Applied Catalysis B: Environmental 200 (2017) 164–173

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Influence of TiO_2 optical parameters in a slurry photocatalytic reactor: Kinetic modelling

A. Tolosana-Moranchel [b], J.A. Casas [b], J. Carbajo [a], M. Faraldos [a], A. Bahamonde [a,*]

[a] Instituto de Catálisis y Petroleoquímica, ICP-CSIC, C/Marie Curie 2, 28049 Madrid, Spain
[b] Sección de Ingeniería Química, Facultad de Ciencias, C/Francisco Tomás y Valiente 7, Universidad Autónoma de Madrid, 28049 Madrid, Spain

ARTICLE INFO

Article history:
Received 20 April 2016
Received in revised form 20 June 2016
Accepted 25 June 2016
Available online 29 June 2016

Keywords:
Photocatalysis
TiO_2
Kinetic model
RTE
VRPA

ABSTRACT

A kinetic model, based on a proposed reaction photo-mechanism and explicitly dependent on the volumetric rate of photon absorption (VRPA), has been performed and analyzed for the photocatalytic degradation of phenol in aqueous suspensions. UVA–vis simulated solar radiation and three commercial TiO_2 powder photocatalysts, with identical chemical structure but with different morphology and hydrodynamic particle size (P25 Aeroxide®, P25/20 VP Aeroperl® and P90 Aeroxide® provided by Evonik) have been used. The effect of TiO_2 hydrodynamic particle size on the optical coefficients has revealed that this property is playing an important role on the absorbed radiation evaluation. Radiation profiles inside the photoreactor were determined by solving the radiative transfer equation (RTE), and the corresponding kinetic parameters were obtained.

A comparative study of TiO_2 loading effect on calculated quantum efficiency (η) revealed P25 was the most photo-efficient catalyst, whereas P25/20 reached similar efficiencies only when higher TiO_2 concentrations were used. On the contrary, P90 presented the lowest photo-efficiency with lower photodegradation rates despite absorbing more radiation.

The obtained kinetic model has been successfully validated by experimental data, being able to reproduce the evolution of phenol photodegradation at a wide range of catalyst concentrations for the three studied TiO_2. In the experimental conditions of this work, low irradiation power conditions can be considered; after simplification, the model adopted a linear dependence on the volumetric rate of photon absorption; showing good agreement between predicted and experimental values, with root-square-mean errors below 5%.

1. Introduction

The heterogeneous photocatalytic process is based on the excitation of a catalytic solid, usually a broad bandgap semiconductor as TiO_2, through the absorption of photons whose energy is equal or greater than their *band-gap* energy. Photo-generated electrons (e^-) and holes (h^+) will react with adsorbed molecules located at catalyst surface, leading to the oxidization of the organic matter by direct hole (h^+) transfer or by indirect hydroxyl radical—oxidation ($HO^\bullet$) [1]. In this context, solar photocatalytic processes contemplate the use of a natural light source such as the sun, environmental friendly, wherein the nanostructured TiO_2 catalysts can improve their final photoefficiency [2]. It is known that photocatalytic processes are affected by different parameters which govern photo-oxidation rates, such as spectral distribution and intensity of the incident radiation, concentration and type of oxidizing agent, mass of catalyst, pH, etc. [1,3]. Therefore, to discriminate the overall performance of a photocatalyst is essential to know its intrinsic kinetic parameters to design new and improved photo-reactors. Then, a crucial requirement to develop novel photoreactors would be to build a kinetic model able to successfully reproduce the experimental rates obtained during photo-catalytic reaction [4]. Analysis of liquid-phase kinetics for titania powder suspensions have relied largely on Langmuir-Hinshelwood (LH) rate forms, which assumes equilibrated adsorption of reactants and implies the existence of a subsequent slow, rate-controlling surface step [5,6]. This kinetic model has demonstrated to well fit the concentration evolution of many organic pollutants in the photocatalytic literature [6]. However to carry out valuable comparison studies of the kinetic parameters among different labs, reactors and research works, it

* Corresponding author.
E-mail address: abahamonde@icp.csic.es (A. Bahamonde).

http://dx.doi.org/10.1016/j.apcatb.2016.06.063
0926-3373/

Nomenclature

%A	Anatase crystalline phase percentage
%R	Rutile crystalline phase percentage
ABS	Value of a absorbance spectrophotometric measurement
a_V	Interfacial area per unit suspension volume, m^{-1}
BG	Band-gap, eV
C_{cat}	Mass catalyst concentration, g cm^{-3}
C_{Ph}	Molar phenol concentration, mmol L^{-1}
d_A	Anatase mean diameter, nm
d_{PHD}	Hydrodynamic particle diameter, μm
d_R	Rutile mean diameter, nm
e^a	Volumetric rate of photon absorption, Einstein cm^{-3} s^{-1}
f	Spectral energy distribution of the lamp
I	Specific radiation intensity, Einstein cm^{-2} s^{-1}
k	Kinetic constant, its units depend on the step considered
K	Equilibrium constant
LVRPA	Local volumetric rate of photon absorption, Einstein cm^{-3} s^{-1}
p	Function phase, dimensionless
q	Radiation flux, Einstein cm^{-2} s^{-1}
R	Value of a reflectance spectrophotometric reflectance
r_g	Surface rate of electron-hole generation, mol cm^{-2} s^{-1}
$(-r_{Ph})$	Phenol photodegradation rate, mmol L^{-1} min^{-1}
$r_{Fe(II)}$	Fe(II) production rate, mol L^{-1} min^{-1}
S	Relative to a subproduct species
S_{BET}	Catalyst surface are (BET), m^2 g^{-1}
S_{irr}	Area of the inlet radiation window, cm^2
t	Time, min
V_R	Reactor volume, l
VRPA	Volumetric rate of photon absorption, Einstein cm^{-3} s^{-1}

Greek letters

α_1	Kinetic parameter, mmol cm L^{-1} min^{-1}
α_2	Kinetic parameter, cm^2 s $Einstein^{-1}$
α_3	Kinetic parameter, L $mmol^{-1}$
β	Extinction coefficient, cm^{-1}
η	Quantum efficiency, mmol $Einstein^{-1}$
ϕ	Quantum yield, mol $Einstein^{-1}$
$\bar{\phi}$	Mean quantum yield, mol $Einstein^{-1}$
κ	Absorption coefficient, cm^{1}
λ	Wavelength, nm
μ	Director cosine, $\mu = \cos\theta$
θ	Spherical coordinate, rad
Ω	Direction of radiation propagation
ω	Spectral albedo

Subscripts

0	Initial value
λ	Indicates a dependence on wavelength
Cat	Relative to catalyst
Exp	Experimental value
max	Maximum value
min	Minimum value
Mod	Simulated value
Ph	Relative to phenol
S	Relative to a subproduct
T	Total
V_R	Relative to reactor volume

Superscripts

*	Specific properties
±	Direction in which $\mu > 0$
-	Direction in which $\mu < 0$
0	Value at $x = 0$
s	Relative to catalytic area

Special symbols

⟨⟩	Average value over a defined space
[]	Relative to concentration

will be needed to pay attention to intensity of absorbed radiation in any single photoreactor, given that different parameters such as light intensity are grouped in LH model kinetic rate constants.

Therefore, to get a kinetic expression which can be employed within a great range of operating conditions and allow to scaling up the process, the model must have an explicit dependence on the absorbed radiation. Hence, volumetric rate of photon absorption (VRPA) inside photoreactor must be evaluated, since it is involved in the photocatalytic reaction by means of activation step [7]. In this context, the Radiative Transfer Equation (RTE) must be solved to determine the radiation field [8,9]. The RTE describes the radiation intensity at any position along a ray pathway through medium. Besides, it can be also applied to evaluate the radiation field in a heterogeneous system constituted by TiO_2 particles suspended in aqueous suspensions.

Consequently, the aim of this work has consisted on developing an intrinsic kinetic model, where the explicit radiation absorption has been included to reproduce the experimental results obtained with three TiO_2 powder catalysts in the photodegradation of phenol in aqueous suspensions using a slurry photoreactor with external surrounding radiation. TiO_2 catalysts (P25 Aeroxide®, P25/20 VP Aeroperl® and P90 Aeroxide®) with identical chemical structure, but with different morphologic and hydrodynamic particle size were deliberately chosen to study the influence of catalyst loading on phenol photodegradation without any other collateral effect.

The main optical properties (extinction, absorption and scattering coefficients) which affect the overall photocatalytic behavior, have been determined, and its dependence on the hydrodynamic particle size in aqueous suspensions has been settled.

Finally, a comparison study of calculated quantum efficiency for different TiO_2 loading was also analyzed to establish the most photo-efficient catalyst under the studied conditions.

2. Experimental section

2.1. Photocatalysts

Photocatalytic experiments were performed using three TiO_2 commercial catalysts: P25 Aeroxide®, P90 Aeroxide® and P25/20 VP Aeroperl®, all of them provided by Evonik Company.

Analytical grade phenol was purchased from Panreac. All reagents used for chromatographic analyses: (Milli-Q water, Orthophosphoric acid, methanol) were HPLC grade.

2.2. Photocatalysts characterization

Catalysts structural characterization were performed with a X polycrystal PANalytical XíPert PRO using nickel-filtered Cu Kα (1.541874 Å) radiation operating at 40 kV and 40 mA, with a 0.02° step size and accumulating a total of 50 s per point, crystal size was estimated by employing the Scherrer equation [10].

Nitrogen adsorption-desorption isotherms measurements were obtained at 77 K in a Micrometritics Tristar automatic apparatus,