ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 109 (1997) 171–176

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

The fate of organic nitrogen under photocatalytic conditions: degradation of nitrophenols and aminophenols on irradiated TiO_2

V. Maurino [a], C. Minero [a], E. Pelizzetti [a,*], P. Piccinini [a], N. Serpone [b], H. Hidaka [c]

[a] *Dipartimento di Chimica Analitica, Università di Torino, 10125 Torino, Italy*
[b] *Department of Chemistry and Biochemistry, Concordia University, Montreal, Que. H3G 1M8, Canada*
[c] *Department of Chemistry, Meisei University, Tokyo 191, Japan*

Accepted 25 March 1997

Abstract

The photocatalytic transformation of 2-, 3- and 4-nitrophenol (NP) and 2-, 3- and 4-aminophenol (AP) over irradiated titanium dioxide was investigated in aerated aqueous solution. At $pH < 6$, extensive mineralization (more than 90%) of the substituted phenols occurs, whereas, at pH 11, organic carbon is persistently observed. Photocatalysis converts 80% of the nitro group in nitrophenols to NO_3^- through the intermediate formation of NO_2^- ions; the remaining 20% is transformed into NH_4^+ ions. This implies that, even in aerated solutions, reductive pathways are significant, as confirmed by the detection of aminophenol. By contrast, photocatalytic degradation of aminophenols converts the NH_2 group into about 60%–70% NH_4^+ ions and only about 10% NO_3^-, when about 20% of the organic carbon remaining. A slow transformation of the ammonium ions into NO_3^- ions is observed at longer irradiation times. © 1997 Elsevier Science S.A.

Keywords: Aminophenols; Nitrophenols; Organic nitrogen; Photocatalytic transformation; TiO_2

1. Introduction

Processes based on heterogeneous photocatalysis have been demonstrated in numerous reports to be efficient in the conversion of organic compounds into carbon dioxide and inorganic anions [1–3]. In photocatalytic processes involving nitrogen-containing organic compounds, the final oxidation state of nitrogen when mineralization of the organic carbon has occurred may depend on several factors, the most significant being the nature of the initial organic compound, the concentration of molecular oxygen, the pH of the solution, the concentration of the substrate, the loading and nature of the catalyst and the photon fluence from the irradiation source [4].

In an effort to clarify the possible pathways of transformation of the nitro and amino groups in substituted phenols, we examined the photocatalytic degradation of three nitrophenols (NPs), namely 2-, 3- and 4-NP, and the three corresponding aminophenols (APs) in aerated TiO_2 suspensions. The interest in NPs is their inclusion in the US Environmental Protection Agency's list of priority toxic compounds [5], whereas APs are specific intermediates in the manufacture of dyes. It is also worth noting that these NPs and APs are the first intermediate products in the photocatalysed transformation of nitrobenzene and aniline respectively.

2. Experimental details

2.1. Reagents

All the NP and AP isomers were purchased from Aldrich (purity grade, 98%–99%); they were used as received without further purification.

Titanium dioxide P25 was purchased from Degussa; its Brunauer–Emmett–Teller (BET) surface area was about 55 $m^2 g^{-1}$. Before utilization, the photocatalyst was treated by irradiation overnight in an aerated aqueous suspension to eliminate adventitious organic and/or inorganic impurities. It was subsequently washed several times with bidistilled water and then dried in an oven at 70 °C for several hours.

2.2. Irradiation experiments

The aqueous substrate solution (2.5 ml) and catalyst suspension (2.5 ml) were mixed in the reactor cell used for the irradiation experiments which was thermostatically con-

---

[*] Corresponding author.

PII S1010-6030(97)00124-X

trolled by a water bath in the dark to bring the mixture to the working temperature of the lamp housing (approximately 50 °C). The final concentrations were 10 mg l^{-1} and 200 mg l^{-1} for the organic compound and titanium dioxide respectively. The reactor vessel was a cylindrical ($\phi = 4$ cm) Pyrex cell with two parallel windows at the top and bottom. The cell was irradiated from the top; the cell had a lateral aperture (i.d., 1 cm) near the upper window which was closed with a removable cap [6].

Irradiation was achieved with a 1500 W xenon lamp (Solarbox, CO.FO.MEGRA, Milan, Italy) which emitted a spectrum simulating AM1 solar light, but with a UV component nearly twice as intense as that in normal sunlight in the UV range of interest. This Solarbox was equipped with a 340 nm cut-off filter, and provided a total photonic fluence of approximately 1.35×10^{-5} einstein min^{-1} in the 340–400 nm range incident on the reactor cell.

After thermal equilibration, the samples were exposed to light in the reactor and were magnetically stirred. After irradiation for several time intervals, the samples were filtered through a 0.45 μm membrane (cellulose acetate, Millipore HA) and were subsequently analysed directly.

2.3. *Analytical procedures*

Analytical determinations of NPs and APs were carried out isocratically on a Hitachi high performance liquid chromatograph equipped with a UV detector (model L6200), Hitachi Merck pumps (model L6000), a UV source (model L4200) and a reverse phase C-18 column (Lichrocart 5 μm; 150 mm in length). Different mobile phases were used for the NP and AP analyses: for the former substrates, the mobile phase was a 35 : 65 mixture of acetonitrile–phosphate buffer (5×10^{-2} M; pH 2.8); for the AP analyses, the mobile phase consisted of either a 7 : 93 or 5 : 95 mixture of acetonitrile–1-hexanesulphonic acid (1×10^{-2} M in phosphate buffer (5×10^{-2} M); pH 2.8). Under these conditions, the retention times were (min): 2-NP, 6.68; 3-NP, 4.15; 4-NP, 3.75; 2-AP, 7.30; 3-AP, 5.80; 4-AP, 4.40. The detection wavelength was 208 nm.

Non-purgeable organic carbon (NPOC) was measured on filtered samples after adding one drop of concentrated hydrochloric acid and allowing for a purge time of 5 min using a Shimadzu TOC-5000 (catalytic oxidation on Pt at 680 °C) analyser. Calibration of this TOC analyser was achieved using potassium phthalate standards.

Quantification of nitrate and ammonium ions was accomplished by ion chromatography employing, for NO_3^- ions, a Biotronik IC-5000 instrument equipped with a BT1AN separation column, a chemical suppression column and a $K_2CO_3/NaHCO_3$ eluent (1.5 mM in each component) and, for NH_4^+ ions, a non-suppressed Methrom apparatus equipped with a Hamilton PRP-X200 column. For the latter, the eluent was composed of a 70 : 30 mixture of nitric acid (6 mM) and methanol.

The concentration of NO_2^- ions was determined spectrophotometrically at 540 nm using the Griess reagent (Merck).

3. Photocatalysis

Irradiation of titanium dioxide with photons of energy higher than (or equal to) the bandgap (E_g) leads to the formation of a pair of conduction band electrons (e_{CB}^-) and valence band holes (h_{VB}^+)

$$TiO_2 + h\nu \rightarrow e_{CB}^- + h_{VB}^+ \quad (1)$$

The charge carriers thus formed can recombine or be trapped by a defect site at the particle surface and subsurface (intrinsic traps) or by extrinsic surface traps via interfacial electron transfer with adsorbed electron donors $(Red_2)_{ads}$ and acceptors $(Ox_1)_{ads}$

$$h_{VB}^+ + (Red_2)_{ads} \rightarrow (Ox_2)_{ads} \quad (2)$$

$$e_{CB}^- + (Ox_1)_{ads} \rightarrow (Red_1)_{ads} \quad (3)$$

The presence of molecular oxygen and water is essential during the photomineralization process [7], because they contribute to the suppression of electron–hole recombination and provide the necessary oxygen feed for CO_2 evolution

$$h_{VB}^+ + H_2O_{ads} \rightarrow {}^{\bullet}OH_{ads} + H^+ \quad (4)$$

$$h_{VB}^+ + OH_{ads}^- \rightarrow {}^{\bullet}OH_{ads} \quad (5)$$

$$e_{CB}^- + O_{2ads} \rightarrow O_{2ads}^{\bullet -} \quad (6)$$

The superoxide radical anion $O_2^{\bullet -}$ in Eq. (6) can be further reduced to peroxide dianion O_2^{2-} to form surface peroxo species [8]. The evolution of other reactions and the formation of other species depend on the solution pH, and can occur/form on the titanium dioxide particle and implicate the solvent [1–3]. Oxygen-centred species (e.g. $HO_2^{\bullet}$, $O_2^{\bullet -}$, O_2 and H_2O_2) are present either at the interface or in the solution and can participate in the complex degradation scheme which leads to the final mineralization of the organic substrates.

Heterogeneous photocatalytic processes typically involve reactions at the solid–solution interface. In describing some of the homogeneous reactions of $^{\bullet}OH$ radicals and aquated electrons (e_{aq}^-) below, it should be remembered that, in a photocatalytic process, the oxidizing species may (in principle) be the valence band holes or trapped holes (i.e. $^{\bullet}OH_{ads}$), which are more and less oxidizing respectively than the free aqueous $^{\bullet}OH$ radical, and the reducing species may be the conduction band electrons (e_{CB}^-) or trapped electrons (e_T^-), both of which are much less reducing than e_{aq}^-.

4. Nitrophenols

The photocatalysed conversion of the primary compounds and the corresponding disappearance of NPOC at pH 5.5 are shown in Fig. 1. The transformation of the NPs follows a

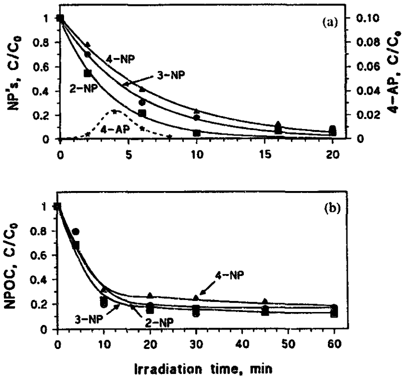


Fig. 1. (A) Photocatalytic degradation of NPs (7.2×10^{-5} M) in the presence of TiO_2 (200 mg l^{-1}) at pH 5.5. Formation of 4-AP from 4-NP is shown on the right scale. (B) Disappearance of NPOC corresponding to (A).

reasonably good first-order rate law [9,10] ($k=(2.7\pm0.3)\times10^{-1}$, $(1.8\pm0.2)\times10^{-1}$ and $(1.5\pm0.2)\times10^{-1}$ min^{-1} for 2-, 3- and 4-NP respectively); the disappearance of about 70%–80% of NPOC also takes place by a similar exponential law. The remaining 20%–30% of NPOC disappears at a much slower rate. The rate of disappearance of NPOC to this level is only slightly slower than the degradation rate of NPs, indicating that the intermediates are also rapidly degraded.

In the case of 4-NP, the degradative process yields hydroquinone and 4-AP (see Fig. 1), as well as other dihydroxynitrobenzene derivatives [11–14]. Hydroxyl radicals (Eq. (5)) induce the elimination of NO_2^- from 4-NP to give 1,4-benzosemiquinone, which subsequently disproportionates into hydroquinone and 1,4-benzoquinone [15]. Other reaction pathways may implicate the initial formation of $HO–C_6H_4–NO_3^-$ (**I**), which can rearrange intramolecularly to give a hydroxyl radical–benzene adduct. The latter disproportionates to NP and dihydroxynitrobenzene. In the presence of oxygen, **I** reacts rapidly ($k=1.7\times10^6$ M^{-1} s^{-1}) [16] to form the same dihydroxynitrobenzene or benzoquinone, together with $HO_2^{\bullet}$ and/or $O_2^{\bullet-}$ radicals. After 15 min of irradiation, the inorganic nitrogen produced accounts for the near-stoichiometric quantity of the initial organic nitrogen (Fig. 2). Thus the remaining organics (NPOC 20%–25% of the initial value) should be assigned to small aliphatic compounds.

The perusal of Fig. 2 shows that the evolution of inorganic nitrogen is independent of the isomeric structure of the NPs. It exhibits two principal features.

1. The initial route of exit of the organic nitrogen from NPs is as the nitrite (NO_2^-) ion. The fast conversion of nitrite to nitrate ions, under similar photocatalytic conditions, accounts for the rise of NO_3^- ions in Fig. 2 [17–19], i.e. nitrate ions originate from nitrite ions.
2. The quantity of ammonium ions formed reaches approximately 20%–30% of the total initial organic nitrogen. Since very small quantities of NH_4^+ ions would originate from nitrite and nitrate ions under the present conditions, direct reduction of the nitro group in NP is an important degradation pathway, even in oxygenated solutions (i.e. oxygen and NPs compete for electrons).

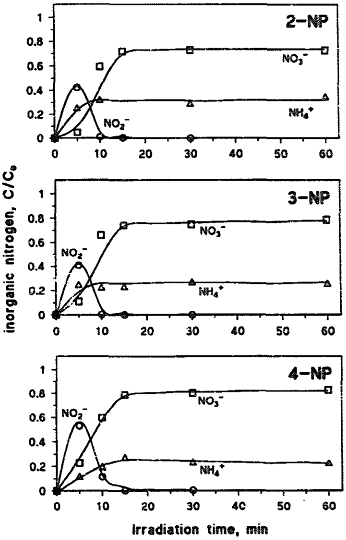


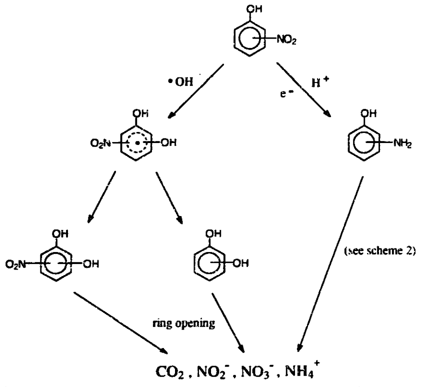
Fig. 2. Time evolution of nitrate, nitrite and ammonium ions in the degradation of 2-NP (top), 3-NP (middle) and 4-NP (bottom). Conditions as in Fig. 1.

Although comparisons have certain limitations, it is nevertheless noteworthy that the reaction of 4-NP with electrons in homogeneous solution is faster (4×10^{10} M^{-1} s^{-1}) than that with $^{\bullet}OH$ radicals (7×10^9 M^{-1} s^{-1}) by an order of magnitude [18]. The formation of the corresponding APs from NPs must implicate a sequence of reductive steps, as observed in the photocatalysed reductive transformation of nitrobenzene [20].

Scheme 1 summarizes the major initial steps in the degradation of NPs.

5. Aminophenols

The temporal photocatalysed conversion at pH 5.5 of the three APs and the corresponding disappearance of NPOC are illustrated in Fig. 3. The degradation kinetics follow a first-order rate law [21]. The rate constants ($k=(4.5\pm0.3)\times$



Scheme 1. Early steps in the oxidative and reductive photocatalytic pathways proposed for the degradation of NPs.

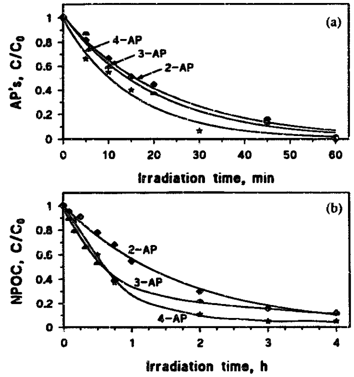


Fig. 3. (A) Photocatalytic degradation of APs (9.2×10^{-5} M) on TiO_2 (200 mg l^{-1}) at pH 5.5. (B) Corresponding disappearance of NPOC.

10^{-2}, $(5.0\pm0.5)\times10^{-2}$ and $(6.7\pm0.7)\times10^{-2}$ min^{-1} for 2-, 3- and 4-AP respectively) are smaller than those experienced for the NPs by a factor of about three, but in the reverse order for the isomers: ortho ≤ meta < para. It is somewhat surprising to note that, although the degradation of oxidizable compounds (e.g. APs) is facile in oxygenated solutions, in the present instance the degradation of APs is slower than that of the corresponding nitro analogues. The initial operating steps in the oxidative conversion of the APs appear to be electron abstraction and/or hydroxyl radical addition to yield semiquinone or quinonimine structures, which are subsequently back reduced efficiently by conduction band (e^-_{CB}) or trapped (e^-_T) electrons [20]. The slower disappearance of NPOC in APs than in NPs suggests that this back reduction may also hold for many of the primary intermediate products, such as polyhydroxyaminophenols.

A comparison of the transformation of the APs, as illustrated by their degradation (Fig. 3(A)) and the formation of inorganic nitrogen (NO_2^-, NO_3^- and NH_4^+ ions; Fig. 4), with the degradation of NPOC (i.e. total organic carbon) (Fig. 3(B)) reveals that, after 1 h of irradiation, the quantity of APs remaining is less than 5%, but the total inorganic nitrogen formed accounts for about 50% of the expected stoichiometric quantity; after 2 h of illumination, the quantity of NPOC is reduced to approximately 10% for 4-AP, approximately 23% for 3-AP and about 30% for 2-AP; by comparison, the corresponding quantity of total inorganic nitrogen formed is about 75% for 4-AP, approximately 60% for 3-AP and approximately 55% for 2-AP; after 4 h, the NPOC remaining is approximately 5% for 4-AP and about 12% for 2- and 3-AP; the total inorganic nitrogen now accounts for approximately 65%, approximately 70% and about 85% for 2-, 3- and 4-AP respectively; irradiation for 24 h leads to a near-stoichiometric recovery of the total inorganic nitrogen for the 4-AP isomer, and approximately 80%–85% for the other two isomers

These observations can be rationalized within the framework of the formation of aliphatic nitrogen-containing compounds following ring opening. These aliphatic intermediates are slowly mineralized (Scheme 2). For 2- and 3-AP, a nitro-

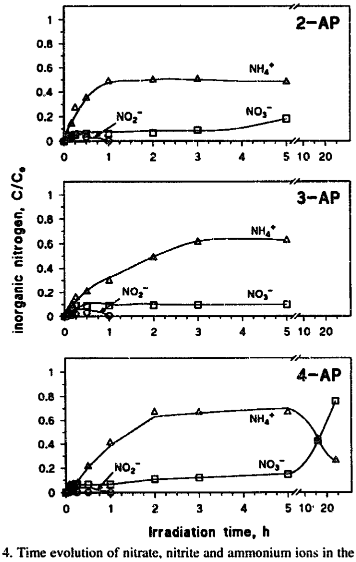
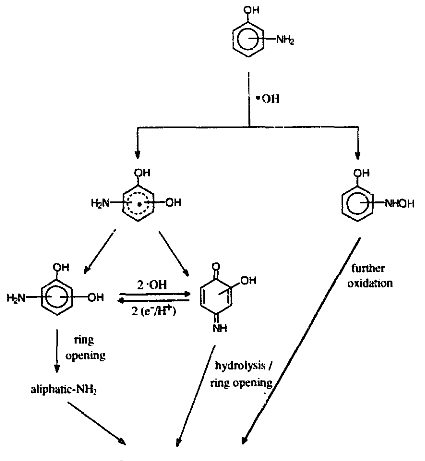


Fig. 4. Time evolution of nitrate, nitrite and ammonium ions in the degradation of 2-AP (top), 3-AP (middle) and 4-AP (bottom). Conditions as in Fig. 3.



Scheme 2. Early steps in the oxidative and reductive photocatalytic pathways proposed for the degradation of APs.

gen defect (about 15%–20%) was observed. The possible formation of volatile nitrogen-containing compounds cannot be ruled out.

It is relevant to note that the predominant inorganic nitrogen species formed in the first 5 h is the NH_4^+ ion. Nitrate ions are formed at a slower rate, reaching about 10%–15% after 5 h of irradiation. Since the NO_3^- species originates only partially from the oxidation of NH_4^+ ions under these conditions (approximately 10% of NH_4^+ is converted to NO_3^- in 5 h), approximately 5%–8% of AP degradation must proceed via an oxidative pathway involving the sequence

$$R\text{–}NH_2 \rightarrow R\text{–}NHOH \rightarrow R\text{–}NO \rightarrow R\text{–}NO_2 \xrightarrow{NO_2^- \text{ or } {}^{\bullet}NO_2} NO_3^- \quad (7)$$

It would appear that the extent of formation of nitrite/nitrate species from the NH_2 group of APs is much less important than ammonium ion formation from the nitro group of the corresponding NPs (cf. Figs. 2 and 4), even in the presence of oxygen. Since the quantity of NPs is below the detection limit, it is probable that the above sequence (Eq. (7)) also operates in the fragments generated by ring opening. An explanation may lie in the high tendency to reduction of nitrosophenol structures due to the tautomeric quinonoid structures, particularly for the ortho and para isomers. Nitrosophenols are indispensable intermediates in the above sequence when R is phenyl. Support for this hypothesis arises from the higher nitrate recovery from the photocatalysed degradation of butylamine under otherwise identical conditions [22].

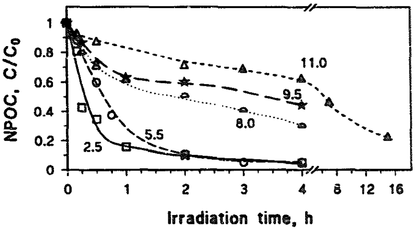


Fig. 5. Time evolution of NPOC in the degradation of 4-AP (9.2×10^{-5} M) on TiO_2 (200 mg l^{-1}) at different pH values.

At long irradiation times (24 h), NH_4^+ ions are converted to NO_3^- ions. The bottom portion of Fig. 4 illustrates the case for 4-AP. Similar observations were made for 3-AP (Fig. 4; 63% NO_3^- and 16% NH_4^+ after 24 h irradiation) and 2-AP (Fig. 4; 78% NO_3^- and 10% NH_4^+ after 24 h illumination).

6. Effect of pH on the mineralization of 4-AP

The effect of pH on the mineralization of these nitrogen-containing phenols has been investigated for the 4-AP isomer. Fig. 5 shows some significant effects when the pH is varied from 2.5 to 11.0. Near-complete mineralization (about 5% of NPOC remains) is achieved at $pH < 6$; at $pH > 8$, a much slower decrease in the quantity of NPOC is observed. Fig. 5 also shows important variations at longer irradiation times at pH 11.0. We believe that negatively charged intermediates (e.g. carboxylate species), formed when the solution pH is greater than the pH_{PZC} of TiO_2 ($pH_{PZC} \sim 6.5$ [8] under the present conditions), is responsible for this behaviour. In this regard, a careful examination of the photocatalytic transformations of small organic molecules at alkaline pH is presently underway and will be reported at a later date [23].

7. Conclusions

NPs photocatalytically degrade faster than APs under aerated and slightly acidic conditions, even though the latter phenols are more easily oxidized. This can be understood on the basis of the facile back reduction of the initial oxidation intermediates (semiquinone and quinonimine species) of APs. Quinonoid related structures formed in the initial oxidation steps are hardly oxidizable, but easily reducible structures [20,24]. These structures cannot directly originate from NPs.

Aliphatic nitrogen-containing compounds are formed during the degradation of APs. The reaction pathways, together with the formation of negatively charged intermediates, such as carboxylate species, account for the slow disappearance of total organic carbon, which is rather remarkable especially at high pH. By contrast, during the degradation of NPs, the formation of almost stoichiometric quantities of inorganic nitrogen occurs after only 15 min of irradiation.

The photocatalytic process involves both oxidative and reductive pathways for the nitro and amino substituents, as illustrated by the formation of ammonium ions from NPs and the formation of nitrite and nitrate species from APs.

Acknowledgements

Financial support for the work in Torino by CNR, MURST and the Progetto Sistema Lagunare Veneziano is gratefully acknowledged; the work in Montreal was supported by a grant from the Natural Sciences and Engineering Research Council of Canada.

References

[1] E. Pelizzetti, C. Minero, M. Vincenti, in: A. Avogadro, R.C. Ragaini (Eds.), Technologies for Environmental Cleaning: Toxic and Hazardous Waste Management, Kluwer, Dordrecht, 1994, p. 101.
[2] D. Bahnemann, J. Cunningham, M.A. Fox, E. Pelizzetti, P. Pichat, N. Serpone, in: G.R. Helz, R.G. Zepp, D.G. Crosby (Eds.), Surface and Aquatic Photochemistry, Lewis Publishers, Boca Raton, FL, 1993, p. 261.
[3] D.F. Ollis, E. Pelizzetti, N. Serpone, Environ. Sci. Technol. 25 (1991) 1522.
[4] G.K.C. Low, S.R. McEvoy, R.W. Matthews, Environ. Sci. Technol. 25 (1991) 460. K. Nohara, H. Hidaka, E. Pelizzetti, N. Serpone, Catal. Lett. 36 (1996) 115.
[5] US Environmental Protection Agency, Nitrophenols, Ambient Water Quality Criteria, Washington DC, 1980.
[6] E. Pelizzetti, C. Minero, V. Maurino, A. Sclafani, H. Hidaka, N. Serpone, Environ. Sci. Technol. 23 (1989) 1380.
[7] M. Barbeni, E. Pramauro, E. Pelizzetti, E. Borgarello, M. Gratzel, N. Serpone, Nouv. J. Chim. 8 (1984) 546.
[8] J. Augustynski, Struct. Bonding (Berlin) 69 (1988) 1.
[9] V. Augugliaro, L. Palmisano, M. Schiavello, A. Sclafani, L. Marchese, G. Martra, F. Miano, Appl. Catal. 69 (1991) 323.
[10] C. Minero, E. Pelizzetti, P. Piccinini, M. Vincenti, Chemosphere 28 (1994) 1229.
[11] E. Lipczynska-Kochany, Chemosphere 22 (1991) 529.
[12] E. Lipczynska-Kochany, Chemosphere 24 (1992) 1369.
[13] A. Alif, P. Boule, J. Photochem. Photobiol. A: Chem. 59 (1991) 357.
[14] P. O'Neil, S. Steenken, H. Van Der Linde, D. Schulte-Frohlinde, Radiat. Phys. Chem. 123 (1978) 13.
[15] C. Suarez, F. Louys, K. Gunther, K. Eiben, Tetrahedron Lett. 8 (1970) 575.
[16] B. Cercek, M. Ebert, Adv. Chem. Ser. 81 (1968) 210.
[17] I. Wagner, H. Strehlow, G. Busse, Z. Phys. Chem. (Wiesbaden) 123 (1980) 1.
[18] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 17 (1988) 513.
[19] C. Minero, P. Piccinini, P. Calza, E. Pelizzetti, New J. Chem. 20 (1996) 1159.
[20] P. Piccinini, C. Minero, M. Vincenti, E. Pelizzetti, J. Chem. Soc., Faraday Trans. 93 (1997) 1993.
[21] C. Pulgarin, J. Kiwi, Langmuir 11 (1995) 519.
[22] V. Maurino, C. Minero, E. Pelizzetti, P. Piccinini, M. Sega, in preparation.
[23] C. Minero, P. Calza, E. Pelizzetti, in preparation.
[24] C. Richard, New J. Chem. 18 (1994) 443.