

## Investigation on the sonocatalytic degradation of parathion in the presence of nanometer rutile titanium dioxide (TiO<sub>2</sub>) catalyst

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### Abstract

The nanometer rutile titanium dioxide (TiO<sub>2</sub>) powder was adopted to act as the sonocatalyst after treatment of high-temperature activation and the ultrasound of low power was used as an irradiation source to induce heat-treated TiO<sub>2</sub> powder performing sonocatalytic degradation of parathion. Although there are many factors influencing sonocatalytic degradation of parathion, the experimental results demonstrate that the optimal degradation condition of parathion can be obtained when the experimental conditions such as initial concentration of 50 mg/L parathion, addition amount of 1000 mg/L nanometer rutile TiO<sub>2</sub>, ultrasonic of 30–50 kHz frequency and 50 W output power, acidity of pH 10.0 and temperature of 20 °C are adopted. The degradation ratio of parathion surpassed 90% within 120 min ultrasonic irradiation in these optimal experiment conditions. The total degradation process of parathion has been monitored by UV–vis spectra and ion chromatography. At last, the parathions in aqueous solution are completely degraded and become some simple inorganic ions such as NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, etc. In addition, the sonocatalytic activities of reused TiO<sub>2</sub> catalysts were also studied and found to decline gradually along with the reused times. In this paper, the research on sonocatalytic degradation kinetics was also been performed and found to follow pseudo first-order reaction. All experiments indicated that the sonocatalytic method in the presence of nanometer rutile TiO<sub>2</sub> powder was an advisable choice for the treatments of non- or low-transparent organic wastewaters in future.

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**Keywords:** Nanometer rutile titanium dioxide (TiO<sub>2</sub>); Sonocatalytic degradation; Parathion

### 1. Introduction

Many tones of organophosphorus insecticides are annually used in agriculture and horticulture, in which some insecticides can be naturally degraded through different pathways such as microbial degradation, chemical hydrolysis and photodegradation. However, the great mass of organophosphorus insecticides is difficult to be naturally degraded within a relatively brief time. Otherwise, during these transformation processes of stepwise degradation, the intermediate products, which may be more toxic than the primary organophosphorus insecticides, are generated. Therefore, the innovative technologies for effectively and completely decomposing all organic pollutants and turning these

organic pollutants into environmental compatible compounds are agog required.

In recent years, the technology of ultrasonic degradation has been studied and extensively used to treat some organic pollutants [1–7]. As known to all, the irradiation of high power ultrasound can result in the acoustic cavitation, namely, the process of the formation, growth and implosive collapse of gas bubbles in liquids and releasing a mass of energies [8]. The acoustic cavitation can generate many hot spots with locally high temperatures and high pressures for short period of time, which give rise to the sonolysis of H<sub>2</sub>O molecules forming the production of some radicals (<sup>•</sup>H, <sup>•</sup>OH and <sup>•</sup>OOH). These radicals can result in the destruction of solutes containing organic pollutants [2,9,10]. Hence, the method of ultrasonic degradation has so many advantages that it is very welcome in domestic and abroad. However, the ultrasonic degradation of organic pollutants using high power ultrasound usually needs lots of electronic

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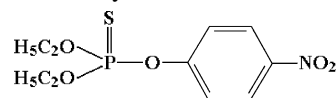
energies, costly equipments and long reaction time [11]. This is a heavy burden for all countries, especially for those developing countries. In order to overcome these drawbacks of ultrasonic degradation, the nanometer titanium dioxide ( $\text{TiO}_2$ ) powders were recently adopted as sonocatalyst because the  $\text{TiO}_2$  powders had already been considered to be a kind of very efficient catalytic material [12]. Furthermore, unlike other semiconductor materials, the  $\text{TiO}_2$  powders are non-toxic, stable, cheap materials and have already been used as the photocatalyst to treat diversified wastewaters all through [13–15]. When the  $\text{TiO}_2$  powders, especially for nanometer anatase  $\text{TiO}_2$  powders, are irradiated by ultraviolet light ( $\lambda \leq 387 \text{ nm}$ ), the photogenerated electrons transit from valence-band to conduction-band and synchronously the formation of electron–hole pairs takes place on the surface or in the interior of  $\text{TiO}_2$  particles [16]. The photogenerated hole is one of the strongest oxidizing agents ( $E = +2.80 \text{ eV}$ ). Thus, these holes not only decompose the organic pollutant adsorbed on the surface of  $\text{TiO}_2$  particles directly, but also degraded the organic pollutant in aqueous solution indirectly through oxidizing  $\text{H}_2\text{O}$  molecules and forming the  $\bullet\text{OH}$  radicals. The method of photocatalytic degradation can almost mineralize all organic pollutants and then finally make them become  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  as well as other simple inorganic ions [17].

However, it is almost helpless to adopt the method of photocatalytic degradation when the non- and low-transparent wastewaters with high concentration or other impurities are treated in practical application. In general, the penetrability of any light except X-ray is very low for non-transparent substances or mediums. Contrarily, the ultrasound has very strong penetrability and the penetrable distance can customarily attain 20–25 cm for any medium. The acoustic cavitation can result in the formation of the lights with broad wavelength range, high temperature and high pressure. Moreover, the ultrasound can usually be competent for catalyzing those chemical reactions that the ultraviolet and visible lights catalyze [18–21]. Hence, in this work, the low power ultrasound was used as an irradiation source instead of ultraviolet light to induce the  $\text{TiO}_2$  particles performing sonocatalytic activities. The research results indicate that the method of sonocatalytic degradation is also feasible in practical application. In the experiment, a kind of typical organophosphorus insecticides, the parathion (O, O-diethyl-O-(4-nitrophenyl)-phosphorothioate), was used as model compound because it was a most common pesticides and possible to use UV–vis spectrum and ion chromatography to monitor its degradation processes and products, respectively. The various affecting factors were reviewed on the sonocatalytic degradation of parathion. Because of the slightly narrow energy gap and appropriate adsorbability, the nanometer rutile  $\text{TiO}_2$  powder after heat-treatment was adopted as sonocatalyst for this work. In conclusion, the method of sonocatalytic degradation has many characteristics such as convenience, safety, credibility and high efficiency, so it is hopeful that this method is extended and applied in the treatment of non- or low-transparent wastewaters on the basis of more research work.

## 2. Experimental

### 2.1. Materials

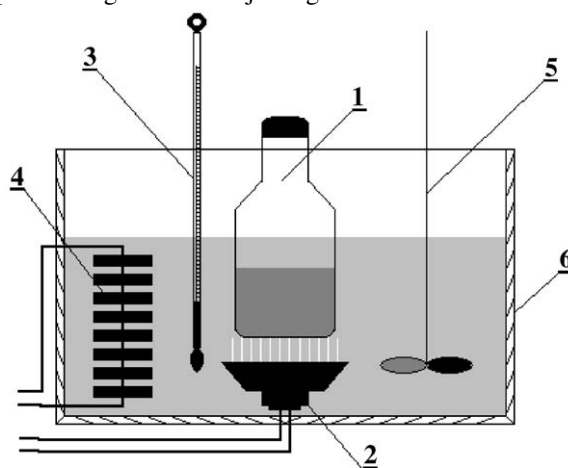
Parathion (O,O-diethyl-O-(4-nitrophenyl)-phosphorothioate, 99.7% purity) was obtained from Shell Research (Sittingbourne, Kent, USA). When the parathion is dissolved in water the UV–vis spectrum shows only one absorption peak at 283 nm. All other chemicals came from high purity Fluka or Aldrich products. The water in this experiment was purified by a Milli-Q water system (Millipore) and was used throughout the experiment. The nanometer rutile  $\text{TiO}_2$  powder (Alleghencyteledyne Company, USA) was used as the titanium source which was heatedly treated for activation.



Molecular structure of parathion

### 2.2. Apparatus

LAMBDA-17 UV–vis spectrophotometer (Perkin-Elmer Company, USA) and ICS-90 Ion Chromatography (DIONEX company, USA) were used to inspect the degradation process of parathion. The parathion solution was irradiated by using KQ-100 Serial-Ultrasonics apparatus (Kunshan Ultrasound Apparatus Company, China), which were operated when the ultrasonic frequency of 20–80 kHz and output power of 20–50 W were adopted through manual adjusting.



Equipment structural diagram

1: glass reactor; 2: energy conversion device; 3: thermometer; 4: heater; 5: stirrer; 6:gullet

### 2.3. Treatment of nanometer rutile $\text{TiO}_2$ catalyst

The nanometer rutile  $\text{TiO}_2$  powder was heatedly treated at  $450^\circ\text{C}$  for 2 h for activation. In order to confirm the crystal phase, the X-ray diffraction (XRD) patterns were recorded on a D8ADVANCE diffractometer (Bruker axs company, Germany) using  $\text{Cu K}\alpha$  radiation with a scan rate of  $2.0^\circ \text{ min}^{-1}$ . Transmission electron microscopy (TEM) was operated using Phillip-EM400T electron microscope (Phillip company, Holand)

at 100 kV was used to describe the size and shape of nanometer rutile TiO<sub>2</sub> particles.

#### 2.4. Experiments of sonocatalytic degradation

The experiments of the sonocatalytic degradation were performed using the self-made glass reactors (bottom area = 50 cm<sup>2</sup>) placed inside an ultrasonic apparatus. Varied output powers of ultrasound from 20 to 50 W and frequencies from 20 to 80 kHz have been used, respectively. The samples were taken out periodically and the degradation ratio of parathion was monitored by the UV–vis spectra, after filtering the liquid with millipore filters to remove the TiO<sub>2</sub> powder. For each experimental process, the pH values were adjusted with diluted NaOH or HCl aqueous solutions. The maximal absorbencies of parathion solution between 0.0 and 50.0 mg/L concentrations abide by Lambert–Beer's law and the calibration curves of standard parathion solutions are used to estimate the degradation ratio.

All spectra of parathion solutions during degradation were recorded by the UV–vis spectrophotometer in the wavelength range from 190 to 600 nm. The changes of degradation ratios were monitored using maximal absorbencies at 283 nm. In order to check up the mineralized degree of parathion, the ion chromatography analyses were performed to monitor the parathion solutions after separating the TiO<sub>2</sub> powders periodically. The degradation products of parathion contain plentiful NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> anions, so the formation yields of NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> anions can express the degradation rate of parathion.

The changes of degradation ratios and pH values of parathion solution were determined every 30 min interval by the UV–vis spectrophotometer and pH meter, respectively. The kinetic result of degradation reaction was also given. The influences of initial parathion concentration, TiO<sub>2</sub> adding amounts, pH values and temperatures of parathion solutions, frequency and output power of ultrasound on the degradation ratios of parathion were measured, respectively. At the same time, the sonocatalytic activities of reused TiO<sub>2</sub> catalyst were also investigated and the results were given. The experimental conditions adopted throughout whole experiments were initial concentration of 50 mg/L parathion, addition amount of 1000 mg/L TiO<sub>2</sub> powder, acidity of pH = 10.0, systemic temperature of 20.0 ± 0.2 °C, ultrasound of 40 kHz frequency and 50 W power except special investigation.

### 3. Results and discussion

#### 3.1. Description of nanometer rutile TiO<sub>2</sub> particles after heat-treatment

As shown in Figs. 1 and 2, the heat-treated nanometer rutile TiO<sub>2</sub> powders are predominantly rutile phase (90% rutile and 10% anatase as determined from XRD) and their particle size are 15–20 nm (as determined from TEM), respectively. Otherwise, the density and the surface area are about 3.56 g cm<sup>-3</sup> and 70 m<sup>2</sup> g<sup>-1</sup>, respectively.

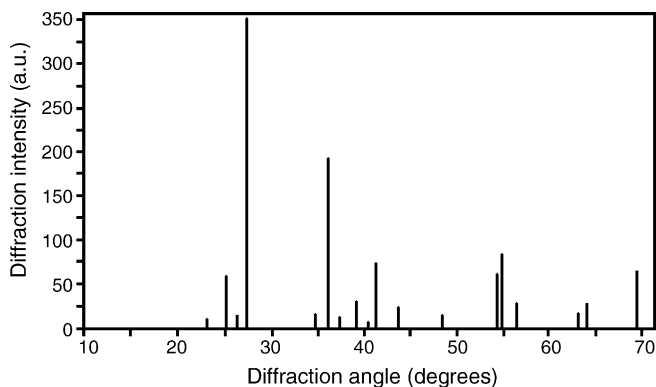


Fig. 1. XRD of nanometer rutile TiO<sub>2</sub> after heat-treatment.

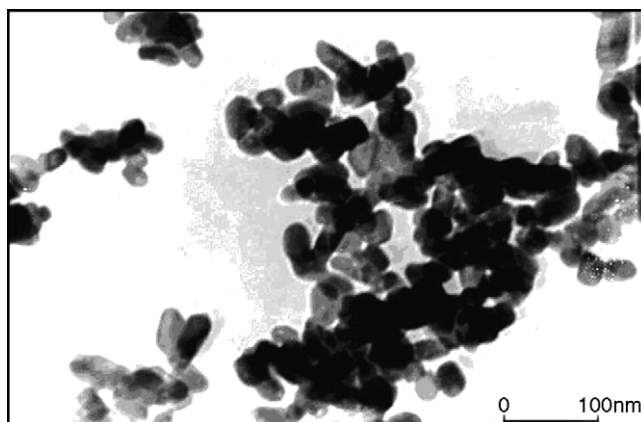


Fig. 2. TEM of nanometer rutile TiO<sub>2</sub> after heat-treatment.

#### 3.2. UV–vis spectra of parathion solution during degradation

In order to exhibit the process of the sonocatalytic degradation of parathion, the UV–vis spectra of the parathion solution before and during degradation in the presence of nanometer rutile TiO<sub>2</sub> powders were determined as shown in Fig. 3. It could be found that the absorption peak of parathion solution at 283 nm declined all through along with ultrasonic irradiation, which indicated that the parathion molecules dissolved in aqueous

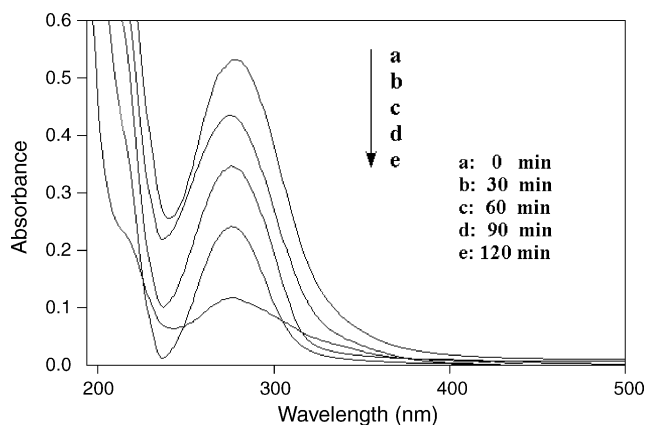


Fig. 3. UV–vis spectra of parathion solutions during degradation: (a) 0.0 min; (b) 30 min; (c) 60 min; (d) 90 min; (e) 120 min.

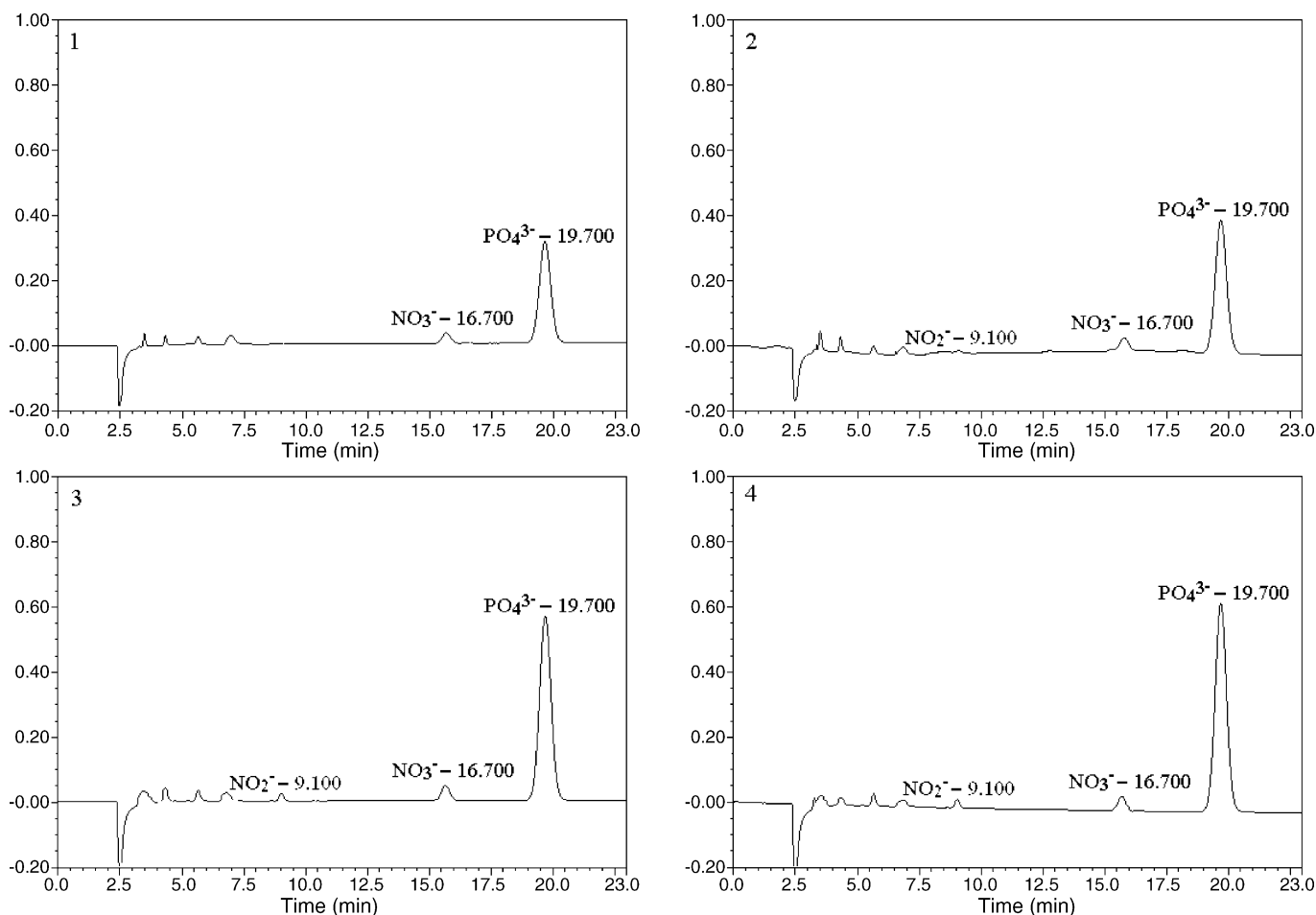


Fig. 4. The ion chromatogram of parathion solution during ultrasonic irradiation: (1) 30 min; (2) 60 min; (3) 90 min; (4) 120 min.

solution and adsorbed on the surface of  $\text{TiO}_2$  particles were decomposed continuously. Otherwise, an unobvious shoulder absorption peak around 235 nm also appears in UV–vis spectra at 30 min ultrasonic irradiation, and then quickly becomes weaker and weaker along with the ultrasonic irradiation and finally undiscerned, which indicates that the intermediate (*p*-nitrophenol) from parathion molecule is also degraded stage by stage until disappears completely.

In fact, the sonocatalytic degradation process of parathion depends on both crystal form and granularity of  $\text{TiO}_2$  particles. For some organic pollutants, the nanometer anatase  $\text{TiO}_2$  powders sometimes display the strong adsorbability. The superfluous adsorption not only makes the  $\text{TiO}_2$  particles be unable to absorb any light or heat energy, but also protect the organic pollutants adsorbed on the surface of nanometer anatase  $\text{TiO}_2$  particles from decomposition. This is the reason why the nanometer anatase  $\text{TiO}_2$  powders are not adopted as the sonocatalyst for this investigation. The adsorbability of nanometer rutile  $\text{TiO}_2$  powders was reviewed in detail. It was found that the absorption peak of parathion solution at 283 nm only slightly declined in the presence of nanometer rutile  $\text{TiO}_2$  powders without ultrasonic irradiation comparing the original parathion solution. In addition, the one-fold ultrasonic degradation in the absence of any  $\text{TiO}_2$  powder was also considered for comparing with the

sonocatalytic degradation. The results show that the absorption peak of parathion solution is unchanged almost under one-fold ultrasonic irradiation, which indicates that such ultrasound of low output power can hardly degrade the parathion in aqueous solution. Hence, the disappearances of parathion attribute to the sonocatalytic degradation, and not one-fold ultrasonic degradation and adsorption of the nanometer rutile  $\text{TiO}_2$  powders.

### 3.3. Ion chromatography of parathion solution during degradation

In order to further prove and explore the degradation process of parathion, the determinations of ion chromatography at different moment under ultrasonic irradiation in the presence of nanometer rutile  $\text{TiO}_2$  powder within 120 min were conducted as shown in Fig. 4. Because of containing the nitrogen, sulphur and phosphorus atoms in parathion molecule, the  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  anions should be produced after degradation. It is a pity that the peak at 21.34 min corresponding  $\text{SO}_4^{2-}$  anion was not found in the ion chromatography except those  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  anions which appear at 9.100, 16.700 and 19.700 min, respectively. In general, under the ultrasonic irradiation, a few of  $\text{TiO}^{2+}$  cations can form in solution. When these  $\text{TiO}^{2+}$  cations encounter  $\text{SO}_4^{2-}$  anions, the insoluble sulphates

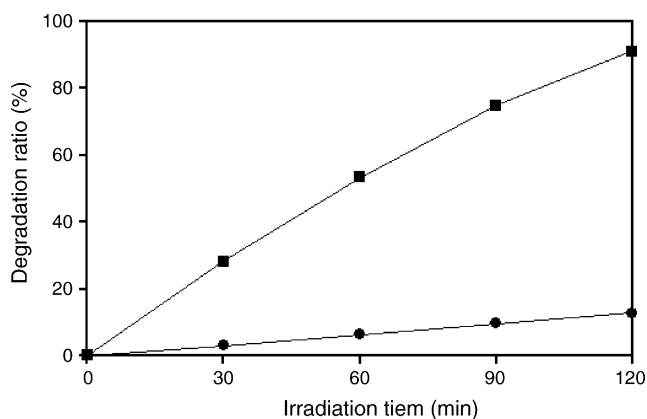


Fig. 5. Effect of irradiation time on degradation ratio: (■) ultrasound + nanometer rutile TiO<sub>2</sub>; (●) only ultrasound.

come into being immediately. Hence, the SO<sub>4</sub><sup>2-</sup> anions were not appear at 21.34 min position in the ion chromatography which belongs to the standard peak of SO<sub>4</sub><sup>2-</sup> anions. Otherwise, the unusually short peak relative to NO<sub>3</sub><sup>-</sup> anion appears at 16.70 min, which indicates that the volatile nitrogen oxides may escape from the reaction system during sonocatalytic degradation. At all events, all peaks gradually increases along with the ultrasonic irradiation, which adequately accounts for the sonocatalytic degradation of parathion.

#### 3.4. Effect of irradiation time on degradation ratio and reaction kinetics

The degradation ratios of parathion under ultrasonic irradiation in the presence of nanometer rutile TiO<sub>2</sub> powder at 30 min interval within 120 min were calculated using the biggest absorbance (at 283 nm) of UV–vis spectra. For the comparison, the degradation ratios of parathion with one-fold ultrasonic irradiation were also given in Fig. 5. It was obviously observed that the degradation ratios of two courses all rose along with increasing irradiation time, but a complete degradation of parathion was achieved at 120 min in the presence of nanometer rutile TiO<sub>2</sub> powder. The considerably low degradation ratio in the absence of any TiO<sub>2</sub> catalyst was only 12.57% in the same ultrasonic irradiation time. These results indicate that the degradation effect of parathion in the presence of nanometer rutile TiO<sub>2</sub> powder combining with ultrasonic irradiation are more obvious than that of using one-fold ultrasonic irradiation.

In addition, the experimental results also demonstrate that the degradation reactions of two cases both follow pseudo first-order kinetics as shown in Fig. 6 and the pseudo first-order rate constants are 0.0195 and 0.0012 min<sup>-1</sup>, respectively, corresponding ultrasonic irradiation integrated nanometer rutile TiO<sub>2</sub> powder and one-fold ultrasonic irradiation.

#### 3.5. Change of pH values during degradation

During the sonocatalytic degradation of parathion, the pH values of parathion solution gradually declined along with ultrasonic irradiation because the organic pollutants were contin-

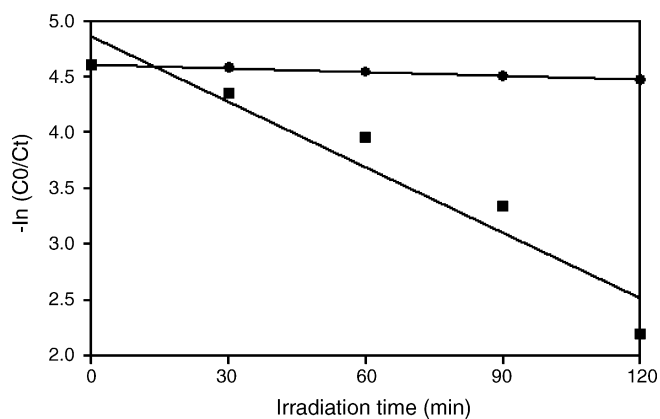


Fig. 6. Reaction kinetics on sonocatalytic degradation of parathion: (■) ultrasound + nanometer rutile TiO<sub>2</sub>; (●) only ultrasound.

uously decomposed and formed those simple inorganic ions such as SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> as well as CO<sub>2</sub>, H<sub>2</sub>O and so on. In fact, this degradation process was accordant with the photocatalytic degradation in the presence of TiO<sub>2</sub> catalyst. Otherwise, it can be seen from Fig. 7 that at every ultrasonic irradiation moment the acidities of the parathion solution in the presence of nanometer rutile TiO<sub>2</sub> powder is higher than corresponding ones in the absence of any TiO<sub>2</sub> catalyst at all times, which also indicate that the degradation effect of parathion in the presence of nanometer rutile TiO<sub>2</sub> powder is the best comparing with the one-fold ultrasonic irradiation. Perhaps it is possible that the change of pH values of wastewater solution can be used to judge the degradation degree of some organic pollutants like parathion.

#### 3.6. Effect of initial parathion concentration on degradation ratio

Different parathion concentrations ranging from 25.0 to 100.0 mg/L were used to discuss the influences of initial concentration on the degradation ratio of parathion. It was found that the best degradation effect was obtained in the presence of nanometer rutile TiO<sub>2</sub> catalyst when the concentration of 50.0 mg/L was adopted as shown in Fig. 8. Afterwards, the degradation effect

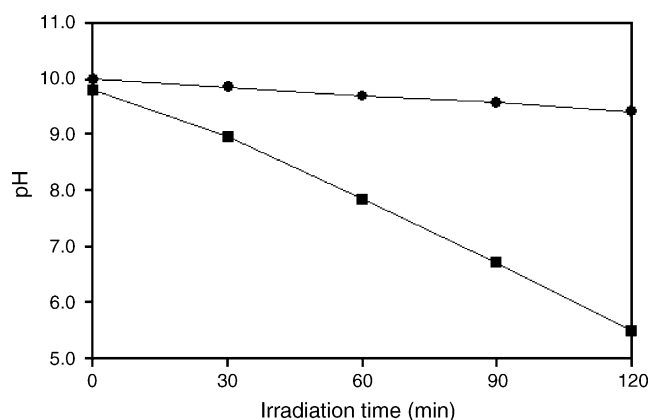


Fig. 7. Change of pH values during degradation of parathion: (■) ultrasound + nanometer rutile TiO<sub>2</sub>; (●) only ultrasound.

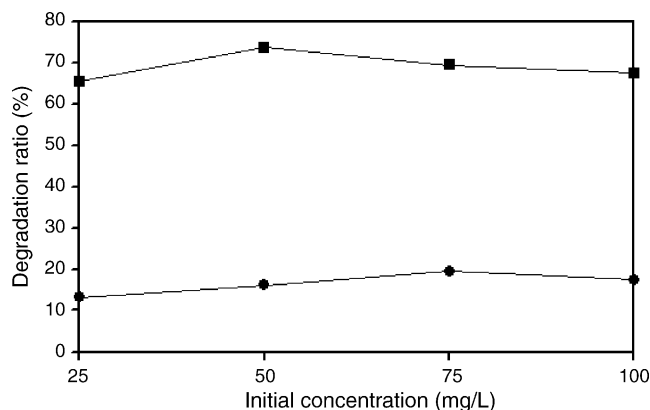


Fig. 8. Effect of initial concentration on degradation ratio of parathion: (■): ultrasound + nanometer rutile TiO<sub>2</sub>; (●) only ultrasound.

slowly fell with increasing concentration of parathion. Perhaps the two following reasons bring on the decrease of degradation ratios. Firstly, the adsorption amounts of nanometer rutile TiO<sub>2</sub> powder attain the saturation for superfluous parathion. The nanometer rutile TiO<sub>2</sub> particles have stated adsorbabilities because of their large surface area. In general, the proper adsorption is of advantage to the sonocatalytic degradation of parathion to a certain extent. However, the excessive adsorption customarily prohibits TiO<sub>2</sub> particles from absorbing light or heat energies resulting from the acoustic cavitation, which has parathion molecules adsorbed on the surface of TiO<sub>2</sub> particles attain the protection. Secondly, the mutual screens between parathion molecules and nanometer TiO<sub>2</sub> particles also increase along with the concentration rising of parathion. Large numbers of parathion molecules in high concentration solution not only absorb the light resulting from acoustic cavitation, but also disturb the transmission of ultrasound. Beyond all doubt, adopting the appropriate concentration is important for complete degradation of organic pollutants.

Whereas, the best degradation ratio in the absence of any TiO<sub>2</sub> catalyst appears at the comparatively high concentration (about 75.0 mg/L), which indicates that the mutual screen among parathion molecules in aqueous solution is not serious. The degradation with one-fold ultrasonic irradiation results from the •OH radicals from acoustic cavitation. Hence, the parathion molecules in high concentration solution can be decomposed all the same.

### 3.7. Effect of TiO<sub>2</sub> addition amount on degradation ratio

In order to optimize the addition amount of nanometer rutile TiO<sub>2</sub> catalyst for the highest sonocatalytic degradation of parathion, the following addition amounts starting from 600 to 1400 mg/L were adopted as shown in Fig. 9. It was found that the degradation ratio in the presence of nanometer rutile TiO<sub>2</sub> powder gradually rose when the addition amount increased from 600 to 1000 mg/L, while it began to decline after the addition amount of nanometer rutile TiO<sub>2</sub> powder surpassed 1000 mg/L. It is understandable that the befitting increase of TiO<sub>2</sub> catalyst is propitious to decompose the organic pollutants in aqueous solution. Whereas, the excessive nanometer rutile TiO<sub>2</sub> parti-

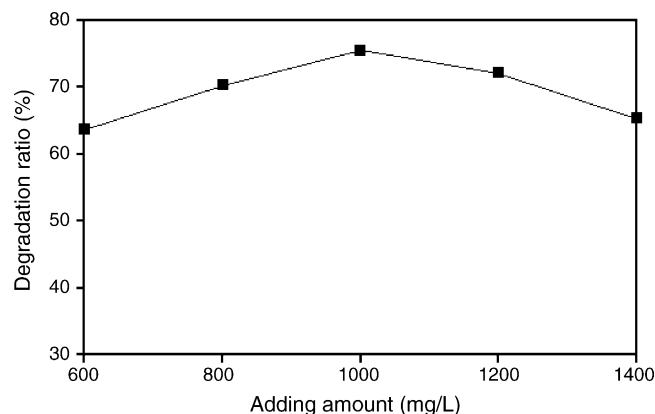


Fig. 9. Effect of TiO<sub>2</sub> adding amount on degradation ratio of parathion.

cles sometimes bring the mutual screens among nanometer TiO<sub>2</sub> particles, which not only make parathion molecules attain the protection, but also reduce the sonocatalytic activity of nanometer TiO<sub>2</sub> powder. The great mass of nanometer rutile TiO<sub>2</sub> particles those do not adsorb the parathion molecules absorb the light and heat energies from acoustic cavitation, but a small quantity of nanometer rutile TiO<sub>2</sub> particles those adsorb the parathion molecules can not absorb the light and heat energies. Considering the influence of mutual screen on the sonocatalytic degradation of parathion the addition amount of 1000 mg/L was used for the parathion solution of 50 mg/L concentration throughout this work.

### 3.8. Effect of initial pH values on degradation ratio

For farther comparison of the sonocatalytic degradations of parathion in the presence of nanometer rutile TiO<sub>2</sub> powder as the sonocatalyst and ultrasonic degradations in the absence of any TiO<sub>2</sub> catalyst, the influences of different initial pH values ranging between 3.0 and 9.0 were also studied. The relationships between the degradation ratio and the initial pH values in parathion solution are shown in Fig. 10. It can be found that the sonocatalytic degradation ratios of parathion gradually increase along with the increase of pH values, that is, the higher the pH value is adjusted, the quicker the degradation rate becomes.

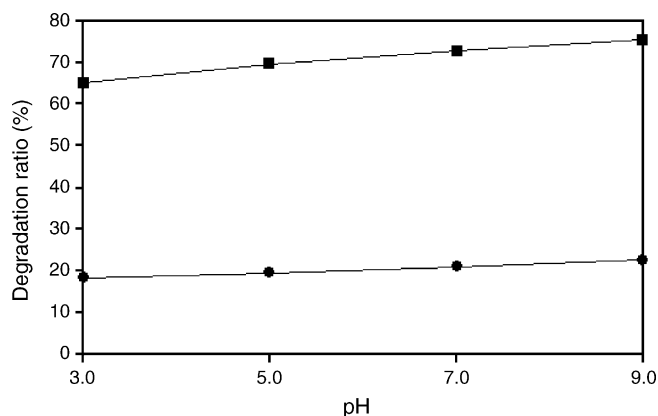


Fig. 10. Effect of initial pH on degradation ratio of parathion: (■) ultrasound + nanometer rutile TiO<sub>2</sub>; (●) only ultrasound.

In general, the point of zero charge (PZC) of nanometer rutile  $\text{TiO}_2$  powder is about pH 6.38. Above this pH value, the surfaces of nanometer rutile  $\text{TiO}_2$  particles are negatively charged, while below this pH value they are positively charged. Some ionic compounds having negative charges after ionization can be adsorbed on the surfaces of nanometer rutile  $\text{TiO}_2$  particles below pH 6.38, contrarily the others having positive charges can be adsorbed above pH 6.38. Although the parathion is a neutral molecular compound almost in all the studied pH range, it can be adsorbed on the surfaces of nanometer  $\text{TiO}_2$  particles above pH 6.38 because of the imbalance of charge distribution and the existence of electronegative sulphur atom and nitril group in parathion molecule. In addition, as well known to all, the  $\text{OH}^-$  anions in alkaline solution can generally act as the getter of holes on the surface of  $\text{TiO}_2$  particles and become  $\bullet\text{OH}$  radicals having strong oxidation ability after losing one electron. Hence, the chances producing  $\bullet\text{OH}$  radicals increase as the pH values heighten.

### 3.9. Effect of temperature on degradation ratio

The effect of systemic temperature on the sonocatalytic degradation of parathion was discussed in the range between 20 and 65 °C. It can be seen in Fig. 11 that both cases of sonocatalytic degradation in the presence of nanometer rutile  $\text{TiO}_2$  powder and ultrasonic degradation in the absence of any  $\text{TiO}_2$  catalyst decrease gradually along with the temperature heightening.

In general, for the most of chemical reactions, the higher the temperature in reaction system is, the quicker the reaction rate becomes, while it has been known that the radical reactions hardly depend on the systemic temperature. However, the acoustic cavitation which produces the holes on the surface of  $\text{TiO}_2$  particles or  $\bullet\text{OH}$  radicals in aqueous solution lies on the change of systemic temperature. It is well known that both sonocatalytic and ultrasonic degradation of organic pollutants relate to the acoustic cavitation. The acoustic cavitation can bring the holes with strong oxidibility on the surface of  $\text{TiO}_2$  particles which either can directly decompose the organic pollutants adsorbed on the surface of  $\text{TiO}_2$  particles or indirectly degrade the organic pollutants in aqueous solution through the  $\bullet\text{OH}$  rad-

icals resulting from hole oxidation of  $\text{H}_2\text{O}$  molecules. When the temperature in aqueous solution becomes exorbitantly high, the vapor or gas bubbles fleetly escape from reaction system so that they do not grow up or collapse betimes, which badly weaken the acoustic cavitation. For the ultrasonic degradation, the  $\bullet\text{OH}$  radicals mainly result from the acoustic cavitation. Hence, the high temperature makes against the ultrasonic degradation. Similarly, the high temperature also makes against the sonocatalytic degradation because the holes on the surface or in the inner of nanometer  $\text{TiO}_2$  particles result from the acoustic cavitation. In addition, the sonocatalytic degradation relates to the adsorbability of  $\text{TiO}_2$  particles. In general, the appropriate adsorbability is propitious to the sonocatalytic degradation. The proper quantities of organic pollutants adsorbed on the surface of nanometer  $\text{TiO}_2$  particles can directly decomposed by the holes. However, the high temperature generally weakens the adsorbability of nanometer  $\text{TiO}_2$  particles, which makes large numbers of organic pollutants freely and fleetly to move in solution and then miss the chance of degradation.

### 3.10. Effect of ultrasonic frequency on degradation ratio

The effect of the ultrasonic frequency on the degradation ratio of parathion was also considered in the range from 20 to 80 kHz. However, up till now, the present experimental phenomena cannot be satisfactorily elucidated because the relationships of ultrasonic frequency with the number of holes produced on the surface or in the inner of  $\text{TiO}_2$  particles are very complicated. In general, neither high nor low frequency ultrasound is propitious to the acoustic cavitation. It is shown in Fig. 12 that the best degradation ratios of parathion were all obtained from the ultrasonic irradiation of 40 kHz for two courses. Hence, the ideal selection should be ones in the range between 30 and 50 kHz because they are gained easily and their noises are smaller than other low frequency ultrasound during treatment of organic pollutants.

### 3.11. Effect of ultrasonic power on degradation ratio

In general, in the case of one-fold using ultrasonic irradiation in the absence of any  $\text{TiO}_2$  catalyst the degradation ratio

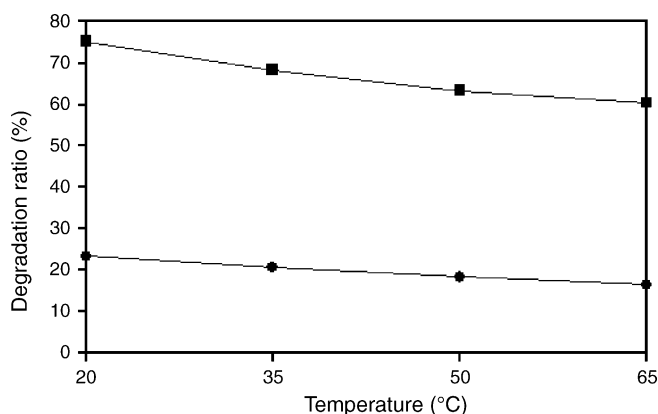


Fig. 11. Effect of temperature on degradation ratio of parathion: (■) ultrasound + nanometer rutile  $\text{TiO}_2$ ; (●) only ultrasound.

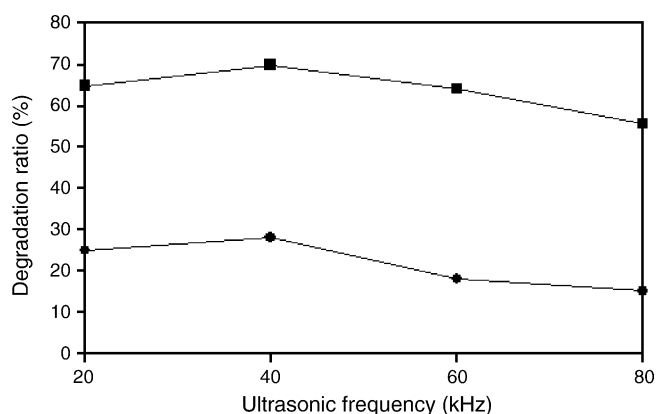


Fig. 12. Effect of ultrasonic frequency on degradation ratio of parathion: (■) ultrasound + nanometer rutile  $\text{TiO}_2$ ; (●) only ultrasound.

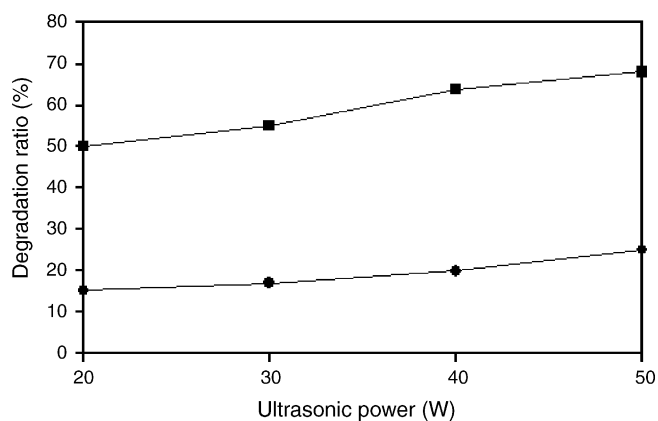


Fig. 13. Effect of ultrasonic power on degradation ratio of parathion: (■) ultrasound + nanometer rutile TiO<sub>2</sub>; (●) only ultrasound.

gradually becomes high with increasing output power of ultrasound. As shown in Fig. 13, the similar phenomena were also found in the sonocatalytic degradation of parathion in the presence of nanometer rutile TiO<sub>2</sub> powder. The reason may be explained as following: firstly, to be similar to the photocatalytic degradation, the ultrasonic irradiation of high output power can provide the chances that the added •OH radicals form on the surface of nanometer rutile TiO<sub>2</sub> particles; secondly, the nanometer rutile TiO<sub>2</sub> particles in aqueous solution can adequately and completely be dispersed by ultrasound of high output power. However, considering the cost of treating organic pollutants and destruction of TiO<sub>2</sub> catalysts from ultrasonic irradiation, it is necessary to use the ultrasound of appropriate output power.

### 3.12. Sonocatalytic activity of reused TiO<sub>2</sub> catalyst

Any catalysts after finishing their tasks in chemical investigation and chemistry industry are expected to reclaim and recycle by proper and simple treatment. Fortunately, in the aqueous solution, not only the high degradation ratios of parathion were obtained, but also the used nanometer rutile TiO<sub>2</sub> catalyst settled down completely after transitory placement and was separated easily from the treated solution. These TiO<sub>2</sub> deposits were washed three times and heated at 350–400 °C and then reused in the next experiments with fresh parathion solution. Fig. 14 shows the relationship between the degradation ratios of parathion and the used times of nanometer rutile TiO<sub>2</sub> catalyst. It was seen that the degradation ratio of parathion in the presence of reused rutile TiO<sub>2</sub> powder was only slightly lower than that of new nanometer rutile TiO<sub>2</sub> powder. It is illuminated that the reused rutile TiO<sub>2</sub> powder can continuously be used to degrade the parathion solution, but it is necessary to search out an effective treatment method for improving and maintaining high sonocatalytic activity.

### 3.13. Possible sonocatalytic degradation mechanism

Up till now, there has been no ready-made mechanism and satisfying explanation yet on the sonocatalytic degradation of organic pollutants in the presence of TiO<sub>2</sub> catalyst. Perhaps the

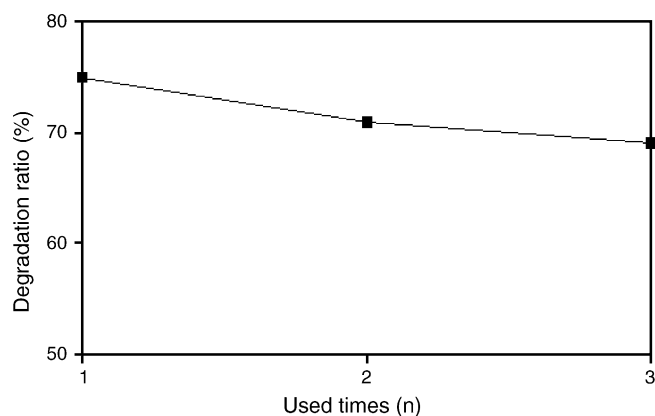


Fig. 14. Effect of reused TiO<sub>2</sub> on degradation ratio of parathion.

following three points of view, namely, sonoluminescence, “hot spot” and oxygen atom escape should be accepted to explain the sonocatalytic degradation process of parathion and other organic pollutants in aqueous solution in the presence of nanometer rutile TiO<sub>2</sub> catalyst. Firstly, it has been well known that the ultrasonic irradiation can result in the formation of the light with a comparatively wide wavelength range because of acoustic cavitation. Those lights whose wavelengths are below 375 nm, beyond all doubt, can excite the nanometer TiO<sub>2</sub> particle acting as a photocatalyst and a great deal of •OH radicals with high oxidation activity should form on the surface of the nanometer TiO<sub>2</sub> particles. In fact, that is the reaction mechanism of photocatalytic degradation. Secondly, as well known, the temperature of “hot spot” also produced by acoustic cavitation in water medium can achieve 10<sup>5</sup> and 10<sup>6</sup> °C, so high temperature sufficiently brings many holes on the surface of TiO<sub>2</sub> particles producing •OH radicals. Thirdly, the shock waves of ultrasound induce some oxygen atoms on the surface of TiO<sub>2</sub> particles to escape from the crystal lattice and then the holes form. Similarly, these holes can decompose the organic pollutant adsorbed on the surface of nanometer TiO<sub>2</sub> particles directly or degrade them in aqueous solution indirectly through the •OH radicals resulted from the reaction of holes and H<sub>2</sub>O molecules. Of course, the detailed mechanism of sonocatalytic degradation is expected to be further and specially studied adopting multifold methods.

## 4. Conclusions

The parathion in aqueous solution can be markedly decomposed by the method of sonocatalytic degradation in the presence of nanometer rutile TiO<sub>2</sub> powder as sonocatalyst. In addition, the research results also demonstrated the feasibilities of the sonocatalytic degradation of parathion and other organic pollutants for treating wastewaters. Especially, the method of sonocatalytic degradation is applicable for those non- and low-transparent wastewaters which is difficult to be treated by the method of photocatalytic degradation. The sonocatalytic degradation of parathion is shown to depend on the initial concentrations of parathion, addition amounts of nanometer rutile TiO<sub>2</sub> catalyst, acidities and temperature of parathion solution, output power and frequency of ultrasound. The optimum conditions for a



high degradation ratio of parathion are considered to be initial concentration of 50 mg/L parathion, addition amount of 1000 mg/L nanometer rutile TiO<sub>2</sub> powder, ultrasonic frequency of 30–50 kHz, output power of 50 W, acidity of pH 10.0 and systemic temperature of 20 °C within 120 min ultrasonic irradiation.

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