

Sonocatalytic degradation of methyl parathion in the presence of micron-sized and nano-sized rutile titanium dioxide catalysts and comparison of their sonocatalytic abilities

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Abstract

Micron-sized and nano-sized rutile titanium dioxide (TiO₂) powders were used as the catalysts for the sonocatalytic degradation of methyl parathion, an organophosphorus insecticide. The ultrasound of low power was used as an irradiation source to induce the catalytic activity of the rutile TiO₂ particles. It was found that the degradation of methyl parathion sonocatalytically progressed more rapidly in the presence of TiO₂ particles than only with ultrasonic irradiation in the absence of TiO₂ catalyst. Moreover, the sonocatalytic activity of the micron-sized rutile TiO₂ particles was obviously higher than that of nano-sized rutile TiO₂ particles. The influences of reaction parameters, such as the species of TiO₂ particles, methyl parathion concentration, TiO₂ amount, pH value, ultrasonic intensity, ultrasonic frequency and temperature have been investigated and the optimal conditions for eliminating methyl parathion have been established. The processes of methyl parathion degradation have been monitored by high performance liquid chromatography (HPLC), ion chromatography and UV–vis spectra. The results showed that methyl parathion in aqueous solution was completely degraded to give simple inorganic ions, such as NO₂⁻, NO₃⁻, PO₄³⁻, SO₄²⁻, etc. The kinetics of the degradation of methyl parathion followed the first-order reaction. The degradation percentage of methyl parathion surpassed 95% within 80 min in the optimal experimental conditions.

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1. Introduction

Recently, there is a growing concern about the damage done to the natural environment due to the human activity. Industry is usually blamed for the introduction of pollutants to the environment. However, the changes in agriculture bring about similar problems. For example, application of fertilizers and pesticides leads to the pollution of soil and ground water. Some of them are resistant to environmental degradation and have the tendency to accumulate in the food chain. Therefore, there is an interest in development of innovative, efficient, cheap and environment-friendly techniques for the degradation of these pollutants. Among such poorly exhausting pesticides, organophosphorus

insecticides have been most heavily consumed in agriculture and horticulture. Hence, a lot of researches have been engaged in the mineralization technology of organophosphorus insecticides. For example, the method of high power ultrasonic irradiation is usually used to treat some dyestuff wastewaters owing to its advantages, such as cleanness, high efficiency and non-secondary pollution [1–3]. As known to all, under the function of ultrasonic irradiation, the dissolved vapors and gases in the liquid become cavitation bubbles and then entrap the organic pollutants, which attain very high temperatures that the organic pollutants are directly decomposed or indirectly oxidized by formed hydroxyl (•OH) radicals during momentary collapse of cavitation bubbles [4–7]. However, the degradation of organic pollutants by high power ultrasound usually needs lots of energy, costly treated equipment and long reaction time [8].

Previously, in order to overcome these drawbacks of mere ultrasonic irradiation, the anatase titanium dioxide (TiO₂)

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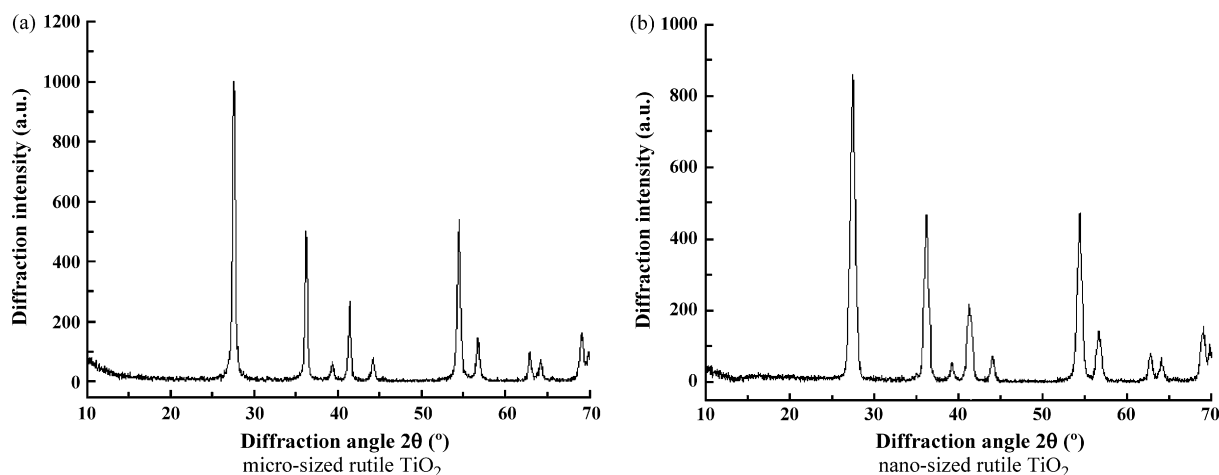
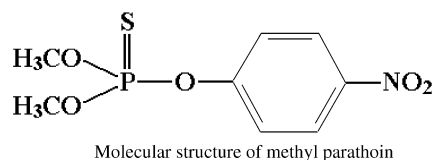


Fig. 1. XRD pattern of rutile TiO_2 powders after treatment: (a) micron-sized rutile TiO_2 and (b) nano-sized rutile TiO_2 .

powders were used as the sonocatalysts combined with low power ultrasonic irradiation to treat methyl parathion solution [9]. Because of the slightly narrow energy gap and appropriate adsorbability, the rutile TiO_2 powder was used after heat-treatment as sonocatalyst in this work and satisfying results were obtained. The influences of reaction parameters were established on sonocatalytic degradation of methyl parathion. In addition, both micron-sized and nano-sized rutile TiO_2 powders were used to compare their catalytic activities. The results indicated that the degradation of methyl parathion sonocatalytically progressed more rapidly in the presence of micron-sized rutile TiO_2 powder than in the presence of nano-sized rutile TiO_2 powder, which is different from the case, where micron-sized and nano-sized anatase TiO_2 powders were used. In the degradation, the TiO_2 powder was used as sonocatalyst because of its unique photochemical, photostable, inexpensive and non-toxic characters [10,11].

Here, the ultrasonic irradiation instead of ultraviolet light was used to degrade the methyl parathion in aqueous solution in the presence of micron-sized and nano-sized rutile TiO_2 powders. In conclusion, the method of sonocatalytic degradation for organic pollutants is expected to be promising as an inexpensive and environment-friendly technology of wastewater purification with huge industrialization prospect on the basis of further

research work.



2. Experimental

2.1. Chemicals

Methyl parathion (99.7%) was obtained from Shell Research (USA). When methyl parathion is dissolved in water the UV–vis spectrum shows only one absorption peak at 278 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 micron-sized and nano-sized rutile TiO_2 particles purchased from Alleghen-tyledyne Company (USA) were used as the catalysts. Before experiments, they were heat-treated for activation at 450 °C. Their XRD patterns and TEM images are shown in Figs. 1 and 2, respectively. According to the Scherrer equation, the size of micron-sized and nano-sized rutile TiO_2 particles are 130–150 and 30–50 nm, respectively.

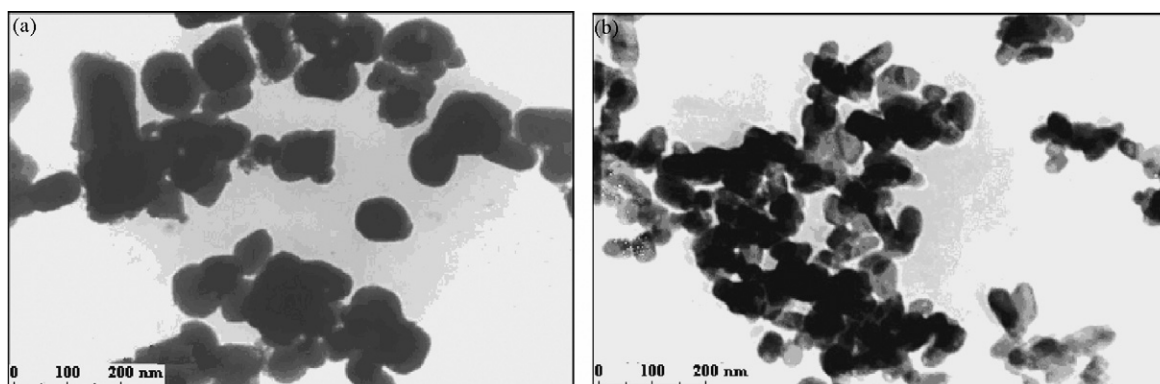


Fig. 2. TEM images of rutile TiO_2 powders after treatment: (a) micron-sized rutile TiO_2 and (b) nano-sized rutile TiO_2 .

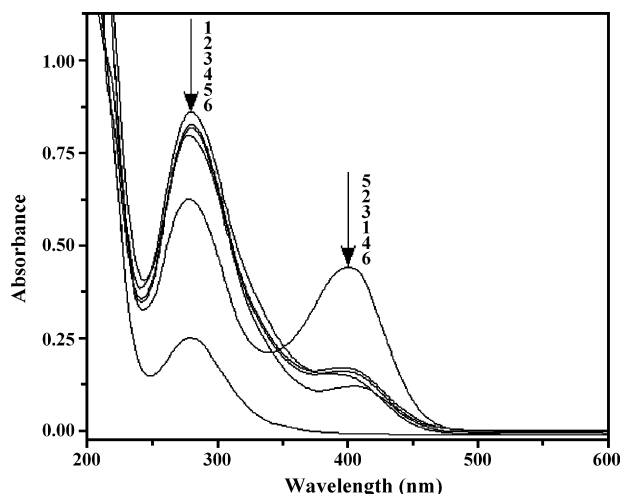


Fig. 3. UV-vis spectra of methyl parathion solution: (1) original solution, (2) nano-sized TiO_2 , (3) micron-sized TiO_2 , (4) only ultrasound, (5) ultrasound + nano-sized TiO_2 and (6) ultrasound + micron-sized TiO_2 .

2.2. Sonocatalytic degradation reaction procedure

In a conical flask, 50 mg micron-sized or nano-sized rutile TiO_2 was mixed with 50 mL of methyl parathion solution (50 mg L^{-1}), and the mixed solution was stirred for 20 h without any irradiation in order to attain the adsorption equilibrium. Then a small amount of the mixed solution was taken out and centrifuged. The separated supernatant methyl parathion solution was used for determining UV-vis spectra as shown in Fig. 3. Then, the mixed solutions were placed inside an ultrasonic apparatus (KQ-100, Kunshan company, China) used as irradiation source. Total ultrasonic intensities and frequencies were varied from 20 to 50 W and 20 to 80 kHz, respectively. The mixed solution was sampled at a definite interval time for tracking the process of methyl parathion degradation until 80 min after. For comparison, the mere ultrasonic degradation without any TiO_2 catalyst was also measured following the same procedure and all the results are shown in Figs. 3 and 4. The experimental conditions adopted throughout the whole experiments were initial methyl parathion concentration of 50 mg L^{-1} , TiO_2 pow-

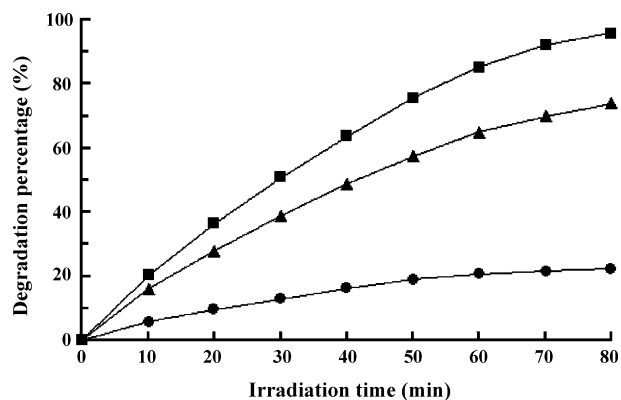


Fig. 4. Effect of irradiation time on degradation percentages: (■) ultrasound + micron-sized rutile TiO_2 , (▲) ultrasound + nano-sized rutile TiO_2 and (●) only ultrasound.

der of 1000 mg L^{-1} , initial pH of 10.0, solution temperature of $20.0 \pm 0.2 \text{ }^\circ\text{C}$ and ultrasound of 40 kHz frequency and 50 W power unless otherwise noted.

2.3. Analyses

Samples were taken out periodically and the degradation percentage of methyl parathion was monitored by the UV-vis spectra (LAMBDA-17, Perkin-Elmer, USA) in the wavelength ranging from 200 to 600 nm as shown in Fig. 3 after filtering the liquid with millipore filters to remove the TiO_2 powder. For each experiment, the absorbance of $0.0\text{--}50.0 \text{ mg L}^{-1}$ methyl parathion solution abide by Lambert-Beer's law and the calibrated curve of standard methyl parathion solutions are used to estimate the degradation percentage. The degradation kinetics was monitored at 278 nm. In order to track the degradation path of methyl parathion, HPLC was performed with a Shimadzu VP series HPLC system equipped with a photodiode array detector (PDAD). The HPLC (with $125 \text{ mm} \times 4 \text{ mm}$ BDS C_{18} column) conditions were: mobile phase 50:50 acetonitrile:water, flow rate of 1.0 mL min^{-1} . The detection wavelength was 278 nm. The injection volume was $20 \text{ } \mu\text{L}$.

3. Results and discussion

3.1. UV-vis spectra of methyl parathion solution during degradation

The UV-vis spectra of methyl parathion solution in the presence of micron-sized or nano-sized rutile TiO_2 powder and in the absence of TiO_2 catalysts under 40 min ultrasonic irradiation are shown in Fig. 3. In addition, for comparison, the absorption curves of mixed solutions in the presence of micron-sized or nano-sized rutile TiO_2 powder without any irradiation as well as the original solution of methyl parathion are also given. It was found that the characteristic absorption peak of methyl parathion solution at 278 nm declined rapidly under ultrasonic irradiation in the presence of either micron-sized or nano-sized rutile TiO_2 powder. Furthermore, it can be judged that the adsorption amounts of methyl parathion on the surface of TiO_2 powders hardly influence the estimation of the degradation percentage in the presence of TiO_2 powders. It is interesting that the absorbance of *p*-nitrophenol at 405 nm appears clearly during the degradation process of methyl parathion in the presence of nano-sized rutile TiO_2 powder, but there is no new absorption peak between 350 and 600 nm in the presence of micron-sized rutile TiO_2 powder. Perhaps, the difference between nano-sized and micron-sized rutile TiO_2 powders results in the different degradation path.

3.2. Effect of ultrasonic irradiation time on degradation percentage

The degradation percentages of methyl parathion under ultrasonic irradiation in the presence of nano-sized or micron-sized rutile TiO_2 powder as well as without any catalyst were examined for 80 min. As shown in Fig. 4, the degradation progressed

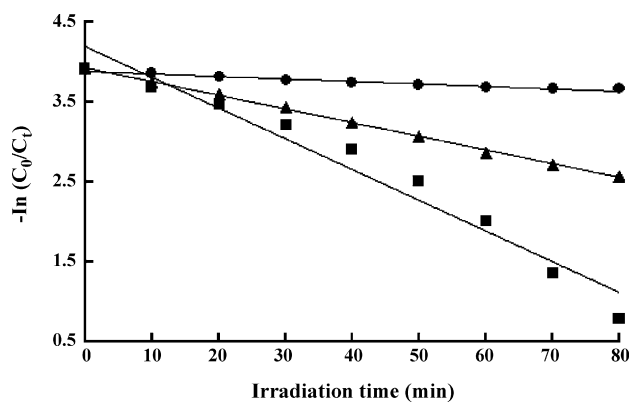


Fig. 5. Reaction kinetics of sonocatalytic degradation: (■) ultrasound + micron-sized rutile TiO₂, (▲) ultrasound + nano-sized rutile TiO₂ and (●) only ultrasound.

gradually along with ultrasonic irradiation time, but a complete degradation (about 95.6%) of methyl parathion was achieved under about 80 min irradiation in the presence of micron-sized rutile TiO₂ catalyst, while the degradation percentage in the presence of nano-sized rutile TiO₂ catalyst was about 74.0%. The considerably low level of degradation (16.3%) of methyl parathion was observed under mere ultrasonic irradiation without any TiO₂ catalyst. These results indicate that the degradation of methyl parathion is more obvious in the presence of rutile TiO₂ catalysts combined with ultrasonic irradiation than in the absence of any TiO₂ catalyst.

Fig. 5 shows that the sonocatalytic degradation of methyl parathion follows the pseudo-first-order kinetics in every case. The rate constants are 0.0385, 0.0171 and 0.0031 min⁻¹ for ultrasonic irradiation combined with micron-sized and nano-sized rutile TiO₂ catalysts and mere ultrasonic irradiation without any TiO₂ catalyst, respectively.

3.3. Ion chromatography of methyl parathion solution during degradation

In order to further prove and explore the different degradation effect of methyl parathion in the presence of micron-sized or nano-sized rutile TiO₂ particles, the ion chromatography after 40 min ultrasonic irradiation were conducted as shown in Fig. 6. Because of the presence of the nitrogen, sulphur and phosphorus atoms in methyl parathion molecule, NO₂⁻, NO₃⁻, SO₄²⁻ and PO₄³⁻ anions should be produced during and after degradation. In fact, the peaks corresponding to NO₂⁻, NO₃⁻, SO₄²⁻ and PO₄³⁻ anions were found indeed in the ion chromatogram. All product anion peaks for methyl parathion degradation in the presence of micron-sized rutile TiO₂ particles are much higher than those in the presence of nano-sized rutile TiO₂ particles, which indicates that the sonocatalytic activity of micron-sized rutile TiO₂ powder is higher than that of nano-sized rutile TiO₂ powder.

3.4. Effect of TiO₂ amount on degradation percentage

For the sonocatalytic degradation in the presence of heterogeneous catalysts, the amount of catalysts is an important

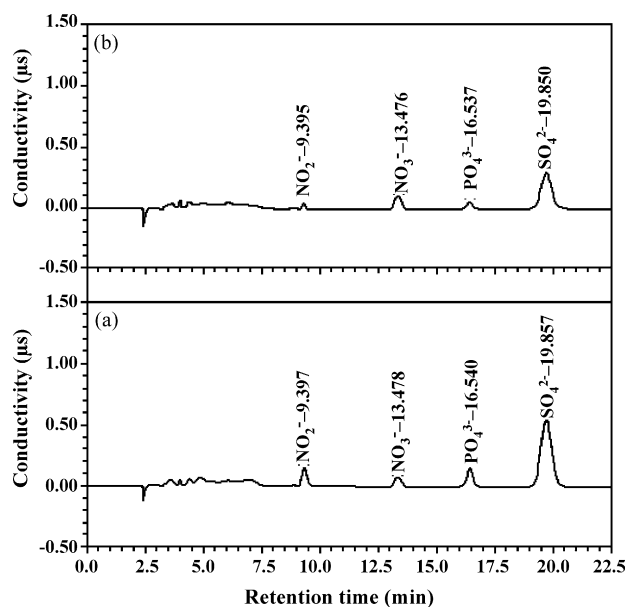


Fig. 6. The ion chromatogram of methyl parathion solution during ultrasonic irradiation (40 min): (a) ultrasound + micron-sized rutile TiO₂ and (b) ultrasound + nano-sized rutile TiO₂.

parameter. The optimal amount depends on the nature of the organic pollutants and many other factors. The effects of TiO₂ amount on the degradation percentage were examined in the range from 250 to 1250 mg L⁻¹. Fig. 7 shows that the degradation percentages of methyl parathion under 40 min ultrasonic irradiation in the presence of either micron-sized or nano-sized rutile TiO₂ increase with increasing amount of TiO₂ below 1000 mg L⁻¹, while they begin to decrease above 1000 mg L⁻¹. Hence, the optimal amount of TiO₂ should be about 1000 mg L⁻¹ for both micron-sized and nano-sized rutile TiO₂ catalysts. This phenomenon may be explained by the close contact and aggregation of TiO₂ particles added in a large amount, which causes the decrease in the surface active sites.

3.5. Effect of initial concentration on degradation percentage

Fig. 8 shows that the highest degradation percentage was obtained with 50.0 mg L⁻¹ methyl parathion for micron-sized

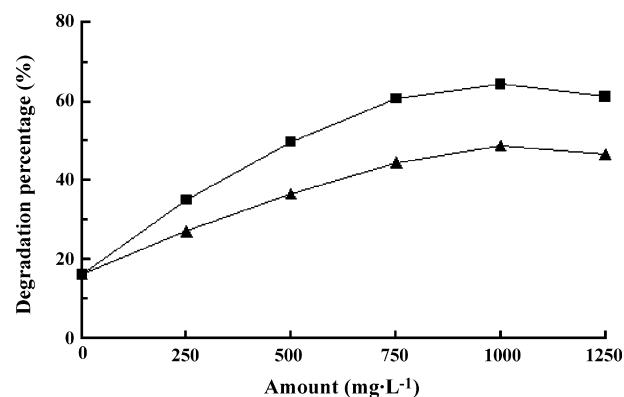


Fig. 7. Effect of TiO₂ amount on degradation percentage: (■) ultrasound + micron-sized rutile TiO₂ and (▲) ultrasound + nano-sized rutile TiO₂.

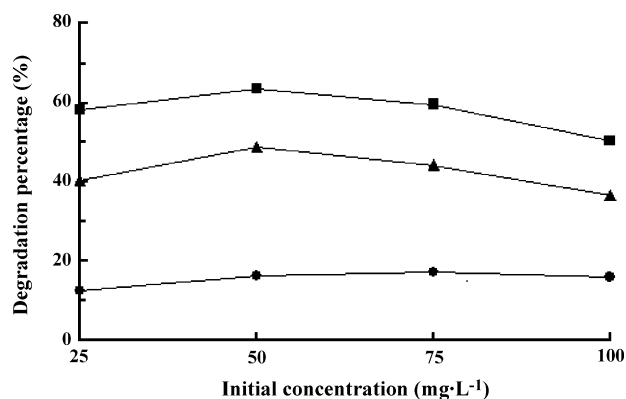


Fig. 8. Effect of methyl parathion initial concentration on degradation percentage: (■) ultrasound + micron-sized rutile TiO₂, (▲) ultrasound + nano-sized rutile TiO₂ and (●) only ultrasound.

or nano-sized rutile TiO₂ catalyst. After 50.0 mg L⁻¹, the degradation percentage slowly decreased with increasing of methyl parathion concentration. This can be explained as follows. The degradation percentage is related to both the quantity of •OH radicals formed on the surface of TiO₂ particles and the probability of reactions between •OH radicals and methyl parathions. For a given concentration range, as the initial concentration increases, the probability of the reaction between •OH radicals and methyl parathions also increases, which leads to the enhancement of degradation percentage. In contrast, when the concentrations surpass the given range, the degradation percentage decreases with the increase in the methyl parathion concentration. Two reasons may exist to explain this phenomenon. On one hand, for any power of ultrasound and any amount of catalyst, the number of •OH radicals produced on the surface of TiO₂ particles is limited. On the other hand, for highly concentrated methyl parathion solution, the surface of TiO₂ particles are generally covered by methyl parathion molecules, which restrains the absorption and transmission of ultrasound. Hence, there is an appropriate initial concentration for high sonocatalytic activity.

3.6. Effect of pH value on degradation percentage

As shown in Fig. 9, the degradation percentage of methyl parathion in the presence of micron-sized and nano-sized rutile TiO₂ catalysts depends on the initial pH values of the solution. It was observed that the higher the pH values, the faster the degradation rate. In general, the point of zero charge (PZC) of rutile TiO₂ powder is pH 6.38. Above this pH value, the surfaces of rutile TiO₂ particles are negatively charged, while below this pH value, they are positively charged. Ionic compounds having negative charges after ionization can be adsorbed on the surfaces of rutile TiO₂ particles in the pH range of below 6.38 and contrarily the others having positive charges can be adsorbed in the pH range of above 6.38. Although the methyl parathion is a neutral compound, as a polar molecule, it can be close to or adsorbed on the surfaces of TiO₂ particles in the pH range of above 6.38, because of the imbalance of charge distribution and the existence of the electronegative sulphur atom and nitro group. In addition, the OH⁻ anions in basic solution can gen-

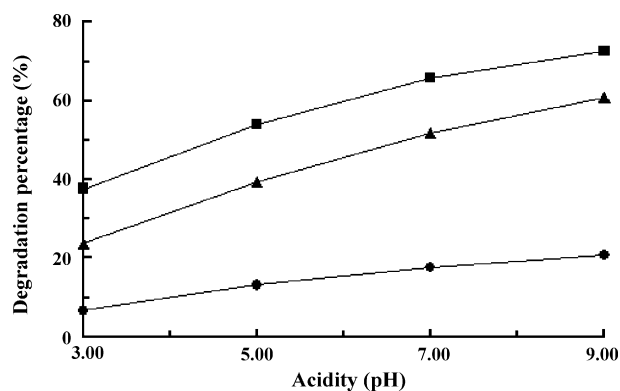


Fig. 9. Effect of the initial pH on degradation percentage: (■) ultrasound + micron-sized rutile TiO₂, (▲) ultrasound + nano-sized rutile TiO₂ and (●) only ultrasound.

erally lose their electrons to capture the holes on the surface of TiO₂ particles and then become •OH radicals having strong oxidation ability. Hence, the chances of producing •OH radicals increase as the pH values are elevated.

3.7. Effect of ultrasonic intensity on degradation percentage

In general, when methyl parathion was irradiated with ultrasound without any TiO₂ catalyst, the degradation percentage gradually increased with increasing output power of ultrasound. As shown in Fig. 10, similar phenomena were also found in the sonocatalytic degradation of methyl parathion in the presence of rutile TiO₂ powder. This may be explained as follows. Firstly, like the photocatalytic degradation, the ultrasonic irradiation of high output power can increase the chances that the •OH radicals are formed on the surface of rutile TiO₂ particles. Secondly, the rutile TiO₂ particles in aqueous solution can adequately and completely be dispersed by high output power ultrasound. However, regarding to the costs of treating organic pollutants and the destruction of TiO₂ catalysts by ultrasonic irradiation, it is necessary to use ultrasound at appropriate output powder.

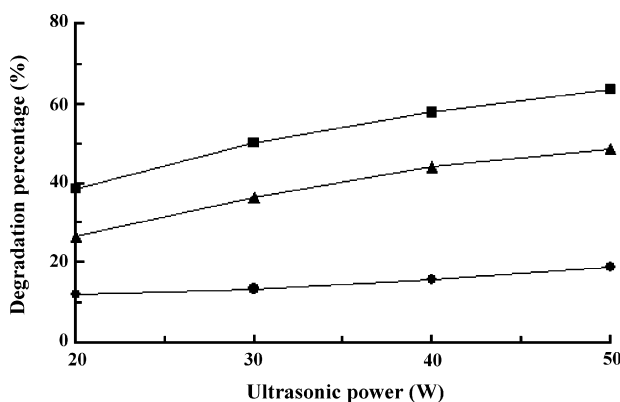


Fig. 10. Effect of ultrasonic power on degradation percentage: (■) ultrasound + micron-sized rutile TiO₂, (▲) ultrasound + nano-sized rutile TiO₂ and (●) only ultrasound.

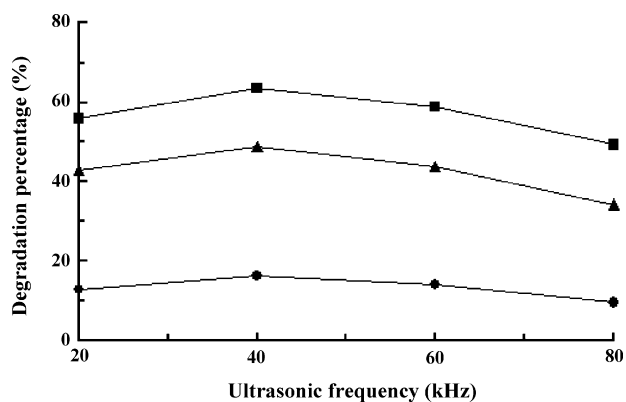


Fig. 11. Effect of ultrasonic frequency on degradation percentage: (■) ultrasound + micron-sized rutile TiO₂, (▲) ultrasound + nano-sized rutile TiO₂ and (●) only ultrasound.

3.8. Effect of ultrasonic frequency on degradation percentage

The effect of the ultrasonic frequency on the degradation percentage of methyl parathion was also examined in the range of 20–80 kHz. However, the experimental phenomena have not been elucidated satisfactorily, because the relationship between the ultrasonic frequency and the number of holes produced on the surface or in the inner of TiO₂ particles is very complicated. In general, neither high nor low frequency ultrasound is beneficial for the acoustic cavitation. Fig. 11 shows that the highest degradation percentages of methyl parathion were obtained with the ultrasonic frequency of 40 kHz in the three cases. Hence, the ideal ultrasonic frequency should be the one in the range between 30 and 50 kHz, because it is easily obtained and its noises are lower than those of low frequency ultrasound.

3.9. Effect of temperature on degradation percentage

The effect of temperature on the degradation percentage of methyl parathion was examined from 20 to 65 °C. It can be seen in Fig. 12 that the degradation percentages in all the three cases increased up to 35 °C, and began to decrease above 35 °C.

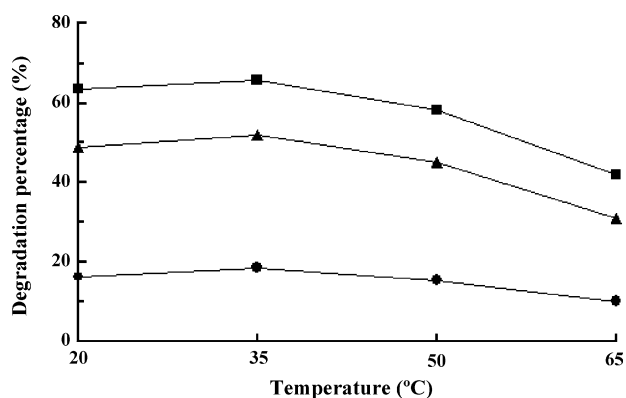


Fig. 12. Effect of temperature on degradation percentage: (■) ultrasound + micron-sized rutile TiO₂, (▲) ultrasound + nano-sized rutile TiO₂ and (●) only ultrasound.

In general, for most chemical reactions, the higher the solution temperature, the faster the reaction rate becomes. However, it is known that the radical reactions hardly depend on the solution temperature. The acoustic cavitation that produces the holes on the surface of TiO₂ particles or •OH radicals in aqueous solution depends on the change of solution temperature. It is well known that both sonocatalytic and ultrasonic degradations of organic pollutants are related to the acoustic cavitation. The acoustic cavitation can produce holes with strong oxidizability on the surface of TiO₂ particles. These holes can either directly decompose the organic pollutants adsorbed on the surface of TiO₂ particles or indirectly degrade the organic pollutants in aqueous solution through the •OH radicals resulting from oxidation of H₂O molecules by holes. When the solution temperature becomes extraordinary high, the vapor or gas bubbles fleetly escape from solution, so that they do not grow up or collapse rapidly, which seriously weakened the acoustic cavitation. For the ultrasonic degradation, the •OH radicals are mainly produced by the acoustic cavitation. Hence, the high temperature is unfavorable for the ultrasonic degradation. Similarly, the high temperature is also disadvantageous for the sonocatalytic degradation, because the holes on the surface or in the inner of TiO₂ particles result from the acoustic cavitation. In addition, the sonocatalytic degradation is related to the adsorbability of TiO₂ particles. In general, the appropriate adsorbability is helpful to the sonocatalytic degradation. The appropriate quantities of organic pollutants adsorbed on the surface of TiO₂ particles can directly be decomposed by the holes. However, the high temperature generally weakens the adsorbability of TiO₂ particles, which makes large numbers of organic pollutants miss the chances of degradation.

3.10. Sonocatalytic degradation process

In order to explore the degradation process, the intermediate products of methyl parathion during sonocatalytic degradation were determined by HPLC for different rutile TiO₂ powders under 30 min ultrasonic irradiation as shown in Fig. 13. As described above, the UV–vis spectra of methyl parathion

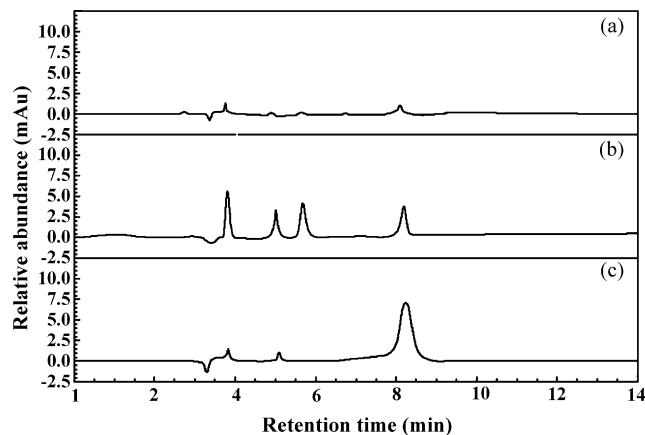


Fig. 13. Liquid chromatogram of methyl parathion solution: (a) ultrasound + micron-sized rutile TiO₂ (30 min degradation), (b) ultrasound + nano-sized rutile TiO₂ (30 min degradation) and (c) original solution.

solution during degradation showed that different degradation reactions take place on the surface of micron-sized and nano-sized rutile TiO₂ powders. For the nano-sized rutile TiO₂ catalyst, the intermediate product, *p*-nitrophenol, appeared after 30 min of ultrasonic irradiation, while such an intermediate product was not found for the micron-sized rutile TiO₂ catalyst. A similar phenomenon was also found from HPLC. It was found that three peaks in Fig. 13b which correspond to the *p*-nitrophenol and other intermediate products appeared at 3.07, 4.54 and 5.35 min, respectively, in the presence of the nano-sized rutile TiO₂ catalyst besides the parent peak of methyl parathion at 8.21 min, which reveals that the radical oxidation take place mainly in aqueous solution. However, for the micron-sized rutile TiO₂ catalyst, the corresponding peaks are very low or hardly appear in Fig. 13a, which indicates that the degradation process belongs to the hole oxidation resulting from the surface of micron-sized rutile TiO₂ particle. Perhaps, this difference is ascribed to the difference in size between nano-sized and micron-sized rutile TiO₂ particles.

3.11. Possible sonocatalytic degradation mechanism

Until now, there has been no established mechanism and satisfactory explanation on the sonocatalytic degradation of organic pollutants in the presence of TiO₂ catalysts. Perhaps the following three points, namely, sonoluminescence, “hot spot” and oxygen atom escape may be accepted to explain the sonocatalytic degradation process of methyl parathion and other organic pollutants in aqueous solution in the presence of rutile TiO₂ catalysts [12]. 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. These lights below 375 nm in wavelength can excite the TiO₂ particle to act as a photocatalyst and a great deal of •OH radicals with high oxidation activity should form on the surface of rutile TiO₂ particle. In fact, that is the reaction mechanism of photocatalytic degradation [13]. Secondly, as well known, the temperature of “hot spot” produced by acoustic cavitation in aqueous medium can reach 10⁵ and 10⁶ °C: such high temperature sufficiently produces many holes on the surface of TiO₂ particle. Thirdly, the strong shock waves from acoustic cavitation may cause some oxygen atoms on the surface of TiO₂ particle to escape from the crystal lattice and then the holes are formed. Similarly, these holes can decompose those organic pollutants adsorbed on the surface of TiO₂ particle directly or degrade them in aqueous solution indirectly through the •OH radicals resulting from the reaction of holes and H₂O molecules. The precise mechanism of sonocatalytic degradation is to be further investigated.

The different degradation processes for micron-sized and nano-sized TiO₂ powders should be attributed to the difference in the particle size. For a micron-sized TiO₂ particle, just like a multi-cell reactor, the whole organic pollutant molecule can

be degraded in a step on its surface. Once a methyl parathion molecule contacts the micron-sized TiO₂ particle having many active sites, it is oxidized completely. However, for a nano-sized TiO₂ particle, like a unit-cell reactor, on such a small surface catalyst an organic pollutant molecule cannot be degraded in a step. Even if a methyl parathion molecule runs up against the nano-sized TiO₂ particle having highly active sites very few in number, it is only oxidized step by step.

4. Conclusions

The methyl parathion in aqueous solution can be completely decomposed by the sonocatalytic reaction in the presence of rutile TiO₂ catalysts, but the sonocatalytic performance of micron-sized TiO₂ powder is obviously better than that of nano-sized rutile TiO₂ powder. The research results demonstrated the feasibilities of sonocatalytic degradation of methyl parathion and other organic pollutants in wastewater. Especially, this method is applicable to the non- and low-transparent wastewater. The degradation of methyl parathion depends on the amount of rutile TiO₂ catalysts, initial concentration of methyl parathion solution, acidities, temperature and ultrasonic frequency and intensity. The optimal conditions for obtaining high degradation percentage of methyl parathion are considered to be initial methyl parathion concentration of 50 mg L⁻¹, micron-sized rutile TiO₂ catalyst amount of 1000 mg L⁻¹, ultrasonic frequency of 40 kHz, output power of 50 W, pH 10.0 and at 20 °C for about 80 min.

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