Photocatalytic Reaction Engineering

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Springer

Library of Congress Cataloging-in-Publication Data

De Lasa, Hugo I.
Photocatalytic reaction engineering / Hugo deLasa [sic], Benito Serrano, and Miguel Salaices.
p. cm.
Includes bibliographical references and index.
ISBN 0-387-23450-0 (acid-free paper)
1. Photocatalysis. 2. Reaction mechanisms (Chemistry) 3. Chemical engineering. I. Serrano, Benito.
II. Salaices, Miguel, III. Title
QD716.P45.D4 2005
541′.395–dc22 2004065093

A C.I.P. Catalogue record for this book is available
from the Library of Congress.

ISBN 0-387-23450-0

Printed in the United States of America

9 8 7 6 5 4 3 2

springer.com

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Preface

The pursuit of knowledge and discovery ebbs and flows. Peaks of innovation and discovery are often followed by periods of calm that invite reflection and reassessment, which in turn motivate renewed efforts towards further advancement. It is our view that the study of photocatalytic reaction engineering is in a phase of reassessment. The very principles of reaction engineering are under review at this time when environmental pressures and social concerns are changing the way we perceive and use technology. The application of photocatalytic reaction technology holds great promise in these changing times.

It is our aspiration to offer with this book a coherent and comprehensive treatment of the subject with thoroughly integrated contributions of the three co-authors.

Chapter I examines the basic principles involved in modeling photocatalytic reaction rates. Clarification in this area is needed as it is often lacking and is required for proceeding with the design, the simulation and the scale-up of the photocatalytic reactor units. Once these concepts are established, Chapter II describes various novel photocatalytic reactors designed by research groups around the world including the Photo-CREC reactors, developed in the context of the authors' research activities at the Chemical Reactor Engineering Centre (CREC), the University of Western Ontario in London, Canada and at the Universidad Autónoma de Zacatecas, Mexico. This chapter provides insight on the opportunities to extend the application of this technology through innovation in chemical reactor engineering.

Chapter III addresses the need of reviewing various types of photocatalysts, power sources and auxiliary equipment available for photocatalytic studies. Description of these matters is of essential importance for establishing radiation source power spectra, their lifetime and their power decay, for describing the available tools for macroscopic radiation balances and for effective kinetic and reaction rate modeling.

Chapter IV elucidates the methodology to develop a macroscopic radiation balance. This methodology allows the effective assessment of absorbed irradiation and irradiation transmission involving apparent extinction coefficients. The focus is put on demonstrating the applicability of these relatively simple functions to make the prediction of photon transfer and photon absorption a tractable mathematical problem. Thus, this chapter provides valuable tools from the perspective of the photocatalytic reactor designer.

Chapter V addresses the important task of accounting for the complex network of photochemical reactions, establishing viable kinetic modeling. This modeling is essentially based on a series-parallel model of the photocatalytic reaction network.

Examples are given to demonstrate the extent of applicability of this approach to the photoconversion of phenol.

Furthermore, the extensive applicability of photocatalysis has essentially become a problem of energy efficiency. As a result, the quantification of these energy efficiency factors is a major issue. Thus, Chapter VI considers these factors from two perspectives: quantum efficiencies and Photochemical Thermodynamic Efficiency Factor (PTEF), the latter being a new efficiency factor introduced by the authors.

Chapter VII addresses the need to account for both physical and chemical phenomena, reaction and adsorption. In fact, consideration of these combined phenomena is, in the view of the authors, essential to provide effective kinetic and rate modeling for the photo conversion of organic and inorganic pollutants. Cases with several organic species are presented including methylene blue, phenol, chloro-phenol, di-chloro-phenol, catechol, and pyrogallol.

Air decontamination is another potential innovative application of photocatalysis. Chapter VIII focuses on air decontamination using Photo-CREC reactors. Several examples are provided by examining the photoconversion of acetone, iso-propanol, and acetaldehyde. Special attention is paid to the quantum efficiencies for air decontamination, exceeding 100% in many cases, which demonstrates the distinctive chain mechanism character of the photoconversion of organic pollutants in air.

Finally, Chapter IX, discusses recent research on the concurrent oxidation-reduction of organic and inorganic compounds and on the inactivation of model microorganisms. These two applications of photocatalysis have the potential of significantly improving the prospects for this novel technology.

In summary, our book contains an up-to-date discussion of photocatalytic reaction engineering and the application of these principles. Altogether it is an invitation to reflect on the possibilities of photocatalysis as a new and unique technique with great potential for air and water treatment. We offer our book as a contribution to the development of reaction engineering in photocatalysis as well as to the extensive potential for application of this technology.

We would like to express our appreciation to the University of Western Ontario, Canada, the Universidad Autónoma de Zacatecas, México and the Instituto de Investigaciones Eléctricas, México for their onthusiastic support of this project.

The authors wish to acknowledge the contributions of Dr. H. Ibrahim, Mr. J. Stuart, Mr. Jesus Moreira del Rio and Salvador Escobedo Salas whose research enriched some of the sections of this book. We are thankful to Ms. Naomi Pavan and Mrs. Graciela Lamana de Lasa who helped with the proofreading and technical editing of the manuscript. We would also like to express our appreciation to Mr. Martin de Lasa who designed the book cover and to Ms. Cristina de Lasa who offered valuable advice for the preparation of this cover. Finally, we are indebted to Mr. Kenneth Howell Senior Editor for Chemistry, Springer who provided guidance from a publisher's perspective.

London, Canada, August 2004

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Establishing Photocatalytic Kinetic Rate Equations: Basic Principles and Parameters

1.1. INTRODUCTION

Heterogeneous photocatalysis is a promising new alternative method for the removal of organic pollutants in water (Carey, 1976). The degradation of organic pollutants in water, using irradiated dispersions of titanium dioxide, is a growing area of both fundamental and applied research.

This chapter reviews the basic principles involved in modeling the rates of photocatalytic reactions. These matters require clarification in order to proceed with the successful design, simulation and scale-up of photo catalytic reactor units.

1.2. THE PHOTOCATALYTIC REACTION AND THE INITIATION STEP

Three components must be present in order for the heterogeneous photocatalytic reaction to take place: an emitted photon (in the appropriate wavelength), a catalyst surface (usually a semi-conductor material) and a strong oxidizing agent (in most cases oxygen). Pasquali *et al.*, (1996) indicated that absorbed photons should be considered to be a nonmaterial reactant, which, like other reacting species, must be present for the reaction to occur.

The heterogeneous photocatalytic process is initiated when a photon with energy equal to or greater than the band gap energy (E_{bg}) of the photocatalyst reaches the photocatalyst surface, resulting in molecular excitation. E_{bg} is defined as the difference between the filled valence band and the empty conduction band of the photocatalyst, in the order of a few electron volts.

This molecular excitation results in the generation of mobile electrons in the higher energy conduction band (E_{cb}) and positive holes in the lower energy valence band (E_{vb}) of the catalyst, according to equation 1-1 and the reaction illustrated in Figure 1.1.

$$photocatalyst \xrightarrow{E_{ph} \geq E_{bg}} e^- + h^+ \tag{1-1}$$

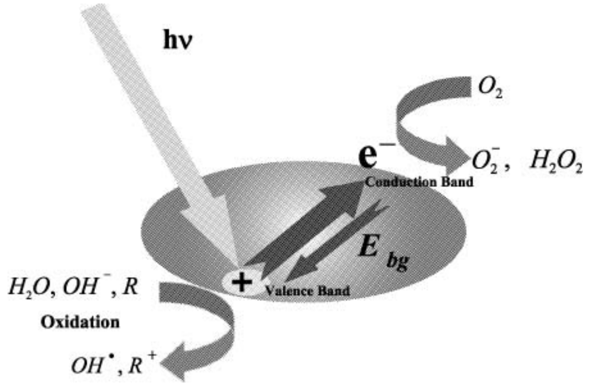

FIGURE 1.1. Schematics of the electron-hole generation in a photocatalyst particle and some of the mechanisms involved: a) Ray promotes the formation of the electron-hole and electron, b) electron-hole is used in the formation of the OH• groups promoting oxidation processes, c) the electron is utilized in a number of reduction processes, d) electron and electron-hole can recombine contributing to process inefficiency.

The photocatalytic reaction proceeds via a series of chemical events, following the initiation step of pair electron-hole formation. This leads to the utilization of both the electron-hole h^+ for oxidation processes and eventually to the capture of the e^- electron for reduction processes, as well as the potential formation of super oxides anions and hydrogen peroxide from oxygen.

Unfortunately, there is a competing electron and electron-hole recombination step (the reverse of equation (1-1)), and this result in process inefficiencies and the waste of the energy supplied by the photon. The electron-hole recombination can be considered as one of the major factors limiting the efficiency of the photocatalytic processes.

Every effort to prevent electron and electron-hole recombination will improve the efficiency of heterogeneous photocatalytic processes and will considerably help to achieve the application of this technique for water and air purification.

1.3. THE PHOTOCATALYTIC REACTION

The heterogeneous photocatalytic reaction can be represented as a number of mechanistic steps (Legrini *et. al.*, 1993; Hoffman *et. al.*, 1995; Turchi and Ollis, 1990).

A photo-excited TiO_2 generates an electron and an electron-hole.

$$TiO_2 \xrightarrow{hv} e^- + h^+ \tag{1-2}$$

Electron transfer from the adsorbed substrate (RX_{ad}), adsorbed water or the OH_{ad} ion, to the electron-hole.

$$h^+ + RX_{ad} \rightarrow RX_{ad}^+ \tag{1-3}$$

$$h^+ + H_2O_{ads} \rightarrow OH_{ads}^\bullet + H^+ \tag{1-4}$$

$$h^+ + OH_{ad}^- \rightarrow OH_{ad}^\bullet \tag{1-5}$$

The third step is of great importance, mostly because of the high concentrations of OH^-, given water dissociation into ions.

$$H_2O \rightarrow OH^-_{ad} + H^+ \tag{1-6}$$

Molecular oxygen acts as an acceptor species in the electron-transfer reaction.

$$e^- + O_2 \rightarrow O_2^- \tag{1-7}$$

Super-oxide anions, (equation 1-7), can subsequently be involved in the following reactions.

$$O_2^- + H^+ \rightarrow HO_2^\bullet \tag{1-8}$$

$$H^+ + O_2^- + HO_2^\bullet \rightarrow H_2O_2 + O_2 \tag{1-9}$$

Photoconversion of hydrogen peroxide gives more $OH^\bullet$ free radical groups.

$$H_2O_2 + h_\nu \rightarrow 2OH^\bullet \tag{1-10}$$

Finally, $OH^\bullet$ radicals oxidize organic adsorbed pollutants (RX_{ad}) onto the surface of the titanium dioxide particles.

$$OH^\bullet_{ad} + RX_{ad} \rightarrow Intermediate \tag{1-11}$$

The $OH^\bullet$ radicals, as described by equation (1-11), are very reactive and attack the pollutant molecule to degrade it into mineral acids including carbon dioxide and water (Al-Ekabi *et al.*, 1993).

There are two possible explanations of photocatalytic reactions. While some authors suggest an indirect oxidation via a surface-bound hydroxyl radical (refer to equations (1-5) and (1-11)) (Mills and Hoffmann, 1993; Terzian *et al.*, 1991; Turchi and Ollis, 1990), another group argues in favor of a direct oxidation via the valence-band hole (equation (1-3) (Draper and Fox, 1990).

In support of the argument for the surface-bound hydroxyl radical mechanism, there is an intermediate presence of hydroxylated structures during the photocatalytic degradation of halogenated aromatics. These hydroxylated intermediates are also found when similar aromatics react with a known source of hydroxyl radicals. Furthermore, ESR studies confirm the existence of hydroxyl and hydro-peroxy radicals in aqueous solutions of illuminated TiO_2 (Hoffman *et al.*, 1995; Linsebigler *et al.*, 1995).

1.4. MODELING PHOTOCATALYTIC REACTION RATES

The modeling of photocatalytic reaction rates is essentially based on a number of mathematical statements, which can be expressed by a set of ordinary differential equations. Each of these equations is established for the key chemical species and therefore species' balances in photocatalytic reactors can be typically described as follows:

$$V\frac{dC_i}{dt} = \left[\sum_k \nu_{i,k}\ R_k\right] W_{irr} \tag{1-12}$$

with V being the total reactor volume in L, C_i being the concentration of the i chemical species in g L^{-1}, t being the time in s, $\nu_{i,k}$ being a dimensionless stochiometric coefficient for i species involved in reaction step k and R_k being the rate of photoconversion of step k based on the unit weight of irradiated catalyst, W_{irr}, in mole $(g_{cat}\ s)^{-1}$.

This equation involves a number of important assumptions satisfied by most photocatalytic reactor units, either in the case of reactors with suspended TiO_2 or in reactors with immobilized TiO_2.

(a) The photocatalytic reactor unit is operated in the batch mode. This condition is typically required because of the relatively low photocatalytic reaction rates.
(b) W_{irr}, the weight of irradiated catalyst is known.
(c) Mixing and fluid recirculation are high enough so that a *quasi* constant reaction rate can be defined in the irradiated reactor section.

Equation (1-12) can be rearranged and simplified in some situations; such as in the case of model pollutant consumption. The rate of photoconversion can then be expressed in terms of measurable parameters and variables

$$r_1 = \frac{V}{W_{irr}}\frac{dC_1}{dt} = \sum_k \nu_{1,k} R_k \tag{1-13}$$

with $i = 1$ and "1" representing the model compound.

The consideration of equations (1-12) and/or (1-13) leads to the advancement of photocatalytic conversion rate models, such as the series-parallel model proposed by Salaices *et al.* (2004) where the derived kinetic parameters are based on the irradiated weight of catalyst. As such, these can be considered as *intrinsic parameters* with phenomenological meaning pertinent to the photocatalytic reaction.

$$\frac{dC_i}{dt} = \frac{-k_i'''C_i}{1+\sum\limits_{j=1}^{n} K_j C_j} \tag{1-14}$$

with k_i representing the kinetic constants for the i species in s^{-1} and K_j is the adsorption constant for the species j (any of the species present) in L mole^{-1}.

A similar approach to that used in equation (1-13) can be adopted by referring the rate of model pollutant photoconversion to A_{irr}, the external area of irradiated catalyst,

$$r_1' = \frac{V}{A_{irr}}\frac{dC_1}{dt} = \sum_k \nu_{1,k} R_k' \tag{1-15}$$

Another possible approach is the use of less meaningful "apparent" rates of photoconversion employing a different basis, such as in the case of V_{irr}, the irradiated reactor volume. Thus, the basic balance, as described in equation (1-12), becomes

$$V\frac{dC_i}{dt} = \left[\sum_k \nu_{i,k}\ R_k^{''}\right]\ V_{irr} \tag{1-16}$$

with V being the total reactor volume in L, C_i being the concentration of the i chemical species in g L^{-1}, t being the time in s, $\nu_{i,k}$ being a dimensionless stochiometric coefficient for i species involved in reaction step k and $R_k^{''}$ being the rate of photoconversion of k step, based in the unit irradiated reactor volume, V_{irr}, in mole (L s)$^{-1}$.

Thus, for the case of a model pollutant photoconversion equation (1-16) can be expressed as follows.

$$r_1^{''} = \frac{V}{V_{irr}}\frac{dC_1}{dt} \tag{1-17}$$

with $i = 1$ and 1 being the model compound.

The definition of the rate of photoconversion then becomes:

$$r_1^{''} = \frac{V}{V_{irr}}\frac{dC_1}{dt} = \frac{(V_{irr} + V_d)}{V_{irr}}\frac{dC_1}{dt} \tag{1-18}$$

with V, the system reactor volume, being the combined irradiated volume V_{irr} and non-irradiated volume (dark reactor volume section) V_d.

During the process of calculating the rates of photoconversion, frequently researchers make no distinction between the total reactor volume, V, and the irradiated reactor volume. It should be stressed that only under very special conditions and designs one can adopt the $V = V_{irr}$ assumption and consider an apparent rate of photoconversion directly obtained from the change in concentration of an i chemical pollutant species.

$$\frac{dC_1}{dt} = \sum_k \nu_{1,k}\ R_k^{'''} \tag{1-19}$$

or

$$r_1^{'''} = \frac{dC_1}{dt} \tag{1-20}$$

with $i = 1$ for the model pollutant.

In summary, one can establish for a model pollutant the following,

$$r_1^{'''} = r_1^{''}\frac{V_{irr}}{V} = r_1^{'}\frac{A_{irr}}{V} = r_1\frac{W_{irr}}{V} \tag{1-21}$$

Thus, when relating the observed changes in concentration of chemical species in a given reactor geometry with the rate of photodegradation, the irradiated catalyst weight

(W_{irr}) or the irradiated reactor volume (V_{irr}) should be carefully considered as two key parameters. This makes photocatalytic rate definition and kinetic parameter calculations phenomenologically sound and meaningful.

The kinetic parameters obtained should otherwise be subjected to corrections using factors suggested by Salaices et al. (2002). For a first order decomposition, apparent reaction parameters should be corrected as follows:

$$k_1''' = k_1'' \frac{V_{irr}}{V} = k_1' \frac{A_{irr}}{V} = k_1 \frac{W_{irr}}{V} \tag{1-22}$$

1.5. EFFECT OF THE LAMP IRRADIATION AND CATALYST LOADING ON THE PHOTOCATALYTIC RATE

Both lamp irradiation and catalyst concentration play very important roles in photocatalytic processes. The effect of the irradiation parameter on the overall (apparent) rate of photoconversion can be represented by a power varying between 0.5 and 1. The influence of the photocatalyst weight can also be considered using a generic function of the irradiated catalyst.

The overall (apparent) initial reaction rate can be represented as the product of several functionalities, which include a function dependent on the i chemical species concentration defined at the initial condition $f_1(C_{i,in})$, a function dependent on the catalyst concentration $f_2(C_C)$ or the catalyst weight, and a function dependant on the rate of absorbed photons $f_3(P_a)$.

$$r'''_{i,in} = f_1(C_{i,in}) f_2(C_C) f_3(P_a) \tag{1-23}$$

In order to clarify the dependence of the initial photoconversion rate with $f_3(P_a)$, Salaices *et al.* (2001) developed experiments with phenol with a changing incident absorbed radiation. As suggested by a number of authors (Okamoto et al., 1985; Ollis, 1991; Pelizzetti et al., 1993; Trillas et al., 1996, 1992; Wei et al., 1994), it is proven that at low levels of absorbed incident radiation there is a linear relationship between the initial photoconversion rate of phenol and the incident absorbed radiation, $r'''_{1,in} = m_3 f_3(P_a) = m_3 P_a^{\delta}$, with $\delta = 1$ and $m_3 = f_1(C_{1,in}) f_2(C_C)$ as the proportionality factor in μ mole L^{-1} einstein^{-1} (refer to Figure 1.2).

This dependence of the photoconversion rate with the incident radiation is established in a Photo-CREC-Water II unit using removable glass tubes and meshes having different openings (for additional details refer to Chapter IV).

The effect of catalyst loading over Degussa P25, $f_2(C_C)$, on the overall initial photoconversion rate is illustrated in Figure 1.3. The catalyst concentration changes from zero to 0.35 g L^{-1}, corresponding to 100 and 0.005 % radiation transmission, respectively. It is observed that a minimum amount of catalyst is required to start the photodegradation, C_{wf}. It is also noticed that the overall reaction rate increases with catalyst loading until it reaches a $r'''_{1,in}$ maximum value of approximately 7.0 μ mole-C (L min)$^{-1}$, at catalyst concentrations higher than 0.14 g L^{-1}.

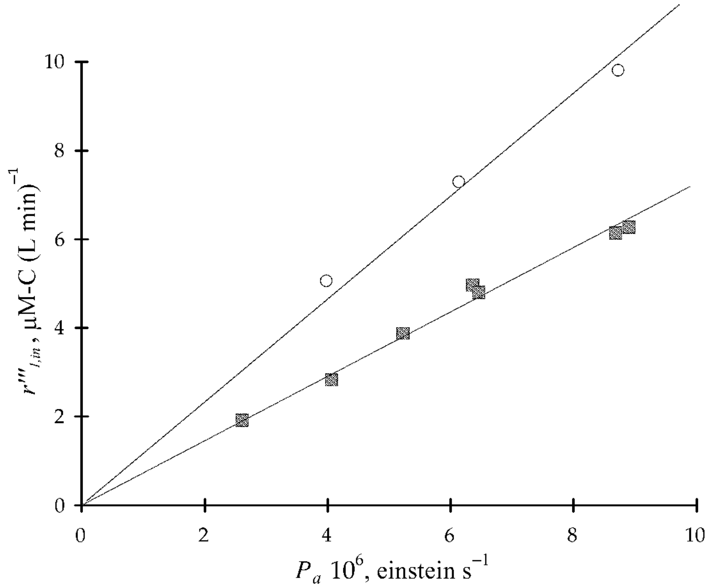

FIGURE 1.2. Initial phenol photoconversion rate ($r'''_{1,in}$) versus incident radiation intensity. (■) Removable 3.2-cm diameter glass inner tube, (○) Removable 5.6-cm diameter glass inner tube. (Reprinted with permission from *Ind. Eng. Chem. Res.*, **40**(23), M. Salaices, B. Serrano and H.I. de Lasa, Photocatalytic conversion of organic pollutants: Extinction coefficients and quantum efficiencies, 5455–5464. Copyright 2001 American Chemical Society).

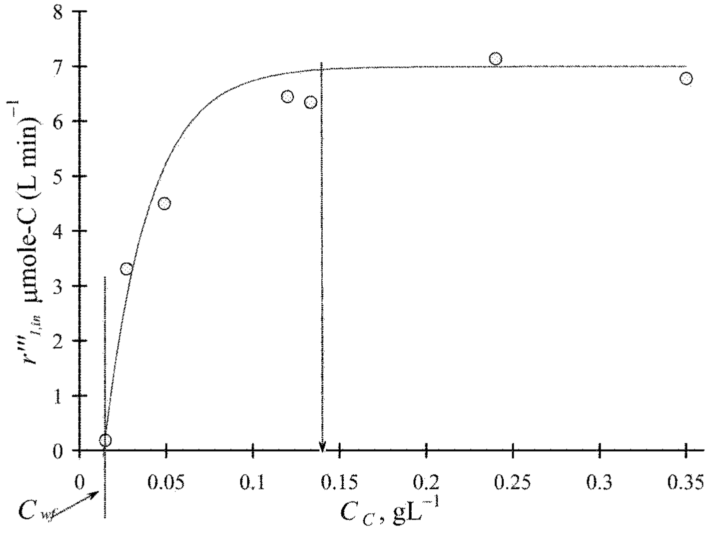

FIGURE 1.3. Initial reaction rate as a function of the catalyst loading. Catalyst: Degussa P25 (Reprinted with permission from *Ind. Eng. Chem. Res.*, **40**(23), M. Salaices, B. Serrano and H.I. de Lasa, Photocatalytic conversion of organic pollutants: Extinction coefficients and quantum efficiencies, 5455–5464. Copyright 2001 American Chemical Society).

These results can be explained as follows:

$$r'''_{1,in} = m_2 f_2(C_C) = m_2 P_i \big|_{C_C \to 0}[1 - \exp(-\alpha C_C)] \tag{1-24}$$

Given $P_i \big|_{C_c \to 0} = P_i - P_{bs}$ (refer to Chapter IV), then,

$$r'''_{1,in} = m_2 P_i[1 - \exp(-\alpha C_C)] - m_2 P_{bs}[1 - \exp(-\alpha C_C)] \tag{1-25}$$

where C_C is the catalyst concentration in g L^{-1}; $m_2 = f_1(C_{1,in}) f_3(P_a)$ is the proportionality constant, μ mole L^{-1} einstein^{-1}; P_i is the rate of photons reaching the inner reactor surface, einstein s^{-1}; P_{bs} is the rate of backscattered photons exiting the system, einstein s^{-1} and α is the effective extinction coefficient of the TiO_2 suspension, L g^{-1}.

It is postulated that the backscattering (refer to Chapter IV) is completed at very low catalyst concentrations, therefore the term $m_2 P_{bs}[1 - \exp(-\alpha C_C)]$ can be approximated to a constant value, $m_2 P_{bs}$, and equation (1-25) is reduced.

$$r'''_{1,in} = a_C[1 - \exp(-\alpha\ C_C)] - b_C \tag{1-26}$$

with $a_C = m_2 P_i$ and $b_C = m_2 P_{bs}$ in μ mole-C (L s)$^{-1}$, α the apparent extinction coefficient in L g^{-1}, C_C the Degussa P25 catalyst concentration in g L^{-1}.

Salaices *et al.* (2001) fitted the a_C, α and b_C parameters to the experimental data reported in Figure 1.3 using a non-linear, least squares method. These parameters can also be calculated independently by using the values for P_i, P_{bs}, α, and m_2 (refer to Chapter IV). These results are summarized in Table 1.1. As noted, the calculated and regressed values are statistically similar, validating the applicability of the proposed model for the prediction of the $f_2(C_C)$ functionality.

Concerning the physical interpretation of C_{wf} in Figure 1.3, this represents the wall fouling catalyst concentration, or the minimum catalyst concentration necessary to start the reaction. It is postulated that, at very low concentrations, the catalyst particles tend to adhere to the system walls, including to some non-illuminated sections. Additionally, a fraction of the irradiated catalyst found close to the reactor walls does not produce any significant photodegradation due to its poor contact with the fluid. It is not until a minimum catalyst loading value is reached that the irradiated catalyst becomes available for the photoconversion reaction. The calculated value of C_{wf} was 0.014 g L^{-1}.

Results of Figures 1.3 and 1.4 show that for $W_{irr} < W_{irr,\max}$ all the catalyst available contribute to the photocatalytic conversion. Beyond this $W_{irr,\max}$ value, additional catalyst does not influence the rate of photoconversion. Thus, one should consider, as suggested in equation (1-12) and shown in Figures 1.4 and 1.5, a photocatalytic reaction rate

TABLE 1.1. Parameter values for the $r'''_{1,in}$ as a function of C_c (equation. (1-26))

Parameter	Value	+/-σ	Calculated	+/-σ
a_c	11.988	2.2032	9.388	1.18
α	38.450	9.012	41.1	3.451
b_c	4.992	2.2488	1.77816	0.7776

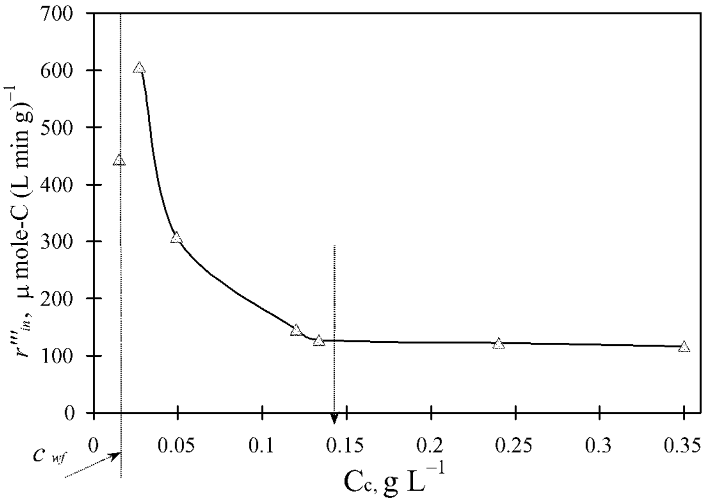

FIGURE 1.4. Change of $r_{1,in}$, the initial reaction rate per unit weight of irradiated catalyst with catalyst loading.

based on the irradiated weight of catalyst for properly expressing the photoconversion using a phenomenologically based rate parameter.

These results highlight: a) Photodegradation reaction rates should be defined on the basis of phenomenologically meaningful parameters, case of W_{irr}, b) Reaction rate evaluation is a task that should be developed carefully, accounting for possible non-idealities in the photocatalytic reactor such as particle wall fouling.

1.6. MODELING PHOTOCONVERSION OF POLLUTANTS: THE PARALLEL-SERIES REACTION MODEL

The functionality of the initial reaction rate on the i chemical species concentration defined at the initial condition $f_1(C_{1,in})$ is illustrated in Figures 1.5 and 1.6.

The ordinates show the phenol concentration (Figure 1.5) and Total Organic Carbon (TOC) (Figure 1.6) changes with reaction time. These results were obtained for different initial phenol concentrations, under the conditions reported by Salaices et al. (2001).

The examination of these experimental data, expanded details are reported in Chapter V, illustrates the basic parallel-series mechanism for photocatalytic reactions including the possible influence of the distribution of photocatalytic site activity.

The model pollutant, phenol, is photo-converted via a first order or pseudo-first order reaction consistent with equation(1-14) considering in this manner all possible sources of phenol consumption.

TOC changes, describing the overall degradation of organic species, follow a near-zero order reaction rate. This shows that some fractions of phenol are fully photoconverted and mineralized into CO_2 at the very early stages of the photocatalytic conversion.