

Variation of Langmuir adsorption constant determined for TiO₂-photocatalyzed degradation of acetophenone under different light intensity

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Abstract

The Langmuir–Hinshelwood (L–H) kinetic model has been used to describe semiconductor photocatalysis. In this report, the L–H rate constant (k_{L-H}) and the Langmuir adsorption constant (K) have been determined under different light intensity for the photocatalytic degradation of poorly adsorbed acetophenone over TiO₂ of Degussa P25 in aqueous medium (pH 6.2). The result shows that K decreases when the irradiation is performed at higher light intensity, while k_{L-H} increases expectedly. It is also demonstrated that the initial time interval selected for the initial rate calculation is quite critical to the final determination for the constants. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Titanium dioxide particles have been used as an efficient photocatalyst for the complete mineralization of various organic compounds in water. It has been postulated that the photocatalytic degradation (PCD) is initiated with attack of the target substrate by active oxygen species such as OH• and O₂•⁻ that are generated from the irradiated TiO₂ [1–4]. For a given system, the initial PCD rate (R_0) has been observed to be a function of the substrate initial concentration (C_0). A linear plot of R_0^{-1} versus C_0^{-1} is often obtained, that gives k_{L-H} as the Langmuir–Hinshelwood (L–H) rate constant and K as the Langmuir adsorption constant of the substrate in the PCD reaction (Eq. (1)). The similarity in this experimentally linear plot has led to an assumption that the PCD primary process occurs between the adsorbed substrate and the adsorbed reactive species on the photocatalyst's surface.

$$R_0 = \frac{k_{L-H} K C_0}{1 + K C_0} \quad \text{or} \quad R_0^{-1} = \frac{1}{k_{L-H} K C_0} + \frac{1}{k_{L-H}} \quad (1)$$

If K truly reflects the adsorption affinity of a substrate for a surface that has no changes upon the light irradiation, K

determined in PCD should be the same as its counterpart measured in the dark from the Langmuir adsorption isotherm. However, there have been several reports showing that K determined in PCD is always larger than the K measured separately in the dark: about 12 times has been observed for weakly adsorbed benzyl alcohol and chlorobenzyl alcohol [4–6], and about 220 times for 4-chlorophenol [7]. Even for the same substrate of phenol or 4-CP in PCD over Degussa P25 TiO₂, a significantly different K value has been also reported by several research groups [2,8,9]. The apparent variability in K may relate to the changes in the adsorptive sites of the TiO₂ surface upon the band-gap irradiation. Then it would be necessary to make a study of the light intensity effect on the K in PCD for a given system.

In this work, the adsorption constant K has been measured under different light intensity for the PCD of poorly adsorbed acetophenone over a popular TiO₂ photocatalyst, Degussa P25. This organic substrate has been employed as a model compound in our system for the activity comparison among various supported-TiO₂ photocatalysts [10,11], partially because of its spectrum that is insensitive to the medium pH. The dark adsorption isotherm was measured, and then the PCD study was carried out in the concentration range of the Langmuir adsorption. The result shows that K varies with the light intensity, and the value is sensitive to the method used for the initial rate calculation.

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2. Experimental section

2.1. Chemicals

Acetophenone (AP, 99%) and 2-hydroxyacetophenone (2HAP, 99%) were purchased from Aldrich and used directly as received. The titanium dioxide photocatalyst was Degussa P25 TiO₂ with a BET surface area of 49 m² g⁻¹. Milli-Q water was used throughout this study, and acetonitrile was HPLC grade.

2.2. Dark adsorption

A 100 cm³ of AP aqueous solution of various initial concentration (0–8.25 × 10⁻⁴ mol dm⁻³ at natural pH) and 1.00 g of TiO₂ powder was mixed in a capped plastic bottle (this bottle had no detectable adsorption toward acetophenone substrate). The suspension was equilibrated at 20 ± 2 °C in a thermostatic shaker for more than 12 h. The slurry was then filtered through a Millipore filter, and the clear filtrate was analyzed by HPLC to obtain the equilibrium concentration C_{eq} . At the same time, a blank sample without addition of TiO₂ was also carried out to confirm the initial concentration C_0 . Then the amount of adsorption, n (mol g⁻¹), was calculated from the decrease in the solute concentration ($\Delta C = C_0 - C_{eq}$). All the samples were covered by an aluminum paper to avoid light illumination.

2.3. Photodegradation

The photochemical reactor was a glass vessel with a flat quartz window (1 cm in diameter) for light illumination. During the experiment, the reactor jacket was circulated by a thermostatic water bath to maintain the reactor at 20 ± 2 °C. The light source was a 200 W Xe-Hg lamp (P.T.I, USA) with a cut-off filter at 350 nm as to avoid direct photolysis of acetophenone [12]. The light intensity was controlled with a 250 LPS power supply. Before irradiation, a suspension containing a 100 cm³ of AP aqueous solution and a 100 mg of TiO₂ was stirred constantly for 2 h to ensure the equilibrium of dark adsorption (no difference was observed between 2 and 12 h of the equilibrium time for the dark adsorption). At each interval of 5 min, a 2 cm³ of the illuminated suspension was withdrawn by glass syringe, filtered through a Millipore filter, and the filtrate was analyzed by standard HPLC method.

The light intensity was roughly estimated by ferrous oxalate actinometry. Since a cut-off filter of 350 nm was used in the present study, the light entered into the reactor was mainly centered at wavelengths (λ_i) 366, 405, 434, 492, 546, and 572 nm with a relative area (A_i) of 21.5, 13, 17, 8.5, 22, and 18%, respectively (the data was provided by P.T.I). Then the total intensity was estimated by a formula of $I_{total} = n_{Fe^{2+}} / \sum A_i \Phi_i$, where Φ_i was the quantum yield of Fe²⁺ at λ_i . The relative intensity effective to TiO₂ excita-

tion was calibrated by $A_{366} I_{total}$, and the obtained result was 0.81, 1.40, and 2.14 × 10⁻⁷ einstein s⁻¹ for the lamp output at 80, 120, and 185 mW, respectively.

3. Results and discussion

3.1. Dark adsorption

In aqueous medium, acetophenone (AP) has rather weak adsorption on the TiO₂ (Fig. 1). There seems two adsorption regions displayed in the adsorption isotherm: one at $C_{eq} < 3 \times 10^{-4}$ mol dm⁻³ appearing of the Langmuir type, and another at $C_{eq} > 3 \times 10^{-4}$ mol dm⁻³ probably taken as the multilayer adsorption. By the Langmuir plot (the insert in Fig. 1) for the first region, the monolayer coverage and the Langmuir adsorption constant K [13] are obtained, that is 1.25 × 10⁻⁶ mol g⁻¹ and 2.44 × 10⁴ dm³ mol⁻¹, respectively. For the PCD studies in the following, the concentration range was then selected at $C_{eq} < 3 \times 10^{-4}$ mol dm⁻³.

3.2. Apparent adsorption constant measured in PCD

Fig. 2A shows the bulk concentration of AP (retention time, RT at 2.1 min) changing with the irradiation time, while Fig. 2B is the corresponding plot for the main intermediate 2HAP (RT=2.5 min) that was detected in the same sample as shown in Fig. 2A (other minor intermediates were also detected at RT=1.2 and 1.4 min, respectively, but they displayed the same trend as 2HAP). We see that the AP substrate degrades continuously with a simultaneous formation of the intermediates, whose concentration firstly increases up to the maximum and then decays with the reaction time. It is also evident from Fig. 2 that the main intermediate accounts for only about 10% in moles of the AP lost even in the first 5 min of the run. This indicates that the intermediate 2HAP, once formed, also experiences the photocatalytical degradation, and the intermediates of several dihydroxyace-

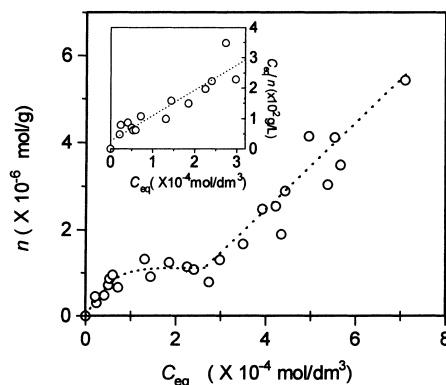


Fig. 1. Adsorption isotherm of acetophenone on a TiO₂ measured at 20 °C. The insert is the Langmuir plot of C_{eq}/n vs. C_{eq} in the region of $C_{eq} < 3 \times 10^{-4}$ mol dm⁻³.

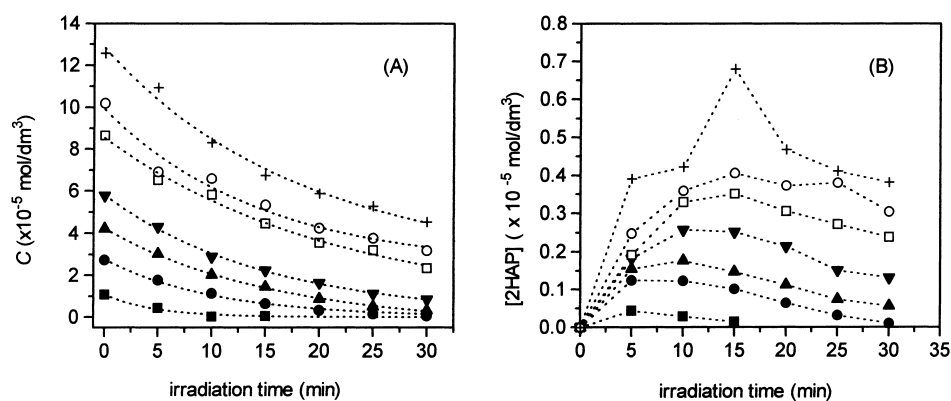


Fig. 2. Concentration of the substrate AP (A) and one of the formed intermediates 2HAP (B) as a function of irradiation time (light intensity, $I=2.14 \times 10^{-7}$ einstein s^{-1}). Each legend corresponds the run using different initial AP concentration.

tophenone isomers have been identified by GC-MS in our previous report [12]. Obviously, it would be then improper to use the formation rate of this intermediate to evaluate the L–H rate constant and adsorption constant by Eq. (1) [5,7].

The decay in the AP concentration (C) appears exponential to the time (t). Then the rate constant of pseudo-first-order (k_{1st}) was calculated by a linear plot of $\ln C$ versus t , and is summarized as a function of initial concentration C_0 in Table 1. It can be seen that the k_{1st} decreases with the initial concentration, quite common in the PCD studies for many other organic compounds in a dilute solution [1,2,4,7]. The concentration-dependence of the k_{1st} indicates that the PCD reaction of AP is not really first order, even though the plot linearity of $\ln C$ versus t is quite well. In fact, the pseudo-first-order can be resulted from the L–H rate equation (Eq. (1)) only when the term KC is much smaller than 1 (and the terms for the intermediates is also not considered). Therefore, it is necessary to determine the rate constant k_{L-H} (Eq. (1)), instead of k_{1st} , when the substrate is used as the model compound for a reliable comparison in activity among different photocatalysts [10,14,15].

Eq. (1) is often applied to evaluate the L–H rate constant k_{L-H} and the adsorption constant K , but it is valid only at initial PCD stage. During the PCD process, the intermediate are formed, and their KC terms must be included in the L–H

rate equation even when their adsorption on the TiO_2 surface may be rather weak. For simplicity, however, it is better to employ the initial PCD rate for the application of Eq. (1). This can be done by an assumption that at initial time interval the intermediate concentration can be considered to be negligible. Definitely such an initial time interval should be shorter as possible. In the practice, however, a considerable error in the analysis could be made easily for such a small conversion of the substrate.

In some reports such as [4,6,8], the initial rate was calculated from the first 20 min, or from the first 10–20% loss of the substrate. It is possible that such a treatment might bring the different K value among laboratories, and might also give K larger than that measured in the dark. It then stimulates us to calculate the initial rate R_0 at each time interval Δt from 5 to 30 min, and then plot R_0 as a function of the initial concentration C_0 for each Δt (Fig. 3), and finally make each plot of R_0^{-1} versus C_0^{-1} (Fig. 4) so as to see whether there is difference in the final k_{L-H} and K among the different trials. The AP concentration decreases non-linearly with the irradiation time (Fig. 2), and it is difficult to extrapolate the initial rate at $\Delta t=0$.

It can be seen that the R_0 versus C_0 plot (Fig. 3) displays the Langmuir-type saturation, similar to the observation in most of the PCD kinetic studies [1]. However, the data appears more highly scattered as the initial rate R_0 is calculated at shorter initial time interval Δt . Consequently, this trend is also reflected in the final plot of R_0^{-1} versus C_0^{-1} (Fig. 4), where the linearity becomes much better at longer Δt . When a linear regression is made to the plot of Fig. 4, a quite different slope appears from one to another, while the intercept looks approximately the same. By Eq. (1), the L–H rate constant k_{L-H} and the Langmuir adsorption constant K can be obtained. These constants are summarized in Fig. 5 as a function of initial time interval Δt (solid square, $I=2.14 \times 10^{-7}$ einstein s^{-1}). Fig. 5 also includes the results determined for two different light intensities of $I=0.81 \times 10^{-7}$ einstein s^{-1} (open cir-

Table 1
Pseudo-first-order rate constant (k_{1st}) at various initial concentration of AP (C_0) (see Fig. 1A)

C_0 ($\mu\text{mol dm}^{-3}$)	k_{1st} (min^{-1})
1.08	0.237
2.74	0.128
4.23	0.0873
5.79	0.0643
8.66	0.0416
10.19	0.03767
12.57	0.0347

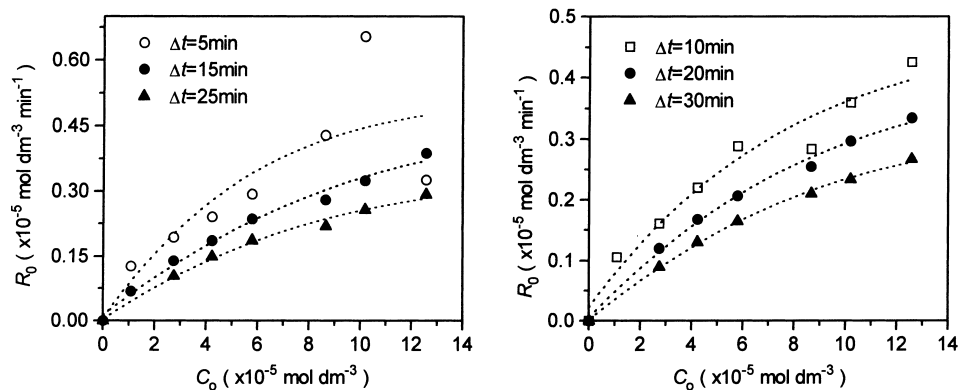


Fig. 3. Dependence of the initial rate (R_0) on the initial concentration (C_0). The R_0 was calculated from Fig. 2A at each time interval of $\Delta t=5, 10, 15, 20, 25,$ and 30 min, respectively.

cle) and 1.40×10^{-7} einstein s^{-1} (solid circle) following the same procedures as for $I=2.14 \times 10^{-7}$ einstein s^{-1} .

There are two characters which appears in the Fig. 5A. The first is that under a stationary light intensity the K value decreases regularly with the time interval Δt , and another is that the K value increases with the decrease in the light

intensity (the data obtained at the lowest I appears more seriously scattered, due to the analysis error for this smallest concentration change among three cases). The result shows that K is a function of light intensity, and the initial time interval Δt chosen for the R_0 calculation is quite critical to the final determination of the absorption constant K . As

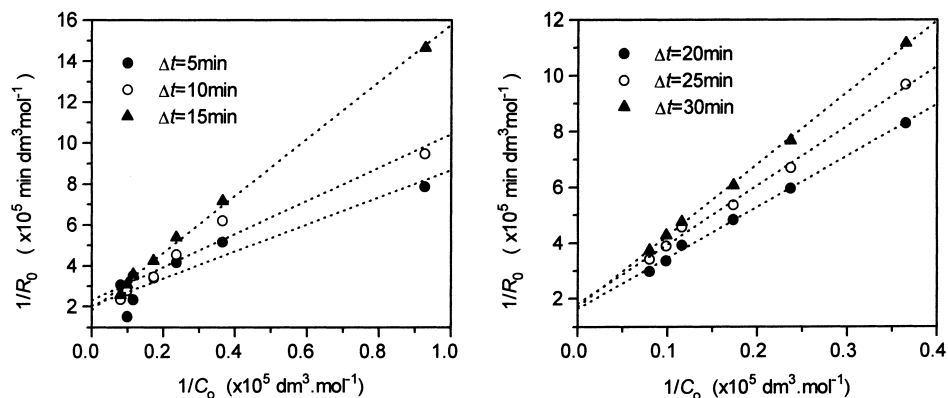


Fig. 4. Plot of the reversal initial rate (R_0^{-1}) vs. the reversal initial AP concentration (C_0^{-1}) for each initial time interval Δt . The data was adopted from Fig. 3.

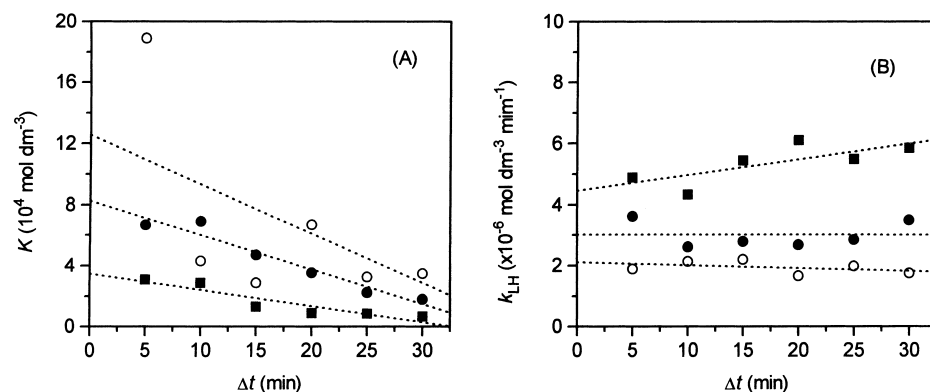


Fig. 5. Effect of initial time interval Δt on the adsorption constant K (A) and rate constant k_{L-H} (B) for three cases measured under different light intensity of $I=0.81$ (open circle), 1.40 (solid circle) and 2.14 (solid square) $\times 10^{-7}$ einstein s^{-1} , respectively.

discussed early, the cause for this K decreasing with Δt has a relation with the intermediate terms that can not be eliminated from Eq. (1) at longer Δt . Therefore, the K value may be obtained by linear extrapolation to $\Delta t=0$ (dotted line in Fig. 5, where for the curve of $I=0.81 \times 10^{-7}$ einstein s^{-1} three initial bad points were eliminated for this linear extrapolation). By this arbitrary treatment, the K value for $I=0.81, 1.40$ and 2.14×10^{-7} einstein s^{-1} is 12.6, 8.33 and 3.46×10^4 $\text{dm}^3 \text{mol}^{-1}$, respectively, all of which are larger than the Langmuir adsorption constant K of 2.44×10^4 $\text{dm}^3 \text{mol}^{-1}$ measured separately in the dark.

Compared to the K , the L–H rate constant k_{L-H} appears less sensitive to the initial time interval Δt (Fig. 5B). By an arbitrary linear regression to the plots, the k_{L-H} value at $\Delta t=0$ may be obtained as 2.11, 3.01 and 4.46×10^{-6} $\text{mol dm}^{-3} \text{min}^{-1}$ for $I=0.81, 1.40$ and 2.14×10^{-7} einstein s^{-1} , respectively. The k_{L-H} increases with increase in the light intensity, as predicted by Ollis, Mills and their collaborators [3,16].

4. Conclusion

The present study for the PCD of acetophenone has shown that the initial rate calculated at longer initial time interval Δt will result in a smaller value of the adsorption constant K . This would be referable to some reports about K [4,6,8] where the initial rate was calculated from the first 20 min, or from the first 10–20% loss of the substrate. It has been also observed that K is a function of the light intensity for the irradiation. Definitely, the electronic properties of the TiO_2 surface will undergo dramatic changes upon illumination, altering the adsorption sites as well. The K measured under

irradiation is thus different from the K measured in the dark. However, it seems difficult to explain why K changes inversely with the light intensity. It may relate to the distribution of the adsorption sites that varies with the light intensity. A further effort is needed to examine this observation.

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