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Effective design of photocatalytic reactors: influence of radiative transfer on their performance

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Abstract

The role of radiative transfer on a photocatalytic reaction occurring in an annular reactor has been investigated by modeling the degradation of chloroform contaminating the processed aqueous stream. From the analysis of the resulting effects it is apparent that the crucial factor in assessing the performance of the reactor is the distribution of radiant energy absorption rate which, in turn, depends on the mass of catalyst and on the way it is dispersed within the reactor. An optimization of the reactor is conceivable through a proper selection of the catalyst dispersion.

Keywords: Photocatalysis; Photoreactor performance; Photoreactor design; Radiative transfer

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1. Introduction

The study of photocatalytic degradation of many organic substances, mainly water contaminants, is receiving increasing attention both from the chemical and the engineering point of view. In the latter field researches have been developed in different directions such as the modeling of the radiation field [1–4], the chemistry of the network of reactions [5,6], the measurement of the optical properties of the photocatalyst suspensions [7] as well as the determination of the intrinsic kinetic rate of the pollutant photocatalytic degradation [8].

Even if the actual developments include technological applications at pilot plant scale and photocatalytic technologies are becoming commercially available to clean up industrial aqueous streams, design methods are still based on empirical or semi-empirical approximations. Up to now the basic principles of reactor engineering have not yet fully exploited in order to obtain an optimal design and a reliable prediction of the performances of photocatalytic reactors.

This work is therefore intended as a contribution to understand the role of the factors which act concurrently to affect the conversion which can be achieved for a given class of photocatalytic degradation reaction.

In particular, attention has been focused on the reliability of the common assumption that, on purely intuitive grounds, conversion depends on the absorbed radiant power and on the quantity of catalyst that is dispersed within the reactor.

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2. Basic relationships

The kinetic equation for the disappearance of a species to be photocatalytically degraded can be given as

$$R(\underline{x}) = k\,c(\underline{x})[\dot{e}'''(\underline{x})]^n,$$

where c is the concentration of the species, $\dot{e}'''$ is the local rate of radiant energy absorption, and its exponent n accounts for the relative weight of the hole–electron generation and recombination rate on the catalyst surface [5,6].

The local rate of radiant energy absorption $\dot{e}'''$ accounts for the availability of absorbed photons which participate in the reaction as non-material reactants. It is therefore likely that the distribution of $\dot{e}'''$ plays a significant role in the overall process.

The absorption capabilities of the reacting medium affect the way the radiative and the chemical reaction problems are linked. When the optical properties vary with the progress of the reaction (direct photoreaction) the two problems are coupled and the solution of the governing equations turns out to be a very complex problem. On the contrary, when the optical properties can be assumed independent of the progress of the reaction, the two problems are uncoupled and the radiative transfer equation (RTE) and the mass balance of the reacting species can be solved sequentially.

Photocatalytic reactions can be safely included in the latter case once the participation of the radiated medium is influenced only by the catalyst particles [2,3]: in this case the actual heterogeneous medium can be assumed to be homogeneous and its optical properties are accordingly evaluated.

The distribution of the local rate of radiant absorption

$$\dot{e}'''(\underline{x}) = \int_{\lambda_1}^{\lambda_2} k_{\lambda'} \int_{4\pi} I_{\lambda'\omega'}\,\mathrm{d}\omega'\,\mathrm{d}\lambda'$$

can be obtained once the solution of the RTE gives, for any position , the value of the intensity of the radiation traveling along any direction $\underline{\omega}$ through and with a wavelength λ within the useful range λ_1 to λ_2.

The RTE for a given wavelength λ and for a given direction $\underline{\omega}$ can be written as [9]:

$$\frac{\mathrm{d}I_{\lambda\omega}}{\mathrm{d}s} = -(k_\lambda + \sigma_\lambda)I_{\lambda\omega} + \frac{\sigma_\lambda}{4\pi}\int_{4\pi} p(\underline{\omega}' \to \underline{\omega})I_{\lambda\omega'}\,\mathrm{d}\omega',$$

where s is a linear coordinate along the direction $\underline{\omega}$ with the origin at the point where the photons enter the system.

The phase function p, which indicates the way the direction of flight can change as the result of scattering, is a property of the catalyst. In the investigated situations its anisotropy is the one typical of diffuse reflecting large spheres [9] so that p can be expressed as

$$p(\underline{\omega}' \to \underline{\omega}) = p(\phi) = \frac{8}{3\pi}[\sin(\phi) - \phi\cos(\phi)],$$

where ϕ is the angle between $\underline{\omega}'$ and $\underline{\omega}$.

k and σ are the absorption and the scattering coefficient, respectively, and are related to the total extinction coefficient β, being $\beta{=}k{+}\sigma$. All these coefficients are proportional to the concentration c_{cat} of the catalyst particles through their specific values β^*, k^*, σ^* which can be assumed as intrinsic properties of the catalyst.

It is however a common practice to characterize the participation of the medium using parameters which are equivalent to the mentioned ones, in particular the optical thickness τ_0 and the single scattering albedo ω_0 defined as

$$\tau_0 = \int_0^{l_o} \beta^* c_{\mathrm{cat}}\mathrm{d}s, \quad \omega_0 = \frac{\sigma}{k+\sigma}.$$

So τ_0 accounts for the ratio between a characteristic linear dimension of the system and the photon mean free path and ω_0 accounts for the probability of a photon/material interaction event to occur as scattering.

3. Situations investigated and solution procedures

The reaction considered in the following is the photodegradation of chloroform:

$$\mathrm{CHCl_3} + 0.5\,\mathrm{O_2} + \mathrm{H_2O} \to \mathrm{CO_2} + 3\,\mathrm{HCl}$$

which has been studied by Martin et al. [8] who proposed the following kinetic equation

$$R = k\, c_{\mathrm{CHCl_3}} \sqrt{\dot{e}'''} \quad \text{with} \quad k = 10.02 \left(\frac{\mathrm{cm}^3}{\mathrm{Einstein}} \right)^{1/2}.$$

The optical properties of the photocatalyst suspension have been estimated on the basis of specific values consistent with those measured by Cabrera et al. [7] and of plausible values of particle concentration. While the optical thickness was varied in order to account for changes in the particle concentration, the single scattering albedo was kept constant at the value ω_0=0.8 in all the investigated situations.

The reaction has been assumed to occur within an annular photoreactor whose internal and external radius are R_1=2 cm and R_2=5.7 cm, respectively, and the length is L=114 cm.

A diffusion coefficient D=1.2×10^{-9} m^2/s has been considered.

Laminar flow was assumed within the annulus with Re=1240.

The lamp, placed on the axis of the reactor, was supposed to be a 100 W linear source, L long, emitting in a diffuse way, typical of fluorescent lamps.

The walls of the reactor have been considered to be pure transparent surfaces.

The RTE has been solved using the Discrete Ordinate Method as described in [4] considering only one wavelength, thus assuming uniform optical behavior in the useful range of wavelengths.

The mass balance of the reacting species has been solved using a control volume approach [10].

4. Results

4.1. The case of uniform catalyst concentration

In Fig. 1 both the total absorbed power $\dot{E}_t$ and the conversion are given as a function of τ_0, i.e. of the catalyst concentration.

It is apparent that the $\dot{E}_t$ curve tends to an asymptotic value which depends essentially on the geometry of the system since when the medium becomes optically thicker, whichever the actual values of the optical properties are, the photons that enter the system cannot escape from it.

The reactant conversion, on the contrary, reaches a maximum and, when the catalyst concentration exceeds a certain value, decreases while the absorbed power increases or remains constant.

This means that the performance of the reactor is not determined simply by the total absorbed power but also and principally by the distribution of the local rate of radiant energy absorption $\dot{e}'''$ which, as it was shown

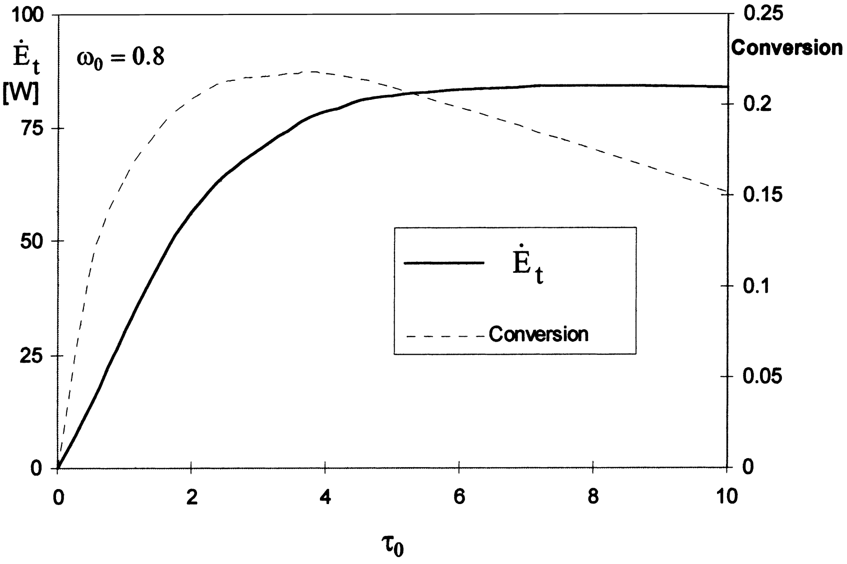

Fig. 1. The total absorbed power and the conversion as functions of the optical thickness.

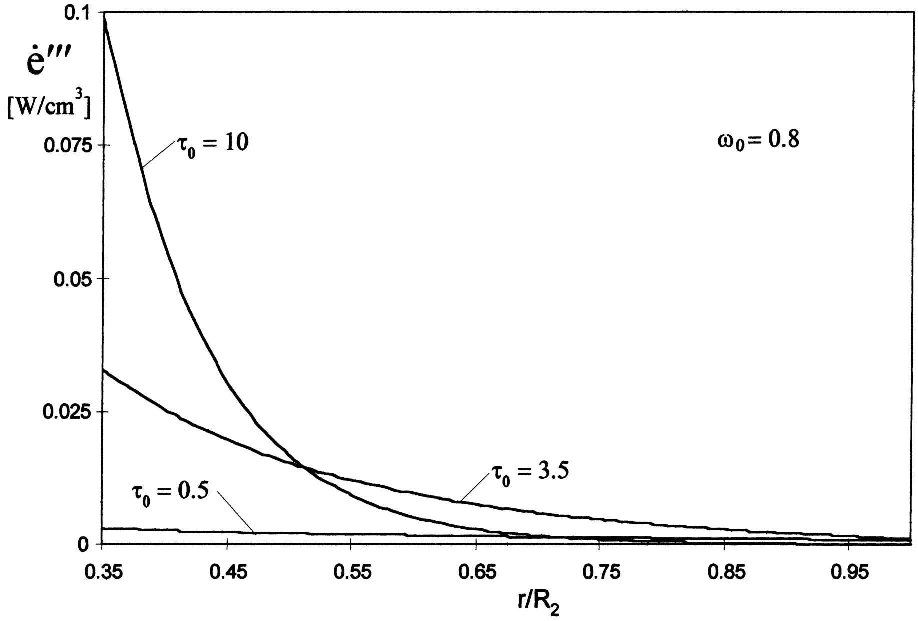

Fig. 2. The radial distribution of the radiant energy absorption rate at the midlength cross flow section of the reactor for different τ_0.

in [11], affects the actually available volume of the reactor and its effective exploitation.

As a matter of fact, conversion is the result of a complex interaction of chemical reaction with radiative transport, flow field and diffusion processes. In liquid systems, such as the one here investigated, the latter phenomena are limited and important conclusions can be drawn from the analysis of the interaction between the residence time distribution resulting from the laminar velocity profile and the exponential-like decreasing trend of the $\dot{e}'''$ distribution.

In order to analyze this latter phenomenon first, the radial distributions of $\dot{e}'''$ at the midlength cross section of the reactor are given in Fig. 2 for different values of τ_0. It is apparent that when τ_0 increases, two effects result:

1. the region where the most of absorption occurs decreases and a dark zone may eventually appear;
2. the distribution of $\dot{e}'''$ becomes less uniform.

The resulting effects on the reaction can be grasped from Fig. 3 where the radial distributions of the dimensionless reactant concentration at the exit cross section are given for different values of τ_0.

It is apparent that the reactant stories are different according to which radial position is considered and to the pertaining level of the radiant energy absorption.

The largest differences result in the central part of the reactor where the residence times are lower and the concentration weight factor $(v_z(r)2\pi r)$ is larger.

Close to the walls the degradation of the contaminant is in any case large due to the large values of the pertaining residence times, with a larger conversion resulting near the inner wall where the largest values of $\dot{e}'''$ occur.

In order to understand the phenomena which take place in the central region of the reactor, it is convenient to follow the evolution of the situation when the concentration of the catalyst is increased.

If c_{cat} is low, the distribution of $\dot{e}'''$ is quite even but with very low values; the whole volume is available but poorly exploited since the concentration of absorbed photons is too low.

When c_{cat} increases the distribution of $\dot{e}'''$ becomes less even but the concomitant increase of the values of $\dot{e}'''$ is the prevailing effect and thus the conversion is enhanced.

Finally if c_{cat} is further increased, the distribution of $\dot{e}'''$ decreases sharply and the central region of the

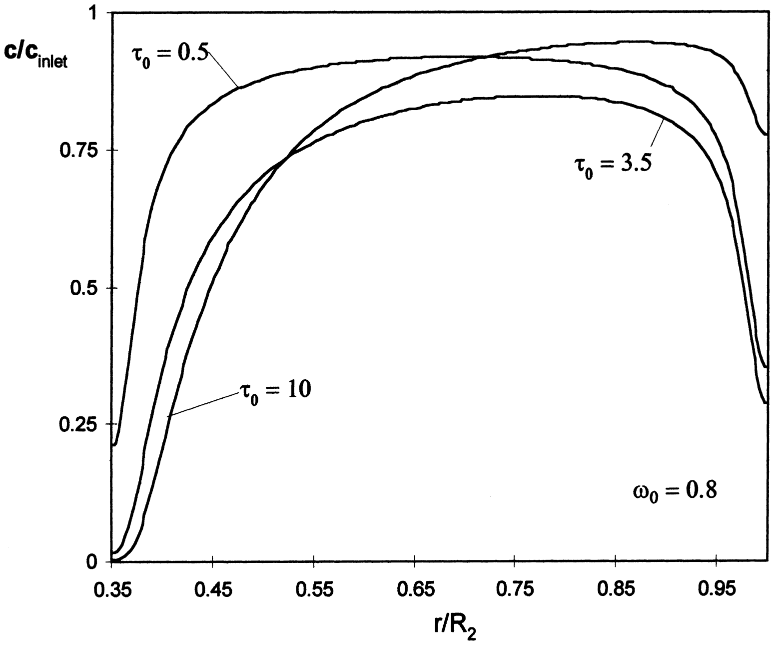

Fig. 3. The radial distribution of the dimensionless reactant concentration at the reactor exit section for different values of τ_0.

reactor becomes almost dark so that a decrease of the conversion is the final result.

It can therefore be concluded that the distribution of $\dot{e}'''$ is essential to assess the final conversion and that to increase, beyond a given value, the mass *M* of the catalyst is not beneficial for the conversion.

4.2. *The case of non-uniform catalyst distribution*

In the real situations it is quite possible that the concentration of the catalyst particles is not uniform as the result of phenomena like particle aggregation, sedimentation, migration, etc.

Since a change in the particle distribution affects the local optical properties of the medium and consequently the distribution of $\dot{e}'''$, the role of non-uniformity of the catalyst distribution has been investigated for a series of values of the mass *M* of the catalyst particles.

At this stage of the analysis, a linear variation of the catalyst concentration along the radial direction has been considered. Even if this situation is somehow unrealistic, nonetheless this choice allows an understanding of the role of non-uniform particle distribution and allows acquisition of information useful for the selection of optimal operating conditions.

It must be noted that in the case of a cylindrical geometry, the elemental volume varies with the radial position: therefore a change in the distribution of the particles causes also a slight change of the optical thickness which does not occur in the case of a plane geometry.

For any value of *M* the catalyst concentration has been assumed to vary with the radial position according to the linear law:

$$c_{\mathrm{cat}}(r) = a\,\bar{c}_{\mathrm{cat}}[1 + b(r - R_1)],$$

where $\bar{c}_{\mathrm{cat}}$ is the average value of the catalyst concentration for the mass *M* considered, i.e.

$$\bar{c}_{\mathrm{cat}} = M/[L\pi(R_2^2 - R_1^2)].$$

The assumed profile has been determined assigning the value of *a*, i.e. the value of the concentration at the inner wall of the reactor ($r{=}R_1$), and evaluating *b* through the condition.

$$M = L\int_{R_1}^{R_2} c_{\mathrm{cat}}(r)2\pi r\,\mathrm{d}r.$$

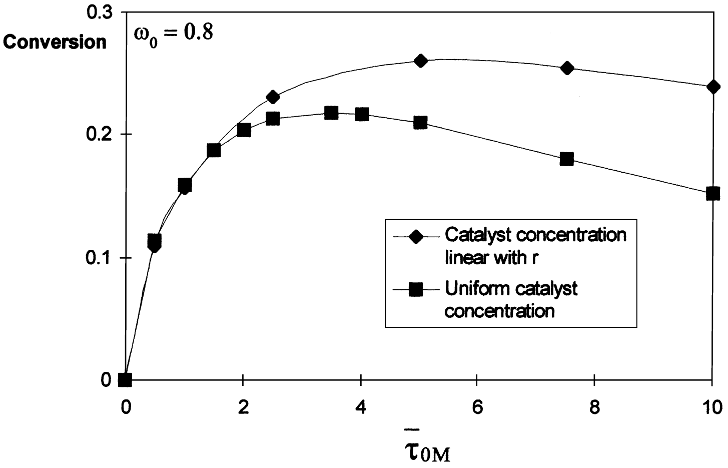

Fig. 4. The conversion as a function of the catalyst mass for different distributions of the particles.

Only a radially increasing concentration profile ($0<a<1$) has been considered since in this case the participation of the medium is low in the inner part of the reactor and increases in the outer one. In this way a more effective use of the reactor volume can be expected in comparison with the uniform distribution case.

In order to make more apparent the investigated effects, a very large non-uniformity (a=0.05) has been considered.

Results for the conversion achievable in both the cases of varying and uniform catalyst distribution are given in Fig. 4 as a function of the catalyst mass M accounted for through a conventional optical thickness $\bar{\tau}_{0M} = \beta^* M/[\pi L(R_2 + R_1)]$, that represents the one pertaining to the uniform distribution of the given mass M.

It is apparent that for the non-uniform situation considered here:

1. the maximum in the conversion is no longer evident as it was in the case of uniform concentration;
2. for large values of M, conversion is significantly larger than in the previous case.

This trend suggests that a more effective use of the reaction volume results from the change in the catalyst distribution: this hypothesis is confirmed by the analysis of Figs. 5 and 6 where the radial profiles of concentration at different axial positions along the reactor and the radial profile of $\dot{e}'''$ at the midlength cross section are given for $\bar{\tau}_{0M} = 5$.

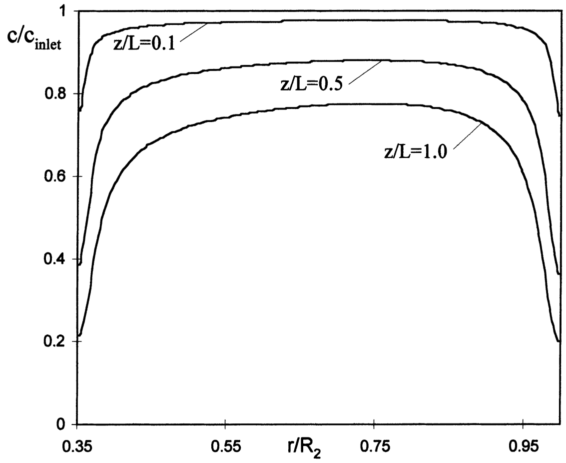

Fig. 5. The radial distribution of the dimensionless reactant concentration at different cross flow sections along the reactor in the case of a linearly varying distribution for $\bar{\tau}_{0M} = 5$.

The more effective use of the central part of the reactor is apparent as the result of the unusual shape of the $\dot{e}'''$ distribution which, as a consequence of the radially increasing participation of the medium, exhibits a maximum just in this region.

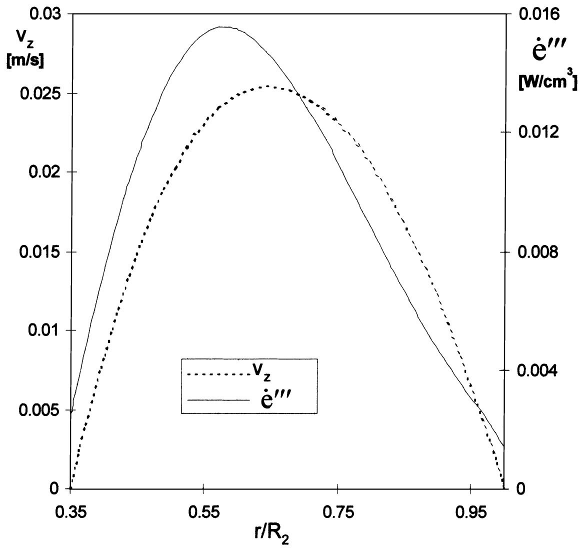

Fig. 6. The radial distribution of the radiant energy absorption rate at the midlength cross flow section and the velocity profile in the case of a linearly varying distribution for $\bar{\tau}_{0M} = 5$.

5. Conclusions

The analysis of the principal factors which affect the conversion in a photocatalytic reaction occurring within an annular photoreactor shows that:

- neither the total absorbed power nor the mass of dispersed catalyst can be comprehensive indices of the conversion;
- the distribution of the local rate of radiant energy absorption is very important in assessing the performance of the reactor since it affects both the fraction of the physical volume of the reactor which is actually available for the reaction and the way how it is exploited;
- the distribution of $\dot{e}'''$ and then the conversion are quite sensitive to the distribution of the catalyst particles.

It appears therefore challenging to investigate further the opportunity of design and operational solutions where conversion is improved as the result of an optimization of the quantity of catalyst particles and of their spatial distribution.

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