Chemical Engineering Journal 262 (2015) 490–498

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Validation of a two-dimensional modeling of an externally irradiated slurry photoreactor

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HIGHLIGHTS

- A two dimensional model of an externally irradiated slurry photoreactor has been validated.
- 4-Nitrophenol was oxidized in the presence of Degussa P25 TiO_2 and 1 to 6 UV fluorescent lamps.
- Least-squares best fitting procedure was carried out by using a properly modified Simpson's rule.
- A good agreement was found between experimental and calculated pseudo-first order constants ($R^2 = 0.83$).
- The model was accurate in a wide range of operating conditions (catalyst, substrate and light radiation).

ARTICLE INFO

Article history:
Received 14 July 2014
Received in revised form 9 September 2014
Accepted 5 October 2014
Available online 12 October 2014

Keywords:
Photoreactor modeling
Externally irradiated photoreactor
Langmuir–Hinshelwood kinetics
Observed rate constant

ABSTRACT

A two-dimensional model describing the behavior of a batch cylindrical photoreactor has been validated through a series of photocatalytic reactivity runs. The light intensity radiation field produced by 1–6 external UV fluorescent lamps was modeled together with Langmuir–Hinshelwood kinetics and 4-nitrophenol (NP) and Degussa P25 TiO_2 were used as the probe molecule and the catalyst, respectively. The experiments were carried out under different conditions of light intensity, photocatalyst amount and substrate concentration. The model parameters were the kinetic constant of substrate adsorption, desorption and degradation and the exponent of the power law expressing the kinetics dependence on the light intensity. A least-squares best fitting procedure was used to fit the experimental data to the model and find the four required parameters. A satisfactory agreement was obtained between experimental and calculated values of the observed pseudo-first order kinetic constant, with a coefficient of determination $R^2 = 0.83$. Notably, the present model is of general interest for cylindrical slurry photoreactors, where different molecules can be oxidized in the presence of several photocatalysts and it can be used, for instance, to accurately compare the performance of a set of catalysts.

1. Introduction

The behavior of photocatalytic reactions depends on several issues and, in particular, on adsorption equilibrium, chemical kinetics and light absorption: furthermore, all of these three factors are dependent one from each other [1–3]. Different reactor configurations and irradiation sources have been modeled in the last decade, but there are no general methods and/or solutions that can be applied to every reaction system due to the different interactions between the substrates and the photocatalytic surface. In all of these studies the knowledge of the radiant field, i.e. the specific radiation intensity at each point of the reaction space and in all the possible directions of irradiation, is essential because the photon absorption rate by the catalyst is the main phenomenon for initiating the photoreaction [4]. The radiation intensity values inside an irradiated scattering medium can be evaluated by solving the radiative transfer equation (RTE), which expresses the radiation intensity balance at a fixed wavelength.

Several mathematical models have been proposed to describe the light irradiation within photochemical reactors (see for instance Alfano et al. [5–6], and Pareek et al. [7]). These models are now becoming truly available thanks to commercial CFD

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http://dx.doi.org/10.1016/j.cej.2014.10.013
1385-8947/

Notations

A [m^2] catalyst surface area (specific surface area multiplied by weight)
b [dimensionless] parameter defined by Eq. (8)
C_{Cat} [$g\ m^{-3}$] catalyst concentration
C_i [$mmol\ m^{-3}$] concentration of I-intermediate
C_{Sub} [$mmol\ m^{-3}$] substrate concentration
$C_{Sub,0}$ [$mmol\ m^{-3}$] substrate initial concentration
e [dimensionless] Napierian extinction coefficient
I_i [$W\ m^{-2}$] light radiation flux coming from "i" lamp
I_0 [$W\ m^{-2}$] light radiation flux coming from one lamp at boundary medium (between light source and reacting suspension)
$I_{0,r1}$ [$W\ m^{-2}$] light radiation flux coming from one lamp at boundary medium as function of r_1
k [m^{-1}] absorption coefficient
k^* [$m^2\ g^{-1}$] absorption coefficient per unit concentration
k' [$mmol\ m^{-2(1-\alpha)}\ W^{-\alpha}\ h^{-1}$] absolute kinetic constant (not depending on light intensity)
k''_1 [$mmol\ m^{-2}\ h^{-1}$] = $k''\theta_{Ox}$ L.-H. surface pseudo-first-order kinetic rate constant
k''_2 [$mmol\ m^{-2}\ h^{-1}$] L.-H. second-order kinetic rate constant
k_{ads} [$m\ h^{-1}$] substrate adsorption kinetic constant
k_{des} [$mmol\ m^{-2}\ h^{-1}$] substrate desorption kinetic constant
K_{Sub} [$m^3\ mmol^{-1}$] reagent equilibrium adsorption constant
K_i [$m^3\ mmol^{-1}$] intermediate products equilibrium adsorption constant
k_{obs} [h^{-1}] observed pseudo first order disappearance rate
k^{Cal}_{obs} [h^{-1}] calculated pseudo first order disappearance rate
k^{Exp}_{obs} [h^{-1}] experimental pseudo first order disappearance rate
l [m] light path length; coordinate along which propagation occurs
N_{Sub} [mmol] phenol moles present in the liquid phase
r [m] distance between light source and a reactant element, i.e., cylindrical radial coordinate
r_0 [m] smaller distance between light source and external reactor wall
r^l_i [m] distance between "i" light source and circumference points farer from the light source
r_i [m] distance between "i" light source and circumference points nearer to the light source
r_{Sub} [$mmol\ m^{-2}\ h^{-1}$] volumetric averaged surface reaction rate
R [m] reactor radius
R_∞ [dimensionless] diffuse reflectance
s [m^{-1}] scattering coefficient
s^* [$m^2\ g^{-1}$] scattering coefficient per unit concentration
S [m^2] cross-sectional area of the photoreactor
t [h] reaction time
V [m^3] reaction volume
W [$einstein\ s^{-1}\ m^{-3}\ sr^{-1}$] gain or loss of energy
x [m] Cartesian coordinate
y [m] Cartesian coordinate
α [dimensionless] parameter varying from 0.5 to 1
θ [rad] cylindrical angular coordinate referred to lamp 1
θ_i [rad] cylindrical angular coordinate referred to "i" lamp
θ_0 [rad] boundary cylindrical angular to be considered
λ [m] radiation wavelength
Ω [sr] solid angle

simulation packages that exploit the high-performance processors. The techniques, used in these models to solve the RTE, are several, including flux zone, Monte Carlo, discrete ordinate and finite volume methods [8,9]. Although the Monte Carlo gives the possibility to establish accurate radiation models, it still presents the main drawback that a very large number of events must be processed for the random path simulation and the ray tracing at each photon collision; moreover, in order to calculate the scattering angle at each collision point, the phase function is required. Indeed, all exact methods (those that do not require any kind of simplifications) are affected by numerical discretization errors (as ray effects and false scattering) the magnitude of which decreases by thickening the directional and spatial grid, with a consequent increase of the calculation time.

The influence of the number of lamps (1, 2 and 3 lamps) on a bench scale photocatalytic reactor for the treatment of a wastewater was investigated [10], whereas the effect of intensity of irradiation with parallel lamps placed in front of the reactor to obtain an optimal surface illumination was studied for monolithic photocatalytic reactors (in dimensionless form) [11]. As far as the lamps placed in axial position is concerned, the light intensity distribution of a multi-lamps photoreactor was deeply explored too [12]. However, to the best of our knowledge, models for externally irradiated cylindrical reactors have been reported only by Yoshihawa et al. [13], Tokumura et al. [14] and – very recently – by Palmisano et al. [15,16].

The present paper is a development of a previous study [15] and proposes a two-dimensional model for the radiation field in a batch cylindrical photoreactor, externally irradiated by 1–6 UV fluorescent lamps, coupled with a modified Langmuir–Hinshelwood kinetics. The model has been validated by comparing the results with those of various photocatalytic runs of 4-nitrophenol (NP) degradation in aerated aqueous suspensions of commercial TiO_2 catalyst. The proposed method does not require neither powerful CPUs nor complicated algorithms, a least-squares best fitting procedure is instead enough and it can be carried out by using the Generalized Reduced Gradient (GRG) non-linear method of MS Excel 2013 Solver, as it was done in the present study.

2. Experimental

A batch cylindrical photoreactor (internal diameter 32 mm, height 188 mm) containing 150 mL of aqueous suspension, externally irradiated by 1–6 fluorescent lamps, previously described [15], was used. The distance between the axis of each lamp and that of the reactor was 75 mm. Fig. 1 shows the scheme of the reacting system.

The experiments were carried out in aqueous suspensions at a natural pH (7.0). The photoreactor was irradiated by 1 to 6 external Actinic BL TL MINI15 W/10 Philips fluorescent lamps. The main emission peak of the fluorescent tubes is in the near-UV region at 365 nm. The radiation intensity impinging on the suspension was measured by a radiometer Delta Ohm DO9721 with an UVA probe. When only one lamp was on, the radiation incident on the reactor wall point nearest to the lamp is 6.50 $W\ m^{-2}$. Oxygen was continuously bubbled during the experiments and the lamps were switched on after 0.5 h from the starting of the bubbling. The starting time of irradiation was taken as the zero time of the photocatalytic run. Degussa P25 was used as the photocatalyst (specific surface area 50 $m^2\ g^{-1}$). Experimental runs were carried out at different NP concentrations (2–24 $mg\ L^{-1}$ range), TiO_2 amounts (0.02–0.9 $g\ L^{-1}$ range) and under different irradiation configurations, i.e. by switching on 1, 2, 4 or 6 lamps. The values of substrate concentration before the addition of catalyst and