Removal of Pesticides Residue in Produce with Ozonated Water Wash

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Abstract. *The objectives of the present study were to determine the susceptibility of the organophosphrous pesticides such as malathion to ozonation. An aqueous model system was developed to study the effects of three pH values and chlorination on malathion degradation over a 30 min treatment period. Aqueous solutions buffered at pH 4.5, 7.0 and 10.7 were prepared and used during testing. For ozonation study, ozone gas was bubbled into each pH solutions doped with 4 ppm malathion. For the chlorination study, an appropriate amount of calcium hypochlorite stock solution was added to each pH solution to bring final chlorine concentration to 50ppm. It was found that malathion degrade rapidly at pH 10.7. With the help of ozonation or chlorination, malathion can be completely degraded in strong alkaline solutions in 5 min. Chlorination was slightly better than ozonation at pH 4.5. However, at pH 7, a neutral and practical condition, ozonation performed better than chlorination in degrading malathion. The tests on grapes indicate that ozonation was effective in removing and decomposing malathion sprayed on grapes.*

Keywords: ozone, ozonation, pesticides, malathion, fruits, vegetables.

Introduction:

Pesticide residues in foods have been an important food safety issue especially for countries where pesticide uses are at alarming levels. There is an increasing need to develop methods to reduce these residue in foods to acceptable levels. Postharvest treatment, such as postharvest water wash and scrub have been traditionally employed to remove debris and dirt, and have been shown to reduce pesticide residues (El-Hadidi 1993). The use of postharvest chlorine dips has shown potential as an effective postharvest treatment in the reducing pesticides residue (Hendrix 1991). However, potential hazards have been associated with chlorine-based compounds(Cheng-I1985). The use of ozonated water dips is an alternative postharvest treatment method(Ong 1996). Ozone is a powerful oxidant which can degrade or eliminate organophosphate pesticide without leaving hazardous compounds on the produce and in the dip water.

The objective of this study was to study the susceptibility of organophosphate pesticide such as malathion to ozonation and determine the effectiveness of ozone and chlorine on the degradation of pesticide in aqueous solution.

Materials and Methods

Materials

Malathion was used in this study to represent organophosphate pesticide. Malathion is a nonsystemic, wide-spectrum organophosphate insecticide. It is suited for the control of sucking and chewing insects on fruits and vegetables, and is also used to control mosquitoes, flies, household insects, animal parasites (ectoparasites), and head and body lice. Malathion may also be found in formulations with many other pesticides.

Malathion was purchased from Sigma Chemical Co. The stock solution of malathion was prepared in D.I. water at concentration of 1000mg/L. The standards were protected from light exposure and stored in the refrigerator at 4 °C. Sodium thiosulfate, calcium hypochlorite, sodium bicarbonate, sodium carbonate, sodium phosphate, sodium acetate were all analytical grade. Methanol, benzene and methylene chloride were HPLC grade.

The commercial pesticide used in this research was a liquid fruit tree spray with fungicide. Its active ingredients include methoxychlor, malathion captan and carbaryl. Malathion is an insecticide that has ability to evoke a variety of behavioral and other effects in several plant insects. Captan is used widely as a non-systemic organosulphur fungicide in the prevention of fungal diseased of grapes.

Methods

Experiments using Aqueous Model Solutions

An aqueous model system was developed to study the effects of ozonation and chlorination (calcium hypochlorite at 50mg/L) on pesticides degradation over a 30 min period at three pH levels (4.5, 7.0 and 10.7).

Aqueous solutions buffered at pH 4.6 (0.2 M sodium acetate), pH7.0 (0.2 M sodium phosphate) and pH 10.7 (0.2 M sodium carbonate and bicarbonate) were prepared. Each buffered solution was doped with pesticide stock solution to give the final concentration of 4 mg/L.

For ozonation study, ozone gas was bubbled into the buffered solution. Forty ml sample was taken out from the container at 0, 5, 15 and 30min intervals. Ozone concentration was monitored before and after each sampling. Forty ml methylene chlorite and 20ml sodium thiosulfate were added immediately to quench the reaction. The pesticide was extracted with 100ml benzene twice. The benzene solution containing the pesticide was subjected to vacuum evaporation, resulting in dry pesticides, which were then dissolved in 5ml methanol and analyzed using GC with on-line EI-MS detection.

For chlorination study, an appropriate amount of pesticide stock solution was added to each pH solution to make the final chlorine concentration to 50mg/L. Sampling method and sample preparation method were the same as described for ozonation study.

Experiments on Grapes

Grapes were bought form the local grocery store. Pesticides were sprayed on the grapes evenly. After 24 hours, all grape samples (control and treated) were stored at 4°C for analysis.

Five grapes (about 40g) were used per replication. Three replications were used for each treatment. Grapes were placed in a 1-liter bucket containing 200 ml of water. Water wash and ozone wash were used as treatments. Each sample (five grapes) was soaked in a treatment solution (water or ozonated water) for 5, 15 and 30 min.

After the wash treatments, 40 ml solution was taken out from the bucket. 40ml methylene chlorite and 20ml sodium thiosulfate were added immediately to quench the reaction. The pesticides in the solution were extracted and analyzed using the same procedures described above.

On the other hand, each treated grape sample was immersed in 100 ml benzene for two times to extract pesticide. The obtained 200ml benzene solution containing the pesticides was subjected to the procedures described above for pesticide extraction and analysis.

Pesticide Residue Analysis

The pesticide residue was analyzed using GC equipped with HP-1 fused silica capillary column (30m $\times$ 0.25 i.d.) with a film thickness of 0.25µm. The oven temperature was programmed to have a gradient from 80 °C to 240°C. Both of the injector temperature and detector temperature were 250°C. The pesticide residue was detected by the on-line EI-MS detector, and quantified at m/z 173.

Results and Discussion

Aqueous Solution Study

Table 1 shows degradation of malathion under different conditions and treatments. Malathion appears to be most stable in neutral media. In strong alkaline condition such as at pH 10.7, malathion degraded very fast even in water. A 5-min ozonation or chlorination can decompose malathion completely at pH 10.7. At pH 4.5, chlorination seems to perform better than ozonation while at pH 7, ozonation was more effective than chlorination. Treatments applied at pH 7 are closer to practical situations, and therefore the results obtained at this pH level are of great significance to practical applications of the treatments.

Table1. Residual malahtion after treatment with water, ozonation solution and chlorination solution.

	Time (min)	Ozonation (%)	Chlorination (%)	Control (%)
pH 4.5	0	100	100	100
	5	36	2.1	95.1
	15	18.8	15.9	94.9
	30	0.3	0.000	88.1
pH 7.0	0	100	100	100
	5	92.4	63.1	100
	15	51.8	71.0	77.0
	30	18.8	44.6	76.0
pH 10.7	0	100	100	100
	5	0	0	17.0
	15	0	0	7.6
	30	0	0	0

Ozone has the property of auto decomposition, producing numerous free radicals, and the most prominent free radical in reaction with water is hydroxyl radical (OH•), (Hwang 2001). OH• is a powerful oxidant which can degrade or eliminate organophosphate pesticide as well as malathion because organophosphate pesticide used contains a phosphoric acid ester linkage which is relatively unstable and more susceptible to oxidation in a strong oxidizing medium (Chiron 2000).

Removal Pesticide Residue on Grapes by Ozonated Water Wash

Generally water washing of produce can remove some pesticide residues on the surface of the produce. However, pesticides may accumulate over time in the wash water, and thus water washing may not lower the pesticide residues on produce satisfactorily. On the other hand, ozonated water, proven to be capable of decomposing pesticides such as malathion, can not only physically remove pesticides on produce but also reduce the pesticide level in the wash water through oxidation. Moreover, ozonated water may penetrate produce skins and attack pesticides below the skinks. Results in Fig. 1 shows the concentration of malathion in water and ozonated water after they were used for washing grapes. The malathion residue concentration in the plain water increased slightly as the washing time was increased, indicating an accumulation of malathion in the wash water and that further increasing washing time would not be effective. The amount of malathion in ozonated water was at much lower levels and decreased with increasing washing time, suggesting that malathion washed off the grapes was decomposed rapidly by ozone. For example, after 5 min, malathion concentration was 5 µg/L in the plain water but only 1.63 µg/L in the ozonated water, a 68% reduction as a result of ozonation. About 98% of malathion residue in the ozonated water was decomposed after 15 min. These results are in agreement with those reported by El-Hadidi (1993) and Ong (1996).

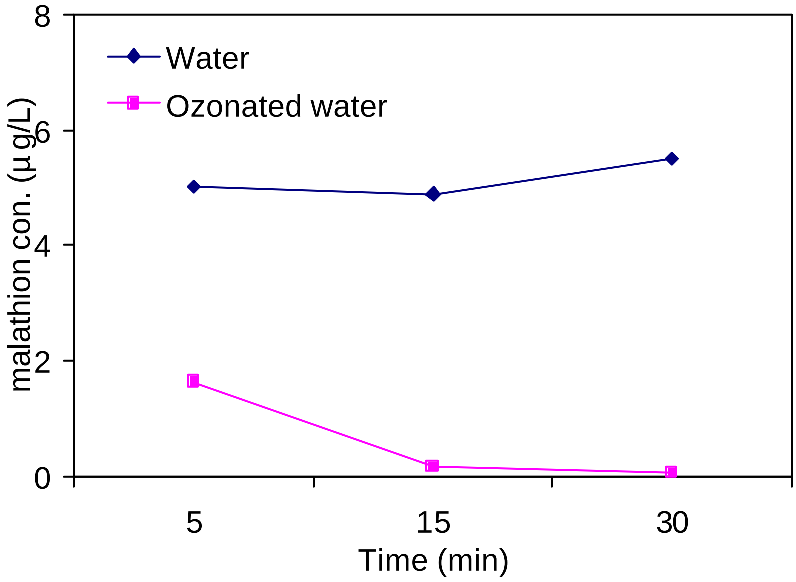

Figure 1. Effectiveness of ozonation treatment on the pesticide residue in the water solution.

Fig. 2 shows the effect of water wash and ozone wash treatments on the pesticide residue in the grape pulp. The total amount of malathion residue on the control water wash grapes was 29 µg/L after 5 min wash. Apparently, there was more malathion residue in the grape pulp than in the wash water. The concentration of malathion in the grape pulp after plain water wash decreased with increasing washing time. The concentration of malathion in the grape pulp with ozonated water wash was about 35% lower than that after plain water wash for all washing times. This is an important finding that supports our earlier hypothesis about the advantage of ozonated water wash over plain water wash, i.e., ozonated water could not only physically remove pesticides from produce surface but also attack pesticides absorbed to the surface layers of produce and reduce pesticide level in wash water.

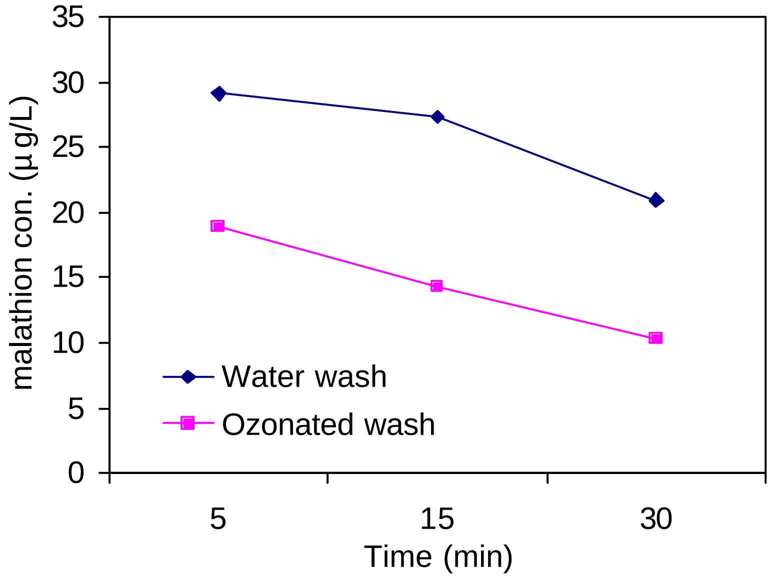

Figure 2. Effectiveness of ozonation treatment on the pesticide residue in the grape pulp.

Conclusions

A laboratory-scale model system was developed to study the effect of ozonated water on degrading pesticides such as malathion. It was found that malathion degraded rapidly in strong alkaline conditions. With the help of ozonation or chlorination, malathion can be completely degraded in strong alkaline solutions in 5 min. Chlorination was slightly better than ozonation in acidic conditions. However, at pH 7, a neutral and practical condition, ozonation performed better than chlorination in degrading malathion. Tests on grapes indicate that ozonation was effective in removing and decomposing malathion sprayed on grapes.

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