

The Mechanistic and Oxidative Study of Methomyl and Parathion Degradation by Fenton Process

Chihhao Fan and Ming-Chu Liao

Abstract—The purpose of this study is to investigate the chemical degradation of the organophosphorus pesticide of parathion and carbamate insecticide of methomyl in the aqueous phase through Fenton process. With the employment of batch Fenton process, the degradation of the two selected pesticides at different pH, initial concentration, humic acid concentration, and Fenton reagent dosages was explored. The Fenton process was found effective to degrade parathion and methomyl. The optimal dosage of Fenton reagents (*i.e.*, molar concentration ratio of H_2O_2 to Fe^{2+}) at pH 7 for parathion degradation was equal to 3, which resulted in 50% removal of parathion. Similarly, the optimal dosage for methomyl degradation was 1, resulting in 80% removal of methomyl. This study also found that the presence of humic substances has enhanced pesticide degradation by Fenton process significantly. The mass spectroscopy results showed that the hydroxyl free radical may attack the single bonds with least energy of investigated pesticides to form smaller molecules which is more easily to degrade either through physio-chemical or biological processes.

Keywords—Fenton Process, humic acid, methomyl, parathion, pesticides

I. INTRODUCTION

THE environmental contamination by organic pesticides has been a serious issue due to their popularity in use. They have been extensively applied to the agricultural activities as well as environmental sanitation implementation due to their chemical characteristics of toxicity, bioaccumulation and persistence [1], [2]. The residual pesticides may become the contamination sources and pose a serious threat to the soil and groundwater environment through the rainfall infiltration process. This contamination becomes even more serious when persistent organic compounds are involved. Among the often-used pesticides, organochlorines are considered most detrimental to the environment because of their persistence and toxicity. However, organophosphorus and carbamate are considered more environmental friendly and become a popular alternative because their residuals in the environment may pose less threat to the public health comparatively in the field application. As a consequence, the abundant uses of these pesticides and their residuals in the environment have also

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drawn a great deal of concerns due to possible environmental contamination.

To mitigate the soil and groundwater contamination by pesticides, many processes based on redox reactions initiated by hydroxyl radicals, such as ozone and Fenton reaction are investigated. These processes have been reported as effective alternatives compared to conventional treatment processes [3]. The hydroxyl radical is a strong oxidizing agent capable of oxidizing various organic contaminants without selectivity. One way to generate hydroxyl radicals is by Fenton reaction, which consists of the decomposition of H_2O_2 catalyzed by Fe^{2+} . The use of Fenton reactions for the treatment of contaminated soil has been reported extensively [4]-[9]. The most advantageous aspect of applying Fenton reactions are the relatively low cost and ready availability of H_2O_2 , the abundance of iron and its massive existence in different mineral species in the form of oxides [10]. Therefore, the aim of the present work is to evaluate the chemical degradation of the organophosphorus pesticide of parathion and carbamate insecticide of methomyl in the aqueous phase through Fenton process. The degradations at different Fenton reagent dosages and humic acid concentrations were investigated. Additionally, the degradation mechanisms for parathion and methomyl were also explored using LC-MS.

II. MATERIALS AND METHOD

A. Reagents

In this study, the reagent grade parathion with 98.7% purity and methomyl with 96.7% purity were purchased from SUPELCO and CHEM SERVICE, respectively. The humic acid was purchased from ALDRICH. The FeSO_4 and H_2O_2 used were reagent grade chemicals purchased from SANTOKU and SHOWA, respectively. The water used in the experiments was deionized water. For the pH adjustment, NaOH and H_2SO_4 used were reagent grade chemicals purchased from Riedel-de Haen and JB Baker, respectively. The quenching agent of KI was purchased from SIGMA.

B. Experiment and analytical procedure

All the Fenton degradation experiments were conducted in the 250 ml beakers under the temperature of $24\pm 2^\circ\text{C}$ at pH 7. The initial concentrations for both pesticides are 20 ppm. For the degradation experiments, initial concentrations of Fe^{2+} were 0, 1.0, 2.0, and 3.0 mM, and initial H_2O_2 concentrations were 0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 and 5.0 mM. At a given Fe^{2+}

concentration, the pesticides were degraded at 8 different H_2O_2 concentrations. In each test, the pesticide concentrations were monitored at 0, 2, 5, 10, 15, 20, 25 and 30 minutes after reaction took place by take an aliquot of the tested solution at each sampling time. The quench agent of KI was added to stop the reaction immediately after the sample was collected. The samples were analyzed using Waters Alliance HPLC and UV detector. The column used was Waters PAH C18 column. The sample volume injected was 20 μL , and the flow rate was 1 ml/min. For parathion, the mobile phase was 15% H_2O and 85% methanol. The UV detector wavelength was 254 nm. For methomyl, the mobile phase was 45% H_2O and 55% methanol. The UV detector wavelength was 238 nm. For the pesticide degradation in the presence of humic acid, the humic acid concentrations were at the concentrations of 0, 2.5, 5, and 10 mg/L, and the Fenton reagent ratios (*i.e.*, H_2O_2 to Fe^{2+}) are controlled at either 4:2 or 2:2.

III. RESULTS AND DISCUSSION

The experiment results for methomyl and parathion are presented in Fig. 1 and Fig. 2, respectively. For methomyl, without the presence of Fe^{2+} , no obvious degradation was observed. As the Fe^{2+} concentration increased, apparent degradation of methomyl occurred. At the Fe^{2+} concentration of 1 mM, the most effective methomyl removal (*i.e.*, 68%) was observed when H_2O_2 was at the concentration of 1.5mM. At the Fe^{2+} concentration of 2 mM, the most effective methomyl removal (*i.e.*, 80%) was observed when H_2O_2 was at the concentration of 2mM. At the Fe^{2+} concentration of 3 mM, the most effective methomyl removal (*i.e.*, 80%) was observed when H_2O_2 was at the concentration of 3mM. Generally, the decrease in concentration ratio of Fe^{2+} to H_2O_2 enhanced the methomyl degradation, resulting in the treatment efficiency increasing from 30% to 80%.

For parathion, at the Fe^{2+} concentration of 1 mM, the most effective parathion removal (*i.e.*, 48%) was observed when H_2O_2 was at the concentration of 3mM. At the Fe^{2+} concentration of 2 mM, the most effective parathion removal (*i.e.*, 40%) was observed when H_2O_2 was at the concentration of 4mM. At the Fe^{2+} concentration of 3 mM, the most effective parathion removal (*i.e.*, 38%) was observed when H_2O_2 was at the concentration of 6mM. In general, the parathion removal efficiency by Fenton process decreases as the concentration ratio of H_2O_2 to Fe^{2+} decreases from 4:1 to 2:1.

In this study, the degradations of methomyl and parathion by Fenton process at the presence of humic acids were also investigated, and the results are presented in Fig. 3. It is found the presence of humic acid enhanced the degradation of methomyl. With the presence of humic acids, the removal efficiency was 81% at the concentrations of H_2O_2 and Fe^{2+} of 2 mM and 2 mM, respectively. The removal efficient was 95% when the concentrations of humic acid, H_2O_2 and Fe^{2+} are 10 mg/L, 2 mM and 2 mM, respectively.

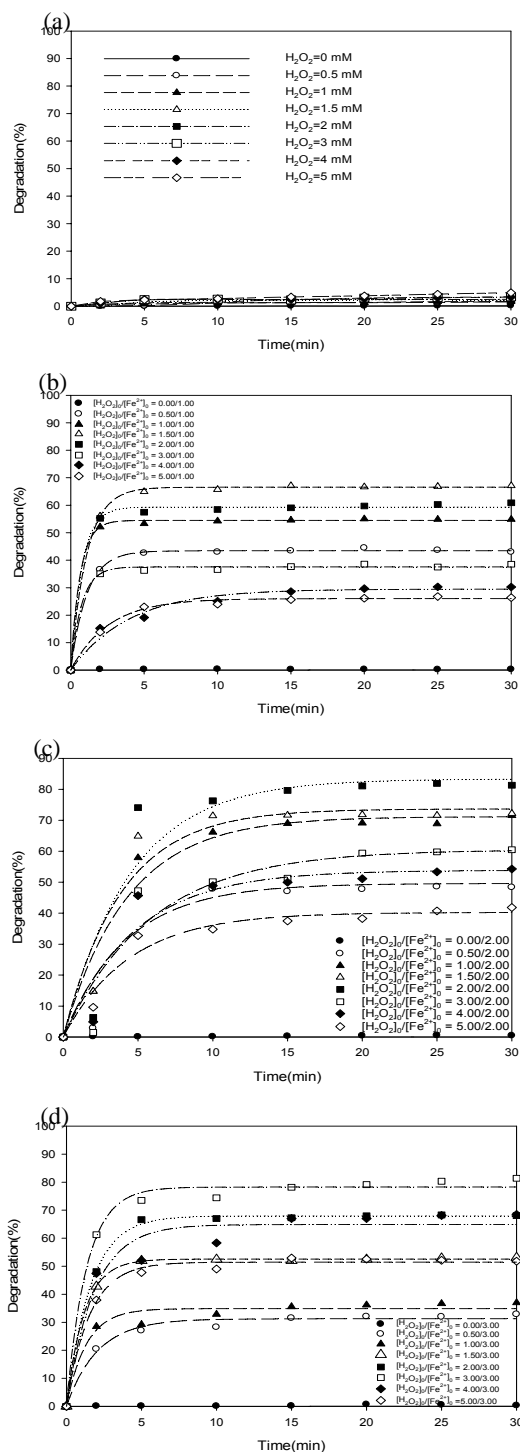


Fig. 1 Mehtomyl degradation at various Fenton reagent dosages of Fe^{2+} concentration at (a) 0 mM, (b) 1 mM, (c) 2 mM and (d) 3mM

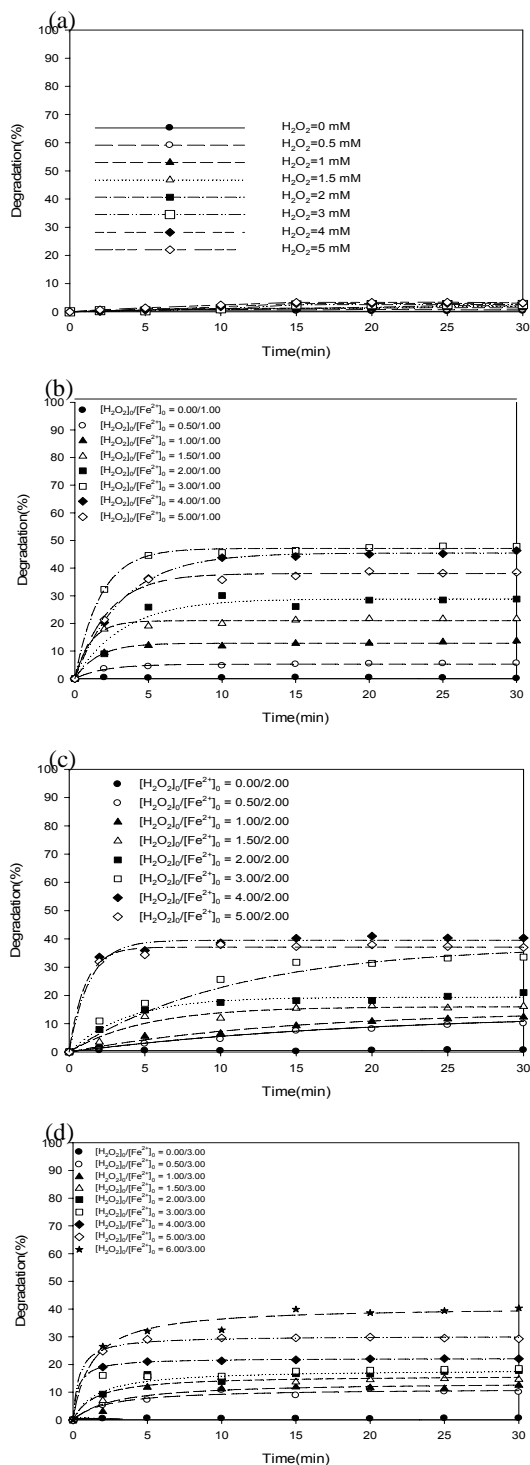


Fig. 2 Parathion degradation at various Fenton reagent dosage of Fe^{2+} concentration at (a) 0 mM, (b) 1 mM, (c) 2 mM and (d) 3 mM

For parathion, the degradation efficiency by Fenton process at the presence of humic acids was 40% when concentrations of H_2O_2 and Fe^{2+} were 4 mM and 2 mM, respectively. Similarly, the addition of humic acids enhanced the degradation of parathion. This removal efficiency increased to 60% when the

concentrations of humic acid, H_2O_2 and Fe^{2+} were 10 mg/L, 4 mM and 2 mM, respectively. The observed enhancement in pesticide degradation may be due to the fact that the protonation of the functional groups of humic substances results in a locally acid environment which is more favorable for Fenton reaction. In order to explore the methomyl and parathion degradation mechanisms in Fenton process, the degradation experiments at H_2O_2 and Fe^{2+} concentrations of 1.0 mM and 0.5 mM, respectively, were conducted. The samples were collected and analyzed with LC-MS. The mass spectroscopic illustrations of methomyl at the reaction times of 0 and 30 minutes are presented in Fig. 4. Fig. 5 shows the spectroscopic illustration of parathion under the same experimental condition.

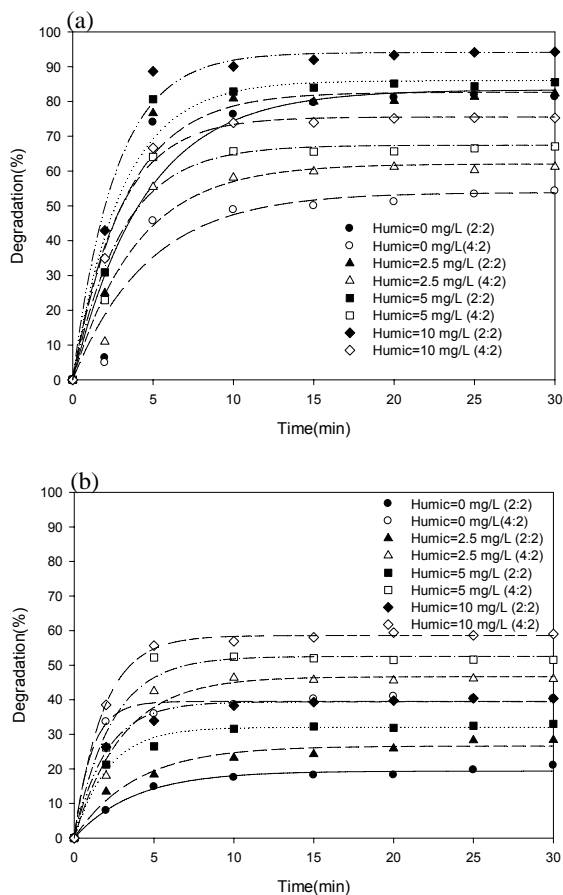


Fig. 3 Methomyl (a) and parathion (b) degradation at the presence of humic acid concentrations of 2.5, 5 and 10 mg/L, the H_2O_2 to Fe^{2+} concentration ratio of 4:2 and 2:2

At the beginning of the methomyl degradation experiment (in Fig. 4 (a)), the most significant signal occurred at 163 amu. In the degradation by Fenton process, a methomyl molecule may break into smaller molecules at the bonds with less energy (*i.e.*, C—O, N—O, or C—N single bond).

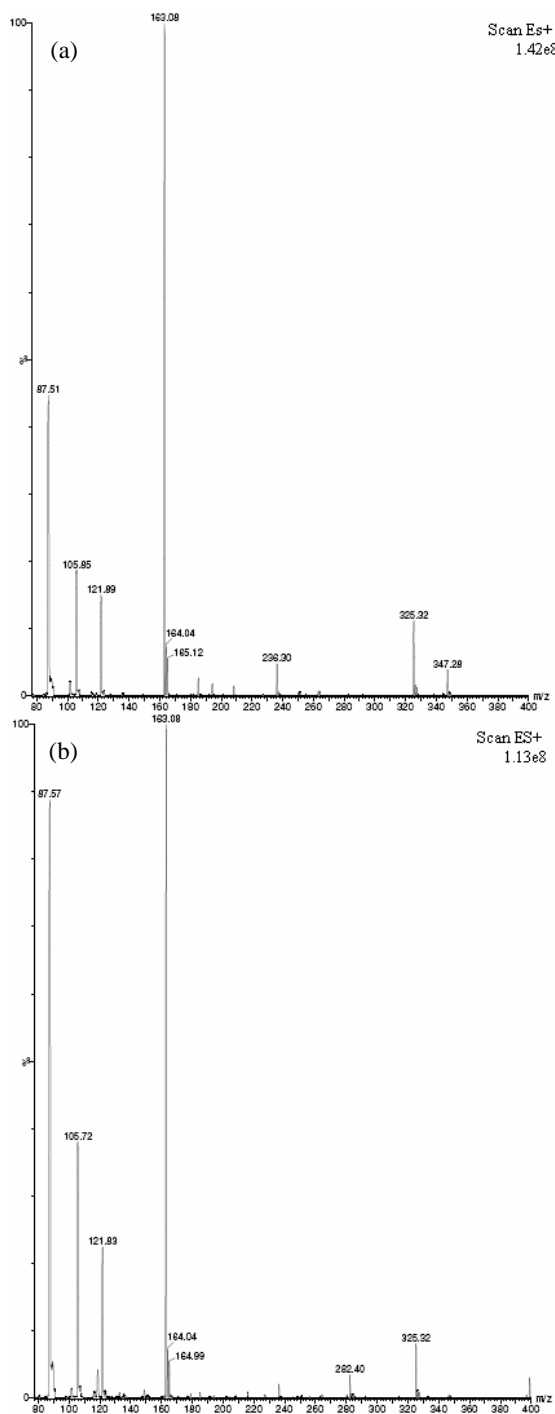


Fig. 4 Mass spectrometry of methomyl degradation of at the reaction time of (a) 0 minute, and (b) 30 minutes, by Fenton reagents H_2O_2 and Fe^{2+} of 1.0 mM and 0.5 mM, respectively

After 30 minutes (in Fig. 4 (b)), the signal for methomyl molecule decreased, and the signals for 121.99, 105.95 and 87.51 amu increased, implying that the hydroxyl radicals have attacked the single bonds of methomyl molecule (the dotted

lines shown in Fig. 6(a)), forming the smaller molecules of C_2H_6NS , C_2H_6NSO and $C_2H_6NSO_2$.

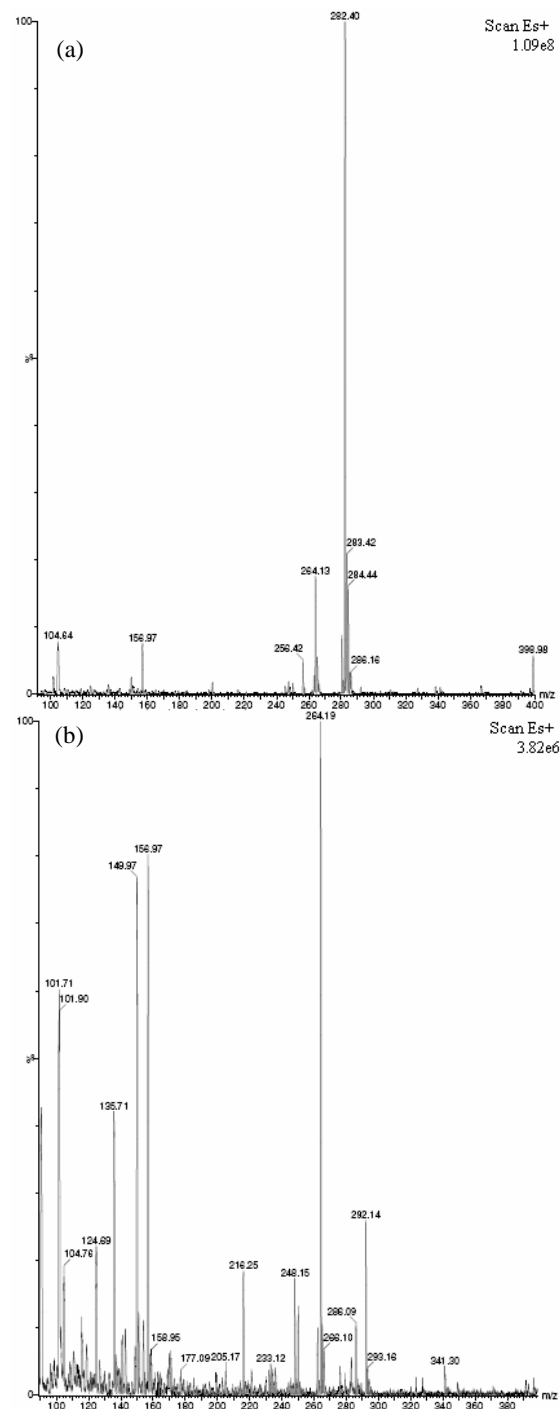


Fig. 5 Mass spectrometry of parathion degradation of at the reaction time of (a) 0 minute, and (b) 30 minutes, by Fenton reagents H_2O_2 and Fe^{2+} of 1.0 mM and 0.5 mM, respectively

In Fig. 5 (a) for parathion degradation, two significant signals are observed at 282 amu and 264 amu. The molecular

for parathion is 291 implying that the 282 amu molecule was formed by losing two methyl function groups with an attachment of sodium ion in the process of ionization during MS analysis, and the 264 amu molecule was formed by losing an ethyl group from a protonated parathion molecule.

After 30 minutes (as shown in Fig. 5 (b)), the signal for parathion molecule decreased, and signals at 156.97, 149.97, 135.71 amu appeared. The 156.97 molecule was formed by losing two $\text{CH}_3\text{CH}_2\text{O}$ groups and one NO_2 from a protonated parathion. The 149 amu molecule might be formed by the cleavage at dotted line 1 in Fig. 6 (b) with subsequent deprotonation. The 135 amu molecule might be formed subsequently by losing a methyl group from the 149 amu molecule.

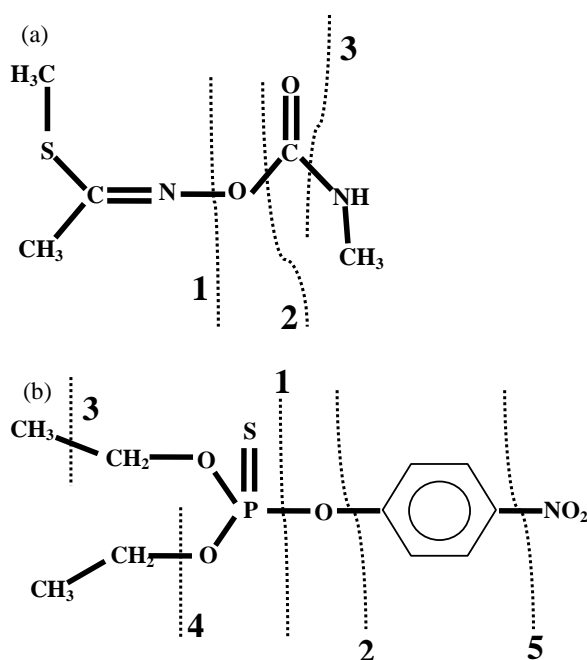


Fig. 6 Illustration of bonds breakage and molecule cleavage for (a) methomyl and (b) parathion molecules in the process of Fenton reaction

IV. CONCLUSION

In this study, the degradations of methomyl and parathion by Fenton process were investigated. It is found that the methomyl degradation by Fenton process is more effective when the reagent dosage of H_2O_2 to Fe^{2+} was 1:1. For parathion, the best removal efficiency occurred at the reagent dosage of H_2O_2 to Fe^{2+} is 3:1. At the presence of humic acids, the methomyl and parathion were degraded more efficiently by Fenton reaction due to the formation of locally acid environment. From the mass spectroscopic analysis for methomyl and parathion, it is found that the free hydroxyl radicals may attack the single bonds with less energy to break the pesticide molecules into small molecule fractions which may be possibly less harmful to the environment as well as more easily to degrade biologically.

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