ELSEVIER
Journal of Photochemistry and Photobiology A: Chemistry 112 (1998) 271–276
Journal of Photochemistry and Photobiology A:Chemistry

EPR spin-trapping of hydroxyl radicals onto photocatalytic membranes immobilizing titanium dioxide, and spin adduct competition, as a probe of reactivity with aqueous organic micropollutants [1]

Roberto Morelli [a], Ignazio Renato Bellobono [b,*], Claudia Maria Chiodaroli [b], Sergio Alborghetti [b]

[a] *C.N.R., Centre for the Study of Relationships between Structure and Reactivity, Milan I-20133, Italy*
[b] *Department of Physical Chemistry and Electrochemistry, University of Milan, via C. Golgi, 19, Milan I-20133, Italy*

Accepted 14 September 1997

Abstract

Spin-trapping of photogenerated $^{\bullet}$OH radicals, with electron paramagnetic resonance (EPR) detection of spin adducts, has been evidenced on to photocatalytic membranes, prepared by photografting, and immobilizing 30 ± 3 wt.% TiO_2 semiconductor. By employing the known rate constant for the reaction of $^{\bullet}$OH radicals with the spin-trap (DMPO), rate constants for the reaction of $^{\bullet}$OH radicals with a given substrate could be obtained by a competition kinetic scheme, using the initial rates of the first step of photodegradation of the substrate. This method used, for a parallel series of runs, also membranes, immobilizing 7 wt.% of trialkyl vanadates as photocatalytic promoters together with the semiconductor, able to yield unitary quantum yields for the photogeneration of $^{\bullet}$OH radicals from semiconductor. Quantum yields for the non-photocatalytically promoted semiconductor membrane could thus be obtained. This method has been validated with phenol, 4-chlorophenol, 2,4-dichlorophenol, atrazine, propazine, prometryn, ametryn, and formate ion, and compared with a similar technique, set up recently in the literature, based on production of $^{\bullet}$OH by homogeneous photolysis of H_2O_2 and direct EPR measurements of the rate of spin adduct formation. © 1998 Elsevier Science S.A.

Keywords: TiO_2 photografted membranes; $^{\bullet}$OH radicals rate constants; Phenols; *S*-triazines; Formate ion

1. Introduction

During the last decade an innovative method for production of reactive membranes has been set up, the membranes having been characterized and tested in a variety of applications (for reviews see Refs. [1–3]). This technology for membrane manufacture is based on a very fast photografting of suitable monomeric and pre-polymeric blends, rheologically controlled, onto convenient supports. Immobilization of massive amounts of sorbents, or catalysts, or reagents occurs within the regular pores of the membrane, by maintaining completely, or nearly completely, active their surface area. Among the manifold applications investigated, advanced oxidation processes have been developed by use of photocatalytic membranes immobilizing TiO_2 and promoting photocatalysts, up to the pre-industrial experience for mineralization of organics in drinking waters and waste waters, as well for inducing integral biodegradability in wastes containing toxic chemicals [4–7] (see also references cited therein). These photocatalytic membranes technologies rely on the formation and use of short-lived oxidative radicals (mainly hydroxyl, but also hydroperoxy radicals, these latter in acid–base equilibrium with oxygen radical anions) generated on to the immobilized semiconductor, following electronic excitation processes which are well known and established, both in pigment [8] and semiconductor [9] TiO_2. Evidence for the formation of reactive hydroxyl radicals was recently obtained on aqueous suspensions of free TiO_2, by the use of spin-trapping electron paramagnetic resonance (EPR) spectroscopy [10]. Otherwise, just previously, it had been elaborated a procedure for determining the primary rate constants for bimolecular attack of $^{\bullet}$OH radicals on micropollutant molecules employing a competition method based on the technique of spin-trapping with detection by EPR spectroscopy [11]. This method produces $^{\bullet}$OH radicals by photolysis of hydrogen peroxide, which has long been known to photolyze cleanly to produce these radicals.

---

* Corresponding author.

[1] Part 63 of the series: 'Photosynthetic Membranes'.

1010-6030/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved
PII S1010-6030(97)00287-6

it thus requires a less expensive facility than that necessary for the pulse radiolysis technology, and is quite applicable also to the production of $^{\bullet}$OH radicals by irradiation of photocatalytic membranes, such as those operated in the present series of papers.

In the investigations performed here, we have first checked the possibility of using a photocatalytic membrane to generate $^{\bullet}$OH radicals heterogeneously in the cavity of an EPR device, when irradiated in situ, in a solution containing dissolved oxygen. Afterwards, we have developed a very simple and convenient membrane technology for evaluating the absolute rate constants for the first step of attack of $^{\bullet}$OH radicals, so produced, on micropollutant molecules. To this aim, the same competition method, by spin-trapping, set up recently [11], has been used, but employing the chemical measurement of initial rate constants of degradation of the substrates, instead of spin-trapping with detection by EPR spectroscopy. As, to this purpose, the measurement of quantum yield for the production of $^{\bullet}$OH radicals by the immobilized semiconductor on to the membrane is necessary, we have devised parallel runs to be carried out on to membranes able to yield a practically unitary yield for this process, as resulting from the validation study reported here. These latter membranes immobilized a synergistic mixture of tri(*t*-butyl)– and tri-(*i*-propyl)vanadate(V), as photocatalytic promoter of immobilized TiO_2, which had proved very efficient [6,12], also as transporters of labile oxygen radical species [13].

2. Experimental

2.1. Materials

The spin-trap used was 5,5′-dimethylpyrroline, *N*-oxide (DMPO), from Aldrich. It was stored at − 20°C in a freezer under nitrogen. It is well known to react with radicals, such as $^{\bullet}$OH, to form relatively stable spin adducts (nitroxides) [11]. Open bottles of DMPO were also stored in the freezer, and only used if the liquid was clear and colorless.

The following compounds were used as substrates: phenol, 4-chlorophenol, 2,4-dichlorophenol, atrazine (6-chloro-N^2-ethyl-N^1-*iso*-propyl-1,3,5-triazine-2,4-diamine), propazine (6-chloro-N^2,N^4-di-*iso*-propyl-1,3,5-triazine-2,4-diamine), ethyl-1,3,5,triazine-2,4-diamine), prometryn (N^2,N^4-di-*iso*-propyl-6-methylthio-1,3,5-triazine-2,4-diamine), ametryn (N^2-ethyl-N^4-*iso*-propyl-6-methylthio-1,3,5-triazine-2,4-diamine), and formate ion. With the exception of *s*-triazines, they were all ≥99.5% pure compounds, obtained from Aldrich. The *s*-triazines were kindly supplied by Oxon Italy (Pero, Milan, I), as samples purified from technical products, up to 99.1–99.4% purity.

2.2. Photocatalytic membranes

Photocatalytic membranes (PHOTOPERM® membranes CPP/313) were supplied by Chimia Prodotti e Processi (Cinisello Balsamo, Milan, I). They immobilized 30 ± 3 wt.% of TiO_2, and were prepared industrially by a pilot plant, as described [4]. In some of the membranes used and tested in the present paper, 7.0 wt.% of a synergistic mixture of tri-(*t*-butyl)– and tri-(*i*-propyl)vanadate(V) was co-immobilised with the semiconductor dioxide, as photocatalytic promoter. This kind of membrane had shown excellent performance with respect to integral photomineralization of organics [4,6,12]: this performance was at least 10× greater than that exhibited by membranes immobilising TiO_2 alone.

2.3. Apparatus and procedure

Stock solutions of the above substrates in 1.0 mM phosphate buffer (pH = 7.0), at constant ionic strength, were diluted with the buffer solution to obtain the final concentrations of the investigated compounds, in the range 0.01–0.15 mM. Solutions were prepared with ultrapure water (maximum content of heavy metal ions 0.004 mg kg^{-1}): this was obtained by cross-flow ultrafiltration on composite membranes immobilizing active carbon and nuclear grade ion exchange resins, as described [14]. To each sample of solution thus prepared, sufficient volumes of a 50 mM DMPO solution in the phosphate buffer were added, so as to reach the final DMPO concentration of 1.0 mM, with a more or less strong excess of the latter with respect to the final concentration of substrates. Solutions were freshly prepared in the dark, just before experiments.

The initial rate of disappearance of all substrates, with the exception of formate ion, was measured by following analytically their concentration, as a function of time, by the technique of solid-phase microextraction (SPME), followed by GC–MS quantitative analysis, as used in previous work [5]. SPME is based on the direct introduction into the aqueous sample of a fused silica fibre coated with an adsorbent material, an adsorption of the analytes on to the fibre coating, and a subsequent thermal desorption directly into the GC, without any clean-up, pre-concentration, or extraction step.

The SPME devices (Supelco, Milan, I) used a fibre coated with a short (10 mm) thin (85 μm) layer of polyacrylate. In order to increase adsorption affinity towards chlorophenols and *s*-triazines, the acrylate layer was previously treated, by grafting photochemically a chlorinated rubber copolymer (Chimia Prodotti e Processi). The fibre was housed in a stainless-steel needle which allowed for penetration of the membrane closing the solution sample vial (1 ml). The fibre was pushed out of the housing and exposed directly to the solution sample for 30–150 min, following the greater or lesser ease of adsorption of the analyte on to the fibre. This time was optimized during the calibration with standard solutions. Afterwards, the fibre was pulled into the housing; the SPME device was removed from the sample and inserted into the injection port of the GC–MS system. For the thermal desorption and substrate analysis, a Varian 3400 with a septum equipped programmable injector was used. In the GC oven a 30 m × 0.52 nm DB5MS megabore column was installed. The temperature programme was optimized during the calibration step. Usually it maintained 50°C for 1 min, followed by a temperature rise of 6°C/min up to the maximum temperature (220–260°C), which was held for 4 min.

As carrier gas He was used at a flow rate of 25 ml/min. The GC was interfaced via jet-separator (0.3 Torr in the separator and 0.01 Torr in the analyser) and a transfer line (270–290°C) to a ITS40 ion trap (ITMS). The ion trap was operated at 300°C in the electron impact mode, scanning from 35 m/z to 550 m/z in 1.5 s. After separation into the GC injection port, the SPME fibre was pushed out and thermally desorbed for 5 min at 270–295°C. By this way the substrates were transferred from the SPME coating to the GC column to be chromatographed. The GC–ITMS data were acquired on a 386/387 Compaq PC with Saturn I software (Varian). Substrates were thus identified by their mass spectrum. Quantification was based on standard solutions, using, as internal standard, standard solutions with fully deuterated substrates (Supelco).

Finally, the initial rate of disappearance of formate was measured by microcoulommetric titration [15], and the formation of hydrogen peroxide, when needed, by the spectrophotometric method, using titanium (IV) in sulphuric acid solution [16].

Experiments for each concentration of a given substrate were repeated several times (at least four) for every stock solution. For every compound, at least three different stock solutions were prepared and examined by the above procedures.

For EPR detection of the spin adduct produced by photocatalytic membranes immobilizing TiO_2, solutions containing 50 mM DMPO only, in ultrapure water, were introduced in a pyrex glass capillary, holding a tiny piece of membrane. The capillary was finally inserted into the cavity of EPR instrument, without any exclusion of air, and irradiated with a UV lamp. The latter was a 500 W high pressure mercury arc lamp (Helios Italquartz, Milan, I), placed at a 25 cm distance from the cavity, to protect it from heating. EPR spectra were recorded on a Varian E-line Century Series EPR, as a function of time. EPR digitized spectra were transferred to a GOULD NP1 main-frame computer through an IBM PS2/80, in order to fit them using the program EPR85 [17].

Irradiation experiments, during the competition kinetic study of hydroxyl radicals with substrate and DMPO, were carried out in the same geometrical conditions as those described for EPR measurements, with the only difference that the solutions, prepared as described above, were introduced into cells formed by pyrex glass tubes, instead than in capillaries. The membranes were placed just on the walls of the cell.

The photon flux reaching the membrane in the cell was integrally absorbed by the membrane, within the absorption range of semiconductor, given the massive amount of immobilized semiconductor per unit membrane surface, and the geometrical position of the membrane inside the cell. The whole radiation flux could be evaluated, by standard ferrioxalate actinometry [18]. By measuring the emission spectrum of the lamp and its integral in the wavelength range of absorption of semiconductor, absorbed photons could then be obtained, as $(1.8 \pm 0.1) \times 10^{-11}$ Einstein s^{-1} ml^{-1} (of solution inside the cell, this latter being introduced in standard amounts, to match the membrane height exactly). The cell was arranged in an ultrasonic field, in order to reach a very strong flow of permeating liquid through the membrane, and a vigorous stirring, so that the reaction between $^{\bullet}$OH radicals in the surface of the membrane and DMPO or substrate could not be limited by diffusion.

3. Results and discussion

3.1. EPR detection of hydroxyl radicals on to irradiated photocatalytic membranes

Typical EPR spectra of spin adducts DMPO–$^{\bullet}$OH are reported in Fig. 1 (upper part), which shows increase of signal intensity when solutions containing 50 mM DMPO, in the presence of the membrane, were irradiated. The signal intensity increased with time up to a maximum, corresponding to equal rates of photochemical formation and thermal degradation. Thermal degradation was given by two concur-

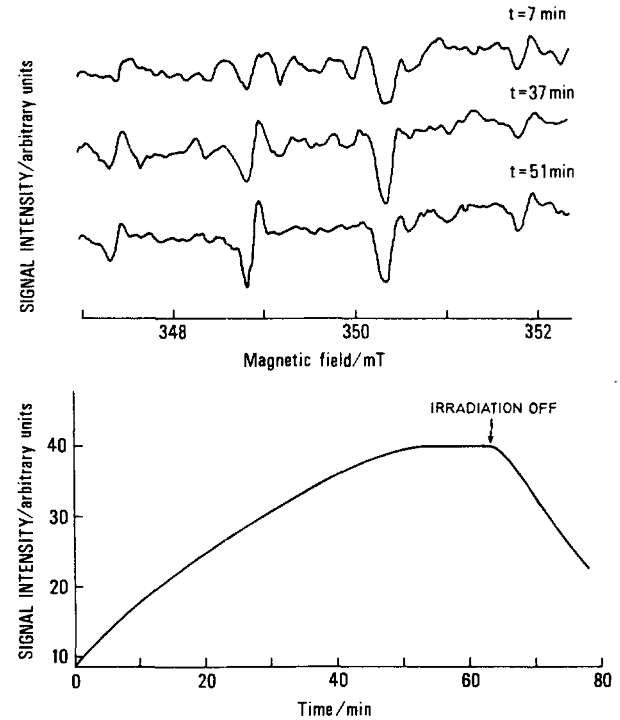

Fig. 1. Upper part: EPR spectra of the DMPO–$^{\bullet}$OH spin adduct, recorded during irradiation of PHOTOPERM CPP/313 standard membranes, immobilizing 30 ± 3 wt.% TiO_2, in the presence of 50 mM DMPO solutions, at various times of irradiation. EPR spectrometer settings: center field = 349.5 mT; sweep width = 10.0 mT; scan time = 60 s. Lower part: Time course of the DMPO–$^{\bullet}$OH signal maximum (low field central peak) of spectra, such as those of the upper part of this figure, during irradiation, and when irradiation was stopped.

rent processes, the first of which was the very fast bimolecular reaction of 2$^{\bullet}$OH radicals to yield H_2O_2, as is well known, and the second of which was the relatively slow decomposition of the spin adduct itself to give non-radical products. As a consequence, after the appearance of this maximum, a gradual decrease of the intensity took place, when irradiation was stopped, as shown in Fig. 1 (lower part), where the signal intensity, in arbitrary units, is reported as a function of time. The experimental evidence of the formation of $^{\bullet}$OH radicals on to the membrane immobilising the semiconductor is thus very clear.

By carrying out experiments, without introduction of DMPO, the presence of H_2O_2, at the end of irradiation, could be detected. No photolysis of H_2O_2 was possible in our experimental conditions, owing to the use of pyrex glass, absorbing all radiation at wavelengths where absorption by H_2O_2 occurs. By H_2O_2 analysis, and by knowing the photon flux absorbed by the membrane, the quantum yield $\Phi(^{\bullet}OH)$ could be calculated, by supposing that H_2O_2 was entirely generated by $^{\bullet}$OH radicals. This should be regarded as an approximate evaluation, since, on one side it is possible that H_2O_2 may be consumed by acting as scavenger of conduction band electrons, but, on the other side, it is also probable that dissolved oxygen exerts this scavenging action, with production of labile radical species, which may ultimately lead, partly at least, to hydrogen peroxide. When using membranes which immobilised semiconductor alone, without any addition of the trialkyl vanadates as photocatalytic promoter, $\Phi(^{\bullet}OH)$ values of 0.09 ± 0.01 were obtained, as mean values, integrated overall the absorption range of semiconductor. These relatively low yields may receive explanation, by taking into account the contribution of electron-hole recombination processes, besides the considerations above. On the contrary, when membranes co-immobilising the trialkyl vanadates were employed, $\Phi(^{\bullet}OH)$ values increased to 0.94 ± 0.06. This may be rationalized, on one side, by the positive action of vanadium(V) catalysts in reducing or almost entirely suppressing the electron-hole recombination process, possibly by sacrificial reaction with conduction band electrons, followed by reversible oxidation by O_2, and, on the other side, by the facilitated oxygen transport towards the conduction band electrons of irradiated semiconductor. This should mean that the photopromoted membranes, being able to yield practically unitary quantum yields for $^{\bullet}$OH radicals production from semiconductor, should be the ideal candidate to act as probes of reactivity for membrane reactions with these radicals. In order to check and to study this possibility, a validation method has been examined, similar to the Kochany–Bolton method [11]. While, however, this latter, based on the competition of $^{\bullet}$OH radicals between DMPO and selected substrates, used spin-trapping with detection by EPR spectroscopy to measure the competition, and photolysis of H_2O_2 to produce $^{\bullet}$OH radicals, the technique devised in this paper employed the chemical measurement of initial rate constants of degradation of the substrates, and the photocatalytic membranes, with or without the trialkyl vanadates as promoters, to generate the $^{\bullet}$OH radicals, with quantum yields $\Phi(^{\bullet}OH)$ for production of these radicals equal to 0.09 and 0.94 respectively, as evaluated above.

3.2. The model of competitive kinetics

Experimental results of competitive kinetics of $^{\bullet}$OH radicals with DMPO and substrate (S) have been analyzed by the following kinetic model

$$TiO_2 \rightarrow {}^{\bullet}OH \qquad (1)$$

(rate of formation of $^{\bullet}$OH radicals: $0.09\,J$)

$$^{\bullet}OH + DMPO \rightarrow DMPO\text{–}{}^{\bullet}OH \text{(kinetic constant } k_2) \qquad (2)$$

$$^{\bullet}OH + S \rightarrow \text{product (kinetic constant } k_3) \qquad (3)$$

(rate of disappearance of S: $-dC_S/dt$) and, with membranes co-immobilizing the trialkyl vanadates,

$$(TiO_2)_{cat} \rightarrow {}^{\bullet}OH \qquad (1a)$$

(rate of formation of $^{\bullet}$OH radicals: $0.94\,J$)

$$^{\bullet}OH + DMPO \rightarrow DMPO\text{–}{}^{\bullet}OH \text{(kinetic constant } k_2) \qquad (2a)$$

$$^{\bullet}OH + S \rightarrow \text{product (kinetic constant } k_3) \qquad (3a)$$

(rate of disappearance of S: $(-dC_S/dt)_{cat}$) where J are the fluxes of absorbed photons (Einstein $s^{-1}\,l^{-1}$), t is time, C are concentrations, and the cat subscript denotes experimental runs with membranes additivated with trialkyl vanadates as photocatalytic promoters. In kinetic scheme above, the photolysis of S is entirely neglected, as it has been generally found relatively insubstantial during experiments with photocatalytic membranes [19], and particularly in those of the present work, where only long wavelength radiation is absorbed by the membranes. As to the possible uncatalysed photooxidation, which is relatively important, in the presence of stoichiometric amounts of hydrogen peroxide [19], or of ozone, it has been found to contribute, to no more than a few percent to overall degradation, in blank runs without the membranes and in experimental conditions of this work, in which only dissolved oxygen was initially present.

On applying a steady-state analysis to the above mechanism, as has been done in the Kochany–Bolton methodology [11], the concentration of $^{\bullet}$OH radicals may be evaluated:

$$C_{^{\bullet}OH} = \Phi(^{\bullet}OH)J/(K_2\,C_{DMPO} + K_3\,C_S) \qquad (4)$$

where $\Phi(^{\bullet}OH)$ is equal to 0.09 and 0.94 in standard and photopromoted membranes respectively, to which a $C_{^{\bullet}OH}$ and a $(C_{^{\bullet}OH})_{cat}$ correspond respectively. By Eqs. (3) and (3a) it follows that

$$(-dC_S/dt) = k_3\,C_S C_{^{\bullet}OH} \qquad (5)$$

and

$$(-dC_S/dt)_{cat} = k_3\,C_S(C_{^{\bullet}OH})_{cat} \qquad (5a)$$

By measuring the initial rates of disappearance of substrate, and by combining Eq. (4) with Eq. (5) or Eq. (5a), in the

Table 1
Rate constants k_3 (M^{-1} s^{-1}) (see Eq. (3)), at pH 7.0, for the reaction of ˙OH radicals, with phenol, chlorophenols, *s*-triazines, and formate ion, as substrates, determined, on to photocatalytic membranes, with (B) and without (A) trialkyl vanadates as photocatalytic promoters of immobilised TiO_2, by the competition method with 5,5′-dimethylpyrroline, *N*-oxide, and the disappearance rate of substrates. Range of literature values [11], obtained by several variants of the Kochany–Bolton model, is indicated in the last column

Substrate	$k_3/(10^{10}$ M^{-1} $s^{-1})$		
	A [a]	*B* [a]	Range of literature values [11]
Phenol	1.5 ± 0.2	1.3 ± 0.2	1.45–1.70
4-Chlorophenol	2.4 ± 0.2	2.5 ± 0.2	2.65–3.20
2,4-Dichlorophenol	4.1 ± 0.4	4.6 ± 0.4	2.65–3.82
Formate ion	0.32 ± 0.3	0.31 ± 0.3	0.27–0.33
Atrazine	0.95 ± 0.08	0.89 ± 0.09	–
Propazine	1.1 ± 0.1	1.0 ± 0.1	–
Prometryn	1.3 ± 0.2	1.4 ± 0.1	–
Ametryn	1.5 ± 0.1	1.5 ± 0.1	–

[a] Uncertainties are given as probable errors of the mean of at least four experimental runs.

cases of standard or photopromoted membranes respectively, k_3 values could be easily calculated in both cases, by assuming that $k_2 = 4.3 \times 10^9$ M^{-1} s^{-1}, as done in the Kochany–Bolton model [11].

To test this method and to compare it with the Kochany–Bolton model [11], we have first used phenol, 4-chlorophenol, 2,4-dichlorophenol and formate as substrates, for which many literature data are available [11], well established also from pulse radiolysis studies. Afterwards, the investigation has been extended to four model *s*-triazines, atrazine, propazine, prometryn and ametryn, the photomineralization data for which are available on to photocatalytic membranes [4,12,20]. The k_2 values, thus obtained, are reported in Table 1, where also the range of the different values determined by several variants of the Kochany–Bolton method [11] is indicated, for comparison.

It may be easily observed that the rate constants for the ˙OH reaction with the substrates examined by the Kochany–Bolton method [11] agree very well, for phenol and formate ion. For 4-chlorophenol and 2,4-dichlorophenol, values of this work are just outside the range of values determined by the time course of EPR signal [11], from the lower and the upper side respectively. For *s*-triazines, the closeness of rate constants values may be remarked, due to similarity of structure. However, the methylthio group of prometryn and ametryn in 6-position, instead of the chlorine of atrazine and propazine, in the same position, seems to carry along a greater reactivity, even if with an effect which is near to the limit of experimental uncertainty.

Anyway, two facts point out to the reliability of the model proposed. The first one is the validation resulting from the comparison with literature values [11], these latter in turn, having been collated with the photolysis or pulse radiolysis methods. The second experimental fact, in connection with the first one, is the close agreement between values determined with standard membranes and those obtained on to photopromoted membranes. This indirectly confirms that the quantum yields values used for the calculation (see Eq. (4)) are substantially correct.

4. Conclusions

(i) The spin-trapping competition method with DMPO, studied in this work, has been shown to be effective for determining absolute rate constants of ˙OH radicals, generated at the membrane surface or within the membrane pores, where the immobilized TiO_2 semiconductor is irradiated, with different kinds of substrates.

(ii) When using a photocatalytic membrane immobilizing trialkyl vanadates, together with TiO_2, quantum yield for production of ˙OH radicals, by irradiation, is substantially unitary. This explains the excellent performance of these membranes during photooxidation and photomineralization of organic micropollutants, in air and water.

(iii) Photocatalytic membranes may consequently be employed satisfactorily as probes to study reactivity of ˙OH radicals, not only with micropollutants, but likely with antioxidants, e.g., to establish behaviour, in vitro or in vivo, of drugs, food products, and so on, particularly for the relevant aspects of these free radicals in biology and medicine.

Acknowledgements

Financial contribution by Italian Ministry of University and Scientific Research (MURST), within the research program on environmentally friendly processes, coordinated by the National Consortium of Environmental Chemistry (INCA), is gratefully acknowledged. The research staff of Chimia Prodotti e Processi, for carrying out analytical determinations, is also gratefully acknowledged.

References

[1] I.R. Bellobono, Some innovative applications of photografting processes, Textile dyeing and printing, Sorbent and reactive composite membranes, in: I.R. Bellobono (Ed.), Grafting Processes onto Polymeric Fibres and Surfaces, Scientific and Technological Aspects, Vol. 85, Conf. Proc. Univ. Milan, Milan, I, 1990, pp. 119–213.

[2] I.R. Bellobono, L. Righetto, Photochemical production of composite membranes and reinforced plastics, in: J.P. Fouassier, J.F. Rabek (Eds.), Radiation Curing in Polymer Science and Technology, Vol. 4, Elsevier, Barking, UK, 1993, pp. 151–177.

[3] I.R. Bellobono, E. Selli, Photochemical production of composite materials and membranes: mechanistic aspects and applications, in: N.S. Allen, M. Edge, I.R. Bellobono, E. Selli (Eds.), Current Trends in Polymer Photochemistry, Ellis Horwood, London, UK, 1995, pp. 102–129.

[4] I.R. Bellobono, B. Barni, F. Gianturco, J. Membr. Sci. 102 (1995) 139.

[5] B. Barni, A. Cavicchioli, E. Riva, L. Zanoni, F. Bignoli, I.R. Bellobono, F. Gianturco, A. De Giorgi, H. Muntau, L. Montanarella, S. Facchetti, L. Castellano, Chemosphere 30 (1995) 2861.

[6] F. Gianturco, L. Vianelli, L. Tatti, F. Rota, P. Bruzzi, L. Rivas, I.R. Bellobono, M. Bianchi, H. Muntau, Chemosphere 33 (1996) 1531.

[7] L. Tatti, D. Niego, F. Rota, P. Bruzzi, A. Moroni, I.R. Bellobono, M. Bonardi, M.M. Bianchi, H. Muntau, Chemosphere 34 (1997) 41.

[8] M. Edge, J. Robinson, Application of microwave methods to study the photoactivity of titanium dioxide in polymers, in: N.S. Allen, M. Edge, I.R. Bellobono, E. Selli (Eds.), Current Trends in Polymer Photochemistry, Ellis Horwood, London, UK, 1995, pp. 238–254.

[9] A.L. Linsebigler, G. Lu, J.T. Jr. Yates, Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results, Chem. Rev. 95 (1995) 735.

[10] H. Hidaka, J. Zhao, E. Pelizzetti, N. Serpone, J. Phys. Chem. 96 (1992) 2226.

[11] J. Kochany, J.R. Bolton, J. Phys. Chem. 95 (1991) 5116.

[12] F. Gianturco, C.M. Chiodaroli, I.R. Bellobono, M.L. Raimondi, A. Moroni, B. Gawlick, Fresenius Environ. Bull. 6 (1997) 461.

[13] I.R. Bellobono, R. Morelli, C.M. Chiodaroli, J. Photochem. Photobiol., A: Chem. 105 (1997) 89.

[14] I.R. Bellobono, R. Tacchi, E. Selli, F. Muffato, Photosynthetic membranes for pure and ultrapure water production, in: A. Green (Ed.), Membrane Separation Processes, BHRA, Cranfield, UK, 1989, pp. 187–193.

[15] S. Siggia, Instrumental Methods of Organic Functional Group Analysis, Wiley-Interscience, New York, 1972, pp. 126–128.

[16] S. Siggia, Instrumental Methods of Organic Functional Group Analysis, Wiley-Interscience, New York, 1972, p. 177.

[17] M. Barzaghi, M. Simonetta, J. Magn. Reson. 51 (1983) 175.

[18] J.G. Calvert, J.N. Pitts, Photochemistry, Wiley, New York, 1966, p. 627.

[19] I.R. Bellobono, A. Carrara, B. Barni, A. Gazzotti, J. Photochem. Photobiol., A: Chem. 84 (1994) 83.

[20] I.R. Bellobono, P.L. Pinacci, G.C. Riva, C. Lagrasta, submitted to publication.