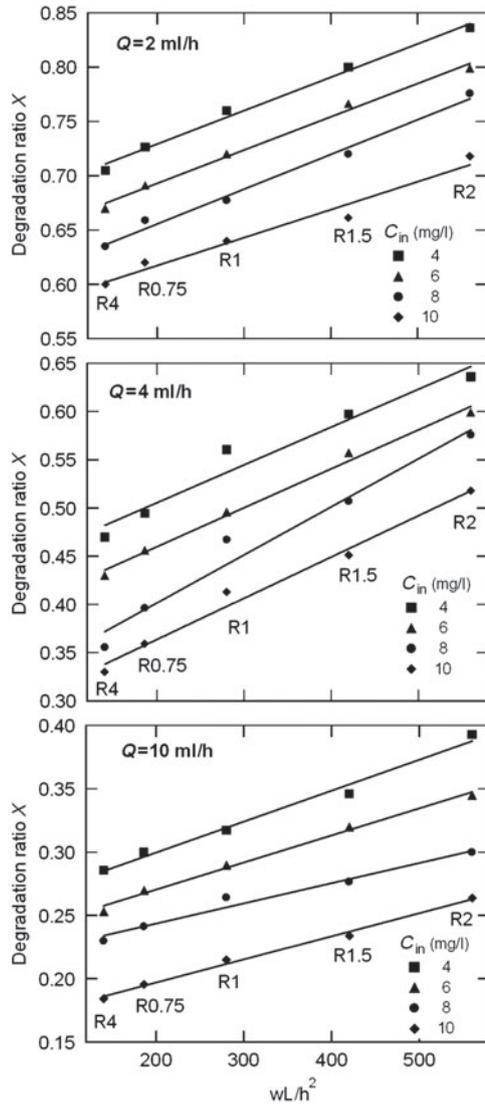


Figure 6 Degradation of salicylic acid as a function of the dimensions of the microchannel reactors (wL/h^2) for different inlet concentrations (C_{in}) and flow rates (Q). w refers to the channel width, L to the channel length, and h to the channel height. The lines represent the best linear fits given by $X=a(wL/h^2)$.

Applying this linear fit to the data of Figure 6 gives the values of the proportionality factor a . All the results are reported in Table 2. A majority of regression coefficients are better than 0.986. For a constant flow rate, the proportionality factor (a) does not depend on the inlet salicylic acid concentration. For $Q=10$ ml/h, all the values equal 0.0002 regardless of the inlet concentration. As the flow rate decreases below 10 ml/h the average values become $a=0.00042\pm 0.00005$ and $a=0.0003$ for flow rates of 4 ml/h and 2 ml/h, respectively. However, the values slightly vary with the flow rate because they range from 0.0002 to 0.0005. Considering all the data, the average proportionality factor is equal to $a=0.00031\pm 0.00009$.

Flow rate Q (ml/h), Inlet concentration C_{in} (mg/l)	Slope a	R^2
$Q=10$ ml/h, $C_{in}=4$ mg/l	0.0002	0.986
$Q=10$ ml/h, $C_{in}=6$ mg/l	0.0002	0.992
$Q=10$ ml/h, $C_{in}=8$ mg/l	0.0002	0.973
$Q=10$ ml/h, $C_{in}=10$ mg/l	0.0002	0.993
$Q=4$ ml/h, $C_{in}=4$ mg/l	0.0004	0.954
$Q=4$ ml/h, $C_{in}=6$ mg/l	0.0004	0.992
$Q=4$ ml/h, $C_{in}=8$ mg/l	0.0005	0.968
$Q=4$ ml/h, $C_{in}=10$ mg/l	0.0004	0.984
$Q=2$ ml/h, $C_{in}=4$ mg/l	0.0003	0.991
$Q=2$ ml/h, $C_{in}=6$ mg/l	0.0003	0.992
$Q=2$ ml/h, $C_{in}=8$ mg/l	0.0003	0.989
$Q=2$ ml/h, $C_{in}=10$ mg/l	0.0003	0.967

Table 2 Parameters obtained from the linear fit $X=a(wL/h^2)$. The linear fits are performed with the data from Figure 6. R^2 is the regression coefficient.

A single value of a represents well the experimental degradation ratios for all flow rates and inlet concentrations.

The linear relationship between the degradation ratio and the dimensionless geometrical parameter indicates that the change in the photocatalytic activity, at a given flow rate and concentration, is fully determined by the dimensions of the microchannel. It is clear that despite its simplicity the empirical relation captures the essential physics of the photocatalytic degradation in a rectangular microchannel reactor in the presence of mass transfer limitation. Owing to the high degree of correspondence for a wide variety of configurations, Eq. (5) can be used to predict the photodegradation behavior as a function of key geometrical parameters such as microchannel length, width, and height. To increase the photocatalytic efficiency, a microchannel with a high value of the ratio wL/h^2 has to be used. For this purpose a channel with large width and length coupled with a low height is highly recommended.

However, it is anticipated that the dimensions of the channel are not the major parameter in order to significantly enhance the degradation. Other parameters such as light intensity (I), flow rate (Q), and inlet concentration (C_{in}) may be more appropriate. Furthermore, all these operating parameters do not have the same relative effect, with some having a more pronounced impact. A method for analysis consists of evaluating the sensitivity of each parameter by calculating the elasticity criteria [34]. Elasticity is a measure of the incremental percentage change in the variable X with respect to an incremental percentage change in another variable Y :

$$E_{X/Y} = \frac{\Delta X/X}{\Delta Y/Y} \quad (6)$$

Operating parameter (Y)	Intensity I (mW/cm ²)	Flow rate Q (ml/h)	Inlet concentration C_{in} (mg/l)	Reactor dimension (wL/h^2)
Range	1–2.8 mW/cm ²	2–10 ml/h	4–10 mg/l	140–560
Fixed experimental parameters	R1.5 $Q=4$ ml/h $C_{in}=10$ mg/l	R1.5 $C_{in}=10$ mg/l $I=1.5$ mW/cm ²	R1.5 $Q=4$ ml/h $I=1.5$ mW/cm ²	$Q=4$ ml/h $C_{in}=10$ mg/l $I=1.5$ mW/cm ²
Elasticity $E_{X/Y}$	0.62	-0.73	-0.31	0.24

Table 3 Values of the elasticity of the degradation with respect to key operating parameters.

The calculation of the elasticity of the degradation with respect to the light intensity is performed using experimental data previously obtained by our groups [19, 20]. The experiments were conducted in reactor R1.5 at different light intensities ranging from 1 to 2.8 mW/cm². Table 3 presents the values of the elasticity of the degradation with respect to the key operating parameters Y (I , Q , C_{in} , or wL/h^2). The two parameters having a great influence (elasticity equal to approx. 0.6–0.7) are the light intensity and the flow rate. As expected, the light intensity is the major factor in photocatalytic reactions, because electron-hole pairs are produced by light energy. It is also demonstrated that the flow rate make a significant contribution to the degradation ratio. The two other parameters (C_{in} and wL/h^2) have a lower influence (elasticity equal to 0.3–0.2). The reactor dimensions, with an elasticity value of 0.24, are a much less sensitive parameter. An elasticity value equals to 0.24 means that an increase of 10% of the dimensionless geometrical ratio wL/h^2 leads to an increase of 2.4% of the degradation ratio.

4 Conclusions

The aim of this paper was to experimentally show the influence of the microchannel dimensions and materials on the photocatalytic efficiency. Rectangular microchannel reactors with immobilized TiO₂ as photocatalyst have been designed, constructed, and tested. The surface of the channel is coated using an aqueous suspension of TiO₂.

The photocatalytic degradation of salicylic acid is investigated as a function of several parameters, including rectangular microchannel size, materials that constitute the reactor (metal or polymer), contaminant concentration, and flow rate. All microchannel reactors show the same behavior. Higher degradation ratio is observed for low pollutant concentrations and flow rates. There is no evidence from the data that the nature of the constituent elements of the reactor affects the photocatalytic process. The almost nil effect of the microchannel reactor materials upon the photocatalytic activity demonstrates that the TiO₂ film is sufficiently thick to mask the possible effect of the catalyst support.

The microchannel dimensions play a role in the degradation performance. Under the same experimental conditions, the highest photocatalytic activity is obtained in the reactor which possesses the largest channel width and the lowest channel height. The results indicate that the reduction of the channel height leads to an enhancement of the photodegradation. This is attributed to the existence of significant mass transfer limitation of salicylic acid from the solution to the catalyst surface. On the opposite, the degradation ratio increases fairly regularly with the microchannel length. To better understand the impact of the design of the microchannel reactors on the photocatalytic activity, a relation between the degradation ratio X and the geometrical dimensions of the channel (L : length, w : width and h : height) is obtained. At a given flow rate and inlet salicylic acid concentration, it is shown that X increases linearly with the dimensionless geometrical ratio wL/h^2 [$X=a(wL/h^2)$]. The product wL emphasizes the uniform irradiance over the entire catalyst surface and confirms that the bottom of the channel covered with TiO₂ is photoactivated. The term in $1/h^2$ can be explained by the diffusion of salicylic acid from the solution to the actual illuminated catalyst surface (mass transfer limitation). The proportionality factor is equal to $a=0.00031\pm 0.00009$ regardless of the flow rate and the inlet concentration.

The empirical correlation can be used to optimize the geometrical dimensions of the microchannel to achieve the desired photocatalytic performance in the presence of mass transfer limitation. To increase the photocatalytic efficiency a microchannel with a high value of the dimensionless geometrical ratio has to be used. For this purpose, a channel with large width and length coupled with a low height is highly recommended.

Acknowledgments: This work was financially supported by grants from the “Region de Lorraine”. The authors would like to acknowledge Hubert Monnier (LRGP, Université de Lorraine) for the useful discussions on this work and the extensive infrastructural support provided by the mechanical division of LRGP-CNRS.

Received March 13, 2012; accepted May 1, 2012; previously published online July 28, 2012

References

- [1] Hoffmann MR, Martin ST, Choi W, Bahnemann DW. *Chem. Rev.* 1995, 95, 69–96.
- [2] Friedmann D, Mendive C, Bahnemann D. *Appl. Catal. B Environ.* 2010, 99, 398–406.
- [3] Herrmann JM. *Appl. Catal. B Environ.* 2010, 99, 461–468.
- [4] Dunlop PSM, Byrne JA, Manga N, Eggins BR. *J. Photochem. Photobiol. A Chem.* 2002, 148, 355–363.
- [5] Mills A, Hill G, Bhopal S, Parkin IP, O’Neil SA. *J. Photochem. Photobiol. A Chem.* 2003, 160, 185–194.
- [6] Dijkstra MFJ, Panneman HJ, Winkelman JGM, Kelly JJ, Beenackers AACM. *Chem. Eng. Sci.* 2002, 57, 4895–4907.
- [7] Ray AK, Beenackers AACM. *AIChE J.* 1998, 44, 477–483.
- [8] Ahmed S, Jones CE, Kemp TJ, Unwin PR. *Phys. Chem. Chem. Phys.* 1999, 1, 5229–5233.
- [9] Gorges R, Meyer S, Kreisel G. *J. Photochem. Photobiol. A Chem.* 2004, 167, 95–99.
- [10] Ehrfeld W, Hessel V, Löwe H. *Microreactors*, 1st ed., Wiley/VCH: Weinheim, 2000.
- [11] Van Gerven T, Mul G, Moulijn J, Stankiewicz A. *Chem. Eng. Process.* 2007, 46, 781–789.
- [12] Choi BC, Xu LH, Kim HT, Bahnemann DW. *J. Ind. Eng. Chem.* 2006, 12, 663–672.
- [13] Shigwedha N, Hua Z, Chen J. *Chem. Eng. J.* 2006, 39, 475–480.
- [14] Mahmoodi NM, Arami M, Limaee NY, Tabrizi NS. *J. Colloid Interface Sci.* 2006, 295, 159–164.
- [15] Oelgemöller M, Shvydkiv O. *Molecules* 2011, 16, 7522–7550.
- [16] He Z, Li Y, Zhang Q, Wang H. *Appl. Catal. B Environ.* 2012, 93, 376–382.
- [17] Teekateerawej S, Nishino J, Nosaka Y. *J. Photochem. Photobiol. A Chem.* 2006, 179, 263–268.
- [18] Chen DH, Ye X, Li K. *Chem. Eng. Technol.* 2005, 28, 95–97.
- [19] Charles G, Roques-Carmes T, Becheikh N, Falk L, Commenge JM, Corbel S. *J. Photochem. Photobiol. A Chem.* 2011, 223, 202–211.
- [20] Charles G. PhD Thesis, University of Nancy, France, 2011.
- [21] Hidalgo MC, Sakthivel S, Bahnemann D. *Appl. Catal. A General* 2004, 277, 183–189.
- [22] Pozzo RL, Baltanas MA, Cassano AE. *Catal. Today* 1997, 39, 219–231.
- [23] Meille V. *Appl. Catal. A General* 2006, 315, 1–17.
- [24] Roques-Carmes T, Marchal P, Gigante A, Corbel S. *Russ. Chem. Rev.* 2009, 78, 375–386.
- [25] Charles G, Corbel S, Carre MC, Roques-Carmes T, Zahraa O. In *Proceedings of the 4th International Conference on Innovative Developments in Design and Manufacturing*, 2010, pp. 431–434.
- [26] Corbel S, Dufaud O, Roques-Carmes T. Materials for stereolithography. In *Stereolithography: Materials, Processes and Applications*, 1st ed., Bartolo PJ, Ed., Springer-Verlag: New York, 2011, pp. 141–159.
- [27] Furman M, Corbel S, Le Gall H, Zahraa O, Bouchy M. *Chem. Eng. Sci.* 2007, 62, 5312–5316.
- [28] Ould-Mame SM, Zahraa O, Bouchy M. *Int. J. Photoenergy* 2000, 2, 59–66.
- [29] Zahraa O, Dorion C, Ould-Mame SM, Bouchy M. *J. Adv. Oxid. Technol.* 1999, 4, 40–46.
- [30] Guinea E, Arias C, Cabot PL, Garrido JA, Rodriguez RM, Centellas F, Brillas E. *Water Res.* 2008, 42, 499–511.
- [31] Kafizas A, Kellici S, Darr JA, Parkin IP. *J. Photochem. Photobiol. A Chem.* 2009, 204, 183–190.
- [32] Herrmann JM, Tahiri H, Ait-Ichou Y, Lassaletta G, Gonzalez-Elipe AR, Fernandez A. *Appl. Catal. B Environ.* 1997, 13, 219–228.
- [33] Commenge JM, Falk L, Corriou JP, Matlosz M. *Chem. Eng. Technol.* 2005, 28, 446–458.
- [34] Matlosz M, Falk L, Commenge JM. Process intensification. In *Microchemical Engineering in Practice*, Dietrich TR, Ed., John Wiley & Sons: Hoboken, NJ, 2009, pp. 325–347.



Guillaume Charles received an engineering degree in chemical engineering from Ecole Nationale Supérieure des Industries Chimiques in Nancy (France) in 2007. He completed his PhD degree in chemical engineering in 2011 at Laboratoire Réactions et Génie des Procédés of Lorraine University. The title of his thesis was “Design and characterization of photocatalytic micro-reactors for water purification”. Since March 2011, he has been working as a postdoctoral scientist at Laboratoire de Génie des Procédés Catalytiques in Villeurbanne (France). He is currently undertaking research on the design and the implementation of a photocatalytic pilot reactor for the treatment of bilge water of ships.



Thibault Roques-Carmes received his PhD degree on polymer adsorption from the Materials and Interfaces Laboratory of the University of Franche-Comté (France) in 2002. He then did postdoctoral work with the Inorganic Materials and Process Group at Philips Research Laboratories in Eindhoven (The Netherlands). He worked on the development of novel electro-optic devices based on electrowetting. Since September 2004, he has been working as an associate professor in Ecole Nationale Supérieure des Industries Chimiques of Lorraine University. He is currently performing research at Laboratoire Réactions et Génie des Procédés at Nancy, France. His research interests include photocatalysis, micro-reactors, wetting, surface treatment, process intensification, and stereolithography.



Nidhal Becheikh received an engineering degree in chemical engineering from Ecole Nationale d'Ingénieurs de Gabès (Tunisia) in 2007. As part of his undergraduate education, he performed a year of industrial experience at Chemical Industries of Fluorine, Tunisia (2008). He then completed a Master's degree in chemical engineering at the University Claude Bernard Lyon (France) in 2009. Since October 2009, he has been working as a PhD student at Laboratoire Réactions et Génie des Procédés at Nancy, France. His research program focuses on the determination of the kinetic constants of a photocatalytic reaction in microchannel reactors in the presence of mass transfer limitation and axial dispersion.



Laurent Falk is director of research at the National Centre for Scientific Research (CNRS) at Laboratoire Réactions et Génie des Procédés at Nancy, France. He received an engineering degree in chemical engineering from the Technical University of Compiègne (France) in 1984. He completed his PhD degree on material engineering in 1989. He is the scientific coordinator of the research group PRISM (25 people) devoted to intensified photonic, catalytic, and reactive process engineering. He has expertise in intensification, micromixing, and reactive flow in chemical reactors. He has taken charge of over 20 key scientific research projects. He has published more than 60 internationally refereed journal papers and book chapters.



Serge Corbel (59 years old) is a senior researcher in the National Centre for Scientific Research (CNRS) in Laboratoire Réactions et Génie des Procédés (LRGP) at the University of Lorraine, Nancy. Dr. Corbel received his PhD in Gas Kinetics (1982) from Nancy-University, and then a Doctorate in combustion from the University of Haute Alsace (1987). He is well known for his books and publications in the fields of photochemistry, photocatalysis, photomaterial, rapid prototyping, and particularly stereolithography.