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Design of photocatalytic reactors made easy by considering the photons as immaterial reactants

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Abstract

While it is quite obvious that photons have an essential role in photochemical and photocatalytic processes, it is not simple to analyse the radiation process.

A simple approach is presented on the assumption that photons can be treated as immaterial reactants. It is then possible to evaluate the radiation process in terms of parameters such as conversion, selectivity and yield, which are common in the conventional reaction engineering, and of an additional parameter, a volume efficiency factor, which accounts for the exploitation of the reaction volume as the result of the inevitable attenuation of the radiation in the transport through the participating medium.

Attention has also been focused on the validation of kinetic data when, as it is usually done, they are interpreted in terms of volume averages.

Finally, guidelines have been prepared to support preliminary phases of analysis and/or design of a photocatalytic reactor.

Keywords: Photocatalysis; Reactor design; Photons; Kinetic analysis; Efficiencies; Titanium dioxide

1. Introduction

A designer of a photoreactor, which contains a suspension of the photocatalyst, has to reach several different objectives, since he must utilize the costly radiant energy as effectively as possible and, at the same time, he must obtain the highest rates of reaction throughout most of the reactor volume. This could be a formidable task as it is often necessary to settle conflicting requirements as it is reported in literature (Camera-Roda and Santarelli, 1982; Cassano et al., 1995; Martin et al., 1999; Minero, 1999; Cassano and Alfano, 2000) and as it will be discussed in the present work. Actually the problem of studying the distribution of

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Nomenclature

$A = C/(kI_0)$ dimensionless parameter
C parameter in the kinetics equation for the reaction rate (Eqs. (1) and (2)); dimensions: $M/(T^3L)$; possible unit: W/m^3
$\dot{e}'''$ local volumetric rate of radiant energy absorption (LVREA); dimensions: $M/(T^3L)$; possible unit: W/m^3
I intensity of the radiation; dimensions: M/T^3; possible unit: W/m^2
I_0 intensity of the radiation entering into the reactor; dimensions: M/T^3; possible unit: W/m^2
k absorption coefficient for the radiant energy; dimensions: L^{-1}; possible unit: m^{-1}
R_i (Eq. (1)), R (Eq. (2)) reaction rates; dimensions: $moles/(TL^3)$; possible unit: $mol/(s\ m^3)$
R_{max} parameter in the kinetics equation for the reaction rate (Eq. (1)); dimensions: $Moles/(TL^3)$; possible unit: $mol/(s\ m^3)$
x spatial coordinate; dimensions: L; possible unit: m

Greek symbols
δ thickness of the slab; dimensions: L; possible unit: m
$\eta_{radiation}$ fraction of the entering radiant energy which is absorbed inside the reactor ("conversion" of the photons); dimensionless
$\eta_{quantum\ yield}$ quantum yield ("selectivity" of the photons); dimensionless
η_{yield} yield of the photocatalytic reaction; dimensionless
η_{volume} productivity of the reactor; dimensionless
$\tau = \tau_0 \frac{x}{L}$ optical thickness at depth x; dimensionless
$\tau_0 = k \times L$ optical thickness of the slab; dimensionless
$\langle\ \rangle$ denotes a volume averaged quantity
[ ] denotes a concentration

Dimensions
M mass
T time
L length

the photon flux inside the reactor has been sometimes disregarded, but recently its importance has been recognized for the analysis of the performances of the reactor and for the interpretation of kinetic data (see e.g. Cassano and Alfano, 2000). Many efforts have been made to derive rules to be used as guide lines in the reactor design, but usually these rules appear rather complex and refer to a very large number of efficiencies (Serpone et al., 1996; Sagawe et al., 2003a,b, 2004) whose meaning is sometimes difficult to be perceived.

The objective of this paper is to obtain simple and meaningful rules, so that they can be profitably used in the reactor design and also in the kinetics analysis of reaction data. This aim can be accomplished through an approach where the photons are treated as conventional, even if immaterial, reactants and effectiveness indices equivalent to those usually adopted in the "conventional" chemical reactor engineering will be introduced and discussed.

The suggested approach can be justified on the basis of some preliminary considerations. It is obvious that the reaction takes place only if there is the simultaneous presence of the photocatalyst, of the reactants and of the photons. In the present work attention is focused on the photons. These latter are absorbed by the photocatalyst to generate the electron–hole pairs, as the primary event of the oxidation mechanism of the organic molecule. So the photons, as the material reactants, are consumed by the reaction, but are not "replaced" as the conventional reactants. In fact the photons do not diffuse according to a Fickian law nor they can be "mixed" by convective motions of the fluid. On the contrary they are transported obeying to the "radiant energy transfer equation" (RTE), with very singular behaviors, as the integro-differential nature of the governing equation reveals. In principle the only way to "mix" the photons is to use "static mixers" ("static" with respect to the photons which travel with the speed of the light), such as reflectors and scattering particles. Unfortunately it is rather difficult to have a good control on the degree of mixing given by this type of "devices", even if in some cases (Spadoni et al., 1978; Camera-Roda et al., 1983; Goslich et al., 1997; Minero, 1999; Cassano and Alfano, 2000) it has been proven that they may increase the conversion.

Since the rate of reactions is affected by the local photon "concentration" (that derives from the local radiation intensity), the first step is to know the radiant energy distribution inside the reactor volume. Many methods, mostly numerical, have been developed to solve the RTE and to get the radiant energy distribution. Then it is possible to calculate the local volumetric rate of radiant energy absorption $\dot{e}'''$ (LVREA), on which it is often assumed the reaction rate depends. The availability of a RTE solver represents only the first necessary tool for the design of the reactor, since many effects must then be considered in order to choice the optimal geometric configuration and the optimal operative condi-

tions (for instance the intensity of the light source, the use of reflectors, the photocatalyst concentration and its distribution, etc.).

It is important to observe that in photocatalytic reactions the quantum yield, which basically expresses the ratio of the reaction rate with respect to the absorbed radiant energy, is not constant with the radiation intensity. It has been shown that it decreases with this quantity. This well known phenomenon (Okamoto et al., 1985; D'Oliveira et al., 1990; Turchi and Ollis, 1990; Ollis, 1991; Ollis et al., 1991; Al-Sayyed et al., 1991; Mills and Morris, 1993; Terzian and Serpone, 1995; Martin et al., 1996; Parent et al., 1996; Serpone et al., 1996; Ohko et al., 1997; Peill and Hoffman, 1998; Greco, 2004) implies that, if the radiant energy is valuable, it should be convenient to have low level of illumination so that this energy is used as effectively as possible. The disadvantage is that with a limited flux of photons the reaction rate is low.

The optimal utilization of the reactor volume is important too. For a given radiation entering the reactor, it is ultimately affected by the choice of the concentration of photocatalyst powders and of the dimensions of the reactor. As said, the radiation has to be absorbed by the photocatalyst in order the reaction to occur and a high concentration of photocatalyst makes absorption more pronounced and potentially increases the availability of active sites per unit volume. Unfortunately absorption makes the radiation less available for the reaction in the zones of the reactor far from the light source. In other words it is rather difficult to exploit effectively all the reactor volume, which can be partly dark and this is especially true for high concentration of photocatalyst or for large geometric thickness of the reactor. The consequence is that (i) it is useless, for a given reactor, to increase the photocatalyst concentration beyond a certain value and (ii) the thickness of the reactor and the concentration of the photocatalyst cannot be chosen independently.

All the previous requirements will be taken into account in the following analysis to derive the practical rules.

2. Kinetics as a basis for the analysis

In all the problems of reactor design, the knowledge of the reaction kinetics is an essential starting point. It is therefore necessary to have a kinetics equation which, for a given photocatalyst, describes the dependence of the reaction rate on the radiation intensity I (or the photon flux), or some other related quantity. In the following analysis the other parameters (e.g. concentration of the substrate and of the electron scavenger) are supposed to be constant, as here the focus is only on the effect of I.

As mentioned in Section 1, the reaction rate in photocatalysis in general increases with the radiation intensity, but with an order of reaction which is not constant throughout the whole range of potential variation of I. It is widely accepted (see e.g. Turchi and Ollis, 1990; Ollis, 1991; Terzian and Serpone, 1995) that the reaction order is one at low illumination level, shifts towards an order equal to 1/2 at intermediate value of I, and it shows to be independent on I (zero order) at high values of the radiation intensity. Actually this variation of the order of reaction appears to be continuous and the shape of the curve is very similar to those represented by a Langmuir–Hinshelwood type kinetics (Minero et al., 1996; Minero, 1999) or even by a Michaelis–Menten type kinetics (Camera-Roda et al., 2003).

The results obtained in our laboratory (see Appendix A for more details) for the photocatalytic degradation of 4-chlorophenol (4CP) confirm this behavior, as it is shown in Figs. 1 and 2. In all the experiments the photocatalyst concentration, the reactor thickness and the UVA source were chosen in order to work with a radiation intensity inside the reactor as even as possible ("photodifferential" reactor). The term "photodifferential" stands to indicate that the radiation is absorbed to attain the reaction, but only at a negligible extent. The concept of photodifferential reactors for photocatalytic reactions is analogue to the well established one of "differential reactor" for conventional reactions (for the definition of the differential reactor see e.g. Levenspiel, 1999). In both cases the aim is to work with a reactor where it could be safely and conveniently assumed that the concentration of the reactants is almost uniform inside the reactor. In the case of photocatalytic reactions the reactants are represented by immaterial reactants,

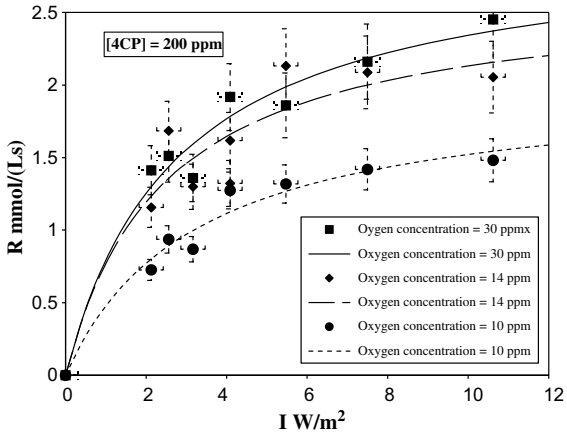

Fig. 1. Initial rate of reaction for the photocatalytic degradation of 4CP as a function of the radiation intensity. Constant substrate concentration and curves for different values of the oxygen concentration.

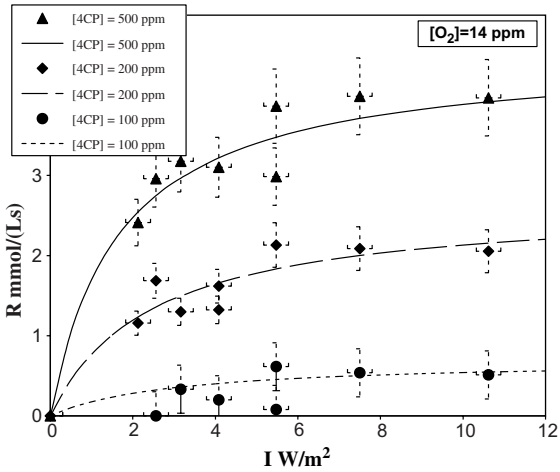

Fig. 2. Initial rate of reaction for the photocatalytic degradation of 4CP as a function of the radiation intensity. Constant oxygen concentration and curves for different values of the substrate concentration.

the photons. The use of photodifferential reactors permits to obtain consistent kinetics data even neglecting the exact radiant energy distribution inside the reactor, as it will be demonstrated afterward. This characteristic is particularly useful in photochemistry and photocatalysis since measuring or modeling the radiation field inside a photoreactor can be very complex.

Various reaction mechanisms have been proposed by different researchers, but most of them ultimately lead to a constitutive equation of the reaction rate that possesses features that can be described by the following kinetic equation:

$$R_i = \frac{R_{\max} k I}{k I + C} \tag{1}$$

where R_i is the reaction rate with the used photocatalyst, k is the radiant energy absorption coefficient, and $R_{\max}$ and C are constants in the hypothesis that the other parameters are kept constant.

Note that Eq. (1) can be obtained by rearranging the equation originally derived by Minero et al. (1996), from a relatively simple model for the mechanism of reaction which takes into account the primary events in the photocatalytic system. Other researchers (see e.g. Okamoto et al., 1985; Turchi and Ollis, 1990; Ollis et al., 1991; Serpone et al., 1996) suggest that the mechanism could be different and that the zero order behavior at high radiation intensity should be caused by mass transfer limitations of the chemical species participating to the reaction. The results reported in Figs. 1 and 2 appear to exclude the hypothesis of mass transfer limitations. In fact, by increasing the concentration of the oxygen or of the substrate, one observes that the shift towards the zero order behavior seems to happen at very similar

Table 1
Values of the constants $R_{\max}$ and C/k in the kinetic equation (1) obtained by best fitting of the experimental data in Figs. 1 and 2

Concentration of oxygen (ppm)	Concentration of 4-chlorophenol (ppm)	$R_{\max}$ (mmol/l s)	C/k (W/m^2)
10	200	2.0	3.2
14	200	2.7	2.5
30	200	3.0	2.8
14	100	0.7	3.0
14	500	4.5	1.7

values of I (also the value of C/k, reported in Table 1, for the different fitting curves plotted in Figs. 1 and 2 do not change very much and show no definite trend with increasing concentrations of the oxygen or of the substrate). On the contrary if the mass transfer were the limiting process this shift should be expected at higher values of I when the concentration of the substrate or when the concentration of the oxygen are increased, even taking into consideration that concurrently the obtained reaction rate is rising.

On the other hand, regardless of which are the intervening mechanisms and even if Eq. (1) could be judged semiempirical, it stands nonetheless as a convenient description of the process. With this meaning it should be regarded as the formulation of a general and consistent reaction rate.

Eq. (1) shows also that the kinetics rate is a function of the product of the radiation times the absorption coefficient. This means that, if different values of the absorption coefficient (e.g. different values of the photocatalyst concentration) are used, the researchers may find different values of the radiation intensity at which the order of reaction shows to vary. This observation can explain some discrepancies for the values reported in literature (Ollis et al., 1991; Parent et al., 1996; Greco, 2004) of this quantity.

In the local mass balance for the participating chemical compounds, a constitutive equation for the local reaction rate is usually adopted in which the product $k \times I$ is replaced with the LVREA (see e.g. Spadoni et al., 1978; Cassano and Alfano, 2000). In the case of a monochromatic radiation, the LVREA is given by $\dot{e}''' = \int_{4\pi} k I_\Omega \, d\Omega'$ where Ω is the direction of propagation and the integral is performed over the solid angle 4π. It should also be pointed out that, if Eq. (1) holds true, this approach is not, in principle, as rigorous as it is usually claimed. In fact, if the intensity reaching the photocatalyst in a given point varies with the incoming direction, then this variation should be taken into account with a proper integration. The integration performed in evaluating the LVREA does not satisfy this requirement, since it counts with the same weight the various different intensities of the radiations incoming from all the direc-

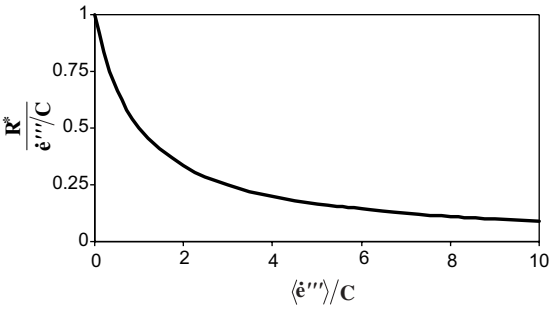

Fig. 3. Quantum yield vs. dimensionless LVREA.

tions, whereas from Eq. (1) it is apparent that the radiation causes a particular intrinsic effect according to its intensity.

Anyway the error which derives from the use of the LVREA in substitution of the product $k \times I$ is negligible in most practical cases of design of a photocatalytic reactor. So, for the sake of simplicity, the following approximate expression of local reaction rate will be utilized:

$$R = \frac{R_{\max}\dot{e}'''}{\dot{e}''' + C} \tag{2}$$

The first consequence of the kinetics depicted by Eq. (2) is that the quantum yield, which is represented in some way by the ratio of R with respect to $\dot{e}'''$, decreases with $\dot{e}'''$, as it is apparent in Fig. 3 where the relevant dimensionless quantities are plotted.

3. Results

3.1. Kinetics analysis

In order to obtain reliable experimental information on the kinetics of reaction, the local values of the reaction rate and those of the radiation intensities from the various directions, or at least of the LVREA, should be known. The use of "photodifferential" reactors may help in getting consistent data, since by definition the intensity is kept almost uniform in this type of reactor.

However very often kinetic analysis is made with reactors of finite dimensions, where the radiation intensity and, as a consequence, the reaction rate are far from being uniform. Furthermore it can be practically impossible to acquire local measurements of these quantities. So it is much easier, and therefore it is a common practice, to use values averaged throughout the volume both of the reaction rate $\left(\langle R \rangle = \frac{\int_V R\,\mathrm{d}V}{V}\right)$, derived from measurements of the extent of reaction, and of the absorbed radiant energy $\left(\langle \dot{e}''' \rangle = \frac{\int_V \dot{e}'''\,\mathrm{d}V}{V}\right)$, obtained by measuring the transmittance. The drawback is that in this manner it may happen to misinterpret the experimental data, or, in other words, the average values should be used only with caution, as it is here demonstrated.

It is easy to understand that, when Eq. (2) holds, it is generally $\langle R \rangle \neq \frac{R_{\max}\langle \dot{e}''' \rangle}{C + \langle \dot{e}''' \rangle}$, since only when $C \gg \langle \dot{e}''' \rangle$ (which implies that R is nearly first order with respect to $\dot{e}'''$) it results that $\langle R \rangle \cong \frac{R_{\max}\langle \dot{e}''' \rangle}{C + \langle \dot{e}''' \rangle}$.

This means that in general the average values cannot be used in substitution of the local values, even if this is a widespread procedure in kinetics analysis and photoreactor design.

As an example a highly ideal, albeit demonstrative, system will be here considered. In a slab photocatalytic reactor in the hypothesis of:

(i) perfect mixing,
(ii) monochromatic radiation travelling only perpendicularly to the surfaces,
(iii) no scattering,
(iv) radiation absorbed only by the photocatalyst,

the radiation intensity for a given wavelength at a depth x is given by:

$$I(x) = I_0 \exp[-\tau]$$

where I_0 is the radiation intensity entering the reactor at $x = 0$, $\tau = \tau_0 \frac{x}{\delta}$ is the optical thickness at the depth x, δ is the geometrical thickness and $\tau_0 = k \times \delta$ is the optical thickness of the slab.

The LVREA in the investigated system can be obtained at each depth, x, as: $\dot{e}'''(x) = k \times I(x)$ where k is the absorption coefficient, which should depend on the concentration of the photocatalyst. It might be convenient, in this case, to define the dimensionless $\dot{e}'''^*$ and $\langle \dot{e}''' \rangle^*$ in this way: $\dot{e}'''^* = \frac{\dot{e}'''}{k \times I_0}$; $\langle \dot{e}''' \rangle^* = \frac{\langle \dot{e}''' \rangle}{k \times I_0}$.

When the governing equations are made dimensionless, the relevant dimensionless parameters turn out to be: τ_0 and $A = C/(kI_0)$. It is clear that for k constant (constant concentration of the catalyst), if the thickness of the slab or the intensity of the entering radiation varies, then the value of τ_0 and A changes, respectively.

In Fig. 4 it is shown how the average reaction rate and the local reaction rate change with the average and the local LVREA, which depend on τ_0 and τ, respectively. When A is low, or in other words when I_0 and/or k are large, the local and the average curves deviate at relatively low values of $\langle \dot{e}''' \rangle^*$. When this happens the use of the average values is unacceptable. Note that $\langle \dot{e}''' \rangle^* = \frac{1 - \exp(-\tau_0)}{\tau_0}$, so that low values of $\langle \dot{e}''' \rangle^*$ correspond to high values of τ_0 and vice versa.

When A is high the difference between the two curves vanishes, because the system works substantially at low reaction rates in the "first order zone". However in this case only this first order behaviour can be observed,

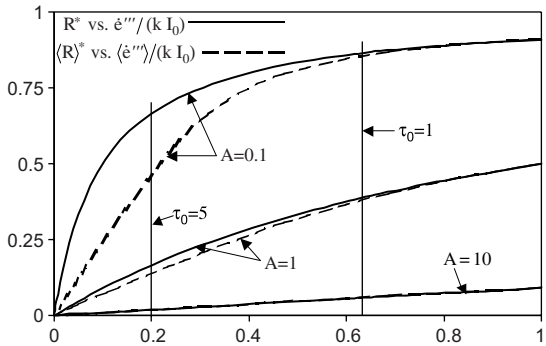

Fig. 4. Comparisons of the average dimensionless reaction rate $\langle R\rangle^* = \langle R\rangle/R_{max}$ with the actual dimensionless reaction rate $R^* = R/R_{max}$ at different values of A.

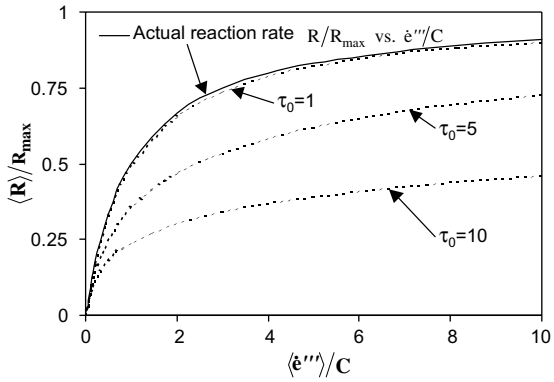

Fig. 5. Comparisons of the average dimensionless reaction rate $\langle R\rangle^* = \langle R\rangle/R_{max}$ with the actual dimensionless reaction rate $R^* = R/R_{max}$ at different values of the optical thickness τ_0.

because the absorption coefficient and/or the radiation intensity are too low to reach the different orders of reaction.

It can be concluded that the direct use of the average values in kinetic analysis is safe when:

- A is high, because only the first order behaviour is possible;
- τ_0 is low, because the distribution of the radiant energy is almost uniform inside the reactor (photodifferential reactor).

One usual way to operate in order to get kinetic data is to keep constant the photocatalyst concentration (k constant) and the thickness of the reactor (L constant) and to vary the intensity of the incoming radiation (I_0 varies). So τ_0 is kept constant. In Fig. 4 the lines at $\tau_0 = 1$ and $\tau_0 = 5$ are vertical lines. It is apparent that the average data obtained at $\tau_0 = 5$ can be used as actual kinetic results only if A is high, whereas when $\tau_0 = 1$ very small deviations from the actual reaction rate curve are obtained at whatever value of A. This is confirmed also by the curves reported in Fig. 5, where the kinetic results obtained operating at constant τ_0 are compared with the actual rate of reaction.

So it can be concluded that it is not necessary to operate at very low values of τ_0 in order to get a "satisfactory" photodifferential reactor, since it could be sufficient that τ_0 is only a little below 1, with benefits for the conversion. This is demonstrated for the present idealized investigated case, with the assumptions reported previously, but it is expected that this conclusion could change only slightly for other practical cases. Finally it must be noted that in order to achieve low values of τ_0 it is more convenient to decrease the thickness L of the reactor than to lower k. In this way sufficiently large values of the product $k \times I$ can be reached without having the necessity to operate with extremely high radiation intensities.

3.2. Reactor design

In conventional chemical reactor design some effectiveness indices are usually considered as a guide for the design choices (see e.g. Fogler, 1986). In view of the observation that, as already discussed, for many characteristics the photons can be considered as immaterial reactants, analogous efficiencies are here introduced for photocatalytic reactors. This approach can simplify the analysis and make clarity in this type of problem, where one of the major difficulties is to conciliate the conflicting requirements of keeping the reaction rate as high as possible in most of the reactor volume and at the same time limiting the radiant energy losses.

The following efficiencies are defined:

$$\eta_{\text{radiation}} = \frac{\text{Absorbed radiant energy in the reactor volume}}{\text{Entering radiant energy}} = \frac{\langle \dot{e}'''\rangle/C \times \delta/(1/k)}{I_0/(C/k)}$$

$$\eta_{\text{quantum yield}} = \frac{\text{Observed reaction rate in the reactor volume}}{\text{Absorbed radiant energy in the reactor volume}} = \frac{\langle R\rangle/R_{max}}{\langle \dot{e}'''\rangle/C}$$

$$\eta_{\text{yield}} = \frac{\text{Observed reaction rate in the reactor volume}}{\text{Entering radiant energy}} = \frac{\langle R\rangle/R_{max} \times \delta/(1/k)}{I_0/(C/k)}$$

$$\eta_{\text{volume}} = \frac{\text{Observed reaction rate in the reactor volume}}{R_{max}} = \frac{\langle R\rangle}{R_{max}}$$

For analogy with conventional chemical reactors $\eta_{radiation}$ represents in some way the "conversion" of the photons inside the reactor, $\eta_{quantum\,yield}$ represents the "selectivity" of the absorbed photons with respect to the "desired reaction", the remaining part of the absorbed photons being actually lost for "undesired reactions" (i.e. mechanisms that finally generate heat), and η_{yield} represents the "yield" of the reaction. As usual it results: yield = conversion × selectivity ($\eta_{yield} = \eta_{radiation} \times \eta_{quantum\,yield}$).

The efficiency η_{volume} is analogue to the "effectiveness factor" that is employed in conventional heterogeneous catalysis in porous catalyst with the observation that, in the present system, it is more convenient to assume the maximum potential reaction rate R_{max} as the reference reaction rate. In fact the optimal, even if purely theoretical, situation is the one in which the reaction rate is uniform in the reactor and equal everywhere to R_{max}, the upper limit of the reaction rate. So η_{volume} gives a measure of how much the behaviour of the reactor deviates from this ideal condition. From another point of view η_{volume} represents also the dimensionless "productivity" of the reactor, that is the moles of the substrate reacted in the reactor per unit of time per unit of volume.

The results presented in the following figures are obtained for the same idealized system previously considered.

In other cases with different geometries and different optical properties the results can be quantitatively, but not qualitatively, different, but the approach is general, as well as the definitions of the efficiencies, that can always be successfully applied to get meaningful indications for the design choices. Of course, when the scattering is taken into account more parameters need to be considered (e.g. the albedo and the scattering phase function), but the approach is still functional.

In Fig. 6 the effects of τ_0 and A are reported for most of the defined efficiencies.

The results show that:

- at low values of $A = C/(kI_0)$, one obtains higher values of η_{volume} (the reaction rate increases with $k \times I_0$), but lower values of $\eta_{quantum\,yield}$;
- at low values of τ_0, one obtains higher values of η_{volume} (the radiation intensity and, consequently, the reaction rate are more uniform inside the reactor, because the radiation is absorbed at a lower extent), but lower values of $\eta_{radiation}$ and $\eta_{quantum\,yield}$;
- $\eta_{quantum\,yield}$ is not very much affected by the optical thickness τ_0;
- $\eta_{radiation}$ does not depend on A whereas it shows a strong dependence on τ_0 (when τ_0 is high almost no radiation exits the reactor);
- most of the variations with τ_0 of the efficiencies take place around $\tau_0 = 1$ (τ_0 is equal to 1 when the mean photon free path is of the same order of magnitude of the reactor thickness);

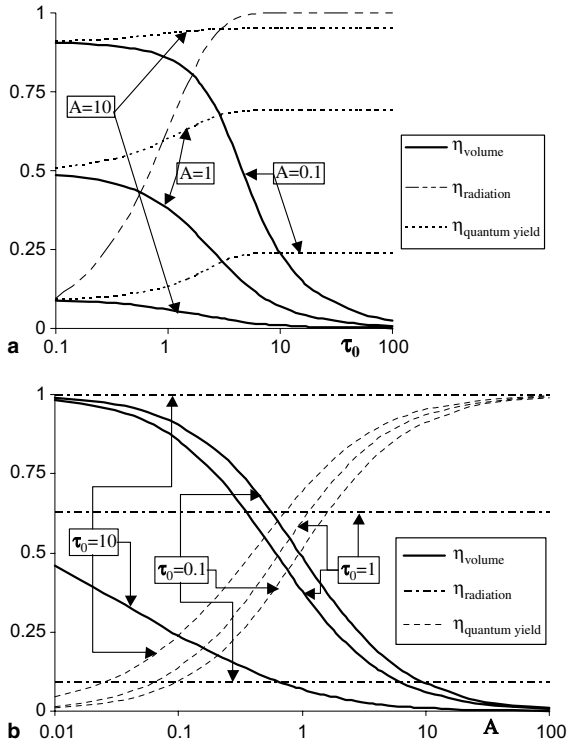

Fig. 6. (a) Various efficiencies vs. the optical thickness τ_0 at different values of A. (b) Various efficiencies vs. the parameter A at different values of τ_0.

- most of the variations with A of the efficiencies take place around $A = 1$.

The different efficiencies have been measured for some of the experiments carried out with the experimental set up described in Appendix A. The results are summarized in Fig. 7a and b, where a comparison is made with the theoretically predicted values of the same efficiencies, calculated by adopting independently measured values of the kinetics parameters and of the optical properties.

The agreement between the measured and the predicted values appears to be good. Therefore it can be concluded that the dependence of these quantities on the intervening parameters A and τ_0 is experimentally confirmed.

The optimal values of A and τ_0 may be chosen also in view of the results presented in Fig. 8.

One observes that:

- At a given entering radiation intensity I_0, that is for a given value of A, if τ_0 increases then η_{yield} ($\eta_{yield} = \eta_{radiation} \times \eta_{quantum\,yield}$) increases, but η_{volume} decreases, because larger parts of the reactor becomes less illuminated;

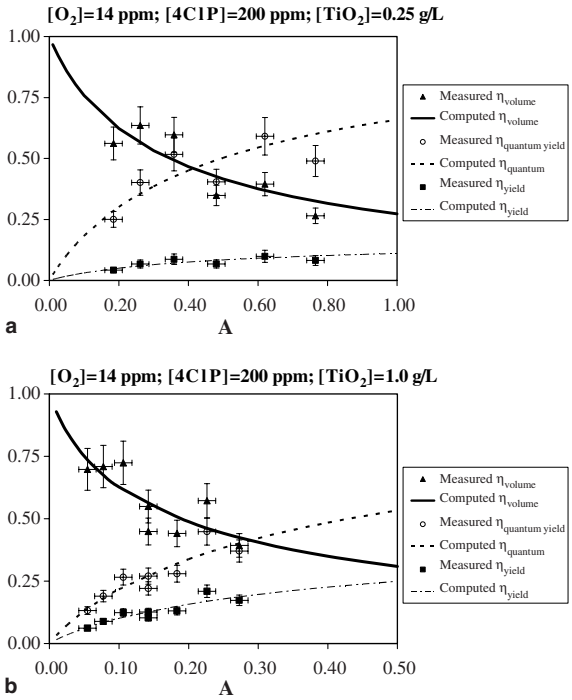

Fig. 7. (a) Comparison of measured and computed efficiencies for $[O_2]$ = 14 ppm, [4CP] = 200 ppm, and $[TiO_2]$ = 0.25 g/l. (b) Comparison of measured and computed efficiencies for $[O_2]$ = 14 ppm, [4CP] = 200 ppm, and $[TiO_2]$ = 1.0 g/l.

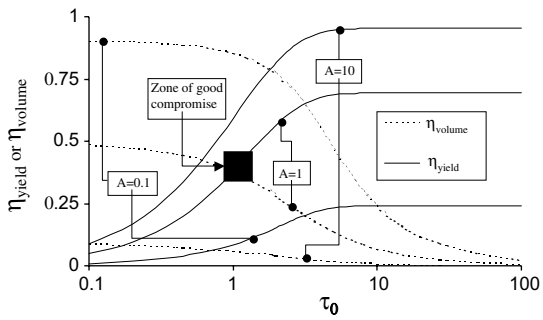

Fig. 8. η_{yield} and η_{volume} vs. the optical thickness τ_0 at different values of A.

- If a high yield is the main aim, it is preferable to use high value of τ_0, but not greater than 10 because it is practically useless, with the awareness that the volume of the reactor is unevenly exploited, i.e. the productivity is low;
- Values of both A and τ_0 around 1 represent a good compromise since in this case $\eta_{radiation}$, $\eta_{quantum\ yield}$, η_{yield} and η_{volume} are all sufficiently high.

The choices suggested by the previous discussion are summarized as follows:

- Use high intensity I_0 of the entering radiation and low optical thickness in order to maximize the productivity and the exploitation of the reactor volume (η_{volume} at its maximum). This could be the choice in the case the radiant energy is inexpensive and the main cost is associated to the reactor;
- Use low intensity I_0 of the entering radiation ($A \approx 10$) and high optical thickness ($5 < \tau_0 < 10$) in order to maximize the utilization of the radiant energy and to work at high values of the quantum yield ($\eta_{radiation}, \eta_{quantum\ yield}$ and η_{yield} at the maximum). This could be the choice if the radiant energy is particularly valuable and the volume of the reactor is of no concern;
- A satisfactory compromise can be reached at intermediate values of the intensity I_0 and of the optical thickness (values of A and τ_0 around the unity).

4. Conclusions

The role of radiation in photocatalytic reactions has been investigated treating photons as immaterial reactants. This assumption allows to relocate photocatalytic processes, but more generally photochemical ones, to the well established framework of conventional reaction engineering making the approach to this class of processes easier for those who are not familiar with radiation and associated phenomena.

On the basis both of experimental results and of theoretical speculations from the open literature a phenomenological rate equation, Langmuir–Hinshelwood type, has been considered to account for the change from 1 to 0 of the reaction order with respect to the radiation absorption rate.

The errors which may derive from the common practice of interpreting kinetic data in terms of volume averaged quantities are then discussed and outlined.

It has finally been shown that, even in view of the utilization of the radiant energy, results can be interpreted in terms of familiar parameters as conversion, selectivity and yield. The peculiar feature of radiation, related to its inevitable attenuation in the transport through a participating medium, is accounted for by an additional parameter, a sort of volume efficiency, which is indicative of how effectively the reaction volume is exploited.

Therefore it has been possible to derive criteria for the selection of the most appropriate operative conditions and to suggest some guide lines which can support practitioners in the acquisition and validation of kinetic

data, as well as in the analysis or design of a photocatalytic reactor.

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Appendix A. Experimental set up

The photoacatalytic rate of degradation of 4-chlorophenol has been analysed in a plane slab reactor (2 mm thick) illuminated from above by two Philips TLD/05 fluorescent lamps with aluminium reflectors. The lamps, each one with a nominal power of 15 W, emit radiation between 300 and 460 nm with a maximum at 365 nm. The reactor volume is confined between two flat pyrex glasses, so that the radiation enters from the upper glass, travels through the reactor and exits from the lower glass, from where it is definitely lost. The illuminated surface of the reactor is 8.3 cm wide and 21.4 cm long and the impinging radiation intensity can be changed by varying the distance between the lamps and the reactor surface. The relative position of the two lamps and the arrangement of the reflectors were designed with the aim of having an uniform distribution of the light entering the reactor. Measurements of the UVA irradiance at different points of the surface, made by a Delta Ohm quantum meter equipped with a UVA probe (HD 9021), confirmed the uniformity of the light distribution. The TiO_2 suspension in water with the organic contaminant exits the reactor, passes through a thermostated tank (volume = 500 ml) and is continuously recycled to the reactor by a membrane pump (Yamada, model NDP-05-FPT) with such a rate that the whole system can be safely considered as a batch perfectly mixed apparatus. The flow inside the reactor is laminar. The oxygen concentration is kept constant by allowing a controlled continuous dissolution in the tank of an appropriate quantity of oxygen.

In all the runs the degradation of 4-chlorophenol (obtained from Fluka) was studied in aqueous solution (water demineralised by both ion exchange and reverse osmosis) with TiO_2 powders (Degussa P25) as photocatalyst.

The TiO_2 suspension was prepared by mixing a weighted amount of powder in a given volume of water, then, before utilization, the slurry was ultrasonicated for 15 min in order to minimize the formation of clusters.

The concentration of the 4-chlorophenol was measured by HPLC (separation column Alltech, Alltima C18 10 U) and the TOC was determined by a Shimadzu TOC-5000 analyser. Both of these two instruments were regularly calibrated and at each calibration a set of comparisons were made between their responses and the known concentration values of reference mixtures to get information about the expected uncertainty. The usual rules for the analysis of experimental data (see e.g. Caporaloni et al., 1998) were then applied to obtain an estimate of the experimental errors (associated to the standard deviation) for the reaction rate, which are reported as error bars in the relevant figures. The error bars for the values of the light intensity are based on the error estimation made by the manufacturer of the utilized Delta Ohm quantum meter equipped with the UVA probe HD 9021.

Only the initial values of the reaction rate have been considered in order to minimize the effect of the presence of the intermediate products, which could compete with 4-chlorophenol for the utilization of the photoactivated sites.

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