

Photocatalytic reactors

M. Bouchy[†] and O. Zahraa[‡]

Département de Chimie Physique des Réactions - UMR 7630 CNRS-INPL

ENSIC, 1 rue Grandville, BP 451, F-54001 - Nancy Cedex, France

ABSTRACT. Fundamental concepts for the design of photocatalytic reactors are recalled: specific rate, modeling of the distribution of the irradiation, description and modeling of transport phenomena on the macroscopic and macroscopic scales. These are required for establishing the reactor mass balance. A brief survey of various reactors is given for solar or artificial light, gas- or liquid-phase, slurry or fixed-bed.

1. INTRODUCTION

Photocatalysis has been a subject of increasing interest during the last twenty years. It has indeed various potential applications such as metal recovery, abatement of NO_x, synthesis of ammonia but the recent developments have been induced mainly by the application to the abatement of organic pollutants both in the aqueous and the gaseous phase. This development participates to the general concern about the environment and the increasing constraints on the toxicity of wastes. The academic studies have been much developed in the fields of organic chemistry, physical chemistry, chemical kinetics and catalyst preparation, but few studies have been dedicated to chemical engineering and the development of reactors. Concomitantly, few industrial processes have been developed.

The aim of this presentation is to give some aspects of studies related to chemical engineering of photocatalysis; far from being exhaustive, it aims at giving an insight into the extent and importance of this topic.

The presentation will deal with three selected subjects: light distribution within a reactor, mass transfer processes and a brief survey of photochemical reactors.

2. BASIC CONSIDERATIONS

2.1. Photocatalytic process. The photocatalytic process results from the excitation by UV-visible light of a solid semiconductor, generating free electrons and holes, which leads to redox processes on the surface and the attack of adsorbed molecules. Direct attack of organic molecules on the surface, or formation of highly reactive hydroxyl radicals results, in the presence of oxygen, in the oxidation of the organic molecules, which, in most cases, leads to a complete mineralization.

2.2. Rate of photocatalytic degradation. The rate of photocatalytic degradation depends on several parameters for a given pollutant and catalyst which are mainly:

- pollutant, oxygen (and other compounds) concentrations,
- temperature,
- irradiation wavelength and flux.

2.3. Specific rate. These parameters are not usually uniform within the reactor. At any given point, the rate per unit catalyst amount q , or specific rate r_{spe} , takes a local value so that the total rate in the reactor is the integration of the elementary rates $dr = r_{\text{spe}} \cdot dq$ over elementary amounts dq of catalyst.

The effect of the irradiation on this elementary catalyst amount is determined by the specific rate of energy absorption $i_{\text{abs}} = dI_{\text{abs}}/dq$, where I_{abs} is the absorbed energy ($E \cdot s^{-1}$ or W), also called LVREA (Local Volumetric Rate of Energy Absorption).

Note that this "amount" of catalyst can be chosen as catalyst mass, suspension volume or support area (immobilised catalyst), depending on the type of reactor used.

2.4. General system. Another problem is that mass transfer phenomena can intervene in the process by reducing the effective local concentration so that the analysis of the reactor must take into consideration:

- the local specific rate,
- the irradiation distribution (the space-dependent LVREA),
- the laws of mass-transfer phenomena (external, internal transfers),
- the mass-balance over the whole of the reactor.

A complete analysis allows accurate information on the laboratory scale to be obtained and the scaling-up of an effective reactor to be carried out. However, the whole

[†]E-mail: Michel.Bouchy@ensic.inpl-nancy.fr

[‡]E-mail: Orfan.Zahraa@ensic.inpl-nancy.fr

problem is complex and requires knowledge of the constitutive laws and of the operative parameters so that simplifying assumptions are often made so as to get a feasible study and practical reactors are designed without a complete ab-initio analysis.

3. SPECIFIC RATE

The basic information which allows a photocatalytic reactor to be designed is an analytical expression for the specific rate of reaction. Data can be found in the literature but are often given as the total rate within the reactor, resulting from an average value of the irradiation rate instead of taking the irradiation distribution into account [1]. A general picture is as follows, although some more elaborate rate expressions are also found:

- a concentration dependence of the Langmuir-Hinshelwood type [2] which leads to first-order kinetics at low concentration and zero-order kinetics at high concentration, with a similar additional effect of oxygen concentration, often referred to as the LHHW model (Langmuir-Hinshelwood-Hougen-Watson),
- a low activation energy,
- an order with respect to absorbed irradiation varying from 1 at low flux to 0.5 at high flux, which is attributed to recombination of reactive species (especially hole-electron recombination).

4. IRRADIATION DISTRIBUTION

There is no feed-back effect between irradiation and chemical conversion as long as the reactants (or products) do not absorb the irradiation in the wavelength range where the catalyst is excited. The catalyst concentration is therefore the only parameter and as this catalyst is by essence a stable compound, the light distribution does not depend on the extent of reaction. This is indeed generally the case in low-concentrated fluids and in near-UV range (wavelength of 350–400 nm). If this were not the case, the concentrations and light distributions would be linked together through the absorption law for the fluid phase, which would add to the complexity of the system.

4.1. Suspension. In the case of a suspension (or a nearly-continuous fixed bed), the LVREA depends on the emission of the light source, both in intensity and spatial distribution, and on the absorption and scattering properties of the reactor filling. If there is no absorption by the compounds in the fluid, the LVREA is dependent on the catalyst only. However, this calculation is much complicated by the scattering.

The master equation is an energy balance along a path ds on any energy flux per unit surface, time and

solid angle $I(\underline{\omega})$ ($E \cdot m^{-2} \cdot sr^{-1} \cdot s^{-1}$) along the direction defined by the unit vector $\underline{\omega}$, which includes:

- loss by absorption (coefficient κ),
- loss by scattering-out (coefficient σ),
- contribution by scattering-in from fluxes in all the directions $\underline{\omega}'$ in space (probability dependent on σ and on the angle between $\underline{\omega}'$ and $\underline{\omega}$, with the probability per unit solid angle (or phase-function) $p(\underline{\omega}', \underline{\omega})$ [1, 3]:

$$\frac{dI(\underline{\omega})}{ds} = -(\kappa + \sigma) \cdot I(\underline{\omega}) + \sigma \cdot \left(\frac{1}{4\pi}\right) \cdot \int_{4\pi} p(\underline{\omega}', \underline{\omega}) \cdot I(\underline{\omega}') d\Omega',$$

where $d\Omega'$ is an element of solid angle in the direction $\underline{\omega}'$.

To solve this equation requires experimentally determining or modelling the absorption and scattering coefficients and also the phase function p . On principle, a theoretical expression for p can be derived from MIE theory but due to the complexity of the derivation, approximate functions have been used (for large spheres [4]) and also simple isotropic scattering.

In addition, solving of this integro-differential equation requires knowledge of a boundary condition. This is the incident flux $I_w(\underline{\omega})$ on the reactor walls. The LVREA is then:

$$i_{\text{abs}} = \kappa \cdot \int_{4\pi} I(\underline{\omega}) d\Omega.$$

Note also that the parameters are dependent on the wavelength λ and that, for a polychromatic source (sun, fluorescent lamp) the spectral density $I_\lambda(\underline{\omega}) = dI(\underline{\omega})/d\lambda$ and corresponding $i_{\text{abs},\lambda}$ should be used instead of $I(\underline{\omega})$ and i_{abs} , which would then be integrated over the wavelength range.

The lamp irradiation flux on the reactor wall $I_w(\underline{\omega})$ can be known from the geometry of the reactor and the distribution of the emission from the light source. The solar emission is well defined as a one-direction uniform flux, but the emission of an artificial lamp is more difficult to assess. The lamps have been considered as of a cylindrical shape and have been simulated as an isotropically emissive medium, either a cylindrical volume (which could ultimately be considered as a thread [5]) or a cylindrical surface (fluorescent lamp). The emission is on principle isotropic in the whole space but a simplified model assumes emission to occur perpendicularly to the lamp axis only.

Once the system is defined, it is a difficult mathematical problem to solve it. If no simplifying assumptions are made, a numerical method is necessary. The Discrete Ordinate Method is a convergent algorithm based on exchange between finite volume elements [1]

or discrete directions in space [3] (about 220). Alternatively, a Monte Carlo approach can be used [3, 5]: in this method, the fate of individual photons is simulated then all these events are averaged over a large number of photons to get the LVREA, a rigorous but time-consuming method.

Analysis of the light distribution is of importance: although a pseudo Beer-Lambert can be used to simulate absorption under some conditions (see below), it can be observed that the increase in catalyst loading can result in a maximum in the rate of the reaction instead of a limiting value [6, 7].

4.2. Thin film-deposited film. A simplification of the general treatment has been suggested [8] where the contribution of scattering-in to the energy intensity can be neglected by a careful design of the reactor (with small light path), which is appropriate for laboratory kinetic studies leading to a pseudo Beer-Lambert law. Such an approximation, has also been used for thin deposits [5, 9], which gives a satisfactory representation of the global properties of the film as measured by an integrating sphere [10]. A simple model [11] considers a finite number of elementary slabs having the same properties of absorption and reflection and exchanging light flows. In an alternative model, originally designed for suspension films [12], the light is assumed to propagate normally to the film plan only: scattering-in is neglected and the total light flow is assimilated to opposite flows coupled to each other by scattering-out. This latter model has the advantage of leading to an analytical expression for the LVREA and has also been applied with some refinement to film deposits [13]. This model has proved satisfactory although out- and in-scattering by thin deposits has been found to be nearly isotropic [14]. Note that the determination of the global properties of a deposited film can also be used to carry out the simulation of reactors equipped with sets of transparent supports of moderately absorbing films.

5. MASS-TRANSFER PHENOMENA

5.1. Coupling with mass transfer. Any consumption of reactant results in a decrease in the local reactant concentration. A concentration gradient then appears and results in a flux of matter. It can be assumed that the QSSA (quasi-stationary-state approximation) is obeyed so that the “photographic” picture of the local situation at any time reveals an exact mass-balance i.e. an equality between transported reactant through mass-transfer phenomena and consumed reactant through the photocatalytic process. The consequence is that the local concentration in the immediate vicinity of the catalyst surface is lower than it is in the bulk of the fluid.

Note that increasing the surface area of the catalyst is profitable as this increases the pollutant adsorption and therefore its degradation and usual catalysts are therefore of a porous or dispersed nature although this increases the possibility of mass-transfer limitation.

Mass-transfer phenomena can be classified as external, within the fluid in the vicinity of the catalyst pellets or deposits (then enhanced by fluid stirring), and as internal within the catalyst pores (independent of the stirring).

5.2. External mass transfer. The rate of external mass transfer is generally expressed according to the model of the boundary layer on the catalyst surface. The rate is then expressed as:

$$r = k_{\text{ext}}(C_b - C_s) \text{ (mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}\text{)},$$

where C_b and C_s represent the bulk and surface concentrations, respectively.

The rate constant k_{ext} depends on the flow regime of the fluid, generally characterised by the non-dimensional Reynolds number Re . It is given by various empirical expressions such as [9]:

$$k_{\text{ext}} = 3.49 \times 10^{-7} Re^{0.77} \text{ (m} \cdot \text{s}^{-1}\text{)}.$$

As the rate constant k_{ext} increases with the flow turbulence, a good stirring is usually enough for the effect of external transfer to vanish, i.e. $(C_b - C_s)/C_b \ll 1$. Experimentally, this can be verified by checking that the rate is not dependent on the flow rate or stirring beyond some minimum value.

In some instances, the oxygen supply has been suggested as a source of rate limitation. Note that the flow in oxygen to the solid particle or deposit results not only from external transfer but also, for aqueous solution treatment with bubbling gas, from dissolution at the gas-liquid interface. This can be taken into account [5] in mass balance with a specific rate of dissolution given by the basic expression:

$$r = k_{G/L}(C_{G/s} - C_b) \text{ (mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}\text{)},$$

where $k_{G/L}$ is the rate constant and $C_{G/s}$ the oxygen concentration in the liquid phase in equilibrium with the gas phase by the gas-liquid interface.

5.3. Internal mass transfer. Internal mass-transfer is more likely to result in rate limitation in a deposited catalyst than it does on a suspended catalyst [15]. Contrary to external mass-transfer, it is not possible to obtain direct evidence of a limitation as the parameters involved (dimension of pores, molecular diffusion coefficient) cannot be varied independently of other kinetic parameters. An indirect way of investigation is to vary the thickness of the catalyst film (an increasing effect of internal mass transfer would lead to a limiting value

of the quantum yield of degradation), or to compare the effect of irradiation from the fluid side and from the (transparent) support side in which case an effect of internal mass transfer would lead to a lower quantum yield of degradation. A measurable [9] or negligible effect [11] has been observed by this technique. The comparison of the rate of adsorption r_{ads} and of photocatalytic degradation r_{deg} can also be compared as r_{ads} is mainly diffusion controlled (in physical adsorption). A partial limitation in suspension of aggregates has thus been shown [6].

The consequence of a mass transfer rate limitation is to alter the true value of the orders with respect to the reactant and the irradiation rate (with a limiting value of 1 for reactants and 0 for the irradiation rate). As a consequence, the effect of internal transfer, if not specifically studied, is often included in an "apparent" specific rate of reaction.

The phenomenon has been modelled either by assuming an exponential expression for the decrease in concentration with the increase in depth within the catalyst [9].

In thermal catalysis, the non-dimensional Thiele and Weisz moduli φ and φ' are defined:

$$\varphi^2 = \frac{r_s L^2}{DC_s}, \quad \varphi' = \langle r \rangle \frac{L^2}{DC_s},$$

where r_s and C_s are the specific volume rate and the concentration at the surface of the film, respectively, D is the diffusion coefficient and L is the characteristic length (ratio of volume to outer area), and where φ' makes use of the effective mean rate $\langle r \rangle$ which is an experimental value.

Models in thermal catalysis correlate to these moduli the effectiveness of the catalyst, that is the ratio $\eta = \langle r \rangle / r_s$. The effectiveness η is equal to or lower than unity as the concentration within the catalyst is lower than C_s if internal diffusion interferes. This description cannot be directly applied to photocatalysis as a gradient in LVREA can take place within the catalyst, but a numerical treatment has been derived for cylindrical pores in the form of an abacus $\eta(\varphi)$ for various values of the optical density [16].

6. REACTOR MASS BALANCE

The local specific rate of reaction r_{spe} is a function of the local bulk concentration C_b and LVREA. The global mass-balance on the reactants then couples the reactant disappearance with the mass transfer over the whole reactor, and leads to the conversion yield.

Ideal reactors can be classified into three categories:

- perfectly-stirred closed reactor (batch reactor),
- perfectly-stirred open reactor (CSR),
- plug-flow reactor (PFR, or integral reactor).

Concentrations are assumed to be uniform in the first two types. On the contrary, they vary during the progress of the fluid within the PFR reactor so that the mass balance must take into account the flow of the reactive medium. Non-ideal reactors will include additional features such as lateral mass transport, or seen as a compound system (reactor with mixing tank). In real reactors the mass transport is bound to the fluid velocity distribution. Perfectly laminar or turbulent flows are often considered, as real flow computation through Navier-Stokes equation is a very complex problem on its own.

A complete ab-initio modelling of the reactor has seldom been carried out but a chosen example will be given as an illustration in the case of a fixed-bed reactor where the catalyst is deposited on packed rings in an annular reactor of cylindrical symmetry [5]. Note that if the rings are small enough, the bed is quasi-continuous so that the treatment is identical to that of a suspension.

The master equation (1) of mass balance for each reactant is written as follows (bulk concentration C , radial variable r and longitudinal variable z):

$$\left\{ v_L \frac{dC_b}{dz} - D \left[\frac{1}{r} \frac{dC_b}{dr} + \frac{d^2 C_b}{dr^2} \right] \right\} h_{\text{up}} = \nu \cdot r_{\text{spe}} \cdot a_{\text{cat}} - k_{G/L} (C_{G/s} - C_b) \cdot a_{\text{gas}} \quad (\text{mol} \cdot \text{s}^{-1} \text{m}^{-3}). \quad (1)$$

The left-hand side represents the differential flow of matter in an tore-shaped element of section $dz \cdot dr$. According to the QSSA, this is equal to the consumption in the same element of space given in the right-hand side expression. The terms of the left-hand side represent the longitudinal transport of matter (interstitial longitudinal rate v_L and the radial diffusion (effective diffusion constant D). The terms of the right-hand side represent the reactant consumption (where r_{spe} ($\text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$) is the specific superficial rate and ν the stoichiometric coefficient) and the appearance (in the case of oxygen only) through gas-liquid transfer. The balance includes weighing terms: a_{cat} the catalyst area, a_{gas} the gas-liquid interface area and h_{up} the liquid hold-up per unit volume. Note that r_{spe} is a function of the concentrations C_s of reactant and oxygen by the surface catalyst and of the LVREA (modelled separately).

In addition, as seen above, external mass-transfer in the boundary layer around the particles verifies the QSSA:

$$k_{\text{ext}} \cdot (C_b - C_s) = r_{\text{spe}} \quad (\text{mol} \cdot \text{s}^{-1} \text{m}^{-2}). \quad (2)$$

Solving (by a numerical method) the whole system of equations of types (1) and (2) for reactant and oxygen, combined with the expression for the r_{spe} including the LVREA requires boundary conditions which are the concentration at the entrance to the reactor and a zero value of (dC_b/dr) on the reactor walls (no flux of matter).

The authors note the importance of the radial diffusion as the LVREA generates a sharp decrease in the rate of the reaction from inner to outer walls. Due to the complexity of the system model simplifications are suggested and validated. A first simplification is done for a highly absorbing medium: the reactor is divided in two zones, a zone by the inner wall where the LVREA is high and the reaction occurs, supplied by mass transfer from the outer second zone. A second simplification for a low absorbing medium is to assume a uniform LVREA. This example deals with a turbulent flow where the fluid velocity is uniform. This is not the case for a laminar flow where the velocity follows a parabolic profile (slit flow or falling film reactor). An analysis has been developed [17] for these cases assuming the annular gap to be small enough to be treated as a planar system (i.e. cancelling of the first diffusion term in (1)), which showed the advantage of a falling film on a slit flow.

Note that the treatments shown here assume that only a surface reaction occurs. This is only approximate as the actual reaction can have a homogeneous part, and be partly photolytic if a reactant absorbs the irradiation light, which requires additional terms of compound consumption in the right-hand side of (1) [17].

7. GEOMETRY OF THE REACTOR

Two main features determine the design of the reactor:

- suspended or immobilised catalyst,
- source of irradiation.

The obvious advantage of an immobilised catalyst is to avoid the separation process after the chemical treatment, a process which can be an expensive (for the filtration) and time consuming (for sedimentation) considering the small size of the catalyst crystals or aggregates (0.05 μm to a few μm). However, mass transfer limitations are more likely to occur within a coat of immobilised catalyst. Various types of support have been used, made mainly of glass (plate, beads, fibreglass mat) but also paper, cotton, fibres.

The source of irradiation can be either natural (solar irradiation) or artificial (lamp). The geometry of the reactor is strongly related to the source of irradiation, in particular it has to be designed so as to collect the maximum of emitted light so as to reduce the energy and investment cost.

7.1. Solar reactors. Considering the unidirectional solar irradiation, the collection of the irradiation is carried out in two ways [18]:

- use of a fixed reactor where a large surface of the solution or suspension is exposed to the sun: trickling on a flat plate supporting a catalyst mesh, flowing a sinuous path [19], flowing

through an array of pipes so as to increase the residence time, or through a flat fixed-bed [20] or exposure within a tank such as those designed for water stations, which can be equipped with impellers designed to ensure a good mixing and aerating of the slurry [7, 21],

- focusing with a mirror (parabolic trough [22]) or more elaborate system (Fresnel lenses, holographic collector) on a reactor of small dimension.

When using a focusing system, the volume of fluid is reduced, which makes it easier to build, and is also a necessity as the whole system (collector + reactor) must be placed on a motorised support so as to track the sun. However, it leads to a high irradiation flux, which may reduce the quantum yield of degradation. In addition, depending on the weather, an important fraction of the sunlight can be diffuse instead of direct, which reduces the efficiency of the focusing system [7, 22].

An interesting compromise is the Compound Parabolic Collector [22] which is fixed, but ensures a partial focusing and a moderate irradiation flux on the catalyst.

7.2. Artificial light reactors. Artificial light sources are on the contrary multidirectional. Two main solutions are:

- to reflect or focus the emitted light to a reactor [4],
- to wrap the light source with the reactor, such as in the coaxial lamp system; this has the additional advantage that the back-scattering of light by the catalyst is not a loss as this scattered light re-enters the reactor.

The main artificial sources are mercury lamps:

- low pressure lamps (254 nm) of high yield "at the plug" (up to 0.5) of low power (about 30 W/m) which require quartz windows,
- fluorescent lamps (around 365 nm), i.e. low pressure lamps equipped with a fluorescent coating, with a decrease of the emitting power of about 50% (so-called black-light lamps),
- medium pressure lamp (UV-visible range), higher in power (about to 3 kW/m) but lower in emission yield,
- high-pressure lamp, nearly punctual, with low part of the emission in the UV range.

High-pressure lamps have a high cost in energy as long as UV light is looked for. Medium-pressure lamps have a very high power which leads to a low quantum yield

of degradation unless the catalyst is placed at a large enough distance to ensure a low enough irradiation flux, which would be space consuming. According to these considerations, fluorescent lamps working with conventional glass vessels are often suggested.

An alternative is the distribution of light over a large area of catalyst by the use of coated optical fibres or hollow tubes [23]. The difficulty of these designs is to collect the maximum amount of light from the source and to ensure a distribution of irradiation of the catalyst along the whole of the light conductor by a careful design of the interface loss through refraction. A summary of reactors is presented below, which although not exhaustive gives an insight into the variation of designs, some of which have been the object of advanced modelling when some others are mainly of an intuitive design.

7.3. Aqueous suspension (slurry). Reactors with suspended catalyst have been the object of fundamental studies (e.g. [1, 4, 5, 24]) with the aim of either getting true kinetic data or allowing large reactors to be designed. Several designs have been studied or suggested. Suspended catalyst has often been used as a flow in an annular space [1, 4] around a linear lamp but a thorough study has been dedicated to a falling film reactor [24], where a thin film runs freely on the outer wall within the annular space. If the reaction is fast enough, a radial concentration gradient in the reactants will take place, this can be reduced by creating a turbulent flow by the presence of baffles of various design. A completely different design is the fountain reactor [25] where a nearly planar horizontal film is exposed to artificial or solar irradiation. These reactors are meant for water treatment where conversion in the reactor is usually very low so that they are coupled with a tank with a continuous recirculation of the fluid. Mass balance for the whole reactor has to take this situation into account although in the case of a low conversion and good stirring of the tank, the reactor is formally analogous to a batch reactor.

7.4. Liquid-phase fixed-bed reactor. Another design for cylindrical reactors is a fixed-bed reactor where the catalyst is fixed onto a support so as to avoid a separation process. The support can be packed Rashing rings [5], fibre mesh whereas an intermediate design between suspended and fixed catalyst uses freely suspended glass beads as catalyst support. Other reactors use large sized supports such as the inner or outer wall of an annular reactor [20]. Confinement of the catalyst onto a practically two-dimensional surface requires a good mixing of the fluid phase in the annular space. Creating a turbulent flow by the use of baffles or foils [26], of a catalyst-coated ridged helix [27], or by inducing a helicoidal swirl [20] is then important. An original solution to this problem is also a vortex reactor where the rotating inner wall induces instability

of the flow due to centrifugal forces and the building-up of successive vortex cells within the annular space as shown in a detailed study [28]. Improving the contact between fluid and catalyst can also be obtained by allowing the fluid to pass through a catalyst loaded mesh on successive flat or conical supports around the lamp [29].

Basically these reactors are built around a single lamp and large reactors can be obtained by a parallel array of elementary reactors. The design can be improved by using an array of light sources in a large tank. Hydrodynamics of such a system is much more complicated than in the case of cylindrical symmetry. Design of the reactor can be helped by the use of fluid dynamics simulation. Such a study, which is very demanding in computational equipment, has been demonstrated on a structure consisting of a cylindrical tank equipped with seven catalyst-coated hollow tubes acting as light conductors [23]. As a homogeneous "dark" reaction can also take place, it can be of interest to accommodate successive periods of irradiation and thermal evolution by a special design of the reactor [26].

7.5. Gas-phase reactors. Gas-phase reactors are most frequently fixed-bed reactors. Crossing of the catalyst bed such as coated glasfibre mesh is often envisaged as it does not lead to a high pressure drop on the one hand and the bed is more resistant to the flow of fluid on the other. A set of closely spaced fins perpendicular to the lamp can also be used [30]. The catalyst bed can be simply a flat mat supported on a rigid grid across a pipe with a normal or high incidence irradiation by a set of lamps [31]. Alternatively a system of annular geometry can be used where the mesh is of cylindrical shape surrounding the lamp, the gas flowing through the mesh outwards [32].

An equivalent of the liquid suspension system is the fluidised bed where the flow of gas through a particle bed creates a pseudo-liquid state when the flow is strong enough to break the particle packing. This has the advantage of creating a lower pressure drop than a fixed bed and provides a good mass transfer. In the rotating fluidised bed, the centrifugal forces take the place of the gravitational forces [32, 33]; this system has the advantage of having a cylindrical geometry which is adapted to usual lamps, and allows, by adjusting the rotating speed, higher flow rates to be used.

8. CONCLUSION

Modelling photocatalytic reactors is of importance in order to get true intrinsic kinetic parameters and to carry out the simulation of industrial-scale reactors so as to select or to improve the reactor design. Many phenomena are involved in the modelling which results in the need for effective parameters and in the complexity of the solving of the problem by numerical

methods. Although a complete treatment appears to be necessary, simplified models have been suggested to avoid tedious numerical treatments. Applied patents often suggest qualitatively efficient set-up so as to abate mass-transfer limitations or make the best use of irradiation sources. A gap still exists between modelling and practical design, which will gradually be reduced with the development of chemical engineering studies in the field of photocatalysis.

REFERENCES

- [1] R. J. Brandi, O. M. Alfano, and A. E. Cassano, *Environ. Sci. Technol.* **34** (2000), 2623, 2631.
- [2] C. S. Turchi and D. W. Ollis, *J. Catal.* **122** (1990), 178.
- [3] G. Scaglari, G. Camera-Roda, and F. Santarelli, *Int. Comm. Heat Mass Transfer* **25** (1998), 651.
- [4] C. A. Martin, G. Camera-Roda, and F. Santarelli, *Catalysis Today* **48** (1999), 307.
- [5] A. Alexiadis, G. Baldi, and I. Mazzarino, *Catalysis Today* **66** (2001), 467.
- [6] H. Y. Chen, O. Zahraa, M. Bouchy, F. Thomas, and J. Y. Bottero, *J. Photochem. Photobiol. A: Chem.* **85** (1995), 179.
- [7] J. Gimenez, D. Curco, and M. A. Queral, *Catalysis today* **54** (1999), 229.
- [8] C. A. Martin, M. A. Baltanas, and A. E. Cassano, *J. Photochem. Photobiol. A: Chem.* **94** (1996), 173.
- [9] D. Chen, F. Li, and A. K. Ray, *Catalysis Today* **66** (2001), 475.
- [10] S. M. Ould-Mame, O. Zahraa, and M. Bouchy, *Int. J. Photoenergy* **2** (2000), 59.
- [11] S. M. Ould-Mame, *Contribution au génie de la dégradation photocatalytique de polluants organiques de l'eau sur TiO₂ en lit fixe*, Ph.D. Thesis, Nancy, 1998.
- [12] A. Brucato and L. Rizzuti, *Ind. Eng. Chem. Res.* **36** (1997), 4740, 4748.
- [13] M. Corboz, private communication.
- [14] H. Dora-Silva, M. Bouchy, and O. Zahraa, *Entropie* **228** (2000), 48.
- [15] M. F. J. Dijksta, A. Michorius, H. Buwalda, H. J. Panneman, J. G. M. Winkelmann, and A. A. C. M. Beenackers, *Catalysis Today* **66** (2001), 487.
- [16] M. E. Edwards, C. M. Villa, C. G. Hill Jr., and T. W. Chapman, *Ind. Eng. Chem. Res.* **35** (1996), 712.
- [17] D. F. Ollis and C. Turchi, *Env. Prog.* **9** (1990), 229.
- [18] J. Blanco and S. Malato, *Solar detoxification technology*, Part B, Chapter 6, UNESCO Publication, 2001.
- [19] B. Volker, M. Müller, D. Bahnemann, D. Weichgrebe, and M. Brehm, *Reaktoren für die photokatalytische Abwasserreinigung mit Stegmehrfachplatten als Solarelementen*, EP Patent 0, 738, 686, A1 (1996).
- [20] A. Gonzalez-Martin, O. J. Murphy, and C. Salinas, *Photocatalytic oxidation of organics using a porous titanium dioxide membrane and an efficient oxidant*, US patent 6, 136, 186, 2000.
- [21] G. Cooper and M. A. Ratcliff, *Method of decontaminating a contaminated fluid by using photocatalytic particles*, US patent 5, 294, 315, 1994.
- [22] J. E. Pacheco, M. R. Prairie, and L. Yellowhorse, *J. Solar Energy Engineering* **115** (1993), 123.
- [23] U. Periyathamby and A. J. Ray, *Chem. Eng. Technol.* **22** (1999), 881.
- [24] G. Li Puma and P. L. Yue, *Chem. Eng. Sci.* **53** (1998), 2993.
- [25] G. Li Puma and P. L. Yue, *Chem. Eng. Sci.* **56** (2001), 2733.
- [26] J. G. Szczechowski, C. A. Koval, and R. D. Noble, *Use of controlled periodic illumination for an improved method of photocatalysis and an improved reactor design*, US patent 5, 439, 652, 1995.
- [27] D. G. Ritchie, *Photocatalytic fluid purification apparatus having helical non transparent substrate*, US patent 5, 069, 885, 1991.
- [28] T. K. Sengupta, M. F. Kabir, and A. K. Ray, *Ind. Eng. Chem. Res.* **40** (2001), 5268.
- [29] H. L. De Lasa and J. Valladares, *Photocatalytic reactor*, US patent 5, 683, 589, 1997.
- [30] J. Say, R. Bonnecaze, A. Heller, S. Sitkiewitz, E. Heller, and P. Haugsjaa, *Apparatus for photocatalytic fluid purification*, US patent 6, 063, 343, 2000.
- [31] H. Ibrahim and H. De Lasa, *Ind. Eng. Chem. Res.* **38** (1999), 3211.
- [32] A. Tabatabaie-Raissi, N. Z. Muradov, and E. Martin, *Apparatus for low flux photocatalytic pollution control*, US Patent 6, 309, 611, B1 (2001).
- [33] D. Firnberg and J. R. Fehlner, *Rotating fluidized bed reactor with electromagnetic radiation source*, US patent 5, 374, 405, 1994.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

