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**Impact of photocatalyst optical properties on the efficiency of
solar photocatalytic reactors rationalized by the concepts of
initial rate of photon absorption (IRPA) dimensionless boundary
layer of photon absorption and apparent optical thickness**

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Abstract

The concepts of “initial rate of photon absorption” (IRPA), “dimensionless boundary layer of photon absorption” and “apparent optical thickness (τ_{app})” are presented to evaluate the radiative transfer phenomena in solar, slurry, planar, photocatalytic reactors. The radiation field produced by suspensions of TiO₂ and goethite, two photocatalysts with profoundly different optical properties used in heterogenous photocatalysis and heterogeneous photo-assisted Fenton reactions, was determined by the six-flux radiation absorption-scattering model coupled to the Henyey-Greenstein scattering phase function (SFM-HG). The concept of IRPA, defined by the differentiation at the local volumetric rate of photon absorption (LVRPA) at the reactor window boundary, is proposed as a new approach to determine the impact of catalyst loading and optical properties on the extinction of light inside a photoreactor. The IRPA showed that the extinction of light follows a second order dependency on the photocatalyst concentration while the impact of the optical properties can be expressed by a decoupled function (Ψ function). The Ψ function increased with photocatalyst concentration and approached a maximum at the same optimal photocatalyst concentration determined from the analysis of the total rate of photon absorption (TRPA) in the reactor. The analysis of TRPA and boundary layer of photon absorption redefined here in dimensionless form, as a function of τ_{app} , determined that the most efficient rate of radiation absorption in solar powered planar reactors occurs at $\tau_{app}=4.1-4.4$, with approximately 10% of the reactor width under darkness. τ_{app} is a similarity dimensionless parameter exclusively derived from the SFM approach, which clusters the effects of photocatalyst loading, reactor dimension and photocatalyst optical properties, providing an ideal parameter for designing and scaling photocatalytic reactors operated with any kind of photocatalytic material.

Keywords: Radiative transfer; Radiation transport; Photoreactor design; Photoreactor model, Optimization.

Nomenclature			
a	SFM parameter, dimensionless	κ^*	absorption coefficient, $\text{m}^2 \text{kg}^{-1}$
b	SFM parameter, dimensionless	λ	wavelength, nm
C_{cat}	photocatalysts concentration, kg m^{-3}	σ^*	scattering coefficient, $\text{m}^2 \text{kg}^{-1}$
g	scattering parameter from the Henyey-Greenstein phase function, dimensionless	τ	optical thickness, dimensionless
$IRPA$	initial rate of photon absorption, W m^{-4}	τ_{app}	apparent optical thickness from SFM, dimensionless
I_0	incident radiative flux, W/m^2	ψ	psi function
I_λ	spectral irradiance, $\text{W m}^{-2} \text{nm}^{-1}$	ω	scattering albedo, dimensionless
L	thickness of the photocatalyst-water film, m	ω_{corr}	corrected scattering albedo from SFM, dimensionless
LVRPA or e^a	local volumetric rate of photon absorption, W m^{-3}	<i>Subscripts</i>	
p_b	SFM probability of scattering in the backward direction, dimensionless	max	maximum
p_f	SFM probability of scattering in the forward direction, dimensionless	min	minimum
p_s	SFM probability of scattering in the sideward direction, dimensionless	UVA	UVA region of the solar spectrum
$TRPA/A$	total rate of photon absorption per unit of transversal surface of the photoreactor, W m^{-2}	Vis	visible region of solar spectrum
x	x coordinate, m	max	maximum
<i>Greek letters</i>			
β^*	extinction coefficient, $\text{m}^2 \text{kg}^{-1}$		
δ	boundary layer of photon absorption		
γ	SFM parameter, dimensionless		

44

45 1. Introduction

46 Platform technologies such as heterogeneous photocatalysis and the photo-assisted heterogeneous
47 Fenton process have shown great potential for the treatment of contaminated water or air [1,2]. The
48 main attraction of these processes is the utilization of solar light as the driving force for the production
49 of highly oxidative radical species, which are then able to complete the conversion of water or air
50 contaminants to innocuous products.

51

52 One very active field of research in heterogeneous photocatalysis is the development and evaluation
53 of new photocatalytic materials. Doping of commercial titanium dioxide (TiO_2) is a common

approach to extend the absorption spectrum of TiO_2 from the UV into the visible region of the solar spectrum [3]. Furthermore, iron oxides, have shown interesting properties as visible light active photocatalyst, as well as, catalysts for photo-assisted heterogeneous Fenton reactions when combined with hydrogen peroxide [4–6].

The intense development in new photocatalysts calls for the development of comprehensive methodologies for the analysis of the radiative transfer behavior of these new materials, particularly in the solar radiation spectrum. These methodologies are necessary for an appraisal of the catalytic performance of new photocatalytic materials and for the design and optimization of solar photoreactors. For this purpose, the optical properties of existing or new photocatalysts (the extinction, absorption and scattering coefficients and the scattering phase function) must be determined or estimated.

Recently several authors have investigated the influence of the optical properties on the photocatalyst performance [7–9], however, the literature has scarce information on the application of these for reactor design. Besides, available information deals almost exclusively with TiO_2 P25 photocatalyst. Furthermore, optimized photoreactor designs have been proposed in conjunction with TiO_2 photocatalytic powders, however, it remain unclear if these designs are also optimal when the reactor is loaded with other photocatalysts, particularly those materials having highly different optical properties than TiO_2 . Process intensification, for instance, is a novel and very interesting approach for optimizing photocatalytical processes [10,11]. One aspect that the intensification process should consider firstly is the optical performance of the photocatalytical material (i.e. its optical properties) for an integral design or correct selection of the photoreactor. In general, the optimization of the reactor performance requires a detailed analysis between the operational parameters such as, optimal photocatalyst loading, which in turn depend on the optical properties of the synthesized material and the rate of absorption of radiation.

In this study, an alternative reaction engineering approach including the impact of the photocatalyst optical properties on the optimization of photoreactors is presented i.e. in the determination of an optimal catalyst loading or photoreactor size. The concepts of “initial rate of photon absorption” (IRPA) and “boundary layer of photon absorption” [12] redefined in dimensionless form are here proposed as new parameters for evaluating the impact of photocatalyst loading on the total rate of photon radiation absorption (TRPA) and to facilitate the optimal design of photoreactors at different scales, from laboratory scale to full scale. The consequence of these are far reaching since the evaluation of the wide range of photocatalysts reported in literature may have to be reconsidered, if the photocatalysts activity was determined at equal loadings in the reactor without accounting the impact of the photocatalysts optical properties.

Goethite (α -FeOOH), an iron oxide used as visible-active photocatalysts [13] as well as for photo-assisted heterogeneous Fenton reactions [14,15], and the extensively explored TiO₂ P25 were selected to illustrate the impact of the above methodology on materials with significantly different optical properties. The use of goethite as one of the model photocatalysts also offers an illustration of the evaluation of the radiative transfer phenomena of a photocatalyst active in the visible range of the solar spectrum, which may be of special interest to the literature. The optical performance of these photocatalysts was evaluated in a simple planar photoreactor geometry, allowing the results and concepts of this study to be easily transferred to other photoreactor geometries. Such geometry is characteristic of falling liquid films [16] and conventional flat-plate photoreactors, with the slurry photocatalyst suspension confined between two walls [17,18]. The six-flux absorption scattering model (SFM) was used to model the solar radiation transport through slurry suspensions of the photocatalysts.

2. Mathematical methods

2.1. Optical properties of photocatalysts and solar spectral irradiation

The spectral absorption and scattering coefficients of the photocatalysts TiO₂ (P25, Evonik) and goethite (α -FeOOH, Aldrich) in aqueous suspensions [19,20] are shown in **Fig. 1** and **Fig. 2**, including the solar radiation data of global irradiance (AM 1.5), incident on a plane tilted 37° facing the sun [21]. The wavelengths range of 310-500 nm was selected since 300 nm is the lower wavelength in which both the goethite and TiO₂ interact with light and 500 nm is the upper limit for goethite, beyond this value Ortiz de la Plata et al. [20] found that the absorption of radiation by goethite was too small to be taken into account. Similarly, the graphical representation of the Henyey-Greenstein scattering factor is presented in **Fig. S1** (Supporting Information (SI)).

Fig. 1 Optical properties of goethite (Aldrich) and solar irradiance for a surface tilted 37° to the sun. The red line separates the UVA and visible regions of the solar spectrum. Absorption and scattering coefficients from [20].

Fig. 2 Optical properties of TiO₂ P25 (Evonik) and solar irradiance for a surface tilted 37° to the sun. The red line separates the UVA and visible regions of the solar spectrum. Absorption and scattering coefficients from [19].

2.2. The Six Flux Model for radiation field calculations

The spatial distribution of the local volumetric rate of photon absorption (LVRPA) inside the planar reactor was evaluated by the SFM as shown in Eq. (1) [22]:

$$e^a(x) = \frac{I_0 \tau_{app}}{\omega_{corr}(1-\gamma)L} \left[\left(\omega_{corr} - 1 + \sqrt{1 - \omega_{corr}^2} \right) e^{-x\tau_{app}/L} + \gamma \left(\omega_{corr} - 1 - \sqrt{1 - \omega_{corr}^2} \right) e^{x\tau_{app}/L} \right] \quad (1)$$

where a , b , ω_{corr} and γ are SFM parameters defined as follows:

$$a = 1 - \omega p_f - \frac{4\omega^2 p_s^2}{1 - \omega p_f - \omega p_b - 2\omega p_s} \quad (2)$$

$$b = \omega p_b + \frac{4\omega^2 p_s^2}{1 - \omega p_f - \omega p_b - 2\omega p_s} \quad (3)$$

$$\omega_{corr} = \frac{b}{a} \quad (4)$$

129

$$\gamma = \frac{1 - \sqrt{1 - \omega_{corr}^2}}{1 + \sqrt{1 - \omega_{corr}^2}} e^{-2\tau_{app}} \quad (5)$$

130 the apparent optical thickness τ_{app} is:

131

$$\tau_{app} = a\tau\sqrt{1 - \omega_{corr}^2} \quad (6)$$

132 For a planar geometry, the optical thickness τ is defined by:

133

$$\tau = (\sigma^* + \kappa^*)C_{cat}L \quad (7)$$

134 where σ^* and κ^* are the spectral averaged specific scattering and absorption coefficients, C_{cat} is the
 135 photocatalyst loading and L is the characteristic length for the extinction of the light inside the reactor.

136 In this study, the planar reactor is positioned orthogonally to the sun and is irradiated by collimated
 137 rays, i.e. L equals the thickness of the depth of the water in the planar reactor (Fig. S2). For such
 138 irradiation conditions in planar geometry, SFM has demonstrated its best performance [23].

139 The scattering probabilities p_f , p_b and p_s were determined from the Henyey-Greenstein phase function
 140 for each photocatalyst, following the procedure described elsewhere [24].

141 **2.3. Radiation field modeling approach**

142 The SFM applied to polychromatic radiation sources conveniently uses the spectral averaged optical
 143 properties of the photocatalyst. TiO_2 only interacts with light (by absorption or scattering)
 144 significantly in the UVA region of the solar spectrum (**Fig. 2**), while goethite absorbs and scatters
 145 light in both the UVA and in a portion of the visible region of the solar spectrum (**Fig. 1**). Therefore,
 146 the net radiation absorbed by the goethite photocatalyst was calculated summing the contributions
 147 from the UVA and the visible regions of the solar spectrum, as shown in [25], also to allow a direct
 148 comparison of the two photocatalyst over the UVA region.

The LVRPA of a TiO_2 suspension was therefore, calculated from the contribution from the UVA region,

$$e_{\text{TiO}_2}^a(x) = e_{\text{UVA}}^a(x) \quad (8)$$

while the net LVRPA of a goethite suspension was calculated summing the two contributions from the UVA and visible regions, as follows:

$$e_{\alpha\text{-FeOOH}}^a(x) = e_{\text{UVA}}^a(x) + e_{\text{Vis}}^a(x) \quad (9)$$

where e_{UV}^a and e_{Vis}^a were determined from Eq. (1) using the specific optical properties of the catalyst averaged over the solar spectrum determined from:

$$\kappa^* = \frac{\int_{\lambda_{\min}}^{\lambda_{\max}} \kappa_{\lambda}^* I_{\lambda} d\lambda}{\int_{\lambda_{\min}}^{\lambda_{\max}} I_{\lambda} d\lambda} \quad (10)$$

$$\sigma^* = \frac{\int_{\lambda_{\min}}^{\lambda_{\max}} \sigma_{\lambda}^* I_{\lambda} d\lambda}{\int_{\lambda_{\min}}^{\lambda_{\max}} I_{\lambda} d\lambda} \quad (11)$$

$$g = \frac{\int_{\lambda_{\min}}^{\lambda_{\max}} g_{\lambda} I_{\lambda} d\lambda}{\int_{\lambda_{\min}}^{\lambda_{\max}} I_{\lambda} d\lambda} \quad (12)$$

The integration limits in Eqs. (10-12) in the UVA region where, $\lambda_{\min} = 310$ nm and $\lambda_{\max} = 400$ nm and in the visible solar spectrum they were, $\lambda_{\min} = 400$ nm and $\lambda_{\max} = 500$ nm. The use of spectral averaged

optical properties is a common approach in literature, which allows a considerable reduction in computational time without introducing considerable distortions in the results [26].

The UVA solar incident radiation flux on the reactor, I_0 in Eq. (1), was set in $I_{UVA} = 30 \text{ W/m}^2$. This value corresponds to an experimentally average value of the solar UVA power for a perfectly sunny day around noon on a surface tilted 37° [27], in agreement with the solar spectral irradiance presented in **Fig. 1** and **Fig. 2**. The visible portion of the incident radiation I_{Vis} was computed ensuring a proportional relationship between the solar spectral irradiances in the UVA and the visible regions of the solar spectrum [28]. Therefore, I_{Vis} is given by:

$$I_{Vis} = I_{UVA} \frac{\int_{400nm}^{500nm} I_{\lambda} d\lambda}{\int_{310nm}^{400nm} I_{\lambda} d\lambda} \quad (13)$$

2.4. The concept of initial rate of photon absorption (IRPA)

The absorption of radiation by the photocatalyst inside the reactor was assumed to be a stationary process [29]. Therefore, in the planar slurry reactor the LVRPA was only a function of the coordinate parallel to the incident rays, denominated as the x -coordinate.

The concept of “initial rate of photon absorption” (IRPA) is here proposed as a new significant parameter for the analysis of the radiation absorption in photoreactors. The importance of the IRPA is that it gives insights on the expected trend of the LVRPA over the entire photoreactor. The IRPA is defined in Eq. (14).

$$IRPA = - \left[\frac{d}{dx} (e^a(x)) \right]_{x=0} \quad (14)$$

By applying this definition to Eq. (1), the IRPA can be expressed as:

$$IRPA = -\frac{I_0}{\omega_{corr}(1-\gamma)} \left(\frac{\tau_{app}}{L} \right)^2 \left[\gamma \left(\omega_{corr} - 1 - \sqrt{1 - \omega_{corr}^2} \right) - \left(\omega_{corr} - 1 + \sqrt{1 - \omega_{corr}^2} \right) \right] \quad (15)$$

By introducing Eq. (6) and (7) in Eq. (15) and by analogy to chemical reactions, the IRPA can be understood as the initial rate of attenuation of the incident photonic energy as results of its “interaction” with the suspended particle of the catalyst. Then, Eq. (15) can be rewritten as:

$$IRPA = -I_0 C_{cat}^2 \psi \quad (16)$$

where ψ is given by,

$$\psi = (\beta^*)^2 \frac{a^2(1-\omega_{corr}^2)}{\omega_{corr}(1-\gamma)} \left[\gamma \left(\omega_{corr} - 1 - \sqrt{1 - \omega_{corr}^2} \right) - \left(\omega_{corr} - 1 + \sqrt{1 - \omega_{corr}^2} \right) \right] \quad (17)$$

where $\beta^* = \sigma^* + \kappa^*$ is the specific extinction coefficient in m²/kg. The psi function ψ has units in m⁴/kg², C_{cat} in kg/m³ and I_0 in W/m², therefore the IRPA has units in W/m⁴.

The mathematical structure of Eq. (16) resembles that of an exponential rate law, generally used to describe the reaction kinetics in conventional chemical reactions. It include three terms: a proportional relationship of the IRPA to the incident radiation I_0 , which from its constant nature can be understood as “the reaction rate constant”; a second order term given exclusively by the catalyst’s loading C_{cat} and a proportional term represented by the psi function, which relates the optical properties of the catalyst, implicit in the SFM parameters, to the catalyst loading included in the initial rate of photon absorption (IRPA) parameter γ (see Eq. (5)).

2.5. The total rate of photon absorption (TRPA)

The TRPA, which is the overall radiation absorbed within the entire reactor volume [24,30] is a useful parameter to determine the efficiency of photoreactors and the optimal photocatalyst concentration

to operate the photoreactor. In a planar photoreactor, uniformly irradiated along the x -coordinate, the TRPA per unit surface area is:

$$TRPA / A = \int_0^L e^a(x) dx \quad (18)$$

2.6. Dimensionless boundary layer of photon absorption for sizing photoreactors

The concept of “boundary layer of photon absorption” has recently been introduced as a useful parameter for designing planar-geometry slurry photoreactors [12]. The boundary layer of photon absorption, in analogy to thermal, hydrodynamic and mass boundary layers, is defined as “the reactor thickness measured from the irradiated photoreactor surface, where 99% of total energy is absorbed” [12]. Mathematically it is defined as:

$$\frac{e^a(0) - e^a(\delta_{abs})}{e^a(0) - e^a(L)} = 0.99 \quad (19)$$

The thickness of the boundary layer δ_{abs} for a given photocatalyst is a function of the catalyst loading and the reactor width (L),

$$\delta_{abs} = f(C_{cat}, L) \quad (20)$$

where δ_{abs} has units of length. This concept has been presented for a planar slurry reactor of 1 cm of thickness operated with different commercial TiO_2 powders [12]. This approach, however, is not dependent on reactor thickness and can be easily extended to any reactor size by introducing a dimensionless form of Eq. (20):

$$\delta_{abs}^* = f(\tau) \quad (21)$$

with $\delta_{abs}^* = \delta_{abs}/L$ representing the fraction of the reactor width in which 99% of the total energy is absorbed. The optical thickness τ in Eq. (21) is a dimensionless parameter that clusters the effects of the catalyst loading and reactor width L (see Eq. (7)).

In order to establish δ_{abs}^* the procedure described by Otálvaro-Marín et al. [12] was followed, by minimizing the objective function Eq. (22) using the Nelder-Mead optimization algorithm:

$$F_{obj}(\delta_{abs}) = \left\{ \left[e^a(0) - e^a(\delta_{abs}) \right] - 0.99 \left[e^a(0) - e^a(L) \right] \right\}^2 \quad (22)$$

The solution of Eq. (22) for a given photocatalyst requires the thickness of the reactor L and the catalyst loading C_{cat} . These two parameters are incorporated in the optical thickness. Any combination of L and C_{cat} that leads to the same value of the optical thickness would produce the same result. Therefore, the “dark zone” of a photoreactor, i.e. the portion beyond the which 99% of the incident energy is absorbed, can be easily determined.

3. Results and discussions

3.1. Photocatalysts optical properties and incident solar radiation on the reactor

The visible component of the incident solar radiation on the reactor was determined from Eq. (13), $I_{vis} = 80.43 \text{ W/m}^2$, by setting the incident UVA radiation component as $I_{UVA} = 30 \text{ W/m}^2$. The numerical values of the integrals in Eq. (13) are shown in Table 1. The fraction of solar power between 400-500 nm is 2.68 times greater than that for the UVA. Goethite, unlike TiO_2 P25, is photoactive between 310-500 nm, therefore, it can absorb a significant larger amount of solar energy (18.62% of the complete solar spectrum).

Table 1. Integrated solar irradiance power for regions in analysis.

Region of the solar spectrum	Integrated irradiance power over the wavelength interval (W/m ²)	Fraction of total spectrum irradiance power (%)
UVA (310-400 nm)	50.61	5.06
Portion of visible (400-500 nm)	135.70	13.56
Complete spectrum (280-4000 nm)	1000.4 ^a	100

a. reported in reference [21]

The optical properties of the photocatalysts calculated from Eq. (10-12) are reported in Table 2, together with the corresponding values of the scattering albedo and corrected scattering albedo (Eq. (4)). The scattering albedo reported for TiO₂ P25 (0.79) was calculated using the optical properties of sonicated TiO₂ slurries reported by [19] ($\kappa^* = 1144.69 \text{ m}^2/\text{kg}$ and $\sigma^* = 4397.30 \text{ m}^2/\text{kg}$). However, since the optical properties are a function of the grade of agglomeration and hydrodynamics [9,31], which for sonicated suspensions can be 2-4 times greater [32], the correction procedure proposed by Toepfer et al. [33] was adopted. Therefore, the specific scattering and absorption coefficient for TiO₂ reported in Table 2 were calculated from $\sigma^* = \beta^* \omega$ and $\kappa^* = \beta^* - \sigma^*$, considering that the specific extinction coefficient of TiO₂ P25 measured under the prevailing conditions of mixing for a solar reactor was $\beta^* = 1470.5 \text{ m}^2/\text{kg}$ [34]. It is worth to note that the specific extinction coefficient is independent of the scattering phase function adopted.

The optical properties of goethite were measured under mixing conditions for a recirculating flow slurry suspension [20].

The specific scattering and absorption coefficients of TiO₂ P25 under UVA irradiation (Table 2) were 289 and 29 times, respectively, greater than those for goethite, although the scattering albedo of TiO₂

(i.e., the probability of scattering photons) was significantly higher than the value for goethite. The corrected scattering albedo ω_{corr} , on the other hand, is a correction made to the conventional scattering albedo, and accounts for the scattering phase function. A predominantly backward scattering decreases the probability of absorbing photons while a predominantly forward scattering increases it, since photons will penetrate deeper in the reactor width [24].

Goethite has very similar optical coefficients in both visible and UVA regions and very low ω_{corr} as results of its low conventional albedo and a g scattering factor near to 1, indicating a highly predominant forward scattering behavior. Such a low value of ω_{corr} could indicate an efficient exploitation of the incident photons. In addition, in comparison to others visible-active photocatalysts reported in literature (Table S1 (SI)) goethite has a comparable absorption coefficient and the lowest scattering albedo in the visible region of the solar spectrum, which means that goethite has superior capacity for absorbing a high proportion of visible radiation from the solar spectrum.

Table 2. Optical properties of catalyst.

Photocatalyst	κ^* (m ² /kg)	σ^* (m ² /kg)	β^* (m ² /kg)	g	ω	ω_{corr}
TiO₂ P25^a	308.8	1161.7	1470.5	0.53	0.79	0.2812
Goethite (UVA region)	10.59	4.32	14.91	0.89	0.29	0.0003
Goethite (Visible region)	9.52	5.28	14.80	0.87	0.36	0.0006

a. Only is considered the UVA region.

3.2. LVRPA profiles

The LVRPA transversal profiles in a planar reactor of thickness $L = 1$ cm uniformly irradiated on the front surface are shown in **Fig. 3**, for both goethite (Fig. 3a-c) and TiO₂ P25 (Fig. 3d). **Fig. 3a-c** show the LVRPA distribution of goethite considering the UVA (Fig. 3a), the visible portion (Fig. 3b) and the full solar spectrum (Fig. 3c), respectively. The visible component of the LVRPA gives the

greater contribution to the net LVRPA since the incident radiation I_{Vis} is higher than I_{UVA} and the optical properties of goethite have similar order in both UVA and visible regions. On the other hand, the LVRPA profile of TiO₂ P25, under solar irradiation, has on average one order of magnitude higher values, which also agrees with the rigorous solution of the Radiative Transfer Equation (RTE) by the discrete ordinate method [20].

Fig. 3 LVRPA spatial distribution on the planar slurry reactor with 0.2 g/L of catalyst. a) Goethite under UVA component of solar radiation b) Goethite under visible component of solar radiation c) Goethite under solar irradiation (UVA + visible components) d) TiO₂ P25 under solar irradiation (UVA component).

The distribution of the LVRPA in the reactor with both catalysts at different catalyst loading is shown in Fig. 4. The LVRPA gradients for TiO₂ increased significantly when the catalyst loading varied from 0.1 to 2.0 g/L. At high catalyst loading, very high LVRPA values are reached near the illuminated boundary of the reactor and a very steep fall results at greater reactor depths. This

behavior is attributed to the relatively high value of scattering albedo of TiO_2 as discussed elsewhere [35].

In sharp contrast to the results shown for TiO_2 , goethite displayed an almost uniform distribution of the LVRPA across the reactor depth at all catalyst loading investigated. The gradients of the profiles were considerably less sensitive to the catalyst dosage, which resulted from the significantly lower values of scattering albedos of goethite, which favored the penetration of photons to greater depths in the reactor, compounded with the higher value of forward radiation scattering (g scattering factor near to 1).

The impact of the scattering phase function on the distribution of the LVRPA can be significant. In this study, the SFM was coupled to the HG scattering phase function model and both catalysts exhibited primarily forward scattering behavior. Therefore, the penetration of photons down the reactor width and the photon absorption efficiency was favored in comparison to other situations. If the SFM is coupled to the diffuse reflectance phase function, which has a predominantly back scattering behavior, the LVRPA at the illuminated boundary would be approximately 2.15 higher than in this study, however, the overall photon absorption efficiency of the reactor would be lower since a higher fraction of photons would escape from the front wall of the reactor [12]. It should be noted that the HG scattering phase function adopted herein has been recently validated as more reliable than the diffuse reflectance phase function for modeling the radiation field of TiO_2 aqueous suspensions [36].

Fig. 4 LVRPA spatial distribution as function of catalyst loading under solar irradiation. a) TiO₂ b) goethite

3.3. Impact of catalyst loading on the initial rate of photon absorption (IRPA)

Fig. 5 and **Fig. 6** show the behavior of the IRPA (Eqs. 16-17) and the squared of the catalyst loading, as function of catalysts loading of TiO₂ and goethite, respectively. In both cases, the IRPA curve (black line) almost overlap the square of catalyst loading (red line). The quadratic nature of the IRPA (Eq. 16) implies a strong dependence from the catalyst loading, in consequence increasing the catalyst

loading produces significantly steeper decays of the LVRPA profiles. Equivalent IRPA values for TiO_2 and goethite were reached at significantly lower catalyst loadings of the former (**Fig. 5** and **Fig. 6**) and as a result, stronger gradients of the LVRPA were observed with TiO_2 (**Fig. 4**) at increasing catalyst loadings, while such dependence was weak with goethite. Such a difference also results since TiO_2 has a specific extinction coefficient 98 times higher than goethite.

Fig. 5 Initial rate of photon absorption as function of catalyst load for TiO_2 P25 for a planar reactor under solar radiation (in black) and the squared catalyst load (in red). The inset figure corresponds to the psi function of Eq. (17).

Fig. 6 Initial rate of photon absorption as function of catalyst load for goethite (Aldrich) for a planar reactor (in black) and the squared catalyst load (in red). The inset figures correspond to the ψ function of Eq. (17).

Despite the quadratic dependence of the IRPA on the photocatalyst concentration, the behavior of the ψ function and its impact on the IRPA is worth of further observations. Table S2 (Supporting Information) shows the fitting of a quadratic equation to initial portions of the IRPA profiles of TiO_2 and goethite. In all three cases, a displacement in the y-intercept of the IRPA curve from zero can be observed, which results from the influence of the ψ function. The impact of the ψ function reduces at increasing catalyst loading as shown in the inset figures in **Fig. 5** and **Fig. 6** until it reaches a plateau at determined values of C_{cat} in both catalysts. The analytical form of such equation can be predicted analytically taking the limits $C_{cat} \rightarrow 0$ and $C_{cat} \rightarrow \infty$.

Eq. (17) at $C_{cat} \rightarrow 0$ reduces to the equation of a straight line with m as its slope and c as the y-intercept:

$$\Psi = m\gamma + c \quad (23)$$

with

$$m = (\beta^*)^2 \frac{a^2(1-\omega_{corr}^2)}{\omega_{corr}} \left(\omega_{corr} - 1 - \sqrt{1-\omega_{corr}^2} \right) \quad (24)$$

$$c = -(\beta^*)^2 \frac{a^2(1-\omega_{corr}^2)}{\omega_{corr}} \left(\omega_{corr} - 1 + \sqrt{1-\omega_{corr}^2} \right) \quad (25)$$

where it has been considered $1 \gg \gamma$ and then $(1 - \gamma) \rightarrow 1$. This approximation is based on the consideration that the highest value possible for γ occurs when $C_{cat} = 0$ which reduces Eq. (5) to

$\gamma = (1 - \sqrt{1 - \omega_{corr}^2}) / (1 + \sqrt{1 - \omega_{corr}^2})$. For instance, at $C_{cat} = 0$, γ equals 0.04 for TiO₂ P25 and 4×10^{-8} for goethite.

On the other hand, at high catalyst loading (i.e. $C_{cat} \rightarrow \infty$), $\gamma \rightarrow 0$, thus Eq. (23) reduces to:

$$\Psi = c \quad (26)$$

The Ψ function predicted by Eq. (23) and Eq. (26) is the specular reflection of the curve for catalyst loading shown in the insets of **Fig. 5** and **Fig. 6**, since γ is inversely proportional to C_{cat} .

Hence, at low catalyst loadings it can be concluded that the attenuation of the LVRPA in a photoreactor, as shown by the IRPA, has a squared contribution from the catalyst loading and a linear dependence from the photocatalyst optical properties, included in the Ψ function. The Ψ function expresses in a decoupled term, the capability of the photocatalyst to absorb and to scatter radiation, which are a function of the catalyst optical properties.

At low catalyst concentration, the contributions of both catalyst concentration and photocatalyst optical properties are relevant on the IRPA, nonetheless at high catalyst loading the IRPA reduces to:

$$IRPA = -k_0 C_{cat}^2 \quad (27)$$

where $k_0 = I_0 c$. At high catalyst loading, the photocatalyst optical properties have a less significant impact on the IRPA and the attenuation of LVRPA with reactor depth is governed by the value of the specific extinction coefficient β^* only and by the concentration of solids. In addition, the fraction of photons escaping from the front wall (the illuminated boundary) of the photoreactor increases and $\gamma = 0$. The analytical behavior of the Ψ function at high and low photocatalyst loading is also supported by experimental observations. Brandi et al. [37] determined that the back-scattered radiation (the photon flux escaping from the illuminated boundary of the reactor) was a linear function of the catalyst concentration at low catalyst loading (below the reported optimal value) and beyond the optimum (once the absorption of radiation in the reactor reached a plateau) the back-scattered radiation became independent from the concentration of solids [37].

3.4. Optimization of rate of photon absorption in planar slurry photoreactors

The optimization of the rate of photon absorption in photoreactors can be accomplished by maximizing the TRPA (Eq. 18) as a function of the photocatalyst loading. The total rate of photon absorption per unit of surface area (TRPA / A) in the planar photoreactor was therefore calculated by integrating the LVRPA across the photoreactor width. The TRPA/A as function of the photocatalyst dosage and apparent optical thickness, τ_{app} , in a 1 cm planar slurry reactor irradiated by solar light is shown in **Fig. 7a-c**. The TRPA/A increases with photocatalyst loading for both photocatalysts approaching plateaus. The concentration of photocatalyst corresponding to TRPA/A changing less than 0.5% can be considered an optimum. Such optimum for TiO_2 is approximately at 0.75 g/L corresponding to an apparent optical thickness of 4.17, which lays within the optimum range reported for planar reactors ($\tau_{app} = 1.8 - 4.4$) [38]. The adoption of the scattering phase function may have a significant effect on the optimum catalyst concentration that maximize the rate of photon absorption. In fact, coupling the SFM to the diffuse reflectance phase function resulted to an optimum TRPA for

TiO₂ at 0.2 g/L, for the same reactor thickness ($L = 1$ cm) [12]. Since the diffuse reflectance phase function favors predominantly backward scattering, sharper LVRPA gradients and diminished penetration of photons across the reactor depth would be expected, therefore the optimum catalyst concentration that maximize the rate of photon absorption occurs at lower values. The higher optimum catalyst loading predicted in this study resulted from the predominant forward scattering phase function (Table 2, g-values). The optimum catalyst concentration reported here agrees with experimental and modeling results by Camera-Roda et al. [39], who reported 0.75 g/L for a planar reactor illuminated with LEDs. This corresponds to $\tau_{app} = 3.91$, which is very close to the value reported in this study.

In sharp contrast, the TRPA with goethite catalyst reached an optimum at significantly higher catalyst concentrations ($C_{cat} \approx 40$ g/L, $\tau_{app} = 4.37$) (**Fig. 7b**), which results from the very low value of the specific extinction coefficient of goethite. Clearly, such value of catalyst loading is not viable in practical application, and further considerations must be done by including the effect of particle agglomeration and hydrodynamics on nanoparticle optical properties as discussed elsewhere [40,41]. However, goethite can reach TRPA / A of similar order to the maximum value observed with TiO₂, at catalyst concentrations in the range 2 - 3 g/L (**Fig. 7b**) since goethite can absorb a significant amount of visible light. Clearly, the results shown in **Fig. 7b** show that very high goethite concentrations are necessary to reach limitations in the transfer of radiant energy, if only the effect of optical properties were considered. However, in practice optimum catalyst loading may have to be considered including other considerations such as expected reaction kinetics, slurry handling, mechanical and hydrodynamics limitations.

The evaluation of the optimum catalyst loading in photoreactors has been the subject of many experimental and modeling studies. It is well known that the TRPA follows an initial linear dependence with the catalyst loading and that excessive loading results in a plateau. This effect has been qualitatively described by some as “the photocatalyst clouding effect” in experimental studies

[42]. In reality, such clouding effect can be rationalized by a simple numerical parameter, which is the apparent optical thickness, τ_{app} (Eq. (6)). τ_{app} is a similarity dimensionless parameter, which in its definition clusters the effects of catalyst loading, reactor dimension and catalyst optical properties, allowing a comparison between photocatalytic systems with similar geometries. The optimum values for the apparent optical thickness are only function of the reactor geometry and the hydrodynamic conditions in the reactor, and typical optimum ranges have been reported in literature for both planar and tubular photoreactors [38,43]. The proximity of the values of the apparent optical thicknesses in which the TRPA approaches a plateau with both goethite and TiO_2 (Fig. 7c) is, therefore, not a casual coincidence.

The behavior of the TRPA/A as function of the catalyst loading observed in **Fig. 7a-b** is similar to that observed for the Ψ function (insets plots in **Fig. 5** and **Fig. 6**). The initial linear dependence with catalyst loading varies until it reaches a plateau. The value in which Ψ reaches a constant value ($\Psi = c$) approaches the optimum catalyst loadings for TiO_2 (0.75 g/L) and goethite (40 g/L), which suggest the existence of a direct relationship between the behavior shown by the Ψ function and the TRPA. Therefore, by similarity to Ψ it can be concluded that the TRPA initially increases linearly with respect to the catalyst concentration, since both absorption of radiation and forward photon scattering are controlling factors of the radiation transport. However, as the catalyst loading and the opacity of the reactor increases, the impact of forward photon scattering becomes less significant, since the photons have a reduced ability to penetrate through the reactor width. Therefore, photon absorption becomes predominant to the transport of radiation through the reactor, back-scattering become significant allowing a higher fraction of photon loss from the reactor front window and the TRPA reaches a plateau with the catalyst loading.

It can be concluded that the Ψ function is an analytical representation of the behavior of the TRPA as a function of the catalyst loading in photoreactors. This represents a new simple way for visualizing

the radiation field in a photocatalytic reactor and for determining optimum catalyst loading, even in non-planar photoreactor geometries (e.g., cylindrical).

Fig. 7 TRPA per unit of surface area in a planar slurry reactor of thickness $L = 1$ cm irradiated by solar light as function of catalyst loading. a) TiO_2 P25 b) goethite and c) TRPA per unit of surface area as function of apparent optical thickness for TiO_2 P25 and goethite.

3.5. Dimensionless boundary layer of photon absorption and its impact on reactor design

Considering a photocatalyst and its optical properties (σ_{λ}^* , κ_{λ}^* and g_{λ}) or more conveniently the corresponding spectral averages (Eqs. 10-12), the conceptual design of a planar photoreactor requires

the determination of an adequate reactor thickness (L) and an optimal catalyst loading, ($C_{cat, opt}$) that maximizes the absorption of the incident radiation. These two design parameters are correlated by the dimensionless parameters: optical thickness τ and apparent optical thickness τ_{app} . These are similarity parameters, since two reactors operated at the same value of τ or τ_{app} will performed similarly in terms of absorption of radiation, independently of photocatalyst loading or reactor dimensions.

Fig. 8 presents the TRPA and the dimensionless boundary layer thickness defined in Eq. (21) calculated by the solution of Eq. (22) for both TiO_2 and goethite photocatalysts, as function of the optical thickness. The optimum optical thicknesses for TiO_2 and goethite are rather different, $\tau_{opt} = 12.18$ and $\tau_{opt} = 6.25$, respectively, while the corresponding apparent optical thicknesses are very similar ($\tau_{app,opt} = 4.17$ and $\tau_{app,opt} = 4.37$ for TiO_2 and goethite) in accordance to the results in Fig. 7c. The dimensionless boundary layer, under the conditions of optimum optical thickness, are $\delta^* = 0.86$ and $\delta^* = 0.89$ for TiO_2 and goethite respectively, which implies that approximately 14% and a 11% of the reactor width can be considered under darkness, respectively.

Fig. 8 TRPA (in black) and dimensionless boundary layer of photon absorption as function of the optical thickness of the reactor (in blue). Black dotted lines indicate the TRPA and δ^* for the optimum optical thickness τ for both catalyst.

Plotting the dimensionless boundary layer as a function of the apparent optical thickness, τ_{app} , instead of the conventional optical thickness, τ , produces one single line irrespective of the photocatalyst optical properties (Fig. 9) (i.e. the blue lines in Fig. 8 overlap). It shows that under optimal conditions for radiation absorption ($\tau_{app} = 4.1 - 4.4$) around 10% of the reactor width will be under darkness. The use of the apparent optical thickness goes beyond the limitations imposed by the use of conventional optical thickness (τ), since τ_{app} is insensitive to the photocatalysts optical properties providing an

ideal similarity parameter for designing and scaling solar photocatalytic reactors with whatever photocatalyst. Particle agglomeration usually observed at very high catalyst concentrations can have a strong impact on the photocatalyst optical properties [40,41] on the optical thickness (τ) and on the optimal design of thin-film photoreactors, but the range of apparent optical thickness (τ_{app}) that would produce an optimum design remain unaffected.

Fig. 9 Dimensionless boundary layer of photon absorption as function of the apparent optical thickness.

4. Conclusions

In this study, a simple and comprehensive reaction engineering approach based on the radiative transfer properties of photocatalysts was presented for evaluating, designing and scaling solar planar photocatalytic reactors. The spatial distribution of the radiation field along the reactor was evaluated by the six-flux radiation absorption-scattering model with the Henyey-Greenstein scattering phase

function considering irradiation by the solar spectrum. Using the SFM approach, the novel concepts of the “initial rate of photon absorption” (IRPA) and “boundary layer of photon absorption” redefined in dimensionless form together with the apparent optical thickness were introduced and combined in order to obtain an alternative basis for photoreactor optimization.

The IRPA allowed a suitable mathematical analysis for determining the impact of catalyst loading and optical properties on the extinction of light inside the photoreactor offering a new way for understanding the radiative transfer phenomena. The IRPA showed that the extinction of light follows a second order dependency from the photocatalyst concentration with the impact of the optical properties expressed by a decoupled term. The common optimization approach that determines the catalyst loading that maximizes the total rate of photon absorption in photoreactors, was complemented with the concept of dimensionless boundary layer of photon absorption, which allowed the determination of the fraction of the reactor under darkness, i.e. not useful for a photocatalytic reaction. The optimum reported in terms of catalyst loading is a strong function of the optical properties of the photocatalysts, which indicates that comparing the performance of photocatalysts having different optical properties at the same catalyst loading may be inconclusive.

The previous concepts when analyzed as function of the apparent optical thickness, which is insensitive to the photocatalyst optical properties, allow some important generalizations. The optimum range for radiation absorption in a planar photoreactor should be determined at ($\tau_{app} = 4.1 - 4.4$) with a fraction of darkness for the reactor width determined from the dimensionless boundary layer of photon absorption of approximately 10%, these results being valid for any photocatalyst. The apparent optical thickness is, therefore, the ideal similarity parameter for designing and scaling photocatalytic slurry reactors.

Finally, it should be highlighted that studies reported in literature comparing the activity of synthesized photocatalytic materials in a slurry suspension, using the same catalyst concentration, may be adversely affected by the differences in the rate of photon absorption, particularly if the

materials present different optical properties. In consequence, some of the conclusions given may need to be revisited.

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665 **Supporting Information**

666 **Impact of photocatalyst optical properties on the efficiency of**
667 **solar photocatalytic reactors rationalized by the concepts of**
668 **initial rate of photon absorption (IRPA) dimensionless boundary**
669 **layer of photon absorption and apparent optical thickness**

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Fig. S1 Henyey-Greenstein scattering factor for goethite and TiO₂ P25 and solar irradiance for a surface tilted 37° facing the sun. The red line separates the regions of the solar spectrum. Spectral data from [19,20]

Fig. S2 Model illustration of the planar, slurry photoreactor.

Table S1. Optical properties of selected visible-active photocatalysts in the visible region of the solar spectrum.

Catalyst	κ^* (m ² /kg)	σ^* (m ² /kg)	ω	Reference
Goethite (Aldrich)	9.52	5.28	0.36	This study
Ag@TiO ₂	4.7	546.0	0.99	[25]
LiVMoO ₆	25-26	170-200	0.88 ^a	[44]

a. Calculated by the arithmetic average of the κ^* and σ^* reported in the table.

Table S2. Fitted quadratic equations to IRPA results in Fig. 5-6.

Catalyst	x-axis data	IRPA quadratic equation	R ²
TiO ₂	0-0.8 g/L	$8 \times 10^6 x^2 + 51637x - 30.149$	1
Goethite -UVA	0-30 g/L	$3594x^2 + 0.4733x + 1.4753$	1
Goethite -Visible	0-30 g/L	$2009.9x^2 - 8020x + 7745.7$	1