ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 150 (2002) 207–212

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Photocatalytic degradation of toluene in the gas phase: comparative study of some TiO_2 supports

A. Bouzaza*, A. Laplanche

Laboratoire CNGE, Ecole Nationale Supérieure de Chimie de Rennes, Avenue du Général Leclerc, 35700 Rennes, France

Received 1 February 2002; accepted 5 February 2002

Abstract

The Langmuir–Hinshelwood (L–H) kinetic model has been used to describe the degradation of the toluene on three TiO_2-based photocatalysts supports. The determination of the L–H rate constant (k) showed that the UV illumination parameter seems to be more important than the quantity of TiO_2 per unit area. The constant k is the greatest for the less density TiO_2 photocatalyst. The comparison between the Langmuir adsorption constant (K) in the dark and under UV irradiation shows that the adsorption constant for the high kinetic catalyst increases while it decreases for the other two. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalysis; Toluene; Titanium dioxide; Langmuir–Hinshelwood; Rate coverage

1. Introduction

Photocatalysis is a subject of great interest in view of its application in effluent decontamination [1–3]. Particularly, it is promising for remediating environmental air pollution by volatile organic compounds (VOCs).

It provides a number of attractive features [4]. First, this process involves the destruction of organic contaminants rather than transfer them from one phase to another, e.g., from gas phase to solid phase in an adsorption process on activated carbon. By employing photocatalysis, one can achieve complete destruction of a wide variety of VOCs to carbon dioxide and water.

Moreover, utilization of this process is energetically interesting because it operates near ambient temperature and the use of solar energy to initiate photocatalytic oxidation reactions is possible [5–8].

In the past, most research on the heterogeneous photocatalytic oxidation of environmental contaminants has focused on the use of TiO_2 photocatalysts for purification of water [9]. However, photocatalytic oxidation in the gas phase has recently attracted more interest. The reason for the increasing interest is that the rates of photocatalytic oxidation of some organic compounds are reported to be orders of higher magnitude in the gas phase than in the liquid phase at similar temperatures and levels of irradiation [10]. Nevertheless, the efficiency of photocatalytic processes in the gas phase needs to be improved. To date, photocatalytic studies have usually employed various TiO_2-based photocatalysts in the form of powder or pellets [9]. Therefore, a major problem associated with using unsupported photocatalysts in a photoreactor is that a large amount of catalyst is needed, but only the thin exterior layer absorbs UV light. Consequently, only a small fraction of the solid is active with respect to its capability to bring about photodegradation reactions. Possible solutions to this problem involve utilization of a thin layer of titania coated on a variety of supports, e.g., glass rings, aluminum sheets, etc., in a novel reactor configurations.

The purpose of this paper is to present the preliminary kinetic studies on the use of three different TiO_2-supported catalysts. The Langmuir–Hinshelwood (L–H) kinetic model will be used to describe toluene degradation. The comparison between the three catalysts will be based on the L–H constants, i.e., k and K the rate and adsorption constants, respectively.

2. Experimental

2.1. Chemical and catalysts

The toluene used is from Prolabo and its purity is about 99%. It is used directly as received.

The catalysts tested are:

- Catalyst A. It is constituted on TiO_2 pellets deposited on glass fibers. The amount of titanium dioxide is about $2.16\ g/m^2$.

---

* Corresponding author. Tel.: +33-22323-8056; fax: +33-22323-8199.
E-mail address: abdelkrim.bouzaza@ensc-rennes.fr (A. Bouzaza).

PII: S1010-6030(02)00088-6

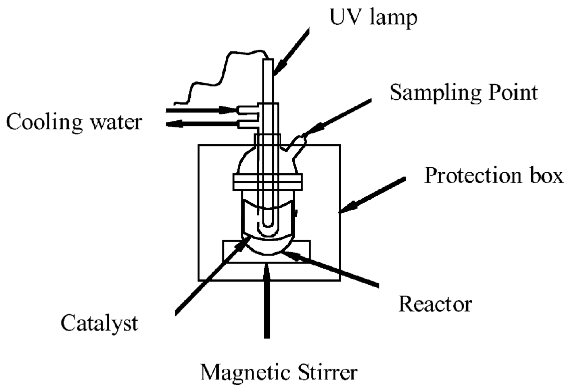

Fig. 1. Experimental photochemical reactor.

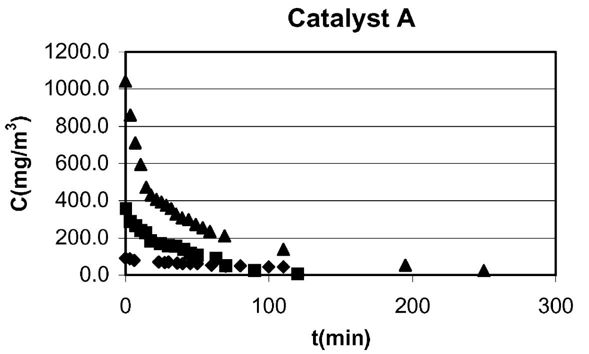

Fig. 2. Concentration of toluene versus irradiation time. The different initial concentrations, C_0 are: 90 (◆), 357 (■), 1043 mg/m^3(▲).

- Catalysts B and C. The first is constituted on 50% TiO_2 and 50% SiO_2 deposited on a mixture support containing polyamide, viscose and cellulose. The amount of titanium dioxide is about 20 g/m^2 of tissue. The second has the same TiO_2–SiO_2 composition deposited on PET and cellulose support.

2.2. Experimental

Experiments were carried out in a Pyrex cell of 1 l capacity. An UV lamp (Heraeus) is placed in the center of the reactor (see Fig. 1), a cooling water flows in the annulus surrounding the lamp in order to maintain a constant temperature during the experiment. The UV light source is low pressure mercury and the wavelength is about 254 nm. A band of catalyst is deposited in the bottom of the reactor. The dimension of the band is $5 \times 29 = 145$ cm^2 witch contains 31.32 mg of TiO_2 for catalyst A and 290 mg of TiO_2 for B and C.

A known quantity of toluene is injected in the reactor. A magnetic stirrer and some glass balls permit the homogenization of the inlet gas phase. When the equilibrium is reached, which allow us to determine the adsorption capacity of the catalyst, the UV lamp is light on. Samples are withdrawn regularly from the reactor for analysis.

The quantitative determination of toluene in the gas phase are performed by gas phase chromatography using fisons chromatograph equipped with an FID detector and chromapack column.

3. Results and discussion

3.1. Photocatalytic oxidation over catalyst A

The bulk concentration of toluene decrease with the irradiation time (Fig. 2). The decay in the toluene concentration appears exponential to the time. For the clarity of the figure, all the experiments are not represented.

Then the rate of pseudo-first-order (k_1) reaction was calculated by a linear plot of $\ln(C_0/C)$ versus t and is summarized as a function of initial concentration C_0 in Table 1. It can be seen that the k_1 decreases with the initial concentration. This is quite common in photocatalytic degradation studies for many organic compounds in dilute solution [11].

The concentration-dependence of the k_1 indicates that the photocatalytic reaction of toluene is not really first-order, even though the plot linearity of $\ln(C_0/C)$ versus t is quite well.

According to the L–H model, the kinetics of the degradation can be represented by the following expression:

$$R_0 = \frac{kKC_0}{1 + KC_0}$$

where R_0 is the reaction rate (mg/m^3 min), k the reaction rate constant (mg/m^3 min) and K the Langmuir adsorption constant (m^3 mg^{-1}).

In fact, the pseudo-first-order reaction can be resulted from the L–H rate equation only when the term KC_0 is much less than 1. Therefore, it is necessary to determine the L–H rate constant k, instead of k_1, when the substrate is used as the model compound for a reliable comparison in activity among different photocatalysts [12,13].

L–H equation is often applied to evaluate the L–H rate constant k and the adsorption constant K, but it is only valid at the initial stage. During the photocatalytic process, the intermediate are formed, and their KC terms must be included in the L–H rate equation even when their adsorption on the TiO_2 surface may be rather weak. For simplicity, however, it is better to employ the initial toluene rate for the application of the equation. This can be done by an assumption that

Table 1
Variation of the pseudo-first-order rate constant (k_1) at various initial concentration of toluene (C_0)

C_0 (mg/m^3)	k_1 (min^{-1})
90	0.0441
357	0.0289
1043	0.0146

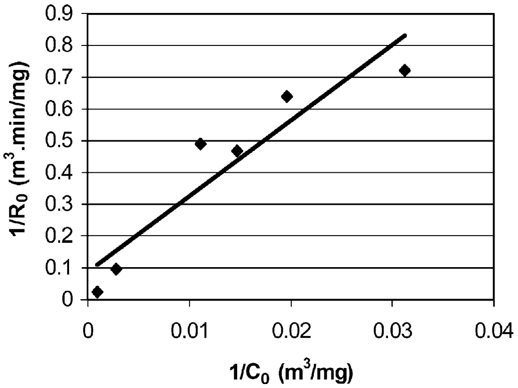

Fig. 3. Plot of the $R_0{}^{-1}$ versus $C_0{}^{-1}$.

at initial time interval the intermediate concentration can be considered to be negligible. Definitely, such an initial time interval should be shorter as possible. In the practice, however, a considerable error in the analysis could be made easily for such a small conversion of the substrate. So for, in our experiments the initial rate will be calculated from the first 10 min.

By representing R_0^{-1} versus C_0^{-1} (Fig. 3), and by linear regression, the L–H rate constant k and the Langmuir adsorption constant K can be obtained.

The data appears scattered. This is probably due to the fact that at 10 min, the hypothesis of no intermediate influence is not really valid. However, the degradation kinetic of the toluene can be represented by L–H model. This means that the chemical reaction is the limiting step of the process.

The value of L–H rate constant and Langmuir adsorption constant were: $k = 11.47\,\mathrm{mg\,m^{-3}\,min^{-1}}$ and $K = 0.004\,\mathrm{m^3\,mg^{-1}}$.

3.2. Photocatalytic oxidation over B and C catalysts

As reported yet, the difference between the two catalysts is based only on the nature of their support. As for catalyst A, the bulk concentration of toluene decrease with irradiation time (Figs. 4 and 5).

The pseudo-first-order rate constant (k_1) is calculated for the two photocatalysts as a function of initial concentration. This is done by plotting $\ln(C_0/C)$ versus t. The results are summarized in Table 2.

As for catalyst A, the concentration-dependence of k_1 indicates that the photocatalytic reaction of toluene is not really first-order for B and C photocatalysts. So it is necessary to determine the L–H rate constant k and the adsorption constant K.

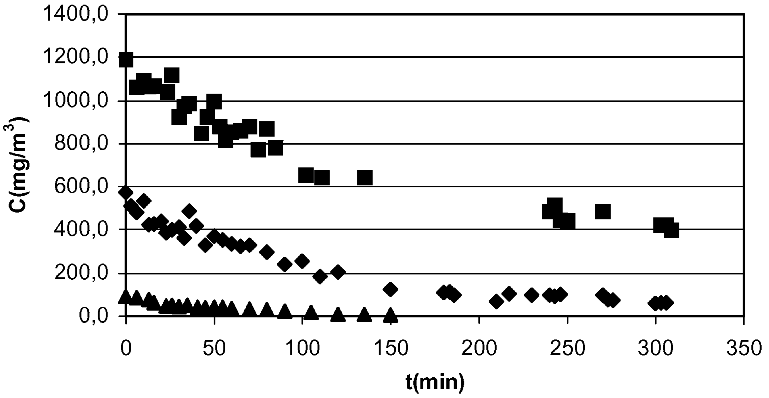

Fig. 4. Evolution of the toluene concentration versus time for photocatalyst B at different initial concentrations, C_0: 93 (▲), 559 (◆), 1190 mg/m^3(■).

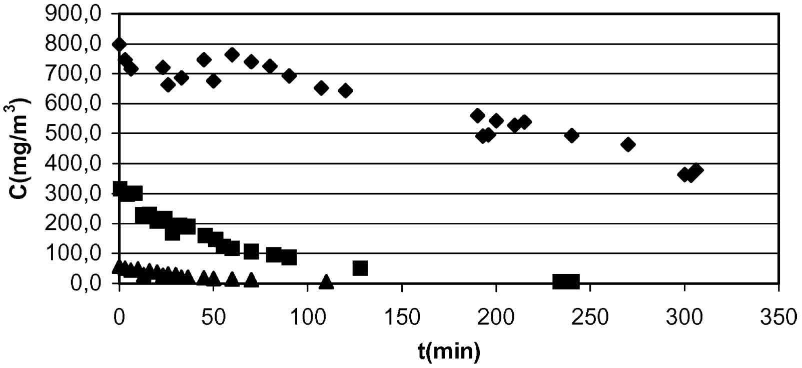

Fig. 5. Evolution of the toluene concentration versus time for photocatalyst C at different initial concentrations, C_0: 58 (▲), 316 (◆), 797 mg/m^3(■).

Table 2
Variation of the pseudo-first-order rate constant (k_1) at various initial toluene concentration (C_0) for B and C photocatalysts

Catalyst B		Catalyst C	
C_0 (mg/m^3)	k_1 (min^{-1})	C_0 (mg/m^3)	k_1 (min^{-1})
93	0.0173	58	0.0230
574	0.0078	316	0.0163
1190	0.0038	797	0.0022

By representing R_0^{-1} versus C_0^{-1} (Fig. 6), and by linear regression, the L–H constants can be obtained. Only the first 10 min data will be used.

The value of L–H rate constant k and Langmuir adsorption constant K determined from Fig. 6 are: for B $k = 5.917\,\mathrm{mg\,m^{-3}\,min^{-1}}$, $K = 0.003\,\mathrm{m^3\,mg^{-1}}$ and for C $k = 2.802\,\mathrm{mg\,m^{-3}\,min^{-1}}$, $K = 0.004\,\mathrm{m^3\,mg^{-1}}$.

The degradation kinetics of toluene can be described correctly by the L–H model. We note that the Langmuir adsorption constants are equal for the two photocatalysts. But the catalyst B rate constant are twofold high than the C's. The two catalysts have the same amount of TiO_2–SiO_2. This difference in the kinetic can be explained by the fact that only a small fraction of TiO_2–SiO_2 is irradiated. This problem will be discussed latter.

3.3. Comparison of the three photocatalysts

The three catalysts used have the same photoactivated matter TiO_2. Even if the support materials are different, we can suppose that they have no role in the photocatalysis mechanism. The materials used for the supports as glass fibers, polyamide, viscose, PET and cellulose have no photocatalytic activity and no adsorption capacity. The results obtained by L–H modelisation are summarized in Table 3.

The value of the Langmuir adsorption constant K is the same for all cases. If K reflects the adsorption affinity of the substrate for the sorbent, then it seems evident that this value be the same. We will see latter that the constant K do not represent only the adsorption affinity [11]. Concerning the rate constant k, we note that the constant for catalyst A is about twice higher than B and four times higher than C. The rate constant of catalyst A is the highest even if the quantity of the TiO_2 per unit area is 10 times lesser than B and C. This means that the kinetic performance of the catalyst A is very high per unit area. This superiority can be due to the site accessibility at UV irradiation. Before discussing this problem, it appears more interesting to express the kinetic degradation of the toluene per unit mass of TiO_2.

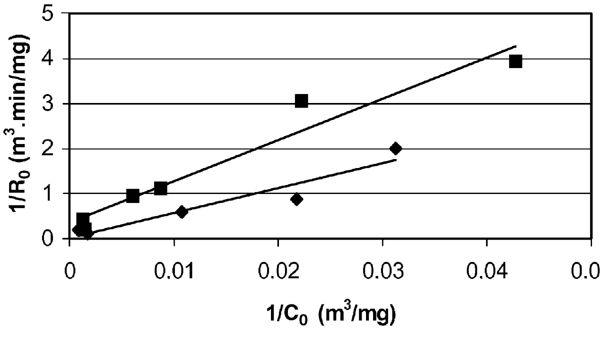

Fig. 6. Plot of R_0^{-1} versus C_0^{-1}. Photocatalysts B (◆), C (■); model (—).

Table 3
The values of k and K for the three photocatalysts

Catalyst	k (mg m^{-3} min^{-1})	K (m^3 mg^{-1})
A	11.47	0.004
B	5.92	0.003
C	2.80	0.004

So the expression of the photocatalytic degradation per unit mass of the catalyst becomes

$$R' = \frac{k'K'C}{1 + K'C}$$

where R' ($\mathrm{mg\,min^{-1}\,g_{cat}^{-1}}$) is the quantity of toluene degraded per minute and per unit mass of the catalyst, k' ($\mathrm{mg\,min^{-1}\,g_{cat}^{-1}}$) the pseudo-L–H rate constant and K' ($\mathrm{m^3\,mg^{-1}}$) the pseudo-Langmuir adsorption constant. The values of k' and K' are given in Table 4.

The pseudo-Langmuir adsorption constant K' is equal for the catalysts A and C and 10 times less for B. We note that this result is different when the Langmuir constant K was calculated per unit surface where the K values was the same. This is probably due to the fact that the calculation of the value of K' is strongly affected by the value of k' the pseudo-L–H rate constant. Concerning the rate constants, the k$'$ for the catalyst A is about twice higher than B and 30-fold higher than C.

In conclusion, the use of the photocatalyst A will give the best performance in the degradation of the toluene and probably for other VOCs.

This difference between the three catalysts is due, in our point of view, to the disposition of the TiO_2 on the supports used. Two reasons can be proposed to explain this difference. First the site accessibility to toluene may be reduced by the disposition of the support material. The second possibility is that some of the catalytic sites is not irradiated by UV. This two hypothesis will be discussed.

3.3.1. Limitation in the site accessibility

The site adsorption accessibility can be approached by calculating the coverage rate (θ) of the support. As reported

Table 4
The values of k' and K' per unit mass of TiO_2

Catalyst	k' (mg min^{-1} g$_{cat}^{-1}$)	K' (m^3 mg^{-1})
A	370	0.004
B	213	0.0003
C	9.66	0.004

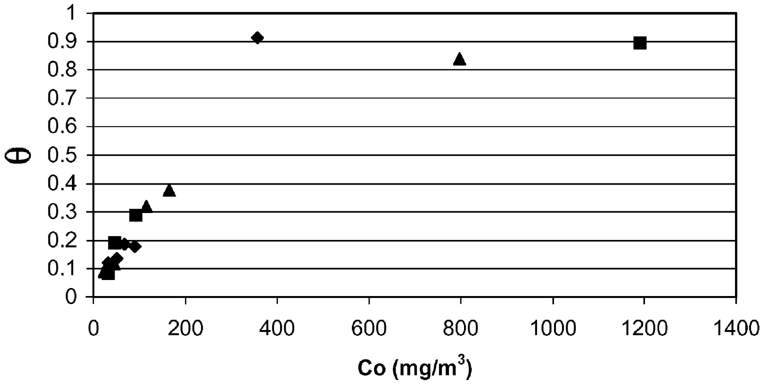

Fig. 7. Evolution of the rate coverage versus initial concentration of catalysts A (◆), B (■), C (▲).

by Chen et al. [14], the reaction rate (R_0) can be expressed by:

$$R_0 = k_i \theta I$$

where k_i is the real rate constant of the overall reaction which is related to illumination intensity I. If illumination intensity, I, is constant, as in our experiments, then $k_i I = k$, the L–H rate constant.

So

$$R_0 = k\theta$$

Then the expression of the coverage rate (θ) becomes

$$\theta = \frac{R_0}{k}$$

the reaction rate R_0 is determined by L–H model. The evolution of the rate coverage versus the initial toluene concentration is represented in Fig. 7.

As shown in Fig. 7, the surface coverage is equal for the three catalyst when the toluene initial concentration is low. This means that the site accessibility for the toluene adsorption is not the discriminating factor when the rate coverage is low. However, at high initial concentration, the surface coverage is higher for photocatalyst A than the photocatalysts B and C. This means that the site accessibility to toluene is more difficult when the toluene concentration increases for the catalysts B and C.

3.3.2. Limitation by UV radiation

The other reason which can explain the difference between the catalysts is that the limitation due to UV irradiation of the activated sites.

Some reports [11] show that the K determined under photocatalytic degradation is different than the K measured in the dark when only adsorption occurs. So we are going to compare this two conditions K values.

When using the catalysts only as absorbers, i.e. with no UV illumination, and by representing the adsorption isotherms by Langmuir model, we obtain (Table 5) the maximum adsorption capacity (q_{max}) and Langmuir adsorption constant (K_{ads}).

Table 5
Determination of the maximum adsorption capacities and Langmuir adsorption constants in the dark

Photocatalyst	q_{max} (mg g_{cat}^{-1})	K_{ads} (m^3 mg^{-1})
A	30.67	0.0015
B	3.45	0.0414
C	2.90	0.0547

As shown in Table 5, we note that the adsorption capacity of catalyst A is about 10 times high, per unit mass, than B and C. This difference in the adsorption capacities is probably due to the site accessibility (see Fig. 7). The variation of K_{ads} in the dark and K under UV illumination is given in Table 6.

We note that the value of K for catalyst A is affected by the use of UV illumination. The value of K increases when the UV is used. It means that the catalyst A is very sensitive to UV light and probably the turn over of the catalyst sites increases.

For B and C catalysts, the adsorption constant K decreases strongly when UV illumination occurs. This means that only a small part of the adsorption sites, about 8%, play a role in the photocatalytic degradation process. On the other hand, we can say that only a small part of the catalyst sites is illuminated.

Some authors as Xu and Langford [11] reported that when increasing the light intensity, the Langmuir adsorption constant decreases. This is not the observed evolution in our experiments when the catalyst A is used. In the case of the catalysts B and C, the evolution is in accord with the reported results of the authors cited above. However, it seems difficult, for the authors, to explain why K change inversely

Table 6
Comparison of the Langmuir adsorption constant in the dark and under UV illumination

Photocatalyst	K_{ads}	K	K_{ads}/K
A	0.001	0.004	0.25
B	0.041	0.003	13.7
C	0.051	0.004	12.75

with light intensity. In our case, the explanation is that probably the constant K express the “virtual” adsorption capacity of the photocatalyst, i.e. K is related to the adsorption step in the photocatalytic reaction.

4. Conclusion

The comparative study of the three photocatalysts has shown that the L–H model can be used to describe the degradation of the toluene. It means that the chemical reaction is the limiting step in the case of the photodegradation of the toluene.

The comparison between the three catalysts showed that the catalyst A has the best kinetic performance. The comparison is based only on the rate constant k which is two to four times higher than the catalysts B and C. We note that the catalyst A is the best photocatalyst unless the density of TiO_2 per unit surface is about 10 times lesser than for B and C catalysts.

This best performance of the catalyst A is due to the fact that all the catalytic sites is irradiated and this is not the case for B and C catalysts. The comparison of the adsorption constants K in the dark and under UV irradiation permit us to express this hypothesis. Finally we can conclude that when we use the photocatalytic process, the most important parameter is the irradiation rate and not the quantity of the photocatalyst used. A further effort is needed to examine this observation.

Acknowledgements

The authors wish to thank M. Dussaud from the Ahlstrom Paper Group (APG) who has furnished the photocatalysts tested.

References

[1] D. Martinez Plaza, S. Malato, Catal. Today 54 (1999) 191.
[2] M. Litter, Appl. Catal. B 23 (1999) 89.
[3] M.R. Hoffmann, S.T. Martin, W. Choi, D. Bahnemann, Chem. Rev. 95 (1995) 69.
[4] X. Fu, W.A. Zeltner, M.A. Anderson, in: P.V. Kamat, D. Meisel (Eds.), Semiconductor Nanoclusters: Physical, Chemical, and Catalytic Aspects, Elsevier, Amsterdam, 1996, p. 445.
[5] R.W. Mattews, Solar Energy 38 (1987) 405.
[6] D. Bahnemann, D. Bockelmann R. Golish, M. Hilgendorff, D. Weichgrebe, in: D.F. Ollis, H. Al-Ekabi (Eds.), Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993, p. 301.
[7] J.E. Pacheco, M. Mehos, C. Turchi, H. Link, in: D.F. Ollis, H. Al-Ekabi (Eds.), Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993, p. 547.
[8] F.W. Wilkins, D.M. Blake, Chem. Eng. Prog. 90 (1994) 41.
[9] A. Sirisuk, C.G. Hill Jr., M.A. Anderson, Catal. Today 54 (1999) 159.
[10] N.N. Lichtin, M. Avudaithai, Environ. Sci. Technol. 30 (1996) 2014.
[11] Y. Xu, C.H. Langford, J. Photochem. Photobiol. A 133 (2000) 67.
[12] Y. Xu, C.H. Langford, J. Phys. Chem. B 101 (1997) 3115.
[13] C. Anderson, A.J. Bard, J. Phys. Chem. B 101 (1997) 2611.
[14] J. Chen, D.F. Ollis, W.H. Rulkens, H. Bruning, Wat. Res. 33 (5) (1999) 1173.