

Study of the degradation behaviour of dimethoate under microwave irradiation

Lei Zhang*, Xingjia Guo, Fei Yan, Mingming Su, Ying Li

College of Chemistry and Chemical Engineering, Liaoning University, Shenyang 110036, China

Received 17 August 2006; received in revised form 6 April 2007; accepted 6 April 2007

Available online 20 April 2007

Abstract

In this work, the degradation of dimethoate under microwave irradiation assisted advanced oxidation processes (MW/oxidants) were studied. The efficiencies of the degradation of dimethoate in dilute aqueous solutions for a variety of oxidants with or without MW irradiation were compared. The results showed that the synergistic effects between MW and $K_2S_2O_8$ had high degradation efficiency for dimethoate. Simultaneously, UV/TiO₂/K₂S₂O₈ photocatalytic oxidation degradation of dimethoate was investigated. The experimental results indicated that the method of microwave degradation of organic pollutants in the presence of oxidant could reduce reaction time and improve product yield. Microwave irradiation was an advisable choice for treating organic wastewaters and has a widely application perspective for non- or low-transparent and fuscous dye wastewaters.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Microwave irradiation; Dimethoate; Degradation

1. Introduction

Dimethoate is a kind of high-effective pesticide that is extensively applied in agriculture; however, its residues have a negative effect on the environment, even on the health of people because of its toxicity and stability. And it is difficult to naturally degrade the organophosphorus insecticides within a relatively short time [1]. Moreover, during the process of stepwise degradation, the intermediate products may be more toxic than the original. Therefore, the innovative technologies for effectively and completely decomposing all organic pollutants and transforming them into environmental compatible forms are imperative required. So a study on treating the organophosphorous wastewaters and transforming the organophosphorous into the inorganophosphate is quite significant. In recent years, the technology of ultraviolet photocatalyst degradation has been studied and extensively used to treat some organic pollutants [2,3]. The investigation showed that nano-TiO₂ photocatalyst could achieve a better effect on treating wastewaters containing dyes, phenol, pesticides and so on [4,5]. However, there are some

defects to nano-TiO₂ photocatalyst. It could only work under the ultraviolet irradiation because of its broad band-gap. Hence, the utilization efficiency of ultraviolet light in the photocatalytic degradation reaction is very low for non- or low-transparent and fuscous dye wastewaters [6,7]. As a result, there are some deficiencies in the application of nano-TiO₂ photocatalyst degradation. But, it has been found that Microwave heating offers increased reaction rates and reduced electrical consumption and increases efficiencies of degradation of pollutants [8–10].

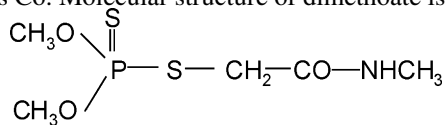
In this paper, the microwave with output power (750 W) was utilized as the irradiation source instead of ultraviolet light and the dimethoate, as a model compound, was treated by advanced oxidation processes. Synchronously, the various influence factors were studied on the effects of microwave irradiation and microwave irradiation/oxidants degradation of dimethoate. And the results were compared between microwave and photocatalytic degradation. Microwave degradation can provide a better result.

2. Materials

Dimethoate (*O,O*-dimethyl *S*-[2-(methylamino)-2-oxoethyl] phosphorodithioate) as a model compound was purchased from Shanghai Sanaisi Reagent Corporation. The water used

* Corresponding author. Tel.: +86 24 62207816; fax: +86 24 62202380.
E-mail address: zhanglei63@126.com (L. Zhang).

throughout the experiment was purified by a Milli-Q water system (Millipore). For increasing photocatalytic activity, the nanometer rutile TiO₂ powder (particle size, 10–20 nm; China) was treated by heating. Analytical grade reagents H₂O₂ (30%), K₂S₂O₈, KIO₄, KBrO₃, KClO₃ were purchased from Tianjin Kemiou Chemicals Co. Molecular structure of dimethoate is as



follows:

2.1. Apparatus

LAMBDA-17 UV–vis spectrophotometer (Perkin-Elmer Company, USA) and Ion Chromatography (2020i, USA) were used to inspect the degradation process of dimethoate. The dimethoate solution was irradiated by using KS-2163-Microwave apparatus (Shenzhaeng Apparatus Company, China), and microwave of output power were in the range from 200 to 850 W.

2.2. Procedure

Dimethoate was oxidized by the following methods:

- (1) microwave irradiation method (MW);
- (2) ultraviolet photocatalytic method (UV/TiO₂);
- (3) an integrated microwave irradiation and H₂O₂, K₂S₂O₈, KIO₄, KBrO₃, KClO₃ process (MW/Oxidants);
- (4) an integrated ultraviolet photocatalytic and K₂S₂O₈ process (UV/TiO₂/K₂S₂O₈).

The experiments of the MW degradation were performed using the self-made glass reactors (bottom area = 50 cm²) placed inside a microwave apparatus. Varied output powers of MW from 200 to 850 W have been used. The samples were taken out periodically and the concentration of PO₄³⁻ was determined with phosphomolybdenum blue colorimetry. The degradation rate of organophosphorous pesticides (η) can be calculated according to the following equation.

$$\eta = \frac{p_t}{p_0} \times 100\%$$

where p_t is the concentration of the inorganophosphorous after MW irradiation; p_0 is the concentration of the organophosphorous before MW irradiation.

For photocatalytic oxidation degradation of dimethoate, the prepared dimethoate solution (1.0×10^{-4} mol/L) and TiO₂ powders (0.1 g/L) were put into a reactor. The high-pressure mercury vapor lamp was hung above the reactor, degradation was carried out below 40 °C, and air was pumped through the reactor from its bottom to ensure a constant dissolved O₂ concentration in the reaction solution. The samples were taken out periodically from the reactor and centrifuged to remove TiO₂. And the concentration of PO₄³⁻ was determined.

3. Results and discussion

3.1. Effect of oxidants

Fig. 1 shows variations of PO₄³⁻ concentrations during oxidation processes, with MW and without MW irradiation. It was found that oxidants could not oxidize dimethoate alone. Dimethoate was degraded up to 2.46% after 6 min of microwave irradiation, but the concentration of PO₄³⁻ was not increasing with time. Therefore, a conclusion was drawn that MW alone could not effectively degrade dimethoate within a short time.

Fig. 1 showed that the efficiencies of the degradation were increased in the presence of oxidants assisted MW. The most effective for degradation of dimethoate was an integrated MW/S₂O₈²⁻ process. In the MW/S₂O₈²⁻ system, almost 100% of dimethoate was degraded in the first 4 min. Whereas oxidation yields of 22.80%, 6.04%, 5.13% and 4.83% were given in the MW/H₂O₂, MW/ClO₃⁻, MW/BrO₃⁻ and MW/IO₄⁻ systems in the first 4 min, respectively. K₂S₂O₈ is different from other oxidants (KIO₄, KBrO₃, KClO₃), strong oxidation agent, and unstable. Free radicals that are produced under MW radiation have longer lifetime and instantly are oxidized and degraded when contacting with dimethoate. But other oxidants have relatively stable structures. Free radicals that are produced by these oxidants under MW radiation have short lifetime and may disappear before contacting with dimethoate.

The microwave irradiation field can induce oxidants to generate free radicals, e.g., •SO₄⁻, •OH, IO₃•, IO₄•, ClO₃• and BrO₃• [11,12]. At the same time, molecules of dimethoate are polarized under MW irradiation [13,14]. Then, the polarized molecules of dimethoate react with the free radicals, and the molecules of dimethoate were degraded in short time. The oxidant K₂S₂O₈ was chosen in all the following experiments.

3.2. Effect of oxidant amount

A series of solutions of 1×10^{-4} mol/L dimethoate containing different amount K₂S₂O₈ were used to investigate efficacies of degradation dimethoate at a fixed output power

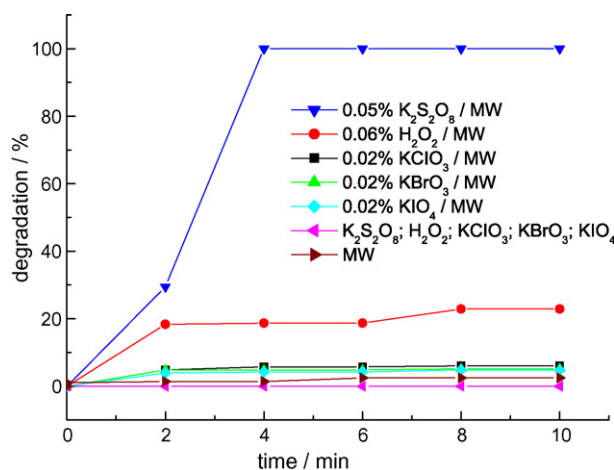


Fig. 1. Influence of different oxidants on degradation ratio.

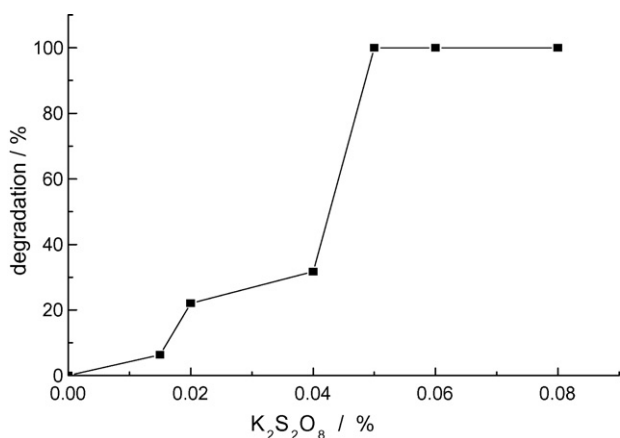


Fig. 2. Influence of K₂S₂O₈ adding amount on degradation ratio.

750 W of microwave irradiation. The degradation rate remarkably increased with the amount of oxidant from 0.01% to 0.05%, whereas the degradation rate did not change for higher concentration (>0.05%). So the optimal amount of K₂S₂O₈ was about 0.05% as shown in Fig. 2.

3.3. Effect of microwave power

Dimethoate aqueous solution (1.0×10^{-4} mol/L) with 0.05% of K₂S₂O₈ was put into the reactor for investigating effect of microwave power. The test results shown in Fig. 3 indicated that degradation rate of dimethoate gradually increased with the microwave power from 200 to 750 W; whereas the degradation rate did not change for higher power (>750 W). So the microwave irradiation of 750 W was chosen throughout the experiments.

3.4. Effect of initial pH

The influences of acidity on the microwave degradation of dimethoate were studied in the range between pH 4.0 and 10.0, and the results were shown in Fig. 4. The values of pH did not nearly influence the degradation rate of dimethoate. Therefore, this experiment was performed at pH 6.8.

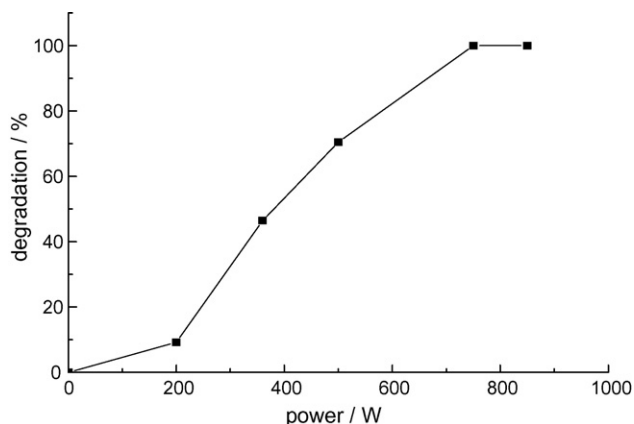


Fig. 3. Influence of microwave power on degradation ratio.

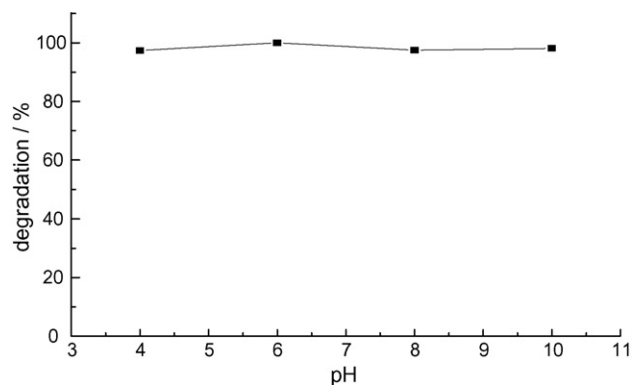


Fig. 4. Effect of initial pH on degradation ratio of dimethoate.

3.5. Effect of irradiation time

The comparisons of degradation rates of dimethoate in different systems MW/K₂S₂O₈ (0.05%), UV/TiO₂ and UV/TiO₂/K₂S₂O₈ (0.1%) were carried out in the mixed solution of 1.0×10^{-4} mol/L dimethoate and 0.1 g nano-TiO₂. It can be observed from Figs. 5 and 6 that the degradation rate of all the three systems gradually increases with irradiation time, but the

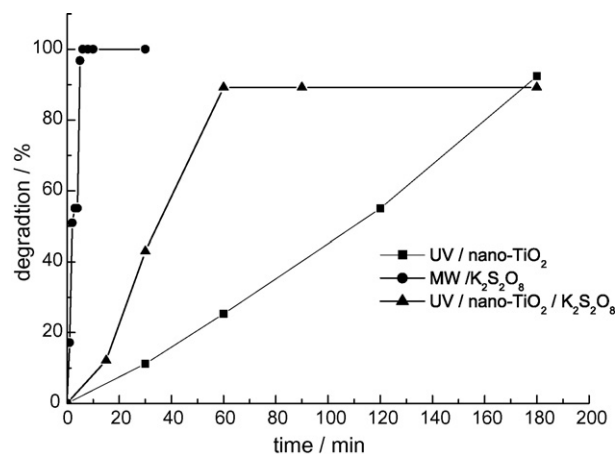


Fig. 5. Influence of acting times on degradation ratio.

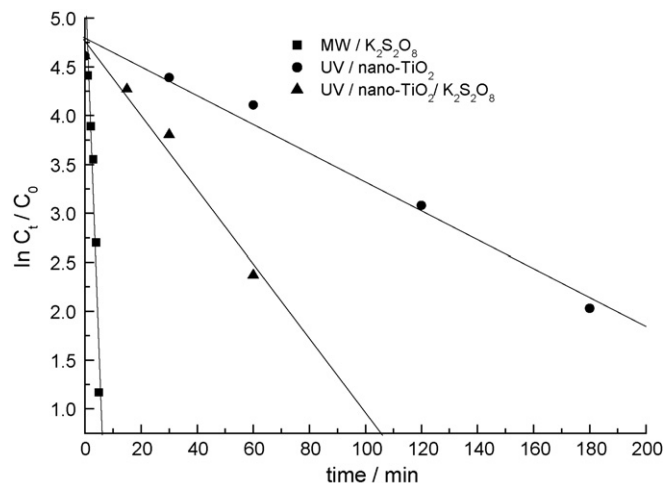


Fig. 6. Reaction kinetics on microwave irradiation–degradation of dimethoate.

degradation rate of dimethoate in the system MW/K₂S₂O₈ is the best. The complete degradation dimethoate achieved at 4 min in the presence of MW/K₂S₂O₈; UV/nano-TiO₂/S₂O₈²⁻ system gave an oxidation yield of 91.24% at 30 min, and there was no change on degradation level after 30 min. The photolytic decomposition products of S₂O₈²⁻, such as SO₄²⁻, were adsorbed on the surface of nano-TiO₂ and competed with dimethoate, which cause no change for degradation rate of dimethoate in the UV//TiO₂/S₂O₈²⁻ system; 92.38% of dimethoate was degraded in the UV//TiO₂ systems following 180 min of treatment. The above results indicate that the degradation of dimethoate in the presence of K₂S₂O₈ combining with MW is the most effective.

Based on the Experimental data fitting was performed by the first order and second order reaction models respectively, the kinetic results of degradation reaction were also given. The results showed that these processes should belong to the pseudo first-order reaction model. The MW/K₂S₂O₈, UV//TiO₂/S₂O₈²⁻ and UV//TiO₂ corresponding kinetic equations are $\ln C_t/C_0 = -0.01474t + 4.7941$ ($r^2 = 0.9902$), $\ln C_t/C_0 = -0.03799t + 4.7608$ ($r = 0.9871$), $\ln C_t/C_0 = -0.767t + 5.445$ ($r^2 = 0.95741$), the pseudo first-order rate constants are 0.767, 0.03799 and 0.0147 min⁻¹, and half-life ($t_{1/2}$) are 0.904, 18.25 and 47.16 min, respectively.

In addition, the experimental results also demonstrate that using microwave heating can reduce reaction time from hours to minutes, remarkably enhance the rates of the reactions, and improve product yield. Besides, the modern microwave technique is easy to control reaction conditions precisely, monitoring temperature and reaction times, saving energy in the process of degrading organic pollutants.

3.6. Mechanism of microwave degrading of dimethoate

The microwave heating is dielectric heating. Microwave irradiation induces changed molecules to migrate or rotate, which results in polarization of these molecules, and the lag between this polarization and rapid reversals of the microwave field creates friction among molecules to generate heat. Because the prompt change from the static to dynamic state is occurring within the molecules, the microwave heating is occurring within the molecules; the microwave heating is described as “inside heating”. The most of the electromagnetic energy is converted into heat.

Dimethoate molecules absorbed microwave energy to make the depression of the activation energy and the increase of reaction activity within the polar bonds, which lead to the rupture of the bond of P–N, P–S, O–N and P–O, etc. K₂S₂O₈ was a strong oxidant with capability of absorbing microwave, and could generate some active free radicals [15] and “heat point”, when the dimethoate molecules contacted with them, which could lead to the oxidations and degradation of dimethoate molecules at reaction temperature. Microwave irradiation makes the efficiencies of dimethoate degradation higher than that of photocatalytic methods. In order to further explore the degradation process of dimethoate under microwave irradiation, degradation

products of dimethoate were determined by ion chromatography, and the concentrations of NO₃⁻, SO₄²⁻ and PO₄³⁻ were 3 mg/L, 6.2 mg/L and 5.12 mg/L, respectively. We conducted that the dimethoate has been completely mineralized and changed into some simple inorganic ions such as NO₃⁻, SO₄²⁻, PO₄³⁻, etc.

4. Conclusions

The Organophosphorous in aqueous solution can be obviously degraded by the microwave reaction in the presence of oxidants assisted. Especially, the research results demonstrated the feasibility of the method, combining microwave with K₂S₂O₈ oxidants for treating dimethoate wastewaters. The optimal conditions of degradation dimethoate (1.0×10^{-4} mol/L) were 0.05% K₂S₂O₈, output power of 750 W microwave irradiation, and pH 6.8. Compared to other methods, the dimethoate could be degraded in shorter time (about 4 min). Moreover, the cost of operating such a simple device is relatively small as the only power needed is the electrical power to drive the domestic microwave oven (in the present case, 750 W). The method of microwave degradation has many advantages such as convenience, safety, economy and high efficiency, so this method has a better prospect in future application.

References

- [1] J.H. Yen, K.H. Lin, Yei Shung Wang, Potential of the insecticides acephate and methamidophos to contaminate groundwater ecotoxicology and environmental safety, *Environ. Res. Sect. B* 45 (2000) 79–86.
- [2] D. Robert, A. Piscopo, J.-V. Weber, First approach of the selective treatment of water by heterogeneous photocatalysis, *Environ. Chem. Lett.* 2 (2004) 5–8.
- [3] S.G. Schrank, H.J. José, R.F.P.M. Moreira, Simultaneous photocatalytic CVI reduction and dye oxidation in a TiO₂ slurry reactor, *J. Photochem. Photobiol. A: Chem.* 147 (2002) 71–76.
- [4] Z. Liu, H. Yang, J. Miao, Kinetic analysis on photocatalytic degradation of Rhodamine B by nano materials titanium dioxide, *Chem. Res. Appl.* 3 (2003) 371–373.
- [5] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, *J. Photochem. Photobiol. A: Chem.* 1 (2000) 1–21.
- [6] B. David, M. Lhote, P. Boule, Ultrasonic and photochemical degradation of chlorpropham and 3-chloroaniline in aqueous solution, *Water Res.* 32 (1998) 2451–2461.
- [7] S. Horikoshi, H. Hidaka, N. Serpone, Environmental remediation by an integrated microwave/UV-illumination method, *Environ. Sci. Technol.* 36 (2002) 1357–1366.
- [8] C. Mesangeau, S. Yous, B. Peres, Pictet–Spengler heterocyclizations via microwave-assisted degradation of DMSO, *Tetrahedron Lett.* 46 (2005) 2465–2468.
- [9] S. Horikoshi, H. Hidaka, N. Serpon, Environmental remediation by an integrated microwave/UV-illumination technique, *J. Photochem. Photobiol. A: Chem.* 161 (2004) 221–225.
- [10] K.S. Jung, J.H. Kwon, S.M. Son, Characteristics of the copper phthalocyanines synthesized at various conditions under the classical and microwave processes, *Synth. Met.* 141 (2004) 259–264.
- [11] W.F. Jardim, S.G. Moraes, Photocatalytic decomposition of 4-chlorophenol over oxide catalysts, *J. Hazard. Mater.* 64 (1999) 313–322.

- [12] F.J. Benitez, J. Beltran–Heredia, T. Gonzalez, Photooxidation of carbofuran by polychromatic UV irradiation without and with hydrogen peroxide, *Ind. Eng. Chem. Res.* 34 (1995) 4099–4105.
- [13] F.J. Benitez, J. Beltran–Heredia, J.L. Acero, Contribution of free radicals to chlorophenols decomposition by several advanced oxidation processes, *Chemosphere* 41 (2000) 1271–1277.
- [14] S. Birgit, L. Gerhard, Oxidative degradation of ptoluene sulfonic acid using hydrogen peroxide, *Chemosphere* 38 (1999) 1035–1047.
- [15] M.A. Boncz, H. Bruning, W.H. Bulkens, Kinetic and mechanistic aspects of the oxidation of chlorophenols by ozone, *Water Sci. Technol.* 35 (1997) 65–72.