Photocatalytic degradation of aromatic sulfonates present in industrial percolates

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Abstract

Photocatalytic treatment in the presence of aqueous TiO_2 suspensions was applied to an aqueous percolate containing various hydrophilic aromatic pollutants, in particular naphthalene sulfonates. A preliminary feasibility study was accomplished on standards of pure compounds, for which a degradation rate trend inversely proportional to the sulfonation degree was found, demonstrating the important role played by the substrate adsorption on semiconductor particles. The evolution of primary processes, the abatement of TOC and the release of sulfate were monitored. Further experiments performed on samples of percolates taken from an abandoned industrial site demonstrated the suitability of photocatalysis for the effective destruction and mineralization of the investigated contaminants in these complex matrices after a few hours irradiation.

1. Introduction

The reduction of fresh water resources in industrialised countries, due in part to the pollution of surface and deep waters, is a crucial problem which must be solved. Besides polluted industrial effluents, water pollution can originate from point sources such as decommissioned industrial sites. In this case the main problems arise from the possible leaching of chemicals present in large amounts as wastes or by-products left unattended after decommissioning the area. The application of suitable remediation technologies is thus required in order to prevent pollution diffusion and eventually to allow site reuse.

In the last 3 years, a multi-approach remediation study has been carried out, in the frame of a wide ranging research project [1], on the ex-ACNA industry site (Cengio, Italy) where dyes and dye intermediates were produced for several decades until about 15 years ago. The main scope of these investigations was to assess the feasibility of recently proposed treatment techniques for soil and water remediation in this abandoned industrial site.

Advanced oxidation processes (AOP) have been demonstrated to be particularly attractive for degradation of organic pollutants present in aqueous wastes since they lead to the transformation of harmful molecules into non-toxic or less toxic products [2]. Among these techniques, heterogeneous photocatalysis performed with irradiated semiconductor dispersions [3–6] is particularly suitable, since it usually leads to the complete mineralization of a broad variety of organic harmful species. The treatment of contaminated aqueous percolates using this approach could thus be of practical interest.

It is well known that photocatalysis is based on a series of light-induced redox reactions occurring when appropriate semiconductor particles are irradiated with light of energy higher than the band-gap. The process involves the generation of electron/hole pairs, species that have potentials capable of reducing or oxidising many organic compounds and, moreover, are able to react with water and oxygen giving rise to the formation of other reactive species (often radicals) which can attack the substrate [7, 8].

Among the semiconductors, TiO_2 (in its anatase form) has been largely employed since it shows very good performance, together with remarkable chemical stability, non-toxic properties and low cost.

In this work, attention was focused on a group of naphthalene sulfonates, widely used as intermediates in dye production, which represent one of the more abundant groups of hydrophilic pollutants found in the examined site, both in groundwater and in percolates taken from the disposal pits. Owing to their good water solubility, once they have reached a water stream, they can be easily transported far from the point of emission.

Although the most studied aromatic sulfonates from the point of view of their biogenic transformation and

toxicity in the environment are those classified as surfactants, the toxicity of naphthalenesulfonates has been also recognized [9].

The influence of degree of sulfonation degree on the primary process was investigated for some pure compounds representative of those found in the percolate. A sample of percolate was treated in order to verify the conditions under which the photocatalytic treatment leads to the effective abatement of total organic carbon content.

2. Experimental and methods

2.1. Materials

3-Hydroxy-2-naphthoic acid (2,3-BON, Aldrich), 1,5-Naphthalenedisulfonic acid disodium salt (1,5-NdS, Aldrich), 1,3,6-Naphthalenetrisulfonic acid trisodium salt hydrate (1,3,6-NtS, Aldrich), 6-Amino-4-hydroxy-2-naphthalenesulfonic acid (6-A-4-H-2-NS, Fluka), 2,6-Naphthalenedisulfonic acid disodium salt (2,6-NdS, Merck) were used as received. Samples of percolate were obtained from the ex-ACNA site in September 2003.

TiO$_2$ P25 from Degussa (composed of ca. 80% anatase and 20% rutile) was used as catalyst in all the experiments. The powder was previously irradiated in Solarbox, washed with water and then dried for 8 h, in order to eliminate any organic impurity. A stock suspension containing 2 g L^{-1} of catalyst in water was prepared.

Acetonitrile (Lichrosolv, Merck) and Octylamine (Fluka), were used to prepare the LC eluents. Na$_2$CO$_3$ and NaHCO$_3$ solutions (Merck) were used as eluents for the IC measurements.

All the reagents used were of analytical grade. Pure water was produced using a Milli-Q^{TM} system (Millipore).

2.2. Instruments

The degradation of individual substrates was followed by HPLC, employing a Merck-Hitachi instrument, equipped with L-6200 pumps and UV–VIS L-4200 detector. A column RP-C18 (Lichro-spher 10 mm, 4 mm i.d. × 125 mm long, from Merck) was used. The eluent was acetonitrile/octylamine (0.6 mM, pH = 6.4) 22/78% (v/v), flow rate 1.0 ml min^{-1}. The HPLC analysis of the percolate was performed by applying a linear gradient, as indicated below:

t/min	0	10	15	20	25	30	35	50
CH$_3$CN/v%	12	16	18	28	35	50	60	60

The detector wavelength chosen for the analysis of individual sulfonate compounds was 226 nm, whereas for 2,3-BON was 232 nm. The degradation of the mixture of components present in the percolate was monitored at 220 nm.

The formation of sulfate was followed by a suppressed ion chromatography, employing a Dionex DX 500 instrument equipped with a 200 mm long × 4 mm i.d. AS9-HC column (Dionex) and an electrochemical detector ED 40 (Dionex). The eluent used was an aqueous solution of K$_2$CO$_3$ (10 mM) and NaHCO$_3$ (4 mM). Elutions were performed at 30 °C, at a flow rate of 1 ml min^{-1}.

The evolution of the organic carbon (TOC) during the photocatalytic runs was followed using a Shimadzu 5000 total organic carbon analyser.

2.3. Photocatalytic experiments

For individual pure compounds, irradiations were performed in stirred cylindrical closed cells (40 mm i.d. × 25 mm high), made of Pyrex glass on 5 ml of aqueous dispersions, containing 0.3 mM of standards and 1 g L^{-1} of TiO$_2$. A 1500 W Xenon lamp (Solarbox, CO. FO. MEGRA, Milan, Italy) equipped with a 340 nm cut-off filter was employed. The temperature within the cell was ca. 55 °C.

The degradation runs performed on the percolate were carried out in a photochemical stirred batch reactor (see Figure 1) from Helios-Italquarz (Milan), equipped with a medium pressure mercury lamp (125 W). A suspension (250 ml) of TiO$_2$ (2 g L^{-1}) was
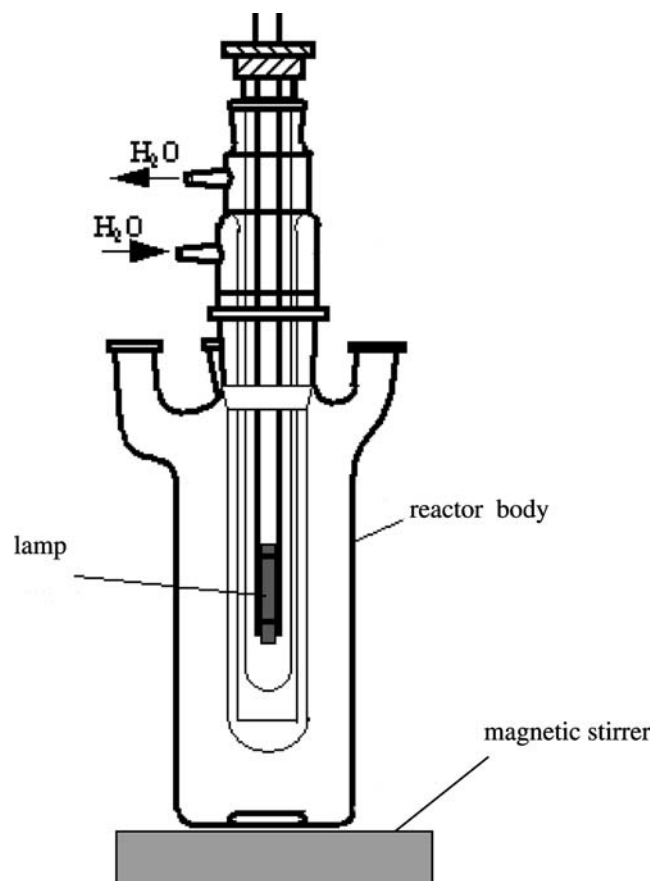

Fig. 1. Schematic representation of the employed reactor.

mixed with 250 ml of percolate. The temperature was kept at 25 °C.

5 ml of aqueous suspension taken from cells or from the laboratory reactor at various reaction times were filtered through a cellulose acetate membrane (HA 0.45μm, Millipore) before the analysis.

3. Results and discussion

The examined percolate sample is a complex mixture for which about 20 naphthalene sulfonates have been identified as major components (see Table 1). Although if the mentioned compounds can be effectively separated and determined using suitable chromatographic and electrophoretic methods, as previously described [10], it is difficult to obtain specific information concerning their degradation behaviour from the study of the real sample. During treatment, many intermediates having structures similar to those of the starting compounds already present are usually formed, thus giving rise to a complex system which cannot be described in terms of evolution of individual compounds.

For the above reasons, a preliminary investigation was performed on some pure standards having a different number of sulfonate substituents. In particular, the behaviour of 1,5-NdS, 2,6-NdS and 1,3,6-NtS was examined and, in order to investigate the effect of the presence of different hydrophilic groups and the absence of sulfonate groups, the derivatives 6-A-4-H-2-NS and 2,3-BON were also considered.

3.1. Degradation of individual components

Figure 2 shows the degradation behaviour of 2,3-BON operating in cylindrical closed cells under different experimental conditions. The first set of runs was

Table 1. Mean content of major organic components present in the percolates

Compounds
1. 1,5-naphthalendisulfonic acid
2. 1,6-naphthalendisulfonic acid
3. 2,3-BON
4. 2,6-naphthalendisulfonic acid
5. 2,7-naphthalendisulfonic acid
6. 2-hydroxy-5-naphthalensulfonic acid
7. 2-hydroxy-6-naphthalensulfonic acid
8. 2-hydroxy-8-naphthalensulfonic acid
9. 2-hydroxy-1,6-naphthalendisulfonic acid
10. 2-hydroxy-3,6,8-naphthalentrisulfonic acid
11. 2-hydroxy-1-naphthalensulfonic acid
12. 2-amino-5,7-naphthalendisulfonic acid
13. 2-hydroxy-6,8-naphthalendisulfonic acid
14. 2-hydroxy-3,6-naphthalendisulfonic acid
15. 3-aminobenzenesulfonic acid
16. 4-aminobenzenesulfonic acid

Concentration range 10–100 mg L^{-1}, compounds: 2, 5, 10, 13.
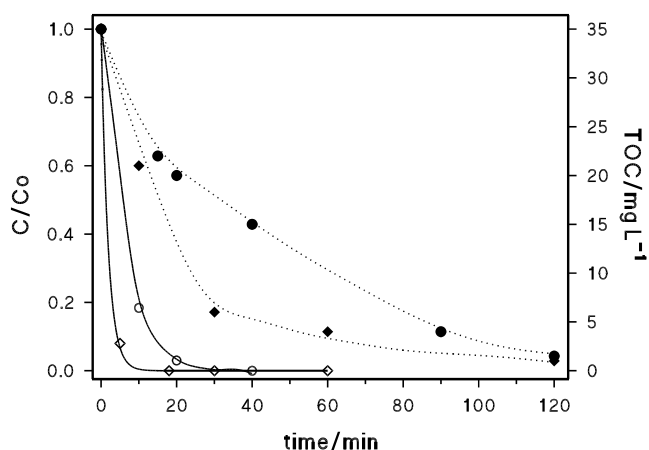Concentration up to 10 mg L^{-1}, all the other compounds.

Fig. 2. Primary process (open symbols) and TOC values (solid symbols) of 2,3-BON degradation in closed (○) and in open cell (◇).

performed keeping the cells closed, without renewal of the total amount of air present. Under these conditions, the substrate completely disappears after ca. 30 min of irradiation, but at this time the organic carbon still present in solution is ca. 50% of the initial concentration.

The corresponding HPLC profile (not shown) indicated the presence of various hydrophilic aromatic products when the complete degradation of the initial substrate was achieved. These results are consistent with those previously found for other aromatic compounds and can be explained taking into account the formation of usual polyhydroxybenzene intermediates. Complete mineralization of 2,3-BON was observed after a much longer irradiation time (ca. 120 min).

In the second set of experiments, the cells were opened for 1 min every 10 min irradiation in order to increase the oxygen content in the system. Under these conditions, a significant increase in degradation rate was observed, leading to complete substrate degradation after shorter irradiation times (ca. 15 min). The trend of TOC decrease was also faster, thus confirming the crucial role played by dissolved oxygen and by surface-adsorbed oxygen in photocatalytic treatments [11].

A similar behaviour was observed during degradation of the examined sulfonate derivatives, for which the release of SO_4^{2-} was also monitored. Figures 3 and 4 show the evolution of the photocatalytic treatment of 2,6-NdS in closed and aerated cells, respectively.

Complete abatement of 2,6-NdS was observed after 50 min, but the stoichiometric concentration of sulfate and the complete mineralization were achieved only after ca. 3 h, thus supporting the hypothesis of the presence of reaction intermediates still containing sulfonate groups, for which degradation proceeds at a slower rate. Also for this substrate, the degradation rate increased by opening the reaction cells at the previously reported time intervals and complete mineralization, with the corresponding stoichiometric formation of sulfate, was achieved after ca. 2 h.
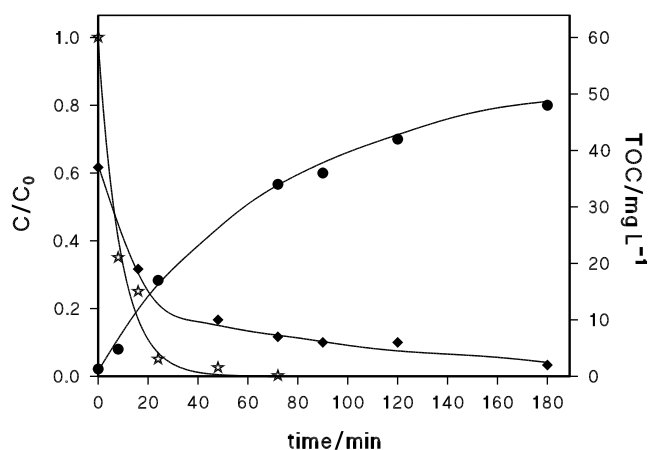
Fig. 3. Degradation of 2,6-NdS in closed cells. (★) Primary process, (◆) TOC (mg L^{-1}) and (●) sulfates evolution (mg L^{-1}).
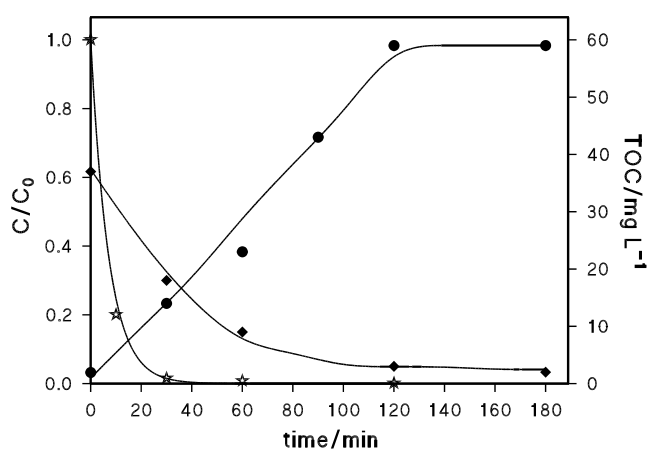

Fig. 4. Degradation of 2,6-NdS in open cells. (★) Primary process, (◆) TOC (mg l^{-1}) and (●) sulfates evolution (mg L^{-1}).

Very similar reaction patterns, not shown for the sake of brevity, were exhibited by the other investigated pure compounds. Table 2 summarizes the degradation conditions for these compounds, comparing the times necessary for their complete degradation (t_{deg}), the times corresponding to their complete mineralization (t_{min}) or, when it was not achieved, the maximum time of irradiation. In this later case, the residual TOC

Table 2. Photocatalytic degradation parameters for the investigated compounds

Compound	System	t_{deg} /min	t_{min} /min	$t_{sulfate}$ /min
2,3-BON	Closed	40	90 (5 ppm)	
	Open	18	90	
2,6-NdS	Closed	60	180	180
	Open	45	120	120
1,5-NdS	Closed	40	180	120
	Open	30	120	120
6-A-4-H-2-NS	Closed	60	120 (5 ppm)	90
	Open	40	120	90
1,3,6-NtS	Closed	120	120	120
	Open	100	120	100

concentration is reported in brackets. The time after which the stoichiometric formation of sulfate occurs is also reported ($t_{sulfate}$).

It appears that, for all the examined pollutants, both carbon mineralization and sulfate evolution are delayed with respect to the primary degradation process. Although deeper studies in this direction were beyond the scope of the present investigation, it could be reasonably hypothesized that the breaking of C–S bond is not the early step in the degradation mechanism. On the other hand, it is known from previously reported studies that sulfate is the typical end-product of sulfur-containing organics, irrespective of its initial oxidation state [5], thus no other products are expected from the photocatalytic degradation of sulfonate derivatives, as confirmed in recent investigations on sulfonated dyes [12]. The stoichiometric conversion of sulfonate groups into SO_4^{2-} was always found in our case, after long term irradiation.

In all the performed experiments, it was confirmed that primary degradation follows pseudo-first order kinetics, according to the equation:

$$-dC_{sub}/dt = k_{obs}C_{sub}$$

where C_{sub} is the substrate concentration and k_{obs} is the observed first-order rate constant. From the corresponding linear plots of $-\ln C/C_0$ vs time, the k_{obs} values were calculated and are reported in Table 3. It can be seen that the k_{obs} values are inversely proportional to the degree of sulfonation of homologous compounds and there are no significant differences between the degradation rate of isomers.

In order to explain the higher value of k_{obs} obtained for 2,3-BON, which is the most hydrophobic among the examined compounds, the influence of sorption of substrates on the surface of TiO_2 particles can be invoked. In fact, previous studies demonstrated that the attack of active radical species present at the semiconductor–solution interface on adsorbed molecules is facilitated [11, 13, 14].

Since under the reported experimental conditions the suspension pH (ca. 6.5) was near the isoelectric point of anatase [15], the TiO_2 particles are practically uncharged. For this reason, low or negligible attractive interactions are expected between the catalyst and the negatively charged naphthalene sulfonates.

In order to confirm this hypothesis, the UV–VIS spectra of 2,3-BON solutions were recorded before and

Table 3. Calculated k_{obs} (min^{-1})

Compound	k_{obs} (closed system)	k_{obs} (periodical cell opening)
2,3-BON	0.35	0.54
6-A-4-H-2-NS	0.11	0.11
1,5-NdS	0.10	0.13
2,6-NdS	0.11	0.13
1,3,6-NtS	0.030	0.033

after contact with semiconductor suspension. The substrate adsorption measured in experiment performed in the dark was ca. 20%, whereas for 2,6-NdS and 1,3,6-NtS practically no substrate adsorption was observed.

3.2. Degradation of percolate samples

Due to the complexity of the percolate matrix, it is difficult and time-consuming to perform an accurate quantitative analysis, also taking into account that the composition of the percolate varies with time and is very sensitive to external factors, such as ambient temperature, rain, wind, bacterial activity, etc. Broad changes of the analyte concentration up to an order of magnitude were, in fact, detected in percolates taken at the same sampling point under different conditions.

For the above reasons, the TOC value was chosen as the reference parameter for the monitoring of the percolate treatment and its corresponding initial value in the sample (76 mg L^{-1}) was determined. The TOC value found is compatible with the maximum content of organic matter usually recommended for an effective application of the photocatalytic approach (TOC up to ca. 1000 mg L^{-1}).

As far as the sulfur mass balance is concerned, the achievement of a constant sulfate concentration has been assumed to correspond to the complete sulfur mineralization. In addition, 8.8 mM (312 mg L^{-1}) free chloride and 460 mg L^{-1} free sulfate were already present in the initial sample. They arise mostly from their corresponding sodium salts, mixed with the residual organic products in the contaminated soil areas.

Figure 5 shows the evolution of the percolate (diluted 1:2 with the TiO$_2$ suspension); the observed TOC decrease was ca. 84% after 8 h irradiation, whereas sulfate concentration reached a constant value of 307 mg L^{-1} after 270 min. If the high content of sulfate initially present in the dilute percolate is considered, the effective contribution coming from the substrates decomposition corresponds to ca. 75 mg L^{-1}. The

reactor vessel was simply kept open during these experiments.

A significant improvement in the degradation performances was achieved by operating the saturation of the irradiated suspension with bubbled air passed continuously through the reaction vessel. Under these conditions, the value of the organic carbon in the irradiated solution dropped to ca. 1 mg L^{-1} (2.6% of the initial content) after less than 5 h, whereas the sulfates approached the observed saturation value (307 mg L^{-1}), move rapidly.

In all the photocatalytic experiments, the concentration of chloride, the other inorganic component found in the examined percolate waste, remained practically constant. This is not unexpected since this anion can take part in the photocatalytic cycle only at higher concentration levels [5].

4. Conclusions

The results clearly indicate that the photocatalytic approach is viable for the abatement of the examined hydrophilic aromatic compounds, the treatment being faster for more hydrophobic and less sulfonated molecules. Efficient reduction of TOC, together with the complete release of the main inorganic product of degradation (SO$_4^{2-}$) can be obtained by operating in photochemical reactors in the presence of abundant dissolved oxygen (air-saturated dispersions), confirming the beneficial influence of this important operating parameter.

Acknowledgements

Fig. 5. Degradation of percolate without (◇) and with a current of air (○). TOC (solid symbols), sulfate (open symbols).

References

1. E. Pramauro, A.B. Prevot, M. Lucchiari, V. Maurino, C. Minero, E. Pelizzetti and D. Vione, in P. Canepa (ed.), Extraction, Concentration and Abatement of Organic Pollutants Present in the ACNA site (Progetto Sisifo, INCA, Mestre 2002) pp. 129–149.
2. O. Legrini, E. Oliveros and M. Braun, Chem. Rev. **93** (1993) 671.
3. N. Serpone and E. Pelizzetti, Photocatalysis. Fundamental and Applications (J. Wiley, New York, 1989).
4. P. Pichat, C. Guillard, C. Maillard, L. Amalric and J.C. D'Oliveira, TiO$_2$ photocatalytic destruction of water aromatic pollutants. Intermediates; properties-degradability correlation; effect of inorganic ions and TiO$_2$ surface area, in D.F. Ollis and H. Al-Ekabi (Eds), Photocatalytic Purification and Treatment of Water and Air (Elsevier, Amsterdam, 1993), pp. 207–223.
5. D. Bahnemann, J. Cunningham, M.A. Fox, E. Pelizzetti, P. Pichat and N. Serpone, in G.R. Helz, R.G. Zepp, D.G. Crosby (eds), Aquatic and Surface Photochemistry. (Lewis, Boca Raton (FL), 1994), Ch. 21, pp. 261–316.
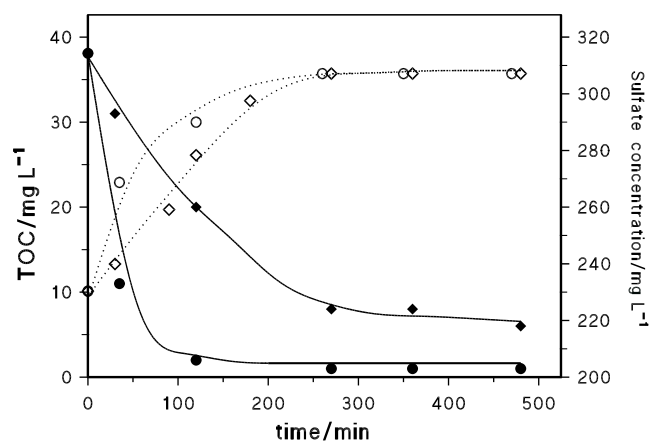6. M.R. Hoffmann, S.T. Martin, W. Choi and D.W. Bahnemann, Chem. Rev. **95** (1995) 69.

7. C.S. Turchi and D.F. Ollis, *J. Catal.* **119** (1989) 483.

8. L.P. Childs and D.F. Ollis, *J. Catal.* **66** (1980) 383.

9. M. Castillo, M.C. Alonso, J. Riu, M. Reinke, G. Klöter, H. Dizer, B. Fischer, P.D. Hansen and D. Barceló, *Anal. Chim. Acta* **426** (2001) 265.

10. S. Angelino, A. Bianco Prevot, M.C. Gennaro and E. Pramauro, *J. Chromatogr. A* **845** (1999) 257.

11. H. Gerischer and A. Heller, *J. Electrochem. Soc.* **139** (1992) 113.

12. A. Bianco Prevot, A. Basso, C. Baiocchi, M. Pazzi, G. Marcì, V. Augugliaro, L. Palmisano and E. Pramauro, *Anal. Bioanal. Chem.* **378** (2004) 214.

13. S.T. Martin, J.M. Kesselman, D.S. Park, N.S. Lewis M.R. Hoffmann, *Environ. Sci. Technol.* **30** (1996) 2535.

14. J.M. Kesselman, N.S. Lewis and M.R. Hoffmann, *Environ. Sci. Technol.* **31** (1997) 2298.

15. J. Augustynski, *Struct. Bonding.* **69** (1998) Berlin, Chap.1.