

U-Shaped Fiber-Optic Detection Elements for Investigation of Photocatalytic Decomposition of Toluene Dissolved in Water

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Received: 23 November 2013 / Accepted: 12 January 2014 / Published: 26 May 2014

Abstract: Several fiber-optic sensing elements consisting of a U-shaped fiber coated by a detection membrane of polydimethylsiloxane have been prepared with arc radii from 0.3 to 2 mm. Angular distributions of the output optical power from the elements have been measured. A high decrease of the transmitted power of paraxial rays has been observed for elements with arc radii below 1 mm. When elements with arc radii above 1 mm were excited by an inclined collimated beam and brought into contact with toluene solutions a maximum sensitivity of 1 dB/mM was determined. Sensing elements have been tested for monitoring the decomposition of toluene dissolved in water by means of photocatalytic TiO₂ nanoparticles applied on silica optical fibers. Differences between concentration data obtained by UV spectrophotometry and those obtained by the element on levels of 10-15% have been observed. Copyright © 2014 IFSA Publishing, S. L.

Keywords: Toluene detection, Photocatalytic decomposition, U-Shaped fiber, Polysiloxane membrane, Inclined collimated beam.

1. Introduction

In last fifty years optical fibers have been applied in telecommunications, environmental protection, medicine, industry, etc. They are broadly used in telecommunication lines as transmission medium, light sources, amplifiers, couplers, etc. where they create performance for achieving high transmission speeds and bandwidths [1]. They have been tested for transmitting high powers of lasers for medicine, lighting, and heating [2-4]. Optical fibers have also been employed in different types of optical sensors for point, remote and distributed sensing especially for chemical sensors [5-9].

However, the ability of optical fibers to controllable transmit light to a particular place have been employed at chemical microreactors for photoreactions [10-12]. Such microreactors allow us to realize photoreactions with micromolar amounts of reactants under controlled illumination. For such a purpose capillary or photonic crystal fibers have been employed in which the air holes can be used as microreactors and the fiber core enables us to transmit light to reactants in the hole. Moreover, light absorbed or emitted by reactant molecules can be employed to detect temporal concentration changes in the holes which enable us to study reaction kinetics.

Optical fibers have also been investigated for realization of photocatalytic reactors [13-15]. In such reactors photocatalyst is applied onto an optical fiber (plastic or silica one) that guides light necessary for exciting the photocatalyst. This arrangement enables the direct transmission of the excitation light to the photocatalyst through low-loss optical fibers and avoids light losses in the reactor medium or on photocatalyst pellets. Moreover, optical fibers coated with photocatalyst can be used in hardly accessible areas with difficult access of light necessary for photocatalyst exciting.

In hardly accessible areas fiber-optic sensors can be used for monitoring the extent of photocatalytic reaction and making possible to employ optical fiber both for photocatalytic reactions and for their control. Such an approach has been used in our previous research on the photocatalytic decomposition of methylene blue in aqueous solutions. In that research photocatalytic TiO₂ nanoparticles were applied onto silica optical fibers and concentrational changes of methylene blue in the solution were detected by a U-shaped silica fiber [16].

In this paper we present results of extending our research to the employment of U-shaped sensing probes for measuring kinetics of photocatalytic decomposition of toluene in aqueous solutions catalyzed by anatase nanoparticles applied on silica optical fibers. Such a research was motivated by looking for advanced methods for detecting and removing environmental pollutants. It is known that toluene has an extensive industrial use and can contaminate water either as a film on water or dissolved in it. A maximum solubility of toluene in water is of about 550 mg/l, however only 0.7 mg/l of toluene is allowed in drinking water. If toluene is released into water, its removal can be rapid or take several weeks, depending on temperature, mixing conditions, and acclimation of microorganisms. Toluene evaporates rapidly from water with an experimentally determined half-life of 2.9 to 5.7 hr for evaporation from 1 m of water with moderate mixing conditions. If toluene is released to the atmosphere, it will degrade by reaction with photochemically produced hydroxyl radicals (half-life 3 hr to slightly over 1 day) or be washed out in rain. It is not subject to direct photolysis.

Recently, photocatalytic decomposition of toluene dissolved in water has been investigated [17-19]. Different photocatalysts, namely TiO₂, ZnO, SnO₂, WO₃, have been tested. The photocatalysts were dispersed in water as suspension [17, 19], or applied onto stainless steel screens as a porous layer [18]. In some experiments surfactant was added into suspension. Gaseous oxygen was bubbled so that increases the reaction speed [17]. Although photocatalysts applied onto optical fibers have been tested for decomposing benzene in gaseous phase [20] no information has been found on using similar reactor for toluene.

In order to study kinetics of photocatalytic toluene decomposition toluene concentrations in

water have been determined in many cases by using high pressure liquid chromatography [17]. However, there is a number of papers dealing with fiber-optic sensors of toluene in water. They include very sensitive bacterial biosensors [21], enzymatic biosensors [22], fluorescence-based sensors [23], sensors employing carbon nanotubes [24]. However, such sensors are a rather difficult to fabricate.

In addition to advanced fiber-optic sensors shown above evanescent-wave fiber-optic sensors provided with polymeric membranes with a high toluene partition coefficient have successfully been developed for toluene sensing. Such sensors have employed spectra of toluene in UV [25], near-IR [26-28] and mid-IR regions [29]. Mid-IR fiber-optic sensors offer detection limits on a level of µg/l while near-IR ones only on a level of 0.1 mg/l. Silica optical fibers and instrumentation for near-IR region are easily available and cheaper than halide fibers and instrumentation for mid-IR region. Thus, some techniques have been developed for improving the detection sensitivity of silica fibers. Coiling or bending silica optical fibers [27] or their excitation by an inclined collimated beam [28] belongs to such techniques.

This paper presents results on detection of toluene dissolved in water by using the special case of coiled silica fibres, namely by U-shaped fibers which are excited by an inclined collimated beam. Several U-shaped sensing elements are introduced which differ in the form of the bent part. The detection sensitivity of these U-shaped elements is based on toluene-induced refractive-index changes of a sensing membrane of polysiloxane polymer applied on these elements. Results of monitoring kinetics of photocatalytic decomposition of toluene in water on silica optical fibers coated with TiO₂-anatase with the developed U-shaped elements are also presented in the paper.

2. Experimental

2.1. Preparation of Fiber-optic Sensing Elements

U-shaped sensing elements were prepared from segments of polymer clad silica (PCS) fibers with a core diameter of 200 and 300 µm and length of about 50 cm. In each preparation an original optical cladding of polydimethylsiloxane polymer (PDMS) polymer, a refractive index of about 1.41) was removed by means of a solution containing hydrofluoric acid from central part of the segment in a length of about 5 cm. The bare silica core was shortly dipped into a mixture of hydrofluoric and nitric acids (1:1) and rinsed with water. Then the center of this silica part was carefully heated in a flame of a hydrogen oxygen burner and manually bent to a designed form.

In order to fix dimensions of the bent part, both fiber arms coated with the PDMS cladding polymer

were fixed in a glass capillary and glued with a thermally curable silicone elastomer. The bent part was dipped into a solution of HF and HNO₃ (1:1), rinsed in water and dried in a stream of air.

Fiber-optic sensing elements were prepared by coating the bent part of the U-shaped segment with a sensing membrane of elastomer Sylgard 184 (PDMS polymer, ELCHEMco, CR). A mixture of the elastomer in toluene with a concentration of 10 vol.% was applied onto the segment by using the dip-coating method and a withdrawing speed of 1 cm/min. An overall length of these sensing membranes was of about 3 cm. Their thicknesses were approximately 100 nm.

2.2. Characterization of Sensing Elements

Forms of prepared sensing elements were characterized by a digital photo apparatus. In these characterizations light from a white, red or green LED was launched into one arm of the sensing element and the photo was taken.

Transmission properties and the sensitivity of the prepared elements to dissolved toluene were determined on a set-up in which the segment was excited by an inclined collimated beam (see Fig. 1). This set-up enabled the optical power to be determined with accuracy better than 0.01 dB in a dynamic range of 110 dB. The set-up used a laser diode emitting an inclined collimated beam at 670 nm and a silicon photodetector. The laser diode was turned around the input element face. By using this set-up and changing the angle of inclination α , angular distributions of the output optical power from the element were measured. Such distributions were measured for the element sensing part placed in air or immersed in a toluene solution in a cell.

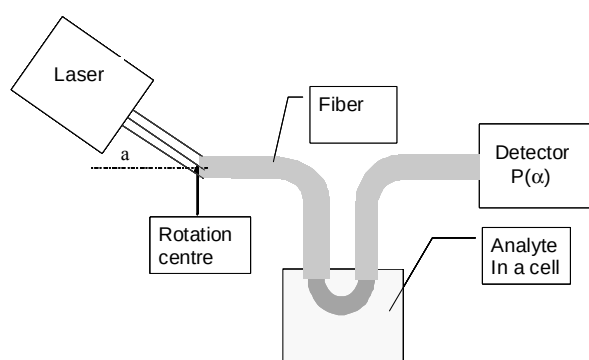


Fig. 1. A scheme of the experimental set-up for characterization of prepared fibers.

By fixing the inclination angle and changing toluene concentrations in the cell, time-response curves of prepared elements were determined. Two types of time-response curves were measured. The first type was determined in experiments in which the element sensing part was continuously placed in

toluene solutions with different concentrations. In these experiments the toluene concentration in the cell with a volume of an immersing solution of 50 ml was changed by removing 2 ml of a solution from the cell and adding 2 ml of the saturated toluene solution in water. The second type of the time-response curves was measured in experiments when the sensing part was after each contact of the sensing part with a toluene solution withdrawn from it and exposed to air (further referred as “discontinuous” approach).

Calibration curves of prepared sensing elements were obtained by plotting steady-state responses of the elements to toluene obtained from measured time-response curves versus the corresponding toluene concentrations.

Toluene solutions used for measuring time-response curves of prepared elements were mixed of a saturated toluene solution and distilled water. The saturated solution was obtained by bringing toluene (Sigma-Aldrich, CR) into contact with distilled water. Of about 1 wgt.% NaCl was dissolved in water in order to increase the detection sensitivity [30].

2.3. Fabrication of Fibers Coated with Photocatalyst

Photocatalytically-active layers were applied onto silica segments with a diameter of about 1 mm and length of about 100 mm. The layers were applied by the dip-coating technique using a dispersion of TiO₂-anatase nanoparticles (Aeroxide®TiO₂ P25, Aldrich, CR) with a concentration of nanoparticles of about 5 %. The applied layers were dried at 420 °C for 30 min. A length of the applied layer was of about 70 mm. Its thickness can be estimated to be of about 200 nm.

The input and output faces of the coated fibers were grinded and polished. A fiber bundle of either coated fibers was used in photocatalytic experiments.

2.4. Photocatalytic Experiments

In these experiments toluene dissolved in water was decomposed on the TiO₂ layer applied on the fiber bundle under effects of UV radiation launched into the fiber bundle from a Xe flash lamp (Oriel, irradiation intensity 30 W/m²). A scheme of the experimental set-up used is shown in Fig. 2. No filter was used with the lamp. Radiation from the lamp was focused to the output face of the bundle by using a focusing unit with silica lenses.

In each experiment the bundle was irradiated by the flash lamp for 24 hours in order to decompose organic compounds on the photocatalytic layer. The, a toluene solution in water (a concentration of 1.2 mmol/l) was poured in the reactor, the bundle fixed in a plastic stop was immersed in the solution and the lamp was switched on. Samples of the solution were taken from the reactor. Toluene

concentrations were determined from bulk absorption spectra of toluene around 180 nm by using a Perkin-Elmer spectrometer and a silica cuvette with an optical path of 1 cm.

In the same sample toluene was detected by using a U-shaped sensing element. The element was exposed to air after each measurement so that the discontinuous calibration curve was used for determining toluene concentrations.

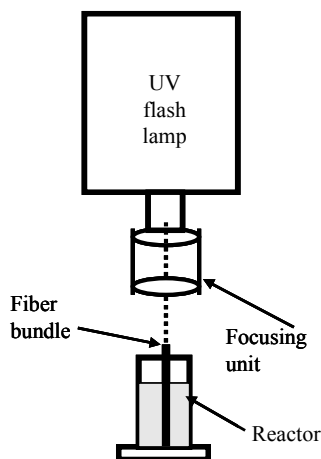


Fig. 2. A scheme of the set-up used in photocatalytic experiments.

3. Results and Discussion

It is known that bending of sensing optical fibers increases the fraction of power transmitted in the optical cladding and therefore increases the sensitivity of the fibers to changes of the refractive-index and absorption coefficient of the cladding [16, 29]. For axially excited bare U-shaped silica sensing elements with an arc radius of 1mm immersed in water the sensitivity to refractive-index changes (RIU) of about 24 dB/RIU can be estimated [16]. From this sensitivity a limit of detection of about 5×10^{-4} RIU can be estimated. However, this value is higher than a refractive-index change of water due to its saturation with toluene that can be estimated on a level of 4×10^{-5} .

A detection membrane of PDMS polymer applied onto the bent part of an U-shaped element enables us to increase the refraction index of the cladding approximately to 1.41 that increases the detection sensitivity by about seven times [16]. Moreover, the membrane increases the toluene concentration in the cladding due to a high partition coefficient of this polymer for toluene that enhances the detection sensitivity as well. This coefficient can be increased by adding NaCl into detected solutions [30]. A further increase of the detection sensitivity can be achieved by using the excitation of the element with an inclined collimated beam that support the propagation of higher optical modes with an increased ratio of power transmitted in the sensing part [28].

Examples of forms of the prepared sensing elements are shown in Figs. 3. Elements with single arcs (Figs. 3a and 3b), arcs in two dimensions (Fig. 3c), or with a very small arc radius below 1 mm (Fig. 3d) can be fabricated by careful heating and manual formatting silica fibers. Final forms of such segments depend on the diameter of the fiber and on personal experience with glass treatment applied at the element fabrication. In cases of elements with very small radii (e.g. 0.1 mm) a small glass drop can be formed at the bent part (see Fig. 3d). Such elements are similar to that prepared by splicing two silica fibers together. The sensing segment in Fig. 3b was used in photocatalytic experiments.



Fig. 3 (a). A photo of a sensing element with an arc diameter of 2 mm (a fiber diameter of 0.2 mm).



Fig. 3 (b). A photo of a sensing element with an arc diameter of 2 mm (a fiber diameter of 0.35 mm).

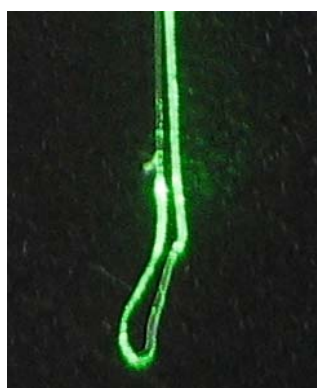


Fig. 3 (c). A photo of a sensing element with an arc diameter of 1 mm (a fiber diameter of 0.35 mm).



Fig. 3(d). A photo of a sensing element with an arc diameter of 0.3 mm (a fiber diameter of 0.35 mm).

Measured angular distributions for the sensing elements depicted in Figs. 3 are shown in Figs. 4. It is evident that these distributions depend on the form of the sensing element. For regular arcs with radii above 1 mm regular distributions can be measured (see Figs. 4a and 4b).

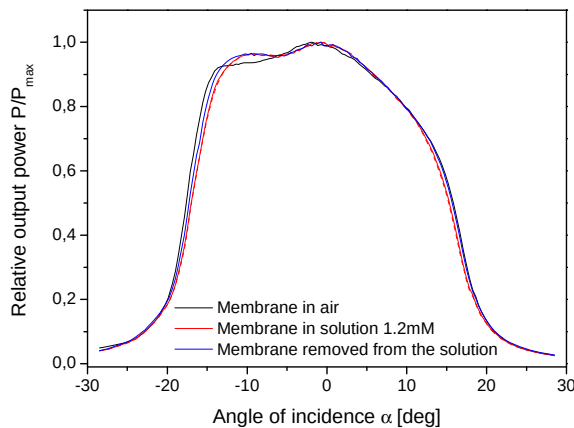


Fig. 4 (a). Angular distributions measured with the sensing element depicted on Fig. 3 (a).

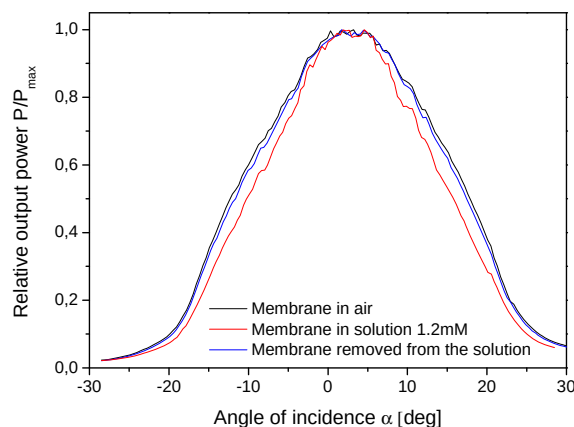


Fig. 4 (b). Angular distributions measured with the sensing element shown on Fig. 3 (b).

These distributions are similar to those determined with straight PCS fibers coated with

xerogel detection layers [28]. From Figs. 4a and 4b one can see that the immersing of the sensing part in a toluene solution caused a decrease of the output power. This decrease can be explained by an increase of the refractive index in the vicinity of the sensing membrane and by the penetration of toluene in the sensing membrane. Both these effects cause a decrease of the reflection coefficient on the core/membrane boundary. The curves in these figures show also the recovery of the initial state of the membrane when the elements were withdrawn from the immersing solution.

For sensing elements with two arcs (see Fig. 3c) or bending radius below 1 mm (see Fig. 3d) immersed in a toluene solution remarkable changes of angular distributions were observed especially for angles of incidence approximately below 15 degs (see Figs. 4c and 4d).

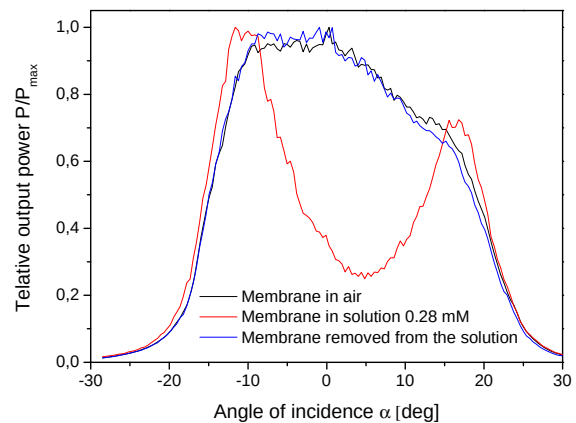


Fig. 4 (c). Angular distributions measured with the sensing element on Fig. 3 (c).

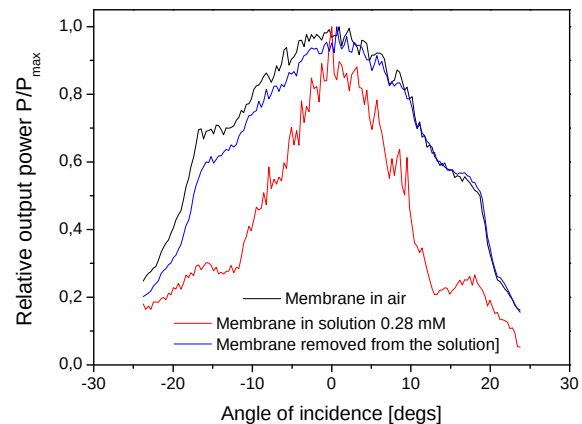


Fig. 4 (d). Angular distributions measured with the sensing element shown on Fig. 3 (d).

These changes can be explained by refraction of paraxial rays on the core/membrane boundary. Such rays can have angles of reflections on the arc on a level of 30 degs. Therefore, they are refracted on the core/membrane boundary and optical power is lost

into the immersing solution. On the other hand rays corresponding to higher optical modes have higher values of the reflection angles than those of paraxial rays. Therefore, their reflection coefficients do not decrease such drastically as those of paraxial rays. The asymmetry of the measured angular distributions especially that in Fig. 4d can be related to irregularities of the sensing elements. Modulations of the curve in Fig. 4c are related to low optical powers and experimental errors. Thus, U-shaped elements with an arc radius above 1 mm have been tested for developing detection elements.

Two types of time-response curves have been measured with prepared sensing elements. The first one, the “continuous” type, can be characterized by continuous contact of a tested element with solution. An example of the time-response curve measured for the element Fig. 3 (b) is shown in Fig. 5 (a). In this figure values of the output power are related to that measured at $\tau=0$ min. In these measurements the sensing part of the element was at first immersed in water. A very rapid drop of the output power followed by its slow decrease was observed after immersing the element in water. The rapid drop can be related to a decrease of the reflection coefficient of the sensing membrane due to replacing air with water. The slow decrease can be explained by penetration of water in the membrane and changing distances of polymeric chains (swelling effects). Each change of the toluene concentration was accompanied by a very rapid decrease of the output power followed by its slow decrease. These effects can be related to an increase of the refractive index of the membrane by toluene and to relaxation effects in the membrane. As the recovery of the initial membrane state was very slow and it was accompanied by strong hysteresis (see the curve at Fig. 5A and times longer than 30 min).

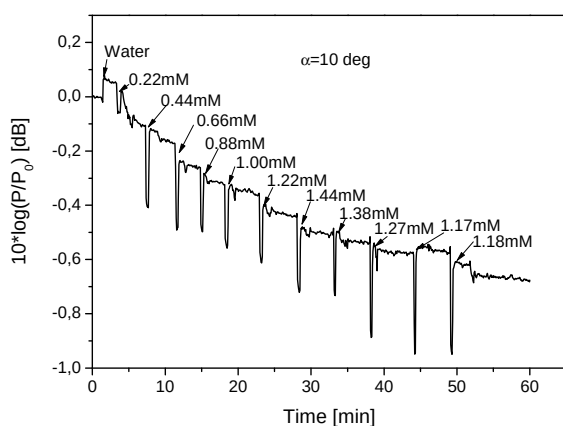


Fig. 5 (a). Time-response curve of the sensing element in Fig. 3 (b) measured at the “continuous” approach.

In measurements of time-response curves of the second “discontinuous” type a sensing element was immersed in a tested solution, then withdrawn and

exposed to ambient air atmosphere. An example of this time-response curve measured for the element is shown in Fig. 5 (b). Measured values of the output power were also related to that at $\tau=0$ min. When the element was immersed in a tested solution a rapid decrease of the output power followed by its slow change was observed. These effects can be explained by decreasing of the reflection coefficient of the sensing membrane and by penetration of toluene into the membrane. The withdrawing of the element from the solution is accompanied by a rapid increase of the output power followed by its slow change. It is evident that the initial state of the membrane is not recovered. However, relaxation changes of the membrane are lower than those observed at the continuous contact of the membrane with solutions which can be seen from comparison Fig. 5 (a) and Fig. 5 (b).

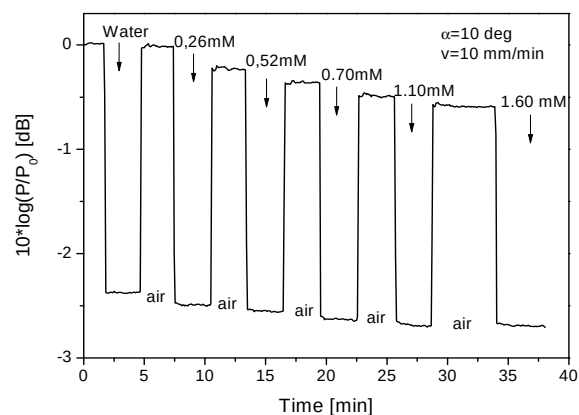


Fig. 5 (b). Time-response curve of the sensing element in Fig. 3 (b) measured at the “discontinuous” approach.

By taking steady-state values of the output power, dividing them by that measured for water and plotting against corresponding concentrations, calibration curves shown in Fig. 6 were obtained for the element depicted in Fig. 3 (b).

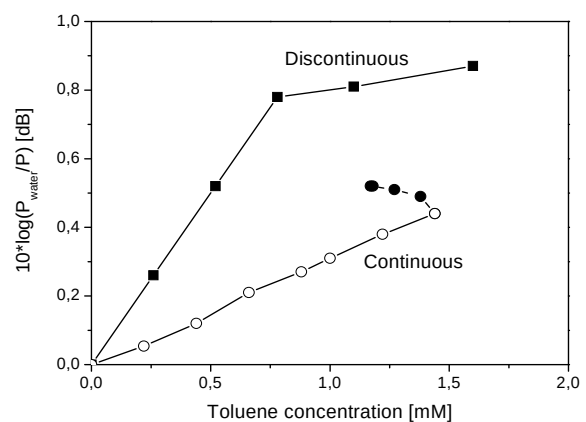


Fig. 6. Comparison of calibration curves for the sensing element operating at the “continuous” and “discontinuous” regime.

The calibration curve obtained in the “continuous” approach is linear in the tested concentration range. In the “continuous” approach the response of the sensing membrane is given both by penetration of toluene in it and relaxation effect of the membrane. The relaxation effects are slow and cause the irreversibility of the detection. A sensitivity of about 0.4 dB/mM can be estimated from the calibration curve.

Relaxation effects can be in large extent suppressed by using the “discontinuous” approach. From Fig. 6 one can see that the calibration curve measured by using this approach consists of two parts. The first linear part up to a concentration of about 1 mmol/l corresponds to a sensitivity value of about 1 dB/mM. The second part of the calibration curve that approximates the tendency of the membrane to be saturated with toluene corresponds to a sensitivity value of 0.12 dB/mM. In the “discontinuous” approach the response of the sensing membrane to toluene is induced mainly by penetration of toluene in it. Although relaxation effects of polymer detection membranes on plastic fibers have already been employed for toluene detection [31], slow relaxation changes have been observed at polysiloxane membranes discussed in this paper.

An example of results of measuring the kinetics of photocatalytic decomposition of toluene is shown in Fig. 7. In this figure experimental data on the solid line were obtained on the basis of the measurements of toluene concentrations by the UV spectrometric technique at 260 nm. Experimental points on the dashed line were obtained by means of the sensing element shown in Fig. 3(b) and the “discontinuous” approach. Differences between both these methods can be related mainly to a lower sensitivity of the sensing membrane at high toluene concentrations (reaction times up to 40 min). This disadvantage can be suppressed by using a detection membrane with a higher detection capacity.

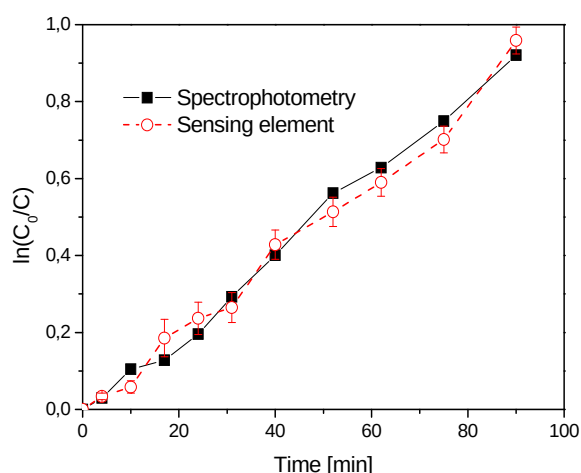


Fig. 7. Reaction kinetics of the photocatalytic toluene decomposition measured spectrophotometrically and by means of the sensing U-shaped element.

The extent of the photocatalytic decomposition of toluene after 90 min was of about 60 %. The employment of the “discontinuous” detection approach for monitoring reaction kinetics in a photocatalytic reactor assumes to take samples from the reactor. A special sampling bypass can be used for such a purpose.

The sensing element shown in Fig. 3(a) was used in several experiments in which it was brought into contact with toluene solutions. It was dried at air for one day after each experiment. Any drastic changes of its sensitivity have not been observed.

4. Conclusions

Several fiber-optic sensing elements consisting of a U-shaped fiber coated by a detection membrane of polydimethylsiloxane have been prepared. Angular distributions of the output optical power from elements with arc radii below 1 mm have shown a high decrease of the power for paraxial rays. One sensing element was tested for measuring the decomposition of toluene dissolved in water by means of photocatalytic nanoparticles applied on silica optical fibers. Differences between concentration data obtained by UV spectrophotometry and those obtained by the element were on levels of 10 to 15 %.

Future experiments will be focused on the development sensing membranes of toluene with suppressed relaxation effects.

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Acknowledgements

This research has been supported by the Czech Science Foundation (contract P102/12/2361).

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