Modelling and Experimental Investigation of Luminous Coupling in UV-LED Driven Optical Fiber Reactors

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Abstract: Background: Photocatalytic oxidation is a promising tool for waste water treatment and decomposition of biologically non digestible substances. Immersed nanoscale catalyst particles from semiconductor materials such as TiO2 and ZnO can be excited by absorbed UV radiation, leading to hydroxyl-ion formation at the surface of the semiconductor and oxidative degradation of pollutants.

Objective: This contribution deals with reactors equipped with catalyst coated light guides to combine the advantages of immobilized catalysts with nearly homogeneous irradiation. With experimental and theoretical methods the coupling and decoupling of radiation were investigated and the performance of catalyst coated light guides was tested by means of methylene-blue degradation.

Methods: Radiation models, known from the recent literature, use single ray, parallel ray or multi ray models to approximate the light transmission. These models neglect Fresnel reflection and consider only coupling into the light guide. In this study, the LED was simulated as a Lambertian radiator using 10 4 rays with angle dependent intensities. This well-known model was extended with Fresnel-reflection, which predicted the measured coupling efficiencies accurately. The simulations predict the decoupling and catalyst activation at the lateral surface of the light guide for two boundary cases, ideal reflection, which predicted the measured coupling efficiencies accurately. The simulations predict the theoretical methods the coupling and decoupling of radiation were investigated and the performance of catalyst coated light guides was tested by means of methylene-blue degradation.

Results: When using matt surfaces, the decoupling rate is very high: 80% of the radiant flux exits the light guide in less than 10 cm. If light guides with reflective surfaces are used, the radiant flux leaving the light guide is low: less than 10% of the radiation exited the light conductor in the first 10 cm. Methylene-blue degradation, seen as a model reaction, was used to determine the reactor performance by comparing the pseudo first order reaction coefficients. Due to the uniform light distribution along the length of the light guides and the resulting even formation of reactive radicals, the quantum yield was increased by a factor of 3, using sol-gel coated light guides, rather than powder coated light guides.

Conclusion: The effectiveness of LED driven optical fiber reactors was intensified, if reflective surfaces are used instead of matt surfaces. These surfaces are achieved by sol gel chemistry. However, to use the complete amount of photons, which entered the optical fiber, very long light guides are needed.

Keywords: Optical fiber reactor, waste water treatment, light guide, photocatalysis, photochemistry, lambertian.

1. INTRODUCTION

The presence of complex organic pollutants in municipal waste waters requires advanced water treatment technologies [1]. There is a significant need for action not only in developing or emerging countries, where people have limited access to potable water [2-7], but also in industrialized countries, where municipal wastewaters are contaminated with nitrate [8] or pharmaceuticals. Pharmaceuticals such as hormones and analgesics [9, 10] cannot be fully broken down by common water treatment technologies [11]. Estrogen, for instance, leads to feminized fish and endanger their population [12, 13].

In recent literature, several processes were found to reduce the concentration of these pollutants [14]. The organic substances can be adsorbed onto activated carbon [15-18] or removed in membrane processes and membrane bioreactors [19-24]. Apart from chlorination [25] photocatalytic oxidation is a very promising method to eliminate organic pollutants. Semiconductors, such as TiO2 and ZnO, can be used as catalysts. Due to narrow band gap excitation by UV radiation, it is possible to induce the formation of hydroxyl radicals at the surface of the semiconductor. The radicals can react with organic molecules contacting the catalyst surface.
Thus, a degradation of polluting solutes is possible. In the development of photocatalytic reactors, it is necessary to consider a mass transfer, mixing pattern, the kind of catalyst installation and catalyst irradiation [14]. For catalyst recovery, an additional solid-liquid separation step is needed if suspended catalyst particles are used. Immobilization of the micro or nanoparticles on an appropriate surface will avoid this, but an efficient illumination of the catalyst is very difficult. As shown by Peill and Hoffmann, light guides are an efficient tool for the irradiation of the reaction volume [26, 27]. By coating light guides with the photocatalyst particles it is possible to combine the advantages of immobilized catalysts with an effective illumination of the catalyst. The effectiveness of catalyst illumination can be evaluated with the quantum efficiency $\varphi$ which is calculated by the following ratio

$$\varphi = \frac{\text{moles converted}}{\text{photons absorbed}}$$  \hspace{1cm} (Eq. 1)

It was shown that the quantum efficiency in a TiO$_2$ coated fiber-optic cable reactor [26, 27] is significantly higher than in a slurry reactor. With the development of UV-LEDs, light sources are available, which are much more energy efficient than collimated lamps and their direct coupling with the light guide is easily possible [28-30].

For the optimization of TiO$_2$ coated light guide-LED systems, it is necessary to analyze the coupling of radiation into the light conductor, the decoupling of the UV-radiation along the length, and finally, the catalytic performance of the optically characterized light guides was evaluated.

This contribution deals with the optical characterization of LED-light-guide-systems and the modelling and simulation of their coupling and decoupling behavior. A multi ray model considering the Fresnel reflection is proposed to predict the coupling efficiency of a LED, which is mounted at the end of a cylindrically shaped light conductor. TiO$_2$ coatings consisted of P25 nano particles or alternatively consisted of sol-gel coatings in order to evaluate the difference between matt and reflective surfaces.

The coated light guides were tested with respect to the degradation of methylene blue in aqueous solution to show the interrelation between the decoupling pattern and the rate constant. According to a German standard procedure (DIN 52980:2008-10), methylene-blue was chosen as a model reactant.

2. MATERIALS AND METHODS

2.1. Simulation

The radiation models, which are known from literature simplify the light transmission with single ray [31, 32] or parallel ray models [28]. While the coupling is displayed by a multi ray model, this approach does not take into account Fresnel reflection at the guide’s light surface [33].

Furthermore, the models do not distinguish between matt and reflective surfaces. In this study, the LEDs are modelled as ideal Lambertian radiators, which are discretized into 100 elementary radiators, each emitting 100 rays, in order to simulate $10^4$ rays with angle dependent intensities.

The model considers Fresnel reflection at the light guide’s surface, the light transmission due to total reflection in the fiber, and the attenuation at matt and at reflective surfaces. The attenuation at matt surfaces is induced by scattering. The attenuation at reflective surfaces, which are caused by the closed layers of TiO$_2$, is induced by partial reflection and refraction.

Fig. (1) shows the coupling of rays into the light guide. A ray with a radiant flux $\Phi_0$ hits the surface and is partially reflected ($\Phi_{\text{refl.}}$) and refracted ($\Phi_{\text{in}}$).

![Fig. (1)](image)

**Fig. (1).** Coupling mechanism: A ray with a radiant flux $\Phi_0$ hits the surface of the light guide. According to the Fresnel-equations, the radiant flux is divided into a reflected $\Phi_{\text{refl.}}$ fraction and into a refracted fraction $\Phi_{\text{in}}$. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

Once the radiation is coupled into the light guide, it is transmitted due to total reflection. If the rays fall onto a matt surface, as seen with nanopowder coatings, the rays are scattered. Therefore, the matt surface emits the radiation as a Lambertian radiator (see Fig. 2). The radiation is partially scattered towards the outside of the light guide and partially towards the inside. Those rays which stay in the light guide, hit the opposite surface of the light guide and are scattered again.

![Fig. (2)](image)

**Fig. (2).** Scattering mechanism for matt surfaces. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

Considering reflective surfaces instead of matt surfaces, the coupling and attenuation mechanism is different. According to the diagram in (Fig. 3) the following mechanism for the refraction/reflection is assumed:

1. The ray reaches the boundary between the light guide and the TiO$_2$ layer.
2. According to the Fresnel-equations there is an average incident angle dependent reflectivity $\bar{\rho}$ and transmissivity $(1-\bar{\rho})$. 
3. The refracted fraction is absorbed in the TiO$_2$ layer according to the Beer-Lambert law. At the boundary between TiO$_2$ and air the conditions for total reflection are fulfilled.

4. As the ray reaches the boundary between TiO$_2$ and glass, the ray is refracted into the glass rod.

Fig. (3). The attenuation in the sol-gel coated light guides is due to the following steps: 1. Refraction at the boundary, 2. Residual intensity according to Fresnel reflection. 3. Absorption in the TiO$_2$ layer. 4. Refraction of the residual intensity into the light guide. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

2.2. Experiments

2.2.1. Coating of the Light Guides

The quartz glass light guides and the LEDs (SEOUL VI-OYS – CUN66A1B) (uv: $\lambda_{\text{max}} = 365$ nm, blue: $\lambda_{\text{max}} = 455$ nm) were obtained from Peschl Ultraviolet GmbH (Mainz, Germany). The PUAS, PUWS and PUDP sols were obtained from Fraunhofer IKTS (Hermsdorf, Germany). These commercial sols are optimized for different applications, as it is stated in (Table 1).

<table>
<thead>
<tr>
<th>P25</th>
<th>Acros Aerioxide P25 Suspended in Ethanol</th>
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<tr>
<td>TTIP</td>
<td>Titaniumisopropoxide in isopropanol 5%vol</td>
</tr>
<tr>
<td>PUDP</td>
<td>Photocatalytic sol</td>
</tr>
<tr>
<td>PUAS</td>
<td>Polymeric Sol</td>
</tr>
<tr>
<td>PUWS</td>
<td>Colloidal Sol</td>
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The quartz glass light guides were cleaned in diluted NaOH solution and rinsed with isopropanol. They were dip-coated with the sols (withdraw speed: 6 cm · min$^{-1}$), and heated for 1 h at 500 °C.

To coat the light guides with the nanopowders, the cleaned light guides were dipped into ethanol - TiO$_2$ slurry. The TiO$_2$ concentration was 0.050 g$_{\text{TiO}_2}$ · g$^{-1}$ solvent. The coated light guides were dried at ambient temperature and heated for 1 h at 500°C.

The p25 coating was white, opaque and matt. The TTIP coating was clear with matt inclusions. The PUDP, PUAS and PUWS coatings were clear and reflective. Furthermore, Newton rings were observable on the surface, which indicates that the coating thickness is in the range of some hundred nanometers. Due to the relatively low calcination temperature of 500 °C for 1 h the dominant modification of the TiO$_2$ catalyst is expected to be anatase [34-37].

2.2.2. Coupling Efficiency

To estimate the relative coupling efficiency patterns between the LED and the light guide, the LED was mounted onto a microscope’s cross table. (Fig. 4) illustrates the relative x- and y-shift of the light guide and the LED. The objective lens was replaced by the light guide. Instead of an eyepiece, a collimator was mounted into the tube and connected to a RGB lasersystems qwave spectrometer. The integration time was normalized to the expected maximum in (0,0) position and kept constant for each measurement.

The real coupling efficiency for a centered light guide (0,0) was measured in a Labsphere illumina Plus integration sphere being 1 m in diameter using a CDS610 spectrometer, calibrated to absolute spectral fluxes. While the lamp was mounted in a PVC box, a 15 cm glass rod of 10 mm diameter was mounted above the LED at a distance of 3 mm. The light guide was roughened on the outer surface, to enable quantitative scattering from the light guide into the integration sphere.

2.2.3. Decoupling Patterns

The decoupling patterns were measured using this setup, which is shown in (Fig. 5). The light guide was mounted onto the LED using a PVC cover, which encapsulates all rays, which do not enter the light guide. The glowing optical rod was covered with a black paper tube, which was vertically raised in 1 cm steps. The whole setup was mounted in an absolute calibrated integration sphere, in order to measure the emitted radiant fluxes.
2.2.4. Kinetic Performance

Finally, the catalytic performance of the optically characterized TiO$_2$ coated light guides were experimentally determined. The methylene-blue degradation was chosen as a test reaction. (Fig. 6) shows a diagram of the reactor, in which the methylene blue degradation took place. The reactor consisted out of a glass cylinder with one lateral and two terminal openings near the top of the reactor. The catalyst coated light guide was placed into the lateral opening. The reaction volume was 25 mL, the recirculation rate from bottom to top was 10 mL·min$^{-1}$. The emission maximum of the LEDs was 365 nm. A photometer with a flow cell was situated in the recirculation stream. The methylene-blue concentration was obtained by measuring the optical absorbance at 665 nm.

The initial methylene-blue concentration was (4.0±0.1) mg·L$^{-1}$. This is a concentration at which the optical absorbance follows Beer-Lambert law. Furthermore, this concentration allows the approximation, as stated in eq. 3. The photochemical reaction is induced by photochemically generated hydroxyl radicals [38] and follows a Langmuir Hinshelwood mechanism [39].

For low reactant concentrations (1 $\gg$ $\sum K_i \cdot c_i$), the initial reaction rate follows a pseudo first order rate law.

$$- \frac{dc_{MB}}{dt} = \frac{k_{cr} K_{MB} c_{MB}}{1 + K_{MB} c_{MB} + K_{prod} c_{MB}}$$

(Eq. 2)

$$- \frac{dc_{MB}}{dt} = k_{cr} \cdot K_{MB} \cdot c_{MB}$$

(Eq. 3)

$$- \frac{dc_{MB}}{dt} = k_{obs} \cdot c_{MB}$$

(Eq. 4)

$$c_{MB}(t) = c_{0,MB} \cdot e^{-k_{obs} \cdot t}$$

(Eq. 5)

$$\ln \frac{c_{MB}(t)}{c_{0,MB}} = -k_{obs} \cdot t$$

(Eq. 6)

3. RESULTS AND DISCUSSION

3.1. Coupling

As shown in equations 7 – 9, the coupling efficiency was defined as the quotient of the radiant flux $\Phi_{in}$, which enters the light guide, and the radiant flux $\Phi_{out}$, which is emitted by the LED.

$$\eta = \frac{\Phi_{in}}{\Phi_{0}}$$

(Eq. 7)

$$\Phi_{in} = \int_{-\alpha}^{\alpha} \int_{-\pi/2}^{\pi/2} I(x, \vartheta) \, dx \, d\vartheta$$

(Eq. 8)

$$\Phi_{0} = \int_{-\alpha}^{\alpha} \int_{-\pi/2}^{\pi/2} I(x, \vartheta) \, dx \, d\vartheta$$

(Eq. 9)

Fig. (7) shows how the coupled intensity decreases with a relative shift of the light guide and the LED, which is shown in x- and y-direction. The coupling efficiencies are given by the color of the pixels. (Fig. 7a) shows the measured data. (Fig. 7b) shows a Gaussian function, which fitted the data accurately. (Fig. 7c) shows the residuals.

As expected, the largest coupling efficiencies were obtained when the light guide was mounted, right in the center of the LED. However, there is a broad plateau, which allows the light guide to be moved 2 mm without a significant loss of coupling efficiency.

(Fig. 8) shows one-dimensional slice of (Fig. 7b) for y = 0. The dashed line shows simulated coupling efficiencies not considering Fresnel-reflection. The solid blue line shows simulated coupling efficiencies considering Fresnel-reflection. The red line shows the fitted experimental data.

While the simple radiation model without Fresnel-reflection shows coupling efficiencies, which are about 20% higher than the experimental data, the extended model predicts the measured coupling efficiencies very well.
Fig. (7). Radiant flux, coupled into the light guide (Diameter $D_F = 10 \text{ mm}$) in relative x/y-position to the LED (Diameter $D_L = 3 \text{ mm}$) after a path length of $d = 3 \text{ mm}$: (a) Data Points, (b) Fit function, (c) Residuals (red = neg. green = pos.) (A higher resolution / colour version of this figure is available in the electronic copy of the article).

Fig. (8). Relative coupling efficiencies $\eta$ versus the relative x-shift between the LED and the light guide (at $y = 0 \text{ mm}$). Light guide diameter $D_R = 10 \text{ mm}$ and a LED diameter $D_L = 3 \text{ mm}$ after a passed path length of $d = 3 \text{ mm}$. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

3.2. Decoupling

Fig. (9) shows the simulation of the relative radiant flux, which leaves a roughened light guide. The rough surface starts at a length of 6 cm and ends at a length of 30 cm.

There is an attenuation in the first 6 cm due to surface inhomogeneities and due to rays, which are larger than the opening angle. When the rough surface starts, there is a steep increase of photons that leave the light guide. After 15 cm, more than 80% of the radiation has left the light guide. After 30 cm, there is only 5% of the radiation left in the light guide. Since, there are some rays with small spreading angles, there is always a residual amount of radiation, which does not leave the light guide.

The experimental data is very similar to the predicted behavior, however, the first data points show higher decoupling rates than the simulation predicts. This is due to inhomogeneities on the light guide’s surface.

Fig. (10) shows the laterally emitted radiant flux, which leaves a light guide, which was coated with p25 nanopowder and had a matt surface. Using a blue LED, the photon flux increases along the whole length of the coated light guide, whereas no ultraviolet radiation leaves the light guide after 6 cm.

Fig. (9). Simulated and measured intensity distribution in a light guide with a rough surface and a diameter of 10 mm. (A higher resolution / colour version of this figure is available in the electronic copy of the article).
The nanopowder coating acts in a similar way as the rough surfaces do and the radiation is scattered at the light guide’s lateral surface as it is shown in (Fig. 2). Since TiO₂ does not absorb visible light, the blue light can pass the layer.

The ultraviolet radiation is scattered in a similar manner, but the layer is dense and thick enough to absorb it completely. Therefore, there is no emitted radiant flux of ultraviolet radiation at places, where the light guide is coated with TiO₂ nanopowder.

Fig. (11) shows the laterally emitted radiant flux of blue and ultraviolet radiation in a light guide, which was coated with titanium isopropoxide. A heterogeneous film of TiO₂ was obtained, which was consisting of a clear TiO₂ matrix and TiO₂ particles.

In the homogeneous film, the radiation follows a mechanism, which is shown in Fig. (3): When a ray hits the lateral surface of the light guide, the radiation is partially reflected and refracted. When the refracted ray hits a TiO₂ particle, it is scattered. The scattered blue radiation is not absorbed by the TiO₂ film and it is laterally emitted, whereas the ultraviolet radiation is absorbed in the TiO₂ film. However, the scattered radiant flux is lower as it with TiO₂ nanopowder. A reasonable amount of radiation remains in the light guide until it leaves the axial end of the light guide at 14 cm, which is shown by the steep increase of the emitted radiant flux.

Figs. (12, 13 and 14) show the laterally emitted radiant fluxes of light guides, which were coated with the PUWS (Fig. 12), PUDP (Fig. 13) and PUAS (Fig. 14) sols. The obtained coatings were clear and reflective and optically similar to each other: Due to the missing scattering particles (only the PUDP sol had a small amount of dispersed TiO₂ particles inside), the reflection/refraction mechanism is strongly according to the model, which is shown in Fig. (3).

In the first 6 cm, there is some lateral emission due to inhomogeneities at the light guide’s surface. After 6 cm when the coating starts, the rays are partially reflected and refracted at the light guide’s surface according to the Fresnel equations. The refracted part is absorbed by the catalyst. Even if it is not absorbed completely, the remaining radiation returns into the light guide. The reflected part remains in the light guide.

A simulation based on this mechanism is shown in (Fig 15). The radiation is emitted much slower in comparison to the model, which was shown in (Fig. 2). Therefore, the largest amount of radiation leaves the light guide at the end (at 14 cm).

The simulated radiation pattern, which is shown in (Fig. 15), is similar to the behavior observed by Spigulis [31]. According to the simulation, the radiant intensity on a surface element is in the range of $10^{12} \cdot \text{cm}^2 \cdot \text{s}^{-1} \cdot \text{photons}$. This is a relatively low radiation intensity. However, the quantum yield increases with a decreasing irradiation rate [38].

These experiments have shown that there are two basic mechanisms for the decoupling of radiation in light guides. 1. Scattering mechanism at matt surfaces, 2. Reflection/refraction mechanism at reflective surfaces. These two cases were predicted by simulation, using geometrical optics.

It is concluded, that reflective surfaces, obtained by sol-gel chemistry, are preferable instead of matt surfaces, obtained by powder coatings, because higher quantum yields are expected.

3.3. Kinetics

Fig. (16) shows the logarithmic methylene blue concentration over time. In the first 1500 s the system was conditioned in the dark. Then, the lamp was turned on. In the range of 2000 s and 5000 s a linear function fits the data. According to equation 6, the rate constant was received from the slope of the fit function. After 7000 s the reaction rate slows down. At this time a significant concentration of intermediates [39, 40] is formed, which are competing with methylene blue for the active sites.

Fig. (17) shows the pseudo first order rate constants in a methylene blue degradation experiment and the relative absorbed photon fluxes using light guides with 10 cm active coating length. An efficiency factor $\eta$ was defined, to characterize the efficiency of the photon absorption from the emitted radiant flux of an empty light guide $\Phi_{empty}$ and a coated light guide $\Phi_{coated}$:

$$\eta = \frac{\Phi_{coated}}{\Phi_{empty}}$$

(Eq. 10)
Fig. (11). Intensity distribution in a light guide with cloudy surface (TTIP coated). (A higher resolution/colour version of this figure is available in the electronic copy of the article).

Fig. (12). Intensity distribution in a light guide with a smooth surface (PUWS coated). (A higher resolution/colour version of this figure is available in the electronic copy of the article).

Fig. (13). Intensity distribution in a light guide with a plain surface (PUDP coated). (A higher resolution/colour version of this figure is available in the electronic copy of the article).

Fig. (14). Intensity distribution in a light guide with a smooth surface (PUAS coated). (A higher resolution/colour version of this figure is available in the electronic copy of the article).
Fig. (15). Simulated intensity distribution in a light guide with smooth surface (diameter = 10 mm). (A higher resolution / colour version of this figure is available in the electronic copy of the article).

Fig. (16). Logarithmic methylene blue concentration versus time. After the system was conditioned during the first 1500 second, the lamp was turned on. A linear function fits the data between 2000 s and 5000 s. After 7000 s and more, the actual reaction rate is significantly lower than the fit function. The initial approximation (eq. 3) is no longer applicable. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

Fig. (17). Comparison of the pseudo first order rate constants and fractions absorption of different coatings. (A higher resolution / colour version of this figure is available in the electronic copy of the article).

Fig. (18). Comparison of the pseudo first order rate constants normalized on the absorption efficiency. (A higher resolution / colour version of this figure is available in the electronic copy of the article).
The powder coated light guides absorb more than 80% of the radiation, whereas, the light guides which were coated by sol-gel chemistry, absorb less. TTIP was the sol, which leads to the cloudiest films and more than 50% of the radiation is absorbed, while the PUAS coatings were very clear and plain. Here, only less than 10% of the radiation was absorbed.

Fig. (18) shows the rate constants, divided by the absorption coefficients, which can be taken as a measure for the quantum efficiency of the photocatalytic methylene blue degradation. Compared to the powder coating (p25), the sol-gel-coating leads to more efficient use of the absorbed radiation. The efficiency is the highest with a highly transparent coating as it was achieved with the PUAS-coating.

A uniform and low absorption of UV-radiation along the length of the light guide leads to high quantum efficiencies. This observation is in agreement with Ohko et al. [38]. High absorption will induce a high formation rate of radicals, but a large part of them cannot be used. Reasons to be named are: the recombination of radicals is a fast reaction [38] and the degradation of the pollutant (here methylene-blue) is slow and can be additionally hindered by film mass transfer.

CONCLUSION

The simple raytracing model, which is known from literature, predicts coupling efficiencies, which are 20% higher, than the experimentally determined coupling efficiencies. The extended model, which uses Fresnel-reflection statements for each ray, predicts coupling efficiencies, which are very congruent with the experimentally determined efficiencies.

The transmission in the light guide, including the catalyst activation, was displayed in two limiting cases: ideal matt surfaces and ideal reflective surfaces. Matt surfaces were realized with nanopowder coatings, while the reflective surfaces were obtained with sol-gel coatings.

The model represents these two cases very accurately. For matt surfaces, the attenuation is very fast [32]. Therefore, the radiation intensities at the beginning of the fiber are high and many radicals are formed. However, the mass transfer resistance of methylene blue is limiting the reaction. Due to the fast recombination of the radicals, the quantum efficiency is very low for high radiation intensities [38].

If sol-gel coated light guides are used, the side scattering effects are very small. Thus, only low irradiation rates are reached at the surface. On the one hand, this lowers the overall performance of a photoreactor by 50%. On the other hand, the quantum efficiency is increased by the factor 3 to 10. Thus, for highly efficient photoreactors sol-gel coatings of the catalyst are preferable.

According to the decoupling pattern, light guides with a diameter of 10 mm have to be much longer than 10 cm. As it was shown by modelling the decoupling, a length of 1 to 2 m is necessary to achieve a nearly complete use of the available ultraviolet radiation.

A reduction of the light guide’s length is only possible if its diameter is reduced. Bundles of fibers with a small diameter will help to overcome this problem.

Finally, it must be stated that an energy efficient photocatalyzed decomposition of pollutants in water with acceptable reaction times will need reactors with a large surface of catalyst coated light guides.

LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Property</th>
<th>Dimension</th>
<th>Explanation</th>
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<tbody>
<tr>
<td>$c_{MB}$</td>
<td>mol·L$^{-1}$</td>
<td>Methylene blue concentration.</td>
</tr>
<tr>
<td>$c_{0,MB}$</td>
<td>mol·L$^{-1}$</td>
<td>Initial methylene blue concentration.</td>
</tr>
<tr>
<td>$c_{prod.}$</td>
<td>mol·L$^{-1}$</td>
<td>Molar concentration of product.</td>
</tr>
<tr>
<td>$d$</td>
<td>m</td>
<td>Incremental path length in axial direction</td>
</tr>
<tr>
<td>$D_L$</td>
<td>m</td>
<td>Diameter of the LED</td>
</tr>
<tr>
<td>$D_R$</td>
<td>m</td>
<td>Diameter of the light guide</td>
</tr>
<tr>
<td>$K_{MB}$</td>
<td>L·mol$^{-1}$</td>
<td>Equilibrium constant for the methylene blue adsorption.</td>
</tr>
<tr>
<td>$K_{prod.}$</td>
<td>L·mol$^{-1}$</td>
<td>Equilibrium constant for the product adsorption.</td>
</tr>
<tr>
<td>$k_{cr}$</td>
<td>s$^{-1}$</td>
<td>Intrinsic rate constant for the surface reaction</td>
</tr>
<tr>
<td>$k_{obs.}$</td>
<td>s$^{-1}$</td>
<td>Observable rate constant for the chemical reaction.</td>
</tr>
<tr>
<td>$t$</td>
<td>s</td>
<td>Time.</td>
</tr>
<tr>
<td>$x,y$</td>
<td>m</td>
<td>Relative shift between the light guide and the LED.</td>
</tr>
<tr>
<td>$\eta$</td>
<td>l</td>
<td>Coupling efficiency, absorption efficiency.</td>
</tr>
<tr>
<td>$\Phi_{in.}$</td>
<td>W</td>
<td>Radiant flux, which is coupled into the light guide.</td>
</tr>
<tr>
<td>$\Phi_{em.}$</td>
<td>W</td>
<td>Cumulated radiant flux emitted at the distance x.</td>
</tr>
<tr>
<td>$\Phi_0$</td>
<td>W</td>
<td>Total radiant flux, emitted by the light guide/ by the LED.</td>
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CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

Not applicable.

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CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.
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Declared none.

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