Quantum efficiencies in a multi-annular photocatalytic reactor

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Abstract Radiative energy efficiencies of a multi-annular photocatalytic reactor were evaluated and analysed. The total quantum efficiency, defined as the ratio of the number of molecules of the pollutant reacted to the number of photons emitted by the lamp, is expressed as the product of three factors: (i) the reactor radiation incidence efficiency, (ii) the catalyst radiation absorption efficiency, and (iii) the overall reaction quantum efficiency. By means of a detailed mathematical model, the numerical values of each one were 83, 92, and 0–2.5%, respectively. The dependence of the overall reaction quantum efficiency upon operating variables was also studied.

Keywords Mathematical modelling; photocatalytic reactor; quantum efficiencies

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Introduction

Photocatalytic reactions using TiO_2 catalysts are an effective means for elimination of hazardous compounds present in wastewater or contaminated air. The effectiveness of this process for the degradation of many pollutants, such as alcohols, ketones, aromatic organics, nitrogen and halogenated compounds has been demonstrated (Hoffman *et al.*, 1995).

The application of detoxification processes involving both aqueous and gaseous photocatalytic reactors are frequently limited by the operating costs associated with the photons production. Accordingly, in addition to the effort directed at obtaining high active photocatalysts and at identifying the optimal operating conditions to carry out the degradation reactions, it is also necessary to consider those factors of the reactor design restricting the optimal use of the radiative energy. The apparent quantum efficiency has been widely employed as a way to evaluate the photoreactor energy performance. It can be defined as the ratio of the degradation global rate of the pollutant to the total radiative energy flux entering the photocatalytic reactor. Nevertheless, on the basis of the apparent quantum efficiency only, it is difficult to advance a diagnosis about the factors constraining the energy performance of this type of reactor. A more rigorous analysis can be performed if the impact of each individual event is assessed, starting with the photon emission of the radiation source and ending with its usage in the photocatalytic reaction.

In this work, the quantum efficiencies of a multi-annular photocatalytic reactor were analysed. The total quantum efficiency, defined as the ratio of the number of molecules of pollutant reacted to the number of photons emitted by the lamp, was expressed as the product of the following factors: the reactor radiation incidence efficiency, the catalyst radiation absorption efficiency and the overall reaction quantum efficiency. Based on a rigorous physical and mathematical model of the photoreactor, the quantum efficiencies analysis was made. The multi-annular reactor can be used for environmental detoxification of water and air. In the present work, it was employed for perchloroethylene (PCE) removal from contaminated air streams.

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Methods

The photocatalytic reactor consists of four concentric, borosilicate glass tubes (Figure 1) which are transparent to UVA radiation (300–420 nm). A tubular UV lamp (Philips TL 18 W) was placed at the reactor central axis. The tube walls were covered with thin layers of TiO_2 deposited on them using a sol-gel technique (Yamazaki-Nishida *et al.*, 1993). The air stream carrying PCE, water vapour and photocatalytic reaction products, flows through the annular spaces, entering the reactor by the external annular space and leaving it by the internal one. The reactor was fed with a mixture of PCE and chromatography-quality air with controlled humidity and temperature (Figure 2). The radiation incident on the catalytic film was modified by means of neutral density filters. The PCE concentrations in the inlet and outlet streams were determined by gas chromatography.

Results and discussion

The full modelling and simulation of a multi-annular photocatalytic reactor requires a through physical analysis of all the concurrent phenomena determinant of its performance. In a previous work (Imoberdorf *et al.*, 2005), the degradation kinetics of PCE from a moist air stream was studied for different values of PCE feed concentrations, relative humidities, and irradiation levels in a flat-plate reactor without mass transfer limitations. For the experimental conditions used:

$$r_{PCE} = -\alpha \frac{C_{PCE}}{1 + K_{H_2O} C_{H_2O}} e^{a,s} \tag{1}$$

where the kinetic parameters were regressed from experimental data using the Levenberg-Marquardt method. The obtained results are: $\alpha = 1.54 \times 10^8\,\mathrm{cm^3\,Einstein^{-1}}$ and $K_{H_2O} = 3.21 \times 10^{-4}\mathrm{m^3 mg^{-1}}$.

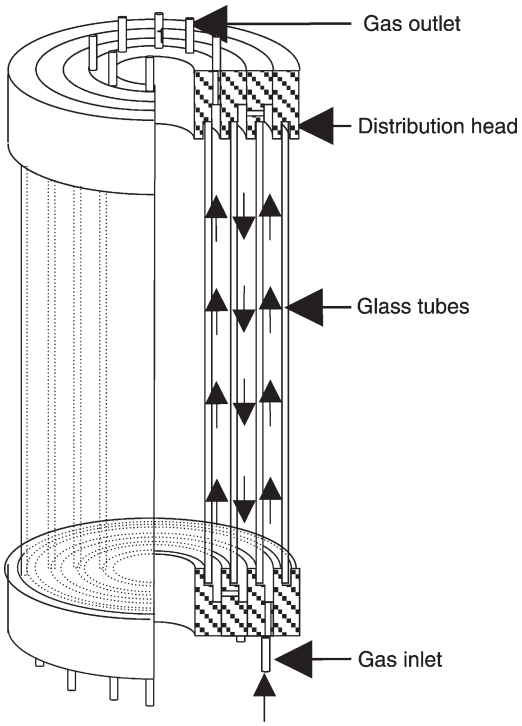

Figure 1 Multi-annular photocatalytic reactor

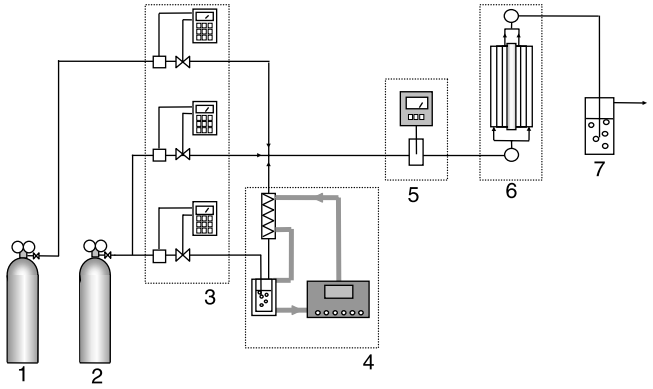

Figure 2 Experimental setup. (1) PCE + air, (2) air, (3) mass flowmeters, (4) humidifier, heat exchanger, thermostatic bath, (5) thermohygrometer, (6) photoreactor and sampling devices, and (7) gas scrubber

A radiation field model was developed to predict the spectral net radiative flux on the area of the reactor wall of radiation entrance and the local superficial rate of photon absorption (LSRPA) at each point on the reactor catalytic walls:

$$q_{\lambda,RW} = \int_{\phi_{\min}(R_W)}^{\phi_{\max}(R_W)} \int_{\theta_{\min}(R_W,z,\phi)}^{\theta_{\max}(R_W,z,\phi)} \frac{P_{\lambda,\mathrm{L}}}{2\pi^2 R_\mathrm{L} Z_\mathrm{L}} \cos\phi \sin^2\theta \; \mathrm{d}\theta \; \mathrm{d}\phi \tag{2}$$

$$e^{a,s}(r,z) = \sum_{\lambda=300nm}^{420nm} \int_{\phi_{\min}(r)}^{\phi_{\max}(r)} \int_{\theta_{\min}(r,z,\phi)}^{\theta_{\max}(r,z,\phi)} \frac{P_{\lambda,\mathrm{L}}}{2\pi^2 R_\mathrm{L} Z_\mathrm{L}} \exp\left(-n_\mathrm{g}(r)\frac{\kappa_{\lambda,\mathrm{g}} e_\mathrm{g}}{\cos\alpha_\mathrm{n}} - n_\mathrm{f}(r)\frac{\kappa_{\lambda,\mathrm{f}} e_\mathrm{f}}{\cos\alpha_\mathrm{n}}\right) \times \left[1 - \exp\left(-\frac{\kappa_{\lambda,\mathrm{f}} e_\mathrm{f}}{\cos\alpha_\mathrm{n}}\right)\right] \cos\phi \sin^2\theta \; \mathrm{d}\theta \; \mathrm{d}\phi \tag{3}$$

where $P_{\lambda,\mathrm{L}}$ is the spectral emission power of the lamp; R_L and Z_L are the radius and length of the lamp, respectively; $\kappa_{\lambda,\mathrm{f}}$ and $\kappa_{\lambda,\mathrm{g}}$ are the spectral absorption coefficients of the TiO_2 film and of the glass tubes; e_f and e_g are their corresponding thicknesses; α_n is the angle between the ray trajectory and the film outwardly directed normal; and n_g and n_f are the number of times that a radiation beam has been attenuated by a glass tube wall or by a TiO_2 film, respectively, before its incidence at the (r,z) position on the catalytic surface.

The mean value of the LSRPA on the reactor catalytic surface (A_R) is the surface rate of photon absorption (SRPA), defined as:

$$\langle e^{a,s} \rangle_{A_\mathrm{R}} = \frac{\int_{A_\mathrm{R}} e^{a,s}(r,z)\mathrm{d}A}{A_\mathrm{R}} \tag{4}$$

A 2-D mass balance was developed taking into account the intrinsic kinetics (equation 1), as well as mass transfer rate processes and the LSRPA calculated with the radiation field model (equation 3). With the considerations adopted, the differential mass transfer equation can be written as (Imoberdorf *et al.*, 2006):

$$\frac{\partial C_\mathrm{PCE}(r,z)}{\partial z} V_{z,j}(r) = \frac{D^0_{\mathrm{PCE-Air}}}{r} \frac{\partial}{\partial r}\left(r \frac{\partial C_\mathrm{PCE}(r,z)}{\partial r}\right); \quad (j = 1,2,3) \tag{5}$$

with the boundary conditions:

$$D^0_{\mathrm{PCE-Air}} \left.\frac{\partial C_{\mathrm{PCE}}(r,z)}{\partial r}\right|_{r=R_j} = r_{\mathrm{PCE}}\left[C_{\mathrm{PCE}}(R_j,z), e^{as}(R_j,z), C_{\mathrm{H_2O}}\right] \tag{6}$$

$$D^0_{\mathrm{PCE-Air}} \left.\frac{\partial C_{\mathrm{PCE}}(r,z)}{\partial r}\right|_{r=\chi_j R_j} = -r_{\mathrm{PCE}}\left[C_{\mathrm{PCE}}(\chi_j R_j,z), e^{as}(\chi_j R_j,z), C_{\mathrm{H_2O}}\right] \tag{7}$$

The complete mathematical model was numerically solved with an *ad-hoc* developed FORTRAN program. Predicted conversions show good agreement with experimental results with a root mean square error less than 5.6% (Table 1).

The simulation program was used to study the efficiency of the energy usage in the multi-annular photocatalytic reactor. For this purpose, the total quantum efficiency (η_{T}) was defined as the ratio of the number of molecules of PCE reacted to the number of photons emitted by the lamp, and was expressed as the product of the following factors:

$$\eta_{\mathrm{T}} = \eta_{\mathrm{I}} \times \eta_{\mathrm{A}} \times \eta_{\mathrm{R}} \tag{8}$$

Here η_{I} is the incident radiation efficiency of the reactor, it being the ratio of photons entering the reactor to the total number of photons emitted by the lamp; η_{A} is the catalyst radiation absorption efficiency, which is defined as the fraction of photons absorbed by the catalyst films from the total number of photons that have already entered the reactor; and η_{R} is the overall reaction quantum efficiency, defined as the ratio of the number of molecules of PCE reacted to the number of photons absorbed by the catalytic film.

The value of η_{I} depends on the external reactor configuration and dimensions, including the optical properties of the building materials. The reactor radiation incidence efficiency may be obtained as follows:

$$\eta_{\mathrm{I}} = \frac{\int_{A_{\mathrm{RW}}} \int_{\lambda_{\mathrm{L}}} q_{\lambda,\mathrm{RW}}\,\mathrm{d}\lambda\,\mathrm{d}A}{\int_{\lambda_{\mathrm{L}}} P_{\lambda,\mathrm{L}}\,\mathrm{d}\lambda} \tag{9}$$

where A_{RW} is the area of radiation entrance. Notice that $q_{\lambda,\mathrm{RW}}$ may be obtained from equation (2) or resorting to experimental techniques (radiometers, actinometers, etc.).

Table 1 Experimental PCE conversions against model predictions*

Volumetric flow rate ($cm^3\ s^{-1}$)	Relative humidity (%)	SRPA × 10^{-11} (Einstein $cm^{-2}\ s^{-1}$)	X^{exp}_{PCE} (%)	X^{mod}_{PCE} (%)	Absolute error (%)
4.17	48	1.00	52.6	40.55	12.05
7.14	48	1.00	30.1	26.26	3.84
12.55	48	1.00	19.1	15.89	3.21
15.82	48	1.00	14.7	12.82	1.88
20.75	48	1.00	11.3	10.00	1.30
12.50	11	1.00	31.7	32.59	0.89
12.50	30	1.00	22.5	21.22	1.28
12.50	48	1.00	19.1	15.92	3.18
12.50	89	1.00	12.9	10.14	2.76
11.36	47	0.79	16.4	14.00	2.40
11.36	47	1.00	23.5	17.46	6.04
11.36	47	2.74	53.8	40.89	12.91
11.36	47	15.00	100	94.38	5.62
11.36	47	26.50	100	99.38	0.62

*$C^0_{\mathrm{PCE}} = 50\ \mathrm{mg\,m^{-3}}$; $T = 20\ ^{\circ}\mathrm{C}$; $P = 1$ atm

The catalyst radiation absorption efficiency (η_A) depends on the internal reactor/lamp configuration and on the optical properties of its building materials, including the photocatalyst. In some cases the catalyst may absorb almost all the radiation that has entered the reactor, but this is not a frequent situation due to reflections, scattering or low optical length. In the reactor employed in this work the catalyst is immobilised on the internal walls and radiation is partially absorbed by the thin catalytic films; the rest is transmitted through the film or reflected on its surface. The optical properties of the catalyst (absorption and reflection coefficients) present a strong dependence on the radiation wavelength; thus, the catalyst radiation absorption efficiency maintain the spectral dependence. This efficiency is defined as:

$$\eta_A = \frac{\int_{A_R} \int_{\lambda_{Lamp}} e^{a,s}_{\lambda} d\lambda \; dA}{\int_{A_{RW}} \int_{\lambda_{Lamp}} q_{\lambda,RW} d\lambda \; dA} \tag{10}$$

Generally, η_A is determined by numerical computations based on a supporting radiation field model.

It is important to note that both η_I and η_A are parameters related to the inherent characteristics of the reactor/lamp system, depending neither on the reaction taking place, nor on the chosen operating conditions (like, for instance, the flow rate of contaminated stream at the reactor feed point or the pollutant concentration). On the contrary, the value of η_R depends on the specific reaction taking place as well as on the nature of the photocatalyst employed and is strongly affected by the reactor operating conditions. An important feature of this parameter is that it must not depend on the photocatalytic reactor type or configuration. The overall reaction quantum efficiency can be defined as:

$$\eta_R = -\frac{\langle r_{PCE}(r,z)\rangle_{AR}}{\langle e^{a,s}(r,z)\rangle_{AR}} \tag{11}$$

In equation (11), $r_{PCE}(r,z)$ can be evaluated using the mathematical model described before (equations 5–7) and $e^{a,s}(r,z)$ from equation (3). Numerical results of η_I, η_A, and η_R are shown in Table 2.

As explained before, the apparent quantum efficiency has been widely employed as a means of assessing the energy performance of photocatalytic reactors. It is expressed as the ratio of the global rate of degradation of the contaminant species, to the total energy entering the photocatalytic reactor. According to the definitions used in this work, η_{app} is equivalent to the product of η_A and η_R. Although η_{app} can be easily evaluated (without mathematical models), the result gives no indication of the fraction of photons emitted by the lamp that actually enters the reactor, thus leaving aside an important aspect affecting the radiative energy performance of different photocatalytic reactors. Besides, this parameter depends on the reactor configuration. Consequently, it is difficult to compare results obtained in different photoreactors.

Table 2 Numerical values for η_I, η_A, and η_R

	η_I	η_A	η_R
Values	83%	92%	0 to 2.5%
Dependence	External reactor geometry and UV lamp characteristics	Internal reactor geometry, UV lamp characteristics and catalyst optical properties	PCE feed concentration, LSRPA, relative humidity, and mass transfer limitations

The dependence of η_R on the operative variables was studied by means of the mathematical model. This efficiency shows a monotonic dependence upon the local PCE concentration, increasing with larger pollutant concentrations and decreasing with smaller ones. Consequently, η_R dramatically decreases as the PCE conversion increases (with values close to 0% for PCE conversions near 100%). Also, it was found that under constant values of the other operating variables, η_R decreases when the relative humidity is increased. Concerning the diffusive resistances, two different regimens were found: (i) At low irradiation levels ($< 1.0 \times 10^{-10}$ Einstein $cm^{-2} s^{-1}$) the reactor performance is kinetically controlled and mass transfer phenomena are not the determining rate step. Under these operating conditions, PCE radial concentration gradients are negligible. (ii) At high irradiation levels ($> 1.5 \times 10^{-9}$ Einstein $cm^{-2} s^{-1}$), molecular diffusion of PCE from the bulk to the catalytic walls begins to control and noticeable radial gradients start to build up. The mass transfer resistances increase significantly when the reaction takes place in aqueous phase, as a result of the lower diffusivities in this medium compared to the corresponding values in gas phase.

Conclusions

The simulation program developed in this work proved to be a very useful tool for the assessment of the multi-annular photocatalytic reactor energy performance, providing accurate values of the different contributions to the overall quantum efficiency.

For this reacting system, the radiation incidence efficiency (η_I) was 83% and the catalyst radiation absorption efficiency (η_A) was 92%. These values are a function of the reactor-UV lamp characteristics, but do not depend on the particular reaction or operating conditions. Consequently, these values may be used to compare the photon capture ability of various types of photocatalytic reactor configurations for water treatment and for air pollution remediation.

Simulation runs under different operating conditions have shown that the overall reaction quantum efficiency (η_R) decreases when the PCE concentration is decreased or when the relative humidity is increased. Depending on the particular operating conditions, numerical values of η_R are in the 0–2.5% range. It should be noted that η_R does not depend on the photocatalytic reactor configuration, and it may be useful to compare the catalytic activity of different catalysts for the same pollutant or of the same photocatalyst for different pollutants.

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