Available online at www.sciencedirect.com

ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry 190 (2007) 135–140

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

# Malic acid photocatalytic degradation using a $TiO_2$-coated optical fiber reactor

Anne Danion [a,*], Jean Disdier [a], Chantal Guillard [b], Nicole Jaffrezic-Renault [a]

[a] *CEGELY, ECL, 36 avenue Guy de Collongue, 69134 Ecully Cedex, France*
[b] *LACE, UCBL, bât Raulin, 43, boulevard du 11 novembre 1918, 69622 Villeurbanne Cedex, France*

Received 6 November 2006; received in revised form 19 March 2007; accepted 20 March 2007
Available online 27 March 2007

## Abstract

A photoreactor containing a bundle of $TiO_2$-coated optical fibers was employed for the photocatalytic degradation of malic acid, a polycarboxylic acid found in fermentation processes and in biomass. $TiO_2$ film was coated on optical fiber using a dip-coating method. The kinetic behavior of malic acid conversion in this study was found to follow a first-order kinetics with a degradation rate of $6.8 \times 10^{-2}\,h^{-1}$. Laboratory experiments enabled one to detect six intermediates presented in five degradation pathways. Their evolution during the photocatalytic reaction was also investigated. The major one, malonic acid, is initiated by a decarboxylation ("photo-Kolbe") reaction in the α-position with respect to the OH group followed by an OH addition. The others intermediates come from the same process or from H-abstraction or oxidation. The total organic carbon removal after 20 h of treatment was 21%.

A high photonic efficiency of 6% was achieved for experiments operated in the optical fiber photoreactor due to the optimized light utilization.
© 2007 Elsevier B.V. All rights reserved.

*Keywords:* Optical fiber reactor; $TiO_2$; Photocatalytic; Malic acid; Photonic efficiency

## 1. Introduction

The application of photocatalysis using semiconductor particles, with a primary focus on titanium dioxide, $TiO_2$, has found increasing interest to solve a wide variety of problems concerning environmental pollution [1]. The UV-irradiated $TiO_2$ surface can generate highly oxidative electrical holes to decompose various organic compounds present in aqueous and gaseous streams at ambient temperature and pressure conditions [2–7].

The wide range of needs for environmental remediation and clean-up requires the development of immobilized photocatalytic systems instead of the heterogeneous slurry reactor design, requiring a filtration step [8]. Thus, a large number of reactors using fixed $TiO_2$ have been studied [9–13]. However, this kind of reactor presents several disadvantages: (i) low light utilization due to absorption and scattering of the light by the reaction medium and (ii) mass transport limitations.

The employment of optical fibers for the photocatalytic decomposition of organic pollutants has been studied by several research groups [14–26]. Instead of using a single UV light lamp, a bundle of optical fibers is utilized as both light distributor and support for photocatalysts within a photoreactor. Ollis and Marinangeli were the first to propose theoretical studies on this subject between 1977 and 1980 [14,15]. Their calculations conclude that the catalyst could be deactivated due to the heat build-up in the bundled array. In spite of this, reactors based on $TiO_2$-coated fiber-optic bundle have been built firstly in liquid [16–19] and more recently in gas phase [20–24].

However, in almost all studies, the coating method consisted of deposition of Degussa P25 powder on optical fibers. The present work is an extension of our efforts to develop a $TiO_2$-coated optical fiber reactor for water decontamination [25,26]. The optical fibers were coated with $TiO_2$ employing a sol–gel method [26,27]. In this study, we examine the degradation of malic acid (hydroxybutanedioic acid), formerly used in our laboratory as a model compound [28]. In fact, this molecule can be found in fermentation processes and in biomass and its degra-

---

[*] Corresponding author. Present address: Chemical Engineering Department, Ecole Polytechnique de Montréal, C.P. 6079, succ. Centre-ville, Montréal, Que., Canada H3C 3A7. Tel.: +1 514 340 5121x7336; fax: +1 819 821 7955.

*E-mail addresses:* anne.danion@wanadoo.fr, anne.danion@polymtl.ca (A. Danion).

1010-6030/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2007.03.022

dation pathway could produce carboxylic intermediates often found in the degradation chain of organic pollutants [29]. The objective of this study was to investigate the photocatalytic degradation of malic acid in a $TiO_2$-coated optical fiber reactor and to evaluate the achieved photonic efficiency.

## 2. Experimental

### 2.1. Materials and reagents

Malic acid (hydroxybutanedioic acid) (99% purity) was purchased from Merck and used as received. Titanium tetraisopropoxide, isopropanol, $H_2SO_4$, $Na_2S_2O_8$ (analytical grade) were supplied by Aldrich. The solutions were prepared with water from a Millipore Milli-Q water purification system.

### 2.2. Preparation of the thin film photocatalyst as an optical fiber cladding

The optical fibers (3 M Power-Core FT-600-UMT and FT-1.0-UMT, silica core with a polymer cladding, supplied by AMS Electronic, France) with 1 mm diameter were cut into pieces of 30 cm length and their mechanical cladding was mechanically stripped on 18 cm at one end of the fiber. The optical cladding on this part was removed by acetone. The two fiber-ends were polished with abrasive paper.

The fibers were then coated on 13.5 cm by dipping them into a solution of 13% (vol.) titanium tetraisopropoxide in isopropanol. The withdrawal speed was 3.4 mm/s. The coatings were calcined at 450 °C for 1 h [25,27]. The same procedure was repeated in order to obtain five layers. The BET specific area was evaluated to be 51 $m^2/g$ that is similar to the specific area of $TiO_2$ Degussa P25 powder. The average pore size was 2 nm. XRD measurements revealed only the presence of a peak at $2\theta = 25.15^\circ$, characteristic of the anatase phase. The particle size of the $TiO_2$ film measured by AFM was about 20–40 nm. The thickness evaluated by ESEM was about 150 nm for five layers. The catalyst loading after five coatings was calculated to be 177 μg per optical fiber [25].

### 2.3. Optical fiber reactor used for malic acid photocatalytic degradation

The schematic diagram of the multi-fiber reactor system was described in a previous study [25]. A bundle of 57 optical fibers (1 mm diameter, 30 cm length) coated with $TiO_2$ were arranged uniformly in a 220 mL cylindrical reactor (4.5 cm diameter and 13.5 cm length) made of Pyrex glass (Fig. 1). The $TiO_2$ coating thickness was 150 nm (five layers) and the length was 13.5 cm. Malic acid solution (50 mg/L) was introduced into a flask and was recirculated to the optical fiber reactor through a pump (Millipore); the total volume of solution was 300 mL. The fibers were irradiated by a 500 W mercury UV lamp (Oriel Model 6285) [25]. A circulating water cell, used to filter the infrared rays, was equipped with a 340 nm cut-off filter to avoid photochemistry of malic acid. The number of absorbed photons by $TiO_2$ on optical fibers was about $6.14 \times 10^{16}$ photons per second. The radiant flux was measured using a radiometer (United Detector Technology Inc., Model 21A power meter).

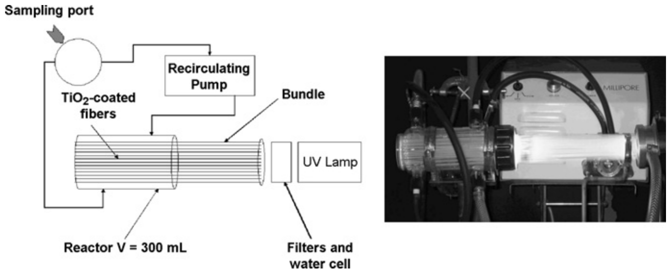


Fig. 1. Schematic diagram of the $TiO_2$-coated optical fiber reactor.

During the irradiation, aliquots of 200 μL of malic acid solution were collected at regular times.

### 2.4. Analytical methods

Liquid chromatography was used to follow the concentration of malic acid and its degradation products. The system is composed by a Waters 600 pump, a Waters 486 UV detector (detection at 210 nm), and a Sarasep CAR-H (300 mm × 4.6 mm) column. The flow rate was 0.7 mL/min. The injection volume was 100 μL and the mobile phase was a $5 \times 10^{-3}$ mol/L $H_2SO_4$ solution. Intermediates were detected, identified and quantified using commercial standard compounds. More analytical details are available in Refs. [28,30,31].

The total organic carbon was determined by using a TOC analyzer Bioritech Model 700.

## 3. Results and discussion

### 3.1. Adsorption of malic acid on $TiO_2$ in the dark

Adsorption of malic acid on $TiO_2$ was investigated. Equilibrium was reached after 1 h. For the following experiments, the treated solution was stirred in the reactor in the dark for 1 h prior treatment. The quantity of malic acid adsorbed represented about 4% of the quantity introduced at the beginning which corresponded to 4.6 molecules/$nm^2$ of $TiO_2$.

### 3.2. Kinetics of degradation of malic acid

Under UV-light (above 340 nm), without titanium dioxide, the decrease of malic acid concentration was negligible. The photocatalytic degradation of malic acid in the optical fiber reactor was performed according to the procedure indicated in the experimental section. The kinetics of the photocatalytic degradation obtained in this reactor is presented in Fig. 2. Under the experimental conditions applied, the experimental results follow a first-order reaction kinetics, according to the equation:

$$\frac{-\mathrm{d}C}{\mathrm{d}t} = k_{\mathrm{obs}} C \qquad (1)$$

where $C$ is the malic acid concentration and $k_{\mathrm{obs}}$ the observed first-order rate constant. Linear plots $\ln C_0/C$ versus time were

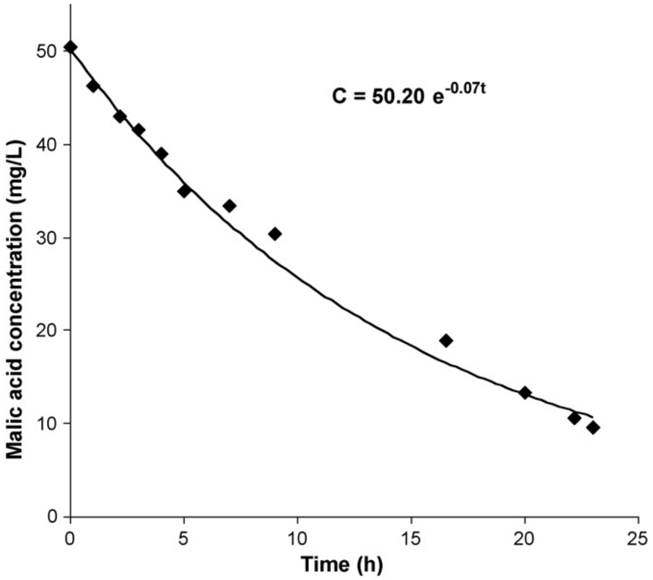


Fig. 2. Photocatalytic degradation of malic acid in a $TiO_2$-coated optical fiber reactor.

obtained as expected, the slope leading to a first-order rate of $6.8 \times 10^{-2}\,h^{-1}$.

This experiment was repeated three times and the photocatalytic activity was similar in each case. In this study, $TiO_2$ coated on optical fiber was not deactivated in aqueous phase.

### 3.3. Identification of the reaction intermediates

Five major intermediates were identified and quantified during the photocatalytic degradation of malic acid in the optical fiber reactor (Fig. 3). Their chemical formulas are given in Table 1.

The oxidative photodegradation may involve two oxidizing agents: photoproduced holes $h^+$ and $OH^\circ$ radicals, known as strong oxidizing agents, generated as follows:

$$(TiO_2) + h\upsilon \rightarrow e^- + h^+ \tag{2}$$

$$(H_2O \leftrightarrow H^+ + OH^-) + h^+ \rightarrow H^+ + OH^\circ \tag{3}$$

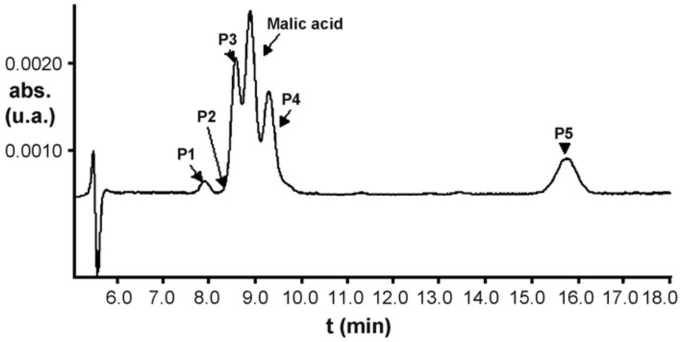
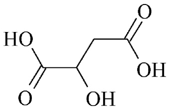
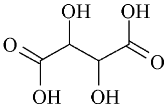
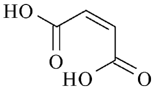
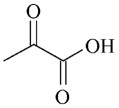
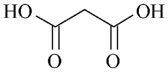
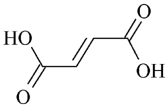


Fig. 3. HPLC-UV chromatogram obtained from 200 μL of the solution after 16 h of irradiation in the optical fiber reactor. Peak assignment is based on the molecules illustrated in Table 1.

Table 1
Intermediates of malic acid during the photocatalytic degradation

| No. | Name | Chemical formula | Molecular weight (g/mol) | Elemental formula |
|---|---|---|---|---|
| Malic acid | Malic acid |  | 134.09 | $C_4H_6O_5$ |
| P1 | Tartaric acid |  | 150.09 | $C_4H_6O_6$ |
| P2 | Maleic acid |  | 116.07 | $C_4H_4O_4$ |
| P3 | Pyruvic acid |  | 88.06 | $C_3H_4O_3$ |
| P4 | Malonic acid |  | 104.06 | $C_3H_4O_4$ |
| P5 | Fumaric acid |  | 116.07 | $C_4H_4O_4$ |

Holes can directly oxidize malic acid according to a photo-Kolbe reaction:

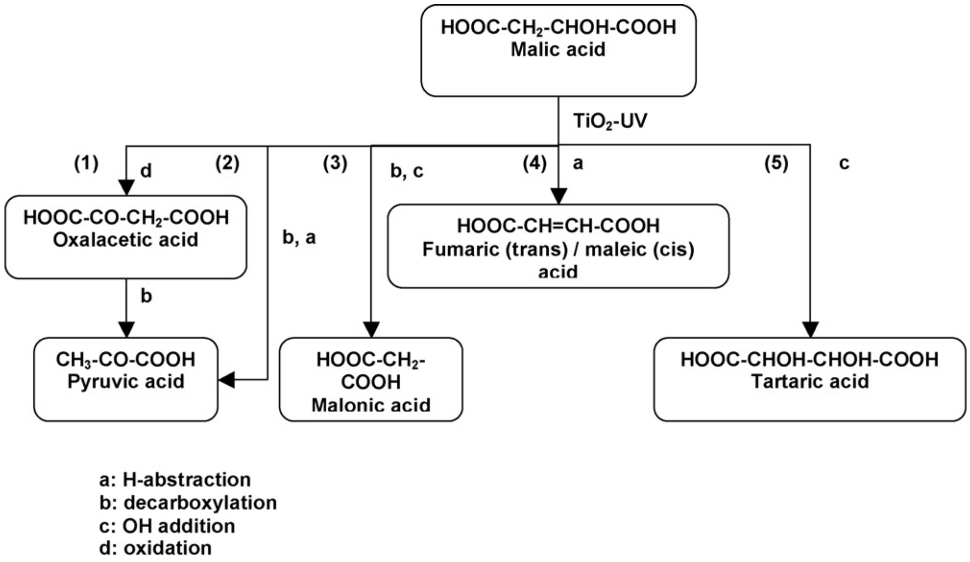
$$RCOO^- + h^+ \rightarrow R^\circ + CO_2 \tag{4}$$

And $OH^\circ$ radicals are prone to abstract an H atom:

$$RCOO^- + OH^\circ \rightarrow R'^\circ\text{-}COO^- + H_2O \tag{5}$$

The radicals thus formed will add $O_2$ and finally give rise to the intermediates as shown in Scheme 1.

Intermediates evolution (Fig. 4a and b) indicates that the main degradation product is malonic acid. Maleic, pyruvic, fumaric and tartaric acids are also identified but at lower concentration whereas oxalacetic acid is present at trace level. From Fig. 4a it appears that malonic acid is rapidly formed and its concentration increases steadily during 20 h of treatment. From Fig. 5, it is shown that the concentration of malonic acid is directly proportional to the concentration of converted malic acid. For each converted μmol of malic acid, 0.8 μmol of malonic acid is created. From these results the Route 3 in Scheme 1 seems to be the main one. The photo-Kolbe process (Eq. (4)) appears to be predominant, with decarboxylation in the α-position from the OH group followed by an OH addition. This suggests that the preferential mode of adsorption of malic acid is related to the binding of the carboxylic group in the α-position from the OH group to the amphoteric hydroxyls at the surface of titanium dioxide [28]. The other carboxylic group of malic acid can also be linked to the surface since pyruvic acid is also formed after 11 h of reaction via the photo-Kolbe process followed by an H abstraction (or via a decarboxylation of oxalacetic acid) (Scheme 1).



Scheme 1. Photocatalytic degradation pathway of malic acid in a $TiO_2$-coated optical fiber reactor.

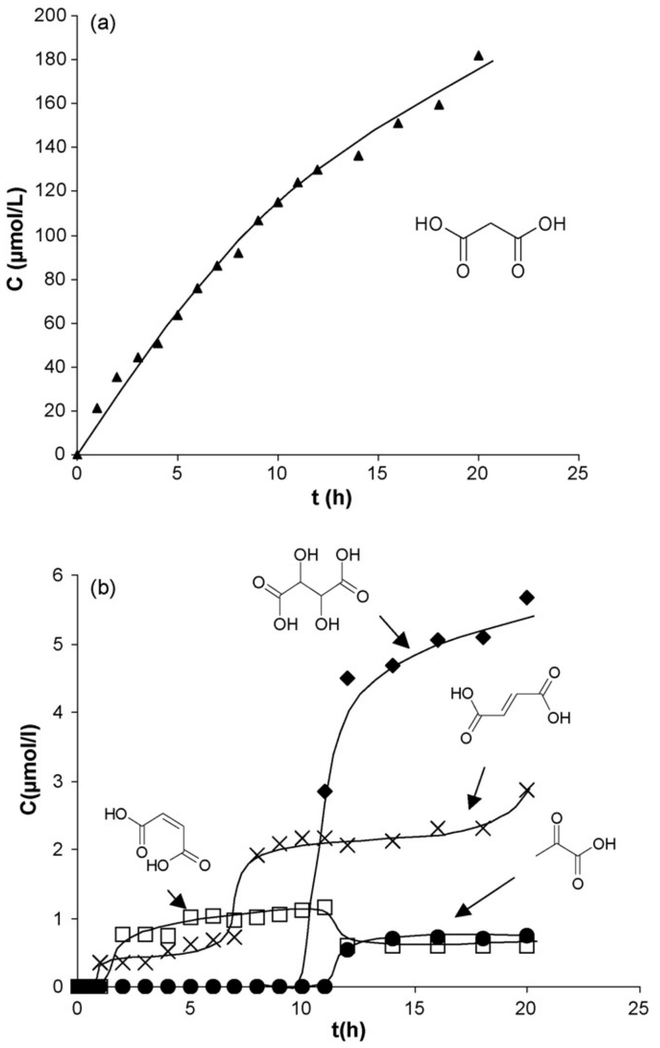


Fig. 4. (a) Formation of malonic acid (▲). (b) Formation of fumaric (×), maleic (□), tartaric (⧫) and pyruvic (✹) acids.

The competitive oxidation route via OH° radicals also takes place, since fumaric and maleic acids also appear from the first hours of irradiation and tartaric acid is detected after 11 h of irradiation (Fig. 4b). The two actions of OH° radicals consist in H atom abstraction or in OH addition [28]. For the first 7 h of reaction, maleic acid (*cis*) is present at a higher concentration than fumaric acid (*trans*). However, after 7 h of irradiation, concentration of fumaric acid becomes two times higher than maleic acid concentration that decreases after 11 h of reaction.

Traces of oxalacetic acid were detected between 7 and 11 h of reaction: it was obtained from the hydroxyl group in malic acid that gets oxidized into a ketone.

The intermediates found in this study are within agreement with a previous study in a slurry reactor [28].

### 3.4. Total organic carbon removal

The total organic carbon concentration during the photocatalytic degradation of malic acid is presented in Fig. 6. After 20 h

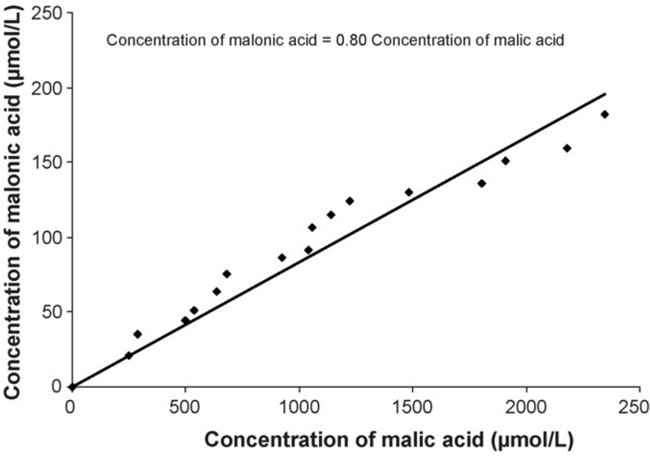


Fig. 5. Concentration of malonic acid as a function of the concentration of malic acid degraded during the photocatalytic reaction.

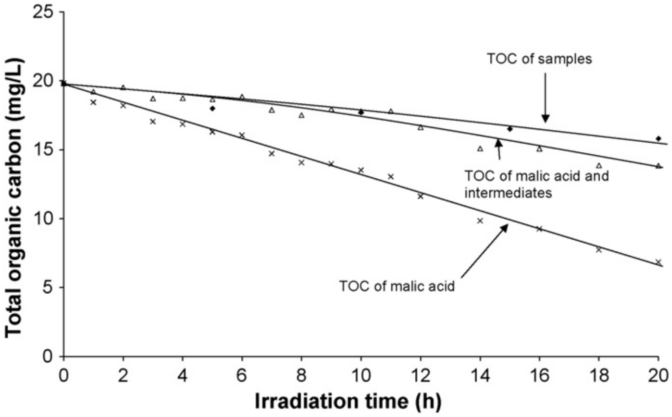


Fig. 6. Total organic carbon (TOC) during the photocatalytic degradation of malic acid in an optical fiber reactor (♦: TOC of samples; ×: TOC of malic acid; △: TOC of malic acid and intermediates).

of treatment, the final total organic carbon (TOC) is 15.8 mg/L which corresponds to a total organic carbon removal of 21%.

From Fig. 6, it is shown that the TOC of malic acid does not correspond to the TOC of samples: this difference could be attributed to intermediates products or to carbon mineralization during the photocatalytic process. Since there is a gap of 18% between the TOC of identified intermediates with malic acid and the TOC of samples, the identified intermediates only cover 3% of the carbon transformation.

### 3.5. *Photonic efficiency*

In order to avoid any confusion with the quantum yield used in photochemistry, Serpone [32] has defined precisely the photonic efficiency ($\xi$) as the number of molecules $N_{\mathrm{mol}}$ undergoing an event (conversion of reactants or formation of products) relative to the number of quanta $N_{\mathrm{photons}}$ absorbed by the photocatalyst:

$$\xi = \frac{N_{\mathrm{mol}}\,(\mathrm{mol/s})}{N_{\mathrm{photons}}\,(\mathrm{Einstein/s})} = \frac{\upsilon\,(\mathrm{molecules/s})}{\phi\,(\mathrm{photons/s})} \qquad (6)$$

$\phi$, the amount of photons absorbed or scattered by the $TiO_2$ coating on the optical fiber, was calculated following the equation:

$$\phi = E_{\mathrm{abs}} \times 10^{-3} C_{\mathrm{f}} S \qquad (7)$$

where $E_{\mathrm{abs}}$ is the light energy absorbed or scattered by $TiO_2$ (mW/cm$^2$), $C_{\mathrm{f}}$ the number of photons ($\mathrm{W}^{-1}\,\mathrm{s}^{-1}$) emitted by the lamp at 365 nm and $S$ is the entrance area of the photoreactor.

Light transmitted by all fibers was measured with a radiometer before and after coating them with $TiO_2$: a Teflon plate with 57 holes was adapted to the radiometer in order to measure only the light transmitted by the bundle of 57-optical fibers. The difference between the two values leads to the light energy absorbed or scattered by the $TiO_2$ coated on the fibers ($E_{\mathrm{abs}}$) [25]. The results obtained with the $TiO_2$-coated optical fiber reactor are shown in Table 2. It appears that the photonic efficiency in the optical fiber reactor is about 6.0%. This value is much higher than that (2.8%) obtained in the conventional system [33]. This indicates that higher efficiency of light utility can be achieved by employing the optical fiber type reactor.

Table 2
Photonic efficiency obtained in a $TiO_2$-coated optical fiber reactor

| | |
|---|---|
| Reactor | Optical fiber; Lamp: oriel 6285 |
| $E_{\mathrm{abs}} \times S$ (mW) | 89 |
| $C_{\mathrm{f}}$ (photons/W s) | $6.9 \times 10^{17}$ |
| $\phi$ (photons/s) | $6.1 \times 10^{16}$ |
| $\upsilon$ (molecules/s) | $3.6 \times 10^{15}$ |
| Photonic efficiency, $\xi$ (%) | 6 |

## 4. Conclusion

Photocatalytic oxidation of malic acid was carried out using optical fibers bundle as both a light transmitter and a catalyst support.

The adsorption equilibrium was obtained after 1 h and corresponded to 4.6 molecules/nm$^2$ of $TiO_2$.

The conversion showed a first-order kinetic behavior under the present experimental conditions with a degradation rate of $6.8 \times 10^{-2}\,\mathrm{h}^{-1}$.

Malonic, maleic, pyruvic, fumaric, tartaric and oxalacetic acids were detected as transformation products. Malonic acid was found to be the main intermediate suggesting that photo-Kolbe process was predominant in the degradation pathway.

A decrease of 21% was observed for total organic carbon present in solution after 20 h of reaction. However, the identified intermediates only covered 3% of the carbon transformation.

The photonic efficiency evaluated under these experimental conditions reaches 6% that is much higher than the photonic efficiency generally obtained with a “conventional” slurry reactor. Compared with a traditional photoreactor, an optical-fiber provides a medium to transmit light throughout the reactor. Thus light energy can be spread more efficiently. In addition, a higher processing capacity is possible because the catalyst can disperse on a large external area of optical fibers in a given reactor volume.

The data obtained in this work with an optical fiber reactor show a multi-fiber reactor could be successfully applied to photocatalytic water treatment. However, the reaction rate should be improved by increasing $TiO_2$ loading, fiber density and stirring inside the reactor.

The OFR could be a viable option where the direct light illumination is inhibited or the light source is remote from the contaminated site.

## Acknowledgement

This work was supported by the French Ministry of Research through a Ph.D. Scholarship for Anne Danion.

## References

[1] D.M. Blake, Bibliography of work on the photocatalytic removal of hazardous compounds from water and air, RREL/TP-430-22197, National Renewable Energy Laboratory, Golden Co 1997 and 1999.
[2] X. Fu, W.A. Zeltner, M.A. Anderson, P.V. Kamat, D. Meisel (Eds.), Semiconductor Nanoclusters: Physical, Chemical and Catalytic Aspects, Elsevier, Amsterdam, 1996, p. 445.
[3] J.M. Herrmann, J. Disdier, P. Pichat, S. Malato, J. Blanco, Appl. Catal. B: Environ. 17 (1998) 15–23.

[4] R.W. Matthews, Solar Energy 38 (1987) 405–413.

[5] S. Malato, J. Blanco, A.R. Fernandez-Alba, A. Agũera, Chemosphere 40 (2000) 403–409.

[6] C. Minero, E. Pelizetti, S. Malato, J. Blanco, Solar Energy 56 (1996) 411–419.

[7] C. Guillard, J. Disdier, J.M. Herrmann, C. Lehaut, T. Chopin, S. Malato, J. Blanco, Catal. Today 54 (1999) 255–265.

[8] I. Sopyan, M. Watanabe, S. Murasawa, K. Hashimoto, A. Fujishima, J. Photochem. Photobiol. A 98 (1996) 79–86.

[9] A. Fernandez, G. Lassaletta, V.M. Jimenez, A. Justo, A.R. Gonzalez-Elipe, J.M. Herrmann, H. Tahiri, Y. Ait-Itchou, Appl. Catal. B: Environ. 7 (1995) 49–63.

[10] S. Sitkiewitz, A. Heller, New J. Chem. 20 (1996) 233–241.

[11] C. Guillard, J. Disdier, C. Monnet, J. Dussaud, S. Malato, J. Blanco, M.I. Maldonado, J.-M. Herrmann, Appl. Catal. B: Environ. 46 (2003) 319–332.

[12] J.A. Byrne, B.R. Eggins, N.M.D. Brown, B. McKinney, M. Rouse, Appl. Catal. B. Environ. 17 (1998) 25–36.

[13] A. Hilmi, J.H.T. Luong, A.L. Nguyen, Chemosphere 38 (1999) 865–874.

[14] D.F. Ollis, R.E. Marinangelli, AIChE J. 23 (1977) 415–426.

[15] D.F. Ollis, R.E. Marinangelli, AIChE J. 26 (1980) 1000–1008.

[16] K. Hofstadler, R. Bauer, S. Novalic, G. Heisler, Environ. Sci. Technol. 28 (1994) 670–674.

[17] L.W. Miller, M.A. Anderson, J. Adv. Oxid. Technol. 3 (1998) 238–242.

[18] N.J. Peill, M.R. Hoffmann, Environ. Sci. Technol. 29 (1995) 2974–2981.

[19] N.J. Peill, M.R. Hoffmann, Environ. Sci. Technol. 30 (1996) 2806–2812.

[20] W. Choi, J.Y. Ko, H. Park, J.S. Chung, Appl. Catal. B: Environ. 31 (2001) 209–220.

[21] R.-D. Sun, A. Nakajima, I. Watanabe, T. Watanabe, K. Hashimoto, J. Photochem. Photobiol. A: Chem. 136 (2000) 111–116.

[22] S. Hager, R. Bauer, Chemosphere 38 (1999) 1549–1559.

[23] A. Gonzalez-Martin, A.S. Jeevarajan, O.J. Murphy, J. Adv. Oxid. Technol. 3 (1998) 253–260.

[24] W. Wang, Y. Ku, J. Photochem. Photobiol. A: Chem. 159 (2003) 47–59.

[25] A. Danion, J. Disdier, C. Guillard, F. Abdelmalek, N. Jaffrezic-Renault, Appl. Catal. B: Environ. 52 (2004) 213–223.

[26] A. Danion, C. Bordes, J. Disdier, J.-Y. Gauvrit, C. Guillard, P. Lantéri, N. Jaffrezic-Renault, J. Photochem. Photobiol. A: Chem. 168 (2004) 161–167.

[27] C. Guillard, D. Debayle, A. Gagnaire, J.-M. Herrmann, H. Jaffrezic, Mater. Res. Bull. 39 (2004) 1445–1458.

[28] J.-M. Herrmann, H. Tahiri, C. Guillard, P. Pichat, Catal. Today 54 (1999) 131–141.

[29] J.-M. Herrmann, Catal. Today 53 (1999) 115–129.

[30] C. Maillard-Dupuy, C. Guillard, P. Pichat, New J. Chem. 18 (1994) 941–948.

[31] J.C. D’Oliveira, G. Al-Sayyed, P. Pichat, Environ. Sci. Technol. 24 (1990) 990–996.

[32] N. Serpone, J. Photochem. Photobiol. A: Chem. 104 (1997) 1–12.

[33] H. Tahiri, Ph.D. thesis, Université Ibnou Zohr, Faculté des Sciences, Agadir, Maroc, 1997.