CHAPTER 3

OPTIMUM CONDITIONS AND OXIDATIVE DEGRADATION OF TREATED CHLORPYRIFOS SOLUTION BY ULTRASONICATION AND OZONATION

3.1 Introduction

Recent developments in advanced oxidation processes (AOPs) effectively generate free radical species under appropriate conditions. Many researches suggest the use of AOPs for pesticides degradation. Ultrasonication and ozonation have been reported to oxidize organic and inorganic contaminates in aqueous environment. In the combined system, ultrasonication and ozonation were believed to enhance each other in the oxidation of organic pollutants (Xiong *et al*., 2011). The synergetic effect is able to enhance the production of hydroxyl radical generated by the radiolysis of ozonation in the presence of ultrasonic radiation (Yue *et al*., 2008). Weavers *et al*. (1998) pointed out the importance of the rapid degradation of organic contaminants by using ozone and ultrasonication (20 kHz) with an increase in hydroxyl radicals. Ince and Tezcanlí (2001) found that the degradation of a reactive dye was affected by the combination of ultrasonication (520 kHz) and ozonation.

During pesticides degradation, there are some changes in the pesticide solution. Intermediates and products degradation of some pesticides after ultrasonication and ozonation was important study to explain mechanism or degradation pathway during degradation. Many studied intermediates of pesticides during degradation by ultrasonication and ozonation have been observed of many parameters such as temperature, pH, oxidation-reduction potential and anions of the pesticides solution.

Among the different processes, ultrasonication, ozonation and their combined application can be proposed as a suitable tool for chlorpyrifos degradation. Moreover, this chapter was to investigate the effect of ultrasound and its combination with ozone, and to study the oxidative decomposition of chlorpyrifos.

3.2 Materials and methods

Chlorpyrifos and chemicals

Reference standard chlorpyrifos was purchased from Sigma-Aldrich Laborchemikalien GmbH (Stienheim, Germany) with 99.9 % purity. Chlorpyrifos stock solution (1000 mg/l) for pesticide residue analysis was prepared in acetone, high-performance liquid chromatography (HPLC) grade 99.8 %, obtained from RCI Labscan Ltd. (Bangkok, Thailand). The chlorpyrifos solution was diluted with deionized water to the appropriate working concentrations.

Peak areas of standard chlorpyrifos concentration 0.1, 0.5, 1.0, 1.5 and 2.0 mg/l were determined peak area by gas chromatography-flame photometric detector (GC-FPD). Linear equation was obtained to calculate chlorpyrifos concentration (Appendix; Figure 1).

Standard anions such as chloride, nitrate, sulphate and phosphate (Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) for pesticide residue analysis were purchased from Sigma-Aldrich Laborchemikalien GmbH (Stienheim, Germany) with 99.9 % purity. The anion solutions were prepared at eight varying concentrations 0.1, 0.2, 0.4, 0.8 and 1.0 mg/l (Appendix; Figures 2 - 5).

Ultrasonication

Ultrasonic devices with input power of 3 W at varying frequencies of 108, 400, 700 kHz and 1 MHz, were made by Honda Electronics Company (Toyohashi, Aichi, Japan) and utilized for 3 replications. Polyethylene cylinder reactor, 10 cm in diameter, equipped with a transducer at the lower part was used. Chlorpyrifos (25 ml) in a flask was sonicated in an ultrasonic reactor (Figure 3.1).

Ozonation

Ozone gas produced by an ozone generator (Ozonizer, Sky zone model S05AE) was bubbled into chlorpyrifos solution in a flask, with a flow rate of 25 ml/min. Dissolved ozone concentration was determined by ozone sensor (Mettler Toledo, Model Thornton M 300, USA).

Figure 3.1 Ultrasonic devices at 108, 400, 700 kHz and 1 MHz.

3.2.1 Degradation percentage of chlorpyrifos solution by ultrasonication, ozonation and the combination

1) Degradation percentage of chlorpyrifos solution by ultrasonication

The chlorpyrifos standard of 1 mg/l (MRLs of chlorpyrifos in chilli is 0.5 mg/l) was prepared in the ultrasonic reactor mentioned earlier with different frequencies (108, 400, 700 kHz and 1 MHz). Samples were taken out periodically and degradation percentages of each chlorpyrifos were monitored. Concentrations of chlorpyrifos were determined using GC-FPD (Agilent Technologies Model 6890). The standard solutions were analyzed in five replicates. Data were calculated to find the degradation percentage of the chlorpyrifos as follow;

$$\text{Chlorpyrifos degradation (\%)} = \frac{C_0 - C_t \times 100}{C_0}$$

where: C_0 is chlorpyrifos concentration at initial time

C_t is chlorpyrifos concentration at treated time

The degradation kinetics of chlorpyrifos (k) under treatments were calculated from the regression equation of plots $\ln(C_t/C_0)$ versus time.

$$\ln(C_t/C_0) = -kt$$

where: k is an apparent rate constant, degradation kinetic of chlorpyrifos

C_t is chlorpyrifos concentration at treated time

C_0 is chlorpyrifos concentration at initial time

Chlorpyrifos extraction

Chlorpyrifos extraction was done following the improve method used by Department of Agriculture, Thailand (Steinwandter, 1985). In 20 ml sample solution, dichloromethane was added, and then homogenized for 1 min. The process was repeated tree times. Collected extract was dried by evaporator at 340 mbar for 3 - 5 min, redissolved with 2 ml acetone before injection in GC-FPD (Figure 3.2).

GC-FPD analysis of chlorpyrifos

The GC-FPD analysis was performed with an Agilent Technologies (Wilmington, DE) model 6890 gas chromatograph equipped with a flame photometric detector. The GC was carried out using a fused silica capillary column HP-5, 5 % Phenyl Methyl Siloxane, with dimensions of 30 m × 0.32 mm i.d. and a 0.25 µm film thickness. The temperature regime was as follows: initial temperature at 100 ºC, increasing 10 ºC/min to 200 ºC and then 4 ºC/min to the final temperature of 220 ºC. A purified helium carrier gas was used at a flow rate of 3.6 ml/min. The detector temperature was 250 ºC. Sample solution (1.0 µl) was injected in splitless mode and the quantification of chlorpyrifos was performed using chlorpyrifos standard.

Figure 3.2 Gas chromatography-flame photometric detector (GC-FPD).

2) Degradation percentage of chlorpyrifos solution by ozonation

The standard chlorpyrifos 1 mg/l was prepared in the flask and ozone gas was bubbled through the solution. Samples were taken out periodically and the degradation percentages of each chlorpyrifos in samples were monitored. Concentration of chlorpyrifos was determined using GC-FPD. The solutions were analyzed in five replicates. Data were calculated to find the percentage of removal rate of the chlorpyrifos the same procedure as experiment 3.2.1(1).

3) Degradation percentage of chlorpyrifos solution using combination of ultrasonication and ozonation

From last experiments, the treatments which shown good results in chlorpyrifos degradation was used for this experiment. The individual chlorpyrifos standard was prepared in the ultrasonic reactor mentioned earlier. The solution was bubbled with ozone gas from ozone generator. A schematic diagram of experimental set-up is presented in Figure 3.3. Samples were collected for the determination of chlorpyrifos concentration and percentage of removal rate of the chlorpyrifos according to the same procedure as above experiments.

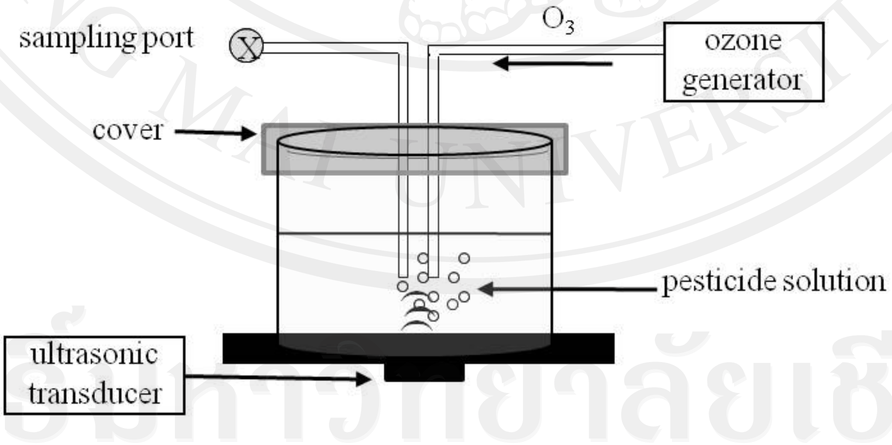


Figure 3.3 Schematic diagram of experimental set-up.

3.2.2 Oxidative degradation of treated chlorpyrifos solution by ultrasonication, ozonation and the combination

Chlorpyrifos concentration at 1 mg/l was treated with ultrasonication and ozonation and then analyzed for oxidative degradation. Ultrasonicated and ozonated chlorpyrifos were detected for the decomposition such as temperature, pH, oxidation reduction potential (ORP) and anion concentration (Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}). The decomposed chlorpyrifos with released anions were analyzed by ion exchange chromatography (IC). Then the degradation products were determined by GC-MS for the decomposition of treated chlorpyrifos solution.

1) Temperature, pH and oxidation-reduction potential (ORP) of standard chlorpyrifos solution after using ultrasonication and ozonation

The oxidative degradation products of treated chlorpyrifos by ultrasonic and ozone treatment were immediately measured for temperature, pH and ORP of the solution by multi-meter (Sartorius, Germany).

2) Anion concentrations of standard chlorpyrifos solution after using ultrasonication and ozonation

Concentrations of anions such as chloride, nitrate, sulphate and phosphate of ultrasonicated and ozonated of chlorpyrifos solutions were determined. The ions released during decomposition of chlorpyrifos at 60 min were analyzed by ion chromatography (Figure 3.4). The amounts of these ions corresponds to the degradation of chlorpyrifos in this study. The ion chromatography analysis was performed by ion chromatograph equipped by column type Metrosep A Supp 5 250/4.0, eluent composition was A Supp5 eluent 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$. Sample solution (10.0 µl) was automatically injected in conductivity mode, and the quantification of chlorpyrifos was carried out by chlorpyrifos standard. An ion chromatography was used at a flow rate of 0.70 ml/min, pressure 12.71 MP and the recording time 28 min. Samples were filtrated by syringe filters size 13 mm, 0.45 µm (Vertical®). Anions concentrations were calculated from peek area compared to the standards anions.

Figure 3.4 Ion chromatography.

3) Oxidative degradation of chlorpyrifos

A gas chromatography-mass spectrometry (GC-MS) was used to analyze oxidative degradation from Agilent Technologies (Wilmington, DE), model 6850 (Figure 3.5). The GC column was a fused silica capillary column HP-5MS, 5 % phenyl methyl siloxane, with the dimensions of 30 m × 0.25 µm i.d. and a 250 µm film thickness. The temperature program started at an initial temperature of 100 ºC, increasing 20 ºC/min to 200 ºC and then 4 ºC/min to the final temperature of 220 ºC hold 2 min. A purified helium carrier gas was used, at a constant flow. MS conditions were TOF-MS, ionization mode electron impact (EI) and EM voltage 1811.8 V (injection volume 1.0 µl in splitless mode). The total ion current chromatograms were recorded between 50 - 400 *m/z*, at a rate of 37 scans per second. EI mass spectrum database searches were carried out in a mass spectral library (National Institute for Standard Technology (NIST) search program version 1.5, Gaithersburg, MD, USA).

Figure 3.5 Gas chromatography-mass spectrometry (GC-MS).

Statistical analysis

All experiments were evaluated with a regression procedure using the SPSS version 17, while the differences among various treatments by Duncan’s New Multiple Range test. The significant difference at $p < 0.05$ was assigned by statistical method.

3.3 Results and discussion

3.3.1 Degradation percentage of chlorpyrifos solution by ultrasonication, ozonation and the combination

1) Degradation percentage of chlorpyrifos solution by ultrasonication

The effect of ultrasonication to reduce standard chlorpyrifos (1 mg/l) was investigated. The chlorpyrifos oxidation in standard solution using different frequencies of ultrasonication and different sonication time was determined by GC-FPD. It was found that the removal of chlorpyrifos residue increase with sonication time. All ultrasonic frequencies significantly increased chlorpyrifos degradation, compared to control. Moreover, ultrasonication at 1 MHz for 60 min was the most effective reducing chlorpyrifos (75.00 %) (Figure 3.6 and Appendix; Table 1). Base on the results, the ultrasonication reduced chlorpyrifos concentration, with increasing time (Figure 3.7A and Appendix; Table 2). It is noticed that the beneficial effect of power on degradation rates is due to increased cavitational activity at higher levels of power. With power and the number of collapsing cavities increasing, degradation rate increase. Klavarioti *et al*. (2009) demonstrated that sonochemical reactions are induced upon high intensity acoustic irradiation of liquids at frequencies that produce cavitation (typically in the range 20 - 1,000 kHz). Thus, cavitation serves as a means of concentrating the diffused energy of ultrasound into micro-reactors with simultaneous release of reactive radicals with each reactor serving as a hot spot. Similarly, Yao *et al.* (2010) reported that the decreasing size of bubbles with the increasing frequency shorten the collapse during, thus optimal frequency for parathion degradation was 600 kHz which was attributed to the much higher $^{\bullet}OH$ yield than 200 kHz.

The plots of $\ln(C_t/C_0)$ vs. sonication time for chlorpyrifos was given in Figure 3.7B, and the deduced parameters for different treatments were listed in Table 3.1. The degradation kinetics of chlorpyrifos (*k*) was related with the chlorpyrifos degradation percentage, the highest *k* value was obtained 2.20×10^{-2} min^{-1} when using ultrasonic frequency at 1 MHz. *k* of parathion degradation increased from 0.0771 to 0.150 min^{-1} with the increasing ultrasonic frequency from 200 to 600 kHz (Yao *et al*., 2010). Zhang *et al*., (2010) observed a similar increase of *k* values and similar decline of $t_{1/2}$ values for malathion and chlorpyrifos when the output ultrasonic power was enhanced from 100 to 500 W. According by Matouq *et al*. (2008), kinetic modeling applied for the obtained results showed that the degradation of diazinon by high ultrasonic frequency wave followed a pseudo-first-model with apparent rate constant around of 0.01 s^{-1}.

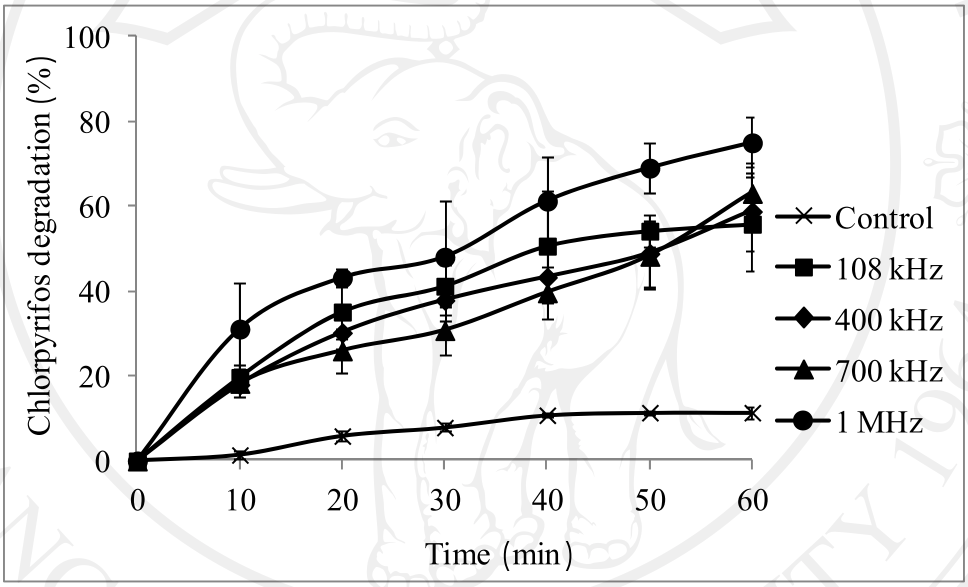


Figure 3.6 Degradation percentage of standard chlorpyrifos (1 mg/l) by ultrasonication.

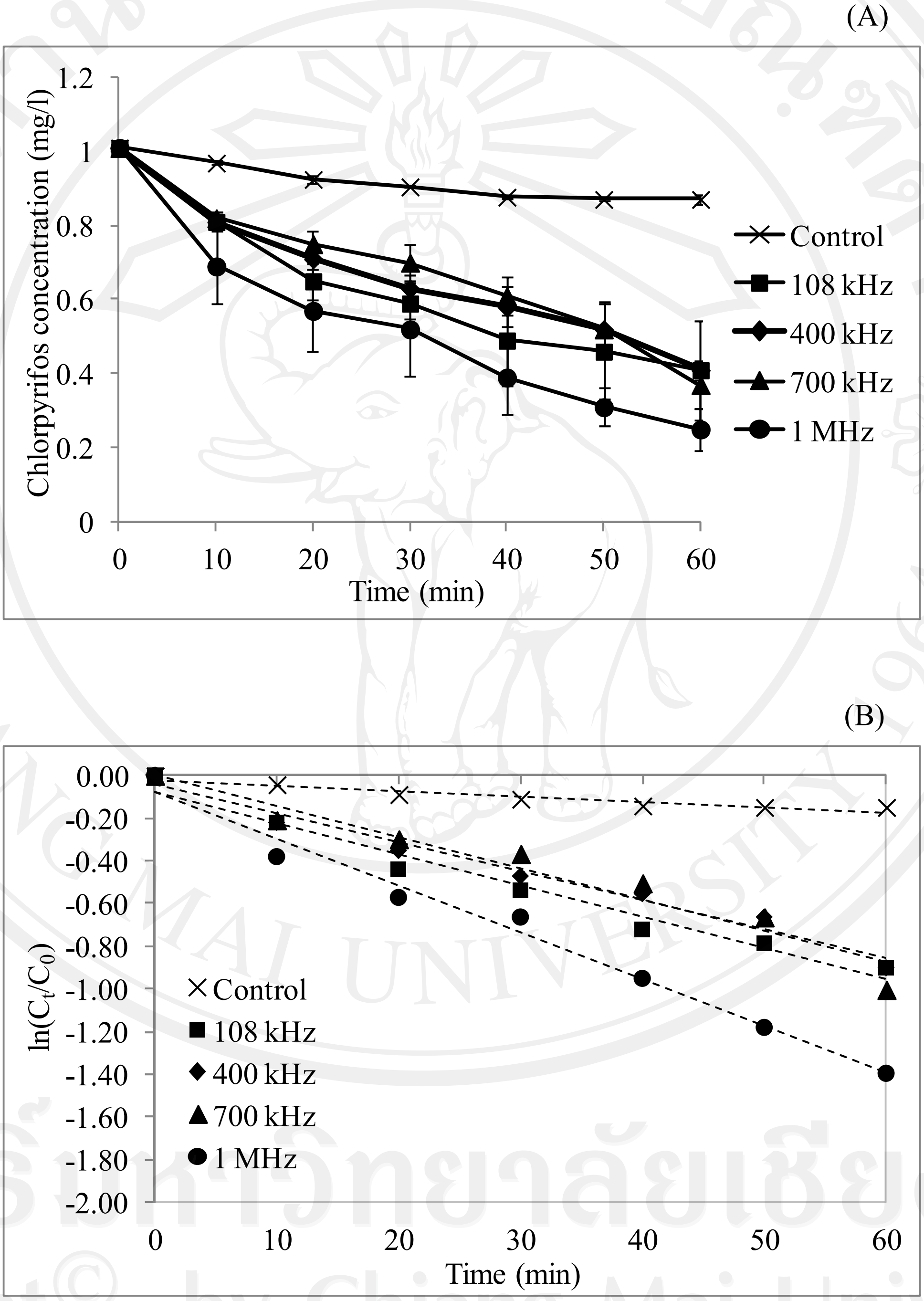


Figure 3.7 The changes of chlorpyrifos concentration (A) and the degradation kinetics of chlorpyrifos (B) under ultrasonication.

2) Degradation percentage of chlorpyrifos solution by ozonation

A result from the ozone treatment of the standard solution of chlorpyrifos against exposure time is shown in Figure 3.8. It was found that the removal of chlorpyrifos residue was directly proportional to the increase in ozone exposure time. At exposure time of 10, 20, 30, 40, 50 and 60 min, the chlorpyrifos degradation significantly increased to 38.33, 44.10, 52.54, 57.42, 61.52 and 64.54 % respectively, when compared with the control (Appendix; Table 1). Chlorpyrifos concentration significantly reduced after treated with ozonation throughout ozone exposure time, compared to the control (Figure 3.9A and Appendix; Table 2). The ozone is a strong oxidant and possibly changed the chlorpyrifos. It may be suggested that ozone is a strong oxidant that either decomposes in water to form hydroxyl radicals which are stronger oxidizing agents than ozone itself, thus inducing the so-called indirect oxidation or attacks selectively certain functional groups of organic molecules through an electrophilic mechanism (Klavarioti *et al*., 2009). These results are in agreement with many studies on the reduction of pesticide in water solution after ozone treatment with a range of contact times (Faust and Gomma, 1972). Benitez *et al*. (2002) reported that carbofuran could be degraded by a combination of ozone and UV treatment. They both improved carbofuran decomposition, in relation to very reactive hydroxyl free radicals, that may attack at the −P=S bond converting to −P=O (oxon derivative) (Magara *et al*., 1994). Catadol (2008) suggested that patulin could be destroyed with ozone both in aqueous solution and in a diluted apple juice. Whangchai *et al*. (2011) observed decomposition of chlorpyrifos in fresh lychee fruit increased with increasing ozone exposure time and, in this study, ozone gas was demonstrated to be more effective for rapid degradation of chlorpyrifos than ozone-containing water. Similarly, Ku *et al.* (1998) reported that the diazinon degradation occurred within 1 h of ozone treatment.

The *k* value of chlorpyrifos degradation by ozonation was 1.64×10^{-2} min^{-1} higher than the control (0.25×10^{-2} min^{-1}) (Figure 3.9B and Table 3.1). The kinetic value of ozonation increased with a chlopyrifos degradation increasing. Pseudo-first order reaction kinetics for reactive Remazol Black B dye degradation in the pure aqueous solution was increased when the decolourisation and mineralisation rate constants increasing (Arslan and Balcioglu, 2001).

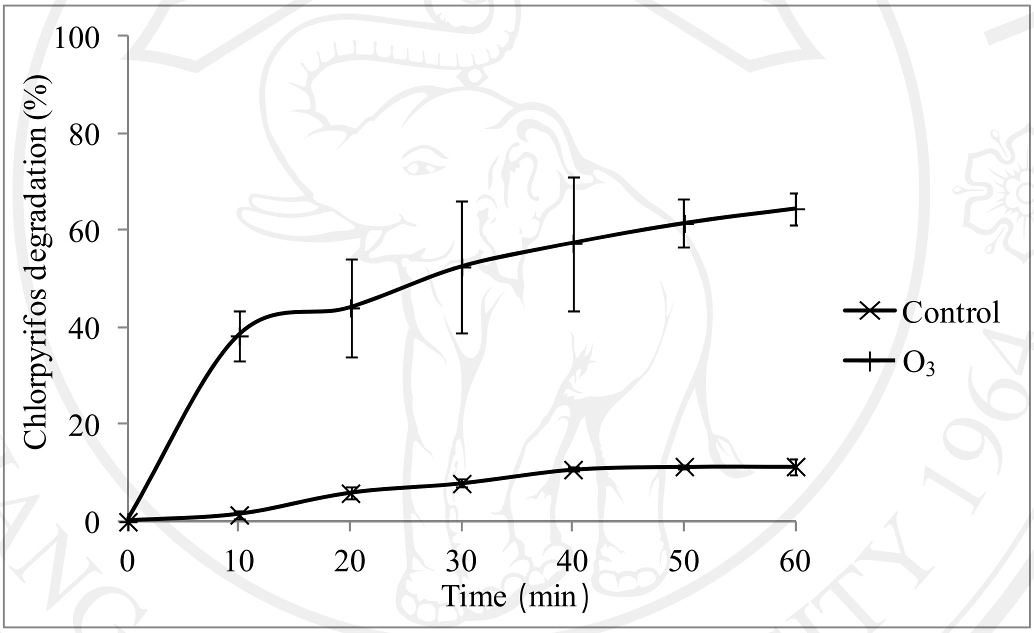


Figure 3.8 Degradation percentage of standard chlorpyrifos (1 mg/l) by ozonation.

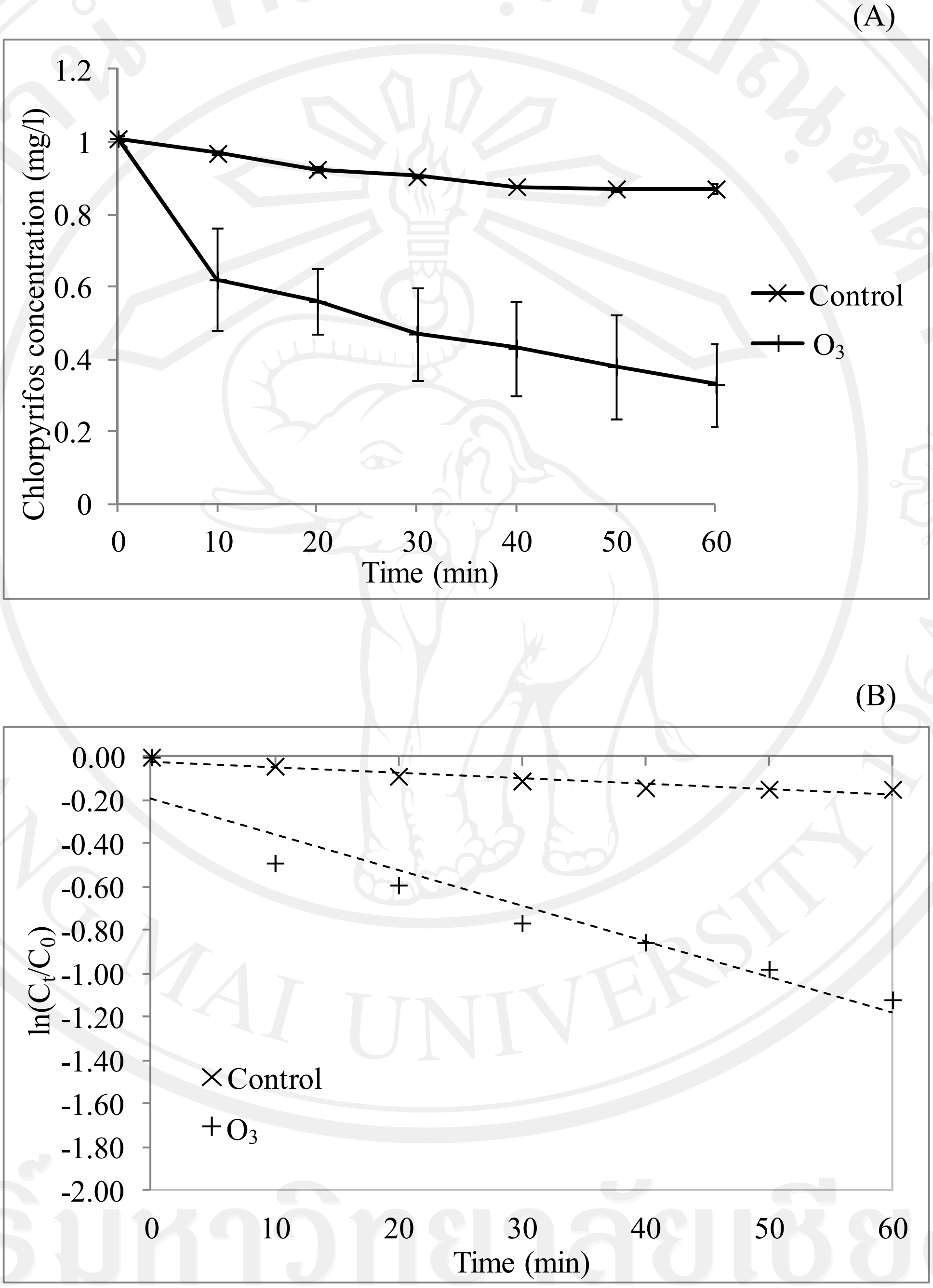


Figure 3.9 The changes of chlorpyrifos concentration (A) and the degradation kinetics of chlorpyrifos (B) under ozonation.

3) Degradation percentage of chlorpyrifos solution using combination of ultrasonication and ozonation

The concentration of standard chlorpyrifos, treated with ultrasonication and ozone applied in combination treatment, decreased with increasing exposure time. During the first 10 min of all treatments, chlorpyrifos degradation was significantly increased, compared with the control. The 1 MHz and ozone combination, applied for 60 min, was the most effective due to the increase of chlorpyrifos degradation up to 83.77 %, compared with the control (Figure 3.10 and Appendix; Table 1), in correlation to the decrease of chlorpyrifos concentration (Figure 3.11A and Appendix; Table 2). Therefore, the chlorpyrifos reduction achieved in conjunction with ultrasonic irradiation was twice as fast as that accomplished by only ozone. The synergistic effect of the combination increased chlorpyrifos removal. The highest rate of chlorpyrifos reduction was obtained when the ultrasonic together with ozone treatment was applied simultaneously. Similarly, Ince and Tezcanli (2001) observed that the ultrasonic combined ozone treatment achieved results twice as quickly as with ozone alone, while no significant removal was observed in the control experiments with ultrasound alone. It is possible that oxidation plays a similar role in ozonolysis, sonolysis and some free-radical pathways, present during ozonation, are similar to those of sonolysis (Schramm and Hua, 2001). The observed synergy was attributed to enhanced ozone diffusion (to promote more rapid electrophilic and radical reaction rates) and enhanced hydroxyl radical formation of some intermediate products of oxidation (Tezcanli and Ince, 2004). The combination produced a myriad of tiny air bubbles by the cavitation effect of ultrasound, allowing most ozone to enter the liquid phase or react on the gas or liquid interface. The physic-chemical properties of the combination enhanced the rate of direct reactions and hydroxyl radical's oxidation of intermediate products (Cui *et al*., 2011). In addition, rapid degradation of organic contaminants, using ozone and ultrasonic irradiation (20 kHz), resulted in an increase of hydroxyl radicals (Weavers *et al*., 1998).

The plots of $\ln(C_t/C_0)$ versus time shown in Figure 3.11B indicated that the *k* values of chlorpyrifos degradation have a tendency to increase when the ozonation combined with increasing of ultrasonic frequency. In addition, the *k* value at 1 MHz combined with ozonation (2.48×10^{-2} min^{-1}) was more than almost 10 folds of the control (0.25×10^{-2} min^{-1}) (Table 3.1). It could be suggested by Xiong *et al*. (2011) the kinetic rate constants of the reaction under ozone involved processes with ultrasonic at 20 kHz (8.4×10^{-3} min^{-1}) higher than with sole ultrasound (3.2×10^{-3} min^{-1}) or ozone (6.7×10^{-3} min^{-1}). The ozone decomposition experiments showed that rate constant of ozone self-decomposition in water with ultrasonic radiation was enhanced by ultrasonic radiation and increased linearly with the increase of ultrasonic power (Zhang *et al*., 2007).

As clearly shown in ultrasonication, ozonation and the combination, the longer the treatments, the greater is the reduction of chlorpyrifos concentration. Further study is needed to explain the exact oxidative degradation and detoxification of treated chlorpyrifos with ultrasonic and ozone treatment.

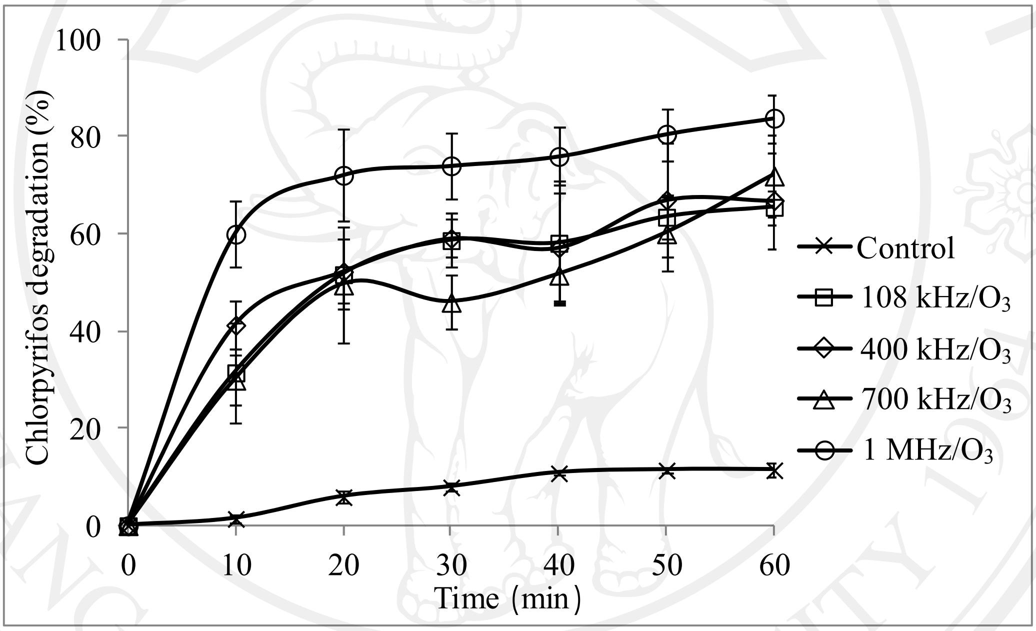


Figure 3.10 Degradation percentage of standard chlorpyrifos (1 mg/l) by ultrasonication and ozonation.

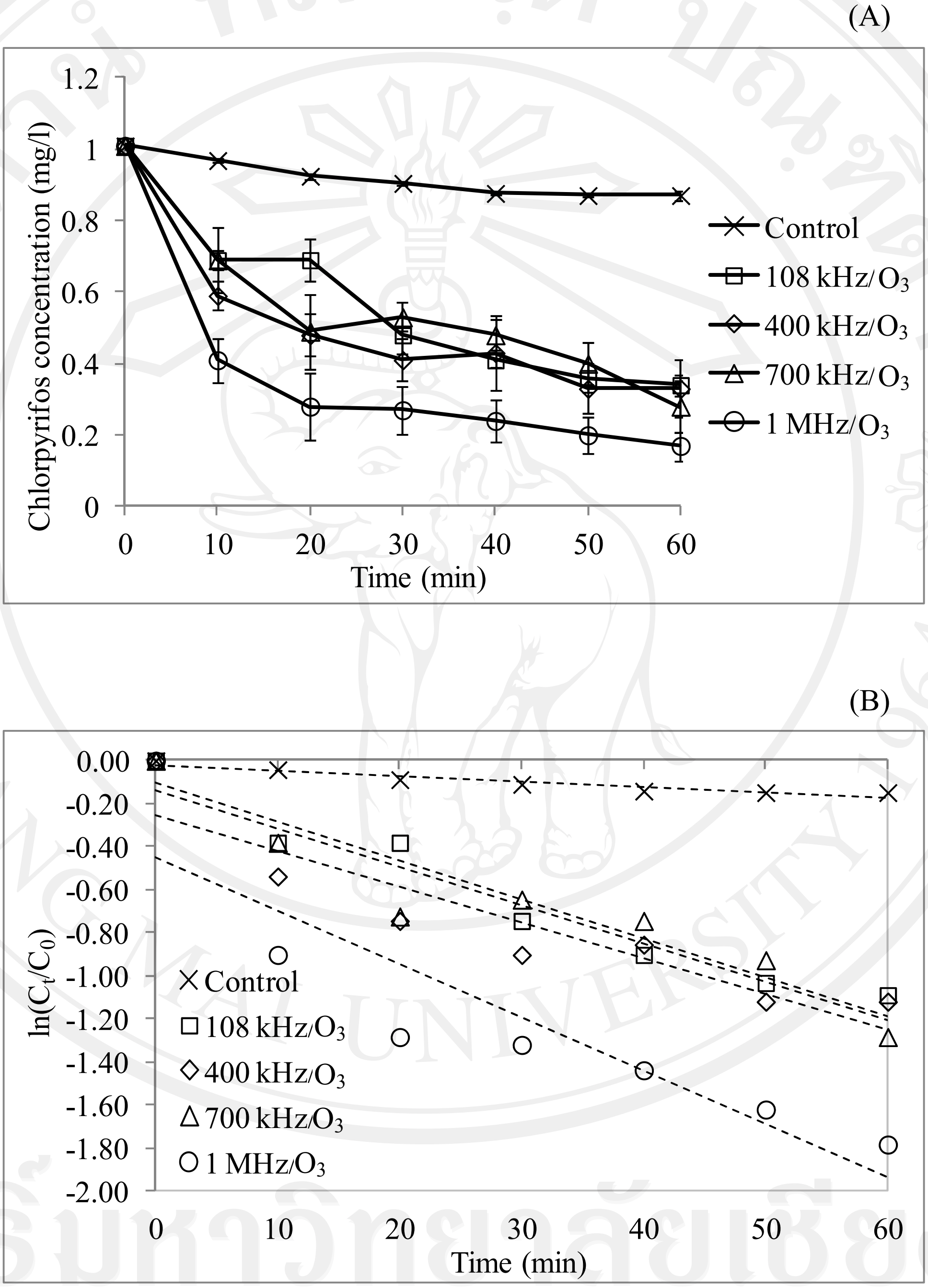


Figure 3.11 The changes of chlorpyrifos concentration (A) and the degradation kinetics of chlorpyrifos (B) under ultrasonication combined with ozonation.

Table 3.1 The first-order kinetic model fitted to the chlorpyrifos degradation.

Treatment	Regression equation	R^2	k (min^{-1})
Control	$\ln(C_t/C_0) = - 0.0025t - 0.0205$	0.9061	0.25×10^{-2}
108 kHz	$\ln(C_t/C_0) = - 0.0147t - 0.0745$	0.9704	1.47×10^{-2}
400 kHz	$\ln(C_t/C_0) = - 0.0135t - 0.0457$	0.9776	1.35×10^{-2}
700 kHz	$\ln(C_t/C_0) = - 0.0148t - 0.0075$	0.9441	1.48×10^{-2}
1 MHz	$\ln(C_t/C_0) = - 0.0220t - 0.0742$	0.9845	2.20×10^{-2}
O_3	$\ln(C_t/C_0) = - 0.0164t - 0.1919$	0.9150	1.64×10^{-2}
108 kHz/O_3	$\ln(C_t/C_0) = - 0.0182t - 0.1017$	0.9460	1.82×10^{-2}
400 kHz/O_3	$\ln(C_t/C_0) = - 0.0165t - 0.2576$	0.8377	1.65×10^{-2}
700 kHz/O_3	$\ln(C_t/C_0) = - 0.0177t - 0.1403$	0.8941	1.77×10^{-2}
1 MHz/O_3	$\ln(C_t/C_0) = - 0.0248t - 0.4486$	0.8102	2.48×10^{-2}

3.3.2 Oxidative degradation of treated chlorpyrifos solution by ultrasonication, ozonation and the combination

The oxidative degradation products of treated chlorpyrifos by ultrasonic and ozone treatment were determined via temperature, pH, ORP, chloride, nitrate, sulphate and phosphate concentrations of chlorpyrifos solution and by-products. The anions concentrations were determined by IC from the treated chlorpyrifos solution after using ultrasonic and ozone treatment.

1) Temperature, pH and ORP changes of standard chlorpyrifos solution after using ultrasonication and ozonation

1.1) Temperature of standard chlorpyrifos solution after using ultrasonication and ozonation

Chlorpyrifos solution after treated with ultrasonication at various frequencies 108, 400, 700 kHz and 1 MHz, showed that in all treatments the temperature was slightly increased in the solution with contact time (Figure 3.12). The increased in temperature at frequency 1 MHz was significantly higher compared with 400 and 700 kHz. No significant different temperature in ozone treatment was observed, whereas a slight increase in temperature of the chlorpyrifos solution was obtained when the combined treatment was applied (Appendix; Table 3). The increase of temperatures generated by the collapsing bubble in chlorpyrifos solution (from hot spot under ultrasonication) probably increases the chlorpyrifos degradation rate. Thus efficiency of chlorpyrifos degradation increases as the temperature increases. Similar, Zhang *et al*. (2011), studied ultrasonic irradiation when increasing temperature from 15 to 25 °C, the degradation of chlorpyrifos and diazinon was considerably improved. He *et al*. (2007) investigated ultrasonication in combination with ozone treatment and found that efficiency of ρ-aminophenol removal increased as the temperature increased. It might be that the rise in solution temperature could reduce the intensity of bubble collapse.

1.2) pH of standard chlorpyrifos solution after using ultrasonication and ozonation

The standard chlorpyrifos solutions were treated with ultrasonication, ozonation and the combination for this investigation. The results showed that pH value of all the treatments decreased when increasing contact time. The pH value of the ultrasonication (1 MHz) and ozone combination for 60 min was rapidly decreased from 7.46 to 4.49 (Figure 3.13 and Appendix; Table 4). The pH-drop of chlorpyrifos solution might be attributed to the chlopyrifos structure decomposed or/and released some acids into solution during oxidation under ultrasonication, ozonation and the combined treatments. Naddeo *et al*. (2009) found that the pH of diclofenac in water was reduced from a nearly neutral to acid values (pH 3.00 - 4.00) after sonolysis and ozonation. Hayashi *et al*. (2009) observed ultrasonic irradiation at 200 kHz in water (pH 3) was positively increased hexachlorobenzene removal ratio, compared to pH 5.6. Concordantly, Park *et al*. (2000), it reported that the rate of degradation of polycyclic aromatic hydrocarbons increased with decreasing pH, because $^{\bullet}OH$ had a greater one-electron oxidation potential in more acidic solutions. According to Devi *et al*. (2009) degradation of chlorpyrifos under UV/solar light showed that the substituent chloro (-Cl) and (-OH) groups may be eliminated as HCl and H_2O. Coelho *et al*. (2009) studied intermediates of diclofenac during degradation by ozonation. They found that ozonation was an efficient treatment for a decrease of pH during diclofenac degradation. Additionally, sonochemical degradation of triphenylphosphine oxide in water was increased. A decrease in solution pH indicates the formation of acidic compounds presumably due to occurrence of hydroxyl radical-mediate oxidation reactions in the liquid (Emery *et al*., 2005). In the case of humic acid, the pH decreased from pH 7.8 (the initial pH) and was equilibrated to 6, 4 and 4 by ultrasonication alone or ozone alone, and their combination, respectively (Cui *et al*., 2011). In the case of this experiment it showed the synergistic effect of ultrasonication and ozonation to reduce pH of the solution. Similarly, the pH-drop of sludge from 6.8 to 5.21 might be attributed to the increase of volatile fatty acid from 61.35 to 111.96 mg/l during the ultrasound combined with ozone treatment process (Xu *et al*., 2010). Under the effect of O_3/ultrasonic, nitro and nitroso are formed after -N=N- bond is broken. Benzene ring is broken and oxidized into carboxylic acid.

Sulfur-group breaks into sulfuric acid. So, pH value of the arsenazo I solution continuously drops down to 3.2 (Wenrong and Haiyan, 2002). Therefore, the decreasing pH may release some acid from the chlorpyrifos solution after the oxidation, which could be confirmed by the result by GC-MS in next experiment.

1.3) ORP of standard chlorpyrifos solution after using ultrasonication and ozonation

All treatments have increased ORP values after chlorpyrifos solutions were treated up to 60 min. ORP values were significantly increased after chlorpyrifos solution were treated with ultrasonication at 1 MHz combined with ozone treatment, compared to other treatments throughout treatment time. Moreover, the first 10 min of the combination markedly increased ORP value (Figure 3.14). In the case of this experiment, the ORP values of treated chlorpyrifos were increased when ultrasonication time increasing (Appendix; Table 5). The increase ORP value may indicate that more $HO^{\bullet}$ radical was produced. Thus, ORP values might relate with the chlorpyrifos degradation. Yasman *et al*. (2004) suggested that sono-electrochemical fenton process for degradation of 2,4-dichlorophenoxyacetic acid and 2,4-dichlorophenol in an aqueous solution, that was related to the oxidative and reductive electrochemical processes and the reactions involved $HO^{\bullet}$ with enhanced efficiency.

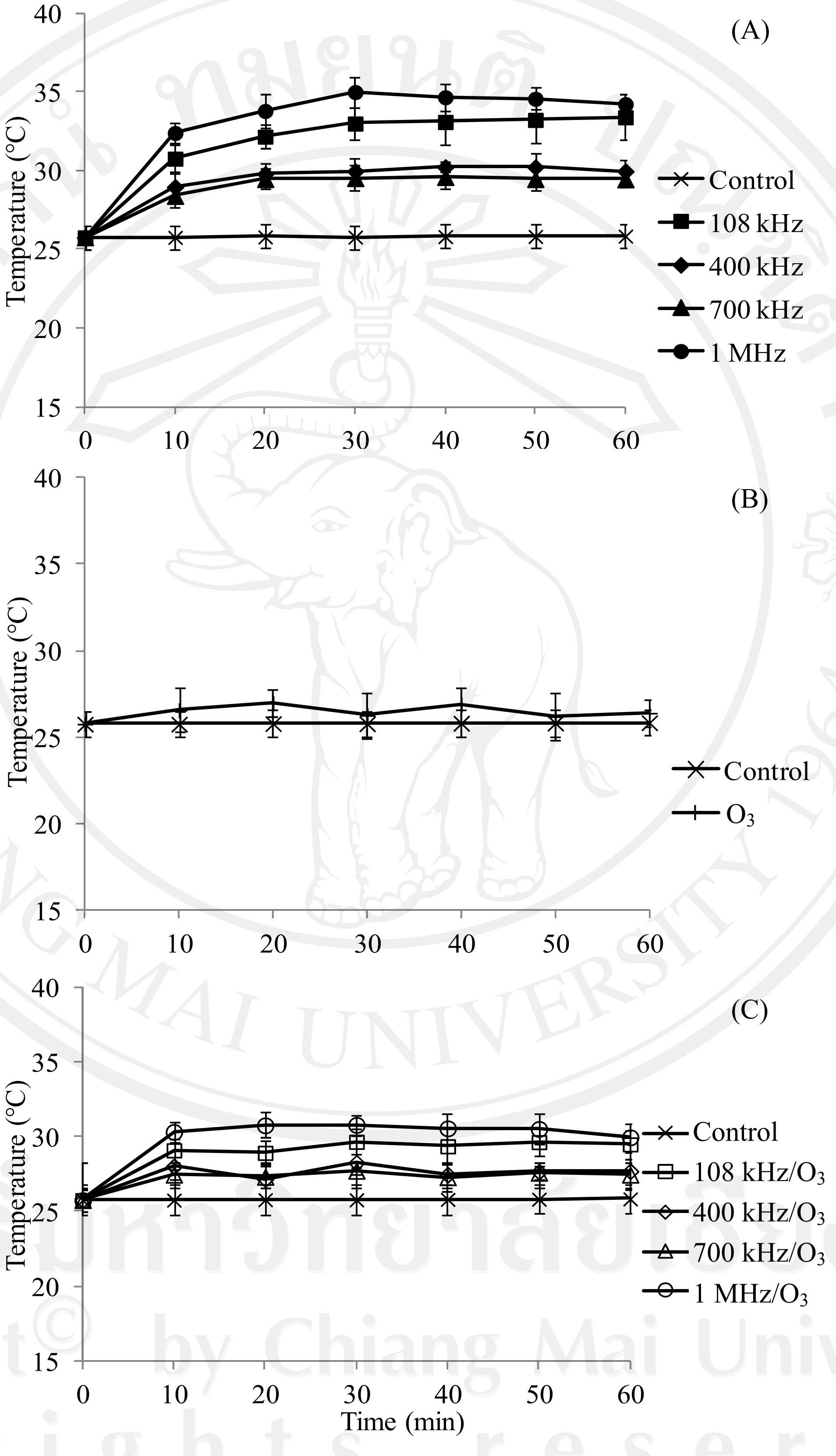


Figure 3.12 Temperature of chlorpyrifos solution after treated with ultrasonication (A), ozonation (B) and the combination treatments (C).

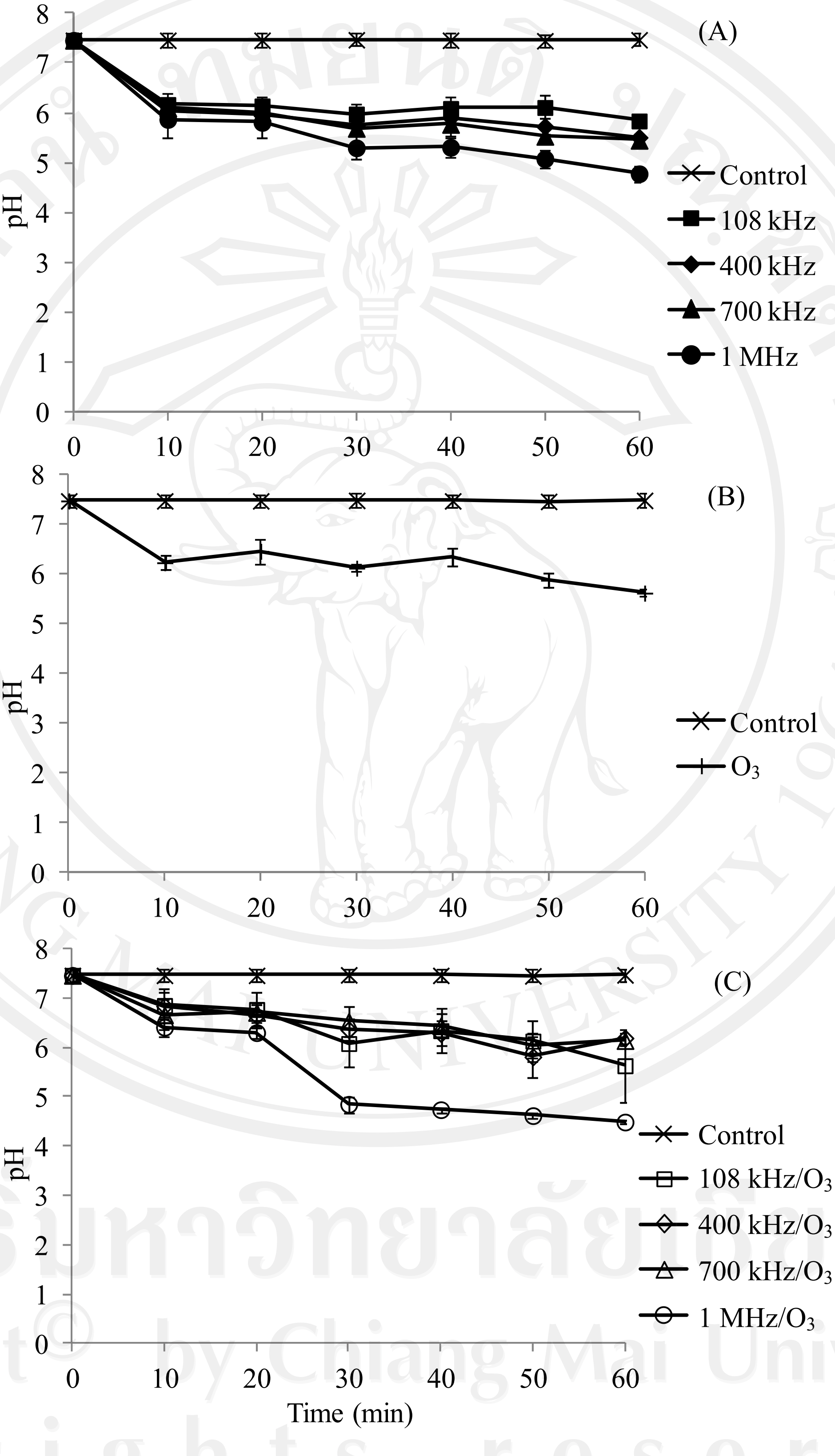


Figure 3.13 pH of chlorpyrifos solution after treated with ultrasonication (A), ozonation (B) and the combination treatments (C).

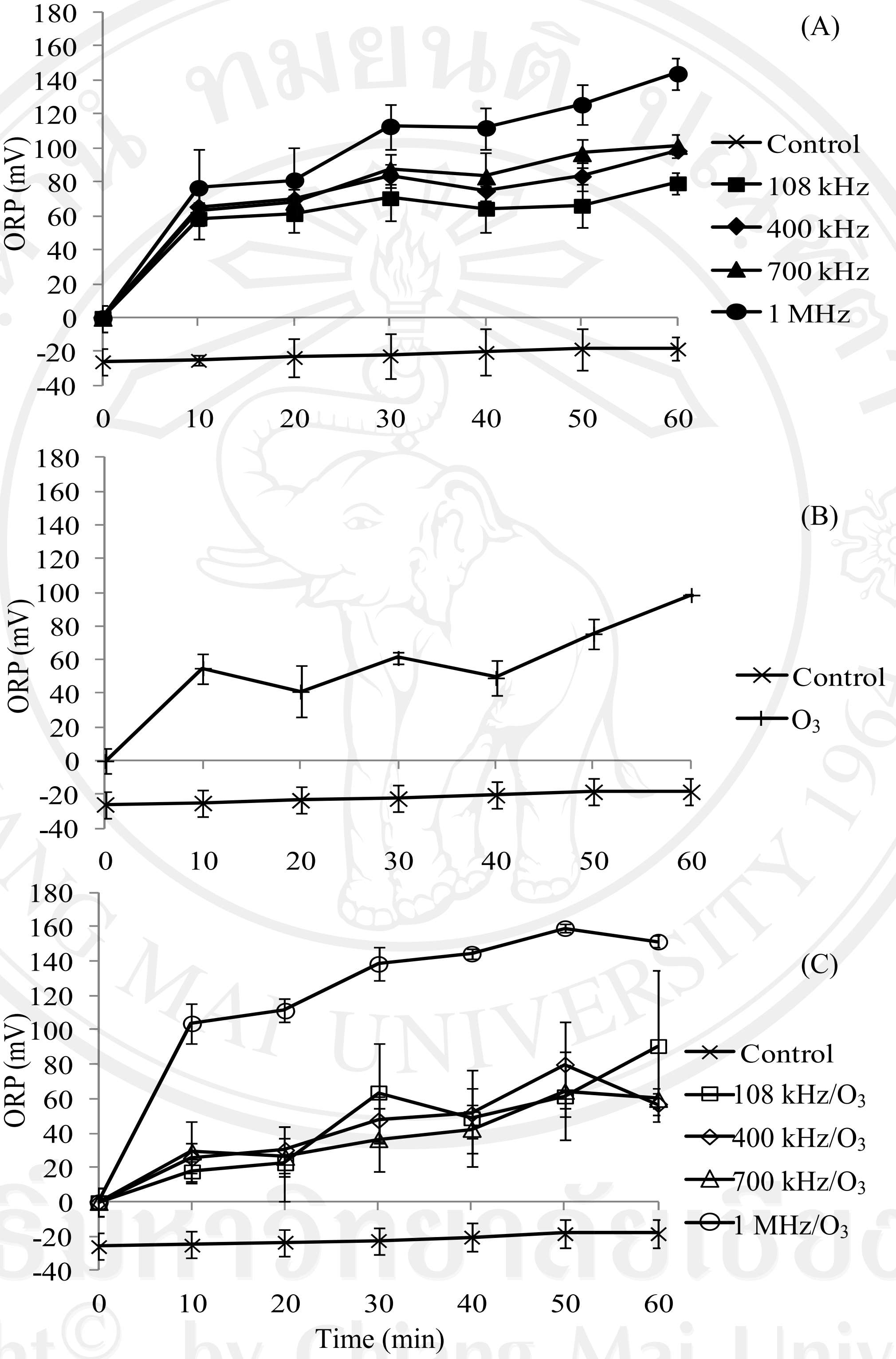


Figure 3.14 Oxidation-reduction potential (ORP) of chlorpyrifos solution after treated with ultrasonication (A), ozonation (B) and the combination treatments (C).

2) Anions concentration of standard chlorpyrifos solution after using ultrasonication and ozonation

Ultrasonication and ozonation on chlorpyrifos solution with anion concentrations were investigated. Phosphate ions were not detected in all the treated chlorpyrifos solution (data not shown). However, chlorpyrifos treated with the combined ultrasonication and ozonation resulted in significantly increased anion concentrations, compared with the control (untreated). Chlorpyrifos, treated with ultrasonication (1 MHz) combined with ozone treatment for 60 min had the highest chloride concentrations, compared with all other treatments. The ions reached a maximum concentration of 0.26 mg/l (Figure 3.15 and Appendix; Table 6). The combination treatment could be C-Cl bond scission and chloride ions releasing from chlorpyrifos structure, which the decomposition product might be HCl. According to the chlorpyrifos degradation was related to decrease pH of treated chlorpyrifos solution. According to Devi *et al.* (2009), it was shown that the degradation of chlorpyrifos under photocatalysis reduced substituent -Cl and -OH groups which may be eliminated as HCl and H_2O. Muhamad (2010) reported that the chloride ions liberated after chlorpyrifos degradation under different types of radiation source and in dark were determined quantitatively. Similarly the chloride ion of dichlorvos rapidly accumulated for the O_2 and Ar/O_2 sparge gases, was nearly reaching the maximum theoretical concentration of 1.0×10^{-3} M after 1 h of sonication at 161 W and 500 kHz (Schramm and Hua, 2001). Coelho *et al*. (2009) found that ozonation was an efficient treatment for diclofenac degradation. In addition chlorine ion and nitrogen as ammonia were released into the aqueous solution during diclofenac degradation. Therefore, it was necessary for determination of the treated chlorpyrifos decomposition. The nitrate and sulphate concentrations were significantly increased after treatment of the chlorpyrifos solution with 1 MHz/O_3 combination for 60 min (Figures 3.16 - 3.17 and Appendix; Tables 7 - 8). Therefore, anions released indicate the chlorpyrifos decomposition. It was suggested by Yao *et al.* (2010) that rapid increased in the first 45 min and then stabilized of sulphate concentration was observed during parathion degradation under ultrasonic irradiation. The concentration of nitrate increased steadily and reached a concentration after 120 min. The formation of nitrate was much slower than the other anions, possibly because of the sequential oxidation of nitrogen-containing species. Similarly, the sulfur group of diazinon was released from the cyclic structure early during the decomposition reaction by the direct oxidation of ozone molecules (Ku *et al*., 1998).

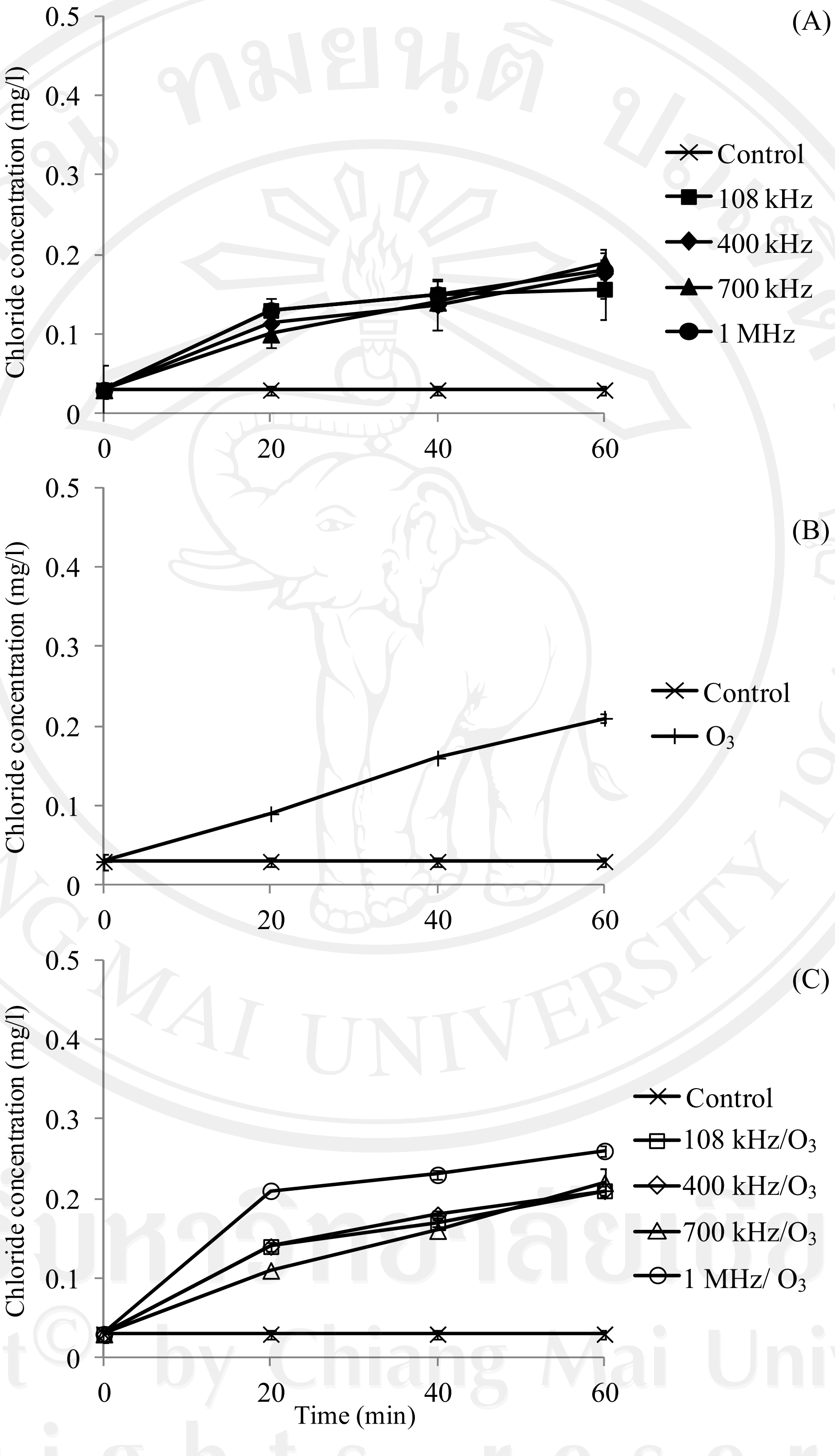


Figure 3.15 Chloride concentration of chlorpyrifos solution after treated with ultrasonication (A), ozonation (B) and the combination treatments (C).

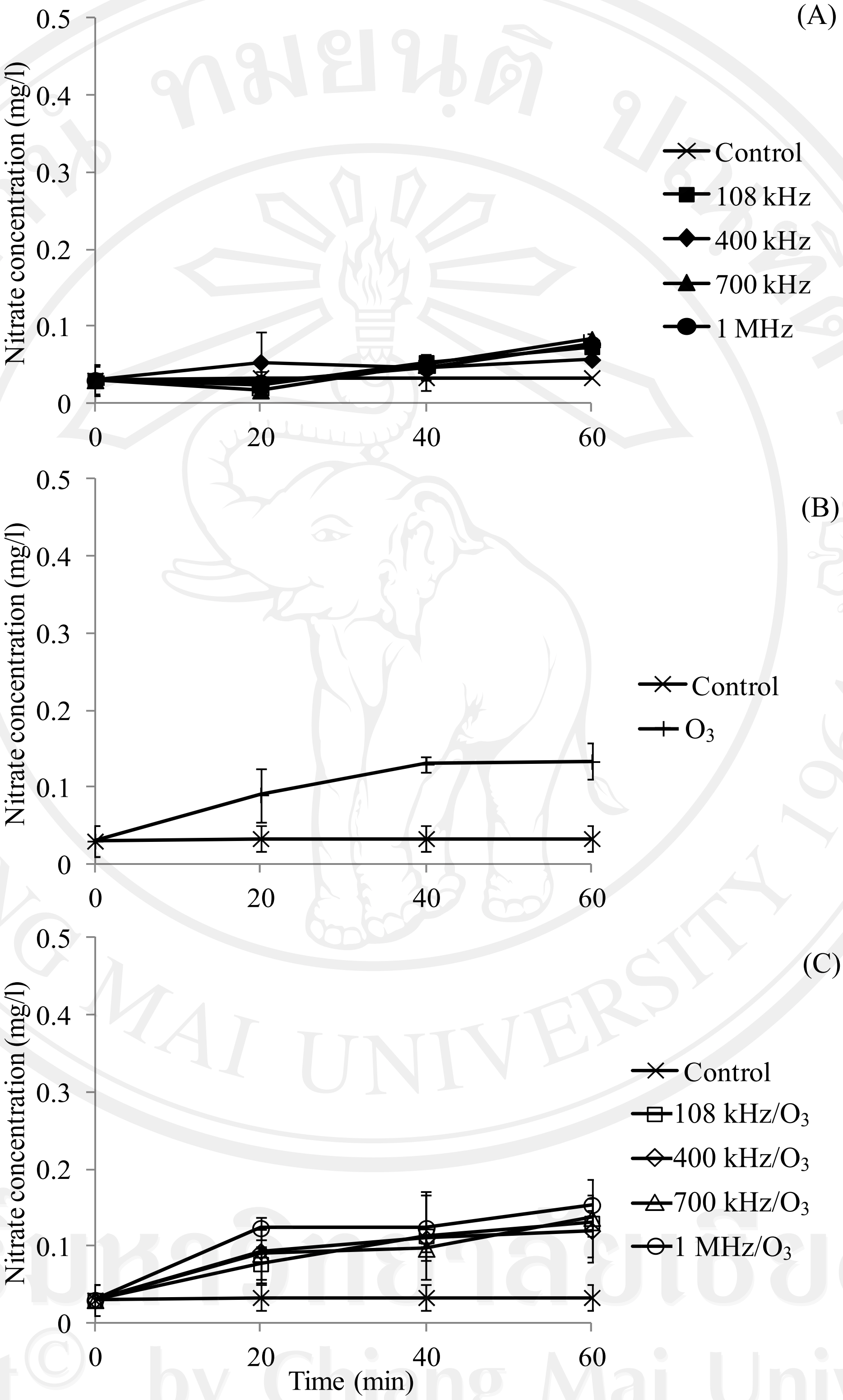


Figure 3.16 Nitrate concentration of chlorpyrifos solution after treated with ultrasonication (A), ozonation (B) and the combination treatments (C).

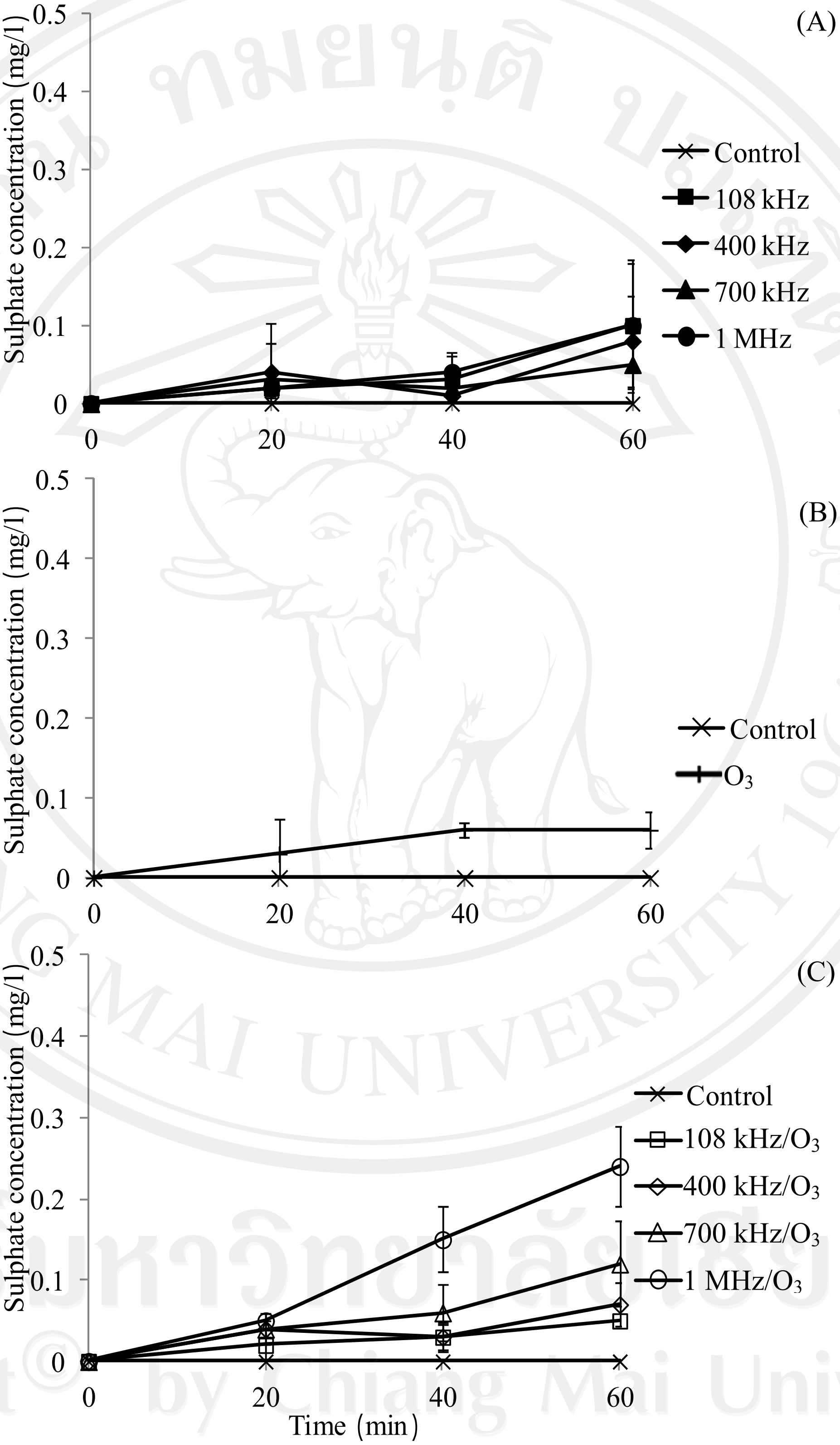


Figure 3.17 Sulphate concentration of chlorpyrifos solution after treated with ultrasonication (A), ozonation (B) and the combination treatments (C).

3) Chlorpyrifos solution after using ultrasonication and ozonation

The treated standard chlorpyrifos of all the treatments for 60 min were analyzed with GC-MS. The result showed GC-MS peak area of chlorpyrifos after treated with the ultrasonication combined with ozonation was positively reduced chlopyrifos concentration, compared to other treatments. This result was similarly to the resulted of the last experiment (Figure 3.18). The results of analyzed mass spectra of the chlorpyrifos were confirmed by the NIST Mass Spectral Library. All treatments resulted in similar main fragment ions. However, chlorpyrifos-oxon could not be determined at *m/z* 335. This formation was due to the result of hydroxyl radicals attack at the –P=S bond converting it to –P=O (oxon derivative), a primary characteristic product, formed during the oxidation of organophosphorous compounds. Moreover, the result showed that the combination treatment produced the main fragment ions at *m/z* 351, 314, 286, 258, 197 and 97 (Figure 3.19). The chlorpyrifos degradation pathway might be described below.

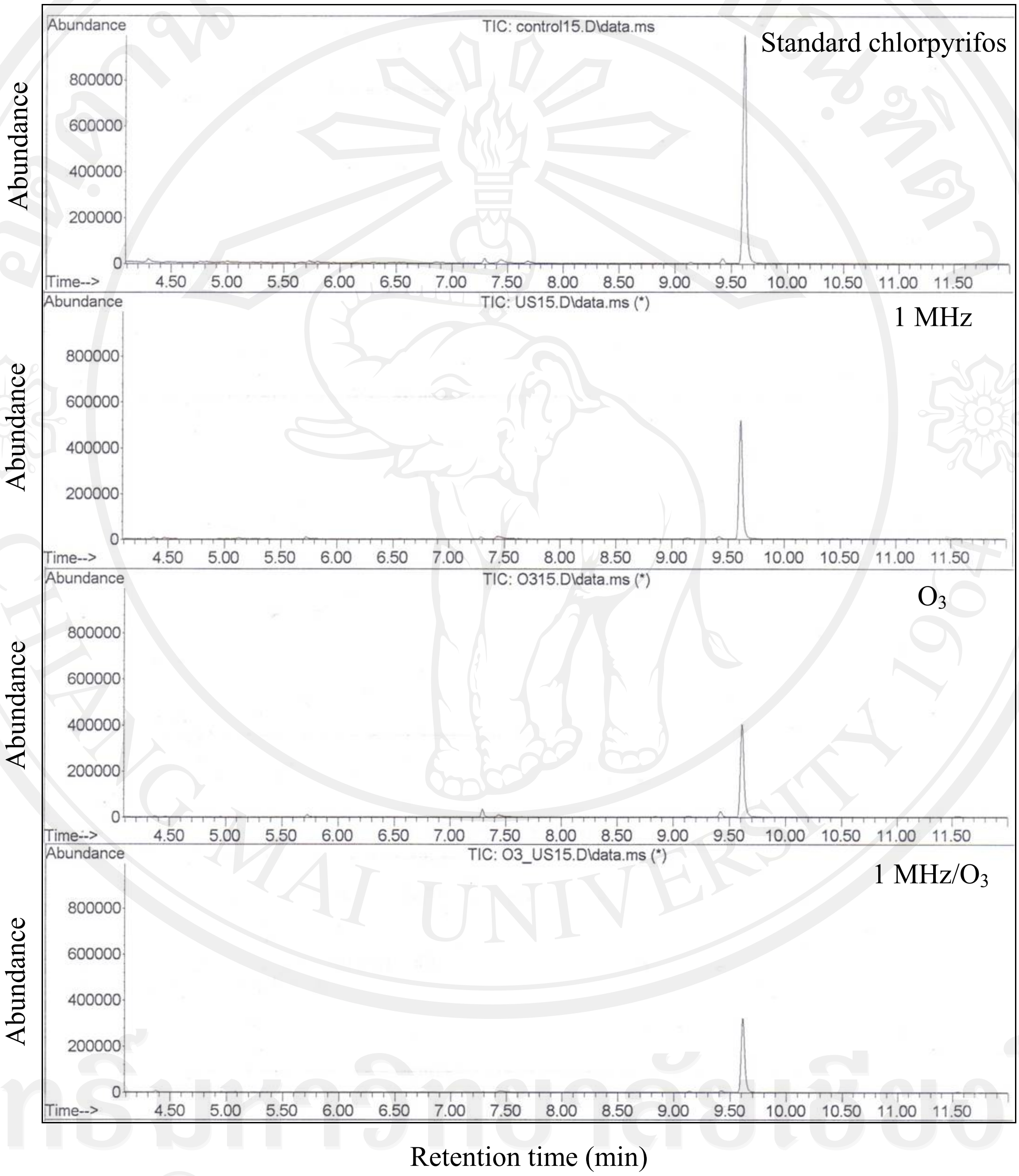


Figure 3.18 GC-MS chromatograms of chlorpyrifos after treated by ultrasonication (1 MHz), ozonation (O_3) and the combination (1 MHz/O_3) for 60 min.

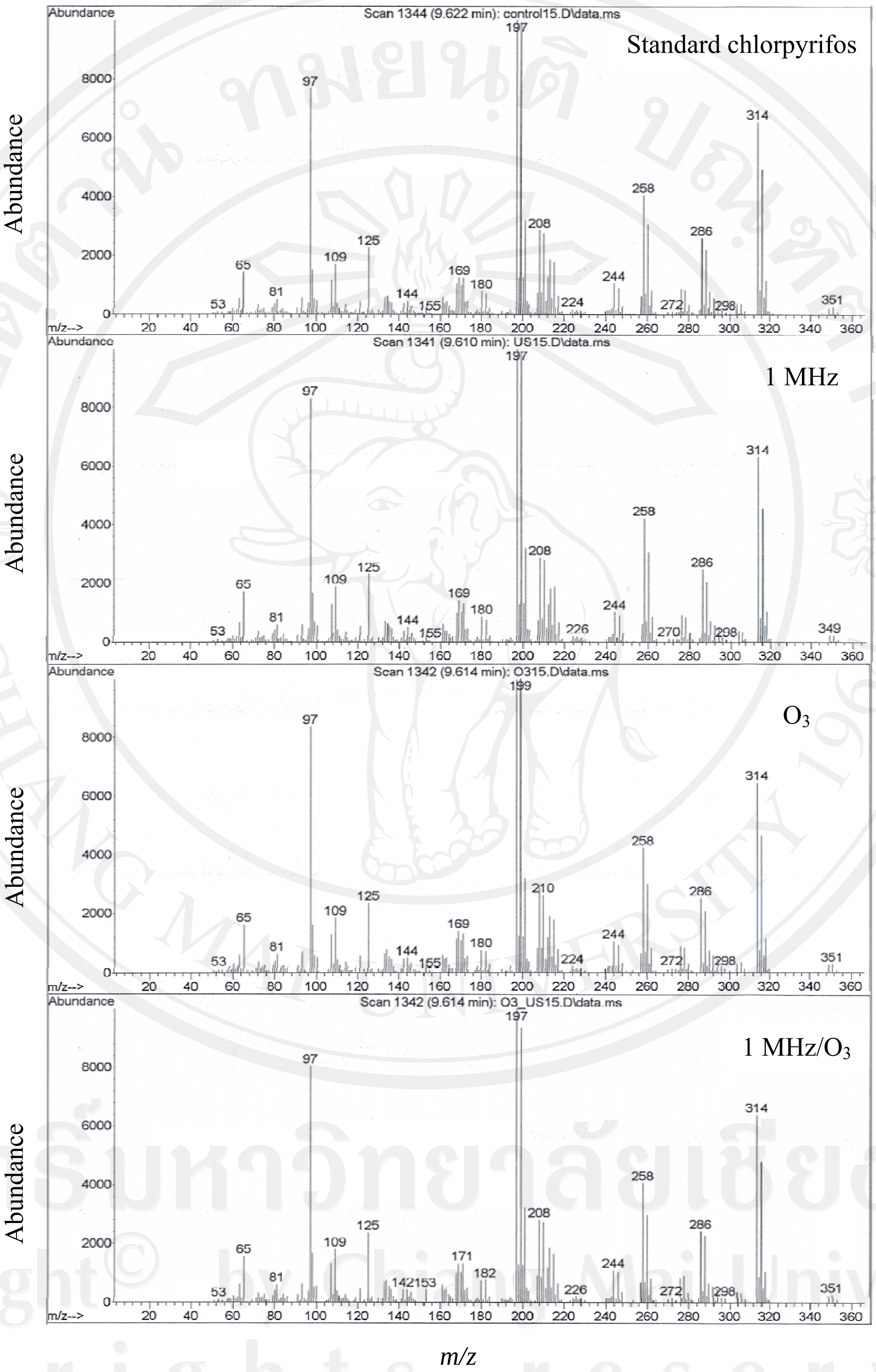
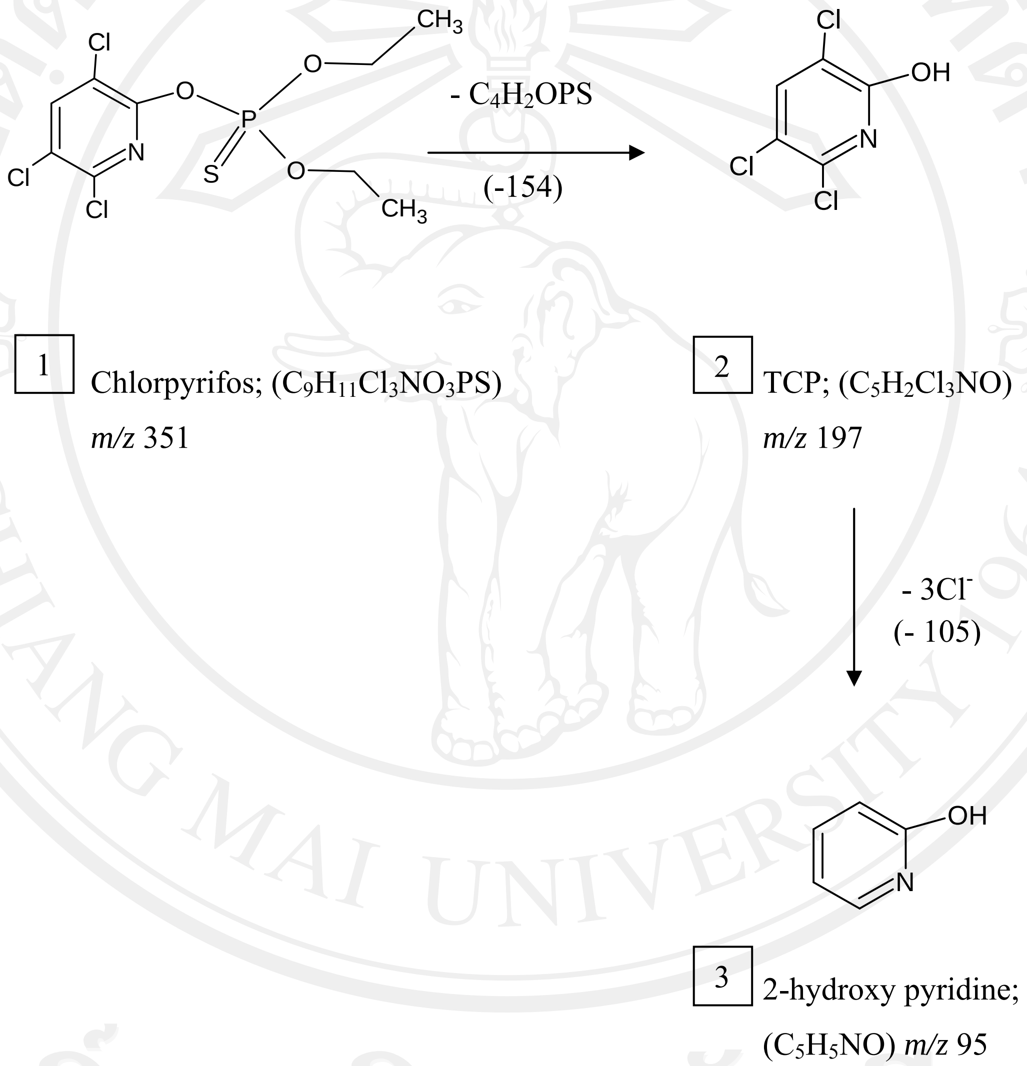


Figure 3.19 GC-MS spectra of chlorpyrifos after treated by ultrasonication (1 MHz), ozonation (O_3) and the combination (1 MHz/O_3) for 60 min.

The chlorpyrifos decomposition by ultrasonication and ozonation possibly can be described from the fragment ions of mass spectra. It could be main 2 decomposition pathways.

1) Figure 3.20 showed the chlorpyrifos degradation. The combination of ultrasonication and ozonation treatments were positively oxidized the side chain (diethylthiophosphate; *m/z* 154) of the chlorpyrifos structure (*m/z* 351) (Figure 3.20, No. 1). Therefore, the side-chains of the structure were lost, and then the decomposition product was substituted with the OH-group. It might facilitate the formation of *m/z* 197 as TCP (3,5,6-trichloro-2-pyridinol, $C_5H_2Cl_3NO$) (Figure 3.20, No. 2) which lower toxicity than chlorpyrifos. Each mass spectrum was normalized to its most intense fragment ion at *m/z* 197, possibly formation of TCP obtained by the loss of the side chain (Mori *et al.*, 2006). Then, the structure might be loss of three chloride ions ($3Cl^-$) from TCP to be 2-hydroxy pyridine (*m/z* 95) (Figure 3.20, No. 3).



1 Chlorpyrifos; ($C_9H_{11}Cl_3NO_3PS$) *m/z* 351

2 TCP; ($C_5H_2Cl_3NO$) *m/z* 197

3 2-hydroxy pyridine; (C_5H_5NO) *m/z* 95

Figure 3.20 Chlorpyrifos degradation pathway 1 by ultrasonication in combination with ozonation.

2) Figure 3.21 describes the chlorpyrifos degradation after ultrasonication and ozonation. The fragment ion at *m/z* 351 should be from molecular ions of chlorpyrifos (Figure 3.20, No. 1). The fragment ion at *m/z* 314 was the result of a lost ^{35}Cl or ^{37}Cl atom from the chlorpyrifos molecular. It might be HCl (*m/z* 36), therefore the *m/z* 314 might be *O*-(3,5-dichloropyridin-2-yl)diethyl phosphothioate (Figure 3.20, No. 2). It related to the results of pH and chloride concentration after ultrasonication and ozonation. Devi *et al*. (2009) reported that intermediates might react with three hydrogen radicals, eliminating all the three chloride ions (Cl^-) groups as HCl, leading to the formation of other intermediates. Base on the mass spectra results, at *m/z* 286 might be due to the loss of ethylene (C_2H_4 *m/z* 28), which led to the formation of *O*-(3,5-dichloropyridin-2-yl)*O*-ethylhydrogen phosphothioate (Figure 3.20, No. 3). Therefore ethylene was released and caused the *m/z* changed from 286 to 258 (*O*-(3,5-dichloropyridin-2-yl)dihydrogen phosphothioate) (Figure 3.20, No. 4). Meng *et al*. (2010) found that the mass fragment at *m/z* 314 was assigned to the daughter ions of chlorpyrifos, after losing a Cl atom during oxidation process by ozone. In addition, the fragment ions at *m/z* 286 and 258 were the result of the loss of one and two ethylene groups (C_2H_4 *m/z* 28) from the fragment ion at *m/z* 314 resulted in the *m/z* 258 which might be *O*,*O*-ethyl-*O*-(3,5-dichloro-2-pyridil) phosphorothioate. The fragment ion at *m/z* 97 was due to the formation of 2-hydroxy pyridine because caused ultrasonication at 1 MHz in combination with ozonation might destroy the side chain of chlorpyrifos structure to be 2-hydroxy pyridine (*m/z* 95) (Figure 3.20, No. 5). This was suggested by Zhang *et al*. (2010) determination of the chlorpyrifos oxon after using ultrasonic treatment. They found that the fragment ion occurred due to the loss of one and two ethylene from the fragment ion. The fragment ion at *m/z* 97 was due to the formation of 2-hydroxy pyridine.

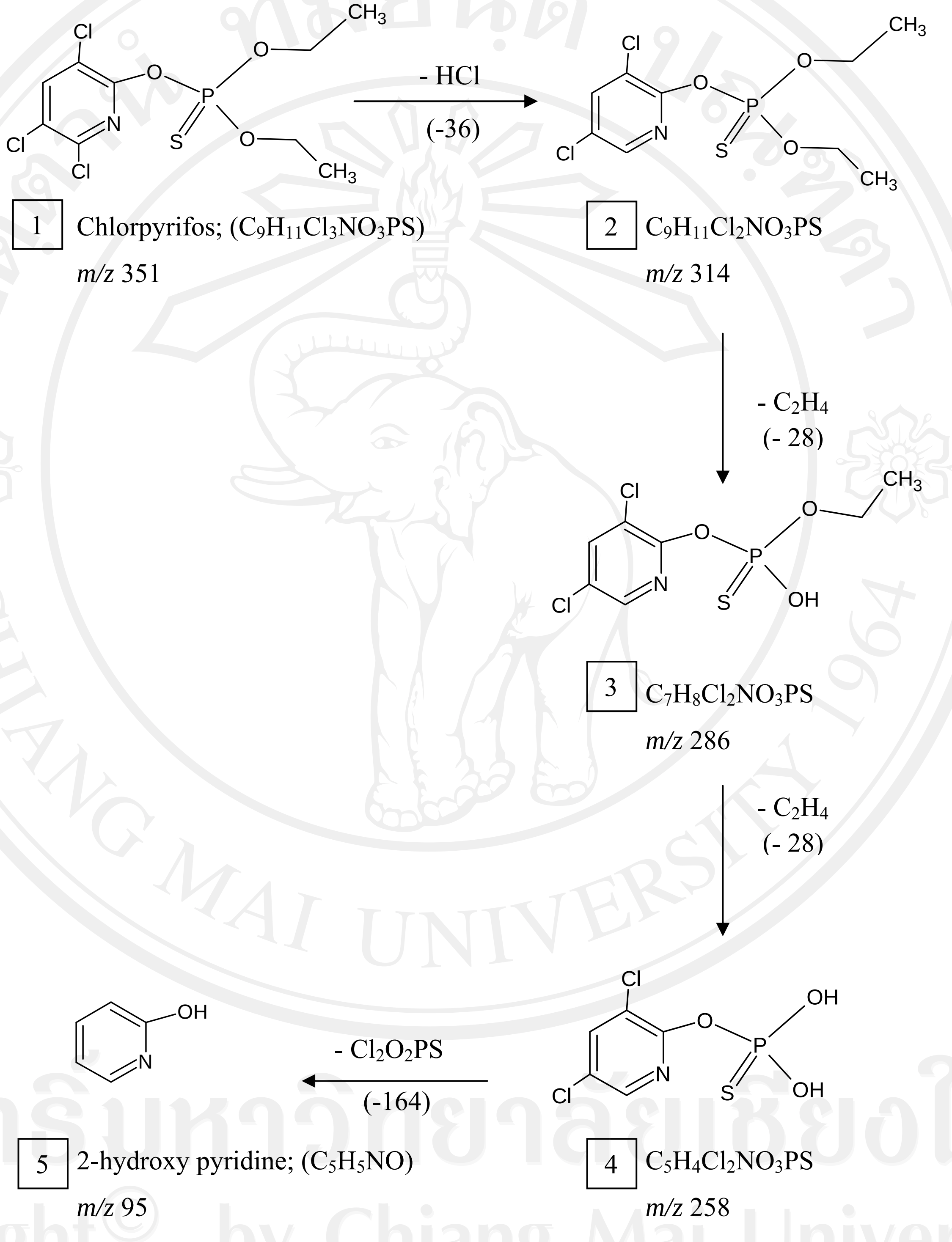


Figure 3.21 Chlorpyrifos degradation pathway 2 by ultrasonication in combination with ozonation.

3.4 Conclusion

Ultrasonication and ozonation enhanced the chlorpyrifos degradation. The degradation of chlorpyrifos increased with contact time and in this study. The highest ultrasonic frequency was demonstrated to be more effective for rapid degradation of chlorpyrifos than lower ultrasonic frequency. Moreover, the combination of ultrasonication (1 MHz) and ozone treatment is the most effective method for degrading chlorpyrifos. It may be concluded that treated chlorpyrifos solutions can increase temperature and ORP value of treated solution when contact time is increased. Whereas, only the 1 MHz/O_3 treatment, can significantly reduced the pH value of chlorpyrifos solution, related to Cl^- concentration and fragment ion from GC-MS. Further degradations of chlorpyrifos solution using ultrasonication in combination with ozonation associated with Cl^-, NO_3^- and SO_4^{2-} anions. The ions which released from the structure of chlorpyrifos during decomposition process might be related with the oxidation by ozone and indirect oxidation by ultrasound-generated $^\bullet OH$.