



## MATHEMATICAL MODEL FOR ESTIMATING THE RADIATION FIELD IN PHOTOCATALYTIC REACTORS

### MODELO MATEMÁTICO PARA LA ESTIMACIÓN DEL CAMPO RADIANTE EN REACTORES FOTOCATÁLICOS

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#### Abstract

This paper proposes a new approach for estimating the radiant field in photocatalytic heterogeneous reactors. The effective radiation field model was developed from the constitutive equations for emission and absorption of energy. The new model considers five components for the radiation energy balance: i) The net energy flux in the volume  $v$ , through  $\alpha$  surface in the system. ii) The total energy is absorbed by catalyst particles. iii) The loss of energy is by scattering. iv) The gain in energy is by scattering (a phase function of the scattered energy is required) and the net energy flux in the volume is through the reactor surface. The model is an integro-differential unidimensional function in terms of an arbitrary nondimensional variable  $\chi$ , where  $\alpha(\chi)$  is the surface area of the reactor,  $\kappa_v$ ,  $\sigma_v$  are the average coefficients of volumetric absorption and scattering, respectively. The model was used for the radiation field simulation with Six Flux Model (for CPC reactor and  $\text{TiO}_2$ -P25). The model allows obtaining good results and is faster than the rigorous solution of radiation field.

**Keywords:** Absorption model, emission model, modeling, photocatalysis, volumetric rate of absorption of energy.

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## Resumen

En este trabajo se propone un nuevo enfoque para la estimación del campo radiante en reactores fotocatalíticos heterogéneos. El modelo de campo de radiación efectiva se desarrolló a partir de las ecuaciones constitutivas para la emisión y absorción de energía. El nuevo modelo contempla cinco componentes para el balance de energía de radiación: i) El flujo neto de energía en el volumen  $v$  a través de la superficie  $\alpha$  en el sistema. ii) La energía total es absorbida por las partículas del catalizador. iii) La pérdida de energía es por dispersión. iv) La ganancia de energía es por dispersión (se necesita una función de fase de la energía dispersada) y el flujo neto de energía en el volumen se da a través de la superficie del reactor. El modelo es una función unidimensional integro-diferencial en términos de una variable arbitraria  $\chi$  adimensional, donde  $\alpha(\chi)$  es el área de superficie del reactor,  $\kappa_v$ ,  $\sigma_v$  son los coeficientes medios de absorción volumétrica y la dispersión, respectivamente. El modelo fue utilizado para la simulación del campo de radiación, con el modelo Six Flux (para un reactor CPC y  $\text{TiO}_2\text{-P25}$ ). Permite obtener buenos resultados y es más rápido que la solución rigurosa de la ecuación de campo radiante.

**Palabras clave:** Fotocatálisis, modelamiento, modelo de absorción, modelo de emisión, velocidad volumétrica de absorción de energía.

## Introduction

The design of solar photocatalytic reactors for water detoxification requires a proper understanding of the dynamics of molecular processes at the semiconductor/solution interface. The main limitation is the formulation of the detailed mechanisms of the photocatalytic processes involving complex substances or mixtures [1, 2].

The heterogeneous photocatalytic processes are strongly influenced by four key components: system reactive (substrate), catalyst (semiconductor), geometry reactor (reactor type) and radiation field (luminous flux) [3 - 5]. The geometry and radiation field introduce a non-intrinsic nature to this type of process (reflected in kinetic of reaction rate). These characteristics are the major differences with the conventional chemical processes.



The performance on photocatalysis depends critically on the amount of incident radiation that can be used to activate the catalyst particles and therefore it requires a correct quantification of volumetric rate of energy absorption (VREA). This, in turn, will allow an adequate description of the kinetic parameters such as quantum yields [6, 7].

Generally, the most appropriate models for the description of radiation fields are based on analysis of fundamental principles of radiant energy balances and transport theory of photons, which give rise to an equation called generalized radiative transfer equation, RTE [3, 4, 8]. Currently, the most researched mathematical approaches focus on the solution of RTE.

Cassano et al. [3, 4] have made great efforts for a proper description of VREA through rigorous solution of the RTE using a complex method known as discrete ordinate (DOM), proposed in 1979 by Duderstadt and Martin [6]. This method allows describing the volumetric rates of photon absorption with minimal discrepancies, however, it requires high computational time and complex numerical methods for their solution.

Li Puma et al. [9-10] have implemented a model called “multi-flux” which has two approaches: the two flux model (TFM) that allows introducing the scattering of energy in two directions (Cartesian coordinates) and the six flux model (SFM) which associate the photons transport paths in six directions in Cartesian coordinates. This model is semi-empirical because it uses experimental solar radiation data and parameter adjustment for stochastic methods.

The standard definition of quantum yield for heterogeneous systems is given as the quotient of the reaction rate at a particular location in the reactor and the local volumetric rate of photon absorption (LVRPA) [11, 12]. In the models that explicitly take quantum yields into account, the quantum yields are calculated by adjusting parameters of the overall reaction rate that are assumed constants in the specific system, independent of operating conditions (except the luminous flux). However, recent research has shown that the process conditions (initial concentration of catalyst and reacting species, pH, wavelength, photon flux), the type of reactor and its geometry, the scale of operation and the type of catalyst affect the overall performance of the process [13].

This paper proposes a new approach to the description of radiation fields, based on a modification of the radioactive transfer equation assuming isotropy field.

## Development of mathematical model

For the formulation of model, we use the next definition or postulate [6]:

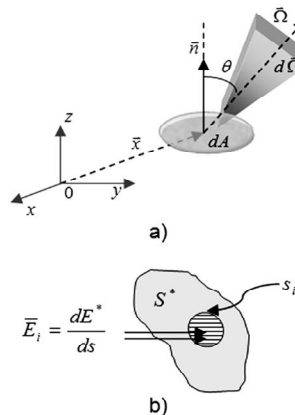
**Definition 1:** the energy radiation field can be calculated by applying the following: “it is possible to redistribute the total energy  $\zeta(\underline{x}, \lambda)$  of an incident photon flux on an energy absorber surface, in a constant energy field  $\langle \xi_N^* \rangle$  which surrounds isotropically the element of absorption, regardless of the direction and spreading frequency”.

**Definition 2:** the radiant field inside the reactor remains isotropic nature and is spread evenly throughout the system volume.

So, the Eq (1) is obtained on the definition of radiation specific intensity  $I_\lambda(\underline{x}, \underline{\Omega}, t)$  [3, 4], this concept is associated with the energy of beam of radiation per unit time (t), per unit solid angle ( $\Omega$ ) from the direction of propagation, per unit surface area (A) as the projected direction  $\theta$  and per unit wavelength interval ( $d\lambda$ ) (see Figure 1a).

Figure 1. (a) Definition of radiation specific intensity, b) incident specific energy

$$I_\lambda(\underline{x}, \underline{\Omega}, t) = \lim_{dA, d\Omega, d\lambda \rightarrow 0} \left\{ \frac{dE^*}{dA \cos(\theta) d\Omega d\lambda} \right\}$$





If  $dE^*$  is the photon flux incident, and maintaining the condition of limit to zero, so:

$$dE^* = I_\lambda(\bar{x}, \bar{\Omega}, t) dA \cos(\theta) d\Omega d\lambda \quad (2)$$

Now,  $ds$  is a differential surface with limit to zero :

$$ds = dA \cos(\theta) \quad (3)$$

If the  $E_i$  is defined as the specific energy per unit differential surface:

$$\bar{E}_i = \frac{dE^*}{ds} = I_\lambda(\bar{x}, \bar{\Omega}, t) d\Omega d\lambda \quad (4)$$

From Figure 1.b,  $\phi_{s,i}^*$  is the fraction of surface area as the relationship differential surface area  $s_i$  and total surface area  $S$  [4]\*:

$$\phi_{s,i}^* \equiv \frac{s_i}{S^*} \quad (5)$$

The global net energy  $\langle E_N^* \rangle$  of the surface  $S^*$  is defined as the contribution of all energy,  $E_i$  of  $N_s$  elements [8]:

$$\langle E_N^* \rangle = \lim_{N_s \rightarrow \infty} \sum_{i=1}^{N_s} \phi_{s,i}^* \bar{E}_i = \lim_{N_s \rightarrow \infty} \sum_{i=1}^{N_s} \phi_{s,i}^* I_\lambda(\bar{x}, \bar{\Omega}, t) d\Omega d\lambda \quad (6)$$

Now, using the conventional definition of spectral incident radiation  $G_\lambda(x,t)$  (Eq. 7) [2, 3], and the fundamental theorem of calculus, we can show that:

$$G_\lambda(x,t) = \int_{\Omega} I_\lambda(\bar{x}, \bar{\Omega}, t) d\Omega \quad (7)$$

$$\frac{dG_\lambda(\bar{x}, t)}{d\Omega} = \frac{1}{d\Omega} \int_{\Omega} I_\lambda(\bar{x}, \bar{\Omega}, t) d\Omega = I_\lambda(\bar{x}, \bar{\Omega}, t) \quad (8)$$

Reorganizing the Eq (8), with the Eq (6) and using the definition to  $\zeta_i(\bar{x}, \lambda) \equiv dG_\lambda(\bar{x}, t) d\lambda$  and the transformation:  $\lim_{N_s \rightarrow \infty} (\sum) = \int$ , so:

$$\langle E_N^* \rangle = S^* \langle \bar{E}_N^* \rangle = \lim_{N_s \rightarrow \infty} \sum_{i=1}^{N_s} \phi_{s,i}^* \zeta_i(\bar{x}, \lambda) = \int_S \zeta(\bar{x}, \lambda) dS \quad (9)$$

Where  $\langle \bar{E}_N^* \rangle$  is the effective net global energy. This model describes an isotropic radiation field.

## Emission model

Using the previous conditions,  $\zeta$  is only a function of wavelength, therefore:

$$\langle \bar{E}_N^* \rangle = \frac{1}{S^*} \int_S \zeta(\lambda) dS \quad (10)$$

The function  $\zeta(\lambda)$  is calculated from the photochemical power source  $\Gamma^*(\lambda)$  over reactor area  $S$ :

$$\zeta(\lambda) = \frac{\int_{\lambda} \bar{Y}_{TR} \Gamma^*(\lambda) d\lambda}{\int_{\lambda} d\lambda} = \frac{\bar{Y}_{TR}}{(\lambda' - \lambda)} \int_{\lambda} \Gamma^*(\lambda) d\lambda \quad (11)$$

The parameter  $\bar{Y}_{TR}$  is the reactor wall average transmittance coefficient:

$$\bar{Y}_{TR} = \frac{1}{4\pi} \int_{\Omega} Y_{TR}(\Omega) d\Omega \quad (12)$$

Finally, the mathematical expression to estimate the energy of isotropic radiation field ( $\langle \bar{E}_N^* \rangle$ ) incident on the surface area ( $S^*$ ) for photocatalytic heterogeneous reactors is:

$$\langle \bar{E}_N^* \rangle = \left( \frac{1}{S^*} \right) \frac{\bar{Y}_{TR}}{(\lambda' - \lambda)} \int_S \int_{\lambda} \Gamma^*(\lambda) d\lambda dS \quad (13)$$

Where  $\bar{Y}_{TR}$  is average transmittance coefficient (dimensionless),  $\Gamma^*(\lambda)$  is a power function from radiation source ( $W/m^2$ ),  $S^*$  is total area of wall reactor absorption ( $m^2$ ),  $(\lambda' - \lambda)$  is wavelength interval (nm) and  $dS$ ,  $d\lambda$  are integration functions.

## Absorption model

The Eq. (9) is a function of the absorption total surface. Now considering the relationship of total particles surface ( $S^*$ ) and volume reactor ( $v_R$ ):

$$\frac{S^*}{v_R} = C_{Cat} S_g \quad (14)$$

Where  $C_{Cat}$  is to catalyst concentration (g/L) and  $S_g$  is the specific surface area of the catalyst ( $m^2/g$ ). If now we use the elementary theorem calculus and Eq. (14), this equation can be transformed to volume function:

$$\langle \hat{E}_N^v \rangle = \frac{1}{v_R^*} \int_{v_R} \zeta^*(v) dv \quad (15)$$



$\langle \hat{E}_N \rangle$  is the overall volumetric rate of energy absorption (OVREA),  $\zeta^*(n)$  is the local volumetric rate of energy absorption (LVREA) [6],  $v_R^*$ ,  $v_R$  and  $v$  are total reactor volume, integration volume and integration function of the volume, respectively. This parameter depends on the reactor volume, besides it is an isotropic function independent of wavelength ( $\lambda$ ) and propagation angle ( $\Omega$ ).

The LVREA can be calculated using the next expression in terms of reactor volume:

$$\zeta^*(v) = \kappa_v \zeta(v) \tag{16}$$

Where  $\zeta(n)$  is net effective energy per catalyst surface area unit ( $E/m^2$ ) and  $\kappa_n$  is a volumetric absorption coefficient ( $m^{-1}$ ).

According to the consideration of postulate 1, the net effective energy in each point of the reactor is estimated through the solution of the radiative transfer equation modified (RTEM). This equation arises from a balance of overall net radiant energy in a volume of differential control (see Figure 2-a).

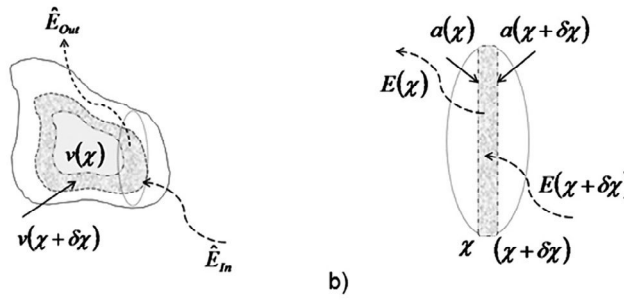


Figure 2. a) Volume of differential control, b) Differential balance element

The Figure 2-b shows the five components for the radiation energy balance: i)  $E_{in}$  is net energy flux entering the volume  $v$  across the surface  $\alpha$  ii)  $E_{abs}$  is total energy absorbed to catalyst particles iii)  $E_{out,Scatt}$  is lost energy by scattering iv)  $E_{in,Scatt}$  is the gained energy by scattering (it needs a phase function from to energy dispersed) v)  $E_{out}$  is net energy flux leaving the volume  $n$  across the surface  $\alpha$ .

In mathematical terms for a reactor volume  $n(\chi)$ , the net effective energy balance is given by the expression:

$$-\frac{1}{\alpha(\chi)} \frac{d}{d\chi} [\alpha(\chi) \cdot \zeta(\chi)] + (\bar{\kappa}_v + \bar{\sigma}_v) \zeta(\chi) = \bar{\sigma}_v \xi_N^*(\zeta) \quad (17)$$

This expression is an integro-differential unidimensional function in terms of an arbitrary dimensionless variable  $\chi$ , where  $\alpha(\chi)$  is surface area of the reactor,  $\kappa_v$ ,  $\sigma_v$  are the average coefficients of volumetric absorption and scattering, respectively,  $\xi_N^*(\zeta)$  is a scattering function.

So, the Eq. (9), Eq. (13) and Eq. (17) show the new concept proposed for estimating the radiation fields in heterogeneous photocatalytic reactors.

### Model validation for solar radiation on CPC reactor

The emission model (Eq. 13) was applied using a similar method reported in [9] for total solar radiation at Cali, Colombia (3° 30' North Latitude) for determination of  $\langle E_N^* \rangle$  incident on the wall photocatalytic heterogeneous solar reactor.

The absorption model, Eq. (17), was applied at CPC solar-scale reactor. This was solved using a numerical coupled for Ray Tracing Technique [9, 10], conventional Runge-Kutta and modified Netwon-Raphson Method [14, 15]. The CPC was simulated with similar operating condition used for Colina-Márquez *et al.*, [9, 10]. We consider 30 W/m<sup>2</sup> for total incident radiation on the solar reactor on clear sunny day. The Figure 3 shows the results for the simulation of radiation field.

These values and performance are similar to values reported previously [9, 10], which were evaluated at different catalyst concentration. For this simulation we used 0.35 g/L of catalyst. However, the description of the radiation field is very satisfactory and is in accordance to the typical distribution light inside of heterogeneous photocatalytic solar reactors. For the solar radiation conditions, on a clear and sunny day with  $I_0 = 30 \text{ W}\cdot\text{h}/\text{m}^2$  as the standard solar irradiance, the performances of the VREA profiles in the CPC reactor is shown in Figure 3. The new model is faster in the time computing and only two the parameters.





The performance of the VREA shows that there is high photon absorption at the reactor boundary layer near the wall or interphase. For the CPC, values of the optical thickness  $\delta$  close to zero show a profile of high energy. However, for high values of  $\delta$ , the energy available for activation is negligible.

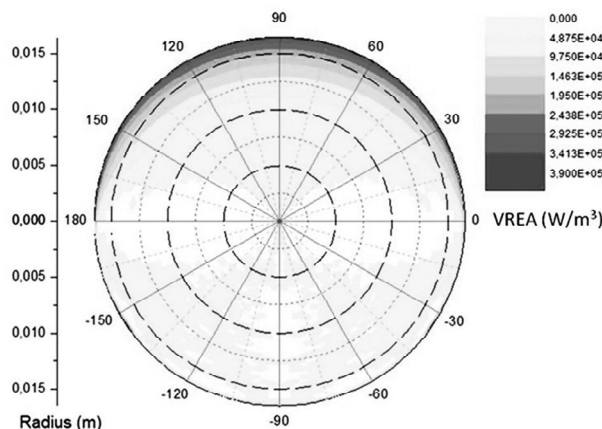


Figure 3. Radiation field simulation with proposed model for CPC reactor on sunny day at  $C_{\text{Cat}} = 0.3 \text{ g/L}$

## Conclusions

A new mathematical approach was proposed for description of radiation fields in heterogeneous photocatalytic reactors, based on isotropic radiation flux.

The model for the estimating radiation in photoreactors was developed for  $\text{TiO}_2\text{-P25}$  and solar irradiation is applicable to any other photocatalytic conditions and it is independent of the operating conditions, the geometry and the scale of the reactor.

The advantage of the new model is that it is easy to apply. The number of setting variables is less than rigorous models and these correspond to the system (reactor and catalyst).

According to the consideration of postulate 1, the net effective energy in each point of the reactor is estimated through the solution of the radiative transfer equation modified (RTEM).

The new model is an integro-differential unidimensional function in terms of an arbitrary dimensionless variable  $\chi$ , where  $\alpha(\chi)$  is surface area of the reactor,  $\kappa_v$ ,  $\sigma_v$  are the average coefficients of volumetric absorption and scattering, respectively,  $\xi_N^*(\zeta)$  is a scattering function.

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### References

- [1] N. Serpone & A. Emeline, Semiconductor Photocatalysis: past, present and future outlook, *J. Phys. Chem. Lett.* vol. 3, pp. 673-677, 2012.
- [2] D. Friedmann, C. Mendive & D. Bahnemann,  $\text{TiO}_2$  for water treatment: parameters affecting the kinetics and mechanism of photocatalysis, *Appl. Catal.*, vol. 99, pp. 398-406, 2010.
- [3] A. Cassano, C. Martin, R. Brandi & O. Alfano, "Photoreactor Analysis and Design: Fundamentals and Applications", *Ind. Eng. Chem. Res.*, vol. 34, pp. 2155 - 2201, 1995.
- [4] A. Cassano & O. Alfano, "Reaction Engineering of Suspended Solid Heterogeneous Photocatalytic Reactors", *Catal. Today*, vol. 58, nº 2-3, pp. 167-197, 2000.
- [5] T. Van Gerven, G. Mul, J. Moulijn & A. Stankiewicz, A review of intensification of photocatalytic processes, *Chem. Eng. Proc.*, vol. 46, nº 9, pp. 781-789, 2007.
- [4] F. Machuca, J. Colina-Márquez & M. Mueses, "Determination of Quantum Yield in a Heterogeneous Photocatalytic System Using a Fitting-Parameters Model", *J. Adv. Oxid. Technol.*, vol. 11, nº 1, pp. 42-48, 2008.
- [5] M. Mueses, J. Colina & F. Machuca, "Degradación fotocatalítica de ácido dicloroacético al aplicar un campo de radiación de baja energía", *Ingeniería y Desarrollo*, vol. 24, pp. 33-47, 2008.
- [6] J. Duderstadt & R. Martin, *Transport Theory*, New York : Wiley, pp. 21-422, 1979.
- [7] G. L. Puma, "Dimensionless analysis of photocatalytic reactors using suspended solid photocatalysts", *Chem. Eng. Res. Desing*, vol. 83 A7, pp. 820-826, 2005.



- [8] G. L. Puma & A. Brucato, "Dimensionless analysis of slurry photocatalytic reactors using a two-flux and six-flux radiation absorption-scattering models", *Catal. Today*, vol. 122, pp. 78-90, 2007.
- [9] J. Colina-Márquez, F. Machuca-Martínez & G. L. Puma, "Photocatalytic mineralization of commercial herbicides in a pilot-scale solar CPC reactor: Photoreactor modeling and reaction kinetics constants independent of radiation field", *Env. Sci. Technol.*, vol. 43, n° 23, pp. 8953-8960, 2009.
- [10] J. Colina-Márquez, F. Machuca-Martínez & G. L. Puma, "Radiation absorption and optimization of solar photocatalytic reactors for environmental applications", *Env. Sci. Technol.*, vol. 44, n° 13, pp. 5112-5120, 2010.
- [11] J. Marugan, R. van Grieken, A. Cassano & O. Alfano, "Quantum efficiency of cyanide photooxidation with TiO<sub>2</sub>/SiO<sub>2</sub> catalysts: Multivariate analysis by experimental design", *Catal. Today*, vol. 129, pp. 143-151, 2007.
- [12] N. Serpone, "Relative photonic efficiencies and quantum yields in heterogeneous photocatalysis", *J. Photochem. Photobiol., A*, vol. 104, pp. 1-12, 1997.
- [13] S. Ahmed, M. Rasul, R. Brown & M. Hashib, "Influence of parameters of the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: a short review", *J. Environ. Manage.*, vol. 92, pp. 311-330, 2011.
- [14] M. A. Mueses, F. Machuca-Martínez, "Modelo matemático para estimación de eficiencias fotónicas no-intrínsecas en reacciones fotocatalíticas heterogéneas", *Información Tecnológica*, vol. 23, n° 3, pp. 43-50, 2012.
- [15] M.A. Mueses, "Modelo de rendimiento cuántico para sistemas simples y mezclas multicomponentes aplicado en escalamiento y simulación de reactores fotocatalíticos heterogéneos", tesis doctoral, Escuela de Ingeniería Química, Universidad del Valle, Cali, Colombia, 2012.

