Intermediate inhibition in the heterogeneous UV-catalysis using a TiO$_2$ suspension system

Yi-Chin Chan [a], Jong-Nan Chen [a], Ming-Chun Lu [b],*

[a] *Institute of Environmental Engineering, National Chiao Tung University, Hsinchu, Taiwan 300, ROC*
[b] *Department of Environmental Engineering and Health, Chia Nan University of Pharmacy and Science, Tainan, Taiwan 71710, ROC*
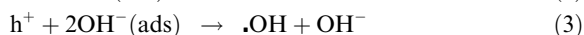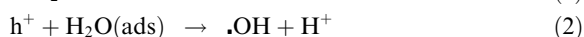
Abstract

Langmuir–Hinshelwood (L–H) kinetic expression was used to develop a basic mathematical model, which could describe the inhibition of intermediates in the photocatalysis of 2-chlorophenol (2-CP) in a suspended TiO$_2$ system. Results showed that the photocatalytic oxidation of 2-chlorophenol followed the L–H type behavior and the reaction by-products displayed an inhibiting effect on the degradation rate. The inhibition was estimated by comparing to observed and estimated half-lives. The higher the initial concentration of 2-chlorophenol, the higher the inhibition of photocatalytic reaction. The L–H kinetic has been modified slightly in this study to rationalize the contrast of inhibited behavior and to improve in favor of a surface reaction. The concentrations of 2-chlorophenol were investigated ranging from 7.78×10^{-5} to 7.78×10^{-4} mol l^{-1}. The degradation of 2-chlorophenol in this reaction condition approximates a first-order kinetics to near-complete degradation. Calculated kinetic profiles are in an excellent agreement with the experimental observation. The results of the theoretical analysis can be used to estimate reaction rates in different initial concentrations of target compound. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: 2-Chlorophenol; Langmuir–Hinshelwood kinetic; Photocatalysis; Titanium dioxide

1. Introduction

The general presence of persistent organic chemicals as pollutants in wastewater effluents from industries and households is a serious environmental problem. Most of these compounds are toxic and difficult to treat using traditional wastewater facilities. In recent years, photocatalytic processes were applied for the removal of organic and inorganic harmful substrates from water or wastewater (Serpone and Pelizzetti, 1989; Fox and Dulay, 1993). The most important reaction in the oxygenated aqueous suspensions is the oxidation of surface water by hydroxyl groups generating reactive hydroxyl radicals, and the electron capture by oxygen generated superoxide anion radical O$_2^-$ (Butler and Davis, 1993). Brezová et al. (1995) has shown that the corresponding photogenerated charge is involved in the reaction and oxidation processes on the TiO$_2$ surface. These radicals are widely believed to be the most important oxidizing species in semiconductor photocatalysis system. If the semiconductor electrode is the photoanode, the liberation of holes (h$^+$) oxidizes one of the redox partners.

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

$$h^+ + H_2O(ads) \rightarrow {}\centerdot OH + H^+ \tag{2}$$

$$h^+ + 2OH^-(ads) \rightarrow {}\centerdot OH + OH^- \tag{3}$$

$$O_2(g) + e^- \rightarrow O_2^-(ads) \tag{4}$$

Several reports have been published recently, describing the principal mechanism of photocatalysis and presenting various examples for its applications. It was found

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* Corresponding author. Fax: +886-6-2667323.
E-mail address: mclu@ms17.hinet.net (M.-C. Lu).

that the dissolved oxygen would influence the reduction of organics in the photocatalysis system.

Interest is now focused on the degradation of phenols and phenol derivatives by irradiation of aqueous TiO$_2$ suspensions (Cheng et al., 1995; Marci et al., 1995; Brezová et al., 1997; Winterbottom et al., 1997). The photocatalytic mineralization of chlorinated hydrocarbon and other organic contaminants in water with illuminated TiO$_2$ was demonstrated. TiO$_2$ dispersions and conventional near-UV radiation were used in most of these studies.

It has been demonstrated that various parameters influence the degradation rate of organic compounds (Al-Sayyed et al., 1991; Augugliaro et al., 1993; İnel and Öket, 1996). Mills and Hunte (1997) have shown that a few degradation kinetic expressions with different compounds have been reported. Unfortunately, almost all these studies investigated the effects of various parameters on the initial degradation rate rather than the whole degradation rate during the photocatalysis process. The mineralization kinetic rate expressions have focused on the initial disappearance rate of organic compounds or the initial formation rate of CO$_2$ (İnel and Öket, 1996). However, initial rate data are (exhausted to obtain) and inclined to variation, reducing the reliability of the results (Chen and Ray, 1998). For the design of a reactor, these kinetic expressions are not always useful. In this study, 2-chlorophenol (2-CP) was chosen as the model compound and the effects of initial 2-chlorophenol in aerated aqueous media on TiO$_2$ suspension. The Langmuir–Hinshelwood (L–H) kinetics, which has been adapted here with some modifications to meet the conditions inherent in solid–liquid reactions, could well explain the decrease of reaction constant with increasing the 2-chlorophenol concentrations. Many reports have used L–H model to describe the degradation characteristic (Lu et al., 1993; Kumar and Davis, 1997; Peill and Hoffmann, 1998; Wang et al., 1998; Zhang et al., 1998). The results of this study may assist in explaining how the intermediates influence the photocatalytic reaction. Derived kinetic expressions are applicable over a range of different initial concentrations.

In order to describe the actual reaction rates and the adsorption constants in photocatalysis system, an L–H model for describing the degradation of 2-chlorophenol in the suspended TiO$_2$ system was used. It is assumed that the reaction is not mass-transport limited for both parent compound and its reaction intermediates in which oxidation occurred on the TiO$_2$ surface.

This research describing the interference of intermediates as a function of adsorption constant and L–H constant are derived. The adsorption rate of intermediates is used as the modified parameter, which is modeled as a function of the interrupting inhibition intensity. The model is tested with the experimental data generated in the suspended TiO$_2$ system for the photocatalytic oxidation of 2-chlorophenol, and the estimated values are compared to the experimental ones.

2. Experimental

All chemicals were of reagent grade and were used without further treatment. The water employed was purified by the Milli-Q/RO system (Millipore) resulting in a resistivity greater than 18 MΩ cm^{-1}. Titanium dioxide P25 (Degussa, Germany), which is predominantly anatase (80% anatase, 20% rutile) with a surface area of 50 ± 15 m^2 g^{-1}, was used in all the photocatalytic experiments. The prepared aqueous suspensions of TiO$_2$ were stirred for 2 h in the ionic strength of 0.05 mol l^{-1} NaClO$_4$ and aerated in the oxygen flow rate of 60 ml min^{-1}. The initial titanium dioxide concentration was 2 g l^{-1} in all experiments. The concentration of 2-chlorophenol varies in the range from 7.78×10^{-5} to 7.78×10^{-4} mol l^{-1}.

Photochemical experiments were performed in a thermostatically controlled reactor of 500 ml capacity. This reactor was made of Pyrex glass with a plain quartz bottom (on which the light beam is focused) equipped with a mechanical stirring bar and gas supplier.

A 1000 W high pressure Xenon lamp (Oriel, USA) was employed as irradiation source, and operated at a power intensity of 800 W. During irradiation, the reaction mixtures were bubbled by oxygen with a flow rate of 60 ml min^{-1} and stirred by a stirrer.

The solution pH was adjusted initially, and then was not kept constant during the reaction. However, it was monitored at intervals in the experimental runs. Dissolved oxygen was detected using a WTW oxygen meter (model OXI 196) with oxygen probe (EO 96). The samples taken from the reactor were filtered on a membrane with 0.2 μm pore size (AFS, USA, cellulose acetate) to separate the catalyst and liquid. The pH was measured using a SUNTEX digital pH-meter (model SP-2200). The 2-chlorophenol was analyzed by an HPLC (LC module I, Waters, USA) with an UV detector adjusted at 284 nm. A reverse-phase column, 15 cm long and 3.9 mm internal diameter packed with RP-18, was used for analysis. The mobile phase was a mixture of acetonitrile (30%) and acetic acid 5% in water (70%); flow rate was 0.7 ml min^{-1}. Comparing the UV spectrum to those of commercial compounds with an UV detector made identification of the eluting compounds.

3. Results and discussion

3.1. Dissolved oxygen and pH

Since Salvador and Gutierrez (1982) have shown that there is a strong dependence on the pH value for the

photocatalytic reaction since the number of basic OH⁻ sites on the TiO$_2$ surface is a controlling factor for the generation of .OH. In this research, the pH was below pH 3 during reaction time and between 3.0 and 2.8 (Fig. 1). Since it was very close, the pH effect could be supposed to have no influence on this experiment. The average oxygen concentration during reaction was 32 mg l^{-1}. The concentration of oxygen values during reaction times and different organic concentrations were all very close, indicating that the initial rate of 2-chlorophenol removal was not limited by oxygen availability over the range of reaction conditions.

3.2. Kinetic analysis

It is important to establish initially whether the degradation reaction takes place in the adsorbed state or the TiO$_2$ semiconductor surface merely provides active species, which desorbs into solution and subsequently react with the organic compound. In the following, we discriminated between the two possibilities invoking the L–H kinetic treatment. The L–H kinetic treatment is known to be a good model for the description of solid–gas reactions. Extrapolation of this model to solid–liquid reactions requires some modifications, especially when the surface is that of TiO$_2$ particles in aqueous solutions, because the TiO$_2$ is known to be covered with hydroxyl groups and molecular water (Zhang et al., 1998). The degradation of 2-chlorophenol in aerated aqueous solutions was carried out in reactor in a recirculation mode. The natural logarithm of normalized concentrations of solute versus irradiated time shows a good linearity under the conditions of experiments. The reactions followed a first-order kinetics during the re-

action time (>75% of 2-chlorophenol). This behavior is rationalized in terms of modified form of the L–H kinetic treatment, which has been used successfully as a qualitative model to describe solid–liquid reactions.

We assume two extreme situations in defining the surface coverage, θ, of the semiconductor particle: (i) both the reactant and solvent compete for the same active sites; (ii) both the reactant and solvent are adsorbed on the surface without competing for the same active sites. However, the initial rate of organic removal in TiO$_2$ photocatalytic systems has been observed by a number of investigators that the reaction follows an L–H rate form (Butler and Davis, 1993; Mills and Hoffmann, 1993; Brezová et al., 1995),

$$r = -\frac{\mathrm{d}C}{\mathrm{d}t} = k_r\theta = \frac{k_r K C_0}{1 + K C_0},\tag{5}$$

where r is the reaction rate for the oxidation of 2-chlorophenol (mol l^{-1} min^{-1}), t the reaction time, C the concentration of organic compound (mol l^{-1}), θ the fraction of surface covered, k_r the specific reaction rate constant for the oxidation of organic compound observed from L–H kinetics (mol l^{-1} min^{-1}), K the equilibrium adsorption constant of organic compound and C_0 is the initial concentration of organic compound.

According to the L–H model, the rate of the unimolecular surface reaction, r, is proportional to θ and follows Eq. (5), when the parent reactant is more strongly adsorbed on the surface than the products (Serpone and Pelizzetti, 1989). Lu et al. (1993) used the L–H expression to analyze the heterogeneous kinetics of photocatalytic oxidation. They found that the reaction by-products displayed an inhibiting effect on degradation rate. The inhibition was also observed by Kumar and Davis (1997) that the electron-withdrawing characteristics of the nitro group had explained the decrease of reaction rates with increasing organic concentration. Photocatalytic degradation of organic reactant has been reported based on the .OH attack (Turchi and Ollis, 1989). The rate equations are shown to produce expressions similar to L–H expressions without regard to the assumptions of reaction that happened on the catalyst surface, in the fluid, or by way of a radical mechanism. The derived kinetic parameters by the investigators' approaches represented fundamentally different reaction and properties to the traditional L–H constants. That is, the conventional L–H kinetics can avoid a complicated mathematical formulation and simply model photocatalytic reaction (Turchi and Ollis, 1989). On the assumption of no competition with reaction, Eq. (5) can express the simplest represent for the rates of the disappearance of 2-chlorophenol.

Eq. (5) can demonstrate linearity of the data when plotted as the inverse initial rate versus initial concentration.
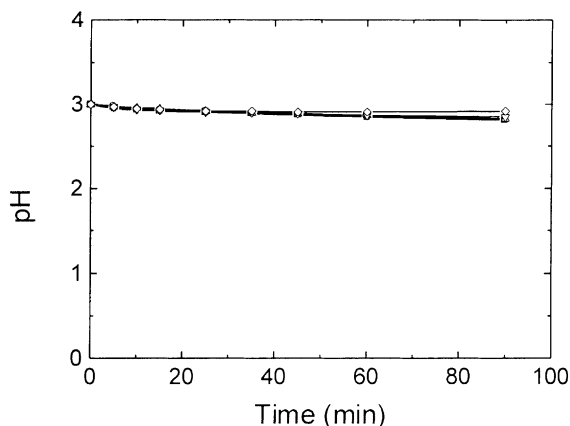

Fig. 1. Variation of pH valued during reaction time, where ($\square$), ($\bigcirc$), ($\triangle$), (∇), and ($\diamondsuit$) were the observed pH values during reaction time in the initial concentration of 2-chlorophenol on 7.78×10^{-4}, 5.83×10^{-4}, 3.88×10^{-4}, 1.94×10^{-4} and 7.78×10^{-5} mol l^{-1}.

$$\frac{1}{r} = \frac{1}{k_r} + \frac{1}{k_r K}\frac{1}{C_0}. \tag{6}$$

In this study, photocatalysis using the formula of linear least squares to fit Eq. (6), gives $k_r = 9.48 \times 10^{-6}$ mol l^{-1} min^{-1} and $K = 7.95 \times 10^3$ mol l^{-1} ($r = 0.975$).

3.3. Competition of intermediates

The hydrated TiO_2 surface is covered with hydroxyl groups and water molecules. Since both 2-chlorophenol (C_0, concentration of organic) and water molecular (C_w, concentration of water) could, in principle, be adsorbed on this surface via hydrogen bonds, their competition for the same active sites cannot be ignored (Serpone and Pelizzetti, 1989). Moreover, to the extent that $C_w \gg C_0$ and that C_w remains essentially constant, the part of TiO_2 surface covered by the solvent is approximately unchanged in all the reactant concentrations used. That is, C_w is a constant. In this work, all conditions such as photointensity, pH, dissolved oxygen, ionic strength and system turbulence were in the same condition. Therefore, C_0 will be the only variable in the initial reactions.

Integrating Eq. (6) during reaction time gives

$$t = \frac{1}{k_r K}\ln\frac{C}{C_0} - \frac{1}{k_r}(C_0 - C), \tag{7}$$

where t is the reaction time during degradation of 2-chlorophenol from concentration C_0 to C. At the half-life time of reaction $C = 0.5C_0$, the reaction time of t is $t^*_{1/2}$. Thus, Eq. (7) becomes

$$t^*_{1/2} = \frac{0.5C_0}{k_r} + \frac{\ln 2}{k_r K}, \tag{8}$$

where $t^*_{1/2}$ is the half-life time of reactions estimated from theory. Eq. (8) indicates that a plot of $t^*_{1/2}$ versus the initial concentration of 2-chlorophenol would be linear. By substituting $k_r = 9.48 \times 10^{-6}$ mol l^{-1} min^{-1} and $K = 7.95 \times 10^3$ mol l^{-1} obtained form Eq. (6) into Eq. (8), the estimated half-lives are obtained. Since half-lives for first-order reaction could also be calculated by

$$t_{1/2} = \frac{\ln 2}{k}, \tag{9}$$

where $t_{1/2}$ is the half-life time of reactions in different concentrations calculated from k, and k is the observed reaction rate constant for the oxidation of 2-chlorophenol in different initial concentrations (mol l^{-1} min^{-1}). When Eq. (8) is true, the estimated values from Eq. (8) would be the same as those obtained from observation. Fig. 2 shows the dependence of $t_{1/2}$ and $t^*_{1/2}$ on the initial concentration of 2-chlorophenol. The difference between $t_{1/2}$ and $t^*_{1/2}$ becomes larger with an increase in the initial 2-chlorophenol. It was suggested that

the reaction by-products might compete with 2-chlorophenol inducing the delay of the half-lives. Thus, the effect of by-products on the reaction rate should be considered. In such a case, Eq. (7) may be modified to give the following equation:

$$r = \frac{-\mathrm{d}C}{\mathrm{d}t} = \frac{k_r KC}{1 + KC + \sum_{i=1}^{n} K_i C_i}, \tag{10}$$

where K_i is the equilibrium adsorption constants of the reaction product i and C_i is the concentration of the reaction product i.

Integration of equation yields the reaction time

$$t' = \frac{1 + \sum_{i=1}^{n} K_i C_i}{k_r K}\left[\ln\frac{C_0}{C} + \frac{K(C_0 - C)}{1 + \sum_{i=1}^{n} K_i C_i}\right], \tag{11}$$

where t' is the experimental reaction time.

For $C = 1/2C_0$, integrating Eq. (11) yields Eq. (12)

$$t'_{1/2} = \frac{0.5C_0}{k_r} + \frac{\ln 2}{k_r K} + \frac{\ln 2\sum_{i=1}^{n} K_i C_i}{k_r K}, \tag{12}$$

where $t'_{1/2}$ are the experimental half-lives of 2-chlorophenol destruction. Theoretically, the quantity of $t'_{1/2}$ modified with the effect of competition should be approximated to those of $t_{1/2}$ observed in the reactions. Comparing Eqs. (8) and (12), the difference, $(\ln 2\sum K_i C_i)/k_r K$, between $t^*_{1/2}$ and $t'_{1/2}$ is found. By assuming that the rate of by-product formation is directly proportional to the initial concentration of parent compound, it can be realized that there shows nearly no evidence of significant difference between $t'_{1/2}$ and $t^*_{1/2}$ at lower initial concentration but an obvious variation at high initial concentration. The induction prompts us to tentatively rationalize the deviation seen in Fig. 2.
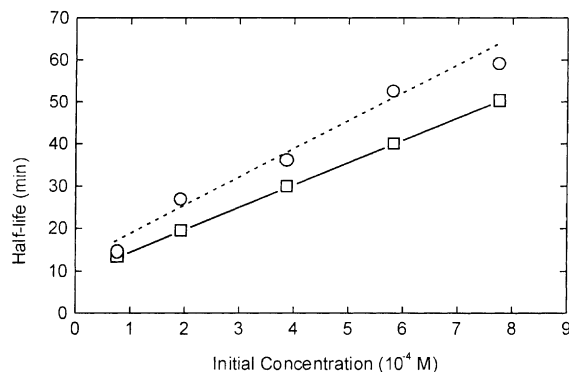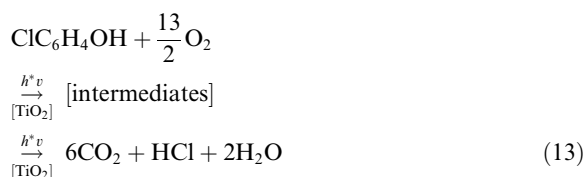

Fig. 2. Half-life profiles of observed and estimated on the different initial concentrations of 2-chlorophenol, where ($\square$) were the estimated half-life and ($\bigcirc$) were the observed half-life in initial concentration of 2-chlorophenol on 7.78×10^{-5}, 1.94×10^{-4} 3.88×10^{-4}, 5.83×10^{-4} and 7.78×10^{-4} mol l^{-1}; (—) was the line of estimate half-life program (--) was the line of observed half-life in the last squire regulation.

3.4. Generation of intermediates

TiO$_2$ is an excellent catalyst in the aqueous photo-oxidation of a variety of aromatic substrates, such as phenol and its derivatives. In the oxidation of phenol by photoactivated TiO$_2$ in aqueous medium, hydroquinone and chatechol are the major products, together with smaller quantities of pyrogallol, 1,2-trihydroxybenzene, hydroxylbenquinone, and some organic acids. Similar hydroxylated species have been identified in the photo-oxidation (Mills and Hoffmann, 1993). The photocatalytic degradation of 2-chlorophenol can be described by the following overall reaction in stoichiometry:

$$ClC_6H_4OH + \frac{13}{2}O_2$$

$$\xrightarrow[\text{[TiO}_2\text{]}]{h^*v} \text{[intermediates]}$$

$$\xrightarrow[\text{[TiO}_2\text{]}]{h^*v} 6CO_2 + HCl + 2H_2O \qquad (13)$$

As shown in other publications, the initial concentration of 2-chlorophenol is a function of the rate and photocatalytic efficiency of the degradation process (Chen and Ray, 1998). When in a certain concentration range, the other parameters, such as the concentration of molecular oxygen, the ionic strength, solution pH, and the light intensity, were kept constant. The reaction rate would be a constant. Therefore, the intermediates were generated from the parent organic (2-chlorophenol in this experiment) and will decompose to the second degree, third degree, and finally decompose to CO$_2$.

$$2 - CP \xrightarrow{k_1} P_1 \xrightarrow{k_2} P_2 \xrightarrow{k_3} \cdots \xrightarrow{k_s} P_S \cdots \xrightarrow{k_N} P_N. \qquad (14)$$
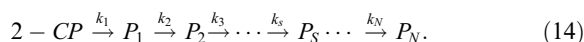
From Eq. (14) the primary decomposition rate constant is k_1 and the next step reaction rate constant from parent compound is

$$k2 = k_1 k_2 \qquad (15a)$$

therefore, decomposition step S will have the rate constant from the parent compound

$$kS = k_1 k_2 \cdots k_S. \qquad (15b)$$

Although there are many parrot reactions for different intermediates in each step, each series of reactions can be

isolated to obtain the relation of Eq. (15b). As the effect of pollutant concentration is of importance in any process of water treatment, it is necessary to investigate its dependence. Many reports showed the different degradation rates at the different initial reaction concentrations (Turchi and Ollis, 1989; Lu et al., 1993; Kumar and Davis, 1997). This is quite different from ordinary thermal reaction. However, all the concentration profiles could be correlated by the following exponential function with good agreement:

$$C_S = C_0 e^{-kSt} \qquad (16)$$

where kS is the reaction constant of step S. Therefore, the constant k_s (l min^{-1}) should be a constant with increases in the initial concentration of organic when other parameters are kept constant. The results summarized in Table 1 show that the photocatalytic degradation of 2-chlorophenol proceeds faster at higher 2-chlorophenol concentration. Because the L–H mode reaction was composed with the surface reaction and the adsorption, in this research the observed rate increased with the concentrations but the rate constant decreased slightly when the initial concentrations increased. That means the effect of adsorption was more than surface reaction in this study.

3.5. Modification of half-life calculation from L–H kinetic

The intermediate concentrations were proportional to the initial concentration of parent compound. It was related with degradation rate because the parent compound, 2-chlorophenol, decomposed into the intermediates. The concentration of intermediates could be expressed as

$$C_i = C_0(1 - e^{-kt}), \qquad (17)$$

where C_i is the concentration of intermediate in the primary degradation. Therefore, the primary intermediates decomposed into the secondary and tertiary intermediates until complete mineralization. In this work, we assume that the decomposition reaction proceeds for S steps from primary organic to mineralization. The concentration of these intermediates in each step could be demonstrated in the theoretical equation.

Table 1
Values of rate, rate constant and correlation coefficient for fit of experimental data to pseudo-first-order equation in different initial concentrations

	Initial concentrations (mol l^{-1})				
	7.77×10^{-4}	5.83×10^{-4}	3.88×10^{-4}	1.94×10^{-4}	7.77×10^{-5}
Reaction constant, k (min^{-1})	1.17×10^{-2}	1.32×10^{-2}	1.92×10^{-2}	2.60×10^{-2}	4.79×10^{-2}
Reaction rate, R (mol l^{-1} min^{-1})	9.10×10^{-6}	7.71×10^{-6}	7.47×10^{-6}	5.04×10^{-6}	3.72×10^{-6}
Correlation coefficient, r^2	0.993	0.983	0.980	0.998	0.895

$$C_{Si} = C_{Si-1,0}(1 - e^{-k_s t}) \qquad (18)$$

where C_{Si} are the concentrations of intermediates in step S, and the $C_{si-1,0}$ shows the initial intermediate concentration before decomposition step S. Since calculation of total intermediates will be a very complex and difficult work, and all steps of degradation will relate with the previous intermediate concentration. It is clear that all of the intermediates in each step are related with the initial concentration of target organic (2-chlorophenol). The difference between Eq. (8) and (12) will become

$$\text{Eq. (12)–Eq. (8)} = \frac{\ln 2 \sum_{i=1}^{n} K_i C_i}{k_r K} = \frac{C_0}{k_r} \left(\frac{\ln 2}{K} \sum_{i=1}^{n} K_i \frac{C_i}{C_0} \right).$$
$$(19a)$$

Since K is the adsorption constant of 2-chlorophenol in TiO$_2$ that must be a constant in the same condition. From Eq. (17) the C_i/C_0 is equal to the $(1 - e^{kt})$ that definition as B_i. Then Eq. (19a) becomes

$$\frac{C_0}{k_r} \left(\frac{\ln 2}{K} \sum_{i=1}^{n} K_i \frac{C_i}{C_0} \right) = \frac{C_0}{k_r} \left(a \sum_{i=1}^{n} K_i B_i \right) = \frac{C_0}{k_r} I, \qquad (19b)$$

where I is the summation of adsorption constant multiple exportation of reaction rate for individual intermediates, a is the $(\ln 2/K)$ and B_i is the exportation of reaction constant for intermediate i. Therefore, Eq. (12) can be rewritten into the following equation:

$$t'_{1/2} = (0.5 + I)\frac{C_0}{k_r} + \frac{\ln 2}{k_r K}. \qquad (20)$$

Since the kinds of intermediate were assumed to be kinds of initial organic, and suppose the reaction mechanism is the same in the same organic compound, therefore, I will be a constant when the initial organic is the same. The constant was also isolated with initial concentration. From Eq. (20), the interference of intermediates can be obtained from the slope. The observed half-lives could have a good linear relationship with initial concentrations as shown in Fig. 2. In consideration of the reaction rate of surface, k_r, it was supposed that no interference induced by the intermediates occurs. Therefore, the real adsorption constant (K) in the reaction could be recalculated in Eq. (20), which is regulated from the observed half-life and initial constant substituted in k_r, obtained from the primary L–H mode (Eq. (8)). Then the true value of K (6.11×10^3 mol l^{-1}) is achieved. Compared with Eqs. (8) and (20), where k_r and K are the constants, then variation C_0 is meaning the increased rate of slope from the estimated to the observed and could be written as Eq. (21). The interference constant I can be quantified in the following equation:

$$\left[\frac{(0.5 + I)}{k_r} - \frac{0.5}{k_r} \right] \Big/ \frac{0.5}{k_r} = 2I. \qquad (21)$$

Therefore, increase of slope was twice the interference constant I. Since the increasing rate of slope was a relatively value, then influence of intermediate (I) could simply define half of the increasing rate of slope.

4. Conclusions

This modified L–H model could be used in estimated observed reaction rate in different initial concentrations. It is a very important fact for operation in wastewater treatment. By the correction of adsorption constant, actually the reaction of suspended TiO$_2$ will be observed more clearly and compared. This could help to differentiate the decomposed mechanism of reaction and adsorption. Inferences of intermediates could quality and quantify by the fact I, which got from the variation of slope.

The modification model was assumed based on the condition of pseudo-first-order reaction and L–H model. There will be some limitations of the applications. If the decomposition rates do not obey the first-order rate mode, then the inference of intermediate will not obey the presumption. Inference of the intermediate may not interfere with reaction rate in the zero-order mode, and a variable in higher order reaction mode. If the adsorptions do not obey the Langmuir mode, the diffusion and multi-site model should be considered. This treatment is subject to the assumptions that sorption of both the oxidant and the reluctant are rapid equilibrium processes in both species present in a monolayer at the solid–liquid interface. Therefore, if the intermediate or the organic species do not follow the assumptions, the model becomes invalid.

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