

Laboratory-scale photomineralisation of *n*-alkanes in aqueous solution, by photocatalytic membranes immobilising titanium dioxide[†]

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ABSTRACT. Kinetics of photocatalytic oxidation of methane, ethane, *n*-heptane, *n*-decane, and *n*-dodecane, to yield intermediates, and photomineralisation of intermediates, to yield carbon dioxide and water, was studied in aqueous solution, by a laboratory-scale photoreactor and photocatalytic membranes immobilizing 30 ± 3 wt.% of TiO₂, in the presence of stoichiometric hydrogen peroxide as oxygen donor. The whole volume of irradiated solution was 4.000 ± 0.005 L, the ratio between this volume and the geometrical apparent surface of the irradiated side of the photocatalytic membrane was 3.8 ± 0.1 cm, and the absorbed power 0.30 W/cm (cylindrical geometry). A kinetic model was used, by which mineralisation of substrate to CO₂ was supposed to occur, by kinetic constants *k*₁, through one single intermediate, mediating the behaviour of all the numerous real intermediates formed in the path from the substrate to CO₂ (kinetic constants of formation of the latter being *k*₂). A competitive Langmuirian adsorption of both substrate and “intermediate” was also supposed to be operative, as expressed by apparent adsorption constants *K*₁ and *K*₂, possessing a, partly at least, kinetic significance. By Langmuir-Hinshelwood treatment of initial rate data, starting values of the *k* and *K* couples were obtained, from which, by a set of differential equations, the final optimised parameters, *k*₁ and *K*₁, *k*₂ and *K*₂, were calculated, able fit the whole photomineralisation curve, and not only its initial segment, as the Langmuirian parameters do. The parameters of present work are critically compared with those obtained in two preceding set of studies relative to *n*-alkanoic acids and to *n*-alkanols. They are interpreted on the basis of a closer behaviour of hydrocarbons to alkanols, from the photocatalytic point of view, than to carboxylic acids are. Discussion of limiting effective quantum yields, and their comparison with maximum, theoretical values, are also carried out.

1. INTRODUCTION

In a preceding set of works of this series [1, 2], the TiO₂-mediated photomineralisation of methanoic, ethanoic, *n*-propanoic, and *n*-decanoic acids was investigated at a laboratory-scale level, in a reactor with cylindrical geometry, both with variable, polychromatic, and with monochromatic 254 nm radiation, in the absorption range of semiconductor, in order to obtain information about the influence of radiant power and concentration of substrate on quantum yields. In these studies, a kinetic model, already used successfully in previous literature, was employed, to interpret photodegradation curves up to complete mineralisation. Quantum yields Φ₀, calculated from initial rates, followed an apparently Langmuirian function of initial concentration, by which Φ_∞ values at “infinite” concentration could be obtained. Limiting Φ_∞ values at 0.10–0.35 W/cm, relative

to polychromatic irradiation substantially coincided with those measured at 0.31 W/cm during monochromatic irradiation at 254 nm. By having thus established that quantum yields of photomineralisation are independent of radiation wavelength, within the absorption range of semiconductor, but dependent on radiant power, the best way to compare different sets of experiments is to refer to series of values obtained with the lowest possible radiant power, in the range above. In fact, at low radiant power values, up to about 0.45 W/cm, quantum yields are independent on radiant power themselves, whatever the radiation wavelength may be.

For this reason, in a successive work [3] experiments on *n*-alkanols, were carried out with polychromatic irradiation at 0.30 W/cm. Kinetics of photocatalytic oxidation of methanol, ethanol, *n*-propanol, *n*-heptanol, and *n*-decanol, to yield intermediates, and photomineralisation of intermediates, to yield carbon dioxide and water, were studied in aqueous solution,

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by a laboratory-scale photoreactor and photocatalytic membranes immobilizing 30 ± 3 wt.% of TiO_2 , in the presence of stoichiometric hydrogen peroxide as oxygen donor, as was done in the preceding work [1, 2]. The whole volume of irradiated solution was 4.000 ± 0.005 L, and the ratio between this volume and the geometrical apparent surface of the irradiated side of the photocatalytic membrane 3.8 ± 0.1 cm. A kinetic model was used, by which mineralisation of substrate to CO_2 was supposed to occur, by kinetic constants k_1 , through one single intermediate, mediating the behaviour of all the numerous real intermediates formed in the path from the substrate to CO_2 (kinetic constants of formation of the latter being k_2). A competitive Langmuirian adsorption of both substrate and "intermediate" was also supposed to be operative, as expressed by apparent adsorption constants K_1 and K_2 , possessing a, partly at least, kinetic significance. By Langmuir-Hinshelwood treatment of initial rate data, starting values of the k and K couples were obtained, from which, by a set of differential equations, the final optimised parameters, k_1 and K_1 , k_2 and K_2 , were calculated, able to fit the whole photomineralization curve, and not only its initial segment, as the Langmuirian parameters do. While in the case of alkanolic acids, values of k_1 and k_2 , representing the kinetic constants of attack of substrate and intermediates, respectively, were roughly coincident, within the limits of reliability of the kinetic model, denoting that the oxidative attack of the "simulating" intermediate by hydroxyl radicals was comparable with that of the substrate, in the case of n -alkanols [1, 2], k_2 values were greater than k_1 of the same molecules. This was interpreted on the basis of the closer behaviour of alkanols to hydrocarbons, from the photocatalytic point of view, than carboxylic acids are, particularly for lower molecular weight substrates. Furthermore, and this is even more important, values of k_2 for methanol were practically the same as those of k_1 of the corresponding acid. This behaviour confirmed the suggestion of being methanoic acid the most representative intermediate for photodegradation of methanol.

In the present paper, the same kinds of experiments, and in the same apparatus and conditions, were carried out by using methane, ethane, n -heptane, n -decane, and n -dodecane as substrates, even if at much lower concentrations than that of n -alkanols and n -alkanoic acids in previous papers.

2. EXPERIMENTAL DETAILS

2.1. Materials. Methane, ethane, n -heptane, n -decane, and n -dodecane were obtained from Fluka (GC purity greater than 99.8%). They were used as received with no further purification. Solutions were prepared with ultra pure water (maximum contents of Na^+ and heavy metal ions 0.02 and 0.004 mg Kg^{-1} respectively):

this was obtained by cross-flow ultrafiltration on composite membranes immobilizing active carbon and nuclear grade ion exchange resins, as described [4]. Concentration of substrates was 0.80 – 2.50 ppm (mass expressed as carbon/volume) for all of the alkanes studied. No buffer system was added to solutions. Initial pH was 6.5 – 6.8 , and it slightly decreased with increasing photomineralisation, reaching a final stabilisation at 4.9 – 5.2 , when mineralisation was greater than 95% with respect to initial concentration of substrate.

2.2. Photocatalytic membranes. The photocatalytic membranes (*PHOTOPERM*[®] *BIT/313*), kindly supplied by B.I.T. srl, Milan, I, were standard membranes, immobilizing 30 ± 3 wt.% of titanium dioxide (P25 by Degussa, D) and no photocatalytic promoter. They were described in previous studies [5, 6].

2.3. Apparatus and procedures. The laboratory-scale photoreactor was the same as that already described [5], with the only difference that it was made gas tight, to avoid any leakage of substrate and/or intermediates through the vapour phase. Overall volume of treated solution was 4.000 ± 0.005 L; the ratio between the overall reacting volume and the apparent, geometrical surface area of the irradiated side of the membrane 3.8 ± 0.1 cm. The high pressure mercury arc lamp with a nominal power of 0.12 KW was employed, kindly supplied by Chimia Prodotti e Processi (Muggiò, Milan, Italy): it was further provided with a step by step power regulation device, so that power absorbed by the membrane, as determined actinometrically, could be varied between 0.10 and 1.05 $\text{W} \cdot \text{cm}^{-1}$. In all the experiments, it was fixed at 0.30 $\text{W} \cdot \text{cm}^{-1}$. The membrane being concentric to the lamp in the photoreactor used, absorbed power per unit length of lamp was also the same, if referred to unit length of membrane. At 0.30 $\text{W} \cdot \text{cm}^{-1}$ the overall power absorbed by the membrane, within the absorption range of immobilized semiconductor, in the experimental conditions of the present work, was 7.50 W, corresponding to 1.10×10^{-5} Einstein s^{-1} . In this paper, as well as in all preceding papers of this series, when concerning laboratory scale experiments carried out in the presence of hydrogen peroxide as oxygen donor, the radiating flux, unless otherwise stated, being filtered by a suitable borosilicate glass corresponded to a radiation wavelength range from the band gap of TiO_2 downwards to 315 nm, so that direct photolysis of hydrogen peroxide to give hydroxyl radicals was inhibited. Owing to the refrigeration system of the lamp, by means of water circulating in the lamp sheath, made of quartz, mean temperature, during the runs, was 308 ± 2 K.

The initial rate r_0 of photodegradation of alkanes was evaluated from curves of their concentration vs. time in the linear range, where zero-order kinetics was apparent. Experiments were repeated for each set of

conditions, essentially for each value of initial concentration C_0 of micropollutant, so that the mean initial rate and its standard deviation could be estimated.

The disappearance of the alkanes, as such, was followed by the technique of solid-phase microextraction (SPME), followed by GC-MS quantitative analysis.

SPME is based on the direct introduction into the aqueous sample of a fused silica fibre coated with a sorbent material, an adsorption/absorption of the analytes by the fibre coating and a subsequent thermal desorption directly into the GC, without any clean-up, pre-concentration or extraction step.

The SPME device for this investigation (Supelco, Milan, Italy) used a fibre coated with a short (10 mm) thin ($85\ \mu\text{m}$) layer of polyacrylate sorbent. The fibre was housed in a stainless-steel needle which allowed for penetration of the membrane closing the water sample vial (1 ml). The fibre was pushed out of the housing and exposed directly to the water sample for 60 minutes (adsorption step). Afterwards the fibre was pulled into the housing and the SPME device was removed from the sample and inserted into the injection port of the GC-MS system. For the thermal desorption and alkanol analysis a Varian 3400 with a septum equipped programmable injector was used. In the GC oven a $30\ \text{m} \times 0.53\ \text{mm}$ DB5MS megabore column was installed with the following temperature programme: $25\ ^\circ\text{C}$ for 1 minute followed by a temperature raise of $5\ ^\circ\text{C}/\text{min}$ to $240\ ^\circ\text{C}$, which was held for 4 minutes.

As carrier gas He was used at a flow rate of $25\ \text{mL}/\text{min}$. The GC was interfaced via jet-separator ($0.3\ \text{torr}$ in the separator and $0.03\ \text{torr}$ in the analyser) and a transfer-line ($270\ ^\circ\text{C}$) to a ITS40 ion trap mass-spectrometer (ITMS). The ion trap was operated at $300\ ^\circ\text{C}$ in the electron impact mode, scanning from $35\ \text{M}/\text{Z}$ to $550\ \text{M}/\text{Z}$ in 1.5 second. After insertion into the GC injection port, the SPME fibre was pushed out and thermally desorbed for 5 minutes at $270\ ^\circ\text{C}$. By this way the alkane was transferred from the SPME coating to the GC column to be chromatographed. The GC-ITMS data were acquired on a 386/387 Compaq personal computer with Saturn I software (Varian). The alkane was identified by its mass spectrum and standard solutions. Quantification was based on seven-point calibration curves using, as internal standard, a standard solution containing the perdeuterated alkanes.

In order to study the relationship between rate of alkane degradation, as such, and the overall rate of organic carbon disappearance, this latter was also followed, by total organic carbon (TOC) analysis. To this purpose, a Shimadzu TOC-W instrument was used, by which the contribution of inorganic carbon present was always evaluated, in order to obtain TOC by difference from total carbon and inorganic carbon determinations. Due to the high sensitivity detector employed and the utilization of ultrapure water for preparation of solutions, determinations were accurate within $5\ \text{ppb C}$.

The instrument was equipped with the ASI-V self sampler.

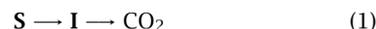
In all the runs of the present paper, stoichiometric hydrogen peroxide was employed as oxygen supplier. This was added, in a standard way, at the beginning of experiments, during the preparation of solutions.

2.4. Kinetic modeling. Kinetic modeling was carried out as described in a preceding paper [7].

3. RESULTS AND DISCUSSION

Photomineralisation of methane, ethane, *n*-heptane, *n*-decane, and *n*-dodecane in aqueous solutions, and in a concentration range corresponding to 0.80 – $2.50\ \text{ppm}$ (mass/volume) of carbon, for all the examined substrates, was studied at $308 \pm 2\ \text{K}$, in a laboratory-scale reactor, by polychromatic irradiation at $0.30\ \text{W}/\text{cm}$ (see Experimental), in the presence of stoichiometric hydrogen peroxide as oxygen donor, by photocatalytic membranes immobilizing $30 \pm 3\%$ of titanium dioxide. Kinetics of both substrate disappearance, to yield intermediates, and total organic carbon (TOC) disappearance, to yield carbon dioxide, were followed.

By employing a kinetic model thoroughly described in preceding papers [7], mineralisation of substrate **S** to CO_2 was supposed to occur through one single intermediate **I**, mediating the behaviour of all possible intermediates formed in the way from **S** to CO_2 , following the Scheme (1)



and to imply that both **S** and **I** showed a competitive apparent Langmuirian adsorption on to the immobilized semiconductor, as expressed by apparent adsorption constants K_1 and K_2 respectively, while the kinetic constants k_1 and k_2 articulate the degradation of **S** and **I** respectively. When both k and K couples, for substrate and "intermediate", are accessible experimentally, as in the present work, that is when initial rate data, relative to substrate, and TOC as well, have been measured, they may be first treated by the classical Langmuir-Hinshelwood equation. The respective values drawn by the Langmuirian model are unable to describe the whole curve of mineralisation: they may be used, however, as starting values of the model represented by Scheme (1), to draw, from the differential equations of this model, an optimisation of the whole temporal kinetic curves of substrate and TOC, until consistency is reached and the best fitting of experimental curves is obtained.

Treating of experimental data by the model above [7] allows, consequently, to obtain two couples of parameters, k_1 and K_1 , k_2 and K_2 , which fit the whole photomineralisation curve, and not only its initial segment, as the Langmuirian parameters generally do. The very satisfactory fitting of experimental kinetic data by this model, notwithstanding its extreme simplicity, is

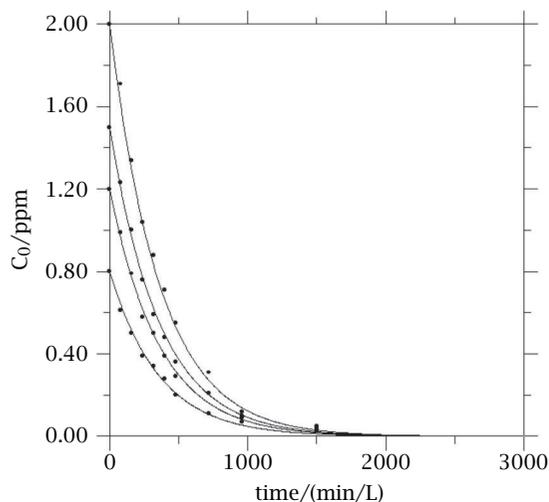


Figure 1. Kinetics of disappearance of methane, as substrate. Concentrations, C_0 /ppm, of methane, expressed as carbon, which was not transformed into intermediates, as a function of time, expressed in min/L, as time necessary to treat 1 L of solution.

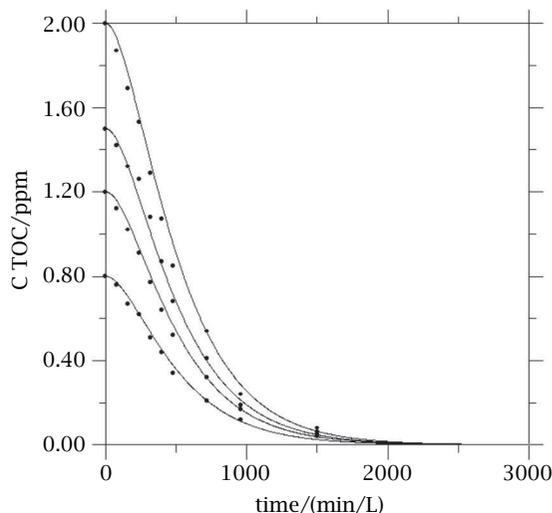


Figure 2. Kinetics of disappearance of total organic carbon (TOC) from aqueous methane solutions, expressed as concentrations, C_{TOC} /ppm of carbon, which was not mineralised, as function of time, expressed in min/L, as time necessary to treat 1 L of solution.

shown in Figures 1 and 2 for the kinetic curves of disappearance of methane as such, and the TOC disappearance from the methane solutions respectively, in Figures 3 and 4 for the kinetic curves of disappearance of *n*-decane as such, and the TOC disappearance from the *n*-decane solutions respectively, at the various initial concentrations specified for the two substrates.

The optimized values for the two k and K couples above are reported in Table 1, together with the corresponding data of *n*-alkanols [3] and *n*-alkanoic acids [1, 2], taken from previous work, but expressed in the same units as those employed in the present work for *n*-alkanes, for comparison. From the observation of these values, some interesting considerations may be drawn.

(a) In most cases examined up to now, by the same technique described in the present and in immediately preceding papers [1–3], and particularly for aromatic substrates [8, 9], k_2 values much less than k_1 were obtained, usually differing by about one order of magnitude. In other words, in these cases, mineralization of I was much slower than transformation of S into I. In the photomineralisation of *n*-alkanoic acids, on the contrary, substantially equal values of the two k and K couples were the best description of the reacting system [1, 2], the uncertainties of data not allowing to show any difference, within the experimental confidence. In these latter cases, the TOC profile as a function of time, with the exception of *n*-decanoic acid, decreased sharply since the very first beginning, without showing the classical plateau, shown by aromatic sub-

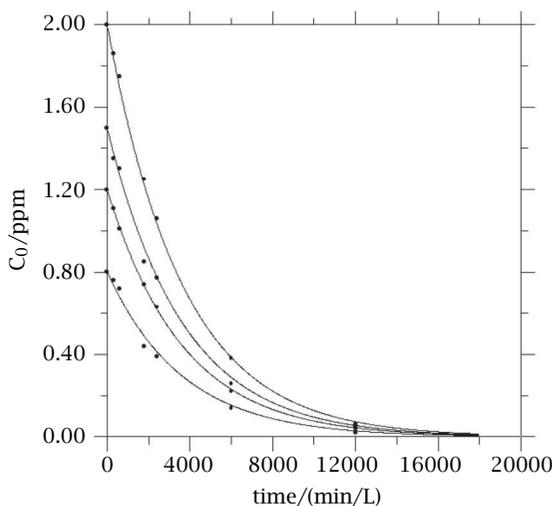


Figure 3. Kinetics of disappearance of *n*-decane, as substrate. Concentrations, C_0 /ppm, of *n*-decane, expressed as carbon, which was not transformed into intermediates, as a function of time, expressed in min/L, as time necessary to treat 1 L of solution.

strates, at values near to those of initial concentrations. This plateau indicates accumulation of intermediates, possessing the same or almost the same number of carbon atoms as those of the starting substrate, and presenting slower rates of transformation than that of the substrate itself. The behaviour of the alkanolic acids

Table 1. Parameters, k_1 and K_1 , k_2 and K_2 (uncertainties are indicated between parentheses and expressed, relatively to the last digits, as probable errors of the means of optimised values from nine sets of runs in the range of concentrations tested), able to fit the whole photomineralisation curve, from disappearance of substrate, to yield intermediates, to formation of carbon dioxide, following Scheme (1), as obtained by optimisation of kinetic curves, by using the set of differential equations corresponding to kinetic model of Scheme (1) [7]. All the parameters are expressed in ppm of carbon units (mass of C/volume) and refer to the photodegradation of *n*-alkanes (present work), *n*-alkanols [3], and *n*-alkanoic acids [1, 2], in the presence of stoichiometric hydrogen peroxide as oxygen donor (treated volume of aqueous solutions 4.00 L; radiant power of polychromatic high pressure mercury arc lamp absorbed by the photocatalytic membranes 0.30 W/cm, corresponding to 6.60×10^{-4} Einstein/min; ratio between volume and geometrical apparent surface of the irradiated side of the membrane 3.8 ± 0.1 cm; PHOTOPERM® BIT/313 membranes immobilizing 30 ± 3 wt.% TiO₂).

Substrate	k_1 (ppm C/min)	k_2 (ppm C/min)	K_1 (ppm C) ⁻¹	K_2 (ppm C) ⁻¹
Methane	0.224(1)	0.584(2)	0.0126(3)	0.0089(3)
Methanol	0.063	0.864	0.103	0.0817
Methanoic acid	0.993	0.993	0.0357	0.0357
Ethane	0.260(3)	0.94(1)	0.0097(3)	0.0069(4)
Ethanol	0.072	0.504	0.0463	0.0477
Ethanoic acid	0.180	0.180	0.0987	0.0987
<i>n</i> -Heptane	0.168(2)	1.171(2)	0.0047(2)	0.0031(1)
<i>n</i> -Heptanol	0.158	1.365	0.0029	0.00271
<i>n</i> -Decane	0.172(3)	1.615(9)	0.0016(1)	0.00195(5)
<i>n</i> -Decanol	0.255	1.74	0.00187	0.00217
<i>n</i> -Decanoic acid	0.750	0.162	0.0171	0.0217
<i>n</i> -Dodecane	0.1853(9)	1.438(4)	0.016(4)	0.00263(3)

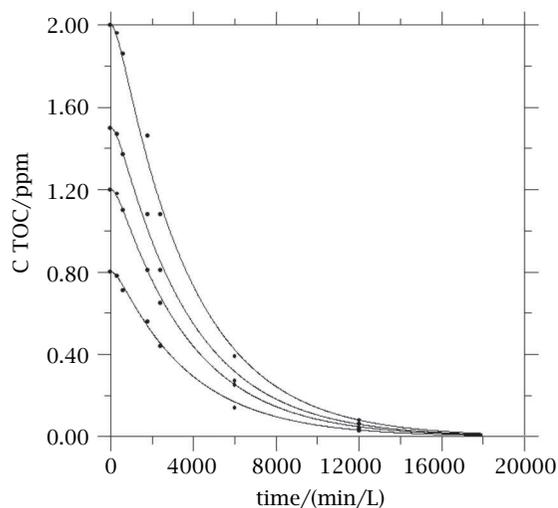


Figure 4. Kinetics of disappearance of total organic carbon (TOC) from aqueous *n*-decane solutions, expressed as concentrations, C_{TOC}/ppm of carbon, which was not mineralised, as a function of time, expressed in min/L, as time necessary to treat 1 L of solution.

with a low number of carbon atoms was interpreted [1, 2] by conjecturing that there were no chemically stable intermediates other than radical species, or at least that chemically stable intermediates with progres-

sively lower number of carbon atoms were in the fairly complicated route from substrate to carbon dioxide. In the case relative to alkanols [3], conversely, k_2 exceeded k_1 values, up to about one order of magnitude for the molecules with higher molecular weight. This has been interpreted [3] as meaning that the rate of conversion of *S* into *I* was, in that particular instance, definitely lower than that of integral mineralisation of intermediates. The result is not entirely surprising, given that the alkanol is a model molecule nearer to a hydrocarbon than the alkanolic acid is, and, consequently, the reaction of the substrate with the attacking hydroxyl radicals, or other oxygen radicals like HO₂·, is a relatively slow process, if compared to further oxidation steps of the intermediates produced earlier.

(b) Along the same line of conclusions, as those drawn from (a), we may also find the comparison between k_1 values of alkanols and those of the alkanes studied in the present paper, thus confirming, as it has been stated previously [3], that, for higher molecular weight substrates, the alcohols are fairly good models of the hydrocarbons behaviour. When the chain is sufficiently long, there is no practical difference between the alkanol and the alkane, the end alcoholic group showing no great influence on the degradation rate of the long hydrocarbon chain. It should be underlined, however, that consideration on rates, based exclusively on k values, following a Langmuir-Hinshelwood model, should not be regarded as fully and absolutely reliable. In fact,

Table 2. Maximum allowable quantum yields and effective extrapolated quantum yields, at "infinite" concentration of substrate, for the photomineralisation of various alkanes, in aqueous solution, with stoichiometric hydrogen peroxide, by PHOTOPERM® BIT/313 membranes immobilizing 30 ± 3 wt.% TiO₂.

<i>n</i> -Alkanes	Maximum allowable quantum yield (mol/Einstein)	Effective quantum yield (mol/Einstein)	Percent quantum yield (%)
Methane	0.125	0.113	90.6
Ethane	0.0714	0.0656	91.9
<i>n</i> -Heptane	0.0227	0.0121	53.3
<i>n</i> -Decane	0.0161	0.00868	53.9
<i>n</i> -Dodecane	0.0135	0.00780	57.8

it has been shown, since long time and unequivocally [5, 6], that also K parameters have a kinetic significance, so that these latter are integral part of a convenient and fitting model, rather than attributing to them a truly and purely physical meaning in the sense of adsorption. This notwithstanding, a rough indication based on k values can be considered, at high concentrations of substrate, as complementary to the use of the rate equation, the latter being anyway the most reliable method to treat experimental data, as has been done, for example in modelling of Figures 1-4, in which the kK factor may play the most relevant role.

(c) As regard the k_1 values, with the short chain hydrocarbons, methane and ethane, it stems out, from values of Table 1, that attack of the hydrocarbon substrates by hydroxyl radicals is a slower process, than that of the corresponding alkanols, by a factor around 3. Even if, physically speaking, the attack of an already substituted carbon atom by radicals, or of an adjacent carbon atom may somewhat be hindered, this should not be considered as an absolute indication, since the kK factor, as stressed in (b) above, may upset this apparent conclusion.

On a pure kinetic basis, such as that employed in the present work, it is impossible to speculate further on mechanisms. Nevertheless, this is not a limitation, because, on one side, mathematical modeling of kinetics is fundamental to the design of membrane photoreactors. Furthermore, on another side, the factors associated with K values, both if interpreted kinetically or as a measure of adsorption-desorption equilibrium, or by both these mechanisms, play a large role [10] in determining rates and consequently overall efficiency as a function of concentration. Isolation of intermediates, which is generally accepted as the most unequivocal proof of the main reaction mechanism, if not accompanied by validation of kinetic scheme, through the determination of the relative constants, may simply denote, as a disturbing possibility, that pathways defined by accumulation of intermediates found in solution are the *inefficient* pathways [10].

Finally, some reflections concerning quantum yields may be carried out, in the hypothesis that the only kind of reaction occurring in the system, and leading to mineralisation, is given by hydroxyl radicals produced from photogenerated holes of semiconductor. This is perfectly reasonable, since no photocatalytic promoter, such as those used in preceding works [1, 11-15] was present in the photocatalytic membranes used in the present investigation. This also corresponds to neglecting any potential and imaginable scavenging action of conduction band electrons by hydrogen peroxide. The stoichiometric number of $\cdot\text{OH}$ radicals necessary to mineralize the alkane molecules amounts to $6n + 2$, where n is the number of carbon atoms present in the molecules. Maximum theoretical quantum yields may be thus evaluated, as reported in Table 2, for the various alkanes, which have been the object of the present work. The calculation of effective quantum yields, at "infinite" concentration, may be carried out, on the basis of k_1 values of Table 1, since the kinetic model reproduces, for the alkane molecules, an experimental situation in which the rate determining step is represented by the attack of the substrate. The relative values are also reported in Table 2, together with the percent ratios between effective and maximum theoretical quantum yields (percent quantum yields).

It may be easily remarked that, in the experimental conditions of this paper, percent efficiencies are nearly quantitative for methane and ethane, and approaching to about 60% for the hydrocarbons possessing greater molecular weights. These values are qualitatively comparable with those relative to the alkanolic acids in the same conditions [1, 2], and, for the substrates with a greater number of carbon atoms, also with those relative to the alkanols [3]. On the contrary, quantum yields relative to low molecular weight hydrocarbons exceed those of the corresponding alcohols [3]. This is again a clear indication of the relatively greater difficulty of mineralising lower molecular weight alcohols by the photocatalytic technology, with respect to the corresponding hydrocarbons, as obtained from k_1 values,

and as underlined in (b) and (c) above. All of this, with the care which should be given to this kind of perusal, on the light of previous comments.

4. CONCLUSIONS

Photomineralisation of model molecules of *n*-alkanes, in the presence of stoichiometric hydrogen peroxide as oxygen donor, by photocatalytic membranes immobilizing $30 \pm 3\%$ of titanium dioxide, has been modelled by a four parameters kinetic model [7], as successfully as that of the corresponding *n*-alkanols [3] and *n*-alkanoic acids [1, 2].

This kinetic model allows a fully reliable fitting of experimental curves, both for the disappearance of substrate as such and for the transformation of total organic carbon into carbon dioxide. Furthermore, this model permits to rationalise quantum yields at "infinite" concentration of substrate, as well as their comparison with maximum allowable quantum yields, on the basis of one hydroxyl radical produced per single photon absorbed by the semiconductor photocatalyst. By this way a fully consistent and trustworthy design of photoreactors may be easily achieved.

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REFERENCES

- [1] L. Rivas, I. R. Bellobono, and F. Ascari, *Chemosphere* **35** (1997), 2899.
- [2] L. Rivas, I. R. Bellobono, and F. Ascari, *Chemosphere* **37** (1998), 1033.
- [3] I. R. Bellobono, C. Lagrasta, M. L. Carbonara, G. Bonizzoni, and P. M. Tozzi, *Fresenius Environ. Bull.* **12** (2003), 1545.
- [4] I. R. Bellobono, R. Tacchi, E. Selli, and F. Muffato, *Membrane Separation Processes* (A. Green, ed.), BHRA, Cranfield, UK, 1989, p. 187.
- [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, and L. Castellano, *Chemosphere* **30** (1995), 1847.
- [6] B. Barni, A. Cavicchioli, E. Riva, L. Zanoni, F. Bignoli, F. Gianturco, A. De Giorgi, H. Muntau, L. Montanarella, S. Facchetti, and L. Castellano, *Chemosphere* **30** (1995), 1861.
- [7] F. Ascari, I. R. Bellobono, and P. M. Tozzi, *Fresenius Environ. Bull.* **12** (2003), 1195.
- [8] F. Rota, M. Cavassi, D. Niego, R. Gorlani, L. Vianelli, L. Tatti, P. Bruzzi, A. Moroni, I. R. Bellobono, M. Bianchi, and H. Muntau, *Chemosphere* **33** (1996), 2159.
- [9] L. Tatti, D. Niego, F. Rota, P. Bruzzi, A. Moroni, I. R. Bellobono, M. Bonardi, M. Bianchi, and H. Muntau, *Chemosphere* **34** (1997), 41.
- [10] G. P. Lepore, A. Vlček Jr., and C. H. Langford, *Photocatalytic Purification and Treatment of Water and Air* (D. F. Ollis, H. Al-Ekabi, eds.), Elsevier, Amsterdam, NL, 1993, p. 95.
- [11] I. R. Bellobono, *Life Chem. Repts.* **13** (1995), 63.
- [12] I. R. Bellobono, B. Barni, and F. Gianturco, *J. Membrane Sci.* **102** (1995), 139.
- [13] F. Gianturco, L. Vianelli, L. Tatti, F. Rota, P. Bruzzi, L. Rivas, I. R. Bellobono, M. Bianchi, and H. Muntau, *Chemosphere* **33** (1996), 1531.
- [14] I. R. Bellobono, F. Gianturco, and C. M. Chiodaroli, *Fresenius Environ. Bull.* **6** (1997), 89.
- [15] I. R. Bellobono, P. Pinacci, G. C. Riva, and C. Lagrasta, *Fresenius Environ. Bull.* **7** (1998), 277.



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