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Optimization of the thickness of a photocatalytic film on the basis of the effectiveness factor

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Abstract

In a supported ‘‘thick’’ photocatalytic film, internal diffusion of the reactant and transport of the photons might hinder the reactivity of the material and limit the obtainable rate of removal of the organic pollutant substrate. The effectiveness factor, η, of the photocatalytic film is the index of the extent of the limitation.

Two dimensionless parameters affect η: the optical thickness, τ_0, and the ratio, α, of the characteristic time of diffusion with respect to the characteristic time of reaction. The analysis demonstrates that the process is controlled by the diffusion of the substrate when the parameter α is high and it is controlled by the transport of the photons when τ_0 is high.

It is also shown that different results are obtained if the film is illuminated from the fluid–film interface (PF) or from the glass–film interface (CF). In PF the observed rate of degradation increases with the film thickness, but no further enhancement of the rate of degradation is obtained when the thickness exceeds the depth where a substantial depletion of the photons or of the substrate takes place. In CF the rate of degradation reaches a maximum at an optimal thickness.

Finally, a new simple procedure to estimate the parameters and then to predict the best thickness is illustrated.

Keywords: Photocatalytic film; Photocatalysis; Optimization

1. Introduction

Detoxification of water streams is one of the most promising applications of photocatalysis [1–8]. Indeed the utilization of photocatalysis is interesting for a complete mineralization of many toxic compounds, in particular if they are present at low concentration and are recalcitrant to a biological degradation. However, in most cases the practicability of the process depends on the attainment of a high efficiency in the utilization of the radiant energy and of the photocatalyst. On the other hand, the interaction between photocatalyst, reagents and photons, which must occur in order to obtain the reaction, makes the optimization and the design of the photocatalytic reactors very complex.

Essentially two types of photocatalytic reactors can be adopted: reactors working with a slurry of photocatalytic powders and reactors with photocatalyst immobilized in films [9].

The use of powders, in particular when their dimension is small (in the scale of 20–100 nm in order to have high surface/volume ratios) involves a series of problems, such as the possible dispersion in the environment of these powders during the manipulation of the photocatalyst and their problematic separation from the effluent streams [10–12].

When a photocatalytic film is used most of the practical drawbacks that are encountered with slurries of the photocatalyst powders [9,13] can be avoided, but other problems arise and additional efforts are required in the design of the reactor. For instance, mass transfer outside the film and/or inside the film can limit the obtainable reaction rate [14–18].

External mass transfer of the reagents in the fluid phase can be enhanced acting on the fluidodynamics or reducing the path of the reagents by decreasing the geometrical dimensions of the cross section of the duct where the fluid flows. In the current paper this phenomenon will not be investigated, since the interest will be restricted to what happens inside the film and it will be assumed that at the interfaces of the film a certain substrate concentration and a certain UVA light intensity are given. It is admitted that locally in the film the simultaneous

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presence of the reagents and of the photons, which for many aspects can be considered as immaterial reagents [19], is necessary for the photocatalytic reaction to occur. The process may then be controlled: by the kinetics of the reaction, or by the transport of the reagents, or by the transport of the radiant energy or by a combination of these phenomena.

Inside the photocatalytic film the reagents are transported by diffusion which can be the limiting process, if the diffusivity is low and the thickness of the film is not very thin. Furthermore, the thickness of the film also affects the distribution of the intensity of the radiant energy inside it. In fact the local availability of the photons, which must be absorbed in order to activate the reaction, depends on the depth that they must penetrate, so that when the optical path is "long" the intensity can be significantly reduced. On the other hand, it must also be taken into account that the quantity of the photocatalyst which is immobilized in the films of a photocatalytic reactor is typically less than the one which is usually present in a slurry system. From this different point of view, thicker films should be preferred in order to increase the quantity of photocatalyst present in the reactor and possibly to absorb more UVA radiant energy [20–24]. It follows that the goal should be to use films as thick as possible, provided that the reaction can take place inside the whole film with sufficient "effectiveness".

An analysis based on the effectiveness factor in a system where the simultaneous presence of reagents and photons plays a significant role in the process was firstly carried out in [25], where a photochemical reactor was studied.

The effectiveness factor of a photocatalytic film was taken into account in Ref. [26], but no attention was given there to the final effect of the thickness on the observed rate of degradation of the substrate. This effect was considered by Chen et al. [27,28] and Herz [29]. In Ref. [27,28] a simplified approach was used to get the values of the effectiveness factor, by considering an exponential decay of the concentration profile which in many cases does not reproduce with satisfactory accuracy the actual concentration profile. Furthermore, the values of the intervening parameters were derived by a rather sophisticated and complex analysis and by fitting the data obtained in multiple experiments [27–29]. On the other hand, it should be advisable to develop simple and sound criteria that allow to easily determine which is the controlling process and to act consequently to enhance its rate and to optimize the system. Indeed it must be noted that the effective diffusivity of the substrate in the film, the kinetic constant that appears in the kinetic equation for the volumetric reaction rate and the optical properties of the film may strongly depend on the physical characteristics of the film, which in turn depend on the deposition method. The various techniques of deposition, such as deposition of photocatalyst powders, sol–gel methods, CVD or plasma-CVD, produce films with very different properties. Even with the same deposition method the properties of the film may change very much if the preparative conditions vary only slightly. The consequence is that it is not possible to extrapolate the values of the parameters for a certain film to another film. The relevant characteristics of the film must be appraised for every preparative condition and it is important that this task is not too complex, expensive and time consuming.

Finally, it is also worth noticing that no one of the cited papers explicitly recognizes the role of the optical properties on the reaction rate so that the subsequent analysis does not give a complete understanding of the effects of the optical thickness of the film.

The aim of the present paper is to identify the intervening parameters which affect the effectiveness, to indicate simple methods to assess the value of the parameters and consequently identify the possible limiting processes, which should be improved, and finally to find which is the optimal thickness that maximizes the obtainable reaction rate.

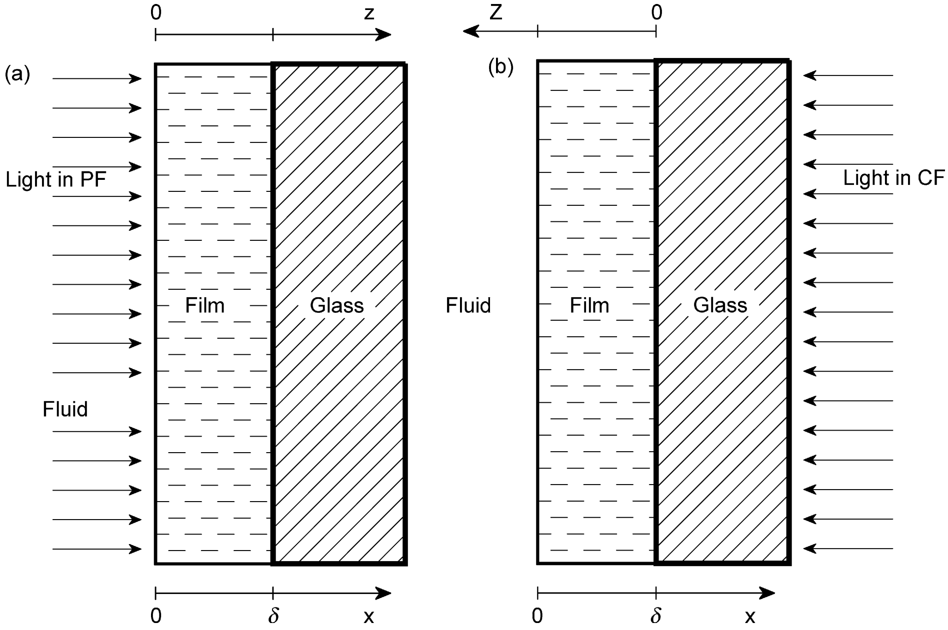

Fig. 1. Schematic representation of the system: (a) PF; (b) CF.

2. Mathematical model

Referring to the scheme in Fig. 1, it is assumed that the reaction takes place inside a plane or an almost plane film where the reactant (the organic pollutant substrate) can diffuse from the fluid–film interface. The light enters the film alternatively from the fluid–film interface or from the glass–film interface. In the first case the photons travel in parallel flow (PF) with respect to the diffusive transport of the reactants and in the second case in counter flow (CF).

In the following analysis, it will be assumed that the absorption coefficient of the radiation, k_a, and the effective diffusivity, D_e, of the substrate in the porous photocatalytic film are uniform within the film. Actually, they depend on the porosity which in some cases decreases with depth. However, in view of the fact that here "thick" films (i.e. with a thickness larger than 1 μm and usually smaller than 10–15 μm) are considered, it is likely that the porosity does not change linearly with the depth and most of the variation is confined in a relatively thin layer close to the film-support interface. In this case, it is safe to neglect the variation with depth of these properties since its overall effect will be minor.

The adopted reaction rate equation is:

$$R = k\,C_S\,\dot{e}''' \tag{1}$$

where k is the kinetic constant, C_S the substrate concentration and $\dot{e}'''$ represents the local volumetric rate of radiant energy absorption, LVREA (see, e.g. [30–32]). Eq. (1) assumes the reaction rate to be first order with respect to both the concentration of the substrate and to the LVREA. Eq. (1) can be considered the simplified form of a more general kinetic equation:

$$R = k'\frac{C_S}{K_C + C_S}\frac{\dot{e}'''}{K_R + \dot{e}'''} \tag{2}$$

when $C_S \ll K_C$ and $\dot{e}''' \ll K_R$.

The dependence of the reaction rate on C_S in Eq. (2) reproduces a Langmuir–Hinshelwood type kinetics and has been largely discussed in many papers (see, e.g. [33]). A discussion on the role of $\dot{e}'''$ on the kinetics of the reaction can be found in [19]. For the system investigated in [19], K_R/k_a was found to vary approximately between 2 and 3 W/m^2. Hence, by considering that the magnitude of $\dot{e}'''$ is given by k_aI, where I is the local radiation intensity, the condition $\dot{e}''' \ll K_R$ can be considered virtually satisfied when the intensity of the UVA radiation in the film is less than about 1 W/m^2. According to other data (see, e.g. [34]) it is sufficient that the intensity is less than "1 solar near-UV equivalent" (about 10 W/m^2) to get a first order reaction with respect to the LVREA. When UVA fluorescent lamps are used, these requirements are often fulfilled throughout most of the film because the emitted UVA flux is typically low and the intensity of the radiation is unavoidably attenuated due to the distance from the light source and due to absorption. At concentrations of organic pollutant substrates normally found in the environment (typically 10–50 mg L^{-1}), it is also verified that $C_S \ll K_C$. On this basis and for the sake of simplicity, Eq. (1) has been adopted in the current analysis. Nonetheless, the present approach can be easily implemented also for the more complex Eq. (2).

Assuming an incident collimated radiation, the beams remain parallel inside the film since the interaction occurs only through absorption [26–29,34,35]: then the LVREA results to be given by $\dot{e}''' = k_aI$, where the intensity I can be conveniently measured in Einstein m^{-2} s^{-1} or, for a given emission spectrum of the lamp, in W m^{-2}.

The attenuation of the radiation is governed by the Lambert–Beer law and then:

$$I(z) = I_0 \exp[-k_a z] \tag{3}$$

where I_0 is the intensity of the radiant energy that enters the film and z the length of the optical path of penetration of the light inside the film. If the light travels perpendicularly to the film surface then the optical path is also the geometrical spatial coordinate that represents the depth inside the film. In this case, defining the optical thickness τ_0 of the film as $\tau_0 = k_a\cdot\delta$ where δ is the geometrical thickness of the film, Eq. (3) becomes:

$$I = I_0 \exp[-\tau_0 z/\delta]. \tag{4}$$

The parameter τ_0 represents the ratio of the thickness of the film with respect to the mean free optical path, $1/k_a$, of the photons.

Since the width and the length of the film are much larger than its thickness the problem is one-dimensional, and the geometry of the system can be schematized as depicted in Fig. 1.

According to the previously illustrated assumptions, the steady state local mass balance equation for the substrate is:

$$D_e\frac{d^2C_S}{dx^2} = R = k\,C_S\,k_a\,I. \tag{5}$$

The boundary conditions are: $C_S = C_{S0}$ at $x = 0$ (fixed concentration at the fluid–film interface) and $dC_S/dx = 0$ at $x = \delta$ (no substrate flux at the film–glass interface).

By using the dimensionless quantities $C_S^* = C_S/C_{S0}$; $I^* = I/I_0$ and $x^* = x/\delta$, the dimensionless form of the previous equation is

$$\frac{d^2C_S^*}{dx^{*2}} = \alpha\,\tau_0\,C_S^*\,I^* \tag{6}$$

where $\alpha = k\,I_0\,\delta/D_e$ with the relevant dimensionless B.C.: $C_S^* = 1$ at $x^* = 0$ and $dC_S^*/dx^* = 0$ at $x^* = 1$.

It must be noted that α depends on the thickness δ of the film and it represents the ratio of the characteristic time of diffusion with respect to the characteristic time of reaction when $\tau_0 = 1$, that is for a film with a thickness equal to the mean free path of the photons. The Thiele modulus ϕ for the photocatalytic film, in analogy with conventional catalysis in porous catalytic particles (see, e.g. [36]), is given by $\phi = \delta\sqrt{k\,I_0\,k_a/D_e} = \sqrt{\alpha\,\tau_0}$ and it is apparent that it depends also on the optical properties, namely the optical thickness, of the film.

The local dimensionless intensity I^* has been calculated by the Lambert–Beer law for radiation entering perpendicularly to the film:

$$I^* = \exp(-t_0 z^*) = \exp(-\tau), \tag{7}$$

where $\tau = k_a z$ is the optical coordinate and $z^* = z/\delta$. The coordinate z^* is given by $z^* = x^*$ for PF and by $z^* = (1 - x^*)$ for CF.

Eq. (6) has been solved numerically by the control volume method [37] to derive the effectiveness factor η defined as:

$$\eta = \frac{\text{observed reaction rate}}{\text{reaction rate at } C_S = C_{S0} \text{ and } I = I_0} = \frac{1/\delta \int_0^\delta R\,dx}{k\,C_{S0}\,k_a\,I_0} \tag{8}$$

It must be observed that the reference reaction rate at the denominator of Eq. (8) represents the reaction rate which would be achieved in the merely ideal case of uniform concentration C_S and uniform intensity I inside the film. In this way the effects of the deviations from the uniformity in the actual distribution of these two quantities can be straightforwardly appreciated and a direct comparison between PF and CF is viable. On the contrary, if other choices of the reference reaction rate were made, then the reference changes according to the investigated case (PF or CF) [26–28] and in the CF case it varies with τ_0 [26].

According to the assumed definition, the effectiveness factor can be computed from the concentration and radiation intensity profiles as

$$\eta = \int_0^1 C_S^* I^*\,dx^* \tag{9}$$

It is obvious that the effectiveness factor depends on the two parameters α and τ_0, as it will be discussed.

The observed rate of degradation of the substrate R_{od} can be evaluated as:

$$R_{od} = \int_0^\delta R\,dx = \delta\,k\,C_{S0}\,k_a\,I_0\,\eta \tag{10}$$

or in dimensionless form as

$$R_{od}^* = \frac{\delta\,k\,C_{S0}\,k_a\,I_0\,\eta}{k\,C_{S0}\,I_0} = \tau_0\,\eta \tag{11}$$

once R_{od}^* is defined as $R_{od}^* = R_{od}/(k\,C_{S0}\,I_0)$.

3. Discussion of the results

Both the photons and the substrate disappear ‘‘due to the reaction’’. The Thiele modulus is an index of the ‘‘hindrance’’ undergone by the substrate to be uniformly present inside the film, since substrate diffuses but is depleted by the reaction. In an analogous way the optical thickness is an index of the ‘‘difficulty’’ of the photons to penetrate inside the film: when travelling through the film they are absorbed and possibly ‘‘utilized’’ by the reaction. As a consequence the profile of the concentration and the profile of the radiant energy intensity become steeper as the Thiele modulus and the optical thickness increase, respectively. This behaviour is evident in Figs. 2 and 3.

In Fig. 3, one can also see the exponential decay of the concentration inside the film which best fits the calculated concentration profile in the case of $\tau_0 = 2.5$ and $\alpha = 5$. The actual concentration profile is the result of complex interactions between the diffusion of the substrate, the transport of the photons and the reaction. These phenomena are almost disregarded by a model assuming a plain exponential decay, which has no theoretical basis, and as a rule the exponential decay is not able to accurately reproduce the actual behaviour of the system: it could be an acceptable casual approximation only in some cases. In Fig. 3, it is evident that when $\tau_0 = 2.5$ and $\alpha = 5$ the divergence between the actual profile and the exponential fitting is indeed significant in the case of PF, even if in the case of CF the exponential decay seems to acceptably fit the actual profile. Of course, when the two profiles diverge, also the evaluation of the effectiveness factor on the basis of the exponential decay profile is unsatisfactory. For instance for PF, $\tau_0 = 2.5$ and $\alpha = 5$ the value of η obtained from the actual concentration profile is 0.222, whereas the value of η computed by assuming the exponential fitting as the concentration profile is 0.242, with a resulting error of +9%.

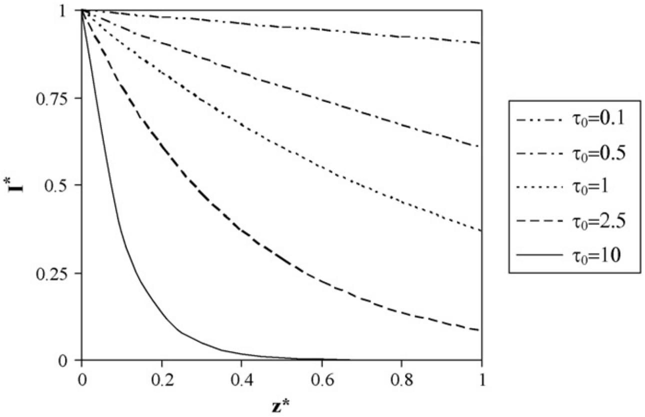

Fig. 2. Profiles of I^* inside the film for various values of the optical thickness.

The effect of a variation of τ_0 on the concentration profiles is shown in Fig. 4.

For a fixed value of α, the concentration profiles become steeper with the increasing of the value of τ_0 provided that τ_0 is not very high. In fact an increase of τ_0 implies that more absorbed radiant energy is utilized by the reaction, but, as it can be observed also in Fig. 2, if τ_0 is significantly larger than 1, e.g. $\tau_0 \geq 10$, the intensity profile is very sharp and the reaction is confined to a fraction of the film, while the rest of the film is practically without light. As a consequence, at high values of τ_0 in PF the concentration profile is almost even in the ‘‘dark’’ zone of the film near the glass-film interface where no reaction takes place and no reagent is consumed. In CF the dark zone is near the fluid–film interface and in this region the concentration profile is almost linear since in the dark zone the reagent diffuses without reaction to reach the ‘‘far’’ region where the light is present and the reagents are consumed by the reaction.

The resulting values of the effectiveness factor are plotted in Figs. 5 and 6.

Firstly, it is observed that the curves for PF are divergent from those for CF demonstrating that different results are obtained illuminating the film from the two opposite directions. This phenomenon is due to the mirror profiles of I in the two

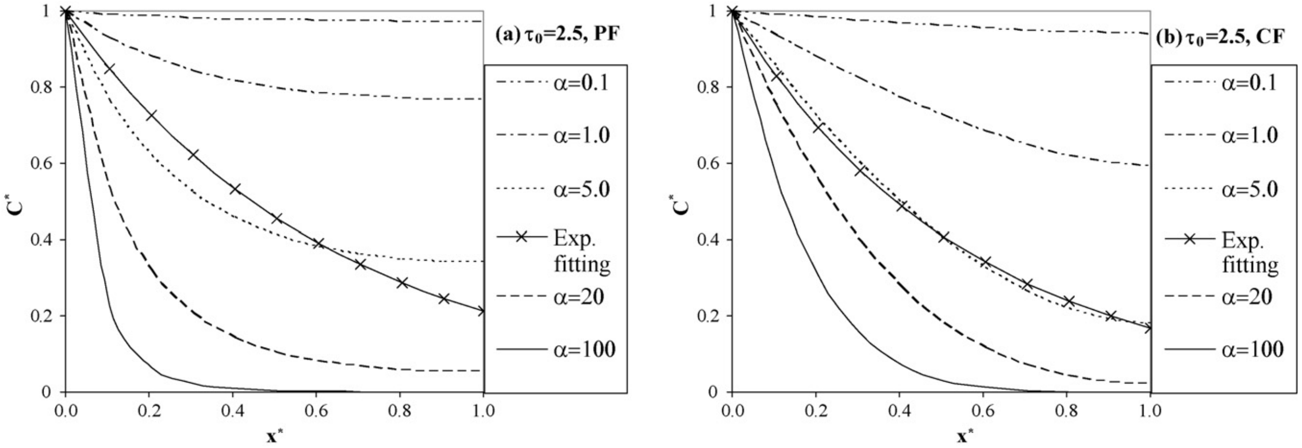

Fig. 3. Substrate concentration profiles inside the film at a fixed value of τ_0 ($\tau_0 = 2.5$) for a range of values of α: (a) PF; (b) CF.

different situations of PF and CF. In Fig. 5, it is apparent that the effectiveness factor decreases by increasing α indicating that, as usual, at high values of α the process is controlled by the diffusion of the substrate inside the film. The asymptotic value of η for $\alpha \rightarrow 0$ decreases by increasing τ_0, since when τ_0 augments the non-uniformity of the radiation intensity becomes more important: as a consequence the whole thickness of the film cannot be exploited effectively by the reaction even if the diffusion is very efficient. In other words when τ_0 is high the process is controlled by the transport of the photons, as it is also clearly shown by the curves in Fig. 6.

Even if η is an index of how effectively the whole thickness of the film (or equivalently the whole mass of the immobilized catalyst) is utilized by the reaction; it does not give a complete knowledge of the yield that can be achieved for the process. It has been shown that an increase of α or of τ_0 implies a decrease of the effectiveness factor. Since these two parameters linearly increase with δ, it results that the smaller is δ the higher is η. However, from the practical point of view, it is more important to investigate the effects on the observed rate of degradation. In view of the fact that it is usually possible to vary the thickness of the film by changing the quantity of photocatalyst deposited in a single deposition or by repeating the deposition of several layers of photocatalyst, the thickness can be chosen in order to maximize the rate of degradation, which is of primary importance for a photocatalytic reactor.

By varying the thickness of a certain type of deposition, the properties (k, D_e and k_a) remain practically the same but the values of the parameters α and τ_0 change. The values of the properties of the material and of the impinging intensity I_0 of the radiation can be lumped into the value of the dimensionless parameter α_1 ($\alpha_1 = k I_0 / k_a D_e$), which represents the value of α at a film thickness that gives a value of τ_0 equal to 1.

The values of the dimensionless observed rate of degradation versus the dimensionless thickness τ_0 of the film are presented in Fig. 7, for some values of α_1.

If the geometrical thickness is made dimensionless with respect to the free mean path of the photons $1/k_a$, τ_0 actually represents the dimensionless thickness of the film. In PF it is evident that the rate of degradation R_{od} monotonically increases with the thickness of the film towards an asymptotic value, whereas for CF R_{od} reaches a maximum at an optimal value of the optical thickness. It is worth noticing that these behaviours have been experimentally observed by some researchers [24,27,28].

These phenomena can be explained by considering the two effects of an increase of δ on (i) the mass of photocatalyst which

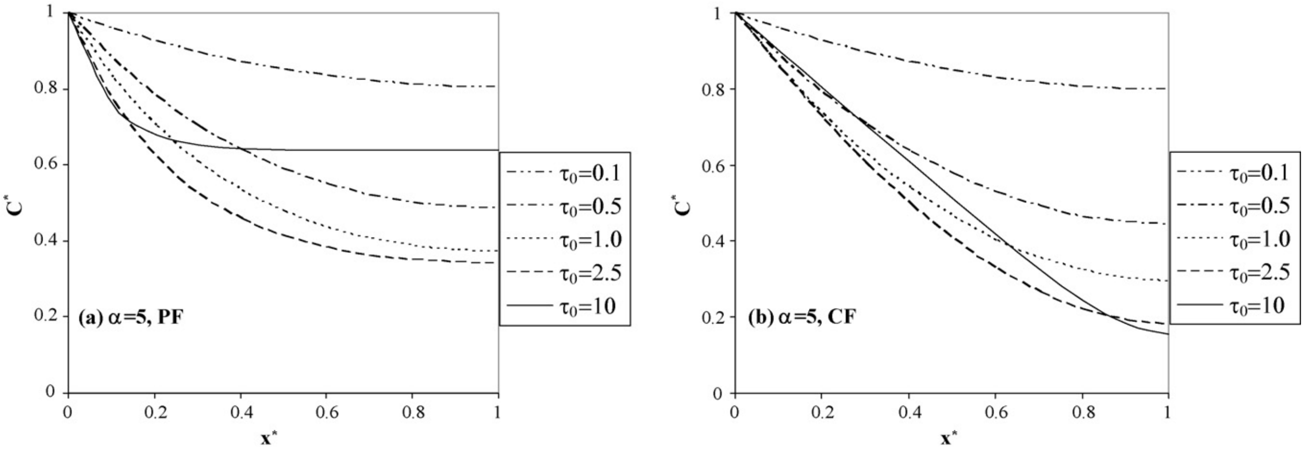

Fig. 4. Substrate concentration profiles inside the film at a fixed value of α ($\alpha = 5$) for a range of values of τ_0: (a) PF; (b) CF.

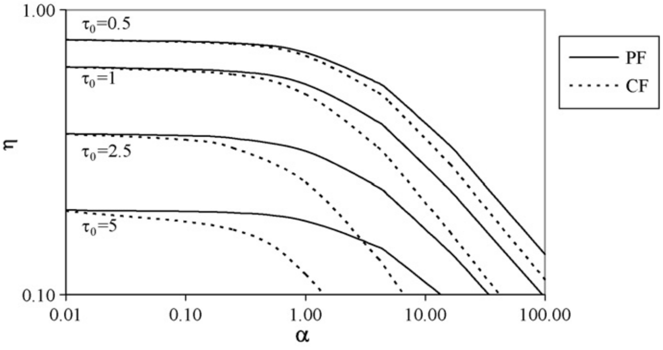

Fig. 5. Effectiveness factor vs. α for a range of values of τ_0.

linearly increases with δ and on (ii) the transport of the substrate and of the photons whose travel inside the film increases with δ. In PF the substrate diffuses in any case through the lighted zone so R_{od} is monotonically increasing with δ due to effect (i); however, no significant enhancement of the rate of degradation can be achieved beyond a certain value of δ which corresponds to the restraining depth where the photons or the substrate are effectively transported. In CF, effect (i) is prevailing on effect (ii) as long as the thickness remains sufficiently small, then, at larger values of δ, effect (ii) prevails since the lighted zone becomes far from the interface from where the substrate diffuses. Both the restraining depth in PF and the optimal thickness in CF decrease by increasing α_1.

For a given film the ratio of the observed reaction rate in PF with respect to the one in CF is given by the ratio between the relevant effectiveness factors and depends on α.

In Fig. 8, this behaviour is shown in two cases: (a) the intensity of the impinging radiation is the same in PF ($I_{0,\mathrm{PF}}$) and in CF ($I_{0,\mathrm{CF}}$) or (b) the intensity $I_{0,\mathrm{CF}}$ is 1.2 times $I_{0,\mathrm{PF}}$. Case (b) might reproduce a situation where the same film is alternatively lighted from the two opposite directions by the same source at the same distance, but the intensity $I_{0,\mathrm{PF}}$ in PF is lower due to additional absorption by the fluid. Case (a) might represent the same situation but with a fluid with negligible absorption. Of course, similar curves can be obtained for whatever value of the ratio $I_{0,\mathrm{CF}}/I_{0,\mathrm{PF}}$.

It is evident that for a given τ_0, that is for a given film, there is an univocal connection between $\eta_{\mathrm{PF}}/\eta_{\mathrm{CF}}$ and α_{PF} or α_{CF} (note that $\alpha_{\mathrm{CF}} = \alpha_{\mathrm{PF}} I_{0,\mathrm{CF}}/I_{0,\mathrm{PF}}$). This observation suggests a simple way to derive important properties of the film which can be used to optimize the system. The intensity $I_{0,\mathrm{PF}}$ and $I_{0,\mathrm{CF}}$ can be easily measured by a UVA radiometer (alternatively $I_{0,\mathrm{PF}}$ can be estimated by measuring the intensity impinging the fluid and measuring by a spectrophotometer the transmittance of the fluid). Also the transmittance of the film can be measured by a radiometer, so that the value of the optical thickness is derived as $\tau_0 = \ln(I_{\mathrm{T}}/I_0)$, where I_{T} is the intensity of the transmitted light, that is at the exit front of the film.

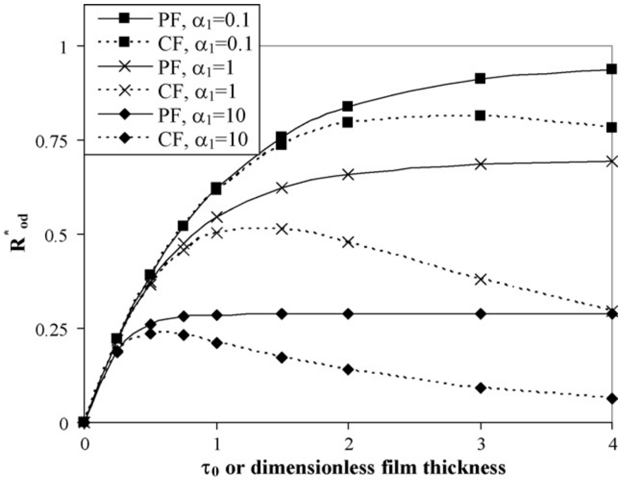

Fig. 7. Dimensionless observed rate of degradation vs. the dimensionless thickness τ_0 of the film for a range of values of α_1.

Then, by performing experiments of photocatalysis in PF and in CF one can measure the observed degradation rates $R_{\mathrm{od,PF}}$ and $R_{\mathrm{od,CF}}$, so that the ratio $\eta_{\mathrm{PF}}/\eta_{\mathrm{CF}} = R_{\mathrm{od,PF}}/R_{\mathrm{od,CF}}$ is obtained. This ratio can be used to get the value of α_{PF} and α_{CF}. When these parameters are known; it is possible to establish which are the possible limiting processes and to optimize the thickness. This procedure has been adopted to elaborate experimental data reported in literature, namely those presented in [27,28]. From the values of R_{od} extracted from the data published in [27,28] it can be evaluated that $\eta_{\mathrm{PF}}/\eta_{\mathrm{CF}} \approx 1.29$ when the thickness of the film gives an optical thickness equal to about 3.5. By assuming $I_{0,\mathrm{CF}}/I_{0,\mathrm{PF}} = 1$, the unique value of α that provides $\eta_{\mathrm{PF}}/\eta_{\mathrm{CF}} = 1.29$ for $\tau_0 = 3.5$ is 0.672, so that $\alpha_1 = 0.672/3.5 = 0.192$. With this value of α_1 the R_{od} curves can be plotted versus the thickness of the film to find the best values of the thickness both in PF and in CF.

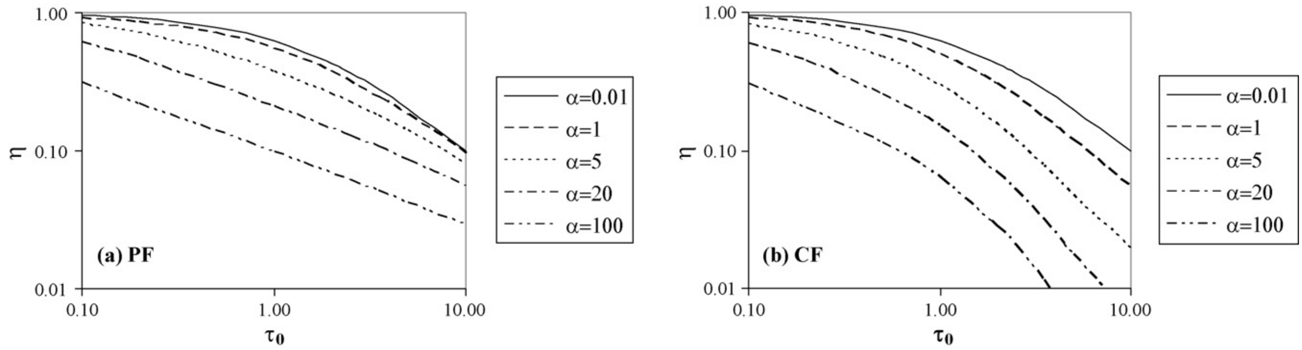

Fig. 6. Effectiveness factor vs. τ_0 for a range of values of α: (a) PF; (b) CF.

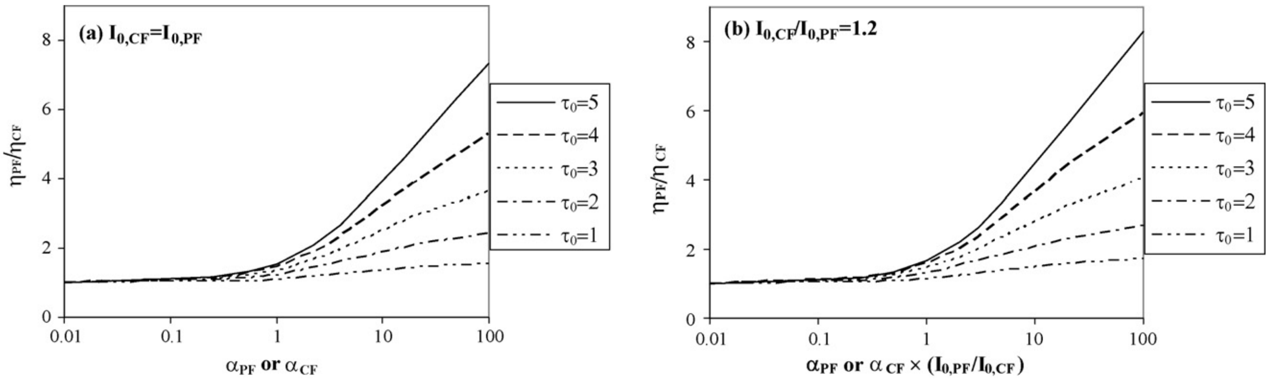

Fig. 8. $\eta_{PF}/\eta_{CF} = R_{od,PF}/R_{od,CF}$ vs. α for a range of values of τ_0: (a) $I_{0,CF} = I_{0,PF}$; (b) $I_{0,CF} = 1.2 \cdot I_{0,PF}$.

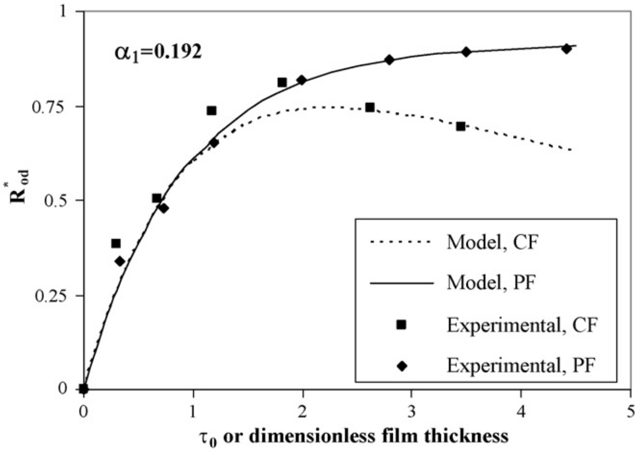

Fig. 9. Comparison between the values of the rate of degradation obtained by experiments [27,28] and by the model applying the procedure described in the text.

In Fig. 9, the curves obtained in this way are compared with the other experimental values extracted from Refs. [27,28] to show that the method works satisfactorily.

4. Conclusions

Photocatalytic reactors with immobilized TiO_2 have valuable intrinsic advantages, though require that the photocatalyst is not only adequately reactive, but also that the quantity of photocatalyst immobilized in the reactor is sufficiently high and it can work at the maximum efficiency. Indeed a film produced with a given technique of deposition should be evaluated on the basis of the observed rate of degradation which is a function not only of the intrinsic kinetics, but also of the optical thickness of the film and of the effectiveness factor. On the other hand, the effectiveness factor depends on the direction the film is illuminated (PF or CF) and on the values of the intervening parameters (the parameter $\alpha = k\, I_0\, \delta/D_e$ and again the optical thickness). Specifically, the research should be directed to the attainment of films which exhibit not only high kinetics (high values of the intrinsic kinetic constant), but also high effective diffusivity of the reagents, for instance by increasing the porosity, and appropriate optical properties.

The analysis on the basis of the effectiveness factor of a photocatalytic film demonstrates that the process is controlled by the diffusion of the substrate when the parameter α is high and it is controlled by the transport of the photons when the optical thickness is high.

In CF a maximum rate of degradation is obtained at an optimal thickness. In PF the rate of degradation is monotonically increasing with the film thickness, nonetheless no significant enhancement of the rate of degradation is obtained beyond a specific value of the thickness.

Finally, it has been shown how the values of the parameters can be obtained just executing a simple test on one film by illuminating it in PF and in CF mode. The conditions to obtain the maximum degradation capability of the film can then be identified by following the indications drawn in the present analysis.

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