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Effects of chlorine, hydrogen peroxide, and ozone on the reduction of mancozeb residues on tomatoes

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Abstract: In this study, the effects of widely used oxidizers (chlorine, hydrogen peroxide, and ozone) on the reduction of mancozeb residues on tomatoes were investigated. Mature tomato samples grown in a greenhouse were treated with mancozeb and collected at different time intervals. Mancozeb residue levels in the samples were determined for each interval using a gas chromatography-mass spectrometry method. A group of the samples with a residue level of approximately 3 mg kg^{-1} was selected for dipping solutions experiments. Selected samples were dipped into the chlorine (10 and 100 mg L^{-1}), hydrogen peroxide (10 and 100 mg L^{-1}), and ozone (1 and 3 mg L^{-1}) solutions for 5, 10, 15, and 20 min. After each experiment, the residues on the samples were analyzed and percent reductions were calculated. The reductions in residual mancozeb were significantly ($P < 0.05$) influenced by dipping into the chlorine, hydrogen peroxide, and ozone solutions as compared to water. The results show that the most effective treatment for the reduction of mancozeb residues from the tomatoes was dipping into the chlorine solution at 100 mg L^{-1} for 20 min.

Key words: Chlorine, dipping solutions, hydrogen peroxide, mancozeb, ozone, tomato

1. Introduction

The tomato (*Lycopersicon esculentum* Mill.) is widely grown and consumed all over the world and thus has been an important staple food in the human diet. World tomato production is 159.023×10^6 t obtained from 4.734×10^6 ha of production area (http://faostat.fao.org). Due to its high economic value, as well as the large number of diseases, insects, and mites that infest tomatoes during growing season, significant quantities of pesticides are often necessary for the protection of this crop. This may lead to residues on (or in) the fruit and vegetable at harvest.

Mancozeb is an important member of ethylene bis-dithiocarbamate (EBDC) fungicides and is used to protect many fruits, vegetables, nuts, and field crops against a wide spectrum of tomato diseases, including downy mildew of tomatoes (http://extoxnet.orst.edu/pips/mancozeb.htm). The official statistics on the use of plant-protection products in the European Union indicate that mancozeb is second on the list of top 10 fungicide active ingredients (mancozeb: 15,946 t, 14.8% of total fungicides) (Nadin, 2007). Chemically, mancozeb is a zinc ion coordination product with a manganese ethylene-1,2-bis-dithiocarbamate polymer. The water solubility of the mancozeb is 6.2 mg L^{-1} at 20 °C, log octanol-water partition coefficient is 1.33, vapor pressure is 0.013 mPa at 25 °C, action mode is nonsystemic, and LD_{50} in mammals is >5000 mg kg^{-1} (http://sitem.herts.ac.uk/aeru/footprint/en/). The toxicity of mancozeb and other metal EBDCs has been attributed to mainly ethylene thiourea (ETU), the major metabolite of mancozeb (Srivastava et al., 2012). ETU is known to have carcinogenic, teratogenic, and goitrogenic effects in rodents (WHO, 1988). Food processing is the major pathway by which exposure to ETU occurs. In particular, thermal treatments are associated with the higher conversion factors of EBDCs to ETU (Knio et al., 2000; Kontou et al., 2004; Kaushik et al., 2009; Certel et al., 2012). Tomato is frequently subjected to thermal treatments such as evaporation, blanching, sterilizing, and canning in order to be consumed as juice, paste, ketchup, or canned products. In addition, home cooking of tomatoes is a common practice. Therefore, mancozeb residues must be removed from tomatoes using proper pesticide residue reducing techniques.

Various techniques have been employed to reduce pesticide concentrations in food commodities (Cengiz et al., 2006, 2007; Basfar et al., 2012; Liang et al., 2012; Yang et al., 2012; López-Fernández et al., 2013). Washing procedures such as dipping into water and rubbing that have been traditionally employed to remove debris and dirt have been shown to reduce pesticide residues. Several

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researchers found that levels of mancozeb residues were reduced by washing procedures (Zhang et al., 1991; Hwang et al., 2001, 2003; Bonnechère et al., 2012; López-Fernández et al., 2013). However, this procedure may be less effective in removing more persistent pesticide residues. Therefore, some chemical agents may need to be added to the washing water to improve the effectiveness of this procedure. The most commonly recommended chemical agents for residue removal purposes are chlorine, ozone, acetic acid, sodium chloride, potassium permanganate, chlorine dioxide, and hydrogen peroxide. The use of these chemical agents has been shown to be effective in the reduction of pesticide residues in food samples (Pugliese et al., 2004; Radwan et al., 2005; Wu et al., 2007; Zhang et al., 2007; Satpathy et al., 2011; Karaca et al., 2012; Liang et al., 2012).

Among various chemical agents, chlorine, hydrogen peroxide, and ozone were selected for this study because they are known to be relatively less toxic and would be good alternatives to complex pesticide reducing techniques. The objective of this study was to determine the effects of these known chemicals on the reduction of mancozeb residues on tomato samples.

2. Materials and methods

2.1. Materials

Carbon disulfide (CS_2) analytical standard was obtained with a purity certificate from Dr. Ehrenstorfer GmbH (Germany). All of the other chemicals were obtained from Merck (Germany). The isooctane was GC grade. Hydrochloric acid (HCl, 37%) and stannous(II) chloride dihydrate were GR grade. Ozone was produced by an ozone generator (Longevity EXT-120; Canada). Dissolved ozone concentration was controlled using the indigo colorimetric method (Clesceri et al., 1998). The water was produced by an ultrapure (18.2 MΩ cm at 25 °C) purification system (Millipore, USA). The commercial mancozeb (Manzate 200) was procured from DuPont (USA).

2.2. Field trials and sampling

Tomato samples were grown in a commercial greenhouse (36°55′54.68″N, 30°43′19.48″E). The absence of mancozeb residues on the samples was confirmed by residue analysis prior to application of commercial mancozeb solution. An aqueous suspension containing commercial mancozeb (wettable powder form) was prepared by mixing 200 g in 100 L of deionized water according to its product label rates. The prepared suspension was uniformly applied to tomato plants using a sprayer.

Mature tomato samples (39 ± 1 g) were collected after a predetermined time interval from the pesticide application. The collected samples were transferred to the laboratory and analyzed immediately. The samples with the residue level of approximately 3 mg kg^{-1}, the maximum residue limit (MRL) value for the mancozeb residue in tomatoes, were selected for dipping solution experiments.

2.3. Dipping solution experiments

All dipping solution experiments were operated in 10-L containers with 5 L of dipping solution to allow for complete submersion of the tomatoes. About 1000 g of tomatoes was placed in the container. The experiments were performed under ambient temperature (ca. 20 °C). The dipping solutions' temperature and pH level were 20 ± 2 °C and 7 ± 0.2 (distilled water), respectively. There were 7 experiments in the study: a) water dipping, b) chlorine dipping at 10 and 100 mg L^{-1}, c) hydrogen peroxide dipping at 10 and 100 mg L^{-1}, and d) ozone dipping at 1 and 3 mg L^{-1}. Control samples were also analyzed prior to each experiment. Selected samples were dipped into the solutions for 5, 10, 15, and 20 min. After each experiment, residues on the samples were analyzed and percent reductions were calculated as compared to the control group.

2.4. Mancozeb residue analyses

Residual mancozeb on the samples was determined using by the method of Cesnik and Gregorcic with some modifications (Cesnik and Gregorcic, 2006). Briefly, 50 ± 0.1 g tomato samples were homogenized with a Warring blender for 3 min at high speed and the obtained homogenate was transferred to sample bottles. Forty milliliters of isooctane and 100 mL of stannous(II) chloride dihydrate solution [4 g of stannous(II) chloride dihydrate in 100 mL of concentrated HCl] were added to the bottle. The bottle was immediately sealed tightly and placed in a shaking water bath at 80 °C for 60 min. Subsequently, the bottle was removed from the water bath and rapidly cooled to room temperature. After cooling, separation of 2 phases (isooctane and tomato homogenate layers) was observed in the bottle. The upper layer, consisting of isooctane, was transferred into a screw-cap sealed vial for the gas chromatography-mass spectrometry (GC-MS) analysis.

A Varian 220-MS GC Ion Trap GC-MS spectrometer equipped with a fused capillary column as VF-5MS (30 m × 0.25 mm × 0.25 µm) was used for the determination of residue in the samples. The oven temperature progression was as follows: a 50 °C initial temperature was held for 2.2 min and then was increased to 270 °C by a rate of 35 °C min^{-1}, and was finally was held for 3 min at this temperature. The injection block, detector, and ion source temperatures were 280, 150, and 230 °C, respectively. Carrier gas (helium) flow through the column was 1 mL min^{-1}. Injection volume was 2 µL and detection was determined in selective ion monitoring mode. Target ion was 76 m/z.

The validation of the analytical method was performed following analytical curves, linearity, limit of detection

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(LOD), limit of quantification (LOQ), and recovery. Linearity was determined by constructing calibration curves with standard solutions. Three injections were performed at each of the 6 concentration levels. The LOD was estimated as 3 times the standard deviation, while the LOQ was estimated as 10 times the standard deviation, which was derived from analyses of 10 independent samples at the lowest calibrated level. For the recovery studies, the mancozeb standard solution was added to chopped blank tomato sample in the blender jar before homogenization.

2.5. Statistical studies

All results were statistically analyzed by analysis of variance ($P < 0.01$). Significant means were subjected to analysis by the Duncan multiple range test ($P < 0.05$). All statistical analyses were performed using the Statistical Analysis System.

3. Results

3.1. Residue analytical methodology

The method used demonstrated acceptable performance for the analysis of mancozeb residues in the tested tomato samples. A good linear relationship with high correlation coefficient values was obtained under the chromatographic conditions. The linearity of the assay was checked by calculating the regression line using the least squares method and expressed by the coefficient of determination, $r^2 > 0.999$. A 6-point calibration curve was obtained in the range from 0.063 to 6.316 mg L^{-1} by plotting the recorded peak area versus the corresponding analyte concentrations. The regression equation for the calibration curve was $y = 4391.550x + 298.440$.

The method was also validated for LOD, LOQ, and recovery studies before the determination of mancozeb levels on the tomato samples. These methodological parameters were optimized by using blank tomato samples. Thus, the LOD, LOQ, and recovery (for 3 mg kg^{-1} mancozeb) were estimated to be 0.013 mg kg^{-1}, 0.043 mg kg^{-1}, and 98.451% (RSD = 1.483, n = 6) respectively. The obtained results from the analytical studies agree with experimental data existing in the literature (López-Fernández et al., 2012).

3.2. Effect of dipping solutions on mancozeb residues

The MRL for mancozeb (as dithiocarbamate) in tomatoes is established as 3 mg kg^{-1} by the European Union (http://ec.europa.eu/sanco_pesticides/public/). Therefore, this level was targeted in our study. The commercial mancozeb solution (200 g 100 L^{-1}) was homogenously sprayed to tomato plants. Mature tomato samples of similar size (39 ± 1 g) were harvested at different time intervals and analyzed in the laboratory for mancozeb residues. Approximately 3 mg kg^{-1} mancozeb was found in the samples, which were collected 24 h after mancozeb treatment. These samples were collected from the greenhouse and treated with various forms of dipping solutions. The percent reductions of mancozeb residues were then calculated by comparing it with the mancozeb residue levels of the control samples.

According to results of variance analysis, significant reductions for mancozeb residue levels were obtained through both types and concentrations of dipping solutions, which were aimed at decreasing pesticide residue ($P < 0.05$). Contact time was also effective on the reduction of mancozeb residue ($P < 0.05$). Water dipping alone was the least effective experiment, while chlorine dipping was the most effective on the reduction of the residue. The initial mancozeb residue level was decreased by 22% in 5 min by the water dipping experiment. No statistical difference was found among the treatment times of 10, 15, and 20 min in these experiments ($P > 0.05$). Obtained results indicate that mancozeb is relatively stable in water for at least 20 min.

Washing is the most common and straightforward form of processing. It is generally the first step in various types of household and commercial food preparation techniques. The residues of contact pesticides that appear on the surface of the plant, loose surface residues, and major portions of polar compounds can be removed with washing processes (Kaushik et al., 2009). In addition, some reducing agents such as chlorine, ozone, and hydrogen peroxide solutions can be used for better reduction of pesticide residues. It was found in this study that chlorine, hydrogen peroxide, and ozone dipping were more effective treatments compared to water dipping. Figure 1 shows percentages of detected average mancozeb residues after chlorine dipping experiments.

It can be seen in Figure 1 that mancozeb residues were gradually decreased, depending on the contact time, at both concentrations of chlorine. The initial mancozeb residue level was decreased by 52% at 10 mg L^{-1} chlorine within

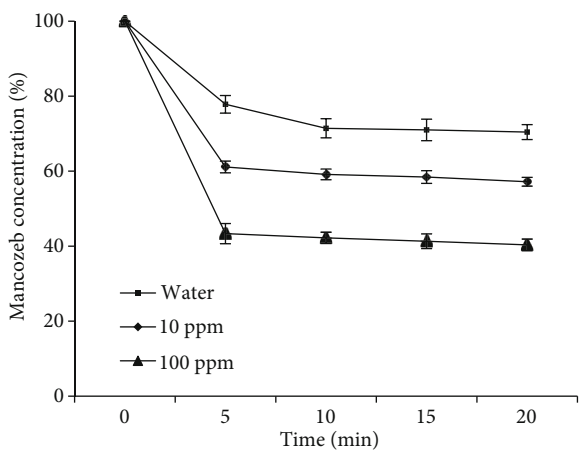

Figure 1. Effect of chlorine solutions treatment on mancozeb residues on tomato samples.

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20 min. On the other hand, a concentration of 100 mg L^{-1} chlorine resulted in substantial reductions of mancozeb residues. This concentration was the most effective in removing residues of mancozeb, with an average of 71% of the residues being eliminated from the samples.

Hydrogen peroxide was the second most effective agent for the reduction of mancozeb residue. The residue levels were decreased by 65% in 20 min by 100 mg L^{-1}. Figure 2 shows the effects of the hydrogen peroxide solutions on the reduction of mancozeb residues on tomato samples. Forty-eight percent and 65% reduction rates were achieved within 20 min using hydrogen peroxide treatment at 10 and 100 mg L^{-1}, respectively.

Dipping into ozonated water resulted in 43% and 60% reductions of the residue levels at 1 and 3 mg L^{-1} ozone concentrations, respectively, within 20 min (Figure 3). Although there was a significant difference between the treated concentrations of ozone, no statistical difference was obtained among 5, 10, 15, and 20 min for each concentration ($P > 0.05$).

4. Discussion

The results showed that the use of chlorine, hydrogen peroxide, and ozone solutions has potential effective postharvest value in the reduction of mancozeb residue on tomatoes.

It was reported that wide ranges of reduction of pesticide residues were obtained by washing treatments. Liang et al. found that the fenitrothion, dichlorvos, dimethoate, trichlorfon, and chlorpyrifos residues in/on cucumber samples were reduced by 13%, 14%, 15%, 22%, and 53%, respectively, by dipping them into tap water for 5 min (2012). Pugliese et al. reported that methidathion, parathion methyl, chlorpyrifos, and pirimicarb residues in/on nectarine samples were decreased by 7%, 15%, 26%, and 34%, respectively, by dipping them into water for 3 min (2004). Cengiz et al. reported that initial diazinon residue level in/on cucumbers was decreased by 22% by rubbing them under running water for 15 s (2006). Satpaty et al. reported that formathion, methyl parathion, fenitrothion, parathion, chlorpyrifos, and malathion residues in tomato samples were reduced by 27%, 32%, 34%, 37%, 39%, and 41%, respectively, by allowing them to be submerged in water for 15 min (2011). It was found that the percentage reduction of mancozeb residues was 29% by dipping in water in this study. These discrepancies among the results of pesticide residue reductions can be attributed to 5 main factors: 1) specifications of the pesticide such as water solubility and octanol-water coefficient, 2) specifications of the food samples such as surface characteristics, 3) conditions during the pesticide application such as temperature and humidity, 4) specifications of the reducing agents such as dissolving properties, and 5) conditions during the reducing agent application such as temperature and pH.

The obtained results from the chlorine experiment were consistent with those of Hwang et al., who found the mancozeb reduction rate to be 56% in apple samples by using 50 mg L^{-1} calcium chloride (2003).

The percent reduction was 64.66 ± 1.71% at 100 mg L^{-1} hydrogen peroxide within 20 min. Hwang et al. (2001) reported that the reduction rate of mancozeb on apples was 82% at 50 mg L^{-1} hydrogen peroxide within 15 min. These differences may be explained by the differences of the surface characteristics between tomatoes and apples. Apple cuticle consists of 44.7% waxes, whereas tomato cuticle contains 6.5% waxes (Chen et al., 2008). The apple cuticle membrane thus contains much higher levels of waxes than that of tomato. Therefore, a weaker interaction might be occurring between mancozeb molecules and

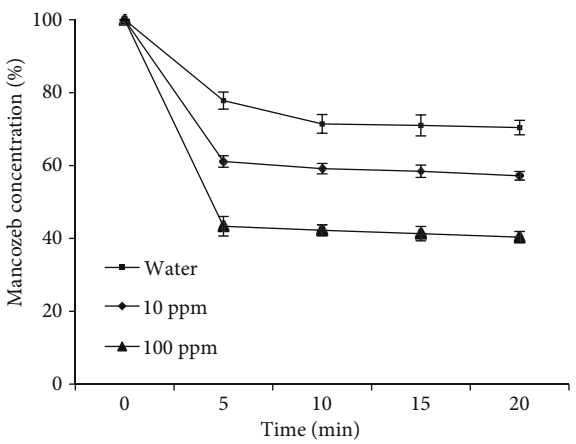

Figure 2. Effect of hydrogen peroxide solutions treatment on mancozeb residues on tomato samples.

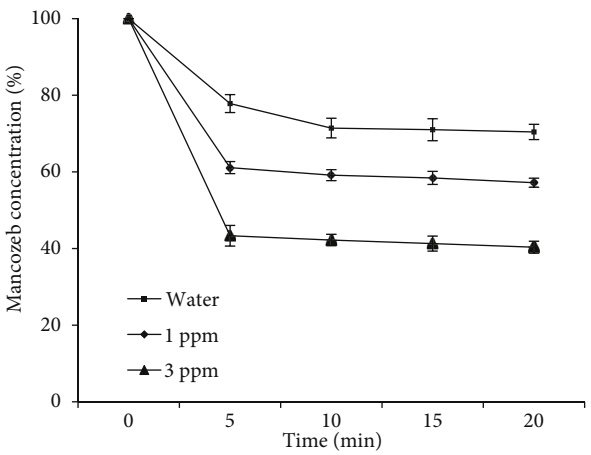

Figure 3. Effect of ozone solutions treatment on mancozeb residues on tomato samples.

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apple cuticle when compared to tomato cuticle. As a result, it can be said that the solution of hydrogen peroxide may be more effective in apples than in tomatoes.

The findings of ozone experiments were consistent with those of Wu et al., who found that 53% of diazinon, 55% of parathion, 47% of methyl parathion, and 61% of cypermethrin were removed from brassicaceous vegetables using 2.0 mg L^{-1} dissolved ozone concentration for 30 min. The authors also reported that the degradation was mostly completed in the first 5 min (Wu et al., 2007). Similar results were obtained in this study. We found that the level of mancozeb was reduced by 60% by dipping into ozonated at water 3 mg L^{-1} ozone concentration and the major reduction of the residue level was observed within 5 min. It could be possible, therefore, that dissolved ozone is unstable. A great proportion of dissolved ozone would escape to the ambient or reduce to oxygen molecules in a few minutes. Therefore, reduction levels of the mancozeb residue remained constant in the ozone treatment.

In 1997, an expert panel of the US Food and Drug Administration reviewed the safety and potential for food-processing use of ozone and declared ozone to be generally recognized as safe for food contact applications. Since that time, interest in developing ozone applications in the food industry has increased. However, it can be argued that toxic intermediates will also be generated under natural environment in exposure to oxygen. Ozone and other oxidants can speed up the mineralization process for complete degradation of the toxic intermediates and ultimately lead to the formation of CO_2. Therefore, the levels of possible by-products and toxic intermediates should be considered at high levels of oxidizing agent treatment. In conclusion, mancozeb has been one of the most commonly used fungicides in commercial use for several decades. Residues of mancozeb have been regularly detected in fruit and vegetables. It has been shown that a significant percentage of ETU may be produced during thermal treatment of food products contaminated with mancozeb. ETU is known to have carcinogenic, teratogenic, and goitrogenic effects in rodents. On the other hand, the tomato is a widely consumed food product that is often subjected to thermal treatment. Therefore, there is an increasing need to develop techniques to reduce mancozeb residue levels in tomatoes. We found that water was the least effective experiment, whereas the 100 mg L^{-1} chlorine solution for 20 min was the most effective treatment in removing mancozeb residues. Further research needs to be done on more effective techniques for the removing of this kind of pesticide and its degradation products.

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