Chemical Engineering Journal 279 (2015) 442–451

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Effective radiation field model to scattering – Absorption applied in heterogeneous photocatalytic reactors

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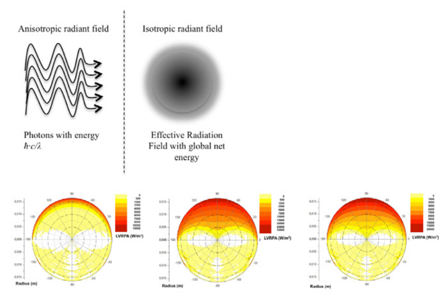
HIGHLIGHTS

- A new concept effective radiation field model for solar heterogeneous photoreactors.
- The model estimates the radiation field for suspension and polychromatic systems.
- Modified radiative transfer equation for several reactors could be used easily.
- The incident photons flow in the photoreactor is an isotropic energy cloud.
- The global energy is independent of the propagation angle and photon frequency.

GRAPHICAL ABSTRACT



Simulation of LVRPA in CPC solar reactor using ERFM to different catalyst concentration

ARTICLE INFO

Article history:
Received 24 February 2015
Received in revised form 14 May 2015
Accepted 15 May 2015
Available online 22 May 2015

Keywords:
Radiation field
SFM
LVRPA
Solar photoreactors
Photocatalyst

ABSTRACT

A new mathematical model for the calculation of the radiation field in heterogeneous photocatalytic reactors using the new concept of "effective radiation field model" or ERFM is proposed. In this concept, the incident radiation associated to the photons flow is an energy cloud. The generated space-phase and the properties of the cloud are considered isotropic and independent of the propagation angle and photon frequency. The isotropic nature of the ERFM concept provides a simple estimation of the radiation field of a catalyst in suspension (particles and fluid) for polychromatic radiation and the solar spectrum.

The ERFM is an alternative model for the calculus of the radiant energy distribution in heterogeneous photocatalytic reactors as an extension of concept to the overall volumetric rate photon absorption – OVRPA. The local volumetric rate of photon absorption (LVRPA) predicted by the ERFM were compared with the Six Flux Model (SFM) and the rigorous solution using Discrete Ordinate Method (DOM) for the radiative transfer equation (RTE).

The calculated LVRPA with the ERFM was found to be closer to the solution of the RTE-DOM. These results were attributed to the performance of the phase function in both models.

1. Introduction

Heterogeneous photocatalysis is a platform technology, for environmental, renewable energy and green synthesis applications. A huge amount of literature exists about the fundamental aspects of photocatalysis [1,2] including the synthesis of

Abbreviations: ERFM, effective radiation field model; OVRPA, overall volumetric rate photon absorption; SFM, Six Flux Absorption Scattering Model; RTE, radiative transfer equation; DOM, Discrete Ordinate Method.

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http://dx.doi.org/10.1016/j.cej.2015.05.056
1385-8947/

photocatalytic materials, the mechanisms of photocatalytic oxidation of contaminants [3], application of photocatalysis for environmental remediation [4], production of renewable energy [5] and for the green synthesis of chemicals [6,7].

The spatial distribution of radiation field and the radiation absorption are key aspects in heterogeneous photocatalytic processes. In the presence of a radiation field made of photons of wavelength with energy higher than the band-gap of the semiconductor photocatalyst, electron–hole pairs can be generated, which produce the reduction and oxidation reactions at the surface of the photocatalyst. Highly reactive radical species such as hydroxyl, peroxyl radicals and superoxide anion, [8–10] are often produced which can oxidize or reduce organic and inorganic contaminants. There is consensus that the evaluation and optimization of the radiation absorption in solar photoreactors is a very important step, in order to achieve better results on the application of the photocatalytic processes [2,8,11].

The direct and indirect radiation with the photoreaction kinetics is associated through of the quantum yield (the photoactivation step of the semiconductor), and the distribution of the local volumetric rate of photon absorption (LVRPA) [10–14]. Efforts in mathematical modeling are centered in the description of the LVRPA to facilitate the prediction of the experimental data in the heterogeneous photocatalytic degradation of contaminants in solution.

The LVRPA is conventionally modeled from the contribution of the *specific radiation intensity* (*i.e.*, *irradiance*) $I_\lambda(\underline{\boldsymbol{x}}, \underline{\boldsymbol{\Omega}}, t)$ integrated over all propagation directions (Einstein·s^{-1}) and the global volumetric coefficient of absorption k_λ (cm^{-1}) [10]:

$$e^a_\lambda = \kappa_\lambda \int_\Omega I_\lambda(\vec{x}, \vec{\Omega}) d\Omega d\lambda \tag{1}$$

The value of $I_\lambda(\underline{\mathbf{x}}, \underline{\boldsymbol{\Omega}}, t)$ is obtained by solving the radiative transfer equation (RTE), which describes photon transport through an immobilized material or though a material dispersed in a fluid. At steady state, the primary form of the RTE used to model the radiation fields in heterogeneous photocatalytic reactors is [15]:

$$\frac{d}{ds} I_\lambda(\vec{x}, \vec{\Omega}) = -[\kappa_\lambda(\vec{x}) + \sigma_\lambda(\vec{x})] I_\lambda(\vec{x}, \vec{\Omega}) + \frac{1}{4\pi} \sigma_\lambda(\vec{x}) \int_{\vec{\Omega}=4\pi} \rho(\lambda' \to \lambda, \Omega' \to \Omega) I_\lambda(\vec{x}, \vec{\Omega}) d\vec{\Omega}' \tag{2}$$

where I_λ is the incident radiation at wavelength λ, s is the generalized coordinate, κ_λ is the absorption volumetric coefficient (m^{-1}), σ_λ is the scattering volumetric coefficient (m^{-1}), $\vec{x}$ represents the coordinate vector, and ρ ($\lambda' \to \lambda$, $\Omega' \to \Omega$) is the scattering phase function (the term in parentheses represents the frequency re-directing in radiation λ and propagation Ω [16,17]):

Usually, the modeling of the radiation field in photocatalytic reactors has been applied on systems using artificial radiation sources (UV lamps). The main modeling approach follows the rigorous solution of the RTE (Eq. (2)) using the Discrete Ordinate Method (DOM) [10,15]. This method has been applied to plane photoreactor geometries [11], tubular photoreactors [10,13,18,19], and compound parabolic collectors (CPC) reactors [11,12,20–22] using monochromatic and polychromatic irradiation.

The RTE solved by DOM method allow an accurate prediction of the radiation field in heterogeneous photocatalytic systems. This approach has been validated with simulation data based on the solution of Mie theoretical equation. Among different expressions of the scattering phase function, it has been found that the isotropic phase function is one of the most appropriate to describe the scattering properties of semiconductor photocatalyst [14,23]. However, since the RTE is an integral–differential equation the application of the DOM for its solution requires a high degree of numerical accuracy, which is reflected in a high computational time [12,13,15,23]. Additionally, boundary conditions need to be evaluated with accurate and specialized actinometric techniques [24].

The above limitations are a disadvantage in the simulation and scaling-up of photocatalytic reactors at the solar scale. Furthermore, diurnal fluctuations of the solar energy do not permit to have a steady incident radiation flux and atmospheric effects and geographical conditions further increase the complexity of the model solutions and actinometric treatment [26–31].

Regarding to solar photocatalytic reactors, the Six-Flux Scattering-Absorption Model (SFM) has been implemented to describe radiation field and rate of photon absorption in pollutants degradation applications [25,32–33]. This method in photoreactors was first proposed as a modification of the Two-Flux Model (TFM) [34,35], and it was validated by a comparison with Monte Carlo simulation of the radiation field in a flat heterogeneous photoreactor [36].

The original SFM describes photon scattering as a diffuse function (although this is not a limiting condition) and considers that incident photons have the probability to disperse in trajectories described by the six directions of the Cartesian coordinates (hence the name) [25,26]. Its mathematical structure is of algebraic nature; therefore, its implementation in reactors to different scales and radiation sources is practical, with a low complexity in numeric procedures and short computational times [36]. Nevertheless, the presence of a diffuse phase function can cause that the method to fail in correctly predict radiant field performances generated by simulation by the solution of Mie theoretical equation [10].

Other approaches in the descriptions of radiant fields in heterogeneous photocatalytic reactors as stochastic models, which are based on Monte Carlo simulation [37–39] and Computational Fluid Dynamics (CFD) [21,40–43] based on the constitutive equations of continuous-medium mechanics. Although these models are as accurate as the DOM solution, they have not been currently implemented at a solar scale due to their high computational time and mathematical cost.

In this study, a new model for the evaluation of the radiation field in heterogeneous photocatalytic reactors of different scales is proposed. The model is based on the concept of effective radiation [20], in which, the radiant field is quantified as isotropic energy flux of photons, which is independent of the propagation direction and is particular suitable for application in solar powered photoreactors.

2. Methodology

2.1. Effective radiation model (ERFM) postulates

The following postulates were made support on the effective-radiation concept [20]:

Postulate 1. In isotropic phase-space, which contains suspended particles in a fluid phase, the net global effective radiant power that arrive to a surface $a(\chi)$, identified by a vector of coordinate $\underline{\boldsymbol{x}}$, can be calculated summing up the energy $E = h\nu$ (with h the Planck constant) by each photon of wavelength λ, frequency ν and propagation direction $\underline{\boldsymbol{\Omega}}$. This net global energy will therefore be independent of the propagation direction and the radiation wavelength (Fig. 1).

Postulate 2. The net global effective energy associated to a phase-space of suspended solid particles is assumed to have an isotropic nature. Thus, the optical properties of suspension can be considered as independent global parameters of the geometric coordinates [20,44].