Photocatalytic oxidation of multicomponent solutions of herbicides: Reaction kinetics analysis with explicit photon absorption effects

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Abstract

The intrinsic reaction kinetics of the photocatalytic oxidation (PCO) of the herbicides isoproturon, simazine and propazine over irradiated TiO_2 (Degussa P25) suspensions was studied in single-component and in multicomponent systems. Experiments were carried out at different photon fluxes and different herbicide concentrations in the range below 1 mg L^{-1}. The results were analyzed in terms of a Langmuir–Hinshelwood (L–H) kinetic model previously established for multicomponent solutions of herbicides, but including the explicit effect of photon absorption. This was accomplished by modeling the radiation field in the reactor with the Six-Flux Absorption-Scattering Model (SFM) (i.e., scattered photons follow the route of the six directions of the Cartesian coordinates) using optical parameters averaged across the spectrum of the incident radiation. The intrinsic reaction kinetic constants of isoproturon, simazine and propazine independent of the radiation field in the reactor were determined. The oxidation rate of the herbicides was found to follow half-order dependence with respect to the local volumetric rate of photon absorption (LVRPA), in the range of photon fluxes investigated. The established model was found to be appropriate to predict the time-dependent degradation profiles of the herbicides in single- and multicomponent systems not only at all radiation intensities investigated in this study but also when one or two herbicides were present in excess of the others in the mixture. Using this simple approach, intrinsic kinetic data can be obtained.
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Keywords: Water purification; Titanium dioxide; Photocatalysis; Photoreactor; Suspensions; Pesticides; Radiation absorption; Radiation scattering; Radiation field; Reaction kinetics

1. Introduction

In our previous study [1], the photocatalytic oxidation (PCO) of the herbicides isoproturon, simazine and propazine over irradiated TiO_2 suspensions was studied in single-component and in multicomponent systems at different initial herbicide concentrations. The time-dependent degradation profiles of each herbicide in a batch-recirculation reactor system were successfully modeled using an approximation of the Langmuir–Hinshelwood (L–H) rate equation, which takes into account the direct effect of intermediate reaction products.

The L–H rate equations were successfully extended to represent the time-dependent degradation profiles of multi-component systems of herbicides, using the kinetic parameters determined in single-component experiments. The binding

constants of the herbicides observed under dark adsorption and under PCO were found to be very similar, therefore it was suggested that the degradation of isoproturon, simazine and propazine and of their mixtures follow a surface or near-surface reaction according to a competitive L–H mechanism. The above findings were observed only at herbicide concentrations less than approximately 1 mg L^{-1} at which monolayer coverage of TiO_2 is attained. Above 1 mg L^{-1} it was concluded that there is a departure from the L–H mechanism due to multilayer adsorption of the herbicides leading to faster herbicide degradation kinetics.

In general, PCO reaction kinetics equations presented in the literature are strictly applicable only to the photoreactor geometry and the experimental conditions under which they have been established, unless an analysis of the radiation field in the photoreactor has been implemented in the kinetic model. Various forms of these rate laws presented in the literature show Langmuirian dependence on the substrate concentration and either power law dependence on the incident photon flux at the

Nomenclature

a	model parameter SFM, dimensionless
b	model parameter SFM, dimensionless
c_{cat}	photocatalyst concentration (kg m^{-3})
C	substrate concentration (kg m^{-3})
C_0	initial substrate concentration (kg m^{-3})
H	length of the reactor (m)
I	radiation intensity (or radiative flux) (W m^{-2})
I_λ	radiation intensity divided wavelength of radiation (W m^{-3} nm^{-1})
k	kinetic constant (mol m^{-3} s^{-1})
k_T	kinetic constant independent of radiation absorbed (mol s^{-1} m^{-3} W$^{-0.5}$)
K	binding constant (m^3 mol^{-1})
L	lamp length (m)
LVRPA	local volumetric rate of photon absorption (W m^{-3})
m	order of the reaction with respect to the VRPA, dimensionless
n	number of herbicides is solution
p_b	probability of scattering in the backward direction, dimensionless
p_f	probability of scattering in the forward direction, dimensionless
p_s	probability of scattering in the side direction, dimensionless
P	relative spectral response of radiometer sensor, dimensionless
r	radial coordinate (m)
r_1	lamp radius (m)
r_j	rate of the reaction with respect to substrate j (mol s^{-1} m^{-3})
r^*	dimensionless radial coordinate ($=r/R$)
R	external radius of annulus (m)
S	radiation emission of lamp per unit time per unit length (W m^{-1})
t	time (s)
V	total volume of fluid in recirculation system (m^3)
V_r	reactor volume (m^3)
W	radiant power (W)
z	axial coordinate (m)
z^*	dimensionless axial coordinate ($=z/H$)

Greek letters

α	geometrical parameter ($=H/L$), dimensionless
α_2	kinetic parameter defined in Eq. (5) in Cabrera et al. [6]
$\alpha_{3,i}$	kinetic parameter defined in Eq. (A.8) in Alfano et al. [16]
β	geometrical parameter ($=L/\eta R$), dimensionless
δ	thickness of the annulus (m)
Φ	scattering phase function, dimensionless
γ	dimensionless parameter SFM, dimensionless
η	ratio of internal radius to external radius of annulus, dimensionless
φ	scattering angle

κ	specific mass absorption coefficient averaged over the spectrum of the incident radiation (m^2 kg^{-1})
λ	radiation wavelength (m)
σ	specific mass scattering coefficient averaged over the spectrum of the incident radiation (m^2 kg^{-1})
τ	optical thickness, dimensionless
τ_{app}	apparent optical thickness, dimensionless
ω	scattering albedo ($=\sigma/(\sigma + \kappa)$), dimensionless
ω_{corr}	corrected scattering albedo SFM, dimensionless
ξ	reaction space radial coordinate (m)
ξ^*	dimensionless reaction space radial coordinate ($=\xi/\delta$)

Subscripts

0	position at inner wall of annulus
j	substrate
l	at the lamp wall
max	maximum
min	minimum
r, r^*	direction along the radial coordinate
w	lamp wall
z, z^*	direction along the axial coordinate
ηR	position at inner wall of annulus
λ	wavelength

Superscript

*	dimensionless variable

front wall of the photoreactor, or power law dependence on the overall radiation absorbed in the photoreactor. The dependence of the apparent reaction kinetic constants on the radiation absorbed within the photoreactor must be established if the kinetic model is to be made generally applicable to photoreactors of any size. To accomplish this, several methods have been proposed including experimental techniques by radiometric and actinometric measurements [2–5] and mathematical methods, which are based on the detailed analysis of the radiation field in the reaction space of the photoreactor [6–10]. The latter methods allow the determination of the amount of radiation absorbed at each position in the reaction space and should therefore allow the derivation of reaction rate laws and reaction kinetic constants which are independent of the radiation field in the reactor. As a result they are more universally applicable to the design and scale-up of photocatalytic reactors.

The key aspect in the modeling procedure of the radiation field in a photocatalytic reactor is the calculation of the local volumetric rate of photon absorption (LVRPA) at each point of the reaction space, which in the most complex cases requires solving the radiative transfer equation (RTE) in the reaction space [11]. As a result of the complex nature of radiation scattering, this leads to a set of integro-differential equations, which can entail demanding numerical computational efforts even in simple reactor geometries.

Statistical approaches involving Monte Carlo methods have also been proposed for the accurate estimation of the LVRPA,