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EFFECT OF OZONATION ON CYPERMETHRIN AND CHLORPYRIFOS PESTICIDES RESIDUES DEGRADATION IN TOMATO FRUITS

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ABSTRACT

This study was conducted to determine the effect of ozonation at concentrations of 0.4 ppm on cypermethrin and chlorpyrifos pesticides residues reduction in spiked tomato fruits at different concentrations. The pesticide residues were extracted from homogenized tomato fruits with acetonitrile using QuEChERS method and the determination was carried out on GC-ECD using splitless injector and HP-5 capillary column. The maximum reduction percentages of chlorpyrifos pesticide after 30 min exposure to ozone at concentration of 0.4 ppm of spiked tomato fruits with 0.05, 0.1, 0.5, 1.0 and 5.0 ppm were 97.9, 97.9, 95.3, 94.9 and 95.9%, respectively, while for cypermethrin pesticide at similar concentrations and conditions were 83.3, 82.8, 83.8, 84.9 and 87.3%, respectively. Results showed that chlorpyrifos pesticide degradation is more sensitive to ozonation than cypermethrin residues. The effect of ozonation at concentration of 0.4 ppm on degradation of chlorpyrifos and cypermethrin residues is time dependent, whenever the exposure time increased, the degradation of chlorpyrifos and cypermethrin residues also increased.

KEYWORDS:
Cypermethrin, Chlorpyrifos, Pesticide residues, Ozonation, GC-ECD.

INTRODUCTION

In modern agricultural practices, pesticides are one of the major inputs used to increase the production of crops. However, the pesticide residues left after harvesting may led to adverse health effects on consumers and affecting the trade of several food commodities. Tomato is one of the most common agricultural products in Jordan. It is the main component for several dishes in the Jordanian people diet. It is estimated that 777820.4 tons of tomatoes were produced in Jordan in 2011 for local use and exportation [1]. The average per capita consumption of tomato fruits in Jordan was about 39.6 kg/year, and it is among the largest rate of consumption for the Jordanian citizen. In addition, Jordan produced 2310 tons of tomato processed products like; tomato paste, tomato soup, tomato juice, and ketchup. The total produced and consumed amount in local market is 6181 tones/year. Furthermore, the per capita consumption of processed tomato products was about 1 kg/year [2].

Tomatoes have been treated intensively with pesticides to control pests. However, many of these pesticides are used in large quantities. Cypermethrin and chlorpyrifos were found to be effective pesticides to control plant pests by contact or systemically and they are classified by the Environmental Protection Agency (EPA) in class II since these pesticides are of moderate toxicity. Monitoring of cypermethrin and chlorpyrifos pesticides residues in Jordan crops showed that these pesticides are the most frequent residues, and in many cases their residues exceeding the maximum residues limits issued by Codex Alimentarius Commission [3].

In the recent years, the word attention has focused on the removal of pesticide residues by different treatments like; cooking, ozonation, UV-radiation, washing and peeling. It is noticed that these treatments are of great benefits to have safe and healthy food. It is well known that ozone was effectively applied to drinking water treatment and wastewater treatment for its powerful oxidization potential. Some researchers demonstrated that certain pesticides, such as 2,4-dichlorophenoxyacetic acid [4,5], carbofuran [6], diazinon [7] and pirimiphos-methyl [8] can be readily degraded in aqueous solution by ozone. Wu et al. [9] showed that the degradation of four pesticides by low concentration of dissolved ozone (1.4 ppm for 30 min) was effective to oxidize 60–99% of 0.1 ppm aqueous diazinon, parathion, methyl parathion and cypermethrin. Ozonation of fortified tomato juice with methomyl, oxamyl and carbosulfan at 0.4 ppm was found to be the most effective treatment; complete degradation of methomyl, oxamyl and carbosulfan were achieved after 30 min of ozone treatment [10].

Ozonated water was mostly effective in cypermethrin removal (>60%) and the efficacy highly depended on the dissolved ozone levels. Hadjikinova et

al. [11] showed that washing, particularly with sodium base (1%) or sodium hydrogen carbonate solutions (1.5%) markedly reduced concentration of chlorpyrifos-methyl insecticide and fenarimol) fungicide in cherries.

Zhanggui et al. [12] observed that pesticide residue levels were reduced in wheat and corn by ozone treatment at 15–20 ppm, with a maximum degradation rate of 12.3% per day. Chen et al. [13] investigated the efficiency of a novel machine to remove permethrin, chlorfluazuron and chlorothalonil pesticide residues from Chinese white cabbage using ozone in a domestic-scale vegetable cleaner consists of a closed cleaning chamber, an ozone generator, a water recirculation pump, and an Oxidation-Reduction Potential (ORP) electrode. The average percentages of pesticides reduction after 15 min of treatment at ozone output rate of 150 mg/h were 51.8%, 55% and 60% for permethrin, chlorfluazuron and chlorothalonil, respectively. However, as the time of treatment increased to 30 min, the percentages of reduction increased up to reach 67% and 64% for chlorfluazuron and chlorothalonil, respectively.

The objective of the current study is to determine the effect of ozonation at concentration of 0.4 ppm for different period of time on reduction percentages of these pesticides.

MATERIALS AND METHOD

Chemicals. Anhydrous magnesium sulphate ($MgSO_4$, assay 99%, Sigma-Aldrich, USA), Acetonitrile (CH_3CN, HPLC-grade, assay of 99.8%, LAB-SCAN analytical sciences, Ireland). Acetic acid (CH_3COOH, assay 99%, J. T. Baker, USA). Acetone (C_3H_6O, GC-grade, assay 99.8%, LabChem, USA). Sodium chloride (NaCl, assay 99.9%, AVONCHEM, UK). Primary Secondary Amine (PSA) sorbent, with 40 – 60 µm particle size was purchased from Agela Technologies, USA. Cypermethrin ($C_{22}H_{19}Cl_2NO_3$) and chlorpyrifos ($C_9H_{11}Cl_3NO_3PS$) pesticides were purchased from Sigma-Aldrich, USA. Aldrin pesticide ($C_{12}H_8Cl_6$, assay 99.5%) and Ditalimifos ($C_{12}H_{14}NO_4PS$, assay 97.5%) were purchased from Sigma-Aldrich, USA.

Sample Preparation and Extraction. Fifty samples of tomato fruits were collected randomly from the local market during the period from July to October 2015. The size of each sample taken for analysis was around 1 kg, as recommended by Codex Alimentarius sampling guidelines [14]. All samples were kept in polyethylene plastic bags, then labelled and refrigerated at 5ºC until pesticides residues analysis within 3 days. QuEChERS method was used for extraction of cypermethrin and chlorpyrifos residues from tomato fruits [15]. This method based on the extraction of pesticides with acetonitrile and partitioning with anhydrous magnesium sulphate. One kilogram of tomato fruits sample was chopped into small pieces with the chopper to get a homogenous sample, then 200 g was taken as subsample and further homogenised with the blender. Then three subsamples were taken, and kept in deep freezing conditions at -18ºC, until analysis. Ten grams from each of homogenised subsample was transferred into 50 ml Teflon centrifuge tube, and 10 ml of acetonitrile with 1% acetic acid solution (v/v) was added and was shaken by the Vortex mixer for 1 min at low speed. Anhydrous $MgSO_4$ (4.0 g) and NaCl (1.0 g) were added to the sample, then vortexed again for 1 min.

Ditalimifos of 1.00 ppm and Aldrin 0.1 ppm concentrations were also added as an internal standard. Finally, sample was Vortexed for 30 s and centrifuged at 3000 rpm for 5 min.

Samples Clean-Up. The same procedures for clean-up were followed for tomato fruits and cucumber, 2 ml of the upper acetonitrile layer was transferred into 10 ml centrifuge tube containing 2*25 mg PSA as sorbent and 2*150 mg anhydrous $MgSO_4$, then it was vortexed for 30 s, as a final step the centrifuge tube was centrifuged at 3000 rpm for 5 min. The extract was transferred into 2 ml GC vial.

Gas Chromatography with Electron Capture Detector Analysis. The chromatographic system consisted of a gas chromatography equipped with electron capture detector, splitless injector and the capillary column HP-5 model No.(19091J-413) with composition of 5% Phenyl and 95% methylpolysiloxane, dimensions are 30 m length, 0.32 mm nominal diameter, and 0.52 µm nominal film thickness. The carrier gas was argon methane. The operating conditions were: injection volume of 1 µl. The temperature program was: injector temperature 250ºC, and detector temperature 300ºC [16]. The oven temperature program was modified to get the best response for cypermethrin and chlorpyrifos as follows: initial temperature 90ºC for 1 min; 20ºC min^{-1} to 150ºC for 1 min; 6 ºC min^{-1} to 270 ºC for 1 min [16]. For data acquisition ChemStation software was used.

Determination of Detection Limits (DL). Three independent blank tomato fruits samples that previously shown not to contain any residues, were separately extracted in the same day to get the amount corresponding to the desired pesticide retention time using GC-ECD. The mean values ($\bar{\square}$) for the amounts of the six replicates and their standard deviation (SD) were calculated separately for each pesticide [17]. The DL for cypermethrin and chlorpyrifos were calculated according to the following equation [18]:

$$DL = \bar{X} + (3 \times SD) \dots\dots\dots\dots\dots\dots\dots (1)$$

After determination of DL for each pesticide, a blank sample was spiked with the desired concentration and determined by GC-ECD.

Blank and Recovery Tests. Blank test was performed to make sure that the solvent and apparatus are free from any residues of cypermethrin and chlorpyrifos. Ten ml of acetonitrile was placed in 50 ml Teflon centrifuge tube, and then the procedures for extraction and GC-ECD analysis were followed as described previously. For recovery test blank tomato juice samples that are previously analysed and proven to be free from any cypermethrin and chlorpyrifos residues were used to perform this test.Ten grams of homogenised blank tomato juice samples were placed in 50 ml Teflon centrifuge tube and spiked separately to obtain 0.1 and 1.0 ppm from each pesticides. The extraction and clean-up procedures were preceded as previously described.

This test was repeated three times for cypermethrin and chlorpyrifos at the spiked amounts of 0.1, and 1.0 ppm to assess the efficiency of QuEChERS method for extraction.

The recovery percentage of each pesticide was calculated according to the following equation:

$$\text{Recovery percentage}(\%) = \frac{\text{ppm pesticide detected}}{\text{ppm pesticide added}} \times 100 \ldots\ldots\ldots\ldots\ldots (2)$$

Effect of Tomato Fruits Ozonation At 0.4 Ppm On Stability Of Cypermethrin And Chlorpyrifos. To investigate the declining pattern in cypermethrin and chlorpyrifos pesticides residues in tomato fruits, the samples were treated as follows:

Samples made of five tomato fruits (1 kg each) (free from cypermethrin and chlorpyrifos) were treated with five different pesticides concentrations 0.05, 0.1, 0.5, 1 and 5 ppm for each of cypermethrin and chlorpyrifos. Each sample was treated with 0.4 ppm ozone for 1, 5, 10 and 30 minutes using the Fruits and Vegetables Washer, which is domestically used to eliminate pesticide residues in fruits and vegetables. The effect of ozone treatment on cypermethrin and chlorprifos were evaluated by analysing tomato fruits samples before and after the treatment. The treated tomato fruits samples were held inside the cleaning chamber during ozone treatment. Samples were taken separately after 1, 5, 10 and 30 minutes for each pesticide determination. Each sample was extracted as previously described and analysed using GC-ECD to determine the recovered amounts of cepermethrin and chlorpyrifos in order to evaluate the efficiency of ozonation on the reduction percentages of cypermethrin and chlorpyrifos with time.

Statistical Analysis. The design of the experiment was Complete Randomised Design (CRD) with three replicates. Mean values and standard error were calculated and analyzed. The obtained data were subjected to statistical analysis using MSTAT-C programme version 1.4, were Least Significant Difference test (LSD) was used at 0.01 probability level.

RESULTS AND DISCUSSION

Pesticides Residues Analysis. The cypermethrin and chlorpyrifos pesticides were identified by comparing their retention times and quantified from the established standards calibration curves for each pesticide.

Blank test. All the blank tests did not show any residues of cypermethrin and chlorpyrifos. These blank tests indicated that there were no contaminations due to reagents and/or equipment.

Detection limits (DL) and retention time. The results in table 1 shows cypermethrin and chlorpyrifos minimum detection limits and the retention time for the analysis of three blank tomato fruit samples.

TABLE 1
Detection limits (DL) and retention time of cypermethrin and chlorpyrifos pesticides, using GC-ECD.

Pesticides	Detection limits*± SE** (ppm)	Retention Time (min)
Cypermethrin	**0.010 ± 0.003**	**28.464**
Chlorpyrifos	**0.003 ± 0.001**	**16.961**

*Values calculated based on six replicates of the blank tomato fruits samples.
** SE= Standard Error

TABLE 2
Recovery percentages of cypermethrin and chlorpyrifos pesticides from tomato fruits samples spiked with different concentration levels.

Pesticide	Spiked amount (ppm)	Recovery %*± SE**
Cypermethrin	**0.05**	**96.0 ± 0.01**
	0.1	**93.0 ± 0.02**
	0.5	**91.4 ± 0.05**
	1.0	**98.9 ± 0.06**
	5.0	**99.6 ± 0 .06**
Chlorpyrifos	**0.05**	**94.0 ± 0.01**
	0.1	**94.0 ± 0.02**
	0.5	**93.2 ± 0.05**
	1.0	**95.3 ± 0.06**
	5.0	**91.0 ± 0.06**

* Values are means of three replicates.
** SE= Standard Error

Recovery test. Recover studies were performed to examine the efficacy of extraction and clean up. Table 2 shows the mean recoveries percentages from blank tomato fruit samples spiked with different concentrations from cypermethrin and chlorpyrifos pesticides.

Effect of Ozonation Treatment At 0.4 Ppm And Exposure Time On Chlorpyrifos And Cypermethrin Reduction Percentages At Different Spiked Levels In Tomato Fruits. Chlorpyrifos. Results presented in table (3) showed the recovered amounts and the reduction percentages of chlorpyrifos after being exposed to ozone at 0.4 ppm in tomato fruits. The recovered amounts of chlorpyrifos decreased sharply after half an hour of exposure to ozone with maximum reduction percentage of 97.87% for the spiked tomato fruits at concentrations of 0.05 and 0.1 ppm, but at 0.5, 1 and 5 ppm the recovered chlorpyrifos amount was 0.022, 0.049 and 0.189 ppm, respectively, with reduction percentages of 95.28, 94.86 and 95.85%, respectively. It must be noted that the ozonation treatment for 30 min could not reduce the concentration of chlorpyrifos in tomatoes fruits lower the European MRL (0.01) ppm for the initial concentration of 0.5, 1.0 and 5 ppm, even the percentage of reduction greater than 90%.

TABLE 3
Effect of tomato fruits ozonation at 0.4 ppm on chlorpyrifos persistence at different spiked concentration levels, using GC-ECD. *

Exposure time (min)	Spiked amount (ppm) 0.05 Amount Recovered (ppm) ± SE	Reduction % ± SE**	0.1 Amount recovered (ppm) ± SE	Reduction % ± SE	0.5 Amount recovered (ppm) ± SE	Reduction % ± SE	1.0 Amount recovered (ppm) ± SE	Reduction % ± SE	5.0 Amount recovered (ppm) ± SE	Reduction % ± SE
0	0.047 ±0.011	0.000^{e}	0.094 ±0.021	0.000^{e}	0.466 ±0.051	0.000^{e}	0.953 ±0.061	0.000^{e}	4.549 ±0.061	0.000$_{e}$
1	0.033 ±0.023	29.79 ± 1.50^{d}	0.068 ±0.000	27.66± 1.11^{d}	0.369 ±0.052	20.82 ± 1.57^{d}	0.766 ±0.131	19.62 ±1.33^{d}	3.931±0.152	13.59 ± 1.88^{d}
5	0.021±0.000	55.32 ± 1.02^{c}	0.044 ±0.000	53.19 ± 1.81^{c}	0.235 ±0.041	49.57 ± 1.93^{c}	0.490 ±0.080	48.58 ±1.20^{c}	2.600±0.181	42.85 ±1.17^{c}
10	0.013 ±0.000	72.34 ± 1.84^{b}	0.025 ±0.020	73.40 ± 0.28^{b}	0.135 ±0.010	71.03 ± 0.96^{b}	0.233 ±0.022	75.55 ± 0.12^{b}	1.440±0.110	68.35 ±0.25^{b}
30	0.001 ±0.000	97.87 ± 0.00^{a}	0.002 ±0.011	97.87 ± 0.97^{a}	0.022 ±0.013	95.28 ± 0.32^{a}	0.049 ±0.051	94.86 ±0.94^{a}	0.189 ±0.091	95.85 ±0.75^{a}

* Values are means of three replicates ± SE.
**Means of reduction percentages within the same column with different letters are significantly different using LSD test at 0.01 probability level.

TABLE 4
Effect of tomato fruits ozonation at 0.4 ppm on cypermethrin persistence at different spiked concentration levels, using GC-ECD. *

Exposure time (min)	Spiked amount (ppm) 0.05 Amount Recovered (ppm) ± SE	Reduction % ± SE**	0.1 Amount recovered (ppm) ± SE	Reduction % ± SE	0.5 Amount recovered (ppm) ± SE	Reduction % ± SE	1.0 Amount recovered (ppm) ± SE	Reduction % ± SE	5.0 Amount recovered (ppm) ± SE	Reduction % ± SE
0	0.048 ±0.011	0.00^{e}	0.093 ±0.020	0.00^{e}	0.457 ±0.053	0.00^{e}	0.989 ±0.063	0.00^{e}	4.978 ±0.062	0.00^{e}
1	0.045 ±0.020	6.25 ± 1.50^{d}	0.087 ±0.002	6.45 ± 1.11^{d}	0.429 ±0.051	6.13 ± 1.57^{d}	0.851 ±0.130	13.95 ± 1.33^{d}	4.240 ±0.150	14.83b± 1.88^{d}
5	0.035±0.00	27.08 ± 1.02^{c}	0.071 ±0.002	23.66 ± 1.81^{c}	0.335 ±0.040	26.70 ± 1.93^{c}	0.626 ±0.082	36.70 ± 1.20^{c}	3.111 ±0.181	37.51 ±1.17^{c}
10	0.015 ±0.00	68.75± 1.84^{b}	0.028 ±0.021	69.89 ± 1.54^{b}	0.135 ±0.012	70.46 ± 0.96^{b}	0.268 ±0.021	72.90 ± 0.12^{b}	1.260±0.115	74.69 ± 0.25^{b}
30	0.008 ±0.00	83.33 ± 0.00^{a}	0.016 ±0.012	82.80 ± 0.97^{a}	0.074 ±0.037	83.81 ± 0.32^{a}	0.149 ±0.055	84.93 ± 0.94^{a}	0.633 ±0.090	87.28 ± 0.75^{a}

* Values are means of three replicates ± SE.
**Means of reduction percentages within the same column with different letters are significantly different using LSD test at 0.01 probability level.

Cypermethrin. The recovered amounts and the reduction percentages of cypermethrin presented in table (4) calculated after ozonation of tomatoes fruits at 0.4 ppm for different periods of time. The reduction percentage of cypermethrin increased to less than 74 ppm after ten minutes for the spiked tomato fruits at concentrations of 5 ppm, while after 30 min the maximum reduction percentage of cypermethrin in tomatoes fruits was 87.28% of the spiked tomato fruits. Cypermethrin EU-MRL on tomatoes fruits equal to 0.5 ppm, this concentration could be exceeded for the initial concentration of 1 ppm after 10 min of ozonation treatment, but for 5 ppm initial concentration it could not be reached even after 30 min of ozonation treatment.

Ozonation treatment at 0.4 ppm for tomato fruits showed significant reduction of chlorpyrifos and cypermethrin for all initial concentrations (0.05, 0.1, 0.5, 1, and 5) ppm. The reduction percentages after 30 min of treatment of tomatoes fruits ranged from 96 % to 98% for chlorpyrifos, and from 83% to 87% for cypermethrin. These findings agreed with Swami et. Al [19] who showed that the reduction percentages of chlorpyrifos after ozonation of apple at rate of 200 mg h^{-1} for 30 min was 95.2%.

Lozowickg et. al [20] found that ozonation treatment at 1 ppm ozone concentration for strawberry was efficient to reduce 16 pesticides residues even after 5 min of treatment. The reduction percentages for chorpyrifos and alpha-cypermethrin were 75% and 58%, respectively, which is agreed with our findings. The ability of ozonation in reduction of these pesticides amount is related to the ability of ozone to generate hydroxyl radicals in aqueous solution, which are highly effective to decompose chlorpyrifos and cypermethrin, so as the time of exposure increased hydroxyl radicals continued to be generated throughout the treatment, and more residues degraded [13]. In general, the effect of ozonation on the degradation of chlorpyrifos and cypermethrin residues is highly affected by the time of exposure, whenever the ozonation increased for long period of time, the degradation of chlorpyrifos and cypermethrin residues also increased. The statistical analysis showed that there were significant differences ($P \leq 0.01$) between chlorpyrifos and cypermethrin residues reduction percentages after ozonation, for all the spiked concentration levels at 3, 5, 10, 15 and 30 min. chlorpyrifos and cypermethrin residues recovered amount decreased significantly with time after ozonation treatment at 0.4 ppm to reach a concentrations that are below the EU-MRL after 30 min of treatment and the reduction percentages were increased with increasing ozonation exposure time. The authors concluded that ozonation treatment could be considered as an efficient treatment to remove high concentrations of pesticide residues if ozone generated continuously for a sufficient time of treatment.

CONCLUSION

Ozonation is an effective method to reduce chlorpyrifos and cypermethrin residues from fruits and vegetables and can significantly reduce the residues below the maximum residue limits. However, chlorpyrifos pesticide is more sensitive to degradation by ozone than cypermethrin. Exposure time to ozone washing was an important factor to reduce the spiked amount below the maximum residue limits.

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