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# Optimization of a single $TiO_2$-coated optical fiber reactor using experimental design

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**Abstract**

The photocatalytic degradation of hydroxybutanedioic acid in a single $TiO_2$-coated fiber-optic reactor was investigated by means of experimental design. The photocatalytic activity was mathematically described as a function of $TiO_2$ film thickness and coating length using the composite design methodology. Optimized values for these two parameters for two fibers with different diameters were determined from the drawing of corresponding response surfaces. A study of light transmission within the coated fiber was then conducted following the same methodology. Finally, the two studies were compared in order to verify the proportionality between the photocatalytic activity and the light absorbed by $TiO_2$.


*Keywords:* Optical fiber; $TiO_2$; Photocatalysis; Composite design; Response surfaces

## 1. Introduction

Heterogeneous photocatalysis using wide band-gap metal oxide semiconductors, such as $TiO_2$, represents an emerging area in pollutant remediation reactions. More than 1700 references both in liquid and gas phase have been recently collected on this subject [1]. This process allows the total destruction and complete conversion of a wide variety of organic contaminants into $CO_2$ and $H_2O$, achieved at ambient temperature and atmospheric pressure [2].

A slurry of $TiO_2$ is usually employed, which requires an expensive filtration step at the end of the process. To avoid this problem, a large number of reactors using fixed $TiO_2$ have been studied [3–8]. 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.

Thus, a novel reactor configuration was developed using a bundle of optical fibers coated with $TiO_2$. The light is transmitted to $TiO_2$ at the fiber core/$TiO_2$ interface. Between 1977 and 1980, Ollis and Marinangeli were the first to conduct studies on this subject [9,10]. Their conclusions were not optimistic: 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 bundles have been built firstly in liquid [11–14] and more recently in gas phase [15–19]. This new type of reactor has been shown to deliver high quantum yields [13].

The influences of the thickness of the coating layer, the coating length and the fiber diameter on the photocatalytic efficiency and on the light transmission through the fiber were reported previously [13–15,20,21]. Optimization of these parameters is assessed by systematic variation of one parameter while the others are maintained constant. However, this approach is unable to predict the best conditions of the process. In this respect, experimental designs are appropriate tools for this purpose. Among experimental designs, second-degree designs such as central composite [22,23] allow process modeling and the determination of optimal conditions. This kind of tool has already been used in several analytical resolution techniques and has been demonstrated to be an adequate tool to improve the analytical

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results [24,25]. Recent studies have applied this methodology to study the photocatalytic degradation of dyes [26,27]. However, so far, we have not found references that have applied chemometric experimental designs to an optical fiber photoreactor.

In this study, we have used a central composite design to optimize experimental conditions of photocatalytic reaction in a reactor composed of a single $TiO_2$-coated fiber (Fig. 1).

## 2. Experimental procedure

### 2.1. Preparation of $TiO_2$ coatings on optical fiber

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 0.6 and 1 mm diameter were cut into pieces of 30 cm length and their mechanical cladding was mechanically stripped for 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 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 [28]. The same procedure was repeated for each coating. Several fibers were prepared with different numbers of layers and different lengths of coating.

### 2.2. Determination of photocatalytic activity

A single coated fiber was placed into a tubular reactor (3 ml) filled with a solution of hydroxybutanedioic acid at a concentration of $3.73 \times 10^{-4}$ mol/l (Fig. 1). The fiber was irradiated by the high-pressure mercury lamp at the end covered by the original cladding. A circulating water cell, used to filter the infrared rays, was equipped with a 340 nm cut-off filter to avoid photochemistry of hydroxybutanedioic acid. After 5 h, the activity was evaluated by HPLC-UV (Waters 600 pump equipped with a Waters 486 UV detector) at 210 nm. The eluent was a solution of sulfuric acid in water at a concentration of $5 \times 10^{-3}$ mol/l. The column (SARASEP CAR-H, 300 mm × 78 mm) was used with a flow rate of 0.7 ml/min, and 20 μl of each sample was injected.

### 2.3. Determination of light intensity absorbed or scattered by a $TiO_2$ film

The light transmission was studied by irradiating a fiber with a 500 W mercury UV lamp (Oriel Model 6285) at one end with a power of 300 W. The transmitted light intensities at the other end were measured by a United Detector Technology (Model 21A) UV radiometer. The difference in light intensity between the light transmitted by a fiber without $TiO_2$ coating and the light transmitted by a coated fiber was taken to be the light absorbed or scattered by the $TiO_2$ film.

### 2.4. Determination of response surfaces

Coefficients for regression models, optimized conditions and response surfaces were calculated using NEMROD (LPRAI, Marseille, France), a software package.

## 3. Results and discussion

### 3.1. Study of photocatalytic degradation of hydroxybutanedioic acid

Relevant factors and their experimental domain were selected in accordance with our preliminary results [21]. The influences of the $TiO_2$ film thickness and the coating length were investigated. As shown in Table 1, the experimental domain for the film thickness is expressed by the number of layers. It is comprised between 1 and 17. Above 17 layers, the photodegradation of hydroxybutanedioic acid is not enhanced. The experimental domain for the coating length was adjusted between 6.5 and 13.5 cm. Below 6.5 cm the photocatalytic activity is too low to be estimated and the length of the reactor is 13.5 cm. Since the different input variables presented different dimensional units, these variables can be compared most easily if they are normalized to a common unit. Therefore, coded variables were used during the modeling procedure. As indicated in Table 1, the coded variables are $X_1$ and $X_2$ for the $TiO_2$ film thickness and the coating length, respectively.

Two types of fibers were studied: one 1 mm fiber and one 0.6 mm fiber. So, two separate experimental designs were conducted.

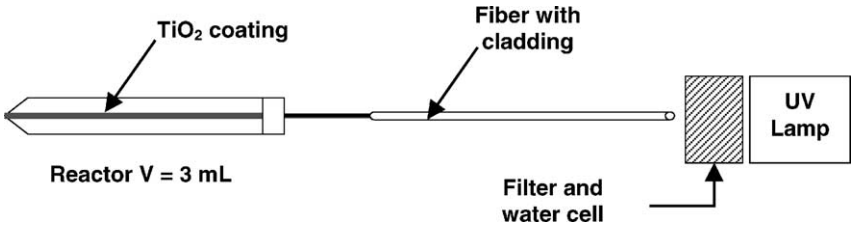


Fig. 1. Experimental setup.

Table 1
Experimental domain

| Natural variable | Coded variable | Parameter | Low level | Center level | High level |
|---|---|---|---|---|---|
| $N_L$ | $X_1$ | Number of layers | 1 | 9 | 17 |
| $L$ | $X_2$ | Coating length (cm) | 6.5 | 10 | 13.5 |

In order to optimize the photocatalytic activity of our single optical fiber reactor, a composite design was carried out following the methodology described by Box et al. [22,23]. This is comprised of a $2^2$ full factorial design (experiments 1–4 in Table 2) and a star point design (experiments 5–8 in Table 2). The center point was repeated three times (experiments 9–11 in Table 2). All experiments were randomly performed. The measured response was defined as the percentage of degraded hydroxybutanedioic acid after 5 h of reaction ($Y_1$ for the 1 mm fiber and $Y_2$ for the 0.6 mm fiber as shown in Table 2).

Multiple regression enables a description of the mathematical relationship between the different coded variables and the experimentally obtained responses. The resulting second-degree model is described by the polynomial expression shown in Eq. (1):

$$Y = b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2 \quad (1)$$

The coefficients $b_i$ and $b_{ii}$ of this model were then calculated for each fiber and the following expressions were obtained:

$$Y_1(1\,\text{mm}) = 39.3 + 6.7\,X_1 + 3.9\,X_2 - 2.9\,X_1^2 - 1.2\,X_2^2 - 0.3\,X_1X_2 (R^2 = 0.876) \quad (2)$$

$$Y_2(0.6\,\text{mm}) = 27.4 + 3.0\,X_1 + 4.7\,X_2 - 2.7\,X_1^2 - 0.9\,X_2^2 - 2.2\,X_1X_2 (R^2 = 0.804) \quad (3)$$

Table 2
Numerical results of the composite experimental design of hydroxybutanedioic acid degradation

| Exp. no. | $N_L$ | $L$ | $Y_1$ (1 mm) | $Y_2$ (0.6 mm) |
|---|---|---|---|---|
| 1 | 4 | 7.5 | 29 | 12 |
| 2 | 15 | 7.5 | 37 | 26 |
| 3 | 4 | 12.5 | 36 | 28 |
| 4 | 15 | 12.5 | 43 | 33 |
| 5 | 1 | 10.0 | 21 | 20 |
| 6 | 17 | 10.0 | 46 | 22 |
| 7 | 9 | 6.5 | 30 | 20 |
| 8 | 9 | 13.5 | 43 | 30 |
| 9 | 9 | 10.0 | 36 | 25 |
| 10 | 9 | 10.0 | 38 | 28 |
| 11 | 9 | 10.0 | 43 | 30 |

From the value of the $b_0$ coefficient for each fiber, which represents the center response, we can assume that the 1 mm fiber is 1.5 times more efficient than the 0.6 mm fiber. This ratio can be explained by the ratio of $TiO_2$ loading on the fibers which is dependant on the diameter ratio (Table 3).

The coefficients of determination ($R^2$) were satisfactory for the two fibers as indicated in Eqs. (2) and (3). As illustrated in Fig. 2, residual error values did not exceed 3.7% for the 1 mm fiber and 4.2% for the 0.6 mm fiber. These values were contained within the range of the experimental standard deviation. No outlier was shown from Fig. 2. Therefore, the two models were accepted.

In order to get the optimal parameter values, the surface responses were then calculated. Fig. 3(a) and (b) show two different behaviors for each fiber. For the 1 mm fiber, under nine layers, the photocatalytic degradation is increased when the number of layers ($N_L$) is increased. After nine layers, the coating length ($L$) must be increased in order to increase the photocatalytic activity. On the contrary, for the

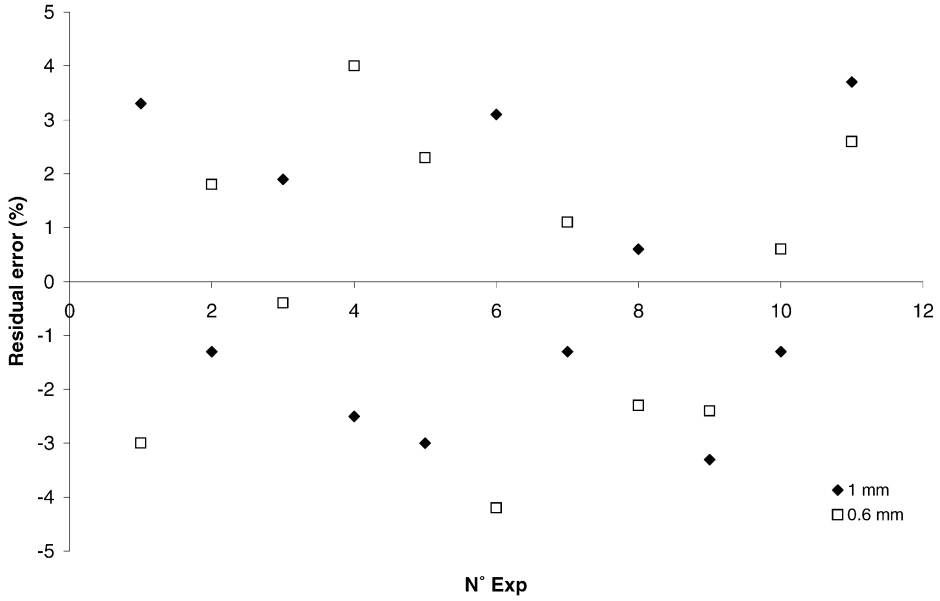


Fig. 2. Residual error for the study of photocatalytic degradation.

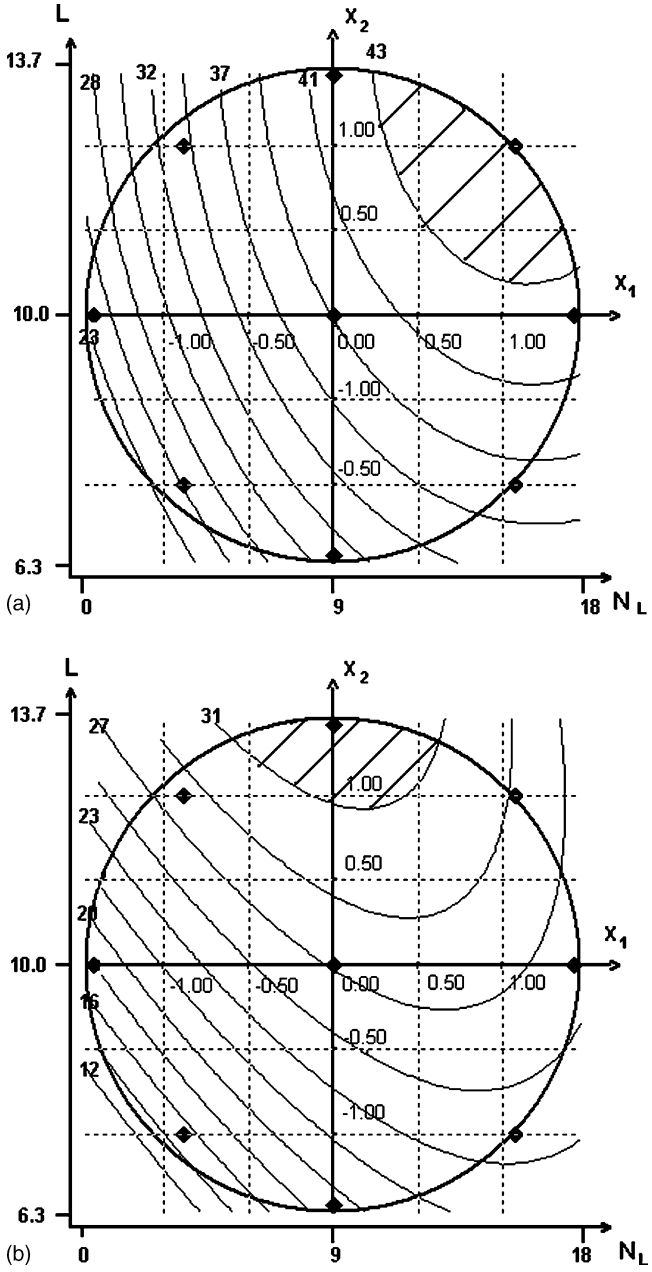


Fig. 3. Response surfaces showing the percentage of degradation of hydroxybutanedioic acid ($Y$) as a function of the number of layers ($X_1$) and coating length ($X_2$): (a) 1 mm fiber (b) 0.6 mm fiber.

0.6 mm fiber, below nine layers, increasing either parameter increases the photocatalytic activity and, above nine layers, only increasing the coating length causes increased photocatalytic activity. As depicted in Fig. 3(a) and (b), the optimal degradation of hydroxybutanedioic acid was obtained for the 1 mm fiber for 15 layers and a coating length of 12.5 cm ($Y_1 = 46\%$) whereas for the 0.6 mm fiber the optimal degradation is obtained for nine layers and a coating length of 13.5 cm ($Y_2 = 32\%$).

The models were then calculated in natural variables and the following expressions are obtained:

Table 3
Coating mass of deposited $TiO_2$

| Number of layers ($N_L$) | Fiber diameter (mm) | Coating mass (μg/cm) |
|---|---|---|
| 4 | 0.6 | 5.8 |
| 4 | 1 | 13.1 |
| 9 | 0.6 | 14.3 |
| 9 | 1 | 27.2 |

$$\%\,\text{deg}\,(1\,\text{mm}) = -16.01 + 3.04N_L + 5.68L - 0.09N_L^2 - 0.19L^2 - 0.02N_L \times L \quad (4)$$

$$\%\,\text{deg}\,(0.6\,\text{mm}) = -32.13 + 3.62N_L + 6.26L - 0.08N_L^2 - 0.14L^2 - 0.16N_L \times L \quad (5)$$

These equations allow to predict any value within the experimental domain using natural variables.

### 3.2. Study of light transmission in a $TiO_2$-coated optical fiber

The light transmission in a $TiO_2$-coated optical fiber was then studied. In fact, from the measurement of the transmitted light through the fiber, we can deduce the light available for the $TiO_2$ activation. The calculations were performed using the same composite design as presented in the former study. The measured response was defined as the percentage of transmitted light within the coated fiber ($Y_3$ for the 1 mm fiber and $Y_4$ for the 0.6 mm fiber as shown in Table 4).

After calculation, the following second-degree models were obtained (coded variables):

$$Y_3\,(1\,\text{mm}) = 64.3 - 10.7X_1 - 4.3X_2 + 0.5X_1^2 + 2.7X_2^2 - 0.2X_1X_2 (R^2 = 0.703) \quad (6)$$

$$Y_4\,(0.6\,\text{mm}) = 22.2 - 14.4X_1 - 2.6X_2 + 8.7X_1^2 - 2.7X_2^2 + 1.1X_1X_2 (R^2 = 0.854) \quad (7)$$

The values of $b_0$ for each fiber suggest that the 1 mm fiber transmits 2.9 times more light than the 0.6 mm fiber. This

Table 4
Numerical results of the composite experimental design of transmitted light

| Exp. No. | $N_L$ | $L$ | $Y_3$ (1 mm) | $Y_4$ (0.6 mm) |
|---|---|---|---|---|
| 1 | 4 | 7.5 | 85 | 32 |
| 2 | 15 | 7.5 | 57 | 16 |
| 3 | 4 | 12.5 | 85 | 27 |
| 4 | 15 | 12.5 | 55 | 15 |
| 5 | 1 | 10.0 | 72 | 70 |
| 6 | 17 | 10.0 | 52 | 15 |
| 7 | 9 | 6.5 | 77 | 26 |
| 8 | 9 | 13.5 | 54 | 16 |
| 9 | 9 | 10.0 | 56 | 21 |
| 10 | 9 | 10.0 | 69 | 25 |
| 11 | 9 | 10.0 | 66 | 23 |

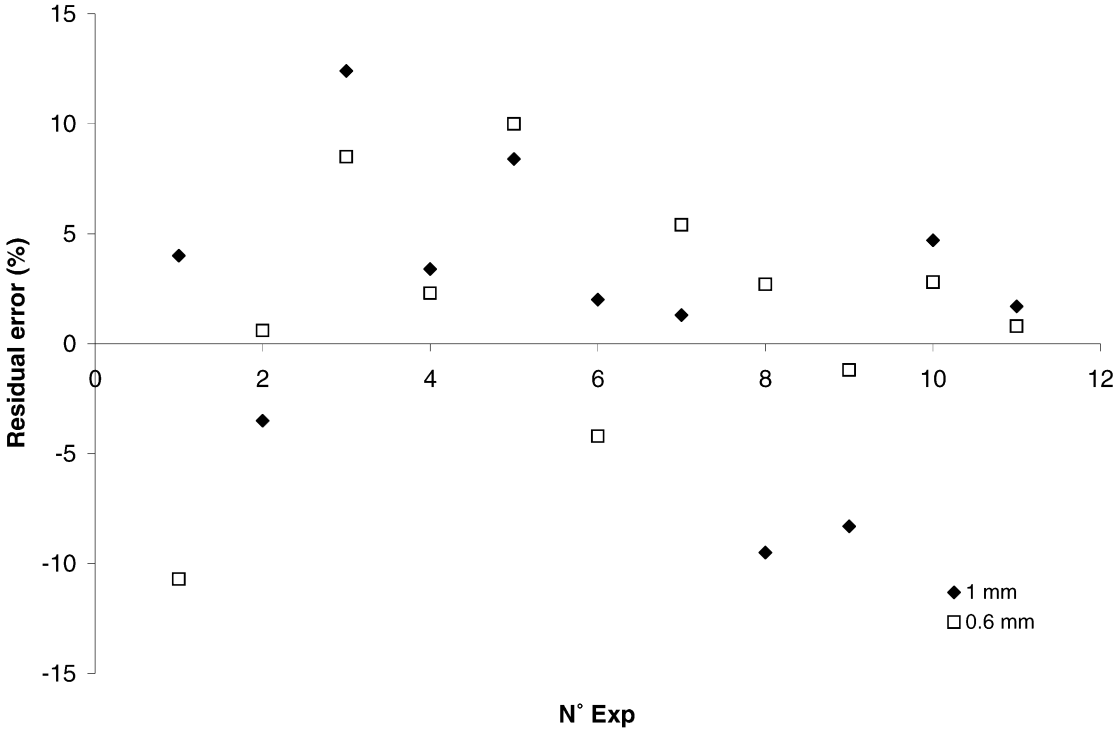


Fig. 4. Residual error for the study of light transmission.

value corresponds to the ratio of the fibers section. As explained by Peill and Hoffmann [14], as the fiber diameter is increased, light undergoes fewer reflections at the core-$TiO_2$ interface for a given length. So, for a larger fiber diameter, more light is transmitted. This result is in agreement with our previous results [21].

The coefficients of determination ($R^2$) were acceptable for the 1 mm fiber and satisfactory for the 0.6 mm fiber as indicated in Eqs. (6) and (7). As illustrated in Fig. 4, residual error values did not exceed 12% for the 1 mm fiber and 10% for the 0.6 mm fiber: these values were contained within the range of the experimental standard deviation. No outlier was shown from Fig. 4. Therefore, the two models were accepted.

The corresponding surface responses were calculated and presented in Fig. 5(a) and (b). As in the former study, two behaviors were observed. For the 1 mm fiber, below and above nine layers, as the layer number ($N_L$) is increased, less light is transmitted. The influence of coating length ($L$) seems to be negligible. On the contrary, for the 0.6 mm fiber, below nine layers, less light is transmitted as the layer number is increased. After nine layers, the light transmission is decreased as the coating length is increased. As shown in Fig. 5(a) and (b), the conditions under which transmission of light is minimal, and therefore more light intensity is available for $TiO_2$, are: 17 layers and a coating length of 11.5 cm for the 1 mm fiber ($Y_3 = 49\%$) and 12 layers and 13.5 cm for the 0.6 mm fiber ($Y_4 = 10\%$).

The models were then calculated in natural variables and the following expressions are obtained:

$$\%\, I_{\text{trans}}(1\,\text{mm}) = 142.86 - 2.05N_L - 10.45L + 0.01N_L^2 + 0.44L^2 - 0.01N_L \times L \quad (8)$$

$$\%\, I_{\text{trans}}(0.6\,\text{mm}) = 40.52 - 8.21N_L + 7.07L + 0.27N_L^2 - 0.44L^2 + 0.08N_L + L \quad (9)$$

These equations allow the prediction of any value within the experimental domain using natural variables.

### 3.3. Comparison between the two studies

In order to investigate a correlation between the loss of transmitted light and the photocatalytic activity, the results obtained by the two studies are gathered. Fig. 6 shows the photocatalytic degradation rate of hydroxybutanedoic acid as a function of the percentage of transmitted light. Two different populations can be observed: the first one is relative to the 1 mm fiber and the second one to the 0.6 mm fiber. Although a certain inaccuracy, probably due to the inhomogeneity of the $TiO_2$ coating, is observed, it can be assumed that the photocatalytic activity increases linearly as the transmitted light is decreased. In other words, the photocatalytic activity is proportional to the light absorbed by $TiO_2$ in our conditions. This result is well-known in photocatalysis [29]. When the photocatalytic activity is compared between the two fibers at a fixed light transmission, the 1 mm fiber is about two times more efficient than the 0.6 mm fiber. This result confirms the result obtained in the photocatalytic study. From this, we can deduce that the 1 mm fiber should

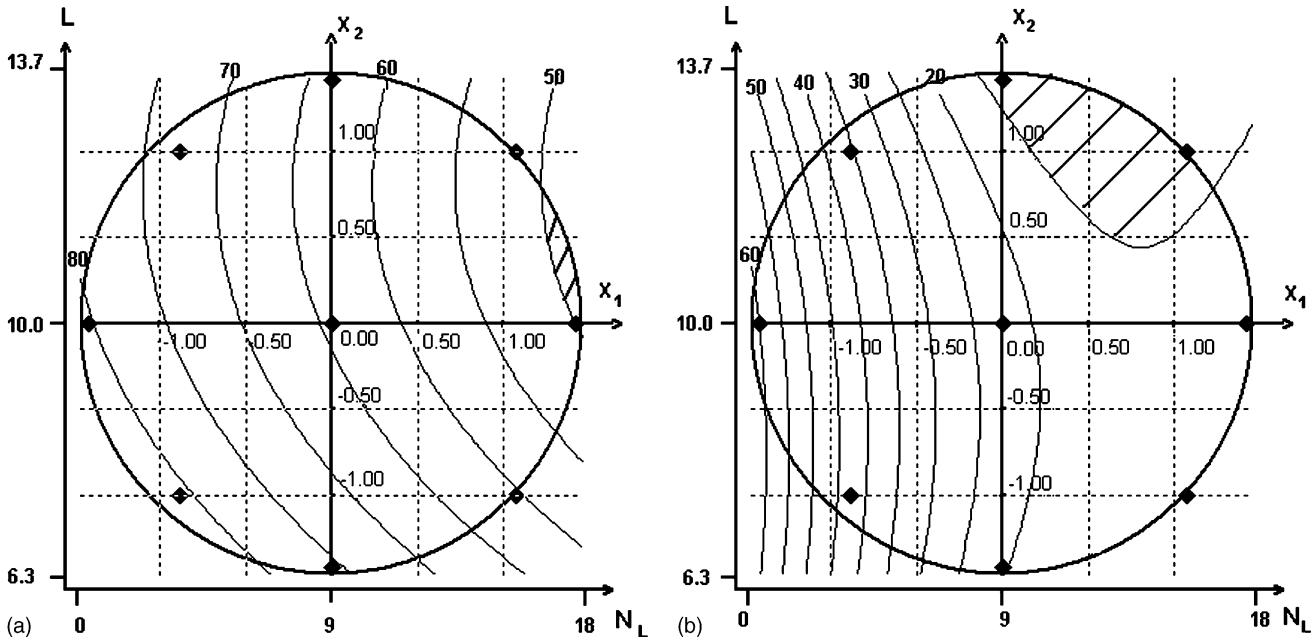


Fig. 5. Response surfaces showing the percentage of transmitted light ($Y$) as a function of the number of layers ($X_1$) and coating length ($X_2$): (a) 1 mm fiber (b) 0.6 mm fiber.

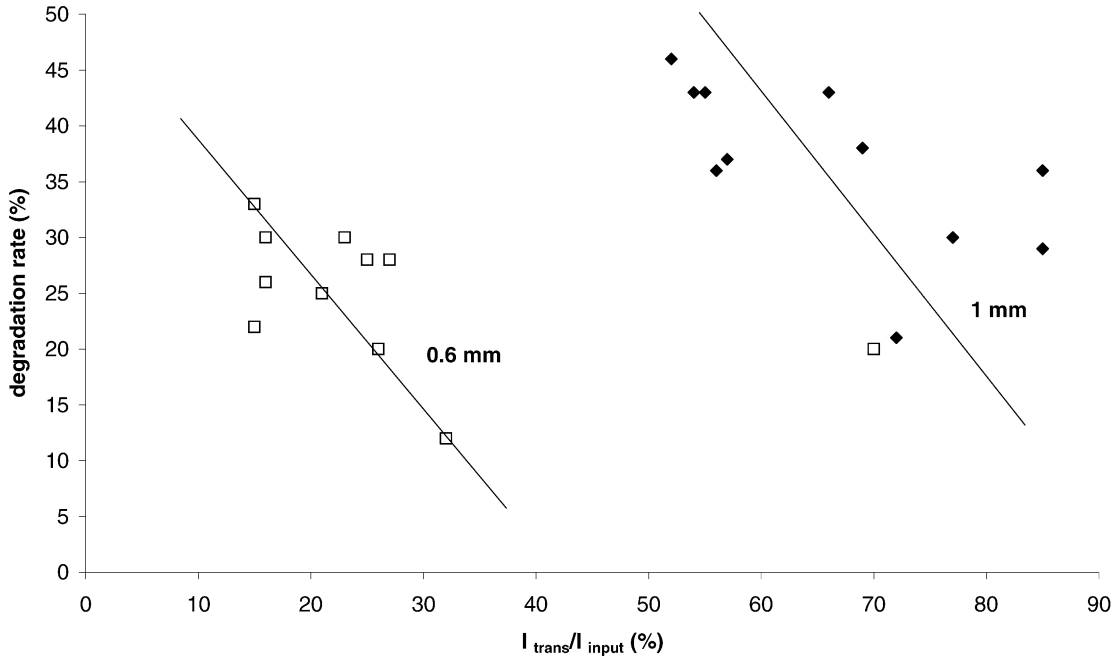


Fig. 6. Photocatalytic degradation rate as a function of transmitted light.

be chosen to improve the photocatalytic degradation rate in further studies.

## 4. Conclusions

Optimization of photocatalytic degradation of hydroxybutanedioic acid in a single optical fiber-based reactor was performed by using a composite experimental design. The ensuing mathematical model enabled the prediction of photocatalytic degradation at any point in the experimental domain as well as the determination of the optimal degradation conditions. The quality of the model was demonstrated by the good agreement between experimental and predicted responses. The same methodology was applied to the study of light transmission within the $TiO_2$-coated fiber. When

the results of the two studies are compared, it is demonstrated that the photocatalytic activity is proportional to the absorbed light.

In further studies, these results will be applied to build a multi-fiber reactor allowing the treatment of a larger volume of polluted water.

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