Modeling UV radiation absorption in a flat-plate photocatalytic reactor

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The modeling of the distribution of radiative energy absorption in photocatalytic systems is an important step for process design and scaling-up. The radiative transfer equation (RTE) solution is the best method to access this information. This equation allows for the calculation of the radiation intensity distribution in a photocatalytic reactor; nevertheless, it is very difficult to solve. The P1-approximation greatly simplifies the solution to this problem. In particular, the P1-approximation will be solved for the general case of a flat-plate reactor. The calculations are compared experimental results obtained in a reactor of the flat-plate geometry.

Keywords: Photocatalysis, Photoreactor, P1 approximation

1. INTRODUCTION

Solar photocatalytic detoxification attracts considerable interest due to the possibility of using a clean energy source to carry out water treatment. The degradation of pollutants in photocatalytic reactors begins with the absorption of near ultraviolet (UV) radiation in a semiconductor catalyst, leading after some steps to the generation of hydroxyl radicals $OH^{\bullet}$ [1,2]. These radicals are very reactive and are able to destroy almost any organic pollutant present in the solution.

The catalyst (usually anatase TiO_2) is often present in the form of suspended particles, which absorb and strongly scatter UV radiation. The efficiency of the reactors is strongly dependent on the way absorbed energy is distributed in the reaction volume. This distribution is greatly affected by the scattering process, and therefore it is necessary to take into account such process to carry out an adequate optical modeling of the reactors [3]. The radiative transfer equation (RTE) is the rigorous tool to carry out such modeling [4,5], but the use of alternate approximate methods is of interest due to the complexity of dealing with it.

2. P1 APPROXIMATION

This analytical aproximation considers that the angular distribution of propagation directions in any point inside the medium is almost uniform. The physical condition for this assumption is to have large amount of scattering, which tends to eliminate preferential propagation directions [10]. The basic equation is

$$\nabla^2 G(\mathbf{r}) = k_d^2 G_\lambda(\mathbf{r}) \qquad (1)$$

where $G_\lambda(\mathbf{r})$ [W cm^{2}μm^{-1}] is the local radiation inside the reactor and

$$k_{d\lambda} = 3\beta_\lambda (1-\sigma_\lambda/\beta_\lambda)^{1/2} \qquad (2)$$

The β_λ and σ_λ parameters are known as extinction and scattering coefficients, respectively, and represent the optical properties of the catalyst particles. The first of them is the sum of the scattering

and absorption κ_λ coefficient. These three coefficients depend linearly on the catalyst concentration and they have been obtained by the present authors, for titanium dioxide (TiO_2) Aldrich type.

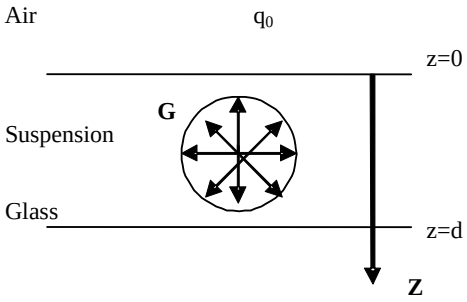

Figure 1: Geometrical scheme for the theoretical model.

The product $k_\lambda G_\lambda(\mathbf{r})$ gives the amount of energy absorbed by the particles, by unit of volume of the suspension and by unit of wavelength, which this directly related to the amount of photons available to carry out the chemical reactions.

Considering a system of rectangular coordinates (flat geometry) and a uniform flux of incident radiation in the face of a reactor, whose lateral dimensions are assumed very large with respect to its height, the solution can depend only on coordinate z (Fig. 1), therefore

$$\frac{d^2G}{dz^2} = k_{d\lambda}^2 G \qquad (3)$$

The general solution of this equation is

$$G(z) = C_1 e^{(k_{d\lambda})} + C_2\, e^{(-k_{d\lambda})} \qquad (4)$$

To obtain the values of the coefficients C_1 and C_2, this solution must be replaced in the boundary conditions of Marshak type [11] for semitransparent surfaces

$$G(d)(1-\rho_f) - \frac{2(dG/dz)_{z=d}}{3\beta_\lambda}(1+\rho_f) = 0 \qquad (5)$$

$$G(0)(1-\rho_s) - \frac{2(dG/dz)_{z=0}}{3\beta_\lambda}(1+\rho_s) = 4q_{0\lambda} \qquad (6)$$

Where ρ_s and ρ_f are the reflectance from the face and the bottom of the reactor, respectively. These boundary conditions represent the radiative flux continuity through a surface. Particularly, $q_{0\lambda}$ represents the incident spectral solar radiative flux in the reactor surface. When replacing the general solution in the boundary conditions the C_1 and C_2 constants are obtained.

From the experimental data the overall reactor transmittance integrated over the solar spectrum is obtained. Therefore, in order to compare the model with the experimental results, it is necessary to obtain the theoretical value of this transmittance, assuming an open top and a glass bottom, as in the experimental setup. This transmittance can be determined as

$$T = (1-\rho_s)\int_\lambda \left[\frac{G_\lambda}{4} - \frac{\nabla G_\lambda}{6\beta_\lambda(1-\sigma_\lambda/\beta_\lambda)}\right]_{z=d} \frac{q_\lambda}{q_0} d\lambda \qquad (7)$$

where

$$q_\lambda = -\frac{\nabla G}{3\beta_\lambda(1-\sigma_\lambda/\beta_\lambda)} \qquad (8)$$

3. EXPERIMENTAL PROCEDURE

In order to carry out the experiments a glass reactor was constructed of flat plate geometry with square base, and opened top surface (fig. 2). The reactor dimensions (0.9m x0.9m x0.06m) are such that the lateral faces do not interfere significantly in the amount of radiation that arrives at the measurement point, which is located at the center of the bottom face. These dimensions were estimated based on the incidence angles and the extinction coefficient previously obtained for the suspensions under consideration. Because a large enough high quality (transparency) glass plate was not available for the construction of

the reactor, standard 0.003m thick glass was used. In spite of this, the measured UV transmittance of this plate gives an average value of 0.7, in the range of interest, which allows the passage of the transmitted radiation in an amount sufficient to be measurable.

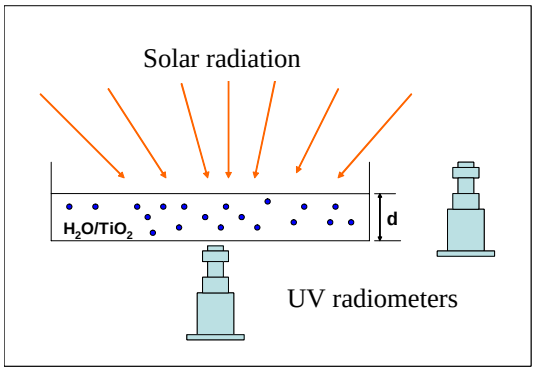

Figure 2: Experimental setup.

The experiments were carried out using two Eppley UV radiometers, TUVR model, both calibrated by the Solar Radiation Laboratory of the UNAM Geophysical Institute. One of them was placed under the center of the reactor, to measure the transmitted radiation, and the other at a side of this device, to measure incident radiation (fig 2). The ratio of both measurements is the overall transmittance of the suspension, over the solar UV region (300-400 nm).

4. RESULTS

In Figures 4, 5 and 6 the obtained experimental results for the transmittance as a function of suspension thickness are shown. They are compared with the theoretical results from eq. (7). Each one of them corresponds to a different catalyst concentration. Depending on the thickness of the suspensions, their appearance goes from a slightly turbid whitish layer that allows seeing the objects clearly through it, to a completely opaque liquid of milky aspect.

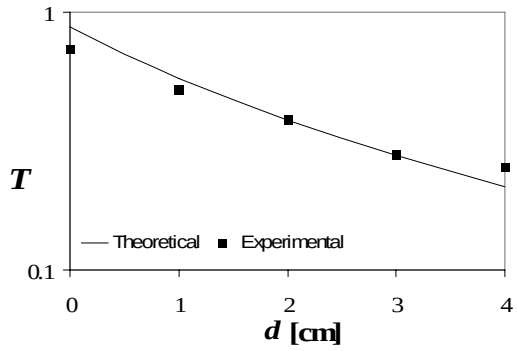

Figure 4: Reactor transmittance as function of suspension thickness, for a catalyst concentration of 0.05 g/L.

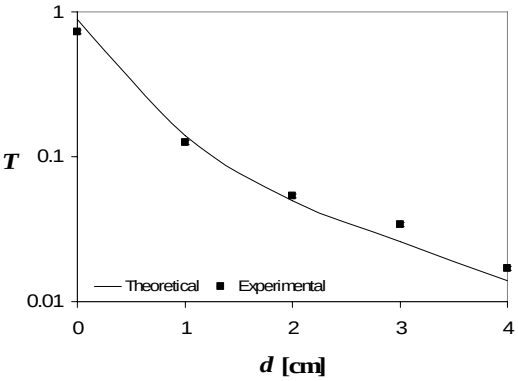

Figure 5: Reactor transmittance as function of suspension thickness, for a catalyst concentration of 0.1 g/L.

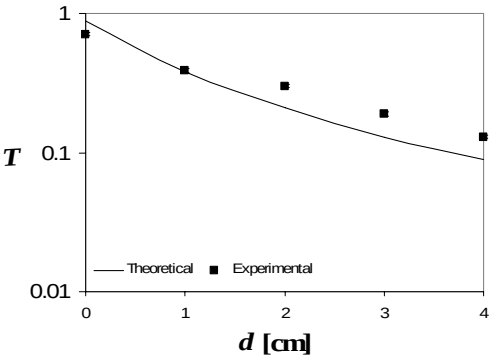

Figure 6: Reactor transmittance as function of suspension thickness, for a catalyst concentration of 0.3 g/L.

As it can be observed in the three figures, in none of the cases is the model

able to reproduce the behavior for small thicknesses. On the other hand, it is also observed in figs. 4 to 6, a very good correspondence of the model with the experiment when either suspension thickness or catalyst concentration is high.

The model failure for low suspension thicknesses can be explained in the following way: The P1 approximation estimates that radiation travels in all directions with almost equal intensity. Nevertheless, this is not realistic for all cases. The incoming radiation on the reactor surface is formed by UV diffuse radiation, which tends to be more or less isotropic on the lower hemisphere, and UV direct radiation, which is strongly directional. In the great majority of the cases the direct and diffuse radiation are comparable. As none of the mentioned contributions to incident radiation is isotropic, it is required that the scattering produced by particles be strong enough to redistribute the radiation in all directions. If the scattering is not so strong, the uniform radiation distribution will never exist and the conditions for the P1 approximation would not be fulfilled. More specifically, the P1 approximation must be valid for media with large optical depths. The optical depth in the present case is defined as $\tau_{opt} = \beta^* C_p d$, where C_p is the particles concentration and $\beta = \beta^* C_p$.

5. CONCLUSIONS

Experiments were made to measure the transmittance of UV solar radiation through a flat plate photocatalytic reactor. Also theoretical calculations were made using the P1 approximation. In general, the theoretical model reflects the transmittance behaviour of the suspensions contained in the reactor. Medium to large optical depths are required to have a good quantitative coincidence in the results, with very important deviations for small depths. However, the later regime is not very interesting from the practical point of view, and we can conclude that the model can be useful tool for the design of reactors.

6. REFERENCES

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