

Oxidative Degradation and Detoxification of Chlorpyrifos by Ultrasonic and Ozone Treatments

Sarunya Pengphol^{1,2}, Jammong Uthaibutra^{2,3}, Orn-anong Arquero^{2,4}, Nakao Nomura⁵ & Kanda Whangchai^{2,3}

¹ Postharvest Technology Research Institute, Graduate School, Chiang Mai University, Chiang Mai, Thailand

² Postharvest Technology Innovation Center, Commission on Higher Education, Bangkok, Thailand

³ Department of Biology, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand

⁴ Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand

⁵ Graduate School of Life and Environmental Science, University of Tsukuba, Tennodai, Tsukuba, Ibaraki, Japan

Correspondence: Kanda Whangchai, Department of Biology, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand. Tel: 66-5394-3346-60 Ext.1204. E-mail: kanda.w@cmu.ac.th

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Abstract

Chlorpyrifos is an organophosphate pesticide, widely used on fruit and vegetable crops. Here, we report on the oxidative degradation of standard chlorpyrifos by individual and combined effects of ultrasonic irradiation (US) and ozone (O₃). A standard chlorpyrifos solution (1 mg L⁻¹) was treated with 1 MHz US, O₃ and its combination (US/O₃) for 0, 10, 20, 30, 40, 50 and 60 min. Reduction of residual chlorpyrifos was determined by gas chromatography with flame photometric detection (GC-FPD) while ion chromatography (IC) was used to determine the concentration of anions as major degradation products. US/O₃ combined treatment had a synergistic effect in reducing chlorpyrifos concentrations, with the highest rate of degradation occurring within the first 10 min. Moreover, chloride, nitrate and sulphate anion concentrations obtained from chlorpyrifos treated with US/O₃ combination, were significantly higher, compared to those treated with ultrasonic irradiation or ozone alone. A sharp decrease in pH from 7.46 to 4.49 was also observed for the combined treatment. The degradation pathway of chlorpyrifos, after treatment, was confirmed by gas chromatography mass spectrometry (GC-MS). All treatments resulted in similar main fragment ions at m/z 351, 314, 286, 258, 197 and 97. The lethal concentration (LC₅₀), over a series (0-100) mg L⁻¹ of standard chlorpyrifos solutions, was estimated and compared to the treated chlorpyrifos. All the treatments directly detoxified chlorpyrifos with LC₅₀ values against brine shrimps (*Artemia salina* L.) of 10.21, 103.54 and 234.09 mg L⁻¹ for US, O₃ and US/O₃ treated chlorpyrifos solutions, respectively. The brine shrimp test showed highest toxicity in standard chlorpyrifos with an LC₅₀ value of 7.22 mg L⁻¹.

Keywords: chlorpyrifos, detoxification, oxidative degradation, ozone, ultrasonic

1. Introduction

Chlorpyrifos is one of the most widely used organophosphate pesticides in agriculture. The intrinsic toxic properties of pesticides allow them to control agricultural insect pests. The annual average global use of chlorpyrifos between 2002 and 2006 was 25 million kg active ingredient, of which 98.5% was used for agricultural purposes. Continuous and excessive use of chlorpyrifos has already led to widespread environmental contamination in many countries. This insecticide has been detected in marine, sediments, streams, sumps, sloughs, rivers, urban storm drains, freshwater lakes, groundwater, fog, rain and air (Whitacre, 2012). Nowadays, consumers and importers demand residue-free products. Being moderately toxic, there are significant concerns about the potential risks posed by chlorpyrifos to humans and the environment. It is therefore of significance to evaluate potential methods of reducing pesticide residue on water and food products.

Ultrasonic irradiation (US) technology effectively reduces a variety of organic and inorganic contaminants (Weavers et al., 1998) and its acoustic cavitations generate many hot spots, with locally high temperatures and pressures, that cause sonolysis of water molecules. Consequently, •H, •OH, •OOH radical species are formed, which directly destroy chemicals in aqueous solution. Wang et al. (2006) reported that methyl parathion is degraded by 40 kHz ultrasonic irradiation. Moreover, ultrasonic irradiation at 640 kHz effectively and rapidly

degrades 2-methylisoborneol (MIB) and geosmin (GSM), with $\cdot\text{OH}$ scavengers playing a major role in chemical degradation (Song & O'Shea, 2007).

Use of ozone (O_3) is a promising method to reduce chlorpyrifos residues in fresh lychee fruits (Whangchai et al., 2011). In addition, Inan et al. (2007) found that after 60 min of ozone exposure, aflatoxin B_1 content is reduced in flaked and chopped red peppers (*Capsicum annuum*) by 80 and 93%, at a rate of 33 and 66 mg L^{-1} , respectively. Wu et al. (2007) demonstrated that using dissolved ozone (1.4 mg L^{-1}) for 60 min effectively reduces methyl-parathion, cypermethrin, parathion and diazinon in aqueous solution.

The combined process of ultrasonication and ozonation offers several advantages over the individual process. The main advantage is the increased mass transfer of ozone from the gas phase to the bulk solution to react with substrate by mechanical effects of ultrasound. Cavitation bubbles from ultrasonication likewise can more readily induce O_3 decomposition under mild conditions yielding molecular O_2 and triplet atomic oxygen, $\cdot\text{O}^3\text{P}$ (Pang et al., 2011). In the combined system, ultrasonication and ozonation were believed to enhance each other in the oxidation of organic pollutants. US/ O_3 combined process was employed to pretreat heterocyclic pesticide wastewater for increasing biodegradability and reducing biological toxicity (Xiong et al., 2011). Moreover, the combined operation effectively renders synergistic effect of ozone and ultrasonic radiation on degradation of chitosan enhancing the production of hydroxyl radical generated by the radiolysis of ozone in the presence of ultrasonic radiation (Yue et al., 2008). The purpose of the research, reported below, was to investigate the combined effects of ultrasonic irradiation on the degradation and detoxification of chlorpyrifos.

2. Materials and Methods

Reference standard chlorpyrifos was purchased from Sigma-Aldrich Laborchemikalien GmbH (Stenheim, Germany) with 99.9% purity. The chlorpyrifos structure is shown in Figure 1. Chlorpyrifos stock solution (1000 mg L^{-1}) was prepared by dissolving standard chlorpyrifos in 99.8% acetone. The solution was diluted with distilled water to the appropriate concentrations.

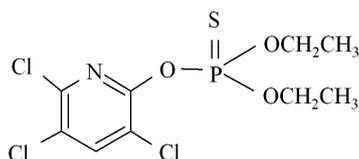


Figure 1. Structure of chlorpyrifos

The ultrasonic device with an input power of 3 W was supplied by Honda Electronics Company (Toyohashi, Aichi, Japan), equipped with a 1-MHz ultrasonic transducer. A 25-mL chlorpyrifos solution was subjected to sonication in a 10-cm diameter polyethylene cylinder reactor fitted with a polyethylene window facing the transducer.

Ozone gas, produced by an ozone generator (Ozonizer, Sky zone model S05AE, Thailand), with a flow rate of 25 mL min^{-1} , was bubbled into the chlorpyrifos solution directly. Dissolved ozone was determined by the indigo colorimetric method (Eaton et al., 2005).

2.1 Reduction of Standard Chlorpyrifos Solution by Ultrasonic and Ozone Treatments

A standard chlorpyrifos solution (25 mL , 1 mg L^{-1}) was prepared then poured inside the ultrasonic reactor and irradiated at 1 MHz. Ozone gas was bubbled through the chlorpyrifos solution at 200 mg L^{-1} . Standard solutions were exposed to individual and combined ultrasonic radiation and ozone treatment. Samples were taken out at 10-min intervals for 1 h. Three replicates of chlorpyrifos samples were analyzed. Chlorpyrifos concentrations were determined by gas chromatography. The analysis was performed in Agilent Technologies (Wilmington, DE) model 6890 gas chromatograph equipped with a flame photometric detector (GC-FPD). The GC column was a fused silica capillary column HP-5, 5% phenylmethylsiloxane, with the dimensions of $30 \text{ m} \times 0.32 \text{ mm}$ i.d. and a $0.25 \text{ }\mu\text{m}$ film thickness (Agilent Technologies). The temperature was programmed to increase at $10^\circ\text{C min}^{-1}$ from an initial 100°C to 200°C and then at 4°C min^{-1} increase to the final temperature of 220°C . A purified helium carrier gas was used at a flow rate of 3.6 mL min^{-1} . The detector temperature was at 250°C . Sample solution ($1.0 \text{ }\mu\text{L}$) was injected in splitless mode. Quantification of chlorpyrifos was performed, using a chlorpyrifos standard as reference.

2.2 Oxidative Degradation and Detoxification of Treated Chlorpyrifos by Ultrasonic and Ozone Treatments

The pH and concentrations of anions such as chloride, nitrate, sulphate and phosphate of ultrasonicated and ozonated chlorpyrifos solutions were determined. Ions, released from the decomposition of chlorpyrifos, were analyzed at 60 min by ion chromatography (IC). The amount of these ions corresponded to degradation of chlorpyrifos in this study. The analysis was performed, using an ion chromatograph equipped with a Metrosep A Supp 5 250/4.0. Eluent composition was A Supp5 eluent 3.2 mM Na₂CO₃ and 1.0 mM NaHCO₃. Samples were filtered by syringe filters of size 13 mm, 0.45 μm (Vertical®). A 10.0 μL sample was automatically injected in conductivity mode, and the quantification of chlorpyrifos was carried out using calibration curves with external standards at a flow rate of 0.70 mL min⁻¹, pressure 12.71 MP and 28 min recording time.

An Agilent Technologies (Wilmington, DE) model 6850 gas chromatograph equipped with a mass spectrometer (GC-MS) was used to analyze oxidative degradation of chlorpyrifos. The GC column was a fused silica capillary column HP-5MS, 5% phenylmethylsiloxane, with the dimensions of 30 m × 0.25 μm i.d. and a 250 μm film thickness (Agilent Technologies). The temperature was programmed to increase at 20°C min⁻¹ from an initial 100°C to 200°C and then at 4°C min⁻¹ increase to the final temperature of 220°C at 2 min holding time. A purified helium carrier gas was used at a constant flow. The MS was operated in electron impact (EI) ionization time-of-flight mode (TOF-MS) at an EM voltage of 1811.8 volts (injection volume 1.0 μL in splitless mode). The total ion current (TIC) 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).

Toxicity estimations were an important tool to test for the treatment efficiency. Diluted solutions with 0, 0.1, 10.0 and 100 mg L⁻¹ chlorpyrifos were prepared in laboratory marine water for US, O₃ and US/O₃ treatment. Five sets of experiment were done for each concentration per treatment at 25-30°C. Ten brine shrimps nauplii were placed in each vial containing 5 mL of treated chlorpyrifos solution. Mortality of nauplii was checked every 6 h eventually after 72 h of incubation. The percent mortality was determined 24 h after application. Probit analysis in SPSS version 17 was used for the calculation of LC₅₀ values.

2.3 Statistical Analysis

All experiments were evaluated with a regression procedure, using the SPSS version 17, while the differences among various treatments were performed using a one-way analysis of variance followed by Duncan's New Multiple Range test ($p < 0.05$).

3. Results and Discussions

3.1 Reduction of Standard Chlorpyrifos Solution by Ultrasonic and Ozone Treatments

The concentration (1 mg L⁻¹) of standard chlorpyrifos, treated with US, O₃ and US/O₃ in combination, decreased with increasing exposure time. During the first 10 min of treatments, chlorpyrifos concentration was significantly reduced, compared with the control. The US/O₃ combination treatment, applied simultaneously for 60 min, was the most effective at reducing chlorpyrifos concentration to 0.17 mg L⁻¹. Therefore, the US/O₃ combination decreased chlorpyrifos concentration, twice as much as that accomplished by O₃ alone (0.33 mg L⁻¹) (Figure 2). Plots of $\ln(C_t/C_0)$ versus contact time (t) are shown in Figure 3. First-order rate constants, k of chlorpyrifos under different treatments are summarized in Table 1. Rate constants varied from 0.30×10^{-2} to 3.51×10^{-2} min⁻¹ with US/O₃ combined treatment's k being the largest. A larger value of k signifies that chlorpyrifos degradation is more rapid in the combined treatment. Similarly, Ince & Tezcanli (2001) observed that the US/O₃ combined treatment achieved results twice as fast as with O₃ alone, while no significant removal was observed in the control experiments with US alone. It is possible that oxidation plays a similar role in both ozonolysis and sonolysis pathways, and some free-radical pathways present during ozonation, are similar to those of sonolysis (Schramm & Hua, 2001). The observed synergy was attributed to enhanced ozone diffusion (promotes more rapid electrophilic and radical reaction rates) and enhanced hydroxyl radical formation of some intermediate products of oxidation (Tezcanli & Ince, 2004). The US/O₃ 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 physicochemical properties of the US/O₃ 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 combined electrochemical cell under ultrasonic irradiation and ozone treatment with simultaneous ultrasonic irradiation led to virtually complete consumption of 1,3-dinitrobenzene, 2,4-dinitrotoluene within a short time (Abramov et al., 2007).

Table 1. The first-order kinetic model fitted to the chlorpyrifos degradation

Treatment	Regression equation	R ²	k (min ⁻¹)
Control	$\ln(C_t/C_0) = -0.0030t$	0.88	0.30×10^{-2}
US	$\ln(C_t/C_0) = -0.0237t$	0.96	2.37×10^{-2}
O ₃	$\ln(C_t/C_0) = -0.0209t$	0.99	2.09×10^{-2}
US/O ₃	$\ln(C_t/C_0) = -0.0351t$	0.80	3.51×10^{-2}

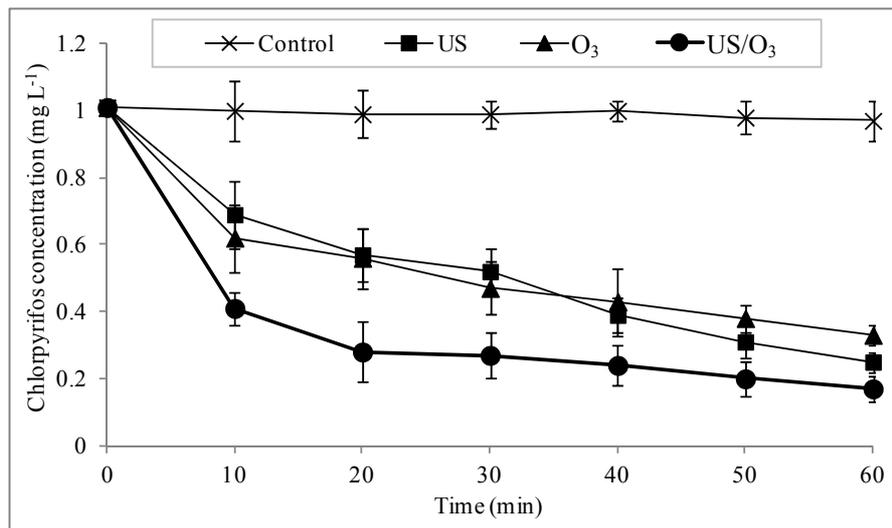
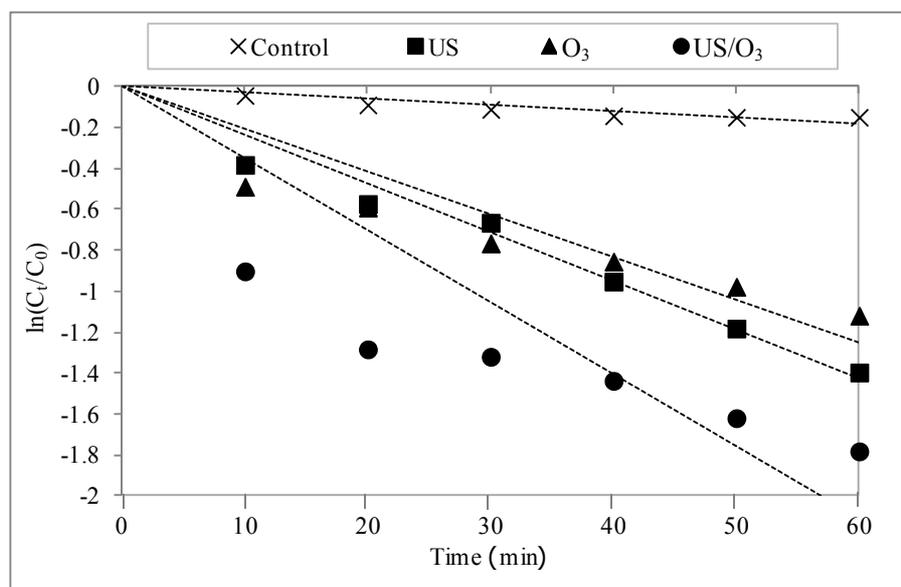
Figure 2. Chlorpyrifos concentrations after treatment with US and O₃ showed statistically significant degradation ($P < 0.05$). The values are expressed as mean \pm S.E. of measurements made on three replicates of treatment

Figure 3. The degradation kinetics of chlorpyrifos under ultrasonic combined with ozone treatments

As clearly shown in US, O₃ and US/O₃ 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.

3.2 Oxidative Degradation and Detoxification of Treated Chlorpyrifos by Ultrasonic and Ozone Treatments

Chlorpyrifos, treated with the US/O₃ combination, resulted in significantly increased anion concentrations, compared with the control. However, phosphate ions were not detected in any of the treated chlorpyrifos solution (data not shown). Chlorpyrifos, treated with US/O₃ for 60 min, significantly ($P > 0.05$) increased chloride concentration compared with all other treatments (Figure 4A). The nitrate (Figure 4B) and sulphate (Figure 4C) concentration were significantly ($P > 0.05$) increased after treatment of the chlorpyrifos solution with US/O₃ combination for 60 min. Therefore, anions released to indicate the chlorpyrifos decomposition. It may suggest that by Yao et al. (2010), observed during parathion degradation under ultrasonic irradiation, that sulphate concentration rapidly increased in the first 45 min and then stabilizes. The concentration of nitrate increased steadily and reached a concentration after 120 min. The formation of nitrate was much slower than for other anions, possibly because of the sequential oxidation of nitrogen-containing species.

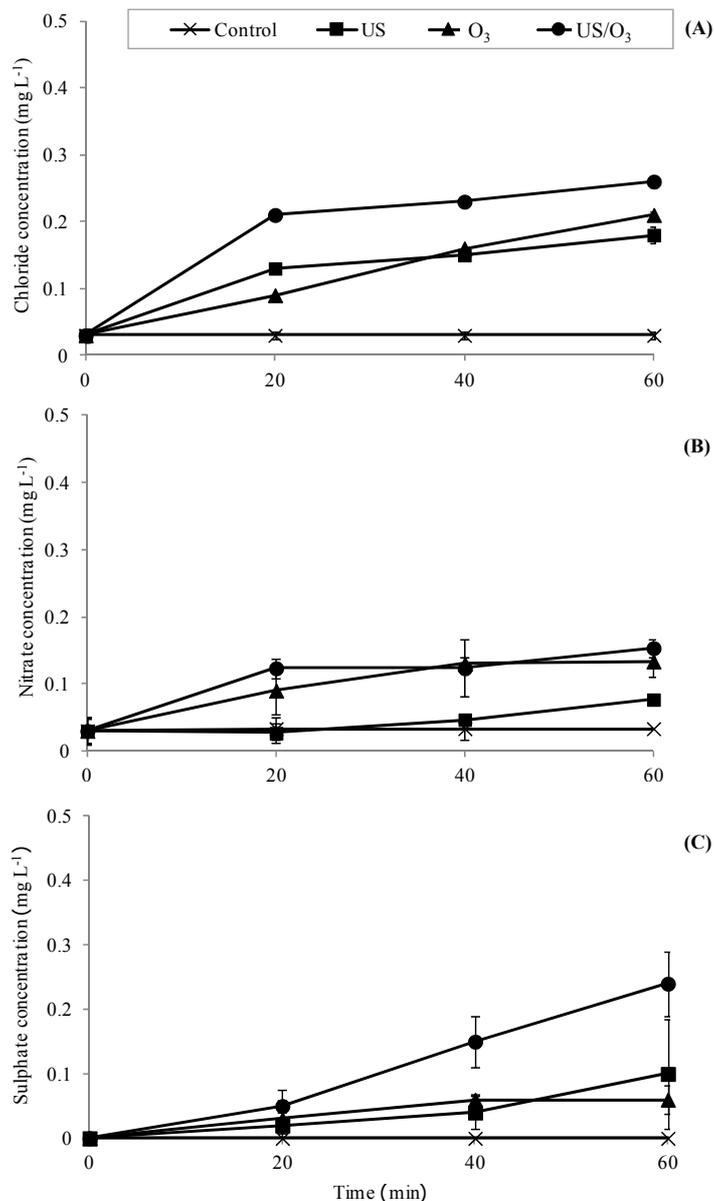


Figure 4. Chloride (A) nitrate (B) and sulphate (C) concentrations in a standard chlorpyrifos solution after application US and O₃ treatments were significantly different according to the Duncan's New Multiple Range test ($P < 0.05$). The values represent mean \pm S.E. of measurements made on three replicates of treatment pH decreased in solutions, treated with US, O₃ and combination of US/O₃. pH decreased with increasing contact time. Notably, the pH of the US/O₃ combination for 60 min rapidly declined from 7.46 to 4.49 (Figure 5). The pH-drop of chlorpyrifos solution might be attributed to the chlorpyrifos structure decomposed or/and released

some acid into solution during oxidation, under US, O₃ and US/O₃ treatments. According to Devi et al. (2009) showed that reduced substituent ⁻Cl and ⁻OH groups may be eliminated as HCl and H₂O. Under the effect of O₃/ultrasonic, nitro and nitroso are formed after -N=N- bond is broken. Benzene ring is broken and oxidized into carboxylic acid. Sulfogroup breaks into sulfuric acid. So, pH value of the arsenazo I solution continuously drops down from 8.4 to 3.2 (Wenrong & Haiyan, 2002). Therefore, reduced pH may release some acid from the chlorpyrifos solution after the oxidation, which could be confirmed by GC-MS. All treatments resulted in similar main fragment ions. Chlorpyrifos-oxon could not be determined at m/z 335. This formation is 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. The US/O₃ combination produced the main fragment ions at m/z 351, 314, 286, 258, 197 and 97 (Figure 6). The fragment ion at m/z 351 was from molecular ions of chlorpyrifos. The fragment ion at m/z 314 was the result of a loss of ³⁵Cl₂ or ³⁷Cl atom from the chlorpyrifos molecular. Similarly, 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 two ethylenes (C₂H₄ m/z 28) from the fragment ion at m/z 314. Each mass spectrum was normalized to its most intense fragment at m/z 197, possibly TCP (3,5,6-trichloro-2-pyridinol, C₅H₂Cl₃NO) obtained by the loss of the side chain (Mori et al., 2006). The fragment ion at m/z 97 was due to the formation of 2-hydroxy pyridine. Intermediates may react with three hydrogen radicals, eliminating all the three chloro (⁻Cl) groups as HCl, leading to the formation of other intermediates (Devi et al., 2009).

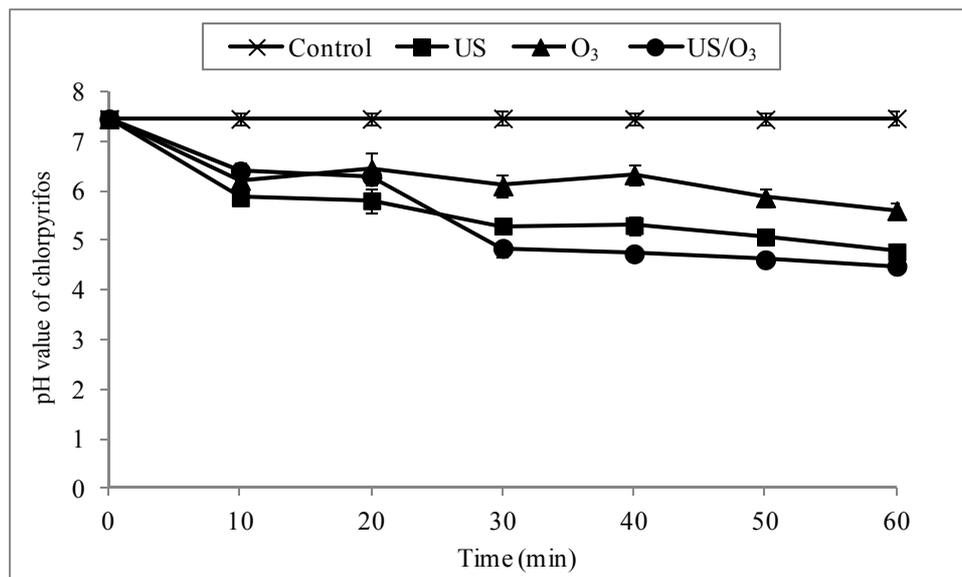


Figure 5. pH of standard chlorpyrifos solution after treatment with US, O₃ and US/O₃. Data are the means \pm S.E. (n=3)

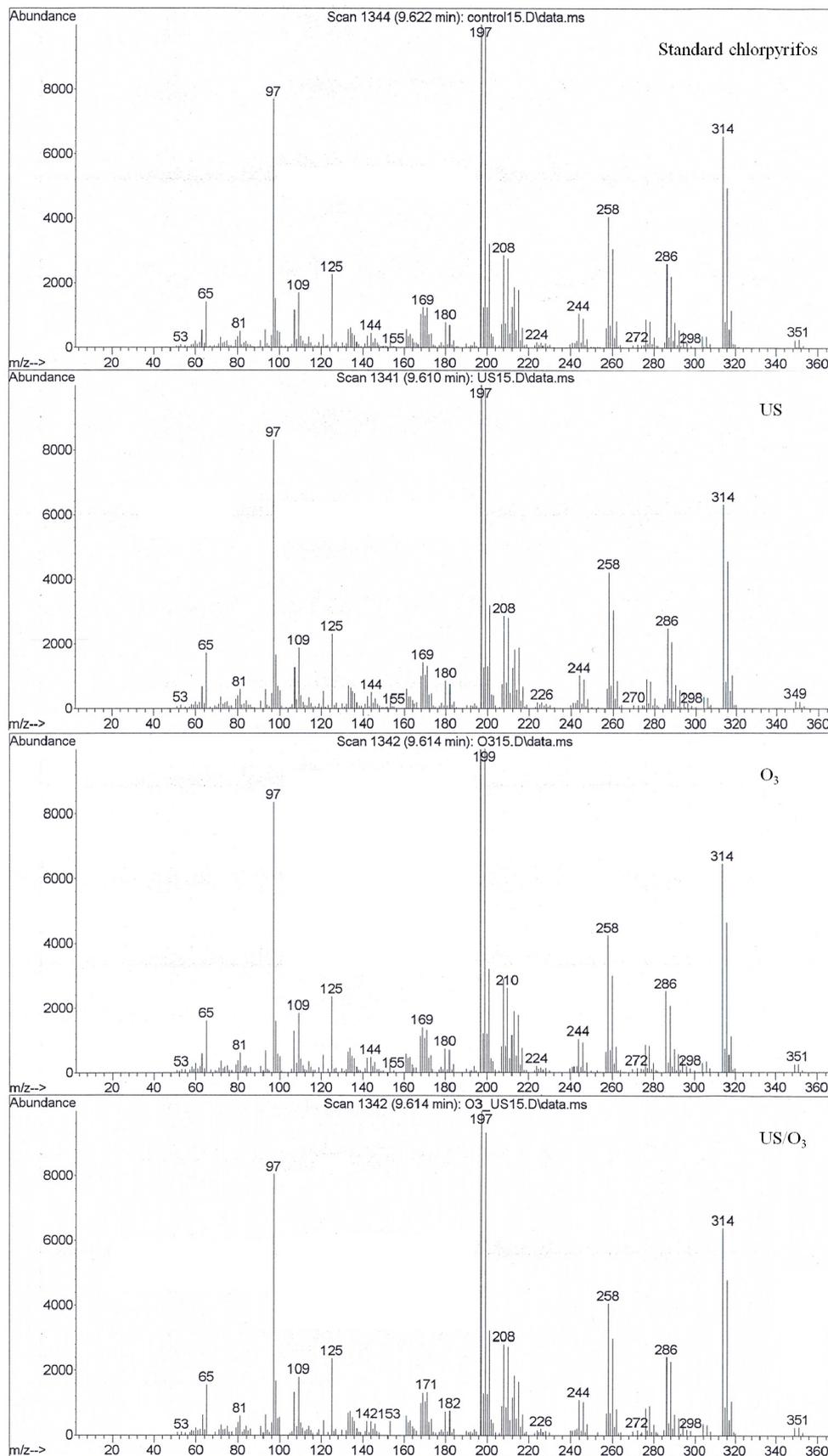


Figure 6. GC-MS spectra of chlorpyrifos after treatment with US and O₃

Toxicity was slightly reduced after treatments as revealed by the LC_{50} values at 24 h which increased from 7.22 to 10.21 $mg L^{-1}$. The O_3 and US/ O_3 treatments increased LC_{50} up to 103.54 and 234.09 $mg L^{-1}$ respectively (Figure 7). The toxicity evaluation indicated the toxicity of chlorpyrifos decreased after US/ O_3 treatment. It may chlorpyrifos concentration degraded by the combination as less toxicity than the other treatment. Tsuda et al. (1997) reported that fish contamination and other aquatic organisms by the oxidized products of diazinon and other organophosphorus pesticides in the environment were low concentration. According by Schneider et al. (2003), the reduction in *Karenia brevis* toxin concentration by ozone in sea water, displayed a positive correlation with the reduction of toxicity as determined by a fish (*Cyprinodon variegatus*) bioassay. The US/ O_3 treatment improved detoxification of the tested chlorpyrifos solutions, suggesting a synergistic effect between US and O_3 in improving the biodegradability of pesticides in wastewater (Xiong et al., 2011).

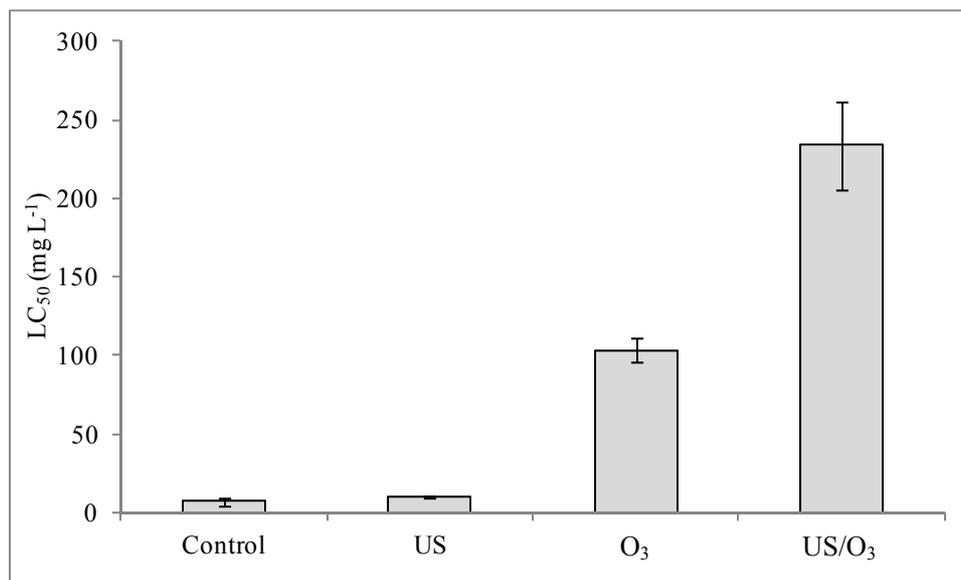


Figure 7. LC_{50} values (24 h) to the brine shrimp (*Artemia salina* L.) toxicity of chlorpyrifos after treatment with US and O_3 .

4. Conclusions

US and O_3 , applied in combination had a synergistic effect in reducing chlorpyrifos concentration with most of the degradation occurring within the first 10 min. Chloride, nitrate and sulphate anions released from the chlorpyrifos structure, during decomposition, might be related with the oxidation by ozone and indirect oxidation by ultrasound-generated $\bullet OH$. The pH of treated chlorpyrifos with US/ O_3 treatment decreased markedly from 7.46 to 4.49, suggesting that chlorpyrifos degradation might have release HCl during the process. The combined US/ O_3 treatments significantly lowered toxicity of chlorpyrifos. The results reported here show that the combination of ultrasonic irradiation and ozone represent a potential.

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