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Journal of Photochemistry and Photobiology A: Chemistry 123 (1999) 7–13

Journal of Photochemistry and Photobiology A:Chemistry

Flow actinometry in a thin film reactor: modeling and measurements

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Received 17 November 1998; accepted 24 February 1999

Abstract

Flow actinometry was planned, modeled and carried out in a thin film (0.04 cm) reactor to study the photomineralization of halogenated organic compounds over a thin TiO_2 layer in a flowing thin film. On the basis of modeling, the parameters were optimized (0.15 M of potassium trioxalatoferrate(III) actinometric solution, an elution time of 3τ where τ is the residence time of the reactor and tubes), and from the emittance spectra the expected light flux was predicted. The possible errors and their elimination are described. Finally the measured light flux of the Xe lamp between 300 and 400 nm was 11.45×10^{16} qu s^{-1}, the expected computed value was 11.5×10^{16} qu s^{-1}; the estimated error of accuracy was less than 1%, i.e. the deviation was 1.1%. The light flux between 300 and 380 nm can be computed by a correction factor 0.562. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Potassium trioxalatoferrate(III) actinometry; Thin film reactor; TiO_2; Photomineralization

1. Introduction

To the best of our knowledge, papers on actinometry in a flowing thin film reactor have never been published. Even in the reviewed literature [1–5] we could not find any paper on the subject. Instead of measuring the light flux with a flowing actinometry solution, usually the output of the lamp was determined with an actinometer cuvette, filled with actinometer solution. This batch actinometry gives a good approximation, but to obtain strictly quantitative results the geometry and the absorbance characteristics of the thin film reactor and the actinometer cuvette have to be the same. This certainly can be achieved but also not without possible errors. Since we wished to study by an ultramicro-electrode the local kinetics of TiO_2-assisted photomineralization of halogenated compounds, we considered it necessary to determine in situ the actual local light flux and light flux density in the flowing thin film system.

Our objective is to determine that part, and only that part, of the near UV–Vis irradiation which is utilized by the titanium-dioxide assisted photomineralization (i.e. between 300 and 380 nm [6]).

2. Experimental

2.1. Chemicals and methods

All solutions were made using Milli-Q water. Iron(III)chloride, potassium oxalate, 1,10-phenanthroline hydrate, sulfuric acid, sodium acetate were purchased from BDH (UK). The actinometry was carried out with solutions of potassium trioxalatoferrate(III), (also called potassium ferrioxalate, denoted by K_3FeOx_3) according to Hatchard and Parker [7], with the necessary additional calculations (see. Section 2.3).

2.2. Instrumentation

The experimental set-up is shown in Fig. 1. The reaction zone of the thin film reactor has a rectangular cross-section with dimensions of $4.3\times1.5\times0.04$ cm^3=0.26 cm^3. The solution of reactant flows along the longest axis, and the light flux of irradiation hits the cell rectangularly on one of its largest sides (4.3×1.5 cm^2). Thus the light is absorbed by a thin film of optical path 0.04 cm. The flow is conducted into the cell through a Teflon tube of inner diameter 0.08 cm and length 210 cm, so the volume of the inlet tube is 1.04 cm^3. The volume of the outlet tube is also 1.04 cm^3. So the residence time τ of the flowing solution [$\tau=(V_{tube}+V_{cell})/(Q/t)$] for the reactor plus either tube is the same. The τ for the first tube plus the reactor is significant when the

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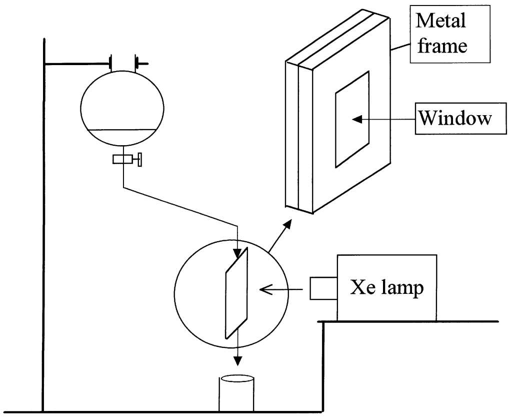

Fig. 1. The experimental set-up: the thin film reactor is zoomed.

K_3FeOx_3 starts to flow in (concentration build-up), while the τ for the second tube with the reactor is important when the Fe(II) photoproduct is eluted. When Q/t is between 100–600 $cm^3\,h^{-1}$, τ is between 8–47 s.

The solution is poured into a funnel and allowed to flow by adjusting the tap of the funnel. The irradiated solution is collected in a 25 cm^3 beaker. The flow is driven by gravity, and controlled by the height of the funnel above the outlet of the second tube.

The irradiations were carried out using an Illuminator 6000 Xenon lamp (Eurosep Instruments, France). For UV–Vis spectrophotometry a Perkin-Elmer 552 instrument was used. All experiments were carried out in a darkroom.

2.3. *Computations*

2.3.1. *Wavelength range selection*

The effective and optimum wavelength range for TiO_2-assisted photomineralization is over 300–380 nm [6]. The TiO_2 can absorb UV radiation shorter than 300 nm but such high energy photons can cause direct photodegradation of the halogenated organics, and direct photolysis is not the objective of our studies.

The short-wavelength UV radiation can be filtered out by Pyrex glass. The transmittance of the glass microscope-plates used in the film reactor is 23% at 300 nm, 6% at 290 nm, and only 1% at 280 nm. As far as visible radiation is concerned, knowing the UV–Vis spectra of the actinometric solution (molar absorbance of which decreases steeply in the visible [8]) and the optical path (0.04 cm), with a properly chosen concentration we can achieve a cut-off between 380–420 nm. We found that one of the traditional actinometric solutions of Hatchard and Parker [7] with the concentration of 0.15 M meets the requirements well: the absorption is above 99% at 380 nm, 50% at 410 nm and only 20% at 420 nm (Fig. 2). These conditions were considered optimum because we measure some light flux above 380 nm as well, but we can measure all photons between 300 and 380 nm, and that number can be calculated from the measured results. At lower concentration of K_3FeOx_3 the cut-off interval becomes too wide: it would be between 330 and 420 nm at 0.02 M of K_3FeOx_3.

2.3.2. *Calculation of the required minimum flow rate* $\{Q/t(l,\Phi)\}$

To maintain full light absorption up to 380 nm the Fe(III)→Fe(II) conversion should not be too high (i.e. $A=\epsilon cd$ should not fall below 2.0 so at least 99% of the entering light will always be absorbed). This requirement determines the minimum flow rate, which depends on the light flux density and on the concentration of K_3FeOx_3.

The conversion (ξ) within the irradiated area cannot be higher than 10%, thus a minimum 99% of the entering light (over 310–380 nm) is absorbed. Note that this is the

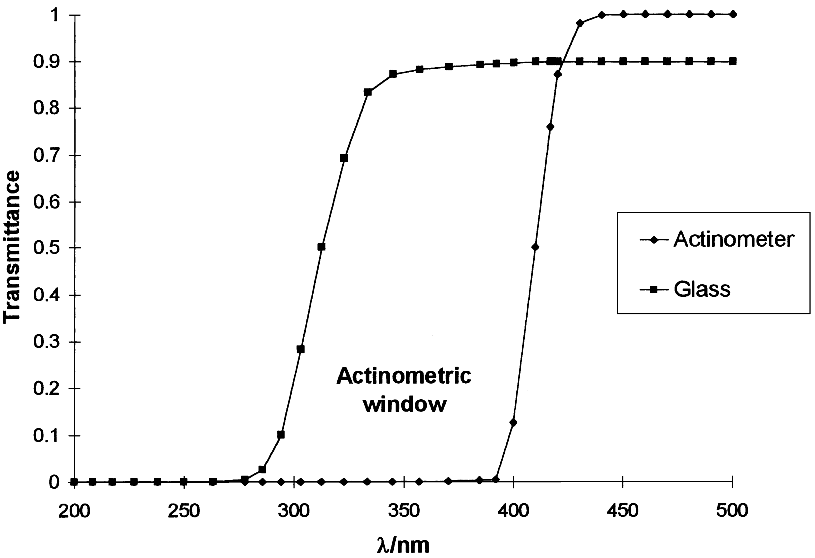

Fig. 2. Selection of the actinometric window by glass cut-off filter below 300 nm, and by the (relative) transparency of the actinometric solution above 400 nm.

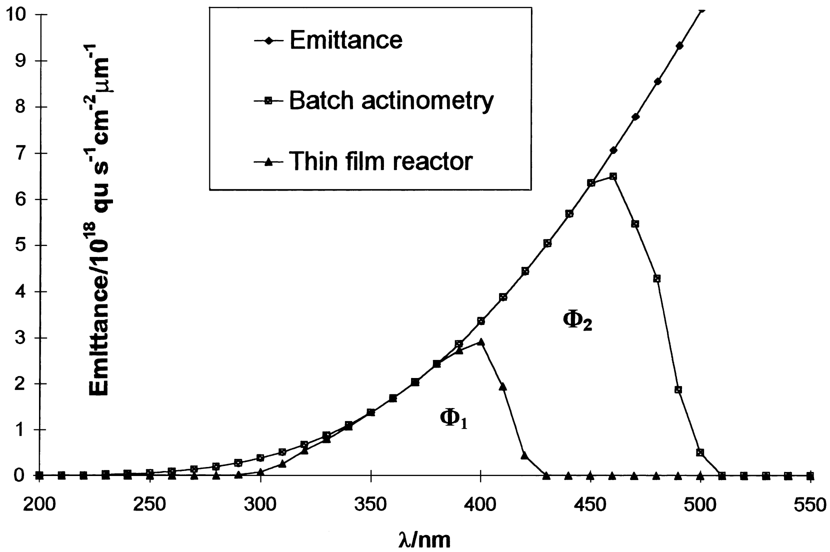

Fig. 3. Derivation of measured light fluxes from the spectral emittance of the Xe lamp. Φ_1: measured light flux in the thin film reactor; Φ_1: light flux measured by batch actinometry. Note that emittance is expressed in photon s^{-1} cm^{-2} µm^{-1}.

maximum permissible *local* conversion (ξ_l), along the longest route where the solution is exposed to light. Since the light spot is circular, there are areas where the local conversion is lower than the maximum; if the light spot does not cover the whole width of the film, then the minimum local conversion will be zero at the edge of the cell. Accordingly the average conversion will be certainly less than 10%.

The maximum local conversion and the light flux density determines the required minimum flow rate (the details are given in the Appendix A):

$$\frac{Q}{t}(\mathrm{cm^3\,h^{-1}}) = \frac{1}{\xi_l}\times\frac{1.25\phi_{\mathrm{LFD}}lw}{N_{\mathrm{A}}c} = 9.51\times10^{-17}\frac{\Phi(\mathrm{qu\,s^{-1}})}{l(\mathrm{dm})}, \qquad (1)$$

where Q/t is the flow rate, ϕ_{LFD} the light flux density (photon cm^{-2} s^{-1}), w the width of the cell, l the maximum route of irradiation exposure, ξ_l the local conversion, N_A Avogadro's number, c the concentration of actinometric solution, and 1.25 is the quantum yield of the K_3FeOx_3 solution over the 300–400 nm interval [7].

The minimum flow rate is 80–160 cm^3 h^{-1} at the light flux used (10×10^{16}–11×10^{16} qu s^{-1}) and light beam diameter (0.67–1.20 cm). We decided to use a flow rate of 200 cm^3 h^{-1} which was suitable for all cases.

2.3.3. Comparison of the batch and thin film actinometry results

Applying K_3FeOx_3 actinometry to a thin film reactor is new territory, so it was advisable to carry out modeling computations to learn what might be expected and whether our experimental results conform to reality.

The output of the Illuminator 6000 xenon lamp was measured by traditional batch actinometry several times [9,10], and was found to be $(38.90\pm0.22)\times10^{16}$ qu s^{-1} between 200 and 480 nm. The question is: how many photons will be absorbed in the film reactor, approximately over the 300–400 nm interval?

To obtain the answer, first of all the spectral emittance (W cm^{-2} µm^{-1}) of the Illuminator 6000 xenon lamp[1] has to be transformed into spectral emittance expressed in photons (quanta cm^{-2} µm^{-1}), then it should be multiplied by the light absorption function $A(\lambda)$ of the actinometer system:

$$F(\lambda) = \frac{\mathrm{d}\Phi}{\mathrm{d}A\mathrm{d}\lambda}A(\lambda). \qquad (2)$$

To compute the absorbed light flux, the definite integral of $F(\lambda)$ is required over the given wavelength interval and emitting area:

$$\Phi = \int_0^A \left\{ \int_{\lambda_1}^{\lambda_2} \frac{\mathrm{d}\Phi}{\mathrm{d}A\mathrm{d}\lambda}A(\lambda)\mathrm{d}\lambda \right\}\mathrm{d}A. \qquad (3)$$

The results are shown in Fig. 3. The absorbed light fluxes are given by the areas under the emittance curves: Φ_1 corresponds to the measured light flux in the thin film reactor, Φ_2 demonstrates the light flux measured by batch experiment in a quartz cuvette of 1 cm optical path. The integral computation was carried out numerically. When the computed spectral emittance of the Oriel lamp matched the data [1], the Φ_1/Φ_2 ratio was 29.5%, so the absorbed light flux in the thin film reactor can be expected to be ca. 11.5×10^{16} qu s^{-1} between 300 and 400 nm.

To obtain the light flux between 300 and 380 nm the definite integral should be computed over the 300–380 nm interval, the result is $\Phi_0=6.45\times10^{16}$ qu s^{-1}. Φ_0 will not be measured with our experimental set-up but can be calculated

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[1] Manual of Illuminator 6000 Xe lamp (Eurosep 1995, France).

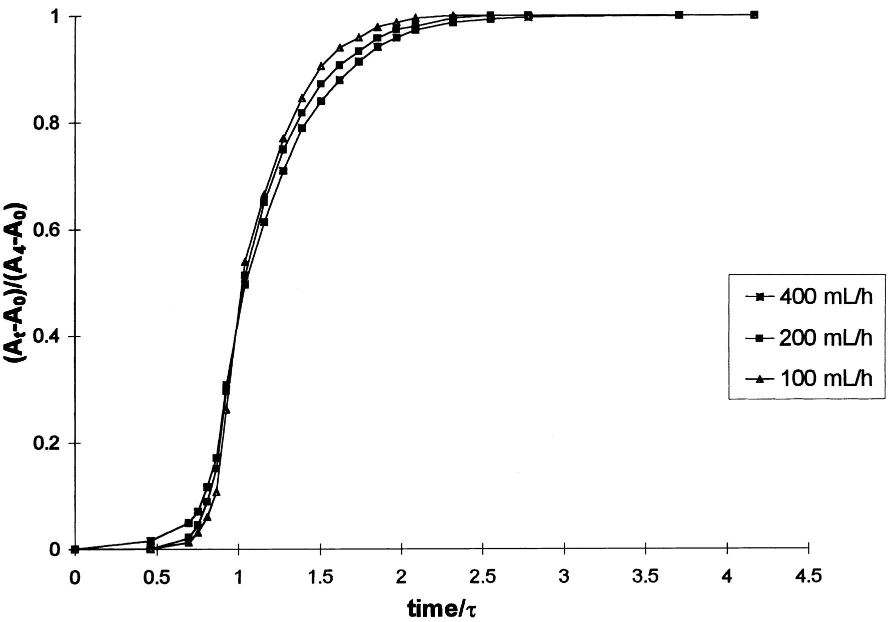

Fig. 4. Transport characteristics of the thin film reactor system.

from the measured Φ_1 by a correction factor 0.562 (i.e. $\Phi_{0,\text{computed}}/\Phi_{1,\text{computed}})^2$.

3. Results and discussion

3.1. Concentration build-up of K_3FeOx_3 and elution of photoproduct

In order to decrease the effect of background light, the actinometric solution is not stored in the experimental set-up but poured into the funnel at the beginning of the experiment. Until that time the reactor and the tubes contain distilled water, so it takes time for the concentration of K_3FeOx_3 to increase to 0.15 M in them.

The corollary of the above mentioned is that when the irradiation ends, the collection of actinometric solution must not be stopped, since both the reactor and the outlet tube contains iron(II) photoproduct. The iron(II) should be completely eluted from the system.

The background light should be kept to a minimum but the dim light of a 25 W bulb is necessary to check the instruments, stopwatches and for safety reasons. Hence the effect of the background light has to be determined and taken into account (to be deducted from the measured light flux).

The necessary time between the beginning of fill-up of the system with actinometer solution, and switching on the lamp depends on the flow rate and on the transport properties of the system. If there were no mixing, there would be distilled H_2O in the system until the residence time was over then 0.15 M K_3FeOx_3 solution would appear in the cell. We measured the concentration build-up in the cell vs. time and flow rate (Fig. 4) and found that at least 2τ is necessary to achieve at least 98% light absorption, but we recommend a figure of 3τ which value is not affected by the flow rate.

When the irradiation is finished, the cell and the outlet tube contains Fe(II) photoproduct which has to be eluted. Based on the transport properties of the system, a waiting time of 2τ results in a 3% loss of the Fe(II) formed, but a waiting time of 3τ results in only a 0.5% loss, which is lower than the expected experimental error.

3.2. Background irradiation

There were two sources of background light affecting the actinometer solution: (i) the dim reading lamp, and (ii) the stray light caused by dispersion of the main light beam during irradiation. The measured background light fluxes are collected in Table 1.

Thus the overall quantity of absorbed background light is

$$N_{\text{bgr}} = t_{\text{total}} \times 6.13 \times 10^{14}\,\text{qu}\,\text{s}^{-1} + t_{\text{irr}} \times 1.324 \times 10^{15}\,\text{qu}\,\text{s}^{1}. \tag{4}$$

This background is rather low; the estimated light flux density (qu $\text{cm}^{-2}\,\text{s}^{-1}$) or irradiance (W cm^{-2}) on the surface

Table 1
Background light flux in the dark room

Light source	Light flux absorbed by K_3FeOx_3 (qu s^{-1})
Reading lamp	6.13×10^{14}
Xe lamp stray light	1.324×10^{15}

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[2] We are grateful to one of our referees who turned our attention to the necessity of this additional correction.

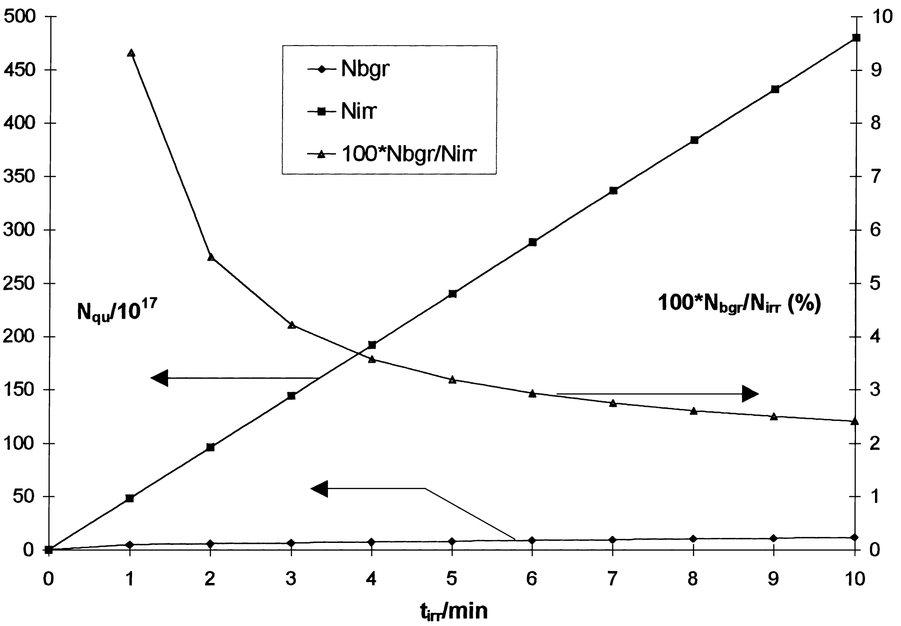

Fig. 5. Dependence of the background light effect on the ratio of irradiation/total time. Total time of experiment was 10 min.

of the actinometric solution is 10^{14} qu cm^{-2} s^{-1} and 60 μW cm^{-2}, respectively. The light flux density in the light beam is about 10^{17} qu cm^{-2} s^{-1}, but the background effect steadily accumulates, especially when the overall exposure to the background is long compared to the actual irradiation. The analysis is shown in Fig. 5.

With proper experimental conditions ($t_{irr}/t_{total} \geq 0.4$–$0.5$), the light absorbed due to the background is less than 4% of the light absorbed from the main beam.

3.3. Actinometry experiments and elimination of error

Six series of measurements were carried out and the results are summarized in Fig. 6. In the first series the K_3FeOx_3 solution collected in a beaker was not stirred before taking samples, resulting in a wide spread in the photoproduct concentration. In the second series this factor was eliminated so the deviation decreased from 17% to 7.6%. At this point the measured light flux (6.7×10^{16} qu s^{-1}) was far from the expected value (11.5×10^{16} qu s^{-1}). The deviation was decreased by taking into account the background, and the accuracy was improved by properly chosen time intervals for concentration build-up and photoproduct elution (t_e). t_b was only 1τ at the series 1 and 2. As t_e was increased to $(1.5$–$2)\tau$, the deviation decreased to 2.3%, and the measured light flux was 90% of the expected value.

The concentration time-profile characteristics were determined to find the optimum t_e, and it seemed to be at 3τ. This assumption was supported by the series 5 and 6: for both series the average light flux was 11.45×10^{16} qu s^{-1}, the deviation was at a minimum at 3τ(1.1%), but at 4τ it increased again (1.5%), presumably because at 4τ the ratio of t_{irr}/t_{total} became too low. The finally measured light flux of $(11.45\pm0.13)\times10^{16}$ qu s^{-1} is equal to the theoretically computed value of 11.5×10^{16} qu s^{-1} within experimental error.

Thus the computing and experimental process described is suitable for the planning and implementation of accurate and precise actinometry in a thin film reactor flowing system.

4. Instructions for use

Summarizing our results here we describe the protocols of thin film reactor actinometry. The required equipment is shown in Fig. 1, but two stopwatches are needed, one to measure the irradiation time, the second to measure the time span of the whole experiment to calculate the effect of background light.

1. Pour 0.15 M K_3FeOx_3 solution (25 cm^3) into a beaker and start stopwatch 1. Put back the flask containing K_3FeOx_3 solution in a dark cupboard.
2. Pour the K_3FeOx_3 solution into the funnel and open the tap 15 s after starting stopwatch 1. At first we proposed 10 s but found that it is very hard to accomplish steps 1 and 2 within 10 s.
3. 4τ minus 10 s after opening the tap (see Table 2) put the sample collector beaker under the end of the outlet tube. Reason: the less unreacted solution we collect the longer can be the irradiation time, since most of the 25 cm^3 volumetric flask will be filled with irradiated solution.
4. 4τ after opening the tap, open the aperture of the Xe lamp and start stopwatch 2.

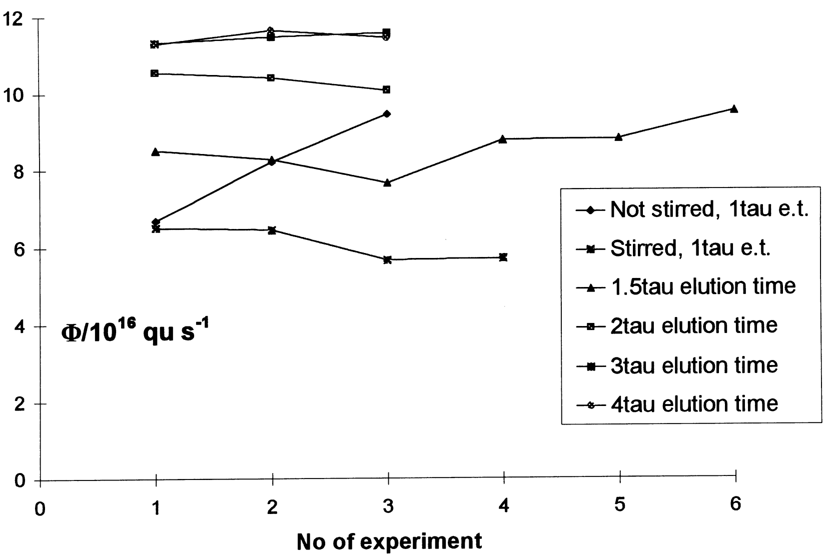

Fig. 6. Improvement of thin film actinometry in its progression of series of experiments. Tau (τ) means residence time.

Table 2
Time spans (s) associated with each step depending on flow rate

Description	100 $cm^3 h^{-1}$	200 $cm^3 h^{-1}$	400 $cm^3 h^{-1}$	Note
Step 1–2	15	15	15	Start
Step 3 ($4\tau-10$ s)	170	80	35	Build-up of K_3FeOX_3
Step 4	10	10	10	
Step 5 irradiation (10τ)	480	240	120	
Step 6 (3τ)	140	70	35	Elution
Step 7	15	15	15	Finish
Total time	970	500	265	
t_{irr}/t_{total}	0.49	0.48	0.45	

Steps 4–6 include the sample collection.

5. Irradiate the system for 10τ, then shut the aperture of the Xe lamp and turn off stopwatch 2.
6. Wait 3τ then close the tap of the funnel.
7. Pour the collected K_3FeOx_3 solution into 25 cm^3 volumetric flask covered with Al-foil for protection from light. Turn off stopwatch 2.
8. Rinse the sample collector beaker once with distilled H_2O, and pour this solution into the volumetric flask as well.
9. Wash the cell and tubes with 2×20 cm^3 distilled H_2O. Now the system is ready for the next actinometric measurement.

Acknowledgements

The financial support of the COST EU grant ERBCIPECT 926097 is gratefully acknowledged.

Appendix A

The objective is to determine that flow rate, Q/t where even the maximum local photoconversion of the K_3FeOx_3 along the diameter of the light beam (l, see Fig. 7) is less than 10%.

In Fig. 7 it is demonstrated that the light flux $\Delta\Phi$ over the area of $\Delta A = l \times \Delta w$ is

$$\Delta\Phi = \phi_{\mathrm{LFD}} \times \Delta A, \tag{5}$$

and the photoreduction rate of K_3FeOx_3 molecules due to the light flux $\Delta\Phi$ is given as

$$\frac{\Delta N}{t} = 1.25 \times \Delta\Phi, \tag{6}$$

where 1.25 is the quantum yield of the 0.15 M actinometric solution over the spectral range 300–400 nm. The required minimum K_3FeOx_3 input of the reactor (expressed in mole-

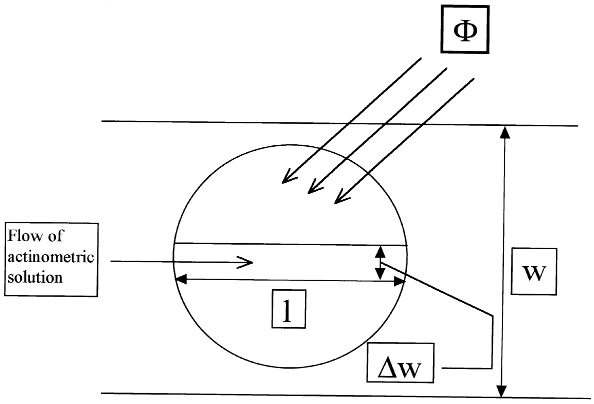

Fig. 7. Position of the light beam on the glass window of the thin film reactor.

cules), considering that the width of the reactor is w and the maximum permitted local conversion is ξ_l,

$$\frac{N}{t}=\frac{1}{\xi_l}\frac{w}{\Delta w}\frac{\Delta N}{t}. \tag{7}$$

Since $n=N/N_A$, and $\Delta N/t$ can be expressed from Eqs. (5) and (6), the required minimum input in mol s^{-1}:

$$\frac{n}{t}=\frac{1}{\xi_l}\frac{w}{\Delta w}\frac{1}{N_A}\times 1.25\frac{4\Phi}{l^2\pi}l\Delta w \tag{8}$$

which can be rearranged to

$$\frac{n}{t}=\frac{1}{\xi_l}\frac{w}{N_A}\frac{5\Phi}{l\pi} \tag{9}$$

and since $c=(n/t)/(Q/t)$, so $Q/t=(n/t)/c$ and thus it can be written:

$$\frac{Q}{t}=\frac{1}{\xi_l}\frac{w}{N_A c}\frac{5\Phi}{l\pi}. \tag{10}$$

Substituting the known values (w=0.15 dm, c=0.15 mol dm^{-3}, 1 dm^3 s^{-1}=3.6×10^6 cm^3 h^{-1}, N_A, π, ξ_l),

$$\frac{Q}{t}(\mathrm{cm^3\,h^{-1}}) = 9.51\times 10^{-17}\frac{\Phi(\mathrm{qu\,s^{-1}})}{l(\mathrm{dm})}, \tag{11}$$

which is the required equation, expressing the required minimum flow rate of the actinometric solution, depending on the absorbed light flux and the diameter of the light beam.

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