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REMEDIATIONOFPESTICIDEPOLLUTEDWATERUSINGOZONATIONASASAFEMETHOD

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Remediation of Pesticide-Polluted Water using Ozonation as a Safe Method

Prof. Dr. Ahmed K. Salama [α] & Khaled A Osman [σ]

Abstract - The effectiveness of ozone to remove the organic compound, chloropyrifos or cypermethrin from water at the two different levels of 1 and 2 ppm, for each and different contact times was studied. The recovered amounts of chloropyrifos or cypermethrin were extracted based on the solid phase extraction (SPE) method and then analyzed by GC-MS. The results demonstrated that the removal of these organic compounds by ozone increased with increasing the contact time. The removal percentages of chloropyrifos following ozone bubbling for different periods of 15, 30, 45 and 60 minutes at room temperature were 10.5, 96.3, 97.4 and 98.5% in case of samples fortified at the level of 1 ppm, while they were 79.6, 93.9, 94.7 and 96.1% at the level of 2 ppm, respectively. In case of cypermethrin, the removal percentages were 68.6, 90.5, 97 and 99.2% at 1 ppm level, whereas they found to be 30.5, 50, 84.7 and 92% at 2 ppm, respectively. Kinetic studies revealed that chloropyrifos and cypermethrin were found to be easily removed from water by ozone treatment. This is clearly reflected in the half-live values ($t_{1/2}$), where $t_{1/2a}$ values of chlropyrifos were 15.0 and 4 minutes at the levels of 1 and 2 ppm, respectively, following ozone treatment. The $t_{1/2a}$ values of Cypermethrin at the same previous levels and treatments were found to be 8.89 and 21.71 minutes. The present results illustrated that ozone may offer an efficient, fast, safe and friendly treatment for pesticide-polluted water.

I. Introduction

The excessive use of pesticides, their volatility and long-distance transports eventually results in widespread environmental contamination. In addition more toxic and environmentally persistent pesticides are used extensively in developing nations, creating serious acute health problems and local and global environmental impacts (Ecobichon, 2001). Several pesticides were detected in groundwater (Garcia deLlasea and Bernal-Gonzales, 2001; Johnson et al, 2001; and Kadian et al 2008). The amount and type of pesticides in the water of a particular area depends largely on the intensity of production and type of crops being cultivated (Belmonte et al, 2005). Also, the rate at which a pesticide is degraded in both surface and subsurface soils is an important factor in determining the groundwater contamination potential of the pesticide (Di et al, 1998). This implies that most of the applied pesticides find their way as 'residue' in the environment into water and the terrestrial and aquatic food chains where they undergo concentration and exert potential, long term, adverse health effects (Ekstrom et al, 1996; Chirone et al, 2000; and Osman and Al-Rehiayani, 2003). Since the late decades, concern about the contamination of water sources has risen due to the increasing number of pesticides detected. Regulations for drinking water are required in order to limit human risks and environmental pollution. These regulations are well defined in North America, depending on the toxicity level of each compound, and Europe (Directive, 1998) setting at 0.1 ppm of pesticide concentration for a single pesticide compound and 0.5 ppm for the sum of all pesticides in water samples. Chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate) is one of the most organo-phosphorus pesticides that is a widely-used for controlling various insect pests in agricultural and urban settings. Chlorpyrifos enters aquatic systems through spray drift, runoff, erosion, and spills (Racke, 1993). Cypermethrin has been widely used in both indoors and outdoors (Kaufman et al, 1981). It is especially effective towards the control of insect pests in many crops, outdoor mosquito control and as an indoor insecticide (Takahashi et al, 1985). Cypermethrin is commonly found in rivers, sediments, soils, and even foodstuffs (Allan et al, 2005 and Amweg et al, 2005). In recent times the removal of organic harmful pollutants present is investigated by means of a variety of chemical procedures. Advanced oxidation processes (AOPs) which are constituted by the combination of several oxidants, have proven to be very effective in treating a wide variety of organic contaminants. These technologies utilize powerful oxidizing intermediates (mainly OH radicals) to oxidize organic pollutants, leading not only to their destruction, but also, given sufficient conditions, to their complete mineralization. The OH radicals can be generated, for example, by the application of ozone/hydrogen peroxide, ultraviolet radiation/ozone, ultraviolet radiation/hydrogen peroxide, ozone/electron beam (Gehringer et al, 1992; Legrini et al, 1993 and Acero et al 2001). Ozone is a triatomic form of oxygen and is referred to as activated oxygen, allotropic oxygen or pure air. It is an unstable gas and the half-life ozone in distilled water at 20 ^{0}C is about 20-30 min and degrades in pure water rather quickly to

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oxygen, and even more rapidly in impure solution (Hill and Rice 1982), while It has a long half-life in the gaseous state (Rice, 1986). Ozone has been approved for use as a disinfectant or sanitizer in foods and food processing in the United States for removing residual pollutants such as pesticides and other pollutants which are difficult to get rid of in biological oxidation processes due to its high oxidability, high reaction rate and absence of any secondary pollution. It is considered as a powerful oxidant having electrochemical oxidation potential of 2.0V versus 2.8V for hydroxyl radical. Consequently, oxidation by ozone have usually been used as an effective method for removing residual pollutants such as pesticides and other hazardous chemicals from raw water used for drinking and for wastewater treatment (Lafi and Al-Qodah, 2006). There is no data about the removal of chropyrifos or cypermethrin from water in KSA and the search for means to improve the production of clean water in KSA is always the target of scientists, politicians and businessmen, who seek new techniques to enhance the quality and safety of this product. A wide range of water and terrestrial ecosystems might be contaminated with chlorpyrifos and cypermethrin (EPA, 1997 and Sapozhnikova et al, 2004) which have increased the public concern to establish an efficient, safe, and cost effective method to remove or detoxify chlorpyrifos and cypermethrin residues in contaminated water. Therefore, the present study was carried out to evaluate the effectiveness of ozone at different contact times as a safe method for removal of chropyrifos and cypermethrin in water samples.

II. Materials and Methods

a) Chemicals

Technical grade standard of chlropyrifos (O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate) was obtained from Chemservice, USA, with purity of 99% purity, while cypermethrin (cyano(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethyl cyclopropanecarboxylate) was purchased from Agrochemicals, Egypt, with purity of 91.5%. Certified HPLC-grade of actone, methanol, cyclohexane and ethyl acetate were purchased from BDH Company, while the Water spe-20G Column Processor designed vacuum manifold capable of processing up to 20 solid phase extraction (SPE) columns and SPE columns (Waters spe™, C18, 500 mg per column) were purchased from Waters, USA. Ultra-pure deionized water of 15 MΩ cm resistivity was obtained from a water purification system (PURELAB Option-R, ELGA, UK) and used throughout this study. All other chemicals used in this study were of the highest grade available.

b) Experimental Procedure

i. *Removal of organic compounds residues from groundwater*

Groundwater samples were collected from different locations at Al-Qassim region. Water samples were fortified with the organic compounds, chlropyrifos and cypermethrin at two levels for each compound (1 and 2 ppm). Removal of organic compounds from water samples was studied at four different contact times to ozone gas (15, 30, 45 and 60 min) at room temperature (25 ± 1^0C). Triplicate random water samples (4 L each) were treated with ozone at the previous mentioned periods. Ozone gas (100 ppm at air flow rate of 2.5 L/min with ozone output of 300 mg/hr) produced by Xetin Ozone Air &Water purifier (Model XT 301, Xetin Co. Ltd, Taiwan) was bubbled into 10 liters deionized water in polypropylene cylinder. The duration of dissolved ozone levels were controlled via adjusting the duration of bubbling. A 500 ml volume of water was withdrawn after different time on intervals and kept at 4^0C until analysis.

ii. *Extraction Procedure*

Water samples were extracted according to the procedure of Quintana et al (2001). with slight modification. In brief, A 500 ml volume of water, in which 5 ml of methanol had been added, was passed over the conditioned sorbent (3 ml of ethyl acetate, 3 ml of methanol and 6 ml of water, the sorbent of SPE was never allowed to dry during the conditioning and sample loading steps.) at a flow-rate of 5 ml/min. The sorbent was afterwards dried under vacuum for 20 min. Elution was performed by soaking the cartridge with 2.5 ml of ethyl acetate at a flow-rate of 0.8 ml/min, eluted with a second portion of 2.5 ml of ethyl acetate and collected in a glass vessel containing 0.5 ml of isooctane. The elute was then dried under vacuum to 0.45 ml. The volume was precisely readjusted to 0.5 ml of isooctane and then analyzed by gas chromatography-mass spectroscopy (GC-MS).

iii. *Recovery Experiments*

Pure water samples were spiked with either chlropyrifos or cypermethrin standard solutions in acetone to give the four levels of 0.25, 0.50, 1 and 2 ppm prior to extraction. They were then prepared according to the proposed procedure as described previously and then absolute recoveries were measured. The recovery values were found to be ranged from 98-104 and 92-106% for chlropyrifos and cypermethrin, respectively.

iv. *Determination of detection and quantitation limits*

The limits of detection (LOD) and limit of quantitation (LOQ) were calculated from the signal-to-noise ratios obtained by analyzing unspiked samples (n = 10); LOD and LOQ were taken to be the concentrations of pesticide resulting in a signal-to-noise ratio of 3 and 10, respectively. The LOD values were

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1.90 and 0.2 ppb, while and LOQ values were 6.30 and 0.67 ppb for chlropyrifos and cypermethrin, respectively.

v. *Gaschromatography-mass spectrometry (GC-MS)*

Gas chromatography (Model GC 450, Varian Inc., The Netherlands) with a mass spectrometry (MS 220.41) detector equipped with split/splitless injector with electronic pressure control was employed. A Fused silica CP-Sil 8 CB-LB/MS capillary column (30 m x 0.25 mm i.d) was used in combination with the following oven temperature programme for chlropyrifos: initial temperature 50 °C, 5 °C/min ramp to 160 °C held for 10 min (first step) and from 160 to 250 °C (20 min) at 15 °C (final step) and 90 °C, 5 °C/min ramp to 160 °C held for 10 min (first step) and from 160 to 250 °C (20 min) at 15 °C (final step) for cypermethrin. The injector temperature was 280 °C and mass range from 50-650 amu. The carrier gas (helium, 99.999%) flow rate was set to a constant head pressure of 200 kPa at flow rate of 1.0 ml min-1 with split ratio of 1: 20 min. The mass spectrometer was operated in electron ionization mode with a transfer line temperature of 280 °C, manifold temperature 40 °C, ion trap temperature 200 °C, ion source 240 °C and selected ion monitoring (SIM) mode. The ion energy for electron impact (EI) was kept at 70 eV. MS Workstation version 6.9.1. was used for data acquisition. For positive identification, both retention time (Rt) and the presence of five fragment ions (z/m ions: 197, 97, 199, 29 and 414 for chlropyrifos and 163, 165, 181, 91 and 77 for cypermethrin) were considered. Figures 1 and 2 represent the GC-MS chromatgrams for chlropyrifos and cypermethrin, respectively.

III. Results and Discussion

The study shows one of the analytical methods that use a solid phase extraction (SPE) to pre-treat the sample and further analysis of the extract by gas chromatograph- mass spectrometer(GC-MS) equipped with electron impact ionization (EI) detector. SPE is particularly suited for the isolation of organic micro-pollutants from water and has now become the method of choice in order to carry out simultaneously the extraction and concentration of many pesticides and metabolites in aqueous samples (Heberer et al, 1994; Font, 1993 and Sabik et al, 2000). The most widely used sorbents are C8 and C18 chemically bonded to silica, carbon black and polymeric resins (Sabik et al, 2000).

a) Removing of chlropyrifos and cypermethrin by ozone treatment

The effect of ozone treatment on either chlropyrifos or cypermethrin residues for different contact times was investigated. The amount of either chlropyrifos or cypermethrin levels was significantly decreased exponentially as the contact time increased in water samples at the two tested levels of the pesticides (1 and 2 ppm) compared to the initial levels, control, (Tables 1-2). The data showed that ozone declined the amount of chlropyrifos in water samples following the all intervals of treatment. The removal percentages were 10.5, 96.3, 97.4 and 98.5% in samples spiked with 1ppm of chlropyrifos after 15, 30, 45 and 60 min, respectively, while they were 79.6, 93.9, 94.7 and 96.1% in samples spiked with 2 ppm. In case of cypermethrin, the removal percentages were 68.6, 90.5, 97 and 99.2% in water samples spiked with 1ppm following ozone bubbling for 15, 30, 45 and 60 min, respectively, whereas they were 30.5, 50, 94.7, 84.7 and 92% at 2 ppm fortification level in the same order.

b) Kinetic Studies

A biphasic model was assumed according to Sigma Plot (2011) in order to carry out the statistical study of the of either chlropyrifos or cypermethrin removal in water (equation 1).

$$C_t = A_0 e^{-\alpha t} + B_0 e^{-\beta t} \quad (1)$$

Where Ct is the recovered amount of pesticide at t min, A_0 and B_0 are the concentrations of the pesticide at t=0, while α and β are the disappearance rate constants for the first and second and phases, respectively. The half-life ($t_{1/2}$) of the exponential decay was calculated according to the equation (2).

$$t_{1/2} = (2.303 \log 2)/ \text{rate constant} \quad (2)$$

The data fitting results in case of all ozone treatment using second order kinetic showed that the coefficients of determination (R2) were 0.829 and 0.999 for chropyrifos as well as 0.9990 and 0.9510 for cypermethrin when the tested levels of pesticide were 1 and 2 ppm, respectively (Tables 5 and 6). The biphasic model is characterized by a rapid phase (first phase), and a much slower phase (second phase). This is clearly reflected in the half- live values ($t_{1/2}$), where $t_{1/2\alpha}$ values for chlropyrifis were 15.0 and 4 min, and $t_{1/2\beta}$ values were 15.1 and 17.96 min, at the spiking levels of 1 and 2 ppm, respectively, following ozone treatment. On the other hand, $t_{1/2\alpha}$ values of cypermethrin were 8.89 and 21.71 min and $t_{1/2\beta}$ values were 9.00 and 21.71 min at the spiking levels of 1 and 2 ppm, respectively, following ozone treatment.

The present findings are in accordance with those of many investigators who reported that the kinetics of pesticide degradation is commonly biphasic with a very rapid degradation rate at the beginning followed by a very slow prolonged dissipation (Alexander, 1994; Jones et al, 1996; Rigas et al, 2007 and Osman et al, 2009). The relative importance of the phases depends on the availability of the pollutants, hydrophobicity, and affinity for organic matter. So it is recommended to use such simple and non-toxic treatment to reduce such residues in water. The present study revealed that removing of either of chlropyrifos or cypermethrin from water depends on the contact times. Also, the amount of pesticide removed by water is

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related to its water solubility and octanol–water partition coefficient.

One of the health concerns of using oxidants to degrade pesticide is the formation of toxic intermediates. The present study investigated the efficacy of ozone to remove chlropyrifos and cypermethrin from water. Ozone was assayed for treatment has a powerful oxidant having electrochemical oxidation potential of 2.0V, and thus, can modify the chemical structure of the selected pesticides creating derived by-products. If these by-products are more toxic than the parent pesticide, such washing treatments should not be utilized to reduce pesticide residue levels in water.

Ozone selectively reacts with compounds containing hetero-atoms such as S, N, O, and Cl via two different pathways, namely direct molecular and indirect radical chain-type reactions Gottschalk et al, 2000). Thus, pesticides, which usually have some hetero-atoms on the molecules, are often expected to be destroyed by ozonation (Reynolds, 1989). However, as has been found by many researchers, the reactivity of pesticides with ozone varies largely due to their diverse structural features (Reynolds, 1989; David et al, 1991) the characteristics of the wastewater to be treated, i.e., pH, concentration of ozone decomposition initiators, promoters and scavengers in the reacting medium (Glaze et al, 1987).

IV. Conclusions

Water is the basic necessity of life and water contaminated with toxic pesticides is associated with severe effects on the human health. Hence it is pertinent to explore strategies that address this situation of water safety especially for the developing countries where pesticide contamination is widespread due to indiscriminate usage. It is therefore of significance to evaluate simple and effective strategies as such ozone to enhance water safety from harmful pesticides. Due to its high oxidability, high reaction rate and absence of any secondary pollution, ozonolysis technique should be used in the sanitization of water especially in the treatment of pesticides which are difficult to get rid of. Results of this work, provided some basic concepts that can be helpful in water treatment for consumers. Therefore, the present study validated that ozone treatment is safe and promising processes for the removal of pesticides from water under domestic conditions. Results found in the present study must not be extrapolated to other pesticides.

V. Acknowledgements

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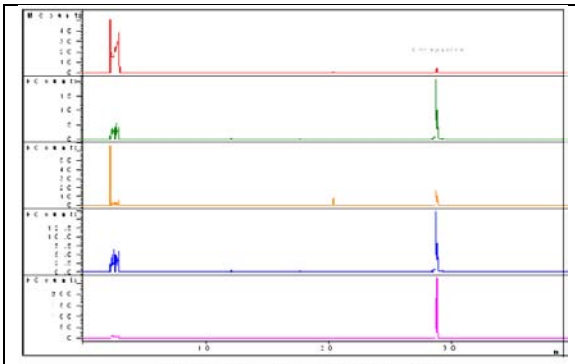


Fig (1). GC-MS profiles for chlorpyrifos

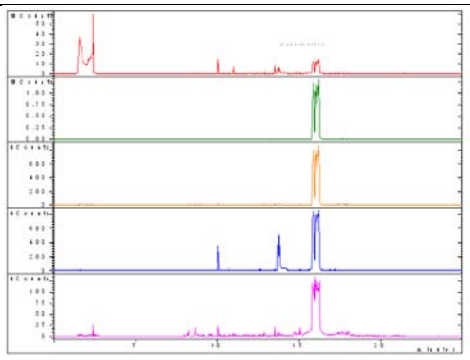


Fig (2). GC-MS profile for cypermethrin

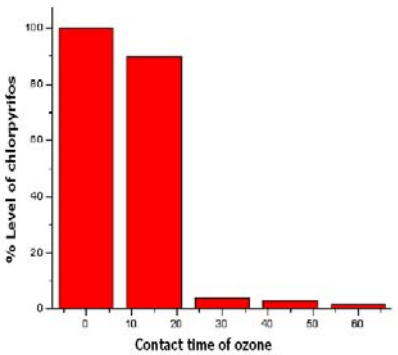


Fig (3). Effect of ozone treatment on removing of chlorpyrifos at 1 ppm level from water

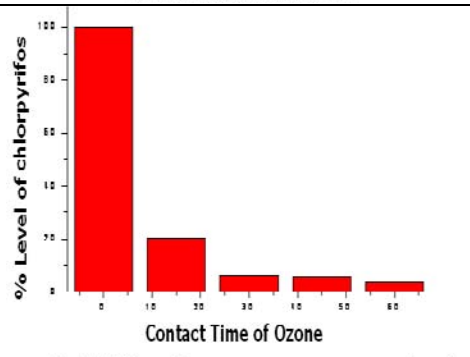


Fig (4). Effect of ozone treatment on removing of chlorpyrifos at 2 ppm level from water

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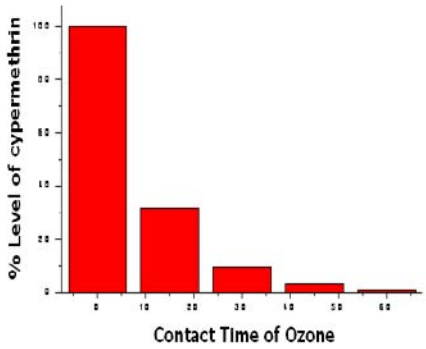


Fig (5). Effect of ozone treatment on removing of cypermethrin at 1 ppm level from water

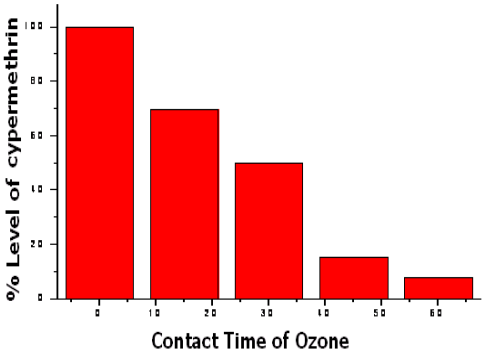


Fig (6). Effect of ozone treatment on removing of cypermethrin at 2 ppm level from water

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Table 1 : Effect of ozone treatment on chlorpyrifos removal from water samples spiked with either 1 or 2 ppm

Contact time (min)	1 ppm			2ppm		
	Chlorpyrifos amounts (ppm)	% of pesticide level	% of pesticide removal	Chlorpyrifos amounts (ppm)	% of pesticide level	% of pesticide removal
0	1.001±0.11	100	0	2.012±0.20	100	0
15	0.896±0.12	89.5	10.5	0.410±0.11	20.4	79.6
30	0.037±0.01	3.7	96.3	0.122±0.009	6.1	93.9
45	0.026±0.01	2.6	97.4	0.107±0.005	5.3	94.7
60	0.015±0.0	1.5	98.5	0.078±0.007	3.9	96.1

Each value is the mean ± S.D of three replicates with 6 determinations

Table 2 : Effect of ozone treatment on cypermethrin removal from water samples spiked with either 1 0r 2 ppm

Contact time (min)	1 ppm			2ppm		
	Cypermethrin amounts (ppm)	% of pesticide level	% of pesticide removal	Cypermethrin amounts (ppm)	% of pesticide level	% of pesticide removal
0	1.006±0.17	100	0	1.998±0.00.9	100	0
15	0.316±0.08	31.4	68.6	1.388±0.030	69.5	30.5
30	0.091±0.012	9.5	90.5	0.919±0.033	50	50
45	0.033±0.010	3.0	97	0.306±0.007	15.3	84.7
60	0.008±0.002	0.8	99.2	0.159±0.006	8	92

Each value is the mean ± S.D of three replicates with 6 determinations

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Table 3 : Kinetic parameters for chlorpyrifos dissipation in water in presence of ozone treatment

Pesticide Level	Kinetic Parameter						
	A_0 (ppm)	α (min^{-1})	$t_{½\,\alpha}$ (min)	B_0 (ppm)	β (min^{-1})	$t_{½\,\beta}$ (min)	Regression coefficient (R^2)
1ppm	56.71	4.62×10^{-2}	15.0	52.11	4.60×10^{-2}	15.10	0.803
2ppm	81.79	1.40×10^{-1}	4.95	18.22	3.86×10^{-2}	17.96	0.999

α and β are the disappearance rate constants for the first and second phases.
$t_{½\,\alpha}$ and $t_{½\,\beta}$ are the half-life times for the first and second phases.
Each value is the mean of three replicates with six determinations.

Table 4 : Kinetic parameters for cypermethrin dissipation in water in presence of ozone treatment

Pesticide level	Kinetic Parameter						
	A_0 (ppm)	α (min^{-1})	$t_{½\,\alpha}$ (min)	B_0 (ppm)	β (min^{-1})	$t_{½\,\beta}$ (min)	Regression coefficient (R^2)
1ppm	50.93	7.79×10^{-2}	8.89	49.11	7.79×10^{-2}	9.00	0.999
2ppm	53.10	3.19×10^{-2}	21.71	50.69	3.19×10^{-2}	21.72	0.951

α and β are the disappearance rate constants for the first and second phases.
$t_{½\,\alpha}$ and $t_{½\,\beta}$ are the half-life times for the first and second phases.
Each value is the mean of three replicates with six determinations.

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