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Removal of organic contaminants in paper pulp treatment effluents by TiO_2 photocatalyzed oxidation

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Abstract

TiO_2 slurries under UV light irradiation were used for the oxidation and removal of the organic load of effluent from the bleaching of paper pulp. TOC was the main analytical parameter used to characterize the reaction progress, although COD, AOX and color also received periodic attention. Conditions such as the catalyst load, light intensity, pH, temperature, and concentration of O_2 and organic matter were changed through several series of experiments in order to determine their effect. A zero order kinetics accounts for the observed variation of TOC with time during most of the reaction, the rate constant being 0.25–0.40 ppm min^{-1} at 25 °C. This behavior is explained in terms of a Langmuir–Hinshelwood rate equation in a highly substrate concentrated system. © 1997 Elsevier Science S.A.

Keywords: Organic contaminants; Paper pulp

1. Introduction

The pulp and paper industry produces large quantities of spent bleach effluent. These liquors are highly colored and contain large concentrations of organic matter, in particular chlorinated organics, most of them being difficult to eliminate by conventional waste water treatment processes and, therefore, being accumulated in the environment [1–6].

Heterogeneous photocatalytic oxidation is a well known procedure for waste water treatment, which can be used to carry out the complete mineralization of a large number of organic compounds [7–10]. It has shown to be particularly efficient for the attack of chlorinated compounds [11] and, for that reason, it is potentially suited for the treatment of paper pulp bleaching effluents.

In the present study samples of bleaching effluents obtained after chlorine dioxide (ClO_2) oxidation of paper pulp were treated with TiO_2 in the presence of UV light and air bubbling. TOC was chosen as the most general parameter for the study of the detoxification and organic content removal, although other characteristics such as AOX (adsorbable organic halogen), COD (chemical oxygen demand) and color were controlled through the experiments. The conditions were varied systematically, so that information about the effect that the catalyst mass, organic load, pH, temperature and O_2 concentration have on the process could be collected. Special attention was paid to the reaction kinetics and the potential of the method for complete removal of TOC content.

2. Experimental section

The effluents used in the present research were obtained in the laboratory after bleaching sequences of a paper pulp made from *Eucaliptus globulus* chips. The Kappa index and viscosity of the resulting pulp were 20.6 and 650 $cm^3\ g^{-1}$ respectively. The bleaching sequence consisted of three steps: (i) acid pretreatment (2 mol l^{-1} H_2SO_4), (ii) bubbling with pressurized O_2 (to reduce the lignin content), and (iii) treatment with chlorine dioxide. The effluent from this last step formed the starting solution of the present research. Only in the experiments where a much higher organic matter content was needed were the acid pretreatment and O_2 bubbling steps avoided.

All chemicals used in this work were at least of reagent grade and were used as received. The titanium dioxide (Degussa P25) was predominantly anatase (80% anatase and

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20% rutile), as shown by X-ray diffraction. The BET surface area, determined from nitrogen adsorption at −196 °C (Accusorb 2100 E Micromeritics) was 59.1 m^2 g^{-1}. The average particle size, determined by scanning electron microscopy, was 27 nm.

Experiments were conducted in a thermostatic cylindrical Pyrex cell of 130 cm^3 capacity. The reaction mixture inside the cell, consisting of 100 ml of organic effluent and the precise amount of TiO_2, was maintained in suspension by magnetic stirring. As a light source, a 125 W Philips HPK medium pressure mercury vapor lamp was used. The intensity of the incident light inside the photoreactor, measured employing a uranyl actinometer, was 9.2×10^{-5} einstein dm^{-3} min^{-1}.

TOC of initial and irradiated samples was determined, after filtering the catalyst, with a Shimadzu TOC 5000 total organic carbon analyzer. COD was detected spectrophotometrically at 620 nm with a specific commercial reagent kit (Hach DR/2000). For AOX measurements a Euroglas analyzer, model ECS2000, was used. Color determination was carried out in a double beam spectrophotometer SP8-300 Pye Unicam at the wavelength of 465 nm using cuvettes of 10 mm light path, according to the standards of the CPPA (Canadian Pulp and Paper Association, Standard H.5, 1991).

3. Results and discussion

The paper pulp treatment effluent, produced as described in Section 2, contained the following contaminating load: 306 ppm TOC, 515 mg O_2 l^{-1} COD, 27.7 ppm AOX, and 250 color units. TOC was chosen as the main parameter of study in the present work because it is the most general quantification of organic matter. Nevertheless determinations of COD, a more extensively used index for water pollution, were also carried out. AOX and color, both particularly important measurements in effluents coming from the paper mill industry, were also sporadically collected.

Blank experiments were carried out in order to ascertain whether photocatalytic oxidation takes place with such an organic content. When 100 ml of the effluent were mixed with 0.2 g TiO_2, a decrease of 9.8 ppm (3.2%) in TOC value after 15 min in the dark was noticed. For longer mixing times no further TOC removal took place. In contrast, the presence of UV light produced a reduction of 16.2 ppm (5.3%) TOC after 15 min, and longer reaction times involved larger reductions. The initial decrease in TOC in the dark is, thus, a consequence of pure adsorption and saturation of the catalyst surface. No appreciable TOC decay was noticed when the solution was irradiated during 1 h in the absence of TiO_2. The mass of TiO_2 suspended is expected to influence the reaction efficiency by providing a larger reactive surface. This point was tested, and the results for three different TiO_2 loads (1, 2 and 6 g l^{-1}) are shown in Fig. 1. As can be seen, in the three cases the reaction rates of TOC removal, which are the slope of the curves, are similar (approximately 0.25 ppm min^{-1}) and suffer no appreciable change with time. The only difference appears in the initial TOC decrease, which is clearly larger in the experiment with 6 g l^{-1} catalyst. This observation agrees with the existence of an initial saturation of the solid surface which would be larger for larger amounts of suspended TiO_2. The other parameters studied follow similar behavior, with larger reductions for increasing mass of catalyst. In this way, after 8 h reaction under irradiation and in the presence of 6 g l^{-1} TiO_2, reductions of AOX and COD of 80% and 64% respectively took place, the reductions obtained with 2 g l^{-1} being 71% and 49%. The improvement in the color reduction was spectacular, going from 21% to 72% for the above mentioned values of mass in suspension and the same reaction time.

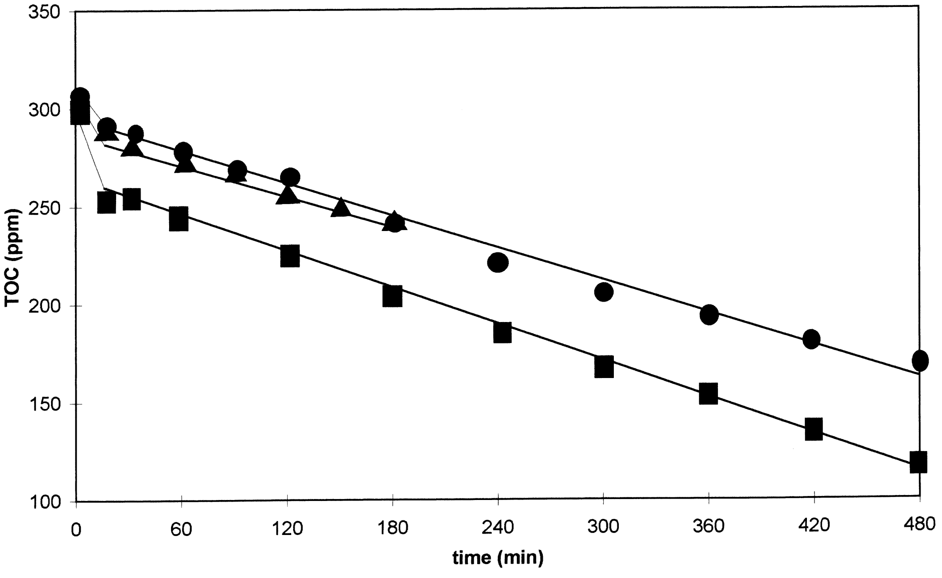

Fig. 1. TOC vs. reaction time for three different catalyst loads: 1 g l^{-1} (▲), 2 g l^{-1} (●), and 6 g l^{-1} (■). AOD sequence effluent, pH ≈ 3, air flow 60 ml min^{-1}, 25 °C, 9.2×10^{-5} einstein min^{-1}.

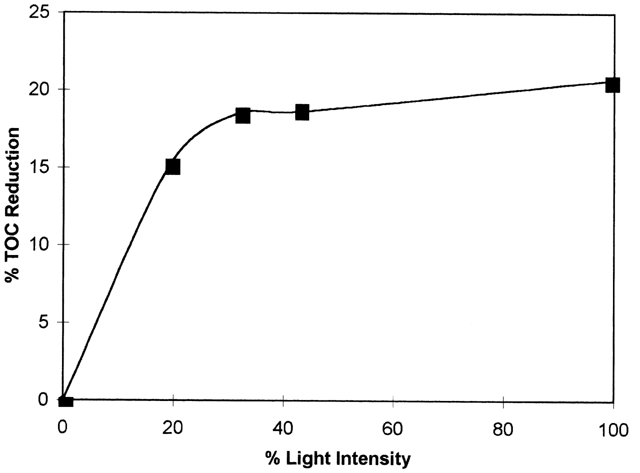

Fig. 2. Effect of relative light intensity on TOC removal. AOD sequence effluent, 2 g l^{-1} TiO_2, pH≈3, air flow 60 ml min^{-1}, 25 °C. Full light intensity 9.2×10^{-5} einstein min^{-1}.

The light intensity was also a variable studied. Fig. 2 presents the removal of TOC vs. the percentage of full lamp intensity used in different experiments. The results clearly indicate no important changes in TOC removal for light intensities going from 30% to 100%. Below 30% of full lamp power the efficiency of the reaction rapidly decreases. An excess of photons is being used in our standard experiments. Different behavior was noticed with AOX, a 35% larger reduction when moving from 100% to 43% light intensity. This fact might well indicate the existence of homogeneous photochemistry among halogen-containing reaction intermediates, which could, through direct activation by photons, react and lose the halogen without complete mineralization. In this way a change in photon flux could produce a decrease in AOX with no influence on the degree of mineralization owing to heterogeneous photochemistry.

The influence of initial pH was also studied. No variations in TOC values in the pH range studied and in the absence of catalyst were noticed, so phenomena such as organic matter precipitation or homogeneous hydrolysis could be ruled out. Fig. 3 presents the TOC-time course for several initial pH. The slope of the curves and, hence, the reaction rates are similar and constant in time, which indicates a lack of influence of pH on photocatalysis under the conditions used here. Nevertheless, the only differences occur again during the initial minutes of the reaction, with a larger TOC adsorption onto the catalyst for pH 6 and 10, which are above the point of zero charge (pzc) of TiO_2 which is 5.5. The behavior of COD and color is similar to that observed for TOC. AOX changes follow again a different direction. The removal of halogen containing species is clearly favored at acid pH (45% reduction after 3 h at pH 3 compared with 30% reduction at pH 6 and 10). The favored adsorptivity of these electronegative species onto the positively charged catalyst surface could explain these phenomena.

Experiments at two different temperatures (25 and 40 °C) were also carried out to detect any possible influence of that variable on the reaction rate. Fig. 4 shows the corresponding data. In this case there is a slight improvement for the higher temperature (0.40 ppm min^{-1} at 40 °C vs. 0.28 ppm min^{-1} at 25 °C). In any case the increase is too low if compared with typical Arrenhius behavior, and the global process could be considered as controlled by the charge transfer step, which is known to be very little affected by temperature [12,13].

As all oxidation processes, photocatalysis is based on the consumption of an oxidant, in the present case the O_2 in solution. O_2 reacts with the photogenerated conduction band electrons keeping the electrical neutrality in the TiO_2 particle. The concentration of O_2 could very well control the oxidation process and experiments were carried out in both air and pure O_2 atmospheres to look for such an effect. Fig. 5 shows very little difference when bubbling these two gases into the TiO_2 slurry, making clear that the amount of O_2 present in solution through all the experiments described so far was enough to

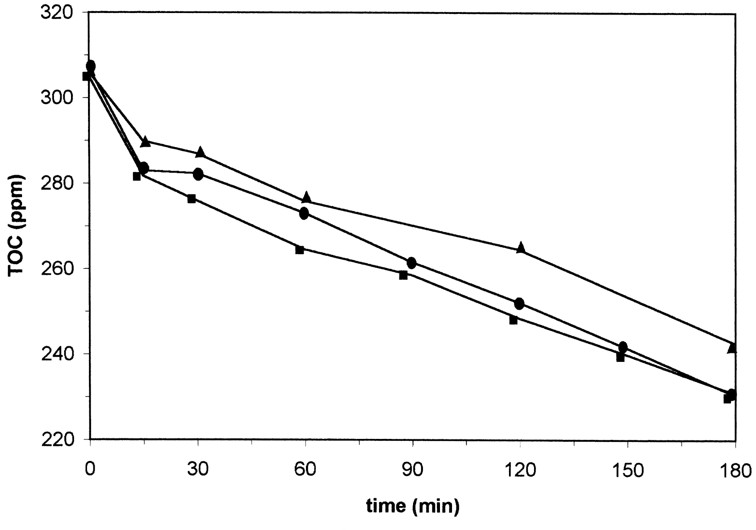

Fig. 3. Time course of TOC for three different initial pH values: pH 3 (▲), pH 6 (●), and pH 10 (■). AOD sequence effluent, 2 g l^{-1} TiO_2, air flow 60 ml min^{-1}, 25 °C, 9.2×10^{-5} einstein min^{-1}.

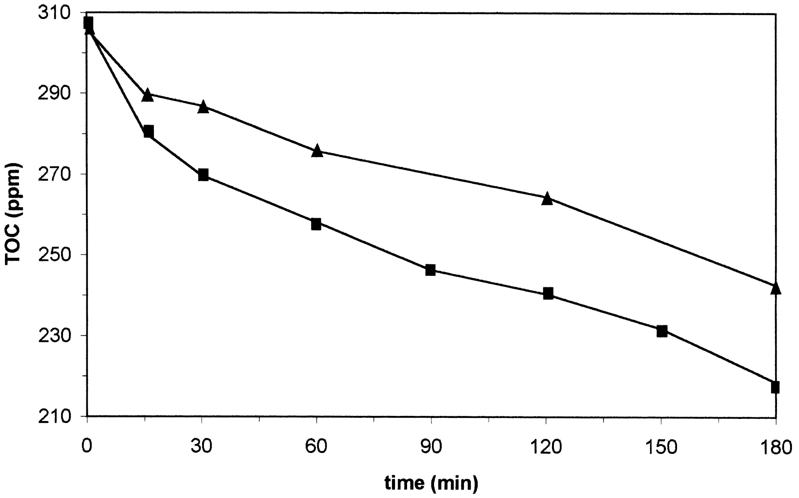

Fig. 4. TOC vs. reaction time data of experiments at 25 (▲) and 40 °C (■). AOD sequence effluent, 2 g l^{-1} TiO_2, pH ≈ 3, air flow 60 ml min^{-1}, 9.2×10^{-5} einstein min^{-1}.

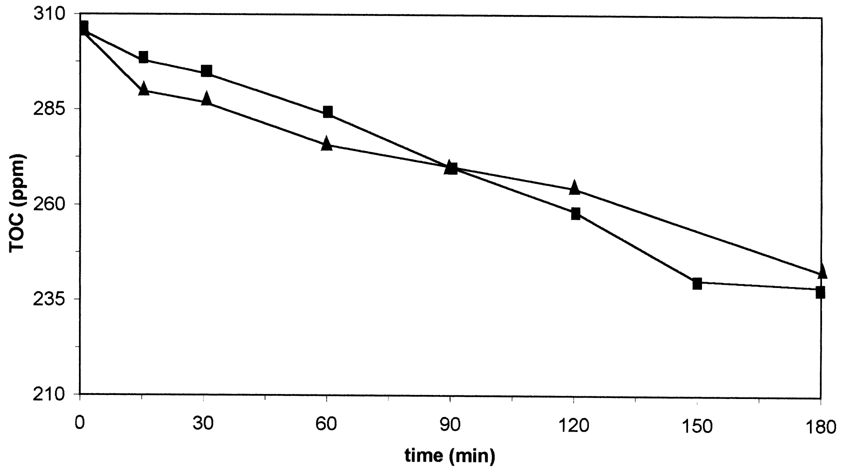

Fig. 5. TOC-time course under two different atmospheres: air (▲) and pure O_2 (■). AOD sequence effluent, 2 g l^{-1} TiO_2, pH ≈ 3, gas flow 60 ml min^{-1}, 25 °C, 9.2×10^{-5} einstein min^{-1}.

saturate the system so that O_2 reduction could not be considered a rate-limiting step. AOX and color reduction behave differently. 55% AOX reduction was attained after only 3 h reaction in the presence of pure O_2, 5 h being necessary to remove the same amount in air atmosphere. On the other hand, while 24% color reduction was obtained after 3 h in O_2 atmosphere, only 20% decrease in this parameter was detected within 8 h of reaction in air atmosphere.

The reaction efficiency for a higher initial contaminant load was examined. To accomplish this a new sequence of paper mill effluent generation was followed, which omits the acidification and O_2 treatment of the paper pulp. The values of the analytical parameters for this effluent were as follows: 1380 ppm TOC, 3700 mg O_2 l^{-1} COD, 69.8 ppm AOX, and 7030 color units. Fig. 6 shows the TOC-time course when two different amounts of TiO_2 (2 and 6 g l^{-1}) were used to prepare slurries for irradiation. Again, the slopes are similar and constant in time, indicating that for this contaminated solution no change is observed in the kinetics of heterogeneous photocatalysis. Only a small increase in reaction rate is noticed when comparing the slopes of these curves with those depicted in Fig. 1 (0.4 ppm min^{-1} and 0.25 ppm min^{-1} respectively).

Finally, a long term irradiation was carried out to ascertain whether the system could undergo complete mineralization and how that would take place. Fig. 7 shows the data collected during that experiment. As is indicated on the figure, three zones of different kinetic behavior are noticed. The narrow band of a few minutes at the beginning of the reaction is due, as previously indicated, to the existence of a dark adsorption onto the catalyst surface. The central zone, which includes the subsequent 500 min is characterized by a zero order. From that moment the reaction rate slows down, being difficult to assign a reaction order. The zero order behavior can be explained by considering that most water phase photocatalytic oxidations described in the literature so far follow the Langmuir–Hinshelwood (LH) equation [14]:

$$r = \frac{kK[A]}{1 + K[A]} \tag{1}$$

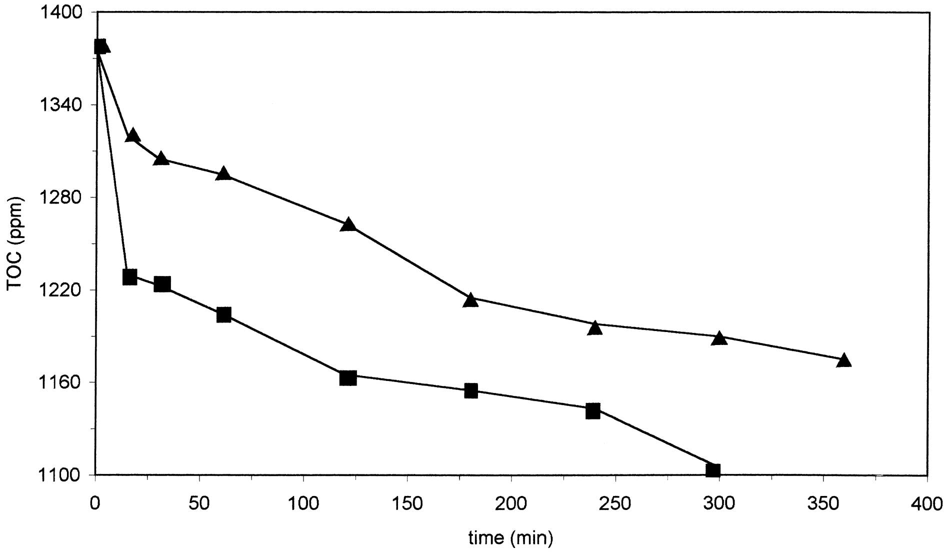

Fig. 6. TOC vs. reaction time for two different catalyst loads: 2 g l^{-1} (▲) and 6 g l^{-1} (■). D sequence effluent, pH ≈ 3, air flow 60 ml min^{-1}, 25 °C, 9.2×10^{-5} einstein min^{-1}.

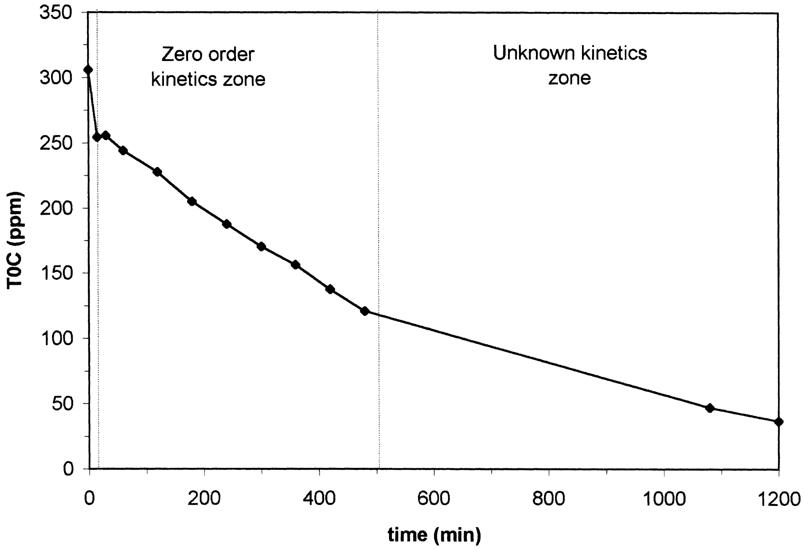

Fig. 7. TOC vs. time for a long term irradiation experiment. AOD sequence effluent, 2 g l^{-1} TiO_2, pH ≈ 3, air flow 60 ml min^{-1}, 25 °C, 9.2×10^{-5} einstein min^{-1}.

where [A] is the reactant concentration (in the present case a mixture of species which is summarized as TOC), K is the adsorption constant of that species onto the TiO_2, and k is the rate constant of the charge transfer reaction itself. If the $K[A]$ product is large enough then $1+K[A] \approx K[A]$ and

$$r = k \qquad (2)$$

This can be the situation when treating paper pulp bleaching effluents: a large concentration of organics (most cases where the LH equation has been applied correspond to a few ppm of organics in solution) and a noticeable adsorption constant. The TiO_2 is rapidly saturated by the TOC containing species so that the surface reaction sees a nearly constant concentration of organics during the central part of the process.

Several reasons can explain the decrease in reaction rate for long irradiation times: the decrease in TOC itself, which would cancel the condition of a large $K[A]$ mentioned above, competition for the surface active sites between reactant and intermediate species, aging of the catalyst surface, agglomeration of particles, changes in pH, etc.

4. Conclusions

Photocatalytic oxidation can efficiently reduce the organic content of contaminated water generated during the pulp bleaching step of the paper making process. During the initial minutes of the reaction the decrease in TOC is due purely to dark adsorption onto the surface of the TiO_2 solid catalyst. The extent of this adsorption depends on the amount of catalyst in contact with the solution, but no important influence of such an experimental parameter was noticed during the photocatalytic process. The light intensity reaching the reaction vessel has an effect on the reaction rate only when levels of photons below 30% of the lamp full output are considered. Neither pH nor temperature have a remarkable influence on the photocatalytic process after the initial dark adsorption has taken place. A 4–5 fold increase in organic content produces only a slight improvement in the reaction rate, and the kinetics of TOC removal during the central part of the process follows a zero order equation; this behavior has been explained as a particular case of the most general Langmuir–Hinshelwood equation. Other interesting contamination indexes, such as COD, AOX and color are systematically reduced during photocatalysis. However, some quantitative divergences arise when comparing the uniformity of these reductions for the different parameters along the experiments.

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References

[1] P.F. Earl, D.W. Reeve, Tappi J. (1990) 179.
[2] C. Rappe, S. Swanson, B. Glas, K.P. Kringstad, F. DeSousa, L. Johansson, Z. Abe, Pulp Paper Canada 90 (1989) T273.
[3] T.Y. Tsai, J.J. Renard, R.B. Phillips, Tappi J. 77 (1994) 149.
[4] S.A. Heimburger, D.S. Blevins, J.H. Bostwick, G.P. Donnini, Tappi J. (1988) 51.
[5] S.A. Heimburger, D.S. Blevins, J.H. Bostwick, G.P. Donnini, Tappi J. (1988) 69.
[6] D.G. Wilson, M.F. Holloran, Pulp Paper Canada 93 (1992) T372.
[7] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[8] D.F. Ollis, in E. Pelizzetti and M. Schiavello (eds.), Photochemical Conversion and Storage of Solar Energy, Kluwer, Dordrecht, 1991.
[9] N. Serpone, E. Pelizzetti, H. Hidaka, Solar Energy Meet. IPS-9, Beijing, China, 1992.
[10] M.A. Fox, M.T. Dulay, Chem. Rev. 93 (1993) 341.
[11] D.F. Ollis, E. Pelizzetti, N. Serpone, Environ. Sci. Technol. 25 (1991) 1523.
[12] J. Kiwi, J. Phys. Chem. 89 (1985) 2437.
[13] J.S. Curran, J. Domènech, N. Jaffrezic-Renault, R. Phillipe, J. Phys. Chem. 89 (1985) 957.
[14] D.F. Ollis, E. Pelizzetti, N. Serponne, in: N. Serpone, E. Pelizzetti (eds.), Photocatalysis Fundamentals and Applications, Wiley, 1989, p. 603.