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Effects of Particle Size of TiO_2 on Photocatalytic Degradation of Methylene Blue in Aqueous Suspensions

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The influence of particle size of TiO_2 on the photocatalytic degradation of methylene blue (MB) in a suspended aqueous solution has been studied. The results suggested that the adsorption rate and adsorbability of MB on suspended TiO_2 particles increased as the particle sizes of TiO_2 decreased. Photocatalytic activity of TiO_2 also increased as the particle size of TiO_2 became smaller, especially when the particle size is less than 30 nm. The half-life ($t_{0.5}$) of the photocatalytic degradation of MB also decreased as the particle sizes of TiO_2 decreased. The first-order reaction rate constant for photodegradation of MB increased as the particle size of TiO_2 decreased. The initial degradation rate of MB in a suspended model was higher than that of a fixed-bed model. This will overcome the difficulty of preparation of ultrafine TiO_2 catalyst particles. Once the problem of separation of fine TiO_2 particles is solved, a TiO_2 suspended photoreactor could be provided on an industrial basis.

Introduction

Studies on photocatalytic features of semiconductors have attracted much attention recently. The application of semiconductor photocatalytic reactions have been focused on in several aspects such as solar conversion and storage,^{1,2} reductive fixation of CO_2 ,^{3,4} organic synthesis,⁵ mineralization, and detoxification of organic compounds.^{6,7} Titanium dioxide (TiO_2) is one of the most popular and promising semiconductor materials, which could be used as a photocatalyst, because of its stability under harsh conditions, commercial availability, and ease of preparation in the laboratory. Photocatalytic activity of TiO_2 can be studied when it is in the fixed-bed form and when it is suspended in a solution.

In the fixed-bed mode, ultrafine TiO_2 particles were supported on large carrier particles packed in a column, while in the suspended state, each individual TiO_2 particle could be available for photocatalysis. According to literature,^{8–10} the photocatalytic activity of suspended TiO_2 in solution strongly depends on the physical properties of TiO_2 (e.g., crystal structure, surface area, surface hydroxyls, and particle size) and operating conditions (e.g., light intensity, oxygen, initial concentration of chemicals, amount of TiO_2 , and pH value). Wei and Wan⁸ have investigated the effects of operating conditions (e.g., pH value, oxygen flux, initial concentration of phenol, and TiO_2 amount) on the photocatalytic degradation of phenol by TiO_2 suspended in solution. Pathirana et al.⁹ have reported the results of photodegradation of 3,4-dichloropropionamide (3,4-DPA) in the presence of TiO_2 suspended in a solution of 3,4-DPA. They have completely degraded and dechlorinated 3,4-DPA by illuminating with artificial light and have found that an acidic medium is suitable for this degradation and dechlorination. Augugliaro et al.¹⁰ have investigated

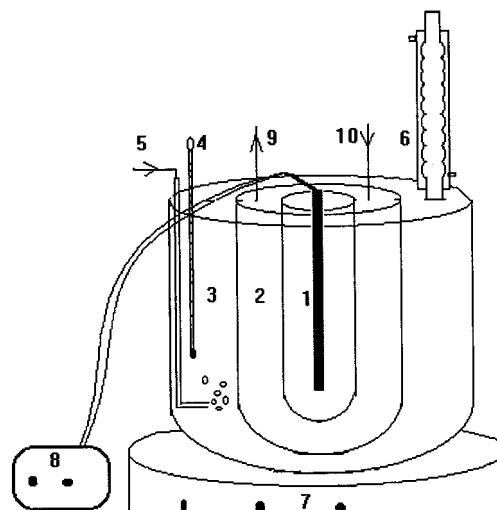


Figure 1. Schematic diagram of experimental setup for a photocatalytic reaction. (1) 300-W mercury lamp; (2) cooling well; (3) reaction container; (4) thermometer; (5) purging gas; (6) cooling tube; (7) magnetic stirrer; (8) control of light; (9) cooling-water outlet; (10) cooling-water inlet.

the effects of operating conditions on photocatalytic oxidation of free cyanides by TiO_2 suspended in an aqueous solution. Their results have showed that the concentration of the catalyst, concentration of chloride ions, and intensity of light affect the kinetics of photo-oxidation of cyanide. It has been independent of the initial concentration of cyanide and initial pH. Very recently, Ohtani et al.¹¹ have reported the effects of crystal structures of TiO_2 in suspension on photocatalytic activity. They have reported that photocatalytic activity of amorphous TiO_2 is negligible, whereas photocatalytic activity of anatase, which is having the same particle size as amorphous TiO_2 , is appreciable. Tanaka et al.¹² studied the photocatalytic degradation of trichloroethylene (C_2HCl_3), dichloroacetic acid (CHCl_2COOH), and phenol using 12 commercially available TiO_2

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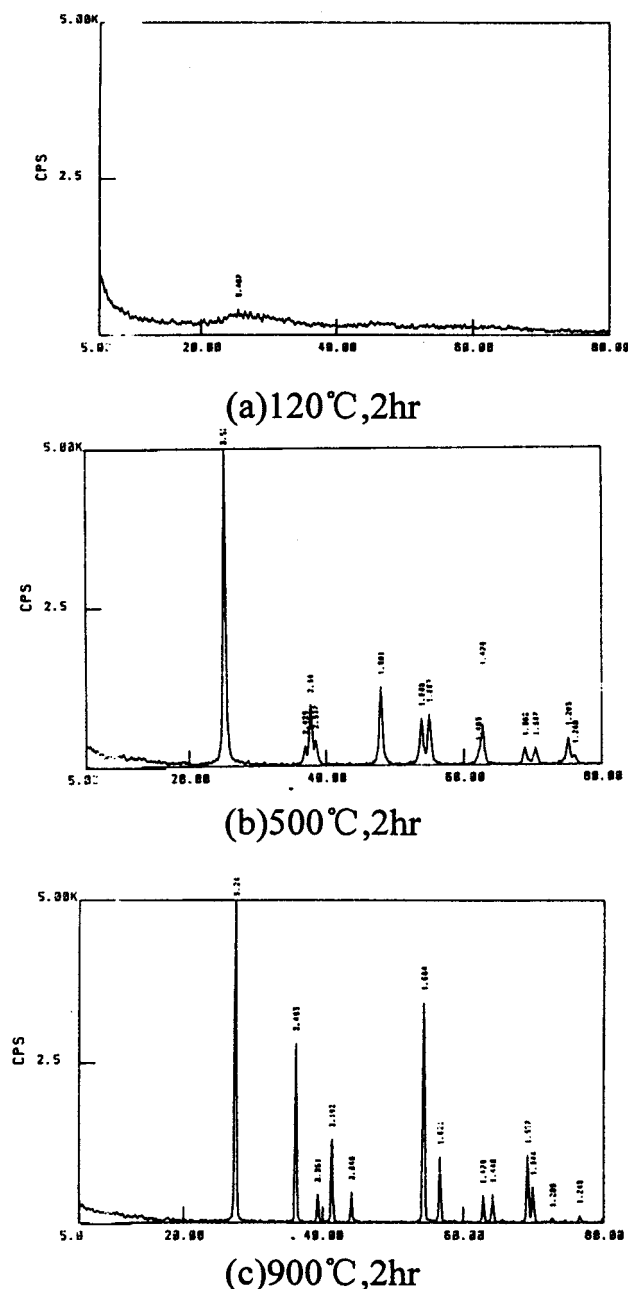


Figure 2. X-ray diffraction patterns of TiO_2 powder at different treatment temperatures.

samples, and some laboratory-prepared TiO_2 of different crystal forms and crystallinities. They have found that the initial rate of degradation was affected mainly by the content of anatase in TiO_2 . Pure anatase has exhibited the best catalytic efficiency on the degradation of the above three compounds, while pure rutile has exhibited the poorest catalytic efficiency. Although many investigations have indicated that the particle size of TiO_2 should affect photocatalytic reactions, the literature contains only a few references on this matter. Also, there are only a few references on the photocatalytic activity of TiO_2 packed as a fixed bed. Anpo et al.¹³ have reported the photocatalytic hydrogenation reactions of propyne (CH_3CCH) in water using a TiO_2 catalyst of extremely small particle sizes. Their results have suggested an increase in photocatalytic activity with a decrease in the particle size of TiO_2 , especially when less than 10 nm. They have suggested that a reduction of the particle size of TiO_2 might result in

some electronic modification of TiO_2 and produce an enhancement of the activities of electrons and holes, and/or suppression of the radiationless transfer of absorbed photon energies. Similar studies have been performed by other researchers, but their attentions have also been focused on research on the mechanism of photocatalytic reactions. The effect of particle size of a photocatalyst on photocatalytic reactions can be studied by using either the particles adsorbed on a carrier or the particles suspended in a solution. Most of the studies on the effect of particle size on photocatalytic reactions have been carried out using the first method. However, it might be more effective to use TiO_2 particles suspended in a solution as a photocatalyst. No reports are available on the effect of the size of suspended photocatalyst particles on photocatalytic reactions.

In the present work, ultrafine TiO_2 particles were prepared by the sol-gel method and were suspended in MB ($[(\text{CH}_3)_2\text{N}]_2\text{C}_{12}\text{H}_6\text{NS}(\text{Cl})$) solution to study the photocatalytic degradation of MB by TiO_2 . Attention was focused on the effect of particle size of the suspended TiO_2 on the photocatalytic reaction.

Experimental Section

Preparation of TiO_2 Powder. The ultrafine particles could be prepared by controlling the hydrolysis process. The preparation of TiO_2 powder was as follows. A predetermined amount of $\text{Ti}(\text{OBu})_4$ (chemically pure) was slowly added into a container that contained alcohol (chemically pure) with continuous stirring. The pH value was then adjusted to 2.0 with nitric acid (chemically pure). Next, deionized water was added to the mixture, and the composition (molar ratio) was controlled at 20:1:2.5 for alcohol: $\text{Ti}(\text{OBu})_4$: H_2O . Stirring the mixture was continued for about 10 min, and the solution was maintained at room temperature for a few days until a gel could be obtained. Then the materials were dried at 60–70 °C in a vacuum for 3 h and then milled. Titanium dioxide powder was obtained by carefully controlling the treatment temperature of the dried powders. The crystal structure of TiO_2 depends on the temperature of heat treatment. Amorphous-, anatase-, and rutile-type TiO_2 could be obtained at 120, 500, and 900 °C, respectively, by heat treatment of the dried powders for about 2–3 h.

Photocatalytic Reaction. The experimental apparatus used to study the photocatalytic reaction is shown in Figure 1. The reactor consists of three parts. The first part is the outside Pyrex glass container (volume, 850 mL). The second part is a Pyrex glass thimble, which is used for recycling the cooling water and filtering the UV light. The reaction temperature is kept at room temperature (25 °C). The third part is an empty chamber in which a mercury lamp (300 W) is immersed. Since the light goes through the Pyrex glass and the water jacket, the infrared fraction, as well as any radiation below 300 nm, is removed. In our study, the TiO_2 powder (0.5 g) was ultrasonically mixed for 10 min with the sample (850 mL) and then transferred into the reaction container and stirred by means of a magnetic stirrer. The solutions were prepared with deionized water and reagent-grade chemicals were used. The initial pH value of each reaction solution was kept at 6.5 by adding NaOH (chemical pure) or HNO_3 (chemical pure) solution.

All samples were taken intermittently for analysis. They were centrifuged at 2000 rpm in order to remove

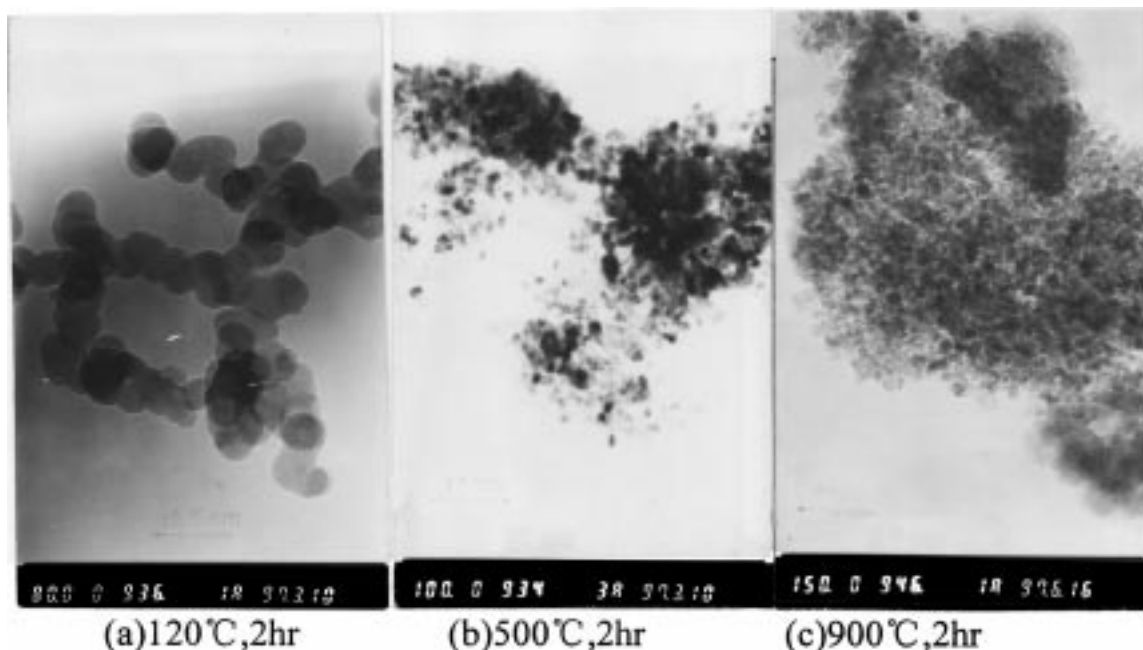


Figure 3. Electron micrographs of TiO_2 powder at different treatment temperatures.

Table 1. Saturated Adsorbabilities and BET Surface Areas of Different TiO_2 Powders at 25 °C

particle size	particle type	saturated adsorbability (mg of MB/g of TiO_2)	BET surface area (m^2/g)
49.0 μm	anatase	0.36	12.44
11.6 μm	anatase	0.66	19.70
6.1 μm	anatase	0.90	27.81
3.0 μm	anatase	1.02	76.72
2.4 μm	anatase	1.16	79.32
30 nm	anatase	2.12	94.17
12 nm	amorphous	3.60	127.14

the particles from the reaction solutions. The MB concentrations were then determined by an UV spectrophotometer.

Results and Discussion

Characterization of Ultrafine TiO_2 Powder. X-ray diffraction patterns of the catalyst of different crystalline structures are shown in Figure 2. Electron micrographs of TiO_2 powder treated at different temperatures are shown in Figure 3. These diagrams confirm that ultrafine TiO_2 particles could be prepared by the sol-gel process. Although the primary particle diameters were less than 10 nm, the agglomeration of particles has increased with an increase in the treatment temperature. The large particles consist of many ultrafine ones. The analysis of normal particle sizes was done by using a photoextinction sedimentation analyzer (Nanjing University of Chemical Technology). The principle for the determination of particle size was mainly that the sedimentation velocity is different for particles with different particle sizes in a solution. The mean value for particle size was weight average. Ultrafine particles were analyzed by using transition electron micrographs.

Ohtani et al.¹¹ has reported that the anatase type of TiO_2 would be desirable for the photocatalytic reaction. In the present work, each photocatalyst was prepared as follows. The dry gel powder was treated at 500 °C for 2 h and then milled into fine particles. The particle

size distribution was very wide after the gel powder was treated at high temperature. Uniform-size particles with different mean diameters could be obtained by sieving and centrifugation. Anatase TiO_2 photocatalysts with six different particle sizes were obtained. The mean particle diameters of the powder were 49.0 μm , 11.6 μm , 6.1 μm , 3.0 μm , 2.4 μm , and 30 nm (Figure 3b), respectively. Figure 4 shows the particle size distributions of five of them. Ultrafine amorphous TiO_2 particles with a mean diameter of 12 nm (Figure 3a) were also prepared in order to make a comparison for different crystal structures.

Effect of the Adsorption of Methylene Blue by the Surface of TiO_2 on Photocatalytic Reaction. The TiO_2 powder prepared by the sol-gel method had high surface areas and porous structures. Their BET surface areas are listed in Table 1. The correlation between particle sizes and surface areas is graphed in Figure 5a. The adsorption of MB on the photocatalyst increases as the particle size of TiO_2 decreases. Thus, it is very important to remove the effect of adsorption intervals at the beginning of the reaction on the results of the photocatalytic degradation of MB.

The adsorption process was studied with the experimental setup shown in Figure 1. TiO_2 powder suspended in MB solution was kept in the container while irradiating in the absence of UV light. The amount of MB added was equal to that contained in the photocatalytic reaction solution. Samples of the solutions, were analyzed at selected intervals, and it was observed that the MB was adsorbed on TiO_2 particles very quickly and saturated in 10 min. The saturated adsorbabilities of the different particles are also listed in Table 1. The relationship between particle sizes and saturated adsorbabilities are graphed in Figure 5a. From Table 1, it can be concluded that the saturated adsorbability increases as the particle size decreases. These results indicate that the photocatalytic reaction should start after the completion of the adsorption process, to eliminate the effect of adsorption on the reactions.

Effects of Particle Size on Photocatalytic Degradation. Previous works^{11,12} have confirmed that

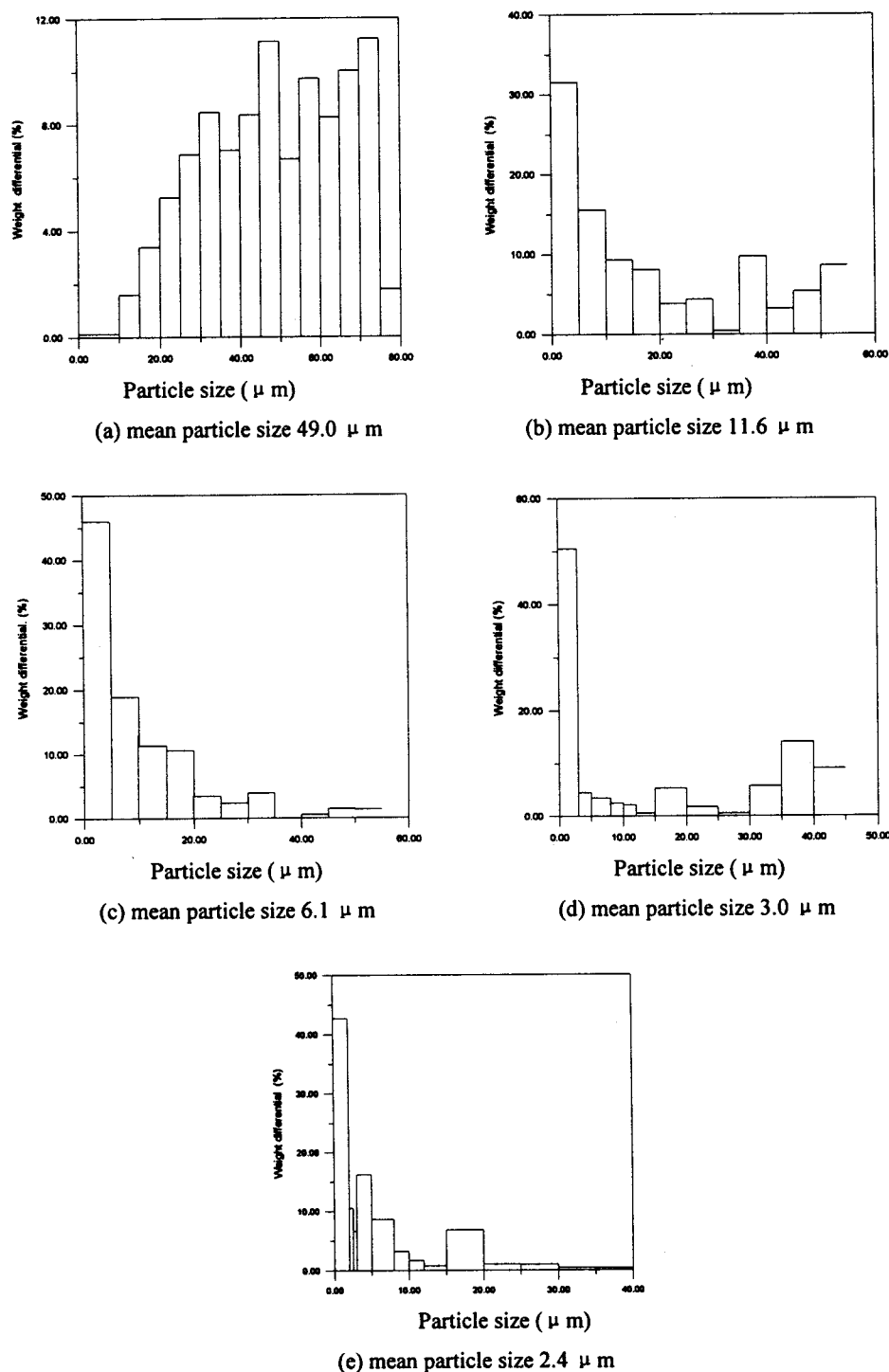


Figure 4. Particle size distribution of anatase TiO_2 .

amorphous TiO_2 has very poor catalytic activity. So only the anatase-type titanium dioxide powders of different particle sizes were used for the photocatalytic degradation of MB. The particle sizes were 49.0 μm , 11.6 μm , 6.1 μm , 3.0 μm , 2.4 μm , and 30 nm, respectively. To eliminate the effects of adsorption, the reaction solution was agitated for 10 min in the absence of the UV light. The results, shown in Figure 6, indicate a change in concentration of MB in solution with irradiation time for different photocatalysts. It also indicates that the photocatalytic degradation of MB in the absence of TiO_2 is low. This result agrees with previous findings for other systems.⁹ The concentration of MB in solution decreased more rapidly with a decrease in the particle

size of anatase-type photocatalysts. Especially, a significant increase of reaction rate was observed when the particle size of TiO_2 was less than 30 nm. These data seem to be similar to those of previous work reported for the fixed-bed mode.¹³ However, in that work, a dramatic increase of the reaction rate has been observed when the particle size of TiO_2 was less than 10 nm. This difference in two cases may be caused by the conditions under which the particles exist. Furthermore, as shown in Figure 5a, the initial reaction rates for photodegradation of MB obtained from the experimental results seem to be parallel to those in the saturated adsorbability rather than those in the BET surface area measurements of the catalysts. The latter increases

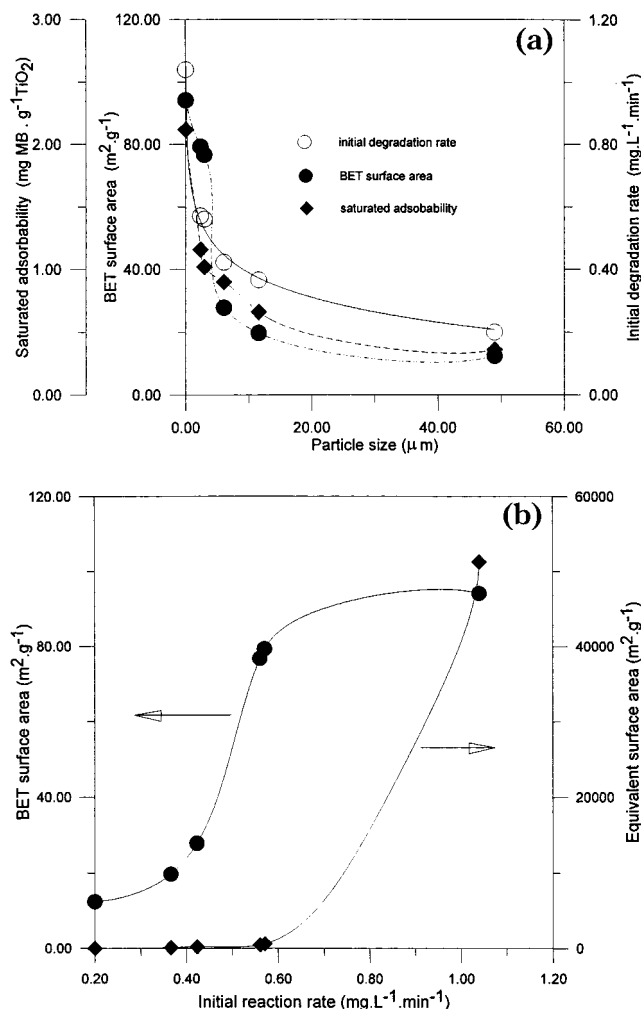


Figure 5. (a) BET surface areas of anatase; saturated adsorptions, and initial degradation rate vs particle sizes. (b) Relationships of initial reaction rate with BET surface area and equivalent surface area.

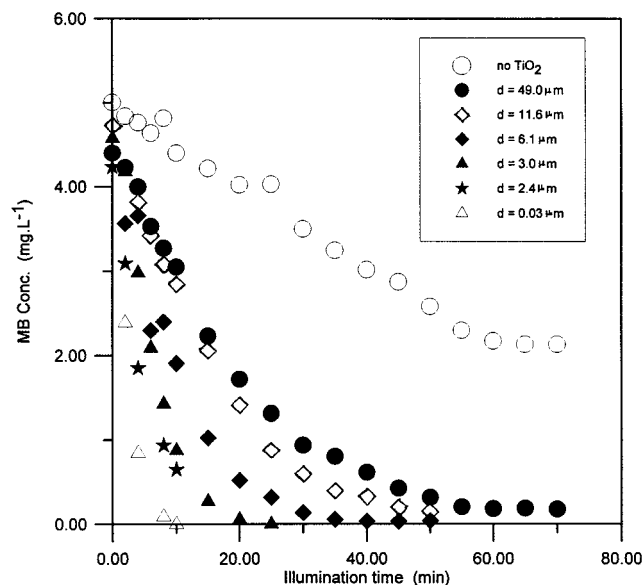


Figure 6. Photodegradation curves of methyl blue using anatase TiO₂ powder of different particle sizes as the catalyst.

slowly with the particle size of the catalyst while the initial degradation rate had a dramatic increase, which could be observed more clearly in Figure 5b. Figure 5b indicates that the activity of the TiO₂ catalyst is affected

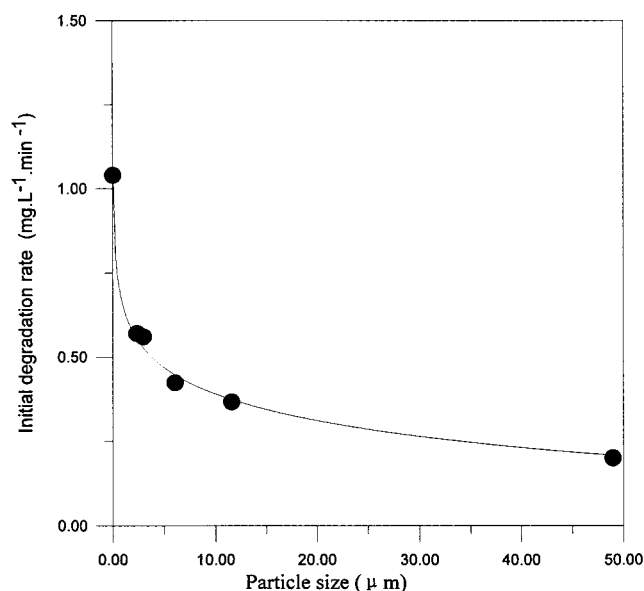


Figure 7. Diagram for the initial degradation rate and particle size.

by its external surface. The equivalent surface area calculated from the mean particle size is the total external surface area that involved in 1 g of TiO₂ catalysts when the particles were regarded as spherical. In conclusion, as reported by Yamashita et al.,¹⁴ in liquid-phase photocatalytic reactions, TiO₂ having a large surface area is a more important factor in achieving high photocatalytic activity. However, they have not mentioned a direct relationship between the BET surface area and the photocatalytic reactivity.

Effects of Particle Size of TiO₂ on the Kinetics of Photocatalytic Reaction. The relationship between the reaction rate and particle size could be determined for the suspended systems by examining the experimental results. The initial rate of degradation of MB increased and the half-life, $t_{0.5}$, decreased with a decrease in the particle size of TiO₂. The mathematical relationship between the initial rate of degradation and particle size could be obtained as follows:

$$a = -0.114 \ln(d) + 0.652 \quad (1)$$

where a is the initial rate of degradation (mg · L⁻¹ · min⁻¹) and d is the particle size (μm). The correlation coefficient is 0.99. The experimental and fitting results were plotted in Figure 7.

The time of half degradation will be shortened with a decrease in the photocatalyst particle size. The mathematical relationship between $t_{0.5}$ and the particle size was also obtained from the experimental data and is as follows:

$$t_{0.5} = 3.905 \ln(d) + 0.707 \quad (2)$$

where $t_{0.5}$ was the time of half degradation (min) and d was the particle size (μm). The correlation coefficient was 0.95. Figure 8 shows a comparison of the experimental and calculated results.

According to experimental results, the photodegradation of MB obeys the first-order reaction law. The first-order rate constant, k , can be obtained from the regression of experimental data.

$$\ln(C) = \ln(C_0) - kt \quad (3)$$

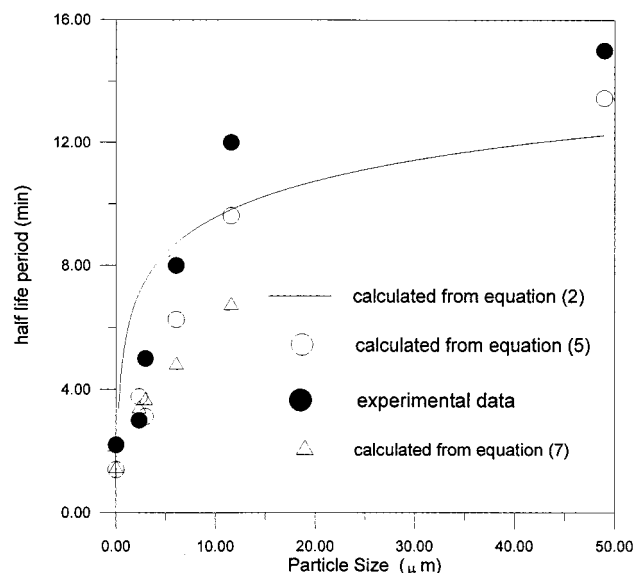


Figure 8. Half degradation time as a function of particle size.

$$C = \exp[\ln(C_0) - kt] \quad (4)$$

where C_0 and C are the initial concentrations of MB and MB at the reaction time t , respectively. k is the first-order photodegradation rate constant of MB.

Hence, the k values could be obtained by regressing the experimental data of $\ln(C)$ and t and are listed in Table 2. Substituting k into eq 4, the curves of MB concentration C versus the reaction time t could be obtained. Figure 9 shows a comparison of the experimental and calculated results.

Following from eq 3, when $C/C_0 = 0.5$,

$$t'_{0.5} = \frac{0.693}{k} \quad (5)$$

could be obtained by substituting k into eq 5. They are also listed in Table 2. A comparison of half degradation periods of MB that depended on particle sizes from experimental results and those calculated from eqs 2 and 5 was graphed in Figure 8. It confirms that eq 2 is reasonable.

Furthermore, it could be found that the k value increases as the particle size decreased. The mathematical relationship was obtained as follows:

$$k = -0.064 \ln(d) + 0.260 \quad (6)$$

where k (min^{-1}) is the first-order reaction constant for the photodegradation of MB and d (μm) is the particle size. Its correlation coefficient is 0.96. The comparison of experimental measurements and correlation results are shown in Figure 10.

Moreover, from Figure 11, one can also find the same form of the correlation between k and d , where k and the saturated adsorbability have a linear relationship and d and the saturated adsorbability have a logarithmic relationship. Subsequently, a linear relation of k versus $\ln(d)$ can be obtained. From this way, a conclusion may be obtained so that the rate constant is mainly decided by the amount of substrate adsorbed on the photocatalyst surface. However, the surface area of particles is mainly affected by the particle size. So the correlation form of k and d is expected to be available for more systems.

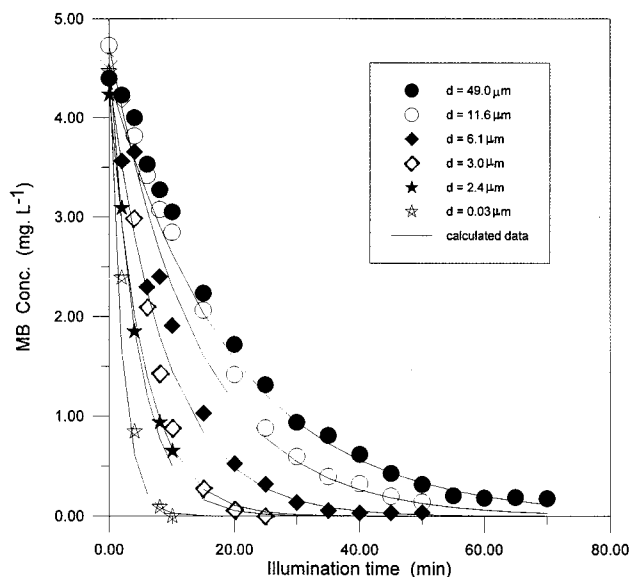


Figure 9. Photodegradation curves of MB for a comparison of experimental and calculated results.

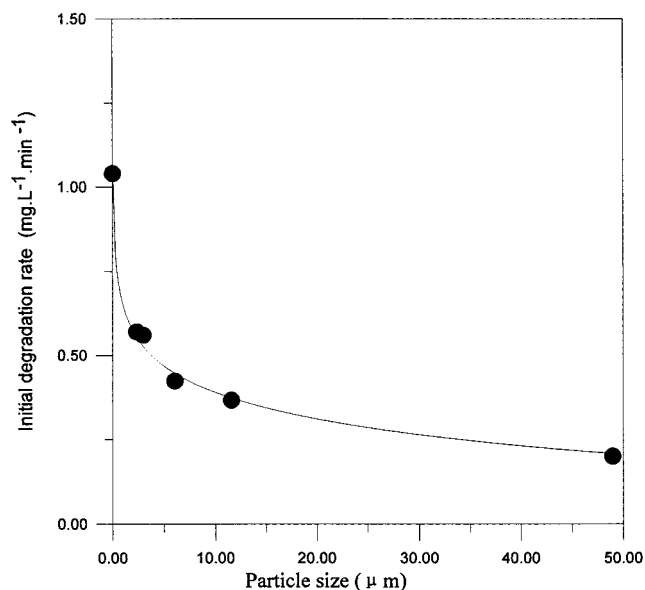


Figure 10. Relationship of first-order reaction constant for the photodegradation of MB and TiO_2 particle sizes.

By the substitution of eq 6 into (5), another expression for $t'_{0.5}$ was obtained as follows:

$$t'_{0.5} = \frac{0.693}{k} = \frac{0.693}{-0.064 \ln(d) + 0.260} \quad (7)$$

Then, data for $t'_{0.5}$ could be calculated from eq 7. The results were also plotted in Figure 8. As shown in Figure 8, the deviations of these data from experimental results were relatively large, especially at a particle size of $49.0 \mu\text{m}$; $t'_{0.5}$ was about 63 min, which might be caused by the deviations transmitted from eq 6.

Conclusions

Ultrafine TiO_2 particles could be synthesized by the sol-gel method. The adsorption process and the photocatalytic degradation of methylene blue (MB) in TiO_2 suspended solution were determined for different particle sizes of TiO_2 . The adsorption rate and adsorbability

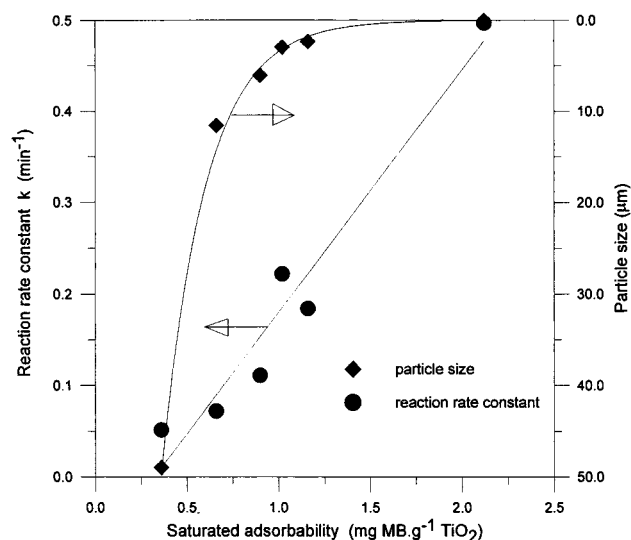


Figure 11. Correlation of reaction rate constant k and particle size d vs saturated adsorbability.

Table 2. First-Order Reaction Rate Constants and Half-Life Period $t_{0.5}$ with Different Anatase Particle Sizes

particle size	rate constant k (min^{-1})	$t_{0.5}$, experimental (min)	$t_{0.5}$, calculated from eq 2 (min)
49.0 μm	0.05	15	13.5
11.6 μm	0.07	12	10.0
6.1 μm	0.11	8	6.3
3.0 μm	0.22	5	3.2
2.4 μm	0.18	3	3.8
30 nm	0.50	2	1.4

of MB on suspended TiO_2 particles increased as the particle sizes decreased. Photocatalytic activity also increased with the decrease in the TiO_2 particle size. The relationship between the initial degradation rate a ($\text{mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$) and particle size d (μm) was logarithmic, $a = -0.114 \ln(d) + 0.652$. The half time for photocatalytic degradation of MB decreased with the decrease in the TiO_2 particle size. The correlation between $t_{0.5}$ (min) and particle size d (μm) was also logarithmic $t_{0.5} = 3.905 \ln(d) + 0.707$. The first-order reaction constant for the photodegradation of MB increased as the TiO_2 particle size decreased. The mathematical relationship of first-order constant k (min^{-1}) and particle size d (μm) was logarithmic, $k = -0.064 \ln(d) + 0.260$. The mathematical relationships between a , $t_{0.5}$, k , and d and were all logarithmic.

The photocatalytic activity increased as the TiO_2 particle size became smaller, especially for sizes less than 30 nm. However, it was below 10 nm for a dramatic increase in a fixed-type reaction to occur. This shows that a TiO_2 suspended-type photocatalytic reaction is more applicable than the fixed-type, as it will overcome the difficulties for the preparation of ultrafine TiO_2 catalyst particles. The equipment for the suspended type is also simpler than the fixed type. The industrialization of the TiO_2 suspended-type photoreactor will be easier once the problem of separation of fine TiO_2 particles is

solved. The application of the ceramic membrane for this problem is now in progress and will be published.

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Nomenclature

a = the initial degradation rate of methylene blue, $\text{mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$
 C = concentration of methylene blue, $\text{mg}\cdot\text{L}^{-1}$
 C_0 = initial concentration of methylene blue, $\text{mg}\cdot\text{L}^{-1}$
 d = titanium dioxide particle size (diameter), μm
 k = first-order reaction rate constant, min^{-1}
 t = illumination time, min
 $t_{0.5}$ = half-life period of methylene blue, min
 $t'_{0.5}$ = half-life period calculated with eq 5 and/or eq 7, min

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