Kinetics of Photocatalytic Degradation of Methylene Blue over TiO$_2$ Particles in Aqueous Suspensions*

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Abstract   The kinetics of photodegradation of methylene blue over UV light illuminated titania particles in aqueous suspensions has been studied with different initial methylene blue concentrations and TiO$_2$ particle sizes. The degradation rate increases with the decrease of initial concentration and particle size. A quasi-experienced model for photodegradation rate is derived based mainly on the coinstantaneous effects of different initial concentrations and particle sizes. The mathematical relationships of model parameters with initial concentration and particle size are given. The model results of the photodegradation rate of methylene blue are coincident with the experimental data.
Keywords   kinetics, photocatalytic, titania

1 INTRODUCTION

The photocatalytic oxidation of organic compounds in aqueous suspensions of titania is a comparatively new method for the removal of impurities from water. It may find applications in the treatment of both waste water and drinking water. The photoactivating wavelengths are near those of UV (<400 nm) or sunlight. Many compounds can be oxidized or degraded by this method[1~3]. The method is available for the destruction of some organic compounds in water which could not be degraded by traditional methods.

For the practical purpose of water treatment, it is expected that more knowledge about the kinetics of photocatalytic degradation of organic compounds should be understood. However, the factors affecting the photocatalytic reactions include the properties and initial concentrations of organic compounds to be degraded, the features of titania powder as photocatalyst, the pH value of solution, the UV light intensity and the load of catalyst particles, *etc.*. They are so complicated that it is difficult to propose an integrated kinetic model for photocatalytic reactions. It is assumed that the kinetics of photocatalytic degradation of organic compounds can be explained with the traditional L-H mechanism and expressed in the form of first-order reaction[4~9], with the interaction of some factors still not clear.

It is noted that the concentration dependence (with identical particle size)[10,11] and particle size dependence (with identical concentration) on photocatalytic reaction rate has been studied[4,5,8]. Matthews studied the kinetics of photoreaction with different initial solution concentrations[10~12]. In fact, the photoreaction rate is dependent on both the reagent concentration and the catalyst particle size, whereas a systematic study of the coinstantaneous effects of the two factors has not yet been reported. The object of this paper is to investigate the kinetics of photocatalytic degradation of organic compounds including the above two factors and to propose a new kinetic model. The new model is verified with the experimental data of photodegradation of methylene blue.

In addition, our previous studies have confirmed that the photocatalytic activity of titania is higher when particles suspend in aqueous solutions than when they are fixed in aqueous solutions[9]. It is believed that the problem of separation of catalysts will be solved with the rapid progress of separation technology. Therefore, the conditions of catalysts being suspended in aqueous solutions are studied in this paper.

2 EXPERIMENTAL

2.1 Materials

Titania with different particle sizes (49, 11, 8, 6, 3, 2 and 1 μm) is used as photocatalyst. It exists mainly in the anatase form and has specific surface areas of 12.44, 19.70, 23.04, 27.81, 76.72, 79.32 and 81.53 m$^2 \cdot$g^{-1}, respectively. The photocatalysts are suspended in a solution containing methylene blue which is to be degraded.

Methylene blue is used as the solute. The reason for it is that methylene blue has strong adsorption characteristics on the surfaces of many solid particles,

good resistance to light degradation and a well defined optical absorption maximum at 660 nm. Solutions are prepared using deionized water and the pH values are adjusted to about 6.5 by adding NaOH or HNO_3.

2.2 Apparatus

The apparatus is the same as described in Ref. [9]. The titania photocatalyst (500 mg) is added into the solution (850 ml) in a glass cylinder 100 mm in diameter and 300 mm high. A 300 W UV light lamp in a borosilicate cooling well is immersed in the solution. The solution is stirred by a magnetic agitator at the bottom of glass cylinder, and air is pumped into the solution continuously. A thermometer and a condenser are used to observe the solution temperature and to cool the volatile vapour respectively. Reaction temperatures are controlled at 15—18°C. The pH value is measured with fine pH indicator paper. The titania powders are dispersed by an ultrasonic disperser.

2.3 Analysis

The changes of methylene blue concentration are measured using a 722-type spectrophotometer, and
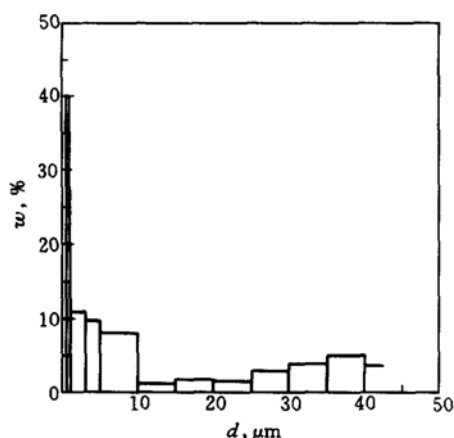
(a) Mean particle size 1.0 μm
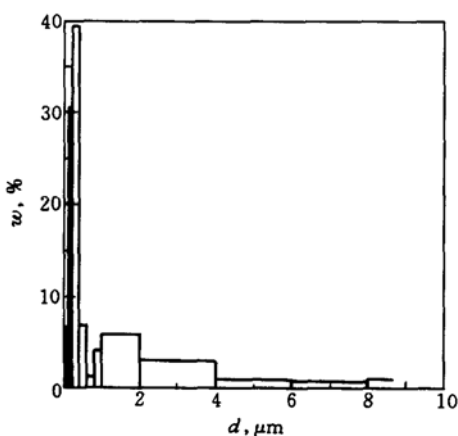
(b) Mean particle size 0.3 μm

Figure 1   Distribution curves of particle size of anatase TiO_2

the calibration curves are prepared using the solutions of known concentrations with an analytical wavelength of 660 nm. Particle sizes are determined by a NSKC-1A photo size analyzer. The distribution curves of particle size with mean particle sizes 1.0 μm and 0.3 μm are showed in Fig. 1; the others can be found in Ref. [9].

2.4 Procedure

The solution of 850 ml is first prepared in a glass container. Then, the pre-dispersed titania powders are added into the solution. The cooling well and lamp are immersed into the solution. The condenser is settled above the glass cylinder, and the thermometer is placed in one of the sockets, and finally the agitator is turned on. Samples are taken at different intervals. In order to eliminate the effects of particles on photo absorption, samples are centrifugalized before analyzed.

3   RESULTS AND DISCUSSION

3.1   Solute concentration

The effects of initial solute concentration on the rate of degradation of methylene blue are studied. The initial degradation rate of methylene blue increases with the increase of initial concentration. The change of concentration with time follows approximately first-order kinetics, and the reaction rate constants increase with the decrease of initial concentration. The reasons for this phenomenon are explained in Section 3.3.

3.2   Particle size

The effects of catalyst particle size on the rate of degradation of methylene blue are shown in Fig. 2, where one identical initial concentration is given as an example. The degradation rate of methylene blue increases as the particle size decreases.
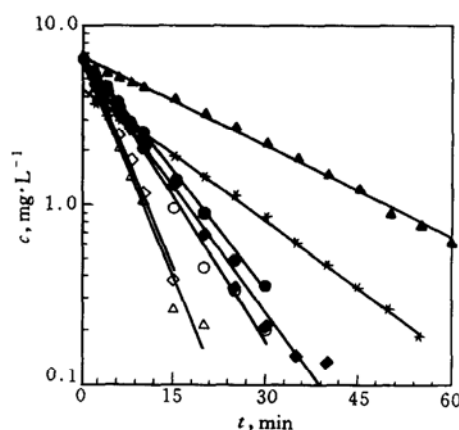

Figure 2   Concentration vs. illumination time for different particle size with the same initial concentration 6.54 mg·L⁻¹
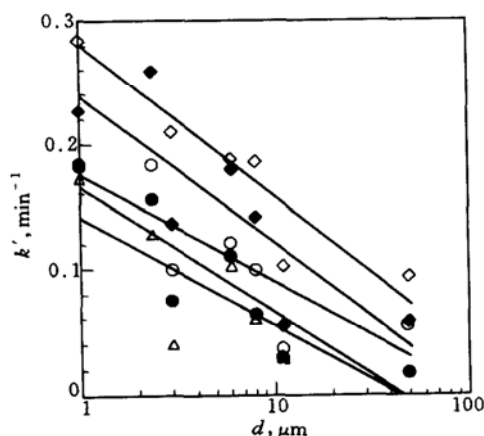
—regression; ▲ * ● ◆ ○ ◇ △ experimental
d, μm: ▲ 49.0; * 11.2; ● 8.1; ◆ 6.1; ○ 3.0; ◇ 2.4; △ 1.0

3.3 Reaction kinetics

It has been confirmed that the rate of photodegradation of organic compounds follows the first-order reaction kinetics[10,11].

$$\ln\left(\frac{c_0}{c}\right) = k't \qquad (1)$$

According to Eq. (1), the plot of the logarithmic value of c $vs.$ t should be a straight line whose slope is $-k'$. Values of k' obtained in this way are illustrated in Fig. 3. k' increased with the decrease of initial concentration, which is coincident with the results presented by R. W. Matthews[10]. It can be explained that the fraction of particle surface area covered by methylene blue decreases with the decrease of its initial concentration, thus both the number of ·OH radicals and the chance of methylene blue to accept photons increase, and eventually, the degradation rate increases. However, the increment of k' is lower than the decrement of the initial concentration. Therefore, the initial degradation rate, $k'c_0$, would decrease with the decrease of initial concentration.

Figure 3   Changes of the first-order reaction constant with TiO$_2$ particle size under different initial methylene blue concentrations
——regression; ◇ ◆ ○ ● △ experimental
c, mg·L^{-1}: ◇ 2; ◆ 4; ○ 6; ● 8; △ 10;

It is known that k' will not vary with initial concentration according to the first-order reaction law. However, k' changes with initial concentration in photodegradation reaction as shown in this work and in previous one[10]. Of course, the change of concentration $vs.$ time still obeys the first-order reaction law. Hence, the Langmuir adsorption isotherm was proposed to illustrate the rate of photocatalytic reaction for different initial concentrations, and it has also been confirmed[9–14]:

$$R = -\frac{dc}{dt} = \frac{k_1 K c}{1 + K c} \qquad (2)$$

where k_1 and K are the constants for a given system related to the reaction properties of solution and adsorption respectively. Matthews[11] suggested that the rate of formation CO$_2$ on the surface may be expressed as

$$R = \frac{k_1 K c}{1 + K c + \sum_i K_i [I_i]} = \frac{k_1 K c}{1 + K c_0} \qquad (2a)$$

where K_i is the equilibrium adsorption constant and I_i is the intermediate degradation product. The simplifying assumption was made as follows

$$Kc + \sum_i K_i [I_i] = K c_0 \qquad (2b)$$

In addition, it was assumed that the adsorption constants for the degradation intermediates are the same as those for the original solute. However, the intermediates are not considered in this work and only Eq. (2) is applied.

In some reports the relationship between the concentration and the apparent rate constant was explained in terms of the integrated form of the Langmuir adsorption isotherm[10].

$$t = \frac{1}{K k_1} \ln \frac{c_0}{c} + \frac{1}{k_1}(c_0 - c) \qquad (3)$$

where t is the time needed for the change of concentration from c_0 to c. When $c/c_0 = 0.5$, it becomes

$$t_{0.5} = \frac{0.693}{k'} = \frac{0.5 c_0}{k_1} + \frac{0.693}{K k_1} \qquad (4)$$

Thus, the plot of half-life time, $t_{0.5}$, $vs.$ the initial concentration c_0 should be a straight line whose slope and intercept are $0.5/k_1$, $0.693/(K k_1)$ respectively. The results are shown in Fig. 4. Values of k_1 and K obtained from Fig. 4 are illustrated in Fig. 5. It can be observed that both k_1 and K increase with the decrease of particle size, while the increment of K is faster than that of k_1. The increase of k_1 and K results from the increase of the number of ·OH radicals and from the increase of the adsorbability and the chance to acquire ·OH radicals, respectively, due to the increase of the specific surface area of particles. Both the increase of k_1 and K will accelerate the photocatalytic reaction rate. It is notable that the adsorbability has important effect on the photocatalytic reaction rate.

Combining the first-order reaction law with L-H mechanism, the reaction rate has the following form

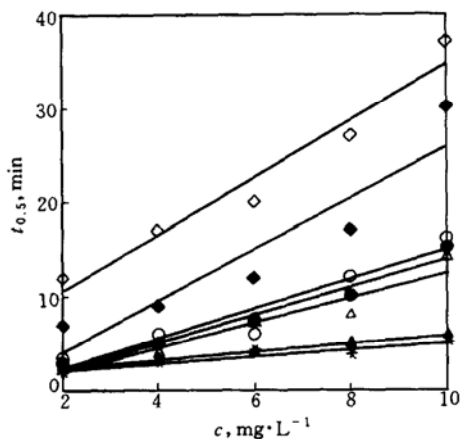$$R = k'(d, c_0)c = \frac{k_1(d) K(d) c}{1 + K(d) c} \qquad (5)$$

Figure 4   Half life time vs. initial concentration for different particle size of TiO₂ used
——regression; ◇ ◆ ○ ● △ ▲ ∗ experimental.
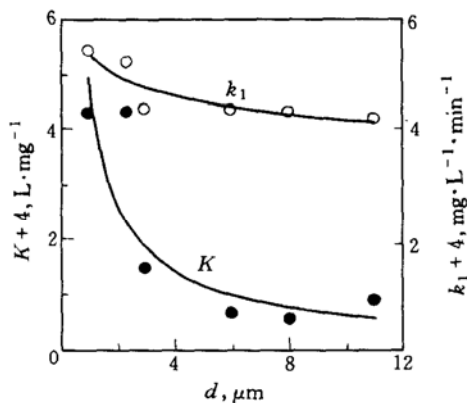d, μm: ◇ 49.0; ◆ 11.2; ○ 8.1; ● 6.1; △ 3.0; ▲ 2.4; ∗ 1.0

Figure 5   The constant k_1 and K vs. particle size
○ ● experimental; —— calculated

where $k'(d, c)$, $K(d)$ and $k_1(d)$ are the functions for the constants k', K and k_1, respectively; d is the mean particle size. These functions can be obtained from Fig. 3 and Fig. 5 by the method of fitting experimental data. The results are as follows

$$k'(d, c) = A \lg d + B \tag{6}$$
$$A = 0.01 \lg c_0 + 0.06$$
$$B = -0.1 \lg c_0 + 0.57$$
$$k_1(d) = 4.59 d^{-0.11} - 4 \tag{7}$$
$$K(d) = 4.96 d^{-0.91} - 4 \tag{8}$$

Therefore, Eqs. (5)—(8) are the desired kinetics of photocatalytic degradation of methylene blue over TiO₂ particle suspended in aqueous solutions.

3.4 Predictions

Under the same experimental conditions as stated in Section 2, solutions with different initial methylene blue concentrations are photodegraded with TiO₂ as catalyst whose mean size and distribution are shown

in Fig. 1(b). Fig. 6 gives a comparison of the experimental data and the data predicted by Eq. (5). Table 1 gives the values of $t_{0.5}$ for both experimental data and those predicted by Eq. (4). The predicted results and the experiment data are approximately coincident.
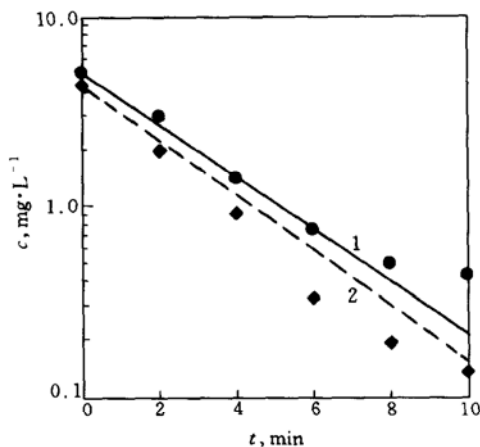

Figure 6   Methylene blue concentration vs. illumination time using a TiO₂ powder with mean particle size 0.3 μm
● ◆ experimental; —— predicted
c_0, mg·L⁻¹: 1—5.07; 2—4.35

Table 1 $t_{0.5}$ of methylene blue using TiO₂ with mean particle size 0.3 μm at different initial concentrations

c_0, mg·L⁻¹	$t_{0.5}$, min		
	Exp.	Cal. from Eq. (1)	Cal. from Eq. (4)
4.35	1.85	2.08	1.81
5.07	2.20	2.19	2.10

However, the factors affecting the photocatalytic reaction rate are complicated and include the load of titania, the intensity of UV light, the pH of solution, the reaction temperature, the preparation method of titania, *etc.* They do not appear in the model. Therefore, the parameters of the model should be modified if the reaction conditions are different from this work.

4   CONCLUSIONS

The kinetics of photodegradation of methylene blue with titania suspended in aqueous solution as photocatalyst has been studied. The effects of particle size and initial concentration are investigated and a model for predicting the kinetics of the photocatalytic reaction is proposed. The results showed that the model is applicable, and it is feasible to find the application of photocatalytic reactions in such field such as environmental protection.

NOMENCLATURE

c	concentration of methylene blue, $mg \cdot L^{-1}$
c_0	initial concentration of methylene blue, $mg \cdot L^{-1}$
d	TiO$_2$ particle size, μm
[I]	concentration of the intermediate degradation product, $mg \cdot L^{-1}$
K	constant of Eq. (3) related to the adsorption, $L \cdot mg^{-1}$
k_1	constant of Eq. (3) related to the reaction properties of the solute, $mg \cdot L^{-1} \cdot min^{-1}$
k'	constant of first-order reaction rate, min^{-1}
R	photocatalytic degradation rate of methylene blue, $mg \cdot L^{-1} \cdot min^{-1}$
t	illumination time, min
$t_{0.5}$	half-life period of methylene blue, min
w	mass fraction, %

Subscripts

i	number of the intermediate degradation product

REFERENCES

1 Fox, M. A., Dulay, M. T., *Chem. Rev.*, **93**, 41 (1993).
2 Kamat, P. V., *Chem. Rev.*, **93**, 267 (1993).
3 Hoffmann, M. R., Martin, S. T., Choi, W., Bahnemann, D. W., *Chem. Rev.*, **95**, 69 (1995).
4 Wei, T. Y., Wan, C. C., *Ind. Eng. Chem. Res.*, **30**, 1293 (1991).
5 Pathirana, H. M. K. K., Maithreepala, R. A., *J. Photochem. Photobiol. A: Chem.*, **102**, 273 (1997).
6 Augugliaro, V., Loddo, V., Marci, G., Palmisano, L., Lopez-Munoz, M. J., *J. Catal.*, **166**, 27 (1997).
7 Tanaka, K., Lapule, M. F. V., Hisanaga,T., *Chem. Phys. Lett.*, **187**(2), 73 (1991).
8 Anpo, M., Shima, T., Kodama, S., Kubokawa, Y., *J. Phys. Chem.*, **91**, 4305 (1987).
9 Xu, N. P., Shi, Z. F., Fan, Y. Q., *et al.*, *Ind. Eng. Chem. Res.*, **38**(2), 373 (1999).
10 Matthews, R. W., *J. Chem. Soc., Faraday Trans. I.*, **85**(6),1291 (1989).
11 Matthews, R. W., *J. Catal.*, **111**, 264 (1988).
12 Matthews, R. W., *Wat. Res.*, **25**(10), 1169 (1991).
13 Turchi, C. S., Ollis, D. F., *J. Catal.*, **122**, 178 (1990).
14 Turchi, C. S., Ollis, D. F., *J. Catal.*, **119**, 483 (1989).