Available online at www.sciencedirect.com
ScienceDirect
Journal of Catalysis 243 (2006) 1–6
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

Dependence of the kinetics of liquid-phase photocatalyzed reactions on oxygen concentration and light intensity

Andrew Mills [a,*], Jishun Wang [a], David F. Ollis [b]

[a] *Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, UK*
[b] *Chemical Engineering Department, North Carolina State University, Raleigh, NC 27695-7905, USA*

Received 3 June 2006; accepted 29 June 2006

Abstract

The initial kinetics of the oxidation of 4-chlorophenol, 4-CP, photocatalyzed by titania films and aqueous dispersions were studied as a function of oxygen partial pressure, P_{O_2}, and incident light intensity, I. The reaction conditions were such that the kinetics were independent of [4-CP] but strongly dependent on P_{O_2}—a situation that allowed investigation of the less-often studied kinetics of oxygen reduction. The observed kinetics fit a pseudo-steady-state model in which the oxygen is Langmuir-adsorbed on the titania photocatalyst particles before being reduced by photogenerated electrons. The maximum rate of photocatalysis depends directly on I^{β}, where $\beta = 1$ for films and 0.7 for dispersions of titania, indicating that the kinetics are dominated by the surface reactions of the photogenerated electrons and holes for the films and by direct recombination for the powder dispersions. Using the pseudo-first-order model, for both titania films and dispersions, the apparent Langmuir adsorption constant, K_{LH}, derived from a Langmuir–Hinshelwood analysis of the kinetics, appears to be largely independent of incident light intensity, unlike K_{LH} for 4-CP. Consequently, similar values are obtained for the Langmuir adsorption constant, K_{ads}, extracted from a pseudo-steady-state analysis of the kinetics for oxygen on TiO_2 dispersions and films in aqueous solution (i.e., ca. $0.0265 \pm 0.005\ kPa^{-1}$), and for both films and dispersions, oxygen appears to be weakly adsorbed on TiO_2 compared with 4-CP, at a rate that would take many minutes to reach equilibrium. The value of K_{ads} for oxygen on titania particles dispersed in solution is ca. 4.7 times lower than that reported for the dark Langmuir adsorption isotherm; possible causes for this difference are discussed.

Keywords: Photocatalysis; Oxygen; 4-Chlorophenol; Titania; Pseudo-first order

1. Introduction

The photocatalytic oxidation of organics dissolved in aqueous solution is a well-studied process [1–4] which can be summarized by the following reaction equation:

$$\text{organic} + O_2 \xrightarrow[\text{SC}]{h\nu \geqslant E_{bg}} H_2O + CO_2 + \text{mineral acids}, \tag{1}$$

where E_{bg} is the bandgap of the semiconductor (SC), invariably titanium dioxide, TiO_2. Research has shown that it is possible to mineralize completely a wide range and number of different organics via reaction (1), including dyes, surfactants, aromatics, insecticides, and pesticides [1–4].

In most studies of the kinetics of reaction (1), the observed variation in the initial rate of loss of the organic, $-r$, with organic concentration, C, is described well by a Langmuir–Hinshelwood-type kinetic equation [1–5],

$$-r = \frac{k_{LH}K_{LH}C}{(1 + K_{LH}C)}, \tag{2}$$

where k_{LH} and K_{LH} are the apparent maximum rate and adsorption constants, respectively. Initially, it was thought that only k_{LH} was dependent on the incident light intensity [1–5], which is directly related to the absorbed light intensity, and that K_{LH}, although not equal to—in fact, usually greater than—the actual Langmuir adsorption constant recorded in the dark, K_{ads}, was nevertheless related to K_{ads}. It is now recognized [6–11] that K_{LH} is also light intensity-dependent, at least in the case of the few organics that have had its kinetics probed in detail,

---

[*] Corresponding author. Fax: +44 141 548 4822.
E-mail address: a.mills@strath.ac.uk (A. Mills).

0021-9517/$ – see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2006.06.025

including 4-chlorophenol (4-CP) [11], phenol (PhOH) [7,10], acetophenone [8], and methyl viologen [9].

A number of different mechanisms have been put forward to account for this light-intensity dependence. Most notably, Emeline et al. [7,10] have proposed several that reveal a kinetic expression of the same form as Eq. (2), for example, an Eley–Rideal-based mechanism, where

$$k_{\mathrm{LH}} = aI \tag{3}$$

and

$$K_{\mathrm{LH}} = b/(dI), \tag{4}$$

and a LH-based model, where

$$k_{\mathrm{LH}} = aI/(e + dI) \tag{5}$$

and

$$K_{\mathrm{LH}} = (e + dI)K_{\mathrm{ads}}/dI, \tag{6}$$

where K_{ads} is the dark Langmuir adsorption constant, I is the incident light intensity, and a, b, d, and e are constants. A brief inspection of Eqs. (3) and (4) or (5) and (6) reveals an important prediction of these two models, namely that a plot of $1/K_{\mathrm{LH}}$ versus k_{LH} will yield a straight line with zero intercept. This prediction is well supported by the values of K_{LH} and k_{LH} determined by these authors using PhOH as the organic [7]. Unfortunately, it does not gain much support from some of the results of kinetic studies of reaction (1) carried out using other organics, such as methyl viologen [9] and 4-CP [11]. In the latter case, reanalysis of the values of K_{LH} and k_{LH} reported therein, determined for 4-CP in a study of the kinetics of reaction (1) as a function of incident light intensity and [4-CP], when plotted as $1/K_{\mathrm{LH}}$ versus k_{LH}, yields a straight line with a clear, positive intercept when either TiO_2 dispersions or films are used as semiconductor photocatalysts. This latter feature, apparently at odds with the models of Emeline et al. [7], is readily explained using the very simple kinetic model proposed recently by Ollis [6] in which the kinetics of adsorption/desorption of the key reactant, A (in this case an organic pollutant), are affected by the oxidation process, that is,

$$\mathrm{A(liquid)} \underset{k_{-1}}{\overset{k_1}{\Longleftrightarrow}} \mathrm{A(ads)} \tag{7}$$

and

$$\mathrm{A(ads)} \xrightarrow{k_{\mathrm{LH}}} \mathrm{products}, \tag{8}$$

so that a pseudo-steady state is set up. In this mechanism, it is assumed that reaction (8) involves oxidation of the organic by a photogenerated surface hydroxyl radical, and, because in the steady state the latter depends on the incident light intensity, it follows that

$$k_{\mathrm{LH}} = \alpha I^{\beta}, \tag{9}$$

where α is a proportionality constant and β is a constant with a value usually 0.5 under high-intensity conditions when recombination dominates or 1.0 under low-intensity conditions when the surface reaction dominates [6]. Note that the intensity threshold at which the transition from $\beta = 1$–0.5 occurs is a matter of some debate, with Emeline et al. [10] suggesting that under moderate illumination conditions ($\cong 10^{16}$ photons $\mathrm{cm}^2\,\mathrm{s}^{-1}$), β is always equal to 1 (i.e., the threshold is $\gg 10^{16}$ photons $\mathrm{cm}^2\,\mathrm{s}^{-1}$), whereas, in contrast, the work of many others [12–16] indicates that it might be much lower. For example, Egerton and King [12] suggested that the transition occurs at as low as 6×10^{14} photons $\mathrm{cm}^2\,\mathrm{s}^{-1}$ in the oxidation of isopropyl alcohol by rutile titania.

The pseudo-steady-state analysis of reactions (7) and (8) proposed by Ollis [6] reveals a kinetic expression for the rate of removal of the organic pollutant with the same form as Eq. (2), that is, a LH kinetics-type expression, where k_{LH} is given by Eq. (9) and

$$K_{\mathrm{LH}} = k_1/(k_{-1} + \alpha I^{\beta}). \tag{10}$$

This simple model predicts not only a light-intensity dependence for K_{LH} and k_{LH}, but also that a plot of $1/K_{\mathrm{LH}}$ versus k_{LH} will yield a straight line of gradient $= 1/k_1$ and a positive intercept of $1/K_{\mathrm{ads}}$, as found for the 4-CP/TiO_2 photocatalytic system and noted above. It also predicts that if the latter plot yields a zero intercept, as it does using the K_{LH} and k_{LH} data reported by Emeline et al. [7] in their study of the photocatalytic removal of PhOH, then this is a special case where $k_{-1} \ll I^{\beta}$, and, as a result, the mechanism effectively involves two sequential, irreversible steps: adsorption followed by reaction [6,10]. Thus, the simple pseudo-steady-state model of Ollis [6] appears to provide a ready interpretation of the observed variations in K_{LH} and k_{LH} as a function of incident light intensity reported to date for 4-CP, PhOH, methyl viologen, and acetophenone [7–11].

In the Ollis model [6], as in all of the kinetic models reported so far, it has been assumed that the kinetics of reduction of the other necessary reactant in reaction (1), namely oxygen, are not rate-determining. To ensure that this is the case in most kinetic studies of reaction (1), the reaction solution is usually saturated with oxygen, and the initial level of organic present is usually set at some very low value (typically <1 mM). However, it follows that it should be possible to probe the initial kinetics of oxygen reduction, and its dependence on light intensity, using a high initial concentration of the organic and low levels of oxygen. Curiously, given the intense interest in the kinetics of reaction (1) with respect to the oxidation of the organic, much less attention has been given to investigating the kinetics of oxygen reduction, even though there is evidence that the latter are slow and in some circumstances possibly rate-determining [17]. In this paper the results of such a study are reported for both TiO_2 dispersions and films and interpreted using the recent Ollis pseudo-steady-state kinetic model [6] for semiconductor photocatalysis.

2. Experimental

2.1. Materials

The TiO_2 used throughout this work was Degussa P25. The 4-CP (99%), along with all other chemicals, were obtained from Aldrich and used as received. The water used to make up solutions was deionized and double distilled. The gases used were of a high purity (>99%) and obtained from BOC. O_2/N_2 gas mixtures of different known composition, spanning the oxygen partial pressure (P_{O_2}) range of 0–101 kPa O_2 (total pressure = 101 kPa), were generated using a gas blender (model 852V5-S, Signal Instruments, Surrey, UK).

2.2. Methods

Details of the photochemical reactor have been reported elsewhere [18]. In brief, the photoreactor comprised two half-cylinders, each containing six 8 W Black Light Blue UVA lamps set against a half-cylinder aluminum reflector. Each of the lamps emitted a narrow range of UVA light, a maximum emission at 355 nm, and a half-band peak width of 20 nm; the number of UVA photons emitted per lamp into the 100 cm^3 reaction solution was found to be 6.4×10^{15} photons s^{-1} per lamp by ferrioxalate actinometry. The reaction vessel presented a total irradiated surface area of 120.5 cm^2. A variation in light intensity, over the range of $(6.4–0.5) \times 10^{15}$ photons $cm^{-2}\,s^{-1}$, was achieved by placing very fine metal mesh screens between the photoreactor and the photoreactor vessel.

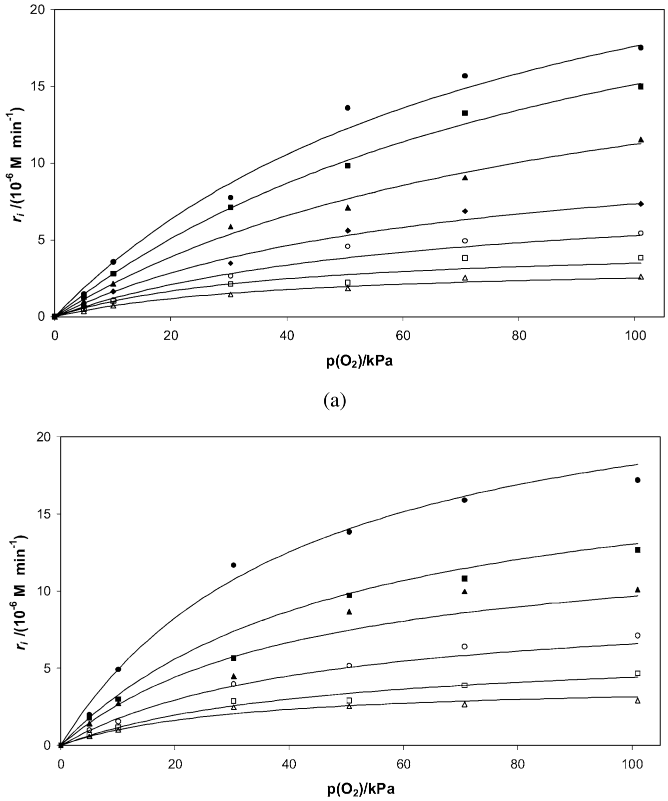
The photochemical reaction vessel was placed in the center of the photochemical reactor. The vessel comprised a 125-cm^3 borosilicate glass Dreschel bottle (4 cm i.d.) fitted with a rubber septum to allow withdrawal of samples from the reaction solution. The vessel had an outer water jacket thermostatted at 30 °C by a circulating water stream. In the TiO_2 film work, the reaction vessel was coated with TiO_2 using a wash coat procedure. The TiO_2 slurry used to coat the inside of the glass reaction vessel was 5% (w/v). After photoreactor was in contact with the stirred coating slurry for 30 min, the slurry was drained off, dried in a stream of air, and then dried in an oven at 100 °C for 1 h. The coat was then washed with excess water to remove any poorly attached TiO_2 and dried again in a stream of dry air. The process was repeated three times to produce a film with optimum activity [19]. The amount of TiO_2 attached to the glass was determined spectrophotometrically as 0.102 mg cm^{-2}, using a simple procedure involving washing the coating off the glass with a strong alkaline solution and measuring the "absorbance" of the resulting alkaline TiO_2 dispersion at 380 nm [20].

A typical reaction solution used in the photochemical reaction vessel comprised 10^{-3} M 4-CP dissolved in 100 cm^3 of 0.01 M $HClO_4$. Either a 0.5-g dm^{-3} dispersion or a 3-coat film of Degussa P25 TiO_2 was used as the photocatalyst. The reaction solution was continually purged with the oxygen/nitrogen gas mixture being tested and magnetically stirred (600 rpm) at least 15 min before, as well as throughout, any irradiation. The level of the oxygen in the gas stream was set using the calibrated gas blender. Initial results indicated that at a stirrer speed >400 rpm, with additional agitation provided by continuous N_2/O_2 purging, the rate of reaction was independent of stirrer speed when a 3-coat film of TiO_2 was used as the photocatalyst. Thus, under the typical reaction conditions used in this work, the observed kinetics were taken to be independent of mass transfer effects. The Thiele modulus for the system was evaluated as 0.043–0.028, implying little or no internal mass transfer effects for this system [21].

HPLC was used to determine the initial rate of disappearance of 4-CP, calculated from the measured decay of [4-CP] with irradiation time over the first 20% of the reaction. In the case of work using a TiO_2 dispersion, samples were taken from the reaction solution using a hypodermic syringe fitted with a 0.2-μm in-line filter to remove the TiO_2 particles. Details of the HPLC apparatus are described elsewhere [22].

3. Results and discussion

The initial rates of removal of a 10^{-3} M 4-CP solution via reaction (1), using a TiO_2 film and a dispersion were determined as a function of incident light intensity, I, varied over the range $(0.5–6.4) \times 10^{15}$ photons $cm^2\,s^{-1}$, with an ambient partial pressure of oxygen, P_{O_2}, which was also varied with each experiment over the range 5–100 kPa. The results of this work are illustrated in Figs. 1a and 1b for a TiO_2 film and dispersion, respectively. These results were analyzed using Eq. (2); the best fit values of K_{LH} and k_{LH}, determined at the different values of incident light intensity used for both TiO_2 films and dispersions, are given in Table 1. These optimized values were used to gen-



(a)

(b)

Fig. 1. Plot of the measured initial rate of removal of 4-CP ($[4\text{-CP}]_0 = 1$ mM) as a function of P_{O_2}, using different relative incident intensities of UVA using TiO_2 films (a) and dispersions (b). In (a) the relative incident light intensities, I, were (from top to bottom): 1, 0.713, 0.616, 0.388, 0.269, 0.143 and 0.084, respectively. In (b) the values of I used were (from top to bottom): 1, 0.713, 0.616, 0.269, 0.143 and 0.084, respectively.

Table 1
LH parameters, k_{LH} and K_{ads}^{app} for the photocatalytic destruction of 4-CP mediated by TiO_2 film or dispersion[a]

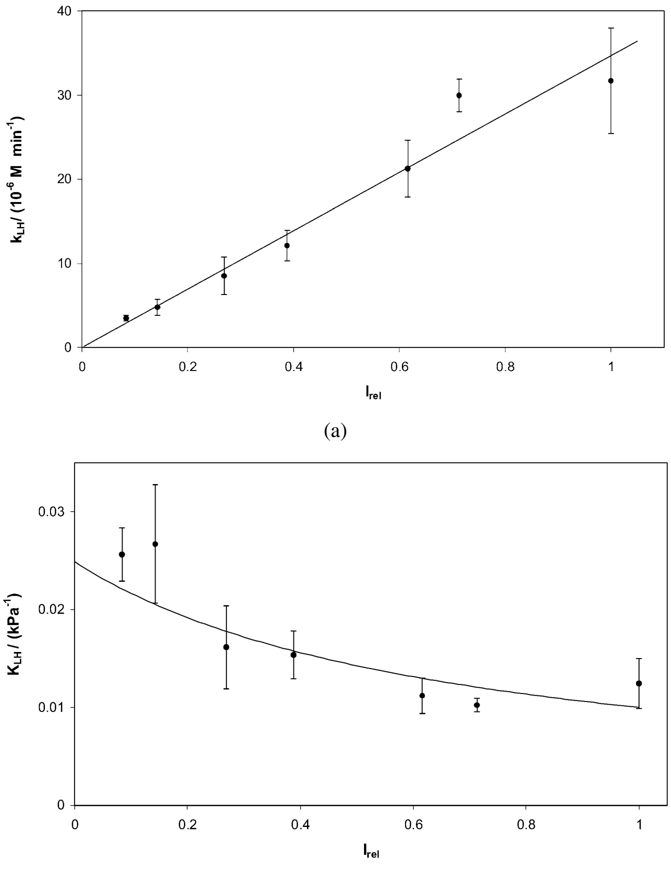
I_{rel}	TiO_2 film		TiO_2 dispersion	
	k_{LH} (μM min^{-1})	K_{LH} (MPa^{-1})	k_{LH} (μM min^{-1})	K_{LH} (MPa^{-1})
1	31.7 (±6.3)	12.5 (±2.5)	25.9 (±2.1)	23.5 (±2.1)
0.713	30.0 (±1.9)	10.2 (±0.7)	17.5 (±3.5)	20.1 (±4.3)
0.616	21.3 (±3.3)	11.2 (±1.8)	13.7 (±3.9)	23.9 (±7.7)
0.388	12.1 (±1.8)	15.4 (±2.4)	–	–
0.269	8.5 (±2.2)	16.2 (±4.2)	9.5 (±2.0)	22.6 (±5.0)
0.143	4.8 (±0.9)	26.7 (±6.1)	6.4 (±1.0)	22.2 (±4.9)
0.084	3.5 (±0.3)	25.6 (±2.7)	4.1 (±0.6)	33.0 (±5.7)

[a] Derived from studies of the initial rate of removal of 4-CP as a function of P_{O_2} at different relative light intensities and use of Eq. (2) to extract values for k_{LH} and K_{abs}^{app} at the different light intensities.

erate the solid lines of best fit to the data illustrated in Figs. 1a and 1b. Plots of these data in the form of K_{LH} and k_{LH}, as functions of relative incident light intensity, I_{rel}, for a TiO_2 film are given in Figs. 2a and 2b, respectively. Similar plots of the data for a TiO_2 dispersion are given in Figs. 3a and 3b.

Assuming a flux-matching model [23], the photogenerated hole and electron transfer rates at the surface of the TiO_2 particles will be the same at steady state. For the observed kinetics for 4-CP removal to be dependent on the O_2 reduction kinetics but independent of the concentration of 4-CP, C, from Eq. (2), the value of C must be sufficiently high so that $K_{LH}C \gg 1$. Previous work on this system [11] revealed that K_{LH} for 4-CP varied from 9 (low intensity) to 2 mM^{-1} (high intensity) M^{-1} over the incident light intensity range used in this work. Thus, in most of the work reported here, in which the initial concentration of 4-CP used was fixed at 10^{-3} M, $K_{LH}C \gg 1$ and the overall initial kinetics of 4-CP removal will depend mainly on the rate at which the oxygen is reduced and will be largely independent of [4-CP].

In the above situation, the key reactant in reaction (8), A, is oxygen and involves the reduction of adsorbed oxygen by trapped photogenerated electrons, possibly at Ti(III) sites. As with the level of surface hydroxyl radicals responsible for the oxidation of the organic, the steady-state level of trapped electrons will depend on the incident light intensity, and it follows that k_{LH} will be related to incident light intensity by an equation of the same form as Eq. (9). Therefore, it is not surprising that a pseudo-steady-state analysis of this low O_2 concentration–high 4-CP concentration system, in which P_{O_2} and the incident light intensity are varied, reveals a kinetic expression identical to Eq. (2), in which the parameters k_{LH} and K_{LH} are related to I by Eqs. (9) and (10), respectively. Note, however, that in this case the values of k_1 and k_{-1} refer to the Langmuir adsorption of oxygen (not 4-CP) on TiO_2 and thus might be expected to be quite different than those reported previously for 4-CP [11].



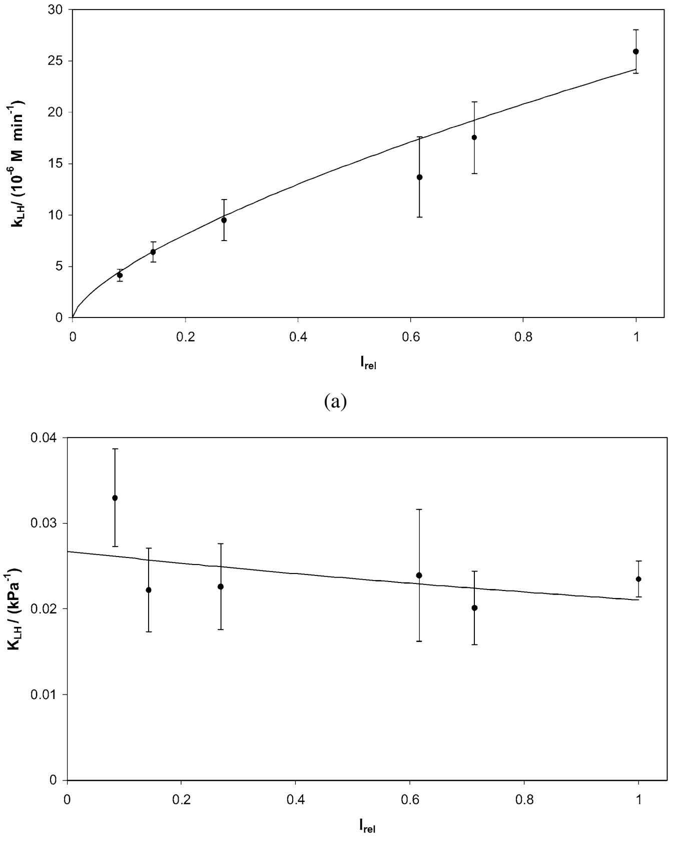
(a)

(b)

Fig. 2. Variation in (a) k_{LH} and (b) K_{LH}, calculated from rate data using Eq. (2), as a function of a relative incident light intensity, I_{rel} ($I_{rel} = 1 \equiv 6.4 \times 10^{15}$ photons $cm^{-2}\,s^{-1}$), for the initial photocatalytic removal of 4-CP sensitized by a TiO_2 film (0.102 mg cm^{-2}, 120.5 cm^2). In both (a) and (b) the solid lines have been calculated using Eqs. (2), (9) and (10) of the pseudo-steady-state model and the optimized fit values, for α, k_1, k_{-1} and θ, given in Table 2.

The variations in K_{LH} and k_{LH} as a function of I in this low [O_2]-high [4-CP] system, determined for TiO_2 films and dispersions, are illustrated in Figs. 2 and 3, respectively, and fit well with the pseudo-steady-state kinetic model of Ollis [6] and the associated key processes (7) and (8). Indeed, the solid lines in the latter figures were generated using Eqs. (9) and (10) derived from this model, and the optimized best-fitting parameters for k_1, $k_{-1}\alpha$, and β are given in Table 2. The kinetics of oxygen reduction by TiO_2 films and dispersions appear to depend on I ($\beta = 1$ and 0.7, respectively) in much the same way as found for the removal of 4-CP ($\beta = 1$ and 0.6, respectively). As predicted by the Ollis kinetic model [6], for both TiO_2 films and dispersions, plots of $1/K_{LH}$ versus k_{LH} yield positive correlations with positive intercepts, as illustrated by the plots of the respective sets of data in Figs. 3a and 3b.

The intercept values of the lines of best fit in the latter plots reveal very similar values for K_{ads} (ca. 0.0265 ± 0.005 kPa^{-1}). This value, at 30 °C, is ca. 4.7 times lower than the value for the Langmuir adsorption constant for O_2 on TiO_2, determined in the dark [i.e., K(O_2 dark)], reported by Rideh et al. [24] at 25 °C for P25 TiO_2 in aqueous solution. However, K_{ads} would



(a)

(b)

Fig. 3. Variation in (a) k_{LH} and (b) K_{LH} as a function of I_{rel} for the photocatalytic removal of 4-CP sensitized by a TiO_2 dispersion (0.5 g dm^{-3}; 100 cm^3). In both (a) and (b) the solid lines have been calculated using Eqs. (2), (9) and (10) and the optimized fit values, for α, k_1, k_{-1} and θ, given in Table 2.

Table 2
Optimized fit parameters to the oxygen kinetic data, based on the pseudo-steady-state model

	θ[a]	α (μM 4-CP min^{-1})[b]	k_{-1}/k_1 (kPa)[c]	k_1 (μM 4-CP min^{-1} kPa^{-1})[c]	k_{-1} (μM 4-CP min^{-1})[c]	K_{ads} (kPa^{-1})[c]
TiO_2 film	0.96 (±0.06)	34.4 (±3.4)	40 (±9.4)	0.58 (±0.17) 0.066*	23.36 (±8.7) 35**	0.026 (±0.005)
TiO_2 dispersion	0.68 (±0.05)	24.2 (±2.8)	38 (±5)	2.4 (±2.1)	90 (±80)	0.027 (±0.004)

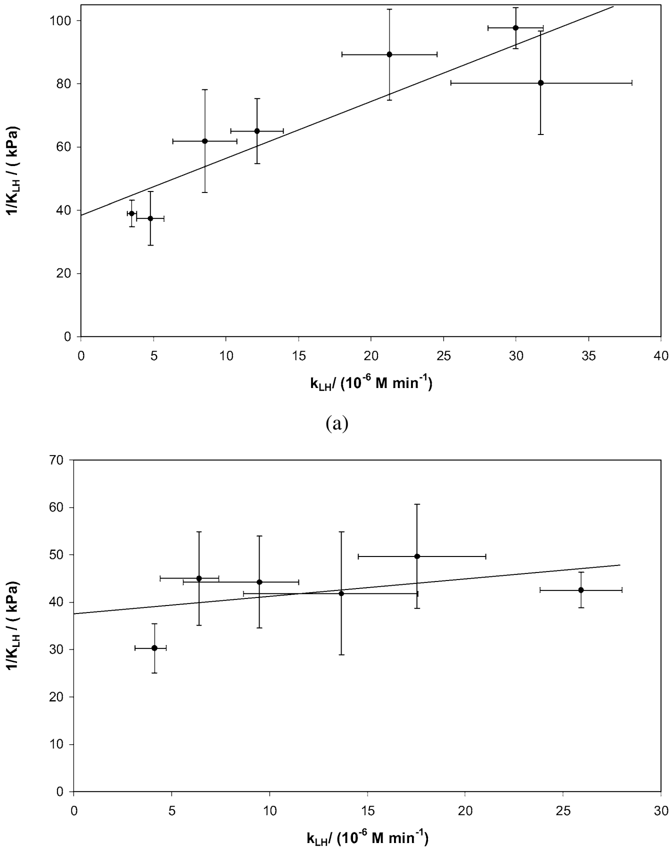
[a] Derived from plots of $\log k_{LH}$ vs I_{rel}.

[b] Derived from plots of k_{LH} vs I_{rel}^{θ}.

[c] Derived from plots of $1/K_{ads}^{app}$ vs k_{LH}.

* Units: min^{-1}.

** Units: μM O_2 min^{-1}.



(a)

(b)

Fig. 4. Plot of $1/K_{LH}$ vs k_{LH} calculated using Eq. (2) for reaction (1) using 4-CP as the organic, sensitized by (a) a TiO_2 film and (b) a TiO_2 dispersion. In both (a) and (b) the solid lines are the lines of best fit based on Eq. (10) and the optimized fit values, for α, k_1, k_{-1} and θ, given in Table 2.

be expected to be lower at the higher temperature used in this work and K_{ads} also may be dependent on pH and ionic strength. In this work a pH of 2 ($HClO_4$) was used, whereas no details of pH or ionic strength are given in the work of Rideh et al. [24]. Finally, it should be noted that Ollis [6] suggested two possible reasons why in a photocatalytic system, $K_{ads} \neq K$ (O_2 dark). The first of these is that there are far fewer active catalyst sites than total surface adsorption sites; the second is that the active sites exist only under illumination. It is not possible at this stage to determine which, if either, of the above is appropriate here; further work is needed.

From the results in Figs. 3b and 4b, it appears that the apparent adsorption constant for oxygen on TiO_2 films and, more strikingly, dispersions is largely independent of the incident light intensity over the range used. This is in notable contrast to the variation of K_{LH} for the adsorption of 4-CP, and other organics, as a function of I observed by us and others [6–11]. The independence of K_{LH} (O_2) on I appears to be due to a high rate of desorption, k_{-1}, so that $k_{-1} \gg \alpha I^{\beta}$ in the pseudo-steady-state model (see Eq. (10)). In other words, the reduction of O_2 by TiO_2 is relatively slow, so that an adsorption equilibrium is nearly achieved, given that the condition for validity of the Langmuir–Hinshelwood rate forming is $k_{LH} \ll k_{-1}$.

In an elegant study of the kinetics of O_2 reduction by TiO_2 films using a channel flow method, Ahmed et al. [14] found a value of $\beta = 0.56$, using incident light intensities much greater (>23 times) than those reported here. Using the same method, the same group [8] also found no evidence of intermediates of the O_2 reduction process and concluded that this occurs predominantly via a 4-electron process. However, the relationship between the removal of 4-CP and the consumption of oxygen is complicated by the likelihood that some will be due to its reaction with the organic radicals produced via the hydroxyl radical attack. In contrast, the removal of 4-CP occurs via the reaction with a $OH^\bullet$ radical, a one-hole process to produce either hydroquinone or 4-chlorocatechol. Thus, it is no surprise to note that the work of Fonseca et al. [15], on a scanning electrochemical microscopy investigation of reaction (1) using TiO_2 films and 4-CP as the test pollutant, indicates that in the initial stages of reaction, the rate of oxygen consumption is ca. 1.5 times that of 4-CP removal. If this initial reaction stoichiometry is assumed to apply here, and given that an aqueous solution saturated with oxygen to a partial pressure of 101 kPa has a dissolved oxygen concentration of ca. 1.3 mM at 25 °C, then it is possible to convert the cumbersome units for k_1 and k_{-1} given in Table 2 into those that relate solely to oxygen, that is, min^{-1} and $\mu\text{M O}_2\ \text{min}^{-1}$, respectively. The values for k_1 and k_{-1} in these latter units for TiO_2 films are $0.066\ \text{min}^{-1}$ and $35\ \mu\text{M O}_2\ \text{min}^{-1}$, respectively (see Table 2). The former is similar to that estimated for the adsorption of 4-CP on TiO_2 films, whereas the latter is about 4 times larger than its 4-CP counterpart; that is, oxygen appears to be more weakly adsorbed than 4-CP. The adsorption of other simple molecules, such as dichloroethane (DCE) on TiO_2 are also similarly slow, ca. $0.084\ \text{min}^{-1}$ for DCE [6], and it is not too surprising that O_2, which is weakly adsorbed onto TiO_2, has a low adsorption rate constant. However, if the assumptions made in calculating the value of k_1 are correct, this highlights the need in such work to equilibrate the reaction solution with oxygen for at least a few minutes to achieve an initial, fully equilibrated system. It also follows that in a photocatalytic system based on reaction (1), in which the rate of organic removal was rapid, the rate-determining step would most likely be the rate of adsorption of oxygen. That this does not appear to be the case in this work indicates that the organic, 4-CP, is not easily oxidized.

4. Conclusion

The pseudo-steady-state model proposed by Ollis for rationalizing the kinetics of organic removal by semiconductor photocatalysis in aqueous solution appears to be also appropriate in the analysis of the kinetics of the concomitant reduction of oxygen [6]. Using this model, similar values were obtained for the Langmuir adsorption constant, K_{ads}, for oxygen on TiO_2 particles and films in aqueous solution. Oxygen appears to be weakly adsorbed on TiO_2 at a rate that would take many minutes to reach equilibrium. In contrast, the rate constant for desorption, k_{-1}, appears high, so that overall, $K_{\text{LH}} \cong K_{\text{ads}}$ for both films and dispersions and is largely independent of I over the incident intensity range used in this work. Further experiments on this and other systems will help prove, or disprove, the general applicability of the pseudo-steady-state model for semiconductor photocatalysis recently proposed by Ollis. For the moment, it appears that this model provides a simple rationale for the observed kinetics associated with the oxidation of the organic and concomitant reduction of oxygen, that is, the reactions that underpin most examples of semiconductor photocatalysis and reaction (1). As such, this model is an encouraging advance from most previous kinetic models.

References

[1] A. Mills, S. LeHunte, J. Photochem. Photobiol. A 108 (1997) 1.
[2] D.F. Ollis, E. Pelizetti, N. Serpone, in: N. Serpone, E. Pelizetti (Eds.), Photocatalysis: Fundamentals and Applications, Wiley–Interscience, New York, 1989.
[3] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69.
[4] M.A. Fox, M.T. Dulay, Chem. Rev. 93 (1993) 34.
[5] C. Turchi, D.F. Ollis, J. Catal. 122 (1990) 178.
[6] D.F. Ollis, J. Phys. Chem. B 109 (2005) 2439.
[7] A.D. Emeline, V.K. Ryabchuk, N. Serpone, J. Photochem. Photobiol. A 133 (2000) 89.
[8] Y. Xu, C.H. Langford, J. Photochem. Photobiol. A 133 (2000) 67.
[9] I. Martyanov, E. Savinov, J. Photochem. Photobiol. A 134 (2000) 219.
[10] A.D. Emeline, V.K. Ryabchuk, N. Serpone, J. Phys. Chem. B 109 (2005) 19515.
[11] A. Mills, J. Wang, Z. Phys. Chem. 213 (1999) 49.
[12] T.A. Egerton, C.J. King, J. Oil Col. Chem. Assoc. 62 (1979) 386.
[13] U. Stafford, K.A. Gray, P.V. Kamat, J. Catal. 167 (1997) 25.
[14] S. Ahmed, S.M. Fonseca, T.J. Kemp, P.R. Unwin, J. Phys. Chem. B 107 (2003) 5892.
[15] S.M. Fonseca, A.L. Barker, S. Ahmed, T.J. Kemp, P.R. Unwin, Phys. Chem. Chem. Phys. 6 (2004) 5218.
[16] G. Al-Fayyed, J.C. D'Oliveira, P. Pichat, J. Photochem. Photobiol. A 58 (1991) 99.
[17] H. Gerischer, A. Heller, J. Phys. Chem. B 95 (1991) 5261.
[18] A. Mills, R.H. Davies, D. Worsley, Chem. Soc. Rev. (1993) 417.
[19] A. Mills, J. Wang, J. Photochem. Photobiol. A 118 (1999) 53.
[20] A. Mills, D. Worsley, R.H. Davies, Chem. Commun. (1994) 2677.
[21] O. Levenspiel, Chemical Reaction Engineering, third ed., Wiley, New York, 1999.
[22] A. Mills, S. Morris, R.H. Davies, J. Photochem. Photobiol. A 70 (1993) 183.
[23] J.M. Kesselman, G.A. Shreve, M.R. Hoffmann, N.S. Lewis, J. Phys. Chem. 98 (1994) 13385.
[24] L. Rideh, A. Behrer, D. Ronze, A. Zoulalian, Catal. Today 48 (1999) 357.