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Photocatalytic inactivation of *Escherichia coli* aqueous suspensions in a fixed-bed reactor

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ABSTRACT

A fixed-bed, annular photoreactor is studied for the photocatalytic disinfection of *Escherichia coli* aqueous suspensions. Experiments were carried out under UV radiation employing P25 titanium dioxide immobilized onto glass Raschig rings. The photoreactor performance has been simulated following a predicted procedure that takes into account explicitly the radiation absorption step and a series-event disinfection mechanism. The modeling of the radiation field was carried out by Monte Carlo simulation. The reactor model has been compared with experimental data, being able to reproduce the evolution of the concentration of viable bacteria under different bacteria initial concentrations and irradiation levels.

1. Introduction

Heterogeneous photocatalysis with titanium dioxide (TiO_2) is a well-known and effective alternative to conventional water disinfection technologies, such us chlorination, ozonization, and germicidal UV-C [1–4]. Aqueous suspensions of fine TiO_2 powder under UV irradiation are mostly employed. Nonetheless, the applicability of photocatalysis on large scale requires the immobilization of TiO_2 in order to avoid the catalyst separation step and to allow carrying out the process in continuous mode. Although the performance of immobilized systems is reported to be lower than that of TiO_2 slurry reactors in deionized water, fixed-bed reactors have shown lesser inhibition by the presence of dissolved organic matter. Besides, immobilized systems have proven to be stable and do not show deactivation after several cycles of reuse, being readily applicable for continuous water treatment systems [5].

Most of the scientific contributions on the photocatalytic inactivation of microorganisms found in the literature have proposed empirical equations or very simple models that take into account only the population of bacteria and kinetic parameters. The effect of the radiation absorption by the photocatalyst is implicitly considered in the macroscopic kinetic parameters estimated from the fitting of the experimental data. Hence, these kinetic expressions for photocatalytic bacterial inactivation are only valid for the experimental setup in which they have been developed; consequently, they cannot be extrapolated to other reactor configurations. Conversely, when a kinetic model is required for designing, optimizing or scaling-up photocatalytic reactors for water disinfection, the proposed kinetic expression must be independent of the shape and configuration of the reactor. In this case, the proposed kinetic model should be based on a reaction scheme that takes into account the radiation activated step and, explicitly, the local rate of photon absorption.

In spite of the corroborated high efficiency of fixed-bed photocatalytic reactors for water treatment, there are only a few approaches to calculate the radiation absorption in such reactors. From the numerical methods available to compute the radiation field in photocatalytic reactors, such as the discrete ordinate (DO) and the Monte Carlo (MC) methods, the latter one is chosen when complex absorption, reflection and refraction interactions between the radiation and the packed bed are involved. To the best of our knowledge, the first contribution on the modeling of a heterogeneous photoreactor using the MC method was presented by Spadoni et al. [6] for a photosensitized reaction in an annular reactor. Imoberdorf et al. [7] proposed a predictive model to solve the radiation transfer equation in a fluidized bed photocatalytic reactor, based on the MC approach coupled with the ray tracing

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Nomenclature

a_v	total bacteria surface area per unit suspension volume, cm^{-1}
$a_{v,int}$	bacteria–catalyst interacting surface area per unit reactor volume, cm^{-1}
$A_{cat,R}$	total catalytic area of the reactor, cm^2
$A^{proj}_{ring,T}$	total projected area of the rings, cm^2
B	bacteria
$e^{a,s}$	local surface rate of photon absorption, einstein cm^{-2} s^{-1}
f_{int}	fraction of bacteria–catalyst interacting surface area, dimensionless
F_λ	normalized spectral distribution of the radiation emitted by the lamp, dimensionless
LSRPA	local surface rate of photon absorption, einstein cm^{-2} s^{-1}
$n_{ph,abs}$	number of photons absorbed in a spatial cell
$n_{ph,T}$	total number of photons considered in the MC simulation
P_{lamp}	emission power of the lamp, einstein s^{-1}
r	superficial reaction rate for bacteria, CFU cm^{-2} s^{-1}
R	volumetric reaction rate for bacteria, CFU cm^{-3} s^{-1}
S_{cel}	specific surface area of the bacterial cells, cm^2 CFU^{-1}
t	time, s
t_k	average thickness of the film, cm
T_f	transmission of the film, dimensionless
V	volume, cm^3
$\underline{x}$	position vector
x	rectangular coordinate, cm
z	rectangular coordinate, cm

Greek letters

α	kinetic parameter, cm $s^{-0.5}$ $einstein^{-0.5}$
α_2	kinetic parameter, dimensionless
α_3	kinetic parameter, dimensionless
θ	polar angle, rad
κ_f	volumetric absorption coefficient of the TiO_2 film, cm^{-1}
λ	radiation wavelength, nm
ξ	distance traveled by a given photon, cm
ρ	reflectivity, dimensionless
φ	azimuth angle, rad

Subscripts

0	initial condition
d	relative to damaged bacteria
i	relative to inactivated bacteria
int	relative to the bacteria–catalyst interacting surface area
p	relative to products of bacteria lysis
pi	relative to products of bacteria lysis
R	reactor
T	total
u	relative to undamaged bacteria
λ	dependence on wavelength

Special symbols

[]	concentration of bacteria species in the bulk, CFU cm^{-3}

technique. Imoberdorf et al. [8] also modeled the radiation field of a packed-bed photocatalytic reactor filled with quartz wool coated with titanium dioxide using the MC technique. Moreira et al. [9] used the MC method along with an optimization technique in a Photo-CREC annular photocatalytic reactor to estimate the wavelength-averaged absorption and scattering coefficients for three different TiO_2 powders. More recently, Zekri and Colbeau-Justin [10] applied the MC approach in a photocatalytic tubular reactor, to study the phenol degradation at different loadings of two commercial TiO_2. Also, Zazueta et al. [11] modeled the radiation field in a multi-plate photocatalytic reactor with the MC algorithm; these results were then employed to optimize the reactor design for air purification. However, most of these contributions with MC simulation were focused on the degradation of chemical contaminants and not on water disinfection.

The aim of this work is to simulate the inactivation of *Escherichia coli* in an annular photocatalytic reactor. The experiments were carried out in a laboratory scale, fixed-bed reactor filled with Raschig rings coated with TiO_2, operating in a closed recirculating system. The proposed model is based on a reaction scheme that takes into account explicitly the local surface rate of photon absorption (LSRPA) inside the reactor. Depending on the type of photocatalytic reactor under analysis, the rate of photon absorption may be expressed per unit reactor irradiated volume or per unit reactor irradiated photocatalytic surface. When modeling a fixed-bed reactor, in which a thin layer of TiO_2 is coated on the surface of an inert support, it is more appropriate to refer the photon absorption rate per unit area of irradiated TiO_2-coated surface [8]. The rate of photon absorption was computed by means of the MC simulation. Results of the LSRPA were then incorporated in the expressions of the kinetic model and the superficial disappearance rates of undamaged and damaged bacteria in the storage tank were solved to obtain their theoretical evolution as a function of time. Finally, the intrinsic kinetic parameters were estimated by applying an optimization procedure between the experimental and simulated results.

2. Experimental

2.1. The reactor

The experimental setup consists of an annular reactor 15 cm long, 3 cm inner diameter and 5 cm external diameter [12]. The reacting system was operated in a closed recirculating circuit driven by a centrifugal pump, with a stirred reservoir tank of 2 L equipped with a device for withdrawal of samples. Experiments were carried out using a total working volume of 1.0 L and a recirculation flow rate of 2.5 L/min. Illumination was carried out with a Philips TL 6W black light lamp placed in the axis of the reactor. The lamp supplies a nominal UV-A radiation power of 0.7 W with a maximum emission peak centered at 365 nm. The UV-A incident photon flow, determined by ferrioxalate actinometry, was 2.77×10^{-6} einstein s^{-1}.

The fixed-bed was prepared by immobilization of P25 TiO_2 (Evonik Industries) onto 6×6 mm glass Raschig rings and placing them into the annular photoreactor volume. Immobilization of TiO_2 has been carried out by a dip-coating procedure. The glass material was first cleaned-up with soap and water and then immersed in a KOH–isopropanol bath (200 g/L) for 24 h. The suspension consists of 150 g/L of Evonik P25 TiO_2 in deionized water at a pH value of 1.5, adjusted with HNO_3. The process was assisted by a Bungard Elektronik RDC-15 equipment working at a controlled withdrawal speed of 0.65 mm/s. After each coating cycle, the glass pieces were dried at 110 °C for 24 h and calcined at 500 °C for 2 h with a heating rate of 5 °C/min. Prior to be used in the reaction, the coated systems were mounted on the photoreactor and cleaned with water for 30 min to eliminate all the TiO_2 particles poorly adhered to the glass.