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# Modelling of Photoreactors for Water Treatment

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Photocatalytic processes are acquiring increasing attention as a means to exploit solar energy to promote chemical transformations. Reactor design and modelling is a fundamental step to set the basis for the possible scale up of the technology. To this purpose, we have modelled the radiation flow depending on reactor geometry for different prototypes of photoreactors, comparing the results with a measured map of irradiance around the emitting source. This is a first step to include photons in a kinetic model as "quasi-reactants" to scale-up photoreactors.

## 1. Introduction

Radiation distribution is the most important component that determines the performance of a photoreactor. In a photocatalytic reaction mediated by a semiconductor photocatalyst, the speed of the initial step (electron-hole pair formation) depends on the radiation intensity (Pareek et al., 2008). The light distribution intensity (Pareek et al., 2008) depends on as the lamp type (Pareek et al., 2005), the reactor geometry (Sun et Xu., 2010), the optical properties of medium (Cassano et al., 1995; Busciglio et al., 2016) and reactor walls (Braun et al., 1991). There are three standard geometrical configurations mostly used: annular (Pareek et al., 2005), elliptical (Serrano et De Lasa., 1997) and parabolic (Cassano et al., 1995). In annular photoreactors, interesting for this study, the lamp is positioned axially and the light intensity distribution may be not uniform (Pareek et al., 2008), since while the points close to the inner surface are illuminated effectively, those far from the inner surface receive very little or no light because of the increased optical thickness. The optical properties of medium are also key factors to design a photoreactor (Cassano et al., 1968). For homogeneous photochemical systems the absorption coefficient k is the only parameter, to be estimated through the Lambert-Beer law (Pareek et al., 2005). For heterogeneous systems, the radiation transport equation (RTE) should be applied, solving a radiation balance by considering photon gains and losses from all possible directions in a control volume (Cassano et al., 1995; Siegel et Howell., 1992). In heterogeneous systems, the RTE contains three parameters: the absorption coefficient (k), the scattering coefficient (σ) and the phase function (p) (Pareek et al., 2008). In this work we developed a Matlab code to estimate the distribution of light intensity in an annular stainless-steel photoreactor with axial lamp. This photoreactor has been used for both the high pressure photoreduction of $CO_2$ (up to 20 bar) and $H_2$ production through photoreforming of carbohydrates. This step will allow mapping the radiation intensity throughout the photoreactor to include photons concentration as "quasi reactants" in the future development of kinetic models for these applications.

## 2. Experimental setup and modelling methods

### 2.1. The photoreactor

The experimental photoreactor in the central part is equipped with a quartz tube containing the radiation source (Figure 1- Left). The tube is transparent to UV radiation and ensures total irradiation of the internal areas of the photoreactor (Rossetti et al., 2015; Galli et al., 2017). The irradiation source consists of two medium pressure mercury UV bulbs (125 W), with maximum emission at 365 nm (Figure 1-Right). The lamp is positioned axially.

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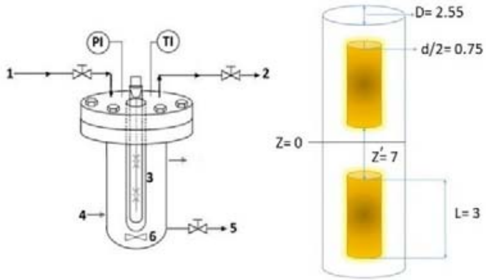


*Figure 1: Left) Schematic representation of the reactor. 1) gas inlet; 2) gas outlet; 3) lamp; 4) heating jacket; 5) liquid outlet; 6) mixer; PI) pressure indicator; TI) temperature indicator. Right) Scheme of mercury vapor bulbs.*

### 2.2. Mathematical model for light distribution

An accurate estimation of the light intensity distribution (LVREA: local volumetric rate of energy adsorption) is essential to implement a reliable design of a photoreactor (Pareek et al., 2008). It is possible to accurately evaluate the distribution of light intensity in each computational domain through the Integro-differential equation of the RTE. For photocatalytic systems, due to the presence of a solid photocatalyst, it is quite difficult to find out the analytical solution for RTE. For this reason, a new and efficient numerical method has been used, to achieve a reliable description of the light distribution in the photoreactor. First, a radiation balance is calculated between the specific photons flow ($dI_v/ds$) as net photons entering and exiting in all directions for a control volume. Energy is exchanged due to Absorption ($W^a$), Emission ($W^e$), in-Scattering ($W^{in}$) and Out-scattering ($W^{out}$) (Pareek et al., 2003).

$$\frac{dI_v}{ds} = -W^a + W^e + W^{in} - W^{out} \quad \left(\frac{W}{cm^2}\right) \qquad (1)$$

To develop our RTE model, the following assumptions were implemented (Pareek et al., 2003): a) the lamp is considered as a uniform surface emitting radiation (Yokota et al., 1981); b) the term related to the in-scattering present in the RTE (3) is separated from the rest of the equation; its contribution to radiation can be added after the formal integration; c) the contribution of in-scattering is considered as the sum of the light intensity dispersed in six different directions; d) reflection and absorption of light by the reactor walls are not considered (this latter assumption is reasonable for thick optical medium, such as 0.5 g/L $TiO_2$ loading (Pareek et al., 2008), in which only a small part of radiation reaches the walls of the reactor). Considering these assumptions, equation (1) can be rewritten as:

$$\frac{dI_v(s,\Omega)}{ds} = -k_v I_v(s,\Omega) - \sigma_v I_v(s,\Omega) + \frac{1}{4\pi}\sigma_v \int_{4\pi} p(\Omega' \to \Omega) I_v(s,\Omega') d\Omega' \quad \left(\frac{W}{cm^2}\right) \qquad (2)$$

Where $p(\Omega' \to \Omega)$ is the phase function, whose value is 1 for an isotropic dispersion. Therefore, the incident light intensity at every point of the reactor, coming from all directions, is:

$$G_v(s) = \int_{\Omega=0}^{\Omega=4\pi} I_v(s,\Omega) d\Omega \quad \left(\frac{W}{cm^2}\right) \qquad (3)$$

The LIVREA at each point of the reactor is given by:

$$E_{tv}(x,y,z) = k_v G_v(x,y,z) \qquad (4)$$

Considering the photocatalytic system, only those photons with wavelength equal or less than the band gap energy $\lambda_{Ebg}$ can contribute to the excitation of the electrons present in the particles of the semiconductors. Therefore, a sum can be made in this wavelength range to evaluate the total LVREA:

$$E(x,y,z) = \sum_{\lambda<\lambda_{Ebg}} E_{l,v}(x,y,z) = \sum_{\lambda<\lambda_{bg}} k_v G_v(x,y,z) \qquad (5)$$

#### 2.2.1. Radiation source model

In order to solve the RTE for a heterogeneous system, boundary conditions are required for the light intensity of the radiation. Consequently, it is necessary to formulate an appropriate model called the "incident model", in which a specific distribution of light intensity (e.g. an exponential decay) is assumed in the reactor space. Furthermore, there is a second class of models called "emission models", in which the amount of photons emitted is used to derive an incident model. In our work we are mainly focusing on the later type since it proved more effective. Hence, the lamp can be seen as a source of light like an illuminative wire with a surface

or an emitting volume (Pareek et al., 2008). According to literature (Pareek et al., 2008), the two types of emission can be considered for the source: a) Specular, b) Diffusive emission (Fig. 2-a).
As shown in Figure 2-a, in the specular emission, the magnitude of the light intensity vectors is independent of the emission angle; this behavior is typical of mercury and neon lamps (Pareek et al., 2008). The diffusive emission is typical of the fluorescent lamps in which the magnitude of the light intensity vectors shows a strong dependence on the emission angle.
The following assumptions have been applied in the present model to obtain a unified structure of the equation and allow a comparison between the different light sources: a) the intensity of light at any point in the reactor due to a lamp element was inversely proportional to the square of the point distance from that element; b) the emission of the radiation takes place with spherical symmetry and the reflection from the reactor surface was negligible; c) the emitted radiation rate was constant throughout the lamp; d) there was no absorption of useful radiation from the cooling elements assembled around the lamp; e) the photon emission rate was independent of the angular coordinate θ.

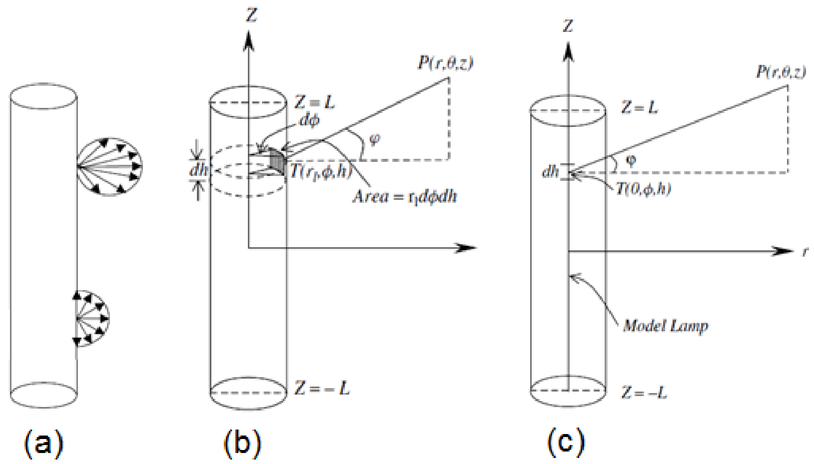


*Figure 2: (a) Types of lamp emission; (b) Model of the emitting surface (2D) for the emission of the lamp; (c) Model of emitting wire source.*

For the study of the distribution of the light intensity emitted by our lamp we used the model of the emitting surface. In this model is assumed that all the emitted radiation comes exclusively from the surface of the lamp (Figure 2-b) (Yokota et al., 1976). An infinitesimal surface area bounded between an angle dφ and a length dh is considered. The emission rate of the photons emitted by the entire surface of the lamp is Kv, the number of photons emitted from the shaded area in Figure 2 (= rl * dφ * dh) per unit of time is:

$$dNv = Kv \times rl \times d\phi \times dh \qquad (6)$$

$$Kv = \frac{Nv}{(4\pi \times rl \times L)} \left(\frac{W}{cm^2}\right) \qquad (7)$$

Where $Nv$ is the total number of photons emitted by the lamp and $rl$ is the radius of the lamp.
For specular emission (independent of the emission angle) (Stramigioli. et al.,1977), the intensity of the incident radiation at point P was given by:

$$dGv = \frac{Kv \times rl \times dh \times d\phi}{4\pi[(rcos\theta - rl \times cos\,\phi)^2 + (rsin\theta - rl \times \sin\phi)^2 + (z-h)^2]} \qquad (8)$$

Integrating on the entire surface of the lamp:

$$Gv\left(\frac{W}{cm^2}\right) = \int_{h=-L}^{h=L}\int_{=-\pi/2}^{=+\pi/2} \frac{Kv \times rl \times d\phi \times dh}{4\pi[(rcos\theta - rl \times \cos\phi)^2 + (rsin\theta - rl \times \sin\phi)^2 + (z-h)^2]} \qquad (9)$$

To solve eq. 9, a code in Matlab was developed to compute the RTE applied to the present photoreactor geometry including 7 inputs. Another script allowed to calculate the intensity of light emitted by a single bulb. To evaluate the accuracy of the code different tests were carried out: a) near field; b) far field; c) box; d) sphere.

*Close field test*

For this we focused on a point located at about 0.8 cm from the lamp axis. At this distance, an observer sees the lamp as a flat emitting surface, consisting of small square surfaces having angle $d_V$ as their base and an infinitesimal length $d_Z$ as height. To obtain the total light intensity emitted by this surface we multiplied the "Intensity" function, calculated at different heights and different angles around the lamp and at a constant distance of 0.8 cm. By solving the equation a light intensity equal to the power of a single bulb of the lamp should be calculated. Accordingly, each single bulb of lamp has a power of 62.5 W/cm$^2$. Applying the close filed test, we reproduced correctly the nominal lamp potential, which confirmed the correctness of the model.

*Far field test*

This assumption is based on considering a position very far from the lamp, at a distance about 15 cm, where the lamp can be compared to an emitting wire. Jacob et al. (Jacob et al., 1968), proposed an emission model considering the emission source as a wire or line particularly for lamps with a relatively small diameter compared to the reactor diameter (Figure 2-c). Considering $K_{v1}$ as a rate of emission of photons per unit area of lamp, therefore, the number of photons emitted by the surface element shown in Fig.2 per unit of time was:

$$dN_v = K_{v1} dh \qquad (10)$$

In which:

$$K_{v1} = \frac{N_v}{2L}\left(\frac{W}{cm}\right) \qquad (11)$$

The $N_v$ is the total number of v-photons emitted by the lamp and L is the semi-length of the lamp. For a specular emission source, the intensity of incident radiation at point P due to this element is obtained by dividing the equation (10) by the area of the sphere with radius TP (=$\sqrt{r^2 + (z-h)^2}$):

$$dG_v = \frac{K_{v1} dh}{4\pi(r^2 + (z-h)^2)} \qquad (12)$$

That integrated on the entire lamp surface is resulting:

$$G_v = \int_{-L}^{L} \frac{K_{v1} dh}{4\pi(r^2 + (z-h)^2)} = \frac{K_{v1}}{4\pi}\int_{-L}^{L} \frac{dh}{(r^2 + (z-h)^2}\left(\frac{W}{cm^2}\right) \qquad (13)$$

The analytical solution to the eq. 13 is written below:

$$G_v = \frac{K_{v1}}{4\pi r}\left(tan^{-1}\left(\frac{z+L}{r}\right) - tan^{-1}\left(\frac{z-L}{r}\right)\right)\left(\frac{W}{cm^2}\right) \qquad (14)$$

The eq. 14, can be easily treated in Matlab. We have considered some boundaries: a) considering a constant distance of 15 cm from the lamp; b) considering the θ angle (Figure 2-c) equal to 0, since the lamp has been considered as an emitting wire; c) a variable Z height.

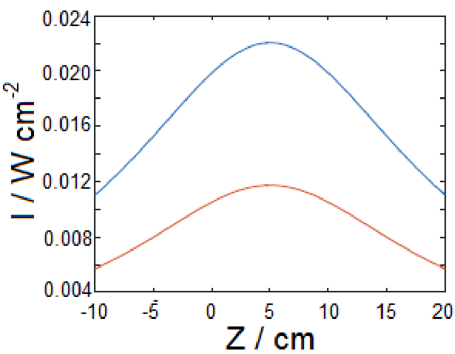


*Figure 3: "Intensity" function and "theoretical wire" function in comparison: in red the intensity of light of the "intensity" function is exactly half the intensity of light of the theoretical function (in blue) as the integral we have elaborated on the angle φ on the XY plane inside the lamp considers as integration interval [-π/2, +π/2]. Therefore, it measures the intensity of light emitted only by half "wire"*

The proposed model provides an integration on a half the length of the lamp. Comparing the result obtained from this model with the integration over the half lamp, with the results obtained from the emitting wire source (integrated on the entire lamp) we expect to obtain an intensity of light equal to half of that provided by the theoretical model. The results are consistent with those expected as shown in Figure 3.

*Test of the box*

Enclosing the lamp in a cylindrical box and estimating the intensity of incident light on the walls and the lids surface of box allowed to measure the intensity of lightas in the near field test but adding the results to the intensity of light reflected on the lids of cylinder. Each lid is divided into a series of rectangles having an infinitesimal angle $d_V$ (angle θ) and infinitesimal length $d_R$ (radius) as height. The upper lid will have Z (observer height) with a constant value of $Z_{max}$ and the bottom lid with a constant value equal to $Z_{min}$. Two loops have been created in order to vary the angle θ (V) and the radius (from 0.8 cm to 1.5 cm), and in each loop the model is multiplied to the area of a single square given by:

$Ai = dR \times dV \times R(p) \quad (15)$

However, the lids are considered not as flat surfaces but as spherical caps, so it was necessary to make the following corrections:

For the upper lid: $\frac{((max(Z)-6.5)^2+R(p)^2)^{0,5}}{(max(Z)-6.5)} \quad (16)$

For the bottom lid: $\frac{((min(Z)-3.5)^2+R(p)^2)^{0,5})}{(-min(Z)+3.5)} \quad (17)$

From the sum of the intensity of light reflected on the walls of the box and on the lids we obtained a value of 62.5 $W/cm^2$, equal to the power of a single bulb. The obtained results confirm the correctness of this model.

*Sphere test*

In this model the lamp was located in the center of a sphere and the intensity of light incident on its surface was then calculated. The surface of the sphere was divided into small squares having an edge of arc given by:

$arc1 = MAX(R) \times dV \quad (18)$

$arc2 = MAX(R) \times dFI \quad (19)$

in which V = angle θ on XY plane; FI = angle φ on XY plane inside the lamp; R = distance from the lamp.
The area of the surface element was:

$Ai = max(R)^{*2} dV \times dFI \quad (27)$

$Ai = max(R)^{*2} dV \times dFI \quad (28)$

Because of the shadow cone created by the lamp itself, the sphere received only half the light emitted by the lamp, so we expect to obtain a result of about 31.25 $W/cm^2$, that is half the power of the bulb. The result instead, has been obtained to be 24.44 $W/cm^2$, which is still far from the estimated value. The discrepancy concerns the consideration of a fixed Z, indeed the Z actually varies with φ. Then we create a FIEXT variable that considers the angle φ as an angle of the sphere and not of the lamp. we write a for loop for FIEXT and we included a definition of Z that varied with FIEXT.

$Z = max(R) \times \sin(FIEXT(i)) + 5 \quad (20)$

We implemented a further correction on the radius of the sphere, as the "intensity" function considered the radius (R) as linear.

The radius was considered as $RAGGIO = max(R) \times cos(FIEXT(i)) \quad (21)$

The surface area of the considered element then became: $Ai = max(R) \times RAGGIO \times dV \times dFIEXT \quad (22)$

By inserting these measures into the model the exact value of 31.25 $W/cm^2$ was obtained.

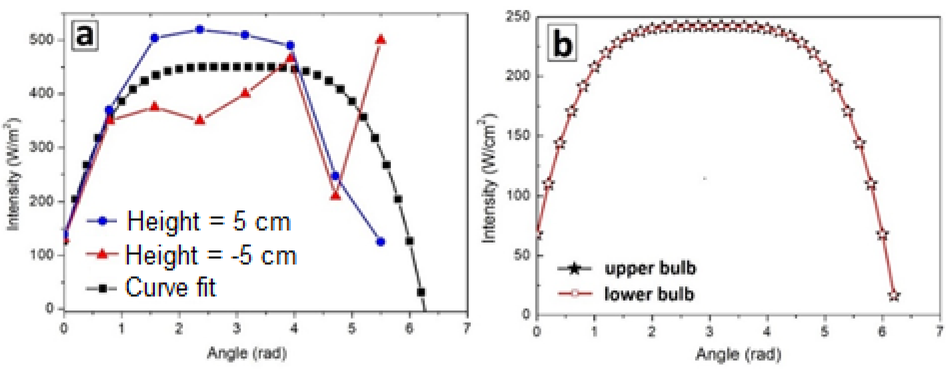


*Figure 4: a) Interpolation of data obtained from remote lamp (d=1.75 cm) mapping; b) Light intensity values emitted by lamp as a function of the angle Θ (d=1.75 cm), at both the upper and lower bulb*

*Two bulbs and Theta angle dependence*

To introduce a dependence of the intensity emitted by the angle θ (Figure 4) the data obtained from the mapping of the lamp at 1.75 cm were considered. The emitted power was measured through of a photo-radiometer (Delta OHM HD2102,2) at 315-400 nm.

The data were divided into two areas and among the least squares methods the exponential regression was used (Figure 4-a).

The calculated intensity at the distance of 1.75 cm from the lamp resulted in the distribution of light intensity according to the angle θ at the upper bulb and the lower bulb as in Figure 4-b, well representing for each bulb the average irradiance experimentally observed (Figure 4-a).

## 3. Conclusions

In this study a Matlab code, appropriately parameterised, was set up to estimate and represent the intensity of light emitted by a lamp as a function of the distance around the bulbs. This model can be considered a good starting point for subsequent computational studies concerning the distribution of light intensity as quasi-reactant in a robust kinetic model for photoreactors scale up and design.

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