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Kinetic analysis of photoinduced reactions at the water semiconductor interface

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Abstract

A reduced kinetic model for the initial steps of the photocatalytic process is presented with the aim to analytically solve the resulting kinetic system. Several possible kinetic models have been explored. Attention was paid to obtain equations with physical meaning and reduced complexity. An analytical equation is obtained for the rate and the quantum yield, which retains the principal features of the photocatalytic process, namely the light induced charge separation and recombination, the oxidative and reductive electron transfers, the formation of a stable oxidized intermediate, and, unlike the previous kinetic models, also the back reaction of the oxidized substrate. Compared to the two-parameter Langmuir–Hinshelwood equation, all the previous features and the dependence on the light intensity are described with only three parameters, which collect all the kinetic constants, and account for experimental concentrations of substrate and electron scavenger, light intensity and catalytic system characteristics. The kinetic behavior of photocatalytic systems under all the possible values of experimental parameters can be graphically presented. The analysis of the obtained rate equation shows that the best utilization of photons is attainable at low light intensities, suggesting that preconcentration of solar light is unnecessary.

Keywords: Photocatalysis; Kinetic model for; Rate equations for; Primary events of

1. Introduction

The photocatalysed conversion of organic species under aerobic conditions has been deeply investigated from basic, mechanistic and practical points of view due to the great potential of the process for pollutant abatement and waste treatment [1]. The basic mechanism was treated in a number of papers [2]. Following the light absorption primary excited species are formed which can either recombine or migrate to the surface of the semiconductor, where several redox reactions may take place. The organic substrate reacts with formed active species (oxidant or reducing) depending on its initial oxidation state and the nature of substituents [3], forming radicals and other species that are further oxidized or reduced. Several complex networks of reaction have been reported on the basis of detailed chemical analyses of the time evolution of substrate and formed intermediates or by-products [4–7].

In photocatalytic processes the degradation rate depends, no matter what the mechanism of degradation is, upon the photon absorption rate. In practical systems the distribution of radiation intensities inside the reactor space is highly non-uniform. Its dependence on reactor geometry, and, for slurries, on the relative contributions of absorption and scattering was deeply investigated [8]. The solution of the integro-differential equation that results is not a simple task even for a

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simple geometry. Equations more manageable may be forecast for thin films. Given the spectral volumetric absorption, the absorption and scattering coefficients, and the distribution function for photon scattering, the incident radiation at any point inside the reactor space can be obtained [8]. The last is directly related to the local photon absorption rate. The photocatalytic degradation rate could be calculated, provided that a chemical kinetic model relating primary chemical events with absorbed photon rate is available.

Owing to the complex network of reactions, even for a chosen substrate it is difficult to develop a model for the dependence of the degradation rate on the experimental parameters for the whole treatment time. All the possible formed species must be identified, their kinetic constants for reaction either with photogenerated species or with other active species (radicals, other intermediates) have to be measured (by independent degradation experiments) or estimated. Since this is a heavy (and perhaps useless) task, kinetic modeling of the photocatalytic process is usually restricted to the analysis of the initial rate of degradation. This is the product of the initial slope and the initial substrate concentration in an experiment in which the variation of the substrate concentration is measured as a function of time. The extrapolation of the rate to time = 0 avoids the possible interference from by-products, both for the kinetic aspect (avoiding the growing complexity of the system as the degradation time increases), and for the possibility that formed species are physisorbed or chemisorbed [9], eventually reducing the possibility of formation of active species, or, in extreme cases, blocking or poisoning surface sites.

However, even under the reduced complexity deriving from the initial rate simplification, the interpretation of the rates obtained in photocatalytic experiments is still under debate. An attempt to model the initial steps of the photocatalytic process and to analytically solve the resulting kinetic system is presented. Attention was paid to obtain equations with physical meaning and reduced complexity. Several possible kinetic models have been explored.

2. The kinetic of photocatalyzed transformation

The common shape observed for the initial rate of degradation r_o as a function of the substrate or catalyst concentration is an increasing function tending to a limiting value (zero order rate), as if the rate would be determined by the adsorption properties of the substrate on the catalyst surface. This was historically, but even now interpreted in terms of the Langmuir–Hinshelwood two-parameter equation either invoking physical reasons or simplicity [10,11].

$$r_o = \frac{k K_{ads} C_o}{1 + K_{ads} C_o} \quad (1)$$

LH equation (Eq. (1)) interprets the rate as the product of a specific rate constant k for reaction of photogenerated surface species with the adsorbed substrate (the extent of adsorption being determined by K_{ads}). The role of other species was coherently interpreted as a competition for adsorption, adding to the denominator the proper terms ($K_i C_i$) for competing species i [11,12]. For the degradation rate of chlorinated haliphatics the LH model was used to justify the inhibiting effect of chloride ions [13,14]. Oxygen (for air equilibrated systems) seems to adsorb on sites different from those on which organic molecules are oxidized, avoiding competition [15]. Thus the rate was supposed as $r = k\, f([\text{organics}]_{surface})\, g([\text{oxygen}]_{surface})$, where $f()$ and $g()$ describe the adsorption of both species in term of a Langmuir isotherm. Interestingly, the LH equation (in the form of a double reciprocal plot of $1/r_o$ versus $1/C_o$) is able to fit also the rate of final product formation (e.g. chloride ions from pentachlorophenol) [16]. This outstanding ability gives rise to doubts about the generality of the physical significance of its parameters.

The LH and related equations are supported by the understanding that the reaction takes place at the catalyst surface. The localization of the degradation process has been deeply debated. From the type of oxidation products observed, similar to those obtained from direct reaction of OH radicals generated in solution [17], direct ESR measurements on aqueous suspensions of TiO_2 [18], and the observation that in non-aqueous solvents there is partial oxidation of the substrate, contrary to that occurring in water [19], it is generally recognized that oxidation proceeds through water related species. However, it was not clear if these species are localized at the surface or are able to migrate in solution. Flash photolysis experiments have been unable to observe the intermediate adduct with OH [20]. In addition, the detected stable intermediates

can be justified either through the reaction with OH or photo-generated holes, followed by reaction with the solvent. By taking into account several hypotheses on the localization of the process (both species are adsorbed, the organic is adsorbed and OH radicals are free in solution, OH radicals are bound to the surface and the organic are free in solution, both species are in solution), the kinetic data alone are unable to give an unambiguous answer [21,22]. A convincing evidence that photogenerated species do not migrate far from the catalyst surface has been derived from the study of the degradation of decafluorobiphenyl (DFBP), a substrate that is strongly adsorbed (>99%) on alumina and TiO_2 [23]. When DFBP is adsorbed on alumina particles and mixed with titania particles, the amount exchanged is very low (<5%). Irradiation of DFBP adsorbed on alumina in the presence of H_2O_2 (generating OH in solution) or titania colloids (supposed to generate OH free or bound to the surface on mobile particles) leads to degradation, whilst DFBP is not degraded when larger titania particles (P25, TiO_2 beads) are present. Pentafluorophenol, which is easily exchanged between the two oxides, is photodegraded in all cases. This makes clear that active species formed upon irradiation do not migrate in solution, whilst the organic substrate may or not migrate to the catalyst surface. Only when both are present at the catalyst surface the degradation takes place.

Thus, the possibility of adsorption is of primary importance. Adsorption may originate either from chelating properties of the organic substrate toward surface metal species, or, because of the low hydrophobicity of the metal oxide surface, from the expulsion of the organic molecules from the bulk of the solution for entropic reasons. Since there is depletion of substrate at the catalyst surface when the degradation takes place, migration from the solution is assisted by the concentration difference in the two environments.

Adsorption is not the single factor influencing the rate of degradation. In general, there is no correspondence between the value of K_{ads} obtained from fits of kinetic data through Eq. (1) and dark adsorption measurements. The degradation rate of phenol (ph, poorly adsorbed) and nonylphenol (nph, strongly adsorbed) differs only by a factor of three [24]. Since it was demonstrated that the aromatic moiety is more susceptible to attack than the haliphatic chain, *k* would be almost identical in the two cases. Owing to the large ratio of $K_{ads}^{nph}/K_{ads}^{ph}(\gg 3)$, it follows that the LH equation is inadequate. The same was demonstrated for pentachlorophenol, [16] and by Cunningham in several papers [21,25,26].

Some additional complexity arises from the possibility of different adsorption sites and the presence of pores, which reflect in non-ideal (not Langmuirian) adsorption isotherms and mass transfer problems. The mass transport can be relatively slow in pores and interparticle spaces (as it is the case of P25, for which in suspension there are particles ranging from 0.2 to 2 μm formed by 30 nm sized primary particles [27]). In such spaces the diffusion coefficient is comparable to liquid diffusion in zeolites [28]. Moreover, when the degradation takes place, intermediate products may be confined in such restricted spaces, being able to back-react with active species favoring a net e^-/h^+ recombination, as recently outlined by Cunningham [29].

According to the preceding discussion, the primary events occurring at the catalyst surface are summarized in reactions 2. The primary photochemical act, following the light absorption by the semiconductor, is the generation of electron/hole pairs (Eq. (2a))

Charge separation

$$\text{semiconductor} \xrightarrow{h\nu} e^-_{CB} + h^+_{VB} \tag{2a}$$

The charge carriers can either recombine where they are formed (bulk, Eq. (2b)) or migrate to the surface where they are trapped (Eq. (2c) and (2d)) or surface recombined (Eq. (2e) and (2f)). In the case of titania the electron may be trapped as a surface Ti(III) [30] (sketched as ≡ $Ti^\bullet$, Eq. (2d)), and the hole as a surface-bound hydroxyl radical (≡ Ti–$O^\bullet$, Eq. (2c)).

Bulk recombination

$$e^-_{CB} + h^+_{VB} \xrightarrow{k_b} \text{heat, light} \tag{2b}$$

Surface trapping

$$h^+_{VB} + \equiv \text{Ti-OH} \xrightarrow{k_c} \equiv \text{Ti-O}^\bullet + H^+ \tag{2c}$$

$$e^-_{CB} + \equiv \text{Ti-OH} \xrightarrow{k_d} \equiv \text{Ti}^\bullet + OH^- \tag{2d}$$

Surface recombination

$$e^-_{CB} + \equiv \text{Ti-O}^\bullet + H^+ \xrightarrow{k_e} \equiv \text{Ti-OH} \tag{2e}$$

$$h^+_{VB} + \equiv \text{Ti}^\bullet + OH^- \xrightarrow{k_f} \equiv \text{Ti-OH} \tag{2f}$$

If electron acceptors (Ox_2, like oxygen) or electron donors (Red_1, as organic substrates) are present at the surface (adsorbed), interfacial electron transfers may occur according to reactions (Eq. (2h) and (2i)). Solution species marked with ($^\bullet$) may be radicals.

Interfacial charge transfer

$$\equiv \text{Ti-O}^\bullet + \text{Red}_1 \xrightarrow{k_3} \text{Ox}_1{}^\bullet + \equiv \text{Ti-OH} \quad (2h)$$

$$\equiv \text{Ti}^\bullet + \text{Ox}_2 + \text{H}_2\text{O} \xrightarrow{k_4} \text{Red}_2{}^\bullet + \equiv \text{Ti-OH} \quad (2i)$$

Direct reaction of holes (and electrons) without surface trapping may also occur [31]. A recent work suggests that the larger the amount of surface OH groups, the more likely the oxidation (Eq. (2h)) via surface trapped holes occurs [32].

Competitive with these are the back reactions (Eq. (2j) and (2k)) which account for the possibility that there is substrate-mediated e/h recombination.

Back reactions

$$\text{Red}_2{}^\bullet + \equiv \text{Ti-O}^\bullet \xrightarrow{k_5} \text{Ox}_2 + \equiv \text{Ti-OH} \quad (2j)$$

$$\text{Ox}_1{}^\bullet + \equiv \text{Ti}^\bullet \xrightarrow{k_6} \text{Red}_1 + \equiv \text{Ti-OH} \quad (2k)$$

The importance of the back reactions increases when the formed radical is trapped near the surface, either for impeded outward diffusion (e.g. in pores) or by its high hydrophobicity. If the law of microscopic reversibility holds, the desorption rate is given by the adsorption rate reduced K_{ads} times. The combined reactions Eq. (2a) and (2b) or Eq. (2c), (2d), (2e) and (2f) or Eq. (2c), (2d), (2h) and (2k) give a net null cycle, without useful transformation of the absorbed light.

The radicals formed are further transformed either by subsequent reaction with photogenerated active species, or through reaction with solvent, other species present in solution (such as O_2, H_2O_2, O_2^-), elimination of molecular groups or ions [4,7] or dimerisation [6]. The additional transformations may lead to the complete degradation of the organic compound to CO_2 and inorganic anions. As we are interested for the reasons outlined above to the analysis of primary events, the kinetic sketch of the evolved system will be neglected.

Degradation

$$\text{Ox}_1{}^\bullet + \equiv \text{Ti-O}^\bullet \xrightarrow{k_7} \text{Ox}_1 + \equiv \text{Ti-OH} \quad (2l)$$

$$\text{Red}_2{}^\bullet + \equiv \text{Ti}^\bullet \xrightarrow{k_8} \text{Red}_2 + \equiv \text{Ti-OH} \quad (2m)$$

$$\text{Ox}_1{}^\bullet + \text{Ox}_2 \xrightarrow{k_9} \text{Ox}_4 \quad (2n)$$

$$\text{Ox}_1{}^\bullet + \text{Red}_2{}^\bullet \xrightarrow{k_{10}} \text{Ox}_3 \quad (2o)$$

$$\text{Ox}_1{}^\bullet + \text{Ox}_1{}^\bullet \xrightarrow{k_{11}} \text{Dimer} \quad (2p)$$

The role of Ox_2 is double: it scavenges e^- (Eq. (2i)) or combines with an organic radical generated by a photohole (Eq. (2n)) (in the case of O_2 generating an organoperoxy radical [33]). In addition to all the preceding reactions, which hold for a substrate that can only be oxidized, there are possible concurrent oxidative and reductive reactions. This is the case observed for halomethanes [7]. In the following these further complications will not be considered. Several kinetic models have been presented based on these primary photocatalytic events [34–39]. A simple kinetic model for periodic illumination based on Eqs. (2a), (2b), (2h) and (2i) and the surface adsorption rate of Ox_2 (O_2) was also developed [40]. Numerical solutions based on the stochastic kinetic analysis of the previously depicted primary events were shown to give the correct predictions of photocatalytic reactions and photochemical experiments [41].

The system of kinetic equations deriving from some of reactions (2) was also solved under the hypotheses of constant illumination intensity, fast reaction of the electron scavenger with photogenerated electrons, and steady state conditions for $\mathrm{d}\left\{e_{CB}^-\right\}/\mathrm{d}t = \mathrm{d}\left\{h_{VB}^+\right\}/\mathrm{d}t = 0$ [42]. No assumptions were made on the steady state concentrations of conduction band electrons, valence band holes, and other transient species. The resulting rate expression showed a Langmuirian shape as a function of light flux, organic and catalyst concentration, independent on the partition properties of the substrate. It was concluded that "whilst experimental data can be fitted by an approximate kinetic solution which has the analytical form of a LH equation, nevertheless the parameters of such working model equation have been demonstrated not to have a physical significance" [16]. The hypothesis that electron scavenging by oxygen or other oxidants is faster than electron/hole recombination is perhaps too restrictive, since it is now recognized that this reaction can be rather slow (see the values of estimated rate constants in Ref. [40]).

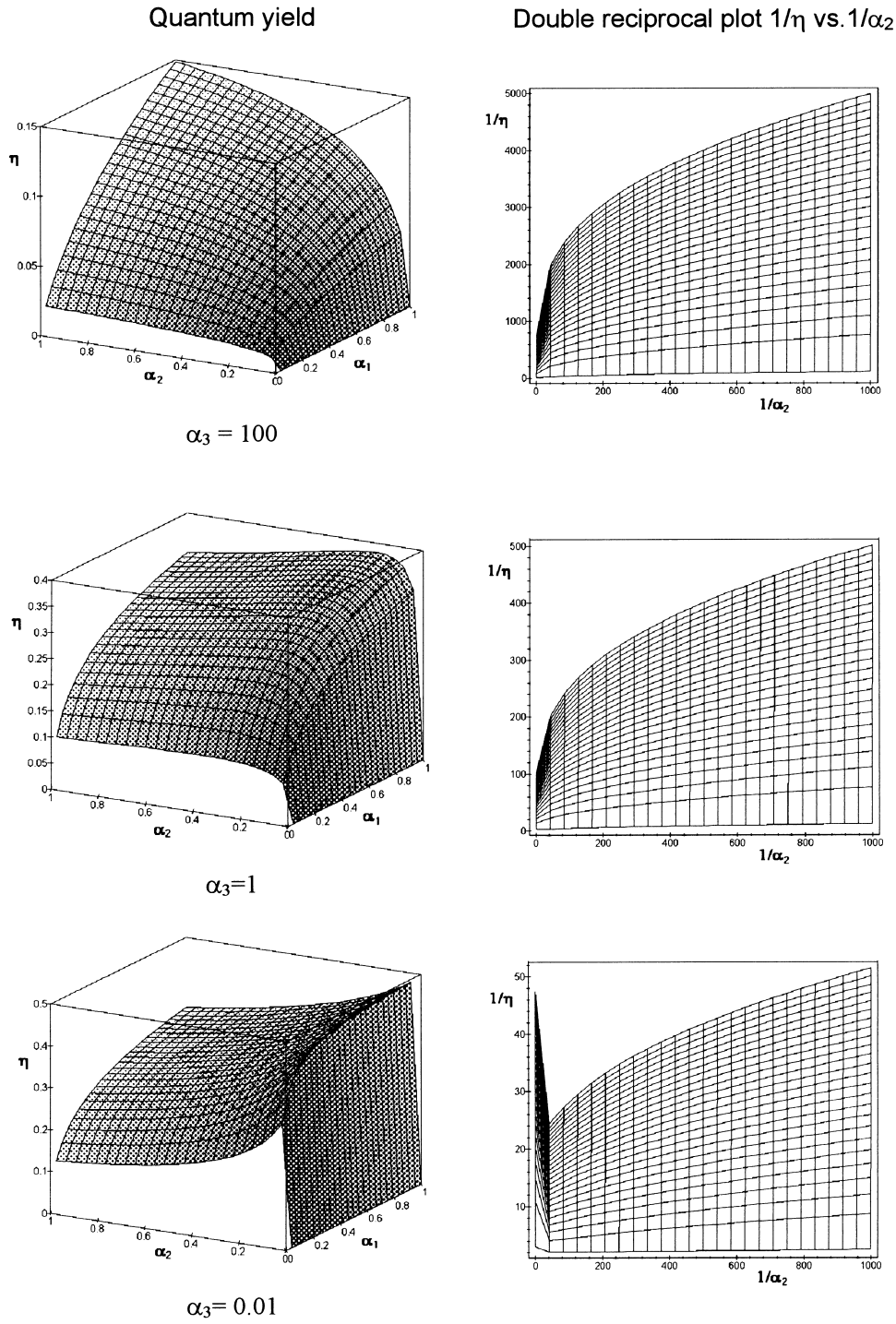

Fig. 1. (left) Quantum yield η (or the rate, that is proportional to η as α_3 is constant) for case A) (see text) as a function of parameters α_2 (left axis) and α_1 (right axis) for different values of α_3; (right) Double reciprocal plots of $1/\eta$ versus $1/\alpha_2$ for simulations at left.

3. Results

The differential kinetic system that can be derived from reactions 2 is not solvable, even under steady illumination, unless numerically with a huge number of parameters. The hypothesis of the steady state can be applied to transient species (e.g. differential equations = 0). Nevertheless, the resulting system has no analytical solution. Its numerical solutions give the dependence of the rate as a function of $\{Red_1\}$ and $\{Ox_2\}$ similar to that reported below (see Fig. 1). Because the number of parameters is high, the applicability of the numerical model into reactor design development would be prohibitive (see for example the applicability to the reactor in Ref. [11]). Scarce information may be obtained when using the model to fit experimental data, or even to have a general overview of the kinetic behaviour of photocatalytic systems.

The kinetic model can be strongly simplified assuming that reactions (2a)–(2f) are reduced to reactions (3a) and (3b), where h^+ and e^- stand for species able to react with adsorbed molecules. They do not necessarily correspond to ≡ Ti-O$^\bullet$ and ≡ Ti$^\bullet$ of system 2, respectively. Thus, although more simplified and with less microscopic detail, the kinetic system includes not only OH-mediated surface reactions, but also possible direct electron transfer reactions [31].

Charge separation

$$TiO_2 \xrightarrow{\phi} e^- + h^+ \quad (3a)$$

Recombination

$$e^- + h^+ \xrightarrow{k_2} \text{heat, light} \quad (3b)$$

Interf. charge transfer

$$h^+ + Red_1 \xrightarrow{k_3} Ox_1^\bullet \quad (3c)$$

$$e^- + Ox_2 \xrightarrow{k_4} Red_2^\bullet \quad (3d)$$

Back reactions

$$Red_2^\bullet + h^+ \xrightarrow{k_5} Ox_2 \quad (3e)$$

$$Ox_1^\bullet + e^- \xrightarrow{k_6} Red_1 \quad (3f)$$

Degradation

$$Ox_1^\bullet + h^+ \xrightarrow{k_7} Ox_1 \quad (3g)$$

$$Red_2^\bullet + e^- \xrightarrow{k_8} Red_2 \quad (3h)$$

$$Ox_1^\bullet + Ox_2 \xrightarrow{k_9} Ox_4^\bullet \quad (3i)$$

Since photocatalytic reactions are surface reactions, from reactions (3) a differential kinetic system results, in which the concentrations of species may be conveniently expressed in term of surface concentrations ({} = moles/unit catalyst surface). This assumption avoids, for the purposes of the model, the problems related to the choice of the proper adsorption isotherm.

In general, the surface concentration is related to the solution concentration by a generalized partition coefficient $K_I = n_{Ibound}/n_{Ifree} = [I_{bound}]/[I_{free}]$, where the concentrations $[I]$ are expressed over the entire volume of the system. The surface concentration is proportional to the solution concentration of I by $\{I\} = K_I\,[I_{free}]/(C_{cat}S)$, where S is the specific surface area (m^2g^{-1}) and C_{cat} is the concentration of powdered catalyst ($g\,l^{-1}$) over the entire volume of the solution. The partition coefficient K_I may be constant as the total analyte concentration $C_I \to 0$, or even a complex function of C_I depending on the adsorption isotherm [43]. When also mass transfer limitations have to be considered, surface concentrations can be related to the solution concentration by the suitable model. These relationships are not developed here in detail.

The surface concentration units are used also for e^- and h^+, that are generated inside the bulk semiconductor, at a maximum distance from the surface equal to the penetration depth of light. The bulk concentrations $[e^-]$ and $[h^+]$ are related to equivalent surface concentrations $\{e^-\}$ and $\{h^+\}$ by $[I] = \{I\}Sd$, where S is the specific surface area of the catalyst (m^2g^{-1}) and d its bulk density. The reaction (3b) sums both bulk and surface recombination reactions, expressed as equivalent surface concentrations. Thus $k_2 = (k_{2,surf} + k_{2,bulk}(Sd)^2)$, where $k_{2,surf}$ (surface dimensions) and $k_{2,bulk}$ ($M^{-1}s^{-1}$) refer to the recombination at the surface and in the bulk, respectively. The constant $k_{2,surf}$ includes also reactions (2c)–(2d) for surface trapping.

If the moles of photons *absorbed* by the unit surface of catalyst and unit time ϕ is considered, for every photon absorbed a bulk e/h pair is formed. Since the recombination reaction is taken explicitly into account in an overall reaction generating heat or light,

the quantum yield of e/h formation in reaction (2a) is unitary. The reduction of system 2 to system 3 does not modify this reasoning. Also in this case the rate of formation of e/h pairs is given by $r_{e/h} = \phi$, where ϕ is expressed in mole (for convenience) of photons absorbed per unit surface and unit time. For a non-porous thin film of definite geometrical surface, and monochromatic light, ϕ is directly related to the absorbed irradiance E (W/m^2), unless a constant due to scattering, through $\phi = E/(N_A h\nu)$. Thus, the rate of formation of e/h pairs is given by $r_{e/h} = k_r E$.

This choice for dimensions of the light flux incoming into the system lets to avoid problems originating from the geometry of illumination, the morphology of the catalyst (thin film or powder), and the related uncertainty due to the scattering, difficult to be evaluated particularly for powders with broad size distribution [8]. The complex relationship between the absorbed radiation inside the entire volume of the reactor and that absorbed by the catalyst at any point inside the reactor space is outside the scope of this paper. However, the degradation rate inside the entire reaction volume may be easily calculated, given the relationship between the locally absorbed light and the degradation rate.

The possible values of the rate constant coefficients of reactions (3) and the literature references are reported in the detailed review of Appendix 1 of Ref. [40]. It was also reported that in reaction (3b) bimolecular carrier recombination never follows second order kinetics. Whilst single excitons decays exponentially, multiple pairs annihilate with second order rate coefficients k asymptotically approaching a ($t^{1/2}$) dependence [41]. In this work we assume under steady state illumination a simple second order kinetics, owing to the average characteristics of the reaction constant k_2, deriving from the bulk (reaction (2b)) and surface recombination reactions (reaction (2e)–(2f)).

If the hypothesis of the steady state is applied to $\{e^-\}$ (Eq. (4a) in system 4), $\{h^+\}$ (Eq. (4b)), $\{Ox_1^\bullet\}$ (Eq. (4c)), and $\{Red_2^\bullet\}$ (Eq. (4d)), assuming constant $\{Ox_2\}$ and $\{Red_1\}$, the system (4) is obtained. Eq. (3i) can be extended also to cover reactions of the first oxidized intermediate with species that, like Ox_2, are supposed at constant concentration.

$$\phi - k_2\{e^-\}\{h^+\} - k_4\{e^-\}\{Ox_2\} - k_6\{e^-\}\{Ox_1^\bullet\} - k_8\{e^-\}\{Red_2^\bullet\} = 0 \quad (4a)$$

$$\phi - k_2\{e^-\}\{h^+\} - k_3\{h^+\}\{Red_1\} - k_5\{Red_2^\bullet\}\{h^+\} - k_7\{h^+\}\{Ox_1^\bullet\} = 0 \quad (4b)$$

$$k_3\{h^+\}\{Red_1\} - k_6\{e^-\}\{Ox_1^\bullet\} - k_7\{h^+\}\{Ox_1^\bullet\} - k_9\{Ox_1^\bullet\}\{Ox_2\} = 0 \quad (4c)$$

$$k_4\{e^-\}\{Ox_2) - k_5\{h^+\}\{Red_2^\bullet\} - k_8\{e^-\}\{Red_2^\bullet\} = 0 \quad (4d)$$

Since the system is still too complex to obtain an analytical solution, the following is assumed: the further reductive reaction of oxidant (reaction (3h), k_8) and the back reaction of oxidant (e.g. $O_2^{\bullet-}$) (reaction (3e), k_5) are neglected. Still in this case an analytical solution in not possible, since a fifth order polynomial comes out.

Two cases are viable for further reduction: case A) the reaction of surface transient radical $Ox_1^\bullet$ with adsorbed Ox_2 is negligible with respect to that with photogenerated active specie h^+ (reaction (3i) is negligible with respect to reaction (3g)); case B) the reverse of case A, that is the reaction of transient radical $Ox_1^\bullet$ with photogenerated active specie h^+ is negligible with respect to that with Ox_2 (reaction (3g) is negligible with respect to reaction (3i)). The second case assumes a fundamental role of adsorbed Ox_2 (i.e. oxygen or other oxidants) in promoting the oxidation of the radical formed by the light promoted oxidation.

3.1. CASE A: the oxidant as a mere scavenger

Under the hypotheses of case A, the system (5) is obtained:

$$\phi - k_2\{e^-\}\{h^+\} - k_4\{e^-\}\{Ox_2\} - k_6\{e^-\}\{Ox_1^\bullet\} = 0 \quad (5a)$$

$$\phi - k_2\{e^-\}\{h^+\} - k_3\{h^+\}\{Red_1\} - k_7\{h^+\}\{Ox_1^\bullet\} = 0 \quad (5b)$$

$$k_3\{h^+\}\{Red_1\} - k_6\{e^-\}\{Ox_1^\bullet\} - k_7\{h^+\}\{Ox_1^\bullet\} = 0 \quad (5c)$$

This approximation to the general kinetic system avoids hypotheses on the relative rate of recombination (reaction (3b)) with respect to that of electron

scavenging as previously reported [42]. The system was solved for $\{e^-\}$, $\{h^+\}$, $\{Ox_1^\bullet\}$, giving a fourth order polynomial for $\{e^-\}$. After quadrature, the rate $= k_3\{h^+\}\ \{Red_1\} - k_6\{e^-\}\ \{Ox_1^\bullet\}$ was evaluated. Among the four solutions, the following has a physical meaning

$$r_o = \frac{\alpha_1\phi}{\alpha_3}\left\{(\alpha_1 - 4\alpha_2 - \beta) + \left(4/\beta\left(\alpha_3(\alpha_1 + 8\alpha_2 - \beta) - \alpha_1^2(\alpha_1 + 4\alpha_2 - \beta) + 8\alpha_2^2(\beta + 4\alpha_1)\right)\right)^{1/2}\right\} \quad (6)$$

where $\beta = (\alpha_1\ (\alpha_1 + 8\alpha_2))^{1/2}$ and $\alpha_1 = k_4k_7\{Ox_2\}$, $\alpha_2 = k_3k_6\{Red_1\}$, $\alpha_3 = 16\phi k_2k_6k_7$.

In Eq. (6) the rate r_o is a function of three experimental parameters (substrate and oxidant concentration, and light flux) and five kinetic constants that retain the principal features of the photocatalytic process, that is the light induced charge separation and recombination, the oxidative and reductive electron transfers, the back reaction of the oxidized substrate, and the formation of a stable oxidized intermediate. Moreover, the eight physical parameters are collected in three parameters α, which account for experimental conditions and catalytic system characteristics. The parameter α_1 is related to the concentration at the catalyst surface of the electron scavenging species $\{Ox_2\}$, its rate constant k_4 for reaction with photogenerated electrons, and the rate constant k_7 for further oxidation of the substrate. The parameter α_2 is related to the surface concentration of the substrate $\{Red_1\}$, its rate constant k_3 for reaction with photogenerated oxidizing species ($\equiv$ Ti-O$^\bullet$ or free holes), and the rate constant k_6 for the back reaction of oxidized substrate $\{Ox_1^\bullet\}$ with photogenerated reducing species. The parameter α_3 is related to the photon flux absorbed (ϕ), the rate constant of recombination k_2, the reductive back reaction (k_6), and the further oxidative degradation step of the substrate (k_7).

Given a substrate (k_3, k_6, k_7), an oxidant (k_4) and an illuminated photocatalyst (ϕ, k_2), the parameter α_1 will depend mainly on the oxidant reactivity and concentration, α_2 on the type and concentration of the substrate, and α_3 on the light flux/geometry of illumination, and the type of catalyst.

Eq. (6) gives also the dependence of the quantum yield $\eta = r_o/\phi$ (degradation rate of the primary compound per unit surface/ absorbed photon flux per unit surface) on experimental parameters. This will depend on α_i. As previously noted [42], the quantum yield for the photocatalytic process will depend on the system on which it is measured (substrate, catalyst, its type, texture, morphological form, and light intensity). The major problem associated with the measure of η is the evaluation of ϕ. When for experimental convenience the absorbed radiation inside a unit volume of the reactor ϕ_{tot}, evaluated by extinction, is used instead of ϕ, the photon efficiency $\eta' = r_v/\phi_{tot}$ is obtained, where $r_v = r_oC_{cat}S$ is the volumetric rate. The photon efficiency takes into account not only the quantum yield of the photocatalytic processes, but also other properties of the semiconductor, like different reflectance and scattering, that are important for engineering purposes [8].

Eq. (6) is the main result of this work. It was investigated for different values of parameters differing for several orders of magnitude. The quantum yield η is reported in Fig. 1 (left), in which η (on the ordinate) is reported as a function of α_1 and α_2 on bottom axes. Fig. 1 shows the kinetic behavior of photocatalytic systems under all the possible values of experimental parameters (concentration of oxidant and substrate, absorbed light flux) and micro-kinetic constants. The values of α_1 and α_2 vary from 1×10^{-6} to 1. Higher values do not change the shape of η. The different figures refer to different values of α_3 (covering a range of 4 order of magnitude), that can be considered as roughly proportional to the total light flux.

The analysis of Eq. (6) and Fig. 1 shows that the rate increases with α_1 (limit $[\text{rate}]_{(\alpha_1\to 0)} = 0$, limit $[\text{rate}]_{(\alpha_1\to\infty)} = \infty$), decreases with light intensity (limit$[\text{rate}]_{(\alpha_3\to 0)}$ = undefined, limit$[\text{rate}]_{(\alpha_3\to\infty)} = 0$) (see also the values on ordinate of Fig. 1 as a function of α_3), and that there is a maximum (or an inversion in the double reciprocal plot) only with respect to α_2, that is for the concentration of the substrate (limit$[\text{rate}]_{(\alpha_2\to 0)} = 0$, limit$[\text{rate}]_{(\alpha_2\to\infty)} = 0$). The rate has a maximum only with respect to α_2. The maximum is sharpest for small values of α_3, little values of α_1 (that is low light flux or concentration of catalyst, or small recombination constant), and small values of α_2. Since $\alpha_2 = k_3\ k_6\ \{Red_1\}$, depending on the type of substrate, the observed rate maximum (at constant ϕ or α_3) will appear at comparatively smaller concentrations of substrate as the back reaction will be more

important (high k_6). The product k_6 $\{Red_1^{\bullet}\}$ in reaction (3f) will increase resulting in a higher apparent k_6 if the outward diffusion is limited by confinement in restricted spaces (e.g. pores) or the intermediate product is very hydrophobic. This kinetic model thus supports recent observations by Cunningham [29], who reported a negative order dependence on $\{Red_1\}$.

Some other experimental data confirm the trend forecast by Eq. (6) on the peaked shape of the degradation rate (unusual reciprocal LH linear transform) observed at low concentration of substrate. Fig. 2 reports the photon efficiency for the degradation of toluene and dodecane with P25 [44], and chloroform with CISE TiO_2 [45]. Whilst for some compounds, as toluene, the rate level off, for others, like dodecane and chloroform, the rate has a maximum. The predicted behavior is qualitatively consistent with these data, and also with the observation reported for thin films [46].

Although the rate (or η) vs. concentration has in some cases a Langmuirian shape (see some sections of graphs in Fig. 1 parallel to the α_2 axes and Fig. 2 for toluene), the preceding kinetic analysis shows that the predictions of the Langmuir–Hinshelwood equation are a coincidence. The double reciprocal plots according to the LH model are reported in Fig. 1 (right). On these plots an approximate linear behavior is always obtained averaging on the experimental error. However, the calculated almost linear LH behavior (at least for high values of $1/\alpha_1$ or $1/\alpha_2$) is obtained taking the concentrations at the surface of the catalyst, without invoking any hypothesis about the partition or isotherm considered.

The zero-order dependence of the observed rate (or quantum yield) on the concentration of substrate is not basically due to the surface adsorption or availability of surface sites (which are not considered in the present model), but to the back reaction of oxidation/reduction of intermediate products. Anyway, the decrease after the maximum along α_2 has no explanation in term of adsorption.

In the case that there is no back reaction (e.g. $k_6 = 0$), the rate $= k_3\{h^+\}\{Red_1\}$ is given by

$$r_o = \gamma \left\{ \left(1 + \frac{\phi}{\gamma} \right)^{1/2} - 1 \right\} \tag{7}$$

where $\gamma = k_3\, k_4\, \{Red_1\}\, \{Ox_2\}/(2\, k_2)$ is for a system with a given substrate (k_3), a given oxidant (k_4, e.g. O_2), and a given semiconductor (k_2) under proper light flux/geometry of absorption (ϕ). Although limited far from the "rate plateau", Eq. (7) may be useful for practical applications, since only one kinetic parameter ($k_3k_4/(2\, k_2)$) is considered. Noting that $\phi_v = \phi\, C_{cat}\, S$, and assuming that $\phi_v = \varepsilon\, C_{cat}\, \phi_{tot}$, it can be easily seen that the volumetric rate r_v has a Langmuirian shape as a function of catalyst concentration, even if K_i is constant (for partitioning of reactants see above).

The kinetic solution given in Eq. (7) shows that, in the absence of the back reaction (reaction (3f)), the rate increases with a square-root like dependence on light intensity (ϕ), $\{Ox_2\}$ and $\{Red_1\}$. It is never possible that the rate has a maximum or a true plateau for some conditions, and possibly decreases at high $\{Red_1\}$. Thus, the Langmuirian or the bell shape of the rate is due to the back reaction (3f). The rate increases as the oxidant is more powerful (k_4), the substrate is less recalcitrant to oxidation (k_3), or the recombination reaction is decreased (k_2). For very small values of γ the rate is proportional to $\sqrt{\{Red_1\}\{Ox_2\}}$ (species at the surface) and to the square root of ϕ. In the limit that $\gamma \to \infty$ the rate equals $\phi/2$, that is the maximum quantum yield is 0.5.

Since the analysis of Eq. (6) showed that the rate has *always* a maximum as a function of α_2, given α_1 and α_3, the maximum attainable rate is always at $\alpha_{2,max}$. Fig. 3 reports $\alpha_{2,max}$ as a function of α_1 and α_3, and the corresponding value of the quantum yield. As previously noted, α_2 is small (i.e. the peak of the rate is observed at low concentration of substrate at a given back reaction rate) when α_3 (light intensity) is small, and α_1 is large (good oxidant present or at high surface concentrations). On the contrary, when α_1 is small and α_3 is large, the peak of the rate will appear at high α_2 (high concentration of substrate).

The maximum quantum yield attainable is depicted in Fig. 3 (right). The quantum yield decreases with α_3 and increases with α_1. Fujishima et al. observed an increase of the photon efficiency decreasing the light intensity [47] as predicted by Fig. 3, right. The rate is proportional to η at constant α_3. Along α_3 axes, at constant α_1, the rate (unless a constant), increases as the product ($\eta\ \alpha_3$). The maximum attainable rate is $\phi/2$, corresponding to $\eta = 0.5$. However, very high values of α_1 can be reached only for oxidants that can reach very high surface concentrations, or are very

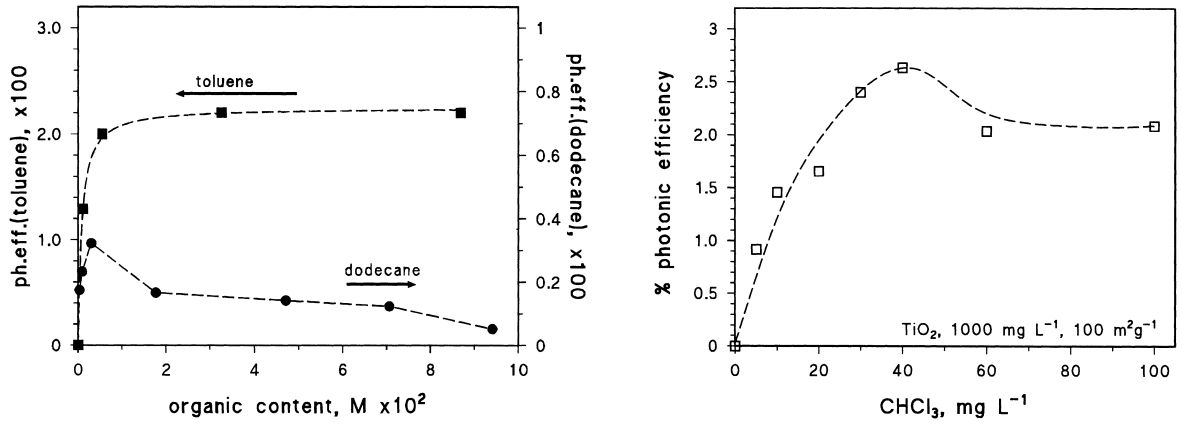

Fig. 2. Percent photon efficiency for the degradation of toluene and dodecane (left), and for chloroform (right), as a function of their total concentration, at constant light flux. Data on left has been obtained on Degussa P25 and redrawn from Ref. [44]. Data on right have been obtained on TiO_2 of nominal surface area of $100\,m^2g^{-1}$, prepared for UE Solardetox project by CISE (Milan).

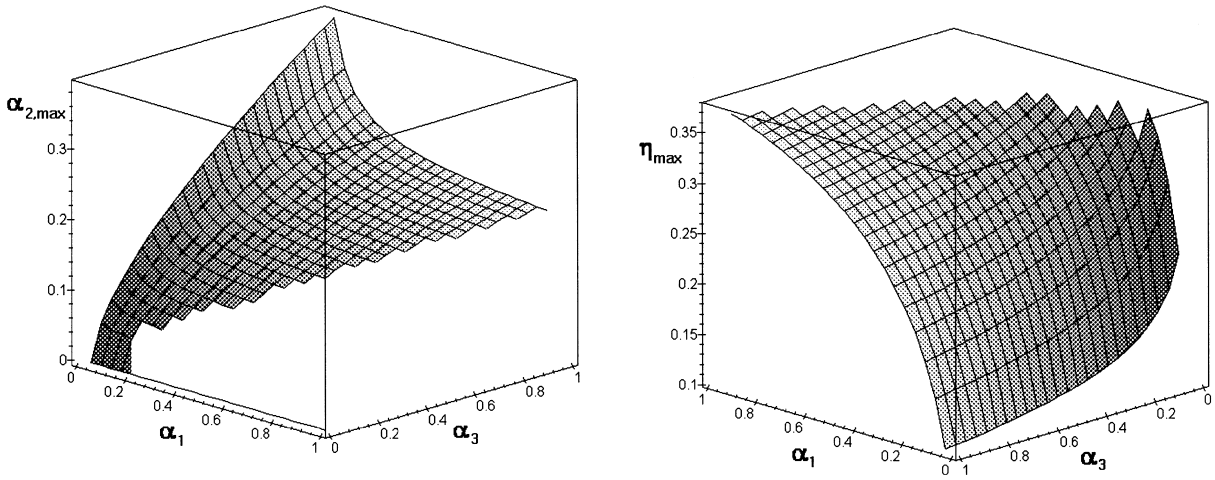

Fig. 3. (left) Values of α_2 for which the rate is maximum ($\alpha_{2,max}$) as a function of α_1 and α_3; (right) Quantum yield corresponding to value of $\alpha_{2,max}$ at left.

effective. Although it is strongly adsorbed on anatase [48], the scarce solubility of oxygen in water can limit its performance. Other oxidants may perform better [49].

The hypotheses under which Eq. (6) was obtained are probably not satisfied at high values of α_1. When the concentration of oxidant is high, the reaction (3i) may be important compared to reaction (3g). This is the case B, previously referred to.

3.2. CASE B: active role of the oxidant

This case assumes a fundamental role of adsorbed Ox_2 (i.e. oxygen or other oxidants) in promoting the oxidation of the radical formed by the light promoted oxidation. In this kinetic regime the reaction of transient $\{Ox_1^{\bullet}\}$ with photogenerated active species h^+ is negligible with respect to that with Ox_2 (reaction (3g)

is negligible with respect to reaction (3i)). Under these conditions the system (4) can be reduced assuming that in Eq. (4c) or in both Eq. (4b) and (4c) the rate $k_7\{h^+\}\ \{Ox_1^\bullet\}$ is negligible. For both these cases the solution of the reduced system (4) is possible in analytical form (the electron concentration is given by a third order polynomial), but the solution is unmanageable and involved, not permitting a collection of kinetic and operational parameters in some ways. Owing to this, and noting that the computation time with the analytical solution may be larger than that required for a numerical solution, the explicit analytical solution will not be reported. Moreover, the efficiency and rate are dependent on five kinetic constant and three experimental parameters ($\{Ox_2\}$, $\{Red_1\}$ and ϕ), which render any simulation useless, or the fit to experimental data very difficult. The general trend of quantum yield is similar to that of Fig. 1, top.

Typical of case B are: (i) The rate does not show maximum with respect to the operational variables as $\{Red_1\}$, $\{Ox_2\}$ and ϕ; (ii) the maximum attainable quantum yield is not limited to 1/2, but tends to 1 under limiting conditions. Thus, kinetic regime of case B) is desirable in practical applications for having best conversion of light.

4. Conclusions

The present kinetic analysis lead to manageable analytical solutions for the dependence of the rate on operational parameters. From a mechanistic point of view, it has been concluded that, when a maximum is observed for the rate as a function of substrate concentration, the reaction of Ox_2 with $Ox_1^\bullet$ is not predominant. On the contrary, when a maximum is not observed, the reaction (3i) may be important, or the conditions of the photocatalytic systems are close to that reported in Fig. 1 top (i.e. α_3 high).

As for the best utilization of (solar) light in photocatalytic reactors, this kinetic analysis suggests that under the kinetic regime previously described as case A, low light intensities (attainable without solar light pre-concentration, α_3 low) are always favorable to have high photon efficiency. Moreover, high surface concentrations of electron scavengers (α_1 high) are always beneficial. When these are limited by water solubility (as for oxygen), the lowest possible concentration of catalyst (thus giving $\{Ox_2\}$ high), compatible with full light absorption in the actual reactor geometry, is advantageous.

The solution given by Eq. (6) is little more involved than the semiempirical equation valid for an oxidative process, which was previously proposed by our group for fitting the data obtained on PCP at the Plataforma Solar de Almeria [16],

$$-\mathrm{d}C_i/\mathrm{d}t = \frac{\beta_1 \phi C_i C_\mathrm{s}}{\beta_2 \phi + \beta_3 C_i C_\mathrm{s}} \tag{8}$$

where C_i and C_s are the concentration of substrate and catalyst, respectively.

Although using the same number of parameters as Eq. (8), with only three parameters Eq. (6) is yet more meaningful on a theoretical basis, and can accommodate the case in which the rate manifests a maximum as a function of the substrate concentration (see Fig. 1, along α_2 axes). By contrast, Eq. (8) shows only a saturative behavior. As far as the two-parameter LH rate equation is concerned, this is silent on the dependence of the rate on the light intensity, and has no mechanistic meaning. Although limited to definite cases, Eq. (7) gives the correct dependence on the substrate concentration, and light flux with only one parameter. Finally, the increase of the calculation time required by the use of three parameters (Eq. (6)) for the solution of the radiation transfer equation and integration of the rate equation over the reactor volume, would be minimal if compared to the two parameters needed by the LH rate equation.

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