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Photocatalytic intrinsic reaction kinetics. II: Effects of oxygen concentration on the kinetics of the photocatalytic degradation of dichloroacetic acid

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Abstract

The effect of oxygen on the reaction kinetics of the photocatalytic oxidation of dichloroacetic acid at pH below the titanium dioxide isoelectric point (pH from 5 to 4) was studied. A kinetic scheme based on the direct hole attack to the dichloracetate ion in conjunction with the classical role of oxygen acting as an electron acceptor is proposed. Oxygen also intervenes in a direct addition reaction to one of the intermediate reaction products. Experiments were conducted in a well-mixed, small, flat plate reactor employing Aldrich titanium dioxide as the photocatalyst in the suspension mode and using polychromatic irradiation with energy in the range from 275 to 385 nm in wavelength. A complete mathematical model, including the effect of the absorbed radiation intensities and catalyst concentration was developed. Experimental data agree well with theoretical predictions employing just two kinetic parameters derived from the proposed reaction mechanism.

Keywords: Photocatalysis; Environments; Kinetics; Oxygen effect; Chemical reactors; Modeling

1. Introduction

Pollution control and pollutant abatement is a subject of increasingly growing importance. New technologies are being studied in substitution of established ones that normally do not produce the complete destruction of the existing toxic compounds. These technologies have received the denomination of destructive processes. Photooxidations have been proposed as a source of potential solutions and have been the subject of intense research efforts in the last years. With the proper operating conditions they produce a complete mineralization of almost all organic pollutants; hence photocatalytic oxidation has the advantage that usually transforms pollutants into water, carbon dioxide and mineral acids. They are part of the so called advanced oxidation technologies from which photocatalytic reactions constitute a significant fraction of the published work. Because of cost, availability, absence of toxicity, chemical stability and lack of selectivity, titanium dioxide has shown to be the most practical catalyst. It absorbs radiation at wavelengths below 385 nm, a fact that can even permit to use solar irradiation as a source of energy.

Activation of the photocatalyst by photon absorption produces a charge separation that renders electrons in the conduction band and leaves holes (positive charges) in the valence band. The mean-life of these electron–hole pairs before recombination is in the order of nanoseconds, a time in which they may be able to move to the catalyst surface and undergo reactions with some of the adsorbed species. Hence, electrons and holes that do not recombine may participate in reduction and oxidation reactions, respectively.

Photocatalytic oxidation processes are carried out in aerobic media; the adsorbed oxygen is the main electron acceptor and upon reaction gives rise to the formation of the

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superoxide radical $O_2^{\bullet -}$. According to Gerischer and Heller (1991) the reaction of the adsorbed oxygen with the photogenerated electron on the surface of the solid semiconductor is rather slow and could become the controlling step in photocatalytic oxidations. In spite of the rate, it is clear that this reaction is important to reduce the significance of electron–hole recombination and thus improving the effectiveness of the oxidative path with the hole participation. Consequently, if electrons are not removed the oxidative degradation of the organic compound could be stopped.

Besides the electron acceptor function, oxygen may participate directly in its molecular form in the oxidation path (Schwitzgebel et al., 1995; Wang and Hong, 2000; Vamathevan et al., 2002). It is interesting to note that this role is seldom considered in most of the proposed kinetic schemes. Moreover, the kinetic effect of the presence of oxygen in photocatalytic reactions has not been quantitatively accessed in the majority of the reported studies. Very often the work is carried out under the following conditions: (i) oxygen concentration is kept constant, (ii) oxygen is always used in excess of the stoichiometric demand and (iii) only the initial oxygen concentration is reported as part of the experimental information if it is reported at all.

A few authors have given an account of the oxygen effect under the apparent form of a Langmuir–Hinshelwood expression in the oxidation of phenol (Augugliaro et al., 1988; Okamoto et al., 1985; Stafford et al., 1997). Turchi and Ollis (1990) proposed a rather general model for the degradation of organic compounds, but they have assumed constant oxygen concentration. Alfano et al. (1997) used an extension of Turchi and Ollis proposal and performed the whole study under constant oxygen concentration and always in excess of the stoichiometric demand. The effect of changes in the oxygen concentration is not included in any of these two models. Almquist and Biswas (2001) proposed a model for the photocatalytic oxidation of phenol in aqueous solution that includes one term for the concentration of dissolved oxygen. Following the general approach employed by Turchi and Ollis and Alfano et al. they have assumed that the oxidation is exclusively produced by the $OH^\bullet$ radical attack formed on the surface of the solid catalyst as a result of the interaction of the hole with the OH^- ion; the direct attack by the hole as well as the direct participation of molecular oxygen in the reaction were not taken into account. Basically, all these reports are made at different initial concentrations of oxygen but the effect of the oxygen concentration evolution existing at each moment of the reaction has not been considered, i.e., none of these models consider that oxygen could be an independent variable in the derived kinetic expression.

More recently, Zalazar et al. (2005a), developed a model for the photocatalytic oxidation of dichloroacetic acid (DCA) with the assumption that direct attack by the hole is the significant oxidative step and that oxygen also participates in an addition reaction with one of the intermediate compounds proposed in the kinetic mechanism. Oxygen is also assumed to be used to trap electrons. However, oxygen concentration—in different initial levels—was also kept constant during the course of the reaction.

In this work the photocatalytic oxidation of DCA is carried out under variable oxygen concentration. Thus, oxygen is considered as one additional reactant that participates in the process and its disappearance rate is also included in the kinetic model. The experiment is completed only when oxygen concentration is very low; moreover, the reaction is carried out even beyond the time when complete consumption of the dissolved gas has occurred. The proposed kinetic model also includes the effect of the catalyst concentration as well as that of the rate of absorbed photons and, consequently, the derived expression incorporates the catalyst concentration and the local volumetric rate of photon absorption (LVRPA) as additional independent variables.

These results are important for those cases where the chemical oxygen demand (COD) of the polluted water is high and the process may become very dependent on the available oxygen in the fluid under treatment. The employed reactor operated with the non-porous, Aldrich titanium dioxide catalyst suspended in the liquid under very good stirring conditions. A lamp with significant emission between 275 and 580 nm was used. Not all of this radiation wavelength range is suitable for the photocatalytic reaction but this fact has been taken into account by the way in which the irradiation boundary condition has been incorporated into the radiation model.

2. A kinetic model

2.1. The reaction scheme

The following kinetic scheme is proposed (see below): The first step (numbered zero) is the catalyst activation till the moment in which electrons and holes are available for the reaction. Thus, in step No. zero ϕ_λ is assumed to be some kind of primary quantum yield that includes all physicochemical steps occurring from the photon absorption up to the moment when the generated electrons and holes reach the surface of the catalyst, i.e., it also includes the recombination reaction inside the catalyst *volume*. With this definition it is known that ϕ_λ must be equal or smaller than one.

Step number	Kinetic step	Parameter
(0)	$TiO_2 \xrightarrow{h\nu} (h^+ + e^-)_{\text{On the surface}}$	ϕ_λ
(1)	$\text{Site} + CHCl_2COO^- \rightleftharpoons CHCl_2COO^-_{ads}$	K_{DCA^-}
(2)	$CHCl_2COO^-_{ads} + h^+\|_{surf} \xrightarrow{k_2} CHCl_2COO^\bullet$	k_2
(3)	$CHCl_2COO^\bullet \xrightarrow{k_3} HCl_2C^\bullet + CO_2$	k_3
(4)	$\text{Site} + O_2 \rightleftharpoons O_{2_{ads}}$	K_{O_2}
(5)	$O_{2_{ads}} + HCl_2C^\bullet \xrightarrow{k_5} CHCl_2O_2^\bullet$	k_5
(6)	$2CHCl_2O_2^\bullet \xrightarrow{k_6} 2COCl_2 + H_2O_2$	k_6