

Design of a micro-channel reactor for decomposition of organic pollutants in waste water treatment

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ABSTRACT: Photocatalytic micro-channel reactor was built by using stereolithography process. A reactor with a micro-channel as a support of TiO_2 photocatalyst was designed in order to reduce dimensions while improving the efficiency. Photocatalytic activity of the micro-reactor at various flow rates was evaluated by the inlet and outlet concentrations of salicylic acid as a model of pollutant. Influence of the initial pollutant concentration, the irradiation intensity on the rate of degradation of the pollutant was studied. A model with the kinetic parameters for the given support geometry was applied to reactor design and scale-up.

1 INTRODUCTION

Methods, such as photochemical treatments, were envisaged for detoxification of the water and air. Among them, photocatalysis is efficient with the advantage of oxidizing most contaminants of water (fertilizers, pesticides, dyes, ...) until their complete destruction (mineralization) (Avila et al, 1998) with no selective transfer of the pollutants and products on the surface of adsorbent. It uses the inexpensive and available UV-A light as sources of irradiation as well as the water and oxygen as oxidizing agents (Hermann et al, 1999).

The simplest processes are the fluidized bed TiO_2 (this poses problems of cost particularly during the stage of separation after purification) or the tubular reactor with catalyst deposited on the walls of reactor, suffering sometimes of limitation of transfer of matter or non homogeneous irradiation. Among the possible solutions for intensification of photocatalytic reactions there is the use of micro-reactors (Van Gerven et al, 2007).

The design and manufacture of micro-reactors by the process of stereolithography, authorizes the fabrication of complex forms with a great flexibility.

The first step of the research has concerned the design and manufacture of a catalytic support whose characteristics are:

- a capacity to overcome the mass transfer,
- the largest ratio of surface on volume in order to obtain a great contact of the pollutant with the catalyst,

- the most important homogeneous irradiation on the whole surface of the structure.

The second step has focused on the study of the influence of geometric characteristics of the support (depth, width, length) on the photocatalytic activity.

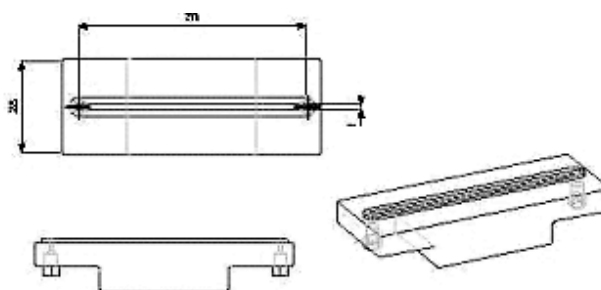


Figure 1. Schematic view of the micro-reactor designed by CAD system; a) Front view; b) side view; c) perspective view.

2 EXPERIMENTAL

The micro-channel reactor with the geometry shown on the Figure 2 has been made in epoxy resin (SI 30) by a self-made stereolithography apparatus using a UV Nd-YAG laser (Corbel et al, 2008).

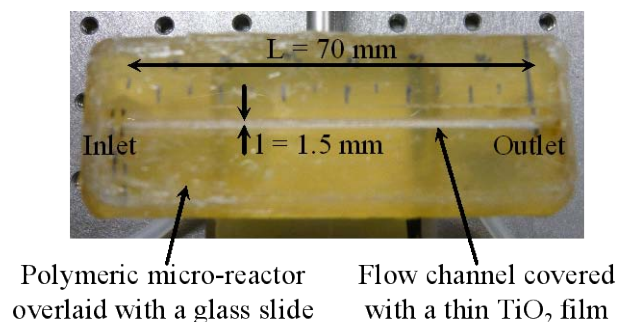


Figure 2. Photographic view of the polymeric micro-reactor. The surface of the channel was coated with a TiO_2 thin film by filling it with an acidic aqueous suspension of TiO_2 (4g/L; adjusted to pH 3 by addition of nitric acid). After drying at room temperature, the surface load was 20 mg/cm^2 , this value being above the minimal load generally required for complete light absorption. The experimental setup used for the photocatalytic tests is shown on Figures 3 and 4.

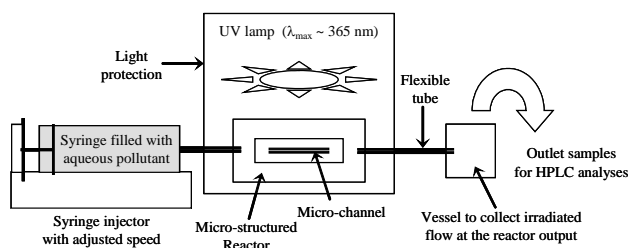


Figure 3. Schematics of the experimental set-up for the degradation in the micro-reactor.

A flow of water containing the pollutant is injected with a syringe at a low speed into the micro-structured reactor. An UV fluorescent lamp (Philips, light power 3W, 56 cm long, $\lambda_{\text{max}} \approx 365 \text{ nm}$) located at 1 cm above the reactor. The incident light power was recorded by a UV radiometer whose spectral response is centered at 365 nm with a half band-width of 12nm. The value of 2.8 mW/cm^2 was fixed at the surface of the catalyst. A flexible tube at the outlet of the reactor allows the collect of the irradiated solution samples.

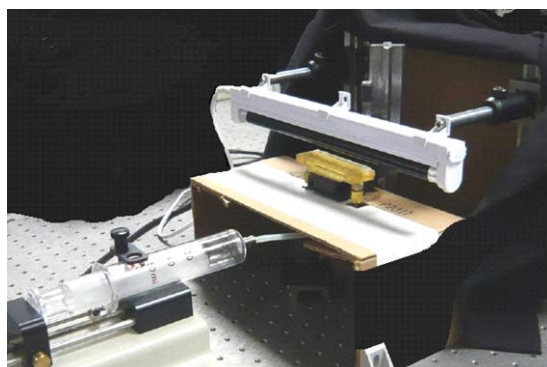


Figure 4. Experimental setup for Photocatalytic reaction with a micro-reactor and syringe used for the injection of the aqueous salicylic acid solution.

In order to validate the micro-structured reactor in a photocatalytic reaction, we have chosen salicylic acid (SA) as model molecule previously studied in the laboratory (Ould-Mame et al., 2000). Its concentration after photoreaction was measured by HPLC with conditions already described. Briefly, the HPLC system is equipped with a variable Shimadzu SPD-20A UV-Vis detector, a Rheodyne Model 7725 injector, a loop size of $20 \mu\text{L}$ and a Shimadzu LC-20AT pump. Reverse-phase chromatographic analysis using a Lichrosorb RP-18 column ($250 \times 4.6 \text{ mm i.d.}$, particle size $5 \mu\text{m}$, Supelco-Inc) was carried out at 25°C , under isocratic conditions (mobile phase consisted of a mixture of methanol and water containing 0.1% volumic of phosphoric acid; 70:30, v/v; 1 mL/min). The column effluent was monitored at $\lambda = 295 \text{ nm}$. Data acquisition was performed using a Varian System (Star Data Acquisition Workstation, System Control Version 5-52).

3 RESULTS AND DISCUSSION

3.1 Photocatalytic degradation of salicylic acid

The efficiency of the monolithic photocatalyst was carried out by estimating the degradation rate R in salicylic acid per volume of reactor (mg/min/cm^3) at different flow rates and inlet concentration of salicylic acid.

$$R = \frac{Q_0 C_0 dX}{dV} \quad (1)$$

where Q_0 = flow rate in mL/min ; dX = experimental conversion of salicylic acid during its contact with the catalyst into the apparent elementary reactor volume dV (cm^3).

The results of photocatalytic degradation carried out with the micro-reactor described previously, will be presented as. the variation of the outlet concentration of salicylic acid C_{out} , obtained at variable flow rate Q_0 , for a constant inlet concentration C_0 .

The value of inlet concentration is 10 mg/L in salicylic acid, and among the geometries tested, we have characterized the performance of the reactor with a 0.5 mm depth channel.

3.2 Modelling photocatalytic reaction with Langmuir-Hinshelwood model (LH)

In photocatalytic studies, the kinetics of photocatalytic degradation is generally represented by the Langmuir-Hinshelwood (LH) model. The reaction rate R is defined by the following relationship (Zahraa et al., 2003).

$$R = k \frac{KC}{1 + KC} \quad (2)$$

Where K is the adsorption constant ($L \cdot mg^{-1}$); C , the concentration of salicylic acid in the liquid-phase ($mg \cdot L^{-1}$) and k , an apparent kinetic constant ($mg \cdot min^{-1} \cdot L^{-1}$). It is also noticeable that the rate is expressed per unit of reactor apparent volume. The importance of substrate pre-adsorption on a given photocatalyst can be evaluated by the use of a LH kinetic model, considering that the adsorption of reaction intermediates and products is not significant. In our case, the disappearance of the pollutant during the photocatalytic process has been followed. Then, if photoreactor considered close to a Plug Flow Reactor (PFR), and a constant flow rate (permanent regime) therefore the mass balance through it is given by the following equation:

$$\frac{dX}{dV} = \frac{R}{Q_0 C_0} \quad (3)$$

with X conversion within the section volume dV of the reactor, where $dX = -dC/C_0$, then :

$$R = \frac{-Q_0 dC}{dV} \quad (4)$$

from of equations (2) and (4) it can be found:

$$\frac{-Q_0 dC}{dV} = k \frac{KC}{1 + KC} \quad (5)$$

Where dV is the elementary volume of the reactor, Q_0 , the volumetric flow rate. The integration of Eq. (5) is possible only when there is no limitation by mass transfer, no difference of concentration between bulk flow and the catalyst surface (Furman et al, 2007, Dingwang et al, 2001). By integrating equation (5) between the reactor inlet and outlet, it follows:

$$\frac{1}{kK} \ln \left(\frac{C_{out}}{C_0} \right) + \frac{1}{k} (C_{out} - C_0) = -\frac{V}{Q_0} \quad (6)$$

Eq. (6) can be written introducing the pollutant conversion $X = 1 - C_{out}/C_0$:

$$\frac{1}{kK} \frac{\ln(1-X)}{C_0 X} - \frac{1}{k} = -\frac{V}{Q_0 C_0 X} \quad (7)$$

A plot of $-V/(Q_0 C_0 X)$ versus $\ln(1-X)/(C_0 X)$ should be linear and will allow the determination of two constants k and K . From this optimization, the values of k and K obtained are respectively $2.66 \cdot 10^{-5} \text{ mmol} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$ and $25 \text{ mmol}^{-1} \cdot \text{mL}$.

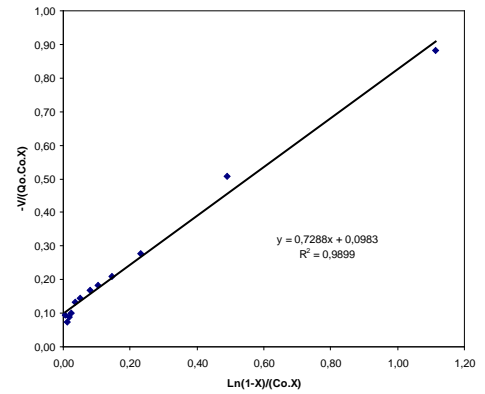


Figure 5. Determination of k and K constants from equation (7).

3.3 Effect of the contact time

The effect of contact time on salicylic acid (SA) outlet concentrations was investigated in the range of 0.06 min to 6.33 min. Figure 6 shows that pollutant outlet concentration decreases according to the contact time $\tau = V/Q_0$.

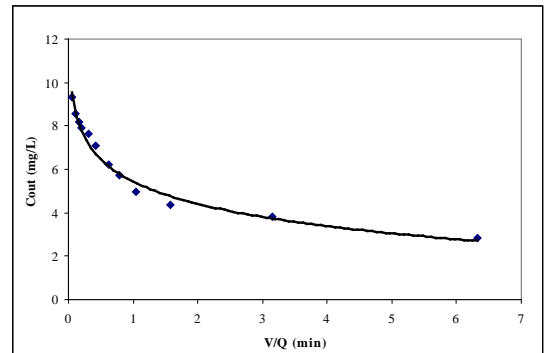


Figure 6. Effect of contact time on the outlet concentration of salicylic Acid.

It has to be noticed that, the effect of the contact time of reactant was studied by varying the volumetric flow rate with a constant concentration of SA. Figure 7 shows that SA conversion increased first rapidly as the contact time increased in the first minutes then slowly until 6.0 minutes. This behavior has been obtained at approximately high concentration where the rate is independent of concentration (zero order kinetic). It can be noticed that the photocatalytic degradation rate is independent of contact time (or volumetric flow rate) in the first part of the curve.

3.4 Influence of the light Intensity

The light flux has been varied by changing the fluorescent lamp and irradiation at two power intensities: 2.8 mW/cm² and 0.3 mW/cm² (Figure 7).

The influence of the irradiation is clear and the conversion increases a little bet at higher irradiation.

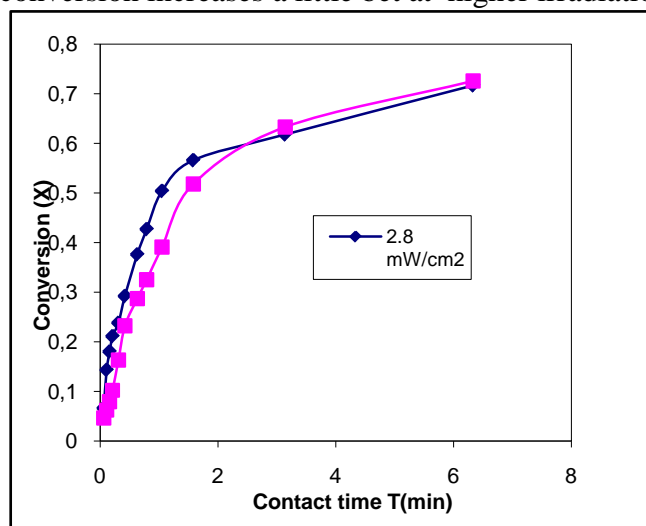


Figure 7. Influence of the Irradiation parameter on the efficiency of the salicylic acid degradation.

4 CONCLUSION

The photocatalytic activity of a micro-reactor has been tested in this study. The experiments have been performed in order to determine, how the geometry influences reaction rate, mass transfer rate and finally the photocatalytic efficiency. It has been shown that the geometry influences the kinetic constant k .

As a consequence, the perspective is the development of a geometry having a great ratio surface to volume. At the same time, a very good accessibility of the photons to the catalytic surface must be achieved.

Besides, the optical properties of the polymer show that the support is not inert since it absorbs the

light and probably leads to a decrease of the reactivity. That is why the use of another material transparent to the UV light, and able to promote favorable interaction with the pollutant will be developed in the future.

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