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Photocatalytic reactor under different external irradiance conditions: Validation of a fully predictive radiation absorption model

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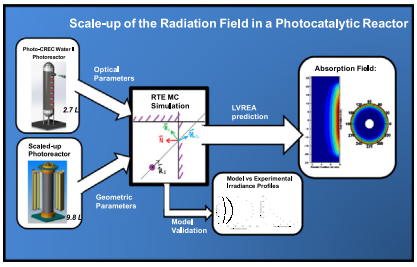
HIGHLIGHTS

- A Monte Carlo radiative model is proposed for scaling up photocatalytic reactors.
- A bench-scaled asymmetric and externally irradiated 9.8 l photoreactor is considered.
- The predictive model uses parameters determined in a 2 l Photo CREC Water II unit.
- Local Irradiance is measured with different photocatalyst loadings and lamp set-ups.
- Errors on simulated LVREA are on average 6%, laying for all cases between 2% and 31%.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study considers the absorption field in an externally-irradiated bench-scale Solar Simulator Photo-CREC Water Reactor with 9.8 l of irradiated volume. This photo reactor consists of an annular slurry region surrounded by four curved and equally spaced reflector units. Each reflector unit consists of a polished metal reflector surface containing of two 15 W UVA lamps. Each pair of lamps can be independently turned "on" or "off", generating different absorption fields within the annular region. Irradiance measurements were obtained at different axial and angular locations and for different external irradiance conditions and photocatalyst loadings. Experimental irradiance data was compared to Monte Carlo (MC) simulations accounting for: (a) Lambertian emission at the lamp surface, (b) specular and ideally diffuse reflection, refraction and absorption at all interfaces and (c) wavelength specific absorption and scattering coefficients. This MC model includes a Henyey–Greenstein (H–G) phase function with a "g" scattering parameter of 0.68. This H–G phase function was first reported in Valades-Pelayo et al. (2014b), using symmetric irradiance and a smaller scale annular reactor unit. This fully predictive model shows good agreement with experimental irradiance data in an ample range of conditions studied in non-symmetrically irradiated units. It is thus concluded that the proposed MC approach as implemented by Valades-Pelayo et al. (2014b) is a reliable predictive tool to scale-up externally and unevenly irradiated photoreactors, as is the case in solar irradiated units.

1. Introduction

Photocatalysis is an emerging technology with potential use in many oxidation and reduction chemical transformations. Photocatalysis

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research was initiated in the 1970s when attractive proposals were considered for water splitting for hydrogen production (Fujishima et al., 1975). It was not until the 1980s, however, that new potential applications were proposed for environmental remediation (Cassano and Alfano, 2000).

Among these new applications, outstanding examples are water purification, air purification, self-cleaning surfaces among others (Bahnemann, 2004). Specifically, heterogeneous photocatalysis was found to be very useful and versatile in the removal of organic contaminants present in water (Moreira et al., 2010). Moreover, as photocatalytic reactions are the result of the interaction of photons, having the appropriate wavelength, with a solid semiconductor (Malato et al. 2002), sunlight can become the main energy source driving the photocatalytic process. Degussa P25 can be regarded as one of the most widely used photocatalysts (Moreira et al., 2010). Degussa P25 is a Titanium Dioxide (TiO_2) based semiconductor, consisting of a mixture of brookite with an 80/20 proportion of anatase/rutile (Bickley et al., 1991). Degussa P25 has an average particle size of 32 nm, forming agglomerates of about 1 μm, depending on operating conditions (Salaices et al., 2002).

On the other hand, the comprehensive design of a photocatalytic reactor requires the description of physicochemical phenomena using constitutive equations (de Lasa et al., 2005). In this respect, many of the strategies for dealing with catalytic reactions can be adapted for photocatalytic reactions (Alfano et al., 2000). There is, however, an important aspect to consider regarding the design and scale-up of photocatalytic reactors: the adequate accounting for radiation absorption. Radiation absorption is at the very origin of photo-oxidation. In fact, in photocatalytic reactions, the reaction initiation is strongly dependent on both radiation intensity and distribution (Cassano and Alfano, 2000). Therefore, an accurate estimation of the radiation field is critical in the design, scale-up and performance evaluation of photoreactors (Pareek et al., 2008).

In the last decade, methodologies to both accurately and efficiently model the radiation fields of photoreactors have been extensively developed. The most prevalent models solve the radiative transfer equation (RTE) in photoreactors using the "P1" approximation, the Two flux, the Six flux and the Monte Carlo model approaches (Li Puma, 2003; Changrani and Raupp, 1999). Given these precedents, there is a special interest in predictive approaches, i.e. models which rely on specific optical properties and are, therefore, independent of reactor geometry.

More specifically, in recent years, advances in RTE modeling for photocatalytic reaction engineering, focused on the development of modeling tools to scale-up small laboratory scale to bench scale photo reactors using irradiance predictions. Imoberdorf et al. (2007) scaled-up a laboratory scale flat plate reactor with an immobilized catalyst to a bench scale (5209 cm^2 of irradiated area) using radiation fundamentals only. Imoberdorf et al. (2008) developed a radiation distribution predictive model for a fluidized bed photocatalytic reactor (approx. 2.15 l). On the other hand, Li Puma and Brucato (2007) scaled up a lab scale annular photoreactor, comparing different numerical methods. Grčić and Li Puma (2013) went a step further and developed a model accounting for the degradation of multiple water contaminants with two different annular photoreactor configurations by using a simplified radiation absorption approach. This method was validated in laboratory scale reactors only.

Furthermore, Marugan et al. (2013) recently simulated a bench scale annular photo reactor (1.25 l) operating at optimum photocatalyst concentration by using a predictive procedure and kinetic data from a laboratory scale photoreactor (0.188 l). Finally, Marugan et al. (2009) reported a methodology to scale-up a slurry annular lab-scale photoreactor (0.12 l) to a bench scale (1.25 l) photoreactor, among others. Thus, it is noticed that predictive models have been shown to be adequate for the scale-up of laboratory to bench scale symmetrically irradiated photoreactors, not surpassing the 2 to 3 l scale.

In spite of the significant progress, the applicability of photocatalytic technologies at larger scales is an area still demanding improved methodologies. This is especially true for energy and economical assessments (Baniasadi et al., 2014). This is likely the case for hydrogen production (Baniasadi et al., 2013; Escobedo Salas et al., 2013). On this basis, it is believed that further developments in photocatalytic reactor engineering are required for the validation of scale-up procedures. These models should be able to predict both the radiation absorption field and the local degradation rates of pilot-plant scale units (Duran et al., 2010; Oyama et al., 2011; Baniasadi et al., 2012).

Furthermore, the majority of the laboratory and bench scale reactors studied up to now were irradiated using both artificial light sources and symmetric irradiance. This type of symmetry, combined with internal irradiation is not expected to be achieved in large scale units, which will most likely be powered by solar energy (Malato et al., 2002). It is expected that changes in scale will also be bound to bring major changes in reactor geometry and, therefore, scale-up procedures.

Our research group studied a bench scale annular photoreactor of 2 l irradiated volume, Photo-CREC Water II reactor (Salaices et al., 2002; Ortiz-Gomez et al., 2007; Moreira et al., 2011; Escobedo Salas et al., 2013). The reactor was irradiated from the center by a 15 W Black-Light (BL) UVA lamp. More recently, (Moreira et al., 2011; Valades-Pelayo et al., 2014a, 2014b) radiation field involving a Monte Carlo simulation was described, by performing radial and axial irradiance measurements at photocatalyst concentrations (Degussa P25) between zero and 400 mg l^{-1}. From these studies, axial and radial irradiance and absorption profiles as well as total rates of photon absorption, were determined. From these data, a lamp emission model, wall properties and more importantly the phase function for Degussa P25 photocatalyst were determined (Valades-Pelayo et al., 2014b).

In spite of all these advancements, predictive irradiance field modeling in photocatalytic reactors is still restricted from laboratory to bench scale reactors, mostly internally and symmetrically irradiated. Thus, there are still important questions that need to be addressed such as: (a) Could an irradiance model such as the one established by Valades-Pelayo et al. (2014a) be extended to photoreactors of larger scale and external-asymmetric irradiance? (b) Could model parameters calculated by Valades-Pelayo et al. (2014b) be used in scaled-up reactors utilizing a fully predictive modeling approach?

In order to address these important issues, the present study, considers a Monte Carlo (MC) model with no adjustable parameters, in an externally irradiated bench-scale photoreactor, called the Photo-CREC Water Solar Simulator. Thus, by developing a physically-based radiation absorption model, this reactor is expected to give valuable insights regarding photoreactor scalability from laboratory to pilot-plant scales. This includes the use of solar-powered photoreactors for a diversity of applications such as hydrogen production and organic pollutant degradation.

The MC method specifically accounts for: (1) a Lambertian-surface emission model at the lamp, (2) specular and ideally diffuse reflection, refraction and absorption at all interfaces, (3) wavelength specific absorption and scattering coefficients and (4) a Henyey–Greenstein (H–G) phase function describing the scattering phenomena. Results of this model are compared with irradiance measurements developed for different outer irradiance conditions. Results show good agreement between predicted and experimental data for photocatalyst concentrations from 20 mg l^{-1} to 400 mg l^{-1}.

Thus, the proposed MC model is able to accurately predict local photon absorption rates in scaled-up reactors with asymmetric