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Effect of pH on the Degradation of Aqueous Organophosphate (methylparathion) in Wastewater by Ozonation

Usharani, K. [1,2*], Muthukumar, M.[2] and Kadirvelu, K.[1]

[1] Division of Environmental Management and Biotechnology, DRDO-BU Center for Life Sciences, TN, India

[2] Division of Environmental Engineering and Technology Lab, Department of Environmental Sciences, Bharathiar University, Coimbatore- 641 046, TN, India

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ABSTRACT: Degradation of *O,O*-dimethyl -*O*-4-nitrophenylphosphorothioate (methylparathion) by ozonation in aqueous solution was studied in a batch reactor under constant ozone dosage and variable pH conditions. The effectiveness of the process was estimated based on the degree of COD (chemical oxygen demand) reduction and conversion of methylparathion. It was observed that ozonation is more effective at alkaline reaction of medium than other conditions. The degree of methylparathion conversion achieved after 120 minutes of the process at pH 9 was 98% compared to 81% and 60% at pH 7 and 3, respectively. Another parameter used to quantify the methylparathion during ozonation was the pseudo first order rate constant *k* (1/min). Results showed that the rate constant of the process was approximately much higher at pH 9 compared to pH 7 and 3. A significant improvement in chemical oxygen demand removal was observed at pH above 7. At pH 9, the reduction in chemical oxygen demand at the end of the process reached 93%. The methylparathion degradation intermediate products were analyzed by gas chromatography–mass spectrometry (GC–MS). The main intermediate product was p-nitrophenol. The result of the study concludes that ozonation is an effective process for the treatment of organophosphate (methylparathion) contaminated wastewater.

Key words: *O,O*-dimethyl -*O*-4-nitrophenylphosphorothioate, Degradation, COD, Kinetics

INTRODUCTION

Water contamination is mainly caused by industrial effluents, agricultural runoff and chemical spills which contain several non-biodegradable substrates that can be harmful to the environment. Their toxicity, stability to natural decomposition and persistence in the environment have been the cause of much concern to the society and regulation authorities all around the world. Although various industries are responsible for contributing the hazardous organic wastes into water resources, pesticide industry is one of the major concerns. Since, the usage of pesticides has recently become an integral part of modern agriculture production. The developed countries have banned many of the pesticides due to their potential toxic effects to man and ecosystem. In many developing countries, the pesticides use is not being properly regulated leading to residues in food which poses health hazards to the consumers (Khan *et al.*, 2009). Developing countries can not stop the usage of certain pesticides due to the cost and efficiency. China is the world's largest producers of vegetables followed by India. Vegetables are susceptible to insect and disease attacks and pesticides are used widely. Therefore, residues of pesticides could affect the ultimate consumer's health especially when freshly consumed. Their fate in the environment is of great concern, since most of them as well as their degradation products have been found both in surface water and ground water. Many studies reported that the main pesticide residues were organophosphate (Bai *et al.,* 2006; Dalal *et al., 2006*; Shen *et al.*, 2002).

Organophosphorous pesticides (OPs) are a group of highly toxic agricultural chemicals widely used in plant protection. Common members of the family are methylparathion, malathion, dimethoate, phosphamidon, phorate, fenitrothion and

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*Corresponding author E-mail: usharaniks2003@yahoo.com

monocrotophos. Among the organophosphate insecticides, methylparathion (MP) was found to be a widely used insecticide in India. Since these pesticides pose a high threat for aquatic systems, it is of great importance to find the effective method for their removal from different sources (Chiron *et al*., 2000). The drinking water directive (Council directive 98/ 83/ EC) sets an allowed contaminant level of 0.1 mg/L for a single pesticide and 0.5 mg/L for the total sum of pesticides. Many studies dealing with the removal of OP pesticides from water have been reported (Laplanche, 1984; Ku *et al*., 1998; Ku and Lin, 2002), relatively few works have reported on the removal of high concentration of pesticides from water.

Among various methods, Ozonation is of significance because of its high oxidation potential, without leaving oxidant residues. Ozone (O_3) has been found to be an effective oxidizing agent for the removal of many organic pollutants from water (Benitez, 2003). Ozonation is very effective in treating wastewaters containing phenolic compounds (Wu *et al*., 2000). Ozone is an attractive and increasingly important method for the degradation of organic pollutants in aqueous solution (Huang *et al*., 2005). Ozonation treatment, both in indirect and direct reaction modes, has been proved effective in degrading of recalcitrant organic contaminants. Ozone is widely used for water and wastewater treatment for decontamination purposes, as well as for the oxidation of common pollutants including pesticides (Ku, and Lin., 2002, Von Gunten, 2007). Ozone can effectively degrade some selected pesticides (including triazine, phosphorus ester, phenylurea herbicides, phenoxycarboxylic acids and miscellaneous pesticides) when its dosage is more than the required disinfection level (Meijers *et al*., 1995; Poche and Prados, 1995). This study aims to investigate the ozonation of methylparathion in aqueous solutions at different pH. A part of work is focused on the kinetic analysis of the data collected during ozonation experiments performed in a batch reactor.

MATERIALS & METHODS

Methylparathion (analytical grade, 98.5 % pure) was obtained from Merck India Ltd., and commercial grade methylparathion (Devithion™ 50% EC) was purchased from Devidayal Agro Chemicals (Mumbai, India). Solvents (HPLC grade) such as dichloromethane, diethylether, n-hexane, methanol and other chemicals (analytical grade) were purchased from Merck India Ltd (Mumbai, India).The organophosphate contaminated synthetic wastewater (0.1%) was prepared using commercial methylparathion (Devithion™ 50% EC). A stock solution of pure methylparathion (98.5%) was prepared by dissolving 1g of this reference material was dissolved in 50ml ethanol and make up to 1000ml with distilled water.

The experimental set-up consisted of an oxygen concentrator (Sim O_2 plus, Italy), ozone generator (Ozonetek Ltd., India) and ozone diffuser with reactor column. Ozone was generated by flowing the oxygen (99.7%) into the ozone generator. A controlled flow rate of 0.5L/min of oxygen was used to produce 4g/h of ozone. Ozone-Oxygen mixture was introduced into the pesticide contaminated synthetic wastewater in the ozonation chamber. The ozonation chamber (reactor) consists of 820mm glass column with 30mm inner diameter having a capacity to hold 1000 ml of effluent. It was provided with a sample port at various points, an ozone gas inlet at the bottom with a ceramic diffuser over the inlet port to diffuse the ozone/oxygen gas mixture through the column and a closed top with a collection port to collect the off-gas for analysis. A teflon tube was used for connecting the ozone outlet port from the ozone generator to the ozone reaction chamber. The volume of sample taken for each experiment was 500 ml. Initial ozone concentration of $4gh^{-1}$ was maintained for all the experiments and it was carried out at room temperature. The experiments were conducted by varying the pH to 3, 7 and 9 using hydrochloric acid (1N) and sodium hydroxide (1N). For each experiment, wastewater samples were collected before and after ozonation and anlaysed for the efficiency of COD removal and methylparathion degradation.

In order to study the effect of variables such as pH, time on chemical oxygen demand (COD) reduction and methylparathion degradation during ozonation, the pH was varied from 3 to 9 and ozonated for a period of 120min. The COD was estimated as per the standard procedure (APHA, 1998). The change in pH of the ozone treated wastewater was monitored using pH meter (ELICO - L1127, India). All experiments were performed in triplicates.

After ozonation the samples were transferred to 250ml separating funnel and extracted with equal ratio of diethylether and n-hexane (1:1) by liquid-liquid extraction method. The organic phase were combined and evaporated with a rotary evaporator to about 5ml, then purged to dryness with high purity Nitrogen. The residue was reconstituted in 1.0 ml methanol and analysed using gas chromatography–mass spectrometry (GC–MS). Intermediate analysis was carried out on GC–MS (Perkin Elmer-Clarus 600, Germany) equipped with a MS capillary column (60 x 250µm). Helium was used as the carrier gas at a constant flow rate of 1 ml min^{-1}. The MS transfer temperature and the ion source temperature was 200°C. The oven temperature program was set as the following: Initial temperature 50°C, hold for 0 min, ramped to 260 °C at 10 °C min^{-1} and hold for 3 min. The scan mode was chosen and the range of m/z was from 50 to 450 Da. Split injections (20:1) was used and the MS data acquisition was set at 3 min post injection after the elution of the solvent peak**.** The injection volume was 5µl. For these operating conditions, the retention time for standard methylparathion was 18.5 min. The ozonated samples after 60 min were analysed for intermediates.

RESULTS & DISCUSSION

The characteristics of the methylparathion contaminated synthetic wastewater are shown in Table 1. It was reported that the pesticide pollution due to wastewater released from formulating or manufacturing pesticide industry were up to 1000 mg/L (Chiron, 1997). Therefore in the present study, synthetic wastewater containing methylparathion with maximum concentration of 1000 mg/L was used. The influence of pH on the effectiveness of MP degradation by ozonation experiments were carried out at pH 3, 7 and 9. The results are shown in shown in Fig. 1. The degradation rate increased as the pH increased from 3 to 9.At pH 3, free radical formation is very low; therefore, radical reactions are expected to be negligible, whereas direct molecular ozonolysis should be highly predominant. The oxidation of aromatic rings, therefore, seems to be provided by ozonolysis of double bonds. Only 60 % of MP and 67% of COD was removed after 120 min of ozonation. In general, ozone molecule itself was one of the main reactive species under acidic conditions, so the degradation of MP exhibited low efficiency (Kasprzyk-Hordern *et al.*, 2003). At pH 7, ozonolysis and OH^- radical reactions are expected to be equally important. Although the total initial concentration of the MP was similar to those of at pH 3, the degradation was (62 % at 90 min), increased by 81 % of MP degradation and 83% of COD reduction. At pH 9, the formation of °OH radicals is fast. Ozonolysis is expected to be negligible because of fast ozone usage for radical formation. Fig.1 shows that the degradation of MP was 63 % up to 60 min of ozonation and reached 97.8% and COD reduction of 93% after 120 min.

Fig. 1 also shows the disappearance of MP at various initial pH levels during the ozonation. As shown, the rates of disappearance of MP were more or less similar, both at neutral and basic conditions. Chu *et al.,* (2003), reported that the hydroxyl radicals may be the important active species in ozonation of 2,4-Dicholrophenoxyaceticacid. As the solution became more basic, the rate of O_3 decomposition to secondary oxidants, such as hydroxyl radicals, increased. The degradation rate of organic compounds by ozonation increases at alkaline condition through the contributions of hydroxyl radicals (Rivas *et al.,*2001; Chu *et al.*, 2003; Beltran *et al.*, 2005; Ye *et al*., 2009). The obtained results indicate that the process effectiveness increases significantly at pH above 7, which is a result of an enhanced Ozone decomposition and the shift towards radical type reaction at pH greater than 7.

For an ionizable organic compound, the reaction rate of O_3 is typically faster with the charged anion form than with the conjugate acid (Hong and Zeng, 2002); however, the expected increases in reaction rate according to abundantly of nitrophenol resulted at higher pH, were observed at pH 9. Most of the reported experimental results indicates the decomposition rate of various organic compounds by ozonation increases with increasing pH due to species distribution of dissolved ozone (in the form of ozone molecules or hydroxyl free radicals) and organic compound (in the form of molecules or ions) in aqueous solution (Ku *et al*., 1998; Beltran *et al*, 1994; Assalin *et al*., 2004). Many organic phosphate pesticides are reported to be dissociative in aqueous solution, the species distribution of these compounds is highly dependent on its dissociation constant and solution pH condition (Ku *et al*., 1998; Beltran *et al*, 1994).

The reaction of ozone with a solute M may be described by the following reaction scheme:

$M+ O_3$ Moxid

In practice, it is usually assumed that the ozone reaction is first order with respect to ozone and solute M concentration, thus the rate law can be formulated as:

$$d[M] / dt = kM [O_3] [M]$$

Where, kM is the rate constant for the degradation of solute M by O_3. Chu and Wong (2003) has confirmed that the ozone concentration can be considered constant, the degradation of organic compound is first order with respect to its concentration. Thus, the degradation of MP was found to follow a pseudofirst-order reaction (Fig. 2). It is well known that the oxidizing ability of ozone comes from either molecular ozone or hydroxyl free radicals (Beltran *et al*., 1998). Eq. 1, therefore, can theoretically interpret the decay rate of MP:

$$d[MP]= kO_3 [MP] [O_3] + kOH [MP] [OH°] \qquad \text{Eq. (1)}$$

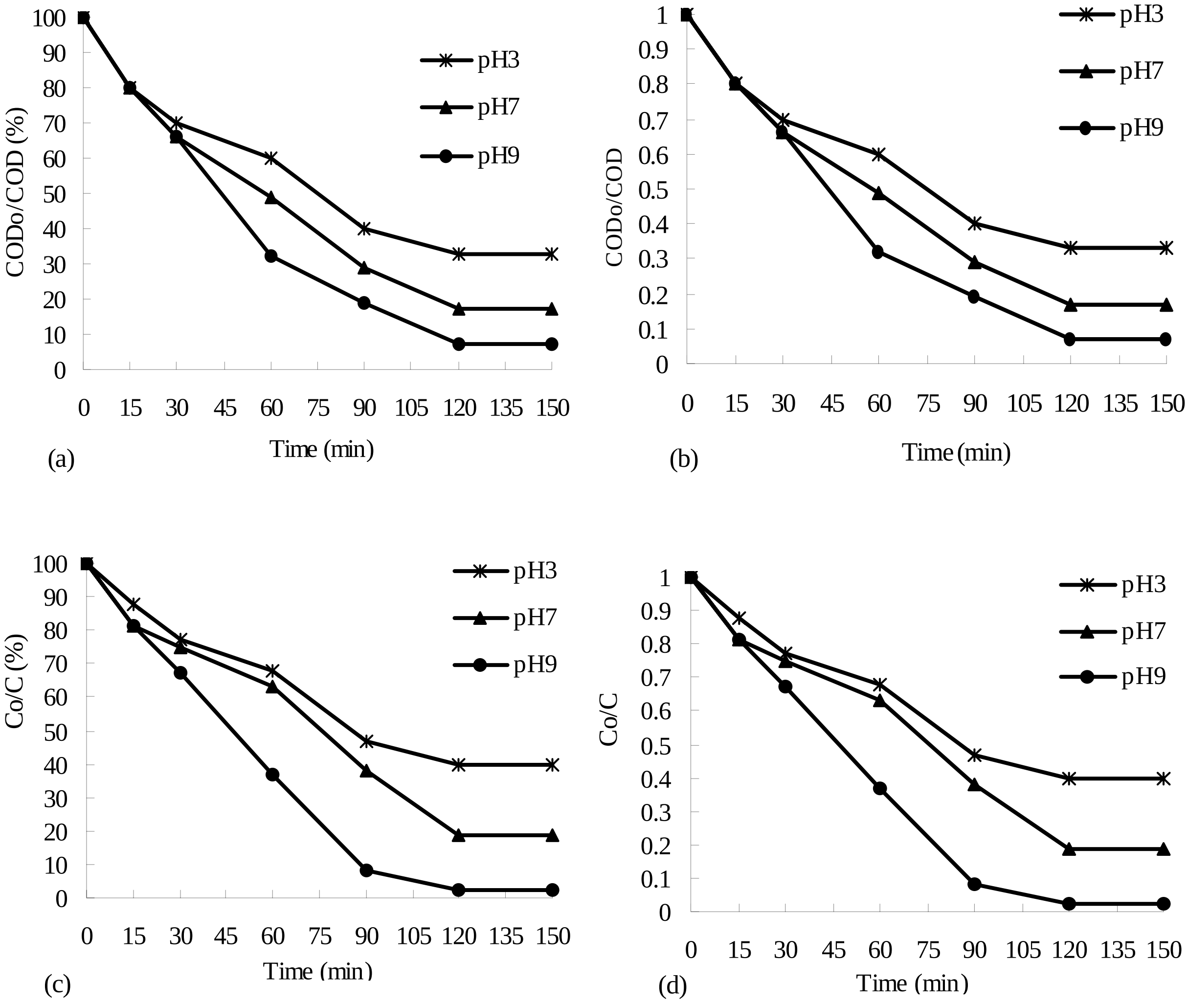

Fig.1. Effect of initial pH on the (a,b) COD reduction and (c,d) methylparathion degradation by ozonation. Initial methylparathion C_0-1000 mg/L; $COD_0$2400 mg/L; ozone dosage- 4g/h

Table 1. Characteristics of methylparathion contaminated synthetic wastewater

Parameters	**Range**	**Mean**	**Standard deviation (SD)**
Colour	Yellow - Brown		
pH	6.8 - 7.2	7	0.282
COD (mg/L)	2380-2420	2400	28.28
Methylparathion (mg/L)	985 - 1,015	1000	21.213

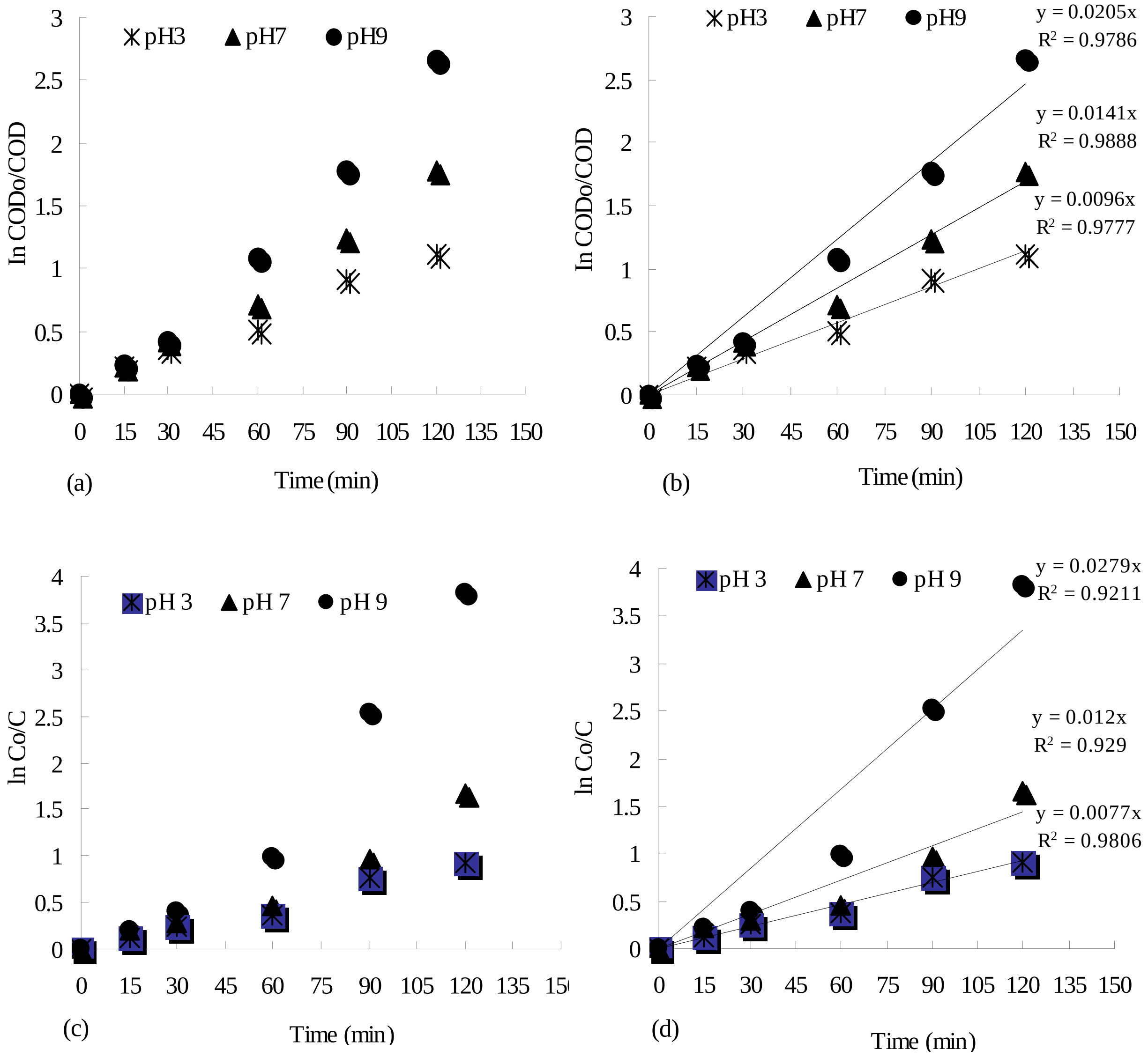

Fig. 2. Rate of (a,b) COD reduction and (c,d) methylparathion degradation by Ozonation from the initial concentration (C0) of 1000 mgL-1; COD0 2400 mgL-1; ozone dosage- 4gh-1

Where, [MP] is the concentration of MP in the solution, $[O_3]$ and [OH°] are the concentrations of ozone and hydroxyl radicals, k_O and k_{OH} are the corresponding rate constants. Since the ozone supply in studied system was presumably in excess, a pseudo steady state condition can be assumed, that is the concentration of ozone and hydroxyl free radicals were close to constant. Eq. 1, therefore, can be rearranged as the following pseudo- first-order equation:

Where, k is the overall pseudo-first–order rate constant:

Eq. (2)

$$d[MP] = (k_{O3}[O_3] + k_{OH}[HO°])[MP] = -k[MP]$$

The degradation rates were shown to be pH dependent (Fig. 2). The decay rate increased with each increment of pH. It was well known that the self decomposition of ozone would be faster at a higher pH. As shown in Fig. 2. the methylparathion degradation and COD reduction kinetics obtained during ozonation fitted a pseudo-first-order curve. Pseudo-first-order rate constants at various pH values are given in Table 2. The rate constants for methylparathion degradation were 0.017, 0.027 and 0.028 per min when pH values were 3.0, 7.0 and 9.0 respectively. The degradation rate increased as the pH increased from 3.0 to 9.0. The rate constants for COD reduction were 0.022, 0.033 and 0.047 per min when pH values were 3.0, 7.0 and 9.0 respectively. The COD reduction rate increased as the pH increased from 3.0 to 9.0. In addition, the relatively high values of R^2 confirm the applicability of this pseudo-first-order model to the methylparathion oxidation process by the ozonation.

From the result of GC-MS analysis, the retention time of methylparathion was observed to be 18.5min for standard and 18.53 for ozone treated wastewater. The compounds with their respective retention times of 14.61 and 18.5 min were identified by library search and by comparison with the authentic standards as p-nitrophenol and the parent MP, respectively. The fragment ions with m/z 263, 125, 109, 93, 79, 63 in the MS spectrum are all characteristic fragment ions of methylparathion ($C_8H_{10}O_5NSP$- 263 MW) (Table. 3). For the parent MP, the fragment ion at *m*/*z* 125 is formed by the loss of *p*-nitrophenol from the molecular ion of *m*/*z* 263. Fragment ion at *m*/*z* 109 is formed by the loss of NO from the nitrobenzene group. Further fragmentation with the loss of an oxygen atom gives $[C_6H_5O]+$ at *m*/*z* 93. In the thiophosphoric moiety, the loss of a methyl and a methoxyl group produced the ion of *m*/*z* 79, followed by the loss of another oxygen atom to give the *m*/*z* 63 ion. Phenol,4-nitro (RT-14.61) and 3-methyl-2-(2-oxopropyl) furan (RT-17.42) were identified as ozonation intermediates of methyl parathion. The fragment ions with m/z 139, 109, 93, 81, 65 in the MS spectrum are all characteristic fragment ions of 4-nitrophenol ($C_6H_5O_3N$- 139 MW). The fragment ions with m/z 123, 109, 81, 69, 55 in the MS spectrum are all characteristic fragment ions of 3-methyl-2-(2-oxopropyl) furan ($C_8H_{10}O_2$- 138 MW) (Table 3).

Table 2. Pseudo-first-order rate constants for the degradation of methylparathion and COD reduction by ozonation process

Temperature (°C)	Ozone dosage (g/h)	Initial MP concentration (g/L)	pH	Pseudo first order k_{MP} (1/min)	MP R^2	Pseudo first order k_{COD} (1/min)	COD R^2
RT	4	1	3	0.01773	0.9806	0.02211	0.9777
RT	4	1	7	0.02764	0.9290	0.03247	0.9888
RT	4	1	9	0.02800	0.9211	0.04721	0.9786

Table 3. GC-MS analysis of intermediates of methylparathion by ozonation process

Compound Name	Formula	Molecular Weight	Retention Time (min)
Methyl parathion	$C_8H_{10}O_5NSP$	263	18.50
3-methyl-2-(2-oxopropyl) furan	$C_8H_{10}O_2$	138	17.42
Phenol, 4-nitro-	$C_6H_5O_3N$	139	14.61

CONCLUSION

In this study, ozonation of methylparathion contaminated synthetic wastewater was carried out in batch process. The ozonation of MP follows pseudo-first-order kinetics; its reaction rates are dominated mainly by initial pH level. Alkaline conditions favor the ozonation rate of the MP, since hydroxyl radical reactions are the main route of MP degradation. It can be concluded that pH is one of the important variables plays a vital role for the removal of MP by ozonation. The main by product of methylparathion degradation was p-nitrophenol. More work is needed to determine the precise mechanisms for the ozonation reported here, and further study may form the basis of important techniques for environmental treatment.

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