Photocatalytic degradation of dimethoate using nanosized TiO$_2$ powder

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Abstract

Photocatalytic degradation of dimethoate using nanosized TiO$_2$ powder at different conditions were investigated in an XPA-II type reactor. The degradation efficiency of dimethoate increases with elevated concentration of TiO$_2$ suspension up to 0.6 g/L, while the efficiency reduced slightly when the concentration of TiO$_2$ is above 0.6 g/L due to the shielding effect. The kinetic rate of dimethoate degradation decreases with increasing initial concentration of dimethoate, which can be described using the first-order model. An alkaline environment and enhanced power of UV-lamp are conducive to dimethoate degradation. The presence of H$_2$O$_2$/K$_2$S$_2$O$_8$ and ultrasonic irradiation can significantly enhance dimethoate degradation. However, the increment in degradation efficiency may be suppressed to some extent due to being scavenged of $\cdot$OH species by excessive H$_2$O$_2$/K$_2$S$_2$O$_8$ at a high concentration level.

Keywords: Photocatalysis; TiO$_2$; Organophosphorous; Dimethoate; Degradation

1. Introduction

The population of organophosphorous pesticides accounts for above 70% of the total 200 types of pesticides used in China [1]. The wide use of organophosphorous pesticides has caused large-scale development of the agrochemical industries. Consequently, increasing amount of organophosphorous pesticide wastewaters in manufacturing process were produced. The concentration of the pesticides in the wastewaters is usually high and needs treatment because a direct discharge of the wastewaters will result in significant contamination of surface and ground waters due to their acutely toxic and carcinogenic nature [2]. This type of contaminants is usually poorly biodegradable or recalcitrant to environmental conditions, and many of them are toxic to microorganisms and may cause direct destruction or inhibition of their catalytic capacities [3]. As a result, effective treatment methods for eliminating
phosphorus pesticides have been in urgent demand. The activated-sludge process was used to treat organophosphorus pesticide wastewaters but did not work efficiently due to the resistance of the pesticides to bacteria degradation [4].

In recent years, nanosized TiO$_2$ has been used as an effective and nontoxic semiconductor photocatalyst for degradation of a wide range of organic contaminants, including organophosphorus pesticides [5]. Compared with the conventional physical, biological and chemical methods, photochemical degradation using nanosized TiO$_2$ as catalyst is especially suitable for eliminating refractory organic contaminants due to a high photocatalytic activity of nanosized TiO$_2$ [6]. Another attractive aspect using this method is that the operation can be carried out at ambient condition.

Photodegradation efficiency of some types of organophosphorus pesticides, for example, dichlorvos, parathion and 2,2-dichlorovinyl dimethyl phosphate (DDVP) have already been investigated [7]. These studies indicated that, although some organophosphorus pesticides could be efficiently degraded at optimal conditions with the final products of PO$_4^{3-}$, CO$_2$ and other inorganic species, many factors such as photocatalytic activity of TiO$_2$, the dosage of catalyst, and light intensity could influence dramatically the photodegradability of those pesticides [8]. Also the photodegradability of this type of pesticides varies substantially depending heavily on their chemical structures. The degradability follows the trend of phosphate > phosphorothioate > phosphorodiethioate. Up to date, some potential factors likely to influence the photodegradability of organophosphorus pesticides have not been well documented [9].

In the present study, the photodegradation of a widely used organophosphorus pesticide, dimethoate [O,O-dimethyl-S-(N-methyl carbamoylmethyl) phosphorodiethioate], was conducted in order to obtain some knowledge of various parameters that may affect the photodegradation efficiency of the pesticide. The chemical structure of dimethoate is shown in Fig. 1. We focused on the following parameters: the dosage of TiO$_2$ catalyst used, the initial concentration and initial pH of dimethoate, the power of ultraviolet light used, and the presence of oxidants H$_2$O$_2$/K$_2$S$_2$O$_8$ and ultrasonic irradiation.

2. Experimental

2.1. Materials

Dimethoate (purity >98%) was purchased from the Dafeng Pesticide Factory, Yancheng, China, and used as received without further purification. Nanosized TiO$_2$ was purchased from the Degussa Company (anatase/rutile: 70/30, mean size 21 nm, specific surface area 50±15 m$^2$/g). All chemical reagents, sulfuric acid, ascorbic acid, ammonium molybdate [(NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O], potassium antimony tartrate [K$\text{SbC}_4\text{H}_4\text{O}_7$.1/2H$_2$O], sodium hydroxide, peroxide hydrogen, and peroxydisulfate [K$_2$S$_2$O$_8$], are of GR grade. A stock solution of dimethoate (0.02 mol/L) was prepared by dissolving 2.3393 g dimethoate in 500 mL deionized water. Dimethoate solutions of various pH were adjusted by dilute HCl or NaOH solutions.

2.2. Photocatalytic degradation experiment

The photocatalytic degradation of dimethoate was conducted in an XPA-II type photochemical reactor (Xujiang Machine Factory, Nanjing, China) equipped with a 300 W or 500 W high-pressure mercury lamp (mean wavelength...
365 nm). The set-up is shown in Fig. 2. A certain amount of TiO₂ catalyst and dimethoate solution were loaded into the reactor and the suspension was dispersed in an ultrasonic wave for 10 min. The reactor was then fitted into the constant temperature water bath (25±1°C), which was fixed on the base of the apparatus. Prior to an UV irradiation, the suspension was magnetically stirred under a 400 ml/min airflow condition for 30 min in order to achieve a maximal adsorption of the pesticide on TiO₂ surface and keep an aeration circumstance. The suspension was kept stirring under airflow condition during the entire degradation process. Aliquots of 10-mL suspension were sampled using a syringe at specific time intervals and filtrated through a 0.22-µm syringe-end filter. The pH of the filtrates was determined immediately after filtration. The filtrates were then stored at 4°C until determination of dimethoate and phosphate (one of inorganic products of dimethoate degradation). Solution pH (2–11.05), dimethoate concentration (0.39×10⁻⁹–9.80×10⁻⁴ mol/L), catalyst dose (0–1.0 g/L), UV light intensity, and the presence of oxidants H₂O₂ or K₂S₂O₈ were investigated for their effects on the photodegradation efficiency.

The effect of ultrasonic irradiation on photodegradation efficiency was also investigated. Briefly, an ultrasonic probe (22 kHz, 800 W), and a 15W UV-lamp (mean wavelength 235.5 nm) fitted in a quartz cold trap were vertically put in a beaker containing 500-mL dimethoate solution (0.39×10⁻⁴ mol/L). The probe was located 5 cm below the surface of the solution. After a combined UV and ultrasonic irradiation for 90 min under airflow condition, the suspension was filtrated using the same method above and the resultant filtrates were stored at 4°C pending determination of dimethoate. For comparison, degradation experiments under ultrasonic irradiation alone and UV irradiation alone were also performed.

2.3. Analytical method

The pH was measured potentiometrically using a glass electrode. The amount of dimethoate degraded was indirectly determined using the
concentration of phosphate because the generation of phosphate stoichiometrically represent the degradation of dimethoate, with one mole of phosphate released for each mole of dimethoate. The concentration of phosphate was determined using the phosphomolybdate blue method [10]. The efficiency was defined as:

$$\eta \% = \frac{C_0 - C_t}{C_0} \times 100\%$$

where $C_0$ (mol/L) is original concentration of dimethoate and $C_t$ (mol/L) the concentration of dimethoate at time $t$.

3. Results and discussion

3.1. Effect of catalyst loading

The effect of catalyst dosage on photocatalytic degradation of dimethoate under an irradiation of a 500W UV-lamp within 120 min is showed in Fig. 3. When the UV irradiation alone was employed, the degradation efficiency was only 3.22%. The presence of TiO$_2$ catalyst significantly enhanced the degradation. After 120 min, the degradation efficiency increased with increasing dose of TiO$_2$ and reached a maximum of 80.15% at a dose of 0.6 g/L, which was followed by a decrease with a further increase in catalyst dosage. Generally, the degradation efficiency can be enhanced with increasing concentration of TiO$_2$ due to the increase in total surface area available for contaminant adsorption. Up to a concentration high enough, however, TiO$_2$ particles may block UV light passage, leading to an increase in the light scattering and consequently a decrease in the exposure of TiO$_2$ particles to the UV light [11]. In this case, a further increase in TiO$_2$ particles could not further enhance, but even decrease, the degradation efficiency as shown in Fig. 3. In subsequent experiments, the dose of 0.6 g/L was chosen as the optimal concentration of TiO$_2$.

3.2. Effect of initial pH of solution

The effect of initial pH of solution on photocatalytic degradation of dimethoate within 60 min is showed in Fig. 4. The initial concentration of dimethoate was $1.96 \times 10^{-4}$ mol/L. The degradation efficiencies at initial pH 2.04, 6.00 and 11.0 were 10.75%, 36.73% and 79.08%, respectively, indicating that the degradation increased significantly with increasing initial pH. The reason is that OH$^-$ ions with elevated concentration would increasingly scavenge photogenerated holes and concurrently yield highly oxidative $\cdot$OH species through H$^+$ + OH$^-$ → $\cdot$OH [12]. In a low pH condition, however, the degradation mainly resulted from photogenerated holes, whose oxidizing ability is somewhat lower than that of $\cdot$OH species [13]. Consequently, the degradation efficiency of dimethoate in 60 min was lower at low pH than at high pH. Similar results were reported in the literature [14,15].

The resultant pH of solutions after degradation decreased to different extent compared with their initial pH values, for instance from initial pH 2.04, 6.00 and 11.05 to 1.97, 3.17, and 4.34, respectively. The reduction were caused mainly by the consumption of OH$^-$ ions in H$^+$ + OH$^-$ → $\cdot$OH process as well as the production of phos-
phorous acid, sulfuric acid, and nitric acid from the oxidation of dimethoate. However, the generation of sulfuric acid, and nitric acid during the degradation of dimethoate was not detected in the present study.

3.3. Effect of initial concentration of dimethoate

The variation in degradation efficiencies of dimethoate and concentration of PO$_4^{3-}$ at varying initial concentrations of dimethoate are shown in Fig. 5(a, b). Obviously, both the degradation efficiencies and kinetic rates decrease significantly with an increase in the initial concentration of dimethoate (Fig. 5a). For instance, when the initial concentrations of dimethoate were $0.39 \times 10^{-4}$ and $9.80 \times 10^{-4}$ mol/L, the degradation efficiencies in 60 min were 83% and 10%, respectively. It is reported that the recombination of photo-generated electrons and holes at the surface of TiO$_2$ can completes within $10^{-9}$ s [16], which implies that the contaminants could not be degraded unless they are adsorbed on the surface of TiO$_2$. Thus surface adsorption process is of paramount importance in controlling the degradation of dimethoate. At a fixed dosage of TiO$_2$ and consequently constant total sites available for absorption, the degradation efficiency is expected to decrease with an increase in the initial concentration of dimethoate.

Based on the result of the increase in PO$_4^{3-}$ concentration with time (Fig. 5b), it is clear that the kinetic rate of PO$_4^{3-}$ production increases with an increase in the initial concentration of dimethoate. However, the rate remains almost unchanged when the initial concentration is up to $9.8 \times 10^{-4}$ mol/L. This is because, with the increase in dimethoate concentration, the amount of adsorbed dimethoate and consequently the rate of PO$_4^{3-}$ production increase; when the surface concentration of dimethoate reaches a steady state, however, the rate of PO$_4^{3-}$ production will remain constant.

As a whole, in the entire photocatalytic process, it was the total adsorption sites available
Fig. 6. The relationship between kinetic rate constant and initial concentration of dimethoate.

being the dominant controlling factor that resulted in different degradation efficiencies between low and high dimethoate concentrations.

Kinetic degradation rate is crucial for evaluating photocatalytic activity of TiO₂ and feasibility of the photocatalytic degradation method. An attempt was made to fit the data for dimethoate degradation at three initial concentration levels using some common kinetic equations and it was found that the kinetics for dimethoate degradation could be satisfactorily described using the first-order rate equations:

\[ \ln \left( \frac{C_t}{C_0} \right) = kt \]

where \( C_0 \) is initial concentration of dimethoate and \( C_t \) is residual concentration at time \( t \), \( k \) is rate constant. The plot of \( k \) vs initial concentrations of dimethoate is given in Fig. 6.

3.4 Effect of UV-lamp power

The effect of UV-lamp power on dimethoate degradation in 120 min is showed in Fig. 7. Within 120 min, the degradation efficiency was appreciably higher under irradiation of a 500W UV-lamp (80.15%) than of a 300W UV-lamp (37.07%). Theoretically, with an increase in UV-lamp power (and thus its light intensity), the photogenerating rate of electron-hole pair at the surface of TiO₂ and consequently the oxidizing ability of the system increase [17]. Therefore, it is expected that the kinetic rate constant \( k \) for dimethoate degradation is directly proportional to the light intensity \( I \). The calculated first-order rate constants \( k \) of dimethoate degradation under the irradiation of a 500W UV-lamp was 0.0125 min⁻¹, significantly higher than that under the irradiation of a 300W UV-lamp (0.0040 min⁻¹), validating the theoretical reasoning above.

3.5. Effect of the presence of oxidant

Effectively preventing recombination of photogenerated electrons and holes is of critical importance to improve photocatalytic ability of TiO₂ catalyst [18]. It is reported that the presence of some oxidants can serve as electron-scavengers to prevent the recombination, and thus dramatically enhance the photodegradation efficiency of organic contaminants [19]. The results of H₂O₂- or K₂S₂O₈-assisted photodegradation of dimethoate in 60 min are shown in Fig. 8.

Obviously, the presence of low concentration H₂O₂ or K₂S₂O₈ (2.0 mmol/L) pronouncedly elevated the degradation of dimethoate. A further increase in degradation efficiency was not
observed with an increase in concentration of H$_2$O$_2$ or K$_2$S$_2$O$_8$. Instead, a slight decrease occurred when the concentrations of H$_2$O$_2$ and K$_2$S$_2$O$_8$ were above 8.0 and 6.0 mmol/L, respectively. As strong oxidants, H$_2$O$_2$/K$_2$S$_2$O$_8$ can serve as efficient scavengers of electrons to prevent electron-hole recombination at the surface of catalyst through the following reactions [18, 20]:

\[
\begin{align*}
  \text{H}_2\text{O}_2 + e^- &\rightarrow \cdot\text{OH} + \text{OH}^- \\
  \text{S}_2\text{O}_8^{2-} + e^- &\rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} \\
  \text{SO}_4^{2-} + e^- &\rightarrow \text{SO}_4^{2-} \\
  \text{SO}_4^{2-} + \text{H}_2\text{O} &\rightarrow \text{SO}_4^{2-} + \cdot\text{OH} + \text{H}^+
\end{align*}
\]

Furthermore, hydroxyl radicals ($\cdot$OH) and sulfate radicals ($\text{SO}_4^{2-}$), two highly oxidizing species produced in the above reactions, would also contribute to the decomposition of dimethoate. But, at a concentration high enough, excessive adsorption of H$_2$O$_2$/K$_2$S$_2$O$_8$ on TiO$_2$ surface probably prevents dimethoate from approaching the surface of TiO$_2$, resulting in a slight decrease in dimethoate degradation as shown in Fig. 8. In addition, it is reported that $\cdot$OH may be scavenged by excessive H$_2$O$_2$ through the following processes [21]:

\[
\begin{align*}
  \cdot\text{OH} + \text{H}_2\text{O}_2 &\rightarrow \text{H}_2\text{O} + \text{HO}_2^- \\
  \cdot\text{OH} + \text{HO}_2^- &\rightarrow \text{H}_2\text{O} + \text{O}_2
\end{align*}
\]

These processes would further reduce the degradation of dimethoate as confirmed by the results shown in Fig. 8 at high concentrations of H$_2$O$_2$. With respect to K$_2$S$_2$O$_8$ at high concentrations, a similar process was expected to occur to retard the degradation of dimethoate, based on the present experimental data (Fig. 8).

### 3.6. Synergetic effect of UV and US (ultrasonic) irradiation

Sonochemical degradation of organic contaminants has been widely studied in recent years [22–24]. US irradiation generates transient cavitation, which gives rise to local high temperature and high pressure sites, where H$_2$O sonolysis occurs with the production of highly oxidative radical species (H$^+$, $\cdot$OH and HOO$^-$), and even a direct destruction of organic pollutants [22,23]. In addition, pitting and cracking of catalyst surface caused by US wave, and the enhanced turbulent flow conditions in the reactor caused by cavitation which increases overall mass transport are all conducive to an increase in degradation rate [25]. The synergetic effect of a combined UV (15W, mean wavelength 235.5 nm) and US (22 kHz, 800 W) irradiations on dimethoate degradation is shown in Fig. 9. At an initial con-
centration of 0.39×10^{-4} \text{ mol/L}, the degradation efficiencies of dimethoate were only 3.18\% and 11.87\%, respectively, when UV irradiation alone and US irradiation alone were applied. The combined application of UV and US irradiation obviously enhanced the degradation to 35.02\%, indicating the existence of synergetic effect of sonochemical and photocatalytic degradations.

4. Conclusion

Photodegradation using TiO_2 as catalyst is an efficient method for eliminating dimethoate and, at optimal operating parameters, the degradation efficiency could reach 99\% in 160 min when the concentration of dimethoate is below 1.96×10^{-4} \text{ mol/L}. Titanium dioxide loading has significant effect on the degradation of dimethoate. The degradation efficiency increases with elevated concentration of TiO_2 suspension up to 0.6 g/L, then the efficiency reduced slightly when the concentration is above 0.6 g/L due to a light-shielding effect. The kinetic rate of dimethoate degradation decreases with increasing initial concentration of dimethoate, which can be described using the first-order model. An alkaline environment and enhanced power of UV-lamp are conducive to dimethoate degradation. The presence of oxidants H_2O_2/K_2S_2O_8 and US irradiation can pronouncedly enhance photodegradation efficiency of dimethoate. However, the increment in degradation efficiency may be suppressed to some extent due to being scavenged of -OH species by excessive H_2O_2/K_2S_2O_8 at a high concentration level.

References