Eight-lamp externally irradiated bench-scale photocatalytic reactor: Scale-up and performance prediction

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HIGHLIGHTS

- A scale up methodology for photocatalytic reactors is established.
- Oxalic acid degradation is carried out at different photocatalyst concentrations.
- Residence time distributions are determined by using glucose as a tracer.
- An efficiency factor is calculated including mixing and charge/recombination.
- Various photocatalyst concentrations and lamp emissions are used for model validation.

GRAPHICAL ABSTRACT
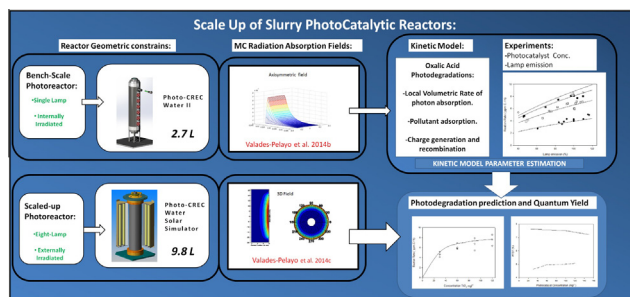
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ABSTRACT

The present study considers a scale-up methodology for photocatalytic slurry reactors. The Photo-CREC Water units used include: (a) a 2.65 L internally irradiated annular photoreactor, (b) a 9.8 L externally irradiated scaled-up unit. The LVREA (Local Volumetric Rate of Energy Adsorption Field) calculations for the bench-scale and the scaled-up reactors at different operation conditions are determined by using approaches established by Valades-Pelayo et al. [40] and Valades-Pelayo et al. [41]. In the bench-scale photoreactor, degradations of oxalic acid are carried out at different photocatalyst concentrations and lamp emissions. Residence time distributions are determined for both the Photo-CREC Water II and the Photo-CREC Water III by using glucose as a tracer. An efficiency factor is calculated in both cases including mixing mechanisms and charge/recombination phenomena using a simplified kinetic model. To avoid cross-correlation issues, all relevant parameters are determined by independent experiments. Model validation is also accomplished by comparing model predictions to experimental degradation rates at different photocatalyst concentrations in the larger Photo-CREC Water III. The proposed methodology confirms the applicability of reaction engineering principles for scale-up, from bench to pilot-plant photoreactors.

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1. Introduction

Heterogeneous photocatalysis has been around for several decades [14]. The interest in this promising technology is steadily increasing [1]. This increasing interest is the result of the diverse advantages of photocatalytic technologies such as the versatility of the photocatalytic process itself; given that it can be used to degrade a wide variety of high stability pollutants [8] or produce high energy molecules [13].

Nevertheless, for photocatalytic technologies to achieve their full potential, several issues still need to be addressed [17]. One

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Nomenclature

A	parameter for free radical source term ($m^3\ g^{-1}\ s^{-1}$)
B	parameter for charge generation/recombination ($mg\ \mu W^{-1}$)
C_{cat}	photocatalyst concentration ($mg\ l^{-1}$)
C_{ox}	oxalic acid concentration (ppm of C)
C_f	adsorbed free radical concentration per unit volume ($mol\ m^{-3}$)
D_z	axial dispersion coefficient (m^2/s)
E	Einsteins (moles of photons s^{-1})
$[e^-]$	electron surface concentration ($mol\ e^-\ m^{-2}$)
g	Henyey–Greenstein phase function dimensionless parameter (–)
$[h^+]$	electron-holes surface concentration ($mol\ h^+\ m^{-2}$)
$[H_2O_{ads}]$	adsorbed water surface concentration ($mol\ H_2O\ m^{-2}$)
I	irradiance, ($\mu W\ cm^{-2}$)
K_A	oxalic acid adsorption constant (ppm^{-1})
k_{all}	kinetic constant for total free radical depletion, sink term ($mol\ OH\ m^{-3}\ s^{-1}$)
k_{rec}	zeroth order constant of recombination of free radicals ($mol\ OH\ m^{-3}\ s^{-1}$)
k_{ox}	zeroth order constant for oxalic acid degradation ($ppm\ s^{-1}$)
k^*	reaction rate constant for dimensionless free radicals conc ($mol\ OH\ s^{-1}\ m^{-3}$)
k^{**}	lumped zero-th order kinetic constant ($ppm\ s^{-1}$)
k_1	reaction rate constant between reaction of $[h^+]$ and $[H_2O_{ads}]$ ($m^2\ mol^{-1}\ s^{-1}$)
k_2	reaction rate constant between reaction of $[h^+]$ and $[H_2O_{ads}]$ ($m^2\ mol^{-1}\ s^{-1}$)
k_3	reaction rate constant between reaction of $[e^-]$ and $[O_{2_{ads}}]$ ($m^2\ mol^{-1}\ s^{-1}$)
k_r	reaction rate constant for charge recombination ($[h^+]$ and $[e^-]$) ($m^2\ mol^{-1}\ s^{-1}$)
k_λ	reaction rate constant $[h^+]$ and $[e^-]$ generation (charges) ($mol\ \mu W^{-1}\ s^{-1}$)
L	length of the photoreactor units (m)
$[OH_{ads}]$	adsorbed OH surface concentration ($mol\ OH\ m^{-2}$)
$[O_{2_{ads}}]$	adsorbed O_2 surface concentration ($mol\ O_2\ m^{-2}$)
$p(\Omega' \rightarrow \Omega)$	phase Function for scattering in RTE (rad^{-1})
r_{ext}	annular section external radius (m)
r_{int}	annular section internal radius (m)
$r_{free\ rad}$	free radicals generated per unit time unit surface ($mol\ OH\ s^{-1}\ m^{-2}$)
r_{all}	overall rate of free radical consumption per unit volume ($mol\ OH\ s^{-1}\ m^{-3}$)
r_{ox}	oxalic acid reaction rate per unit volume ($ppm\ s^{-1}\ m^{-3}$)
s	linear coordinate along the direction Ω, (m)
S_p	external surface area per unit mass ($m^2\ g^{-1}$)
t	time (s)
x, y	cartesian coordinates (m)
z	axial coordinate (m)

Acronyms

BC	Boundary Condition
CI	Confidence Interval
DO	Discrete Ordinate
FV	Finite Volume
H-G	Henyey–Greenstein
LVREA	Local Volumetric Rate of Energy Absorption ($\mu W\ m^{-3}$)
LVRPA	Local Volumetric Rate of Photon Absorption ($E\ m^{-3}$)
MC	Monte Carlo
PTEF	Photochemical Thermodynamic Efficiency Factor (–)
Photo-CREC	Photo Reactor-Chemical Reactor Engineering Centre
RP	Radial Irradiance Profile ($\mu W\ cm^{-2}$)
RTE	Radiative Transfer Equation
RTD	Residence Time Distribution (–)
TREA	Total Rate of Energy Absorption (μW)
TRPA	Total Rate of Photon Absorption (E)
TT	Total Transmittance ($\mu W\ cm^{-2}$)
QY	Quantum Yield (mol OH consumed/mol photons absorbed)

Greek

α	constant for free radicals source term per unit surface area ($mol\ OH\ s^{-1}\ m^{-2}$)
β	extinction coefficient (m^{-1})
β_i	free radicals stoichiometric coefficient (–)
γ	charge recombination kinetic parameter ($m^2\ \mu W^{-1}$)
η	performance factor for the photocatalytic system (–)
θ	azimuth position (rad)
θ_f	free radicals coverage of photocatalyst surface area (–)
κ	absorption coefficient (m^{-1})
v_z	axial velocity ($m\ s^{-1}$)
$\dot{v}$	volumetric flow ($m\ s^{-1}$)
ϑ	dimensionless adsorbed free radicals per unit volume (–)
σ	scattering coefficient (m^{-1})
τ_{tank}	mixing tank average residence time (s)
$\phi_{reactor}$	ratio between reactor volume and total system volume (–)
Ω	solid angle (steradian)

Subscripts and superscripts

λ	indicates dependence on wavelength
f	corresponds to free radicals

of these challenges is to increase the efficiency of photocatalytic systems at larger scales [25]. In this regard, a lot more is needed from engineering design and modelling, for the successful application of the laboratory scale techniques to large-scale operations [15]. Among the main fields of research in heterogeneous photocatalysis, photocatalytic reaction engineering can be regarded as the one that concerns itself with the development and application of constitutive equations towards the design and/or scale-up of photocatalytic reactors [2].

Differences from traditional scale-up procedures in photocatalytic reactor modelling, arise from the fact that the photocatalyst has to fulfill two different functions: (a) it has to absorb radiation inducing charge separation, (b) it has to disperse radiation [7]. Since radiation distribution may be reduced considerably in heterogeneous slurry media (Changrani et al., 1999), it is difficult to investigate kinetic models independently from radiation effects. This is particularly true for bench-scale photoreactors operating at near optimum photocatalyst concentrations [26,25,34].

In this regard, the radiation behaviour is described by the Radiative Transfer Equation (RTE). When solving the RTE, the LVREA is determined [34–36] regarded as a critical parameter for photocatalytic reaction engineering, being able to link radiation modelling with kinetic modelling [6]. Regarding the LVREA, the main parameters affecting it are: (i) the reactor geometry, (ii) the