

EFFECTS OF ENVIRONMENTAL PARAMETERS ON THE ULTRAVIOLET DEGRADATION OF METHYLPHOSPHONATE

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(Received 3rd Apr 2019; accepted 17th May 2019)

Abstract. Considering the heavy presence of methylphosphonate (MPn) and its derivatives in nature and their potential hazard to human health, this paper attempts to clarify the ultraviolet (UV) degradation kinetics of the MPn under different environmental parameters. Several tests were carried out to measure UV degradation efficiency of the MPn with different combinations of the following factors: radiation time, light intensity, pH and initial concentration. The analysis on the test results show that the MPn can hardly degrade under the UV intensity of 400 W but degraded gradually under the UV intensity of 1,200 W, peaking at the rate of 94.5% within 58 h. The degradation kinetics can be described by the first-order reaction model, and the degradation rate constant was calculated as 0.032 h⁻¹. The MPn degradation efficiency varied with the pH values. The different pH media could be ranked as pH 10 > pH 13 > pH 2 > pH 7 in descending order of the efficiency, indicating that the MPn degradation is more efficiency under alkaline condition. In addition, the MPn degradation became less efficient with the growth in initial concentration, as the intermediate products compete with the reactive oxygen species (ROS). The above results provide a valuable reference for environmental protection and pollution control.

Keywords: *methylphosphonate (MPn), degradation efficiency, photo-oxidation, phosphonate*

Introduction

Phosphonates are an important component of organophosphorus compounds and have the general formula $RP(=O)(OR')_2$. With a relatively stable C-P covalent bond, this component is difficult to degrade and easy to reside in nature. The heavy presence of phosphonate compounds in the environment poses a potential hazard to human health.

Methylphosphonate (MPn) is a relatively simple phosphonate. It is the degradation product of neurotoxic agents like Sarin and Soman and flame retardants like methylphosphinate. The MPn serves as a key reactant in the synthesis of metal phosphonate compounds. Such compounds are novel materials for molecular sieves, ion exchange columns and magnetic motion conductors (Maeda et al., 1995; Edgar et al., 2002; Langley et al., 2008; Bauer et al., 2010). The MPn and its derivatives also act as reaction intermediates for the production of fungicides, insecticides and petroleum additives. When these chemicals are produced and utilized, the MPn is carried by wastewater into the environment, and then absorbed in soil particles and chelated with heavy metal ions. All these lead to the wide existence of the MPn exists in soil and water (Shao et al., 2015). Recent studies have considered the MPn as a potential source of methane in the ocean (Karl et al., 2008; Metcalf et al., 2012; Born et al., 2017; Yu et al., 2018). Oceanic methane accounts for about 4% of global methane budget, making up a key link in the global methane cycle (Sandy et al., 2013). As a well-known greenhouse gas, methane has recently been proved as a cause of the greenhouse effect on the Earth surface. Therefore, the degradation and cycling of MPn have a great significance to greenhouse effect and global climate change.

In general, phosphonates can be decomposed through biodegradation, photodegradation, chemical oxidation. The natural photodegradation of organic pollutants mainly occurs under ultraviolet (UV) radiation, which takes up about 5% of the total solar radiation reaching the Earth, and other factors like the atmospheric oxygen (Deanin et al., 1970). For phosphonates, UV degradation exists as one possible pathway of decomposition. The decomposition is thorough and irreversible, bringing fundamental changes to the pollution status in water environment (Lu et al., 2018; Acero et al., 2019; Gao et al., 2019). Therefore, photodegradation promises a bright future for the removal of phosphonate pollutants.

The existing studies on MPn decomposition in nature have focused on the microbial degradation pathway (Matys et al., 2001, 2004), failing to explore the pathway and kinetics of the UV degradation pathway. In fact, the efficiency of phosphonate degradation may be affected by various environmental parameters, such as pH, concentration and light intensity. To promote the MPn removal in water, it is necessary to explore the UV degradation of pollutants under different environmental parameters.

Taking the MPn as a typical phosphonate pollutant, this paper examines the UV degradation kinetics of the MPn under different environmental parameters, including radiation time, light intensity, pH and initial concentration.

Methodology

Materials

All chemicals in this research were purchased from Sigma-Aldrich. Among them, the MPn reaches the purity $\geq 99.9\%$, and the other chemicals are of the analytical grade. The UV source is an Ace Glass 7900 photo-oxidation apparatus with a 1,200 W lamp. The chemical structure of the MPn is shown in *Figure 1* below.

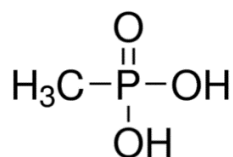


Figure 1. Chemical structure of the MPn

Test procedure

Test on the effect of light intensity

To begin with, 12 mL of 10 mM MPn solution ($\text{pH} \approx 2$) was respectively transferred to two quartz tubes, and separately placed in two photochemical reactors for illumination. One of the reactors has a 400 W mercury lamp and the other, a 1,200 W mercury lamp. The UV emitted from both lamps are consistent with natural UV in composition: primarily UVA (315~400 nm) and UVB (280~315 nm), with a small amount of UVC. The test temperature was controlled below 40°C by a circulating-water air-cooling system. Meanwhile, a control test was carried out to verify whether the MPn can be hydrolyzed by thermolysis in aqueous solution without UV radiation. Specifically, 12 mL of MPn aqueous solution was added to a quartz tube and wrapped in aluminum foil, before being placed in a dark environment. During the reaction,

0.1 mL of sample was taken every 4 h, and diluted 10 times with deionized water, such that the phosphate concentration fell below 1 mM. Next, the phosphate concentration was measured by colorimetric analysis according to the phospho-molybdate blue assay (Murphy and Riley, 1962). All the degradation experiments were run in triplicates.

Test on the effect of pH

The pH of 10 mM MPn solution was respectively adjusted from ~2 to 2, 7, 10 and 13 with 1 M and 5 M NaOH. Then, 12 mL of MPn solution of each pH was transferred to a quartz tube and placed into the photochemical reactor for UV radiation. The UV light was emitted from a 1,200 W mercury lamp. During the radiation, 0.1 mL of sample was taken every 12 h and diluted 10 times for phosphate concentration measurement.

Test on the effect of initial concentration

The MPn aqueous solutions were dispensed separately at the concentrations of 2.5 mM, 5 mM and 10 mM. After shaking, 10 mL of the solution at each concentration was transferred to a quartz tube and relocated to a photochemical reactor for UV radiation. The UV light was emitted from a 1,200 W mercury lamp. During the radiation, 0.1 mL of sample was taken every 12 h and diluted 10 times for phosphate concentration measurement.

Analysis procedure

One of the final products of the MPn is orthophosphate. The formation of orthophosphate can represent the MPn degradation rate, owing to the simple molecular structure of the MPn. In our research, the MPn degradation efficiency is computed by (Yuan et al., 2014):

$$\eta = (C_t / C_0) \times 100\% \quad (\text{Eq.1})$$

where η is the UV degradation efficiency of MPn; C_t is residual concentration of MPn after t-hour radiation; C_0 is the initial concentration of the MPn in the aqueous solution.

The degradation kinetics of the MPn over time was analyzed by the first-order reaction kinetics model below:

$$\ln (C_t / C_0) = -kt \quad (\text{Eq.2})$$

where k is the degradation rate constant of the first-order reaction kinetics, h^{-1} ; t is the reaction time.

Figures and linear fitting analysis were done by OriginPro 2016 software.

Results and Discussion

Effect of radiation time

Figure 2 presents the relationship between radiation time and UV degradation rate of the MPn under the Light intensity of 1,200 W, the initial MPn concentration of 10 mM, the pH of 2 and the temperature below 40°C. It can be seen that the MPn degradation rate increased significantly with the elapse of the radiation time. As the radiation time grew from 0 to 58 h, the MPn degradation rate soared from 0 to 94.5%. In the control

test, no thermolysis degradation was observed during the reaction period, indicating that the MPn will not hydrolyze spontaneously without UV light. Hence, the MPn degradation is attributable to UV radiation.

Much research has been done on the UV degradation mechanism of organic compounds (Chen et al., 2007; Rao and Chu, 2010). Since orthophosphate is a final product of the MPn, the C-P bond dissociation must take place in order to completely decompose the MPn. According to the previous results on UV degradation mechanism, the C-P bond dissociation under UV photolysis can be ascribed to the nucleophilic substitution of the reactive oxygen species (ROS) in the aqueous environment, which are generated by the electronic excitation of the MPn. The UV degradation mechanism of the MPn is detailed below.

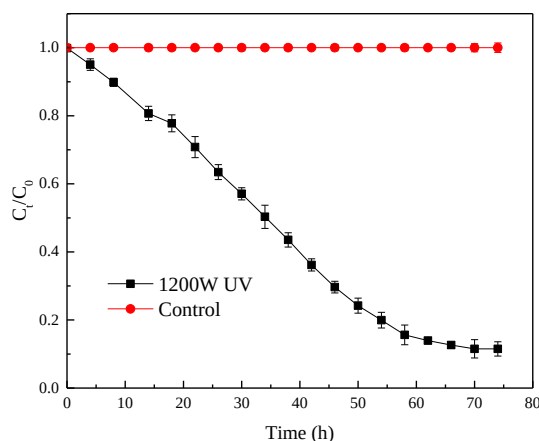


Figure 2. Effect of radiation time on UV degradation efficiency of the MPn

The MPn molecular contains functional groups that can absorb the UV. The absorbed energy will elevate the molecular from the stable ground state to an unstable excitation state (Deanin et al., 1970). The relatively reactive species can transfer electrons to acceptors in the aqueous solution, creating free radicals. In the presence of dissolved oxygen, the free radicals are recombined or hydrolyzed into groups, which then form peroxy radicals through the reaction with oxygen (Bustos et al., 2019). After further photolysis, the peroxy radicals will be converted to hydrogen peroxides (Chen and Liu, 2007), and finally decomposed into hydroxyl radicals that attack the methyl groups in the MPn.

Effect of light intensity

The effective removal of pollutants from wastewater hinges on the optimal UV light intensity for MPn degradation. In this research, the effect of light intensity on MPn degradation is investigated under the UV lights emitted from a 400 W mercury lamp and a 1,200 W mercury lamp. *Figure 3* depicts the relationship between light intensity and MPn degradation rate under the UV intensities of 400 W and 1,200 W, the initial MPn concentration of 10 mM, the pH of 2 and the temperature below 40°C.

As shown in *Figure 3*, the MPn degradation rate was much slower under 400 W UV radiation than 1,200 W. Under the 400 W UV source, only ~3% of MPn were decomposed after an 80 h exposure. The degradation rate was greatly accelerated under

the 1,200 W UV source: the MPn degradation was very fast and then gradually slowed down in the first 58 h, peaking at 94.5%.

As mentioned above, the ROS produced in the aqueous solution is the cause to MPn degradation. Under the 400 W mercury lamp, the amount of ROS generated per unit time was very limited. Coupled with the intense energy required to cleavage the C-P bond, the limited amount of ROS makes it slow for the MPn to be degraded under the 400 W UV source.

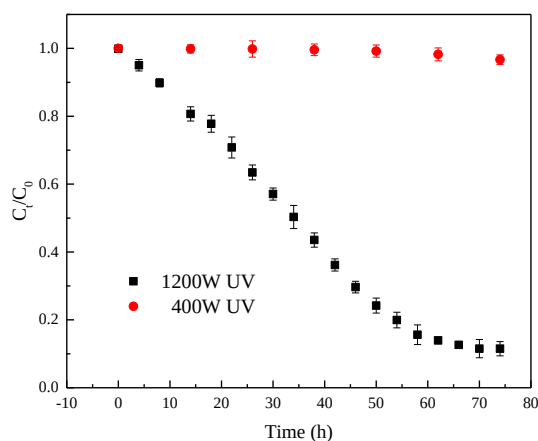


Figure 3. Effect of light intensity on the UV degradation efficiency of the MPn

The MPn degradation reflects the typical degradation kinetics of organic compounds: the degradation proceeds rapidly at the beginning, and gradually slows down near the peak rate. Here, the degradation kinetics of the MPn under different UV intensities are described by the first-order reaction equation (Eq.2) and the results are shown in Figure 4. Obviously, the first-order reaction equation described the reaction process well ($R^2=0.97$).

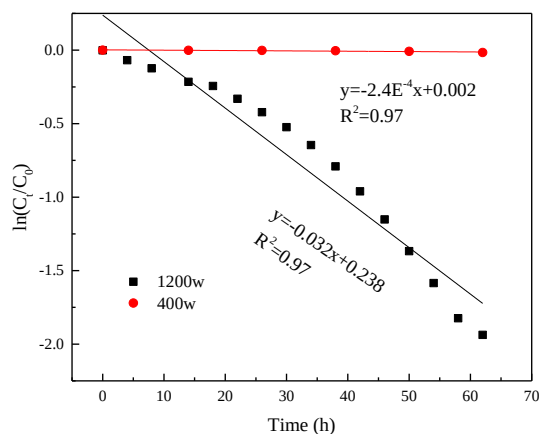


Figure 4. UV degradation kinetics of the MPn under different UV intensities

The calculated kinetics parameters are listed in Table 1. It can be seen that the degradation rate constant (k) of the MPn was only $2.4E^{-4} \text{ h}^{-1}$ under 400 W UV radiation. During the radiation, only 3% of the MPn was decomposed. By contrast, under 1,200 W

UV radiation, the degradation rate constant increased 133 times to 0.031 h^{-1} , and the photolysis half-life reduced to 21.66 h. It can be concluded that the UV intensity plays a significant positive role in the MPn removal in wastewater treatment.

Table 1. Kinetics parameters of UV degradation of the MPn under different light intensities ($C_0=10\text{mM}$)

Light Sources	Photolysis Equation	Rate Constant k (h^{-1})	Photolysis Half-Life $t_{1/2}$ (h)	Coefficient of Determination (R^2)
1,200W Mercury Lamp	$\ln(C_t/C_0) = -0.032 t$	0.032	21.66	0.97
400W Mercury Lamp	$\ln(C_t/C_0) = -2.4\text{E}^{-4} t$	2.4E^{-4}	2,888.11	0.97

Effect of pH

In nature, the pH value differs from one aquatic environment to another. The pH is essential to the degradation of the organic pollutants, as it can affect the photochemical reaction kinetics in pollutant treatment. Under different pH values, the organic pollutants have different molecular forms, and thus exhibit varied physicochemical properties and toxicities.

Figure 5 displays the relationship between pH and MPn degradation rate under the UV intensity of 1,200 W, the initial MPn concentration of 10 mM, the pH of 2, 7, 10 and 13 and the temperature below 40°C . As can be seen from the figure, the different pH values could be ranked as $\text{pH } 10 > \text{pH } 13 > \text{pH } 2 > \text{pH } 7$ in descending order of MPn degradation efficiency. The degradation efficiency increased in acidic and alkaline solutions. Within 50 h exposure to UV radiation, 96% of the MPn in acidic and alkaline media were decomposed, while only 84% were degraded in the neutral solution.

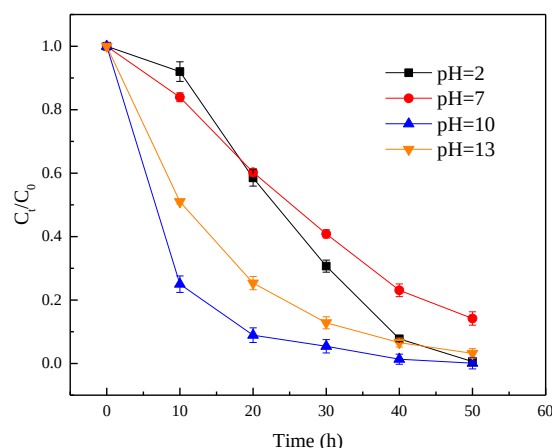


Figure 5. Effect of pH on the UV degradation efficiency of the MPn

Many scholars (Wei et al., 2000; Santos-Beneit, 2015) agree that organophosphorus compounds are more easily to photolyze in acidic and alkaline solutions than in neutral medium. In aqueous solutions, the molecular forms of organophosphorus compounds depend on the pH value. For instance, Li et al. (2016) studied the effect of pH on the photolysis of sulfamethazine (SMZ), concluding that the SMZ photolysis efficiency

varies greatly with pH values: the SMZ degrades much faster in strong alkaline and acidic conditions than in neutral and alkaline condition. This is because the SMZ mainly ionizes in the form of SMZ^- and SMZ^+ in alkaline and acidic conditions, respectively, but exists in the stable molecular state in neutral condition. The ionization of the SMZ in different pH media affects its photolysis kinetics.

As an organic acid, the MPn ionizes in the form of $\text{CH}_3\text{PO}(\text{OH})_2^{2+}$ and $\text{CH}_3\text{PO}(\text{OH})(\text{OH}_2)^+$ in acidic condition. When the pH is adjusted to alkaline condition by NaOH solution, the MPn mainly exists as $\text{CH}_3\text{PO}(\text{OH})\text{O}^-$ and $\text{CH}_3\text{POO}_2^{2-}$. The ionization weakens the molecular bond energy, pushing up the speed of photolysis reaction.

The first-order reaction model (Eq.2) was used to describe the UV degradation kinetics of the MPn at different pH values. The linear fitting results of $\ln(C_t/C_0)$ to time t are shown in Table 2. It is observed that the UV degradation of the MPn was well described by the first-order reaction model ($R^2 \geq 0.97$). The kinetics parameters were calculated and listed in Table 2. As shown in the table, the photolysis half-life of MPn in the solution was 17.32 h, 23.1 h, 10.05 h and 7.07 h respectively at the pH of 2, 7, 10 and 13. The degradation rate constants k at the four pH levels were 0.04, 0.03, 0.069 and 0.098, respectively. The MPn degradation rate at the pH of 10 was 3.3 times that at the pH of 7 and 2.5 times that at the pH of 2.

Table 2. Kinetic parameters of UV degradation of the MPn at different pH values ($C_0=10\text{mM}$)

pH	Photolysis Equation	Rate Constant k (h^{-1})	Photolysis Half-Life $t_{1/2}$ (h)	Coefficient of Determination (R^2)
2	$\ln(C_t/C_0)=-0.040t$	0.04	17.32	0.97
7	$\ln(C_t/C_0)=-0.030t$	0.03	23.10	0.98
10	$\ln(C_t/C_0)=-0.098t$	0.098	7.07	0.99
13	$\ln(C_t/C_0)=-0.069t$	0.069	10.05	0.97

The formation of hydroxyl radicals ($\text{HO}\cdot$) in aqueous solution is the key to the UV degradation of organophosphorus compounds (Evgenidou et al., 2006; Manassero et al., 2010). In alkaline medium, the abundance of hydroxyl groups (OH^-) in solution may boost the formation of hydroxyl radicals, thus speeding up the degradation reaction. To sum up, the pH condition is very important for UV degradation of the MPn and the alkaline medium is preferred for MPn wastewater treatment.

Effect of initial concentration

Figure 6 illustrates the relationship between initial concentration and the UV degradation rate of MPn under the UV intensity of 1,200 W, the initial MPn concentration of 2.5, 5 and 10 mM, the pH of 2 and the temperature below 40°C. As shown in the figure, the three initial concentrations could be ranked in descending order as 2.5 mM > 5 mM > 10 mM by the degradation efficiency. It took about 20 h, 30 h and 50 h for the 2.5, 5 and 10 mM MPn solutions to reach the peak efficiency, respectively. In general, the lower the initial concentration, the more efficiency the MPn degradation.

The above results echo that of Yuan (2007) on photolysis kinetics of paclobutrazol at different initial concentrations: the photolysis efficiency is negatively correlated with the initial concentration. This correlation can be explained as follows. Under the same UV intensity, the amount of ROS produced in solution is fixed at a certain volume and

time. With the increase in MPn concentration, the ratio of ROS to the MPn continues to fall, leading to the decline in degradation efficiency. In addition, the intermediate products of MPn degradation compete with the ROS, thus reducing the degradation rate. The denser the MPn, the greater the number of intermediate products.

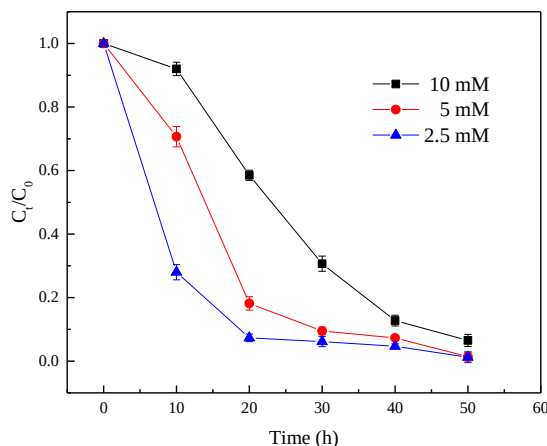


Figure 6. Effect of initial concentration on the UV degradation efficiency of MPn

Conclusions

The environmental parameters are key factors for UV degradation of the MPn. The MPn can be easily degraded under the UV intensity of 1,200 W, and exhibit typical degradation features of organic compounds over time. However, the MPn is difficult to degrade under a low UV intensity (400 W). The optimal pH for UV degradation of the MPn is the pH of 10. The MPn can be degraded more efficiently under a low initial concentration. These conclusions provide a valuable reference for the MPn removal in wastewater treatment.

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