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REDUCTION OF PESTICIDE RESIDUES FROM SURFACE OF FRESH TOMATOES USING OZONE (MICROBUBBLE) TREATMENT

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Abstract: The research has looked at the effectiveness of washing tomatoes with ozonated water before processing. Washing was done by immersion in water with O_3 micro bubbling at 2.5 mg L^{-1} for 5 and 10 minutes, respectively at the temperature of 15°C. The removal of residues generated by treating tomatoes with Cyperguard 25 EC, Dithane M-45 and Topsin 70 WDG was examined. Mass spectrometry was used to determine the residues. At V1, the variant treated with Cypermethrin, the second and fourth peak have recorded the values of 0.6 mg/kg > 0.5 mg/kg, the value accepted as the maximum allowed limit. The analysis data confirmed that the solution used was significantly effective in removing pesticide residues, applied before the harvest.
Keywords: ozone; immersion; bubbling; pesticide residues

INTRODUCTION

The requirements regarding the existence of safe foods on the market, makes the food industry promote innovative technologies, in order to obtain high quality products with a high retention of nutrients and a sensory quality able to satisfy consumer demand.

In the case of vegetable origin food production, the problem of eliminating contaminants generated by the treatments carried out against pathogenic and harmful agents on the raw materials (vegetables and fruits) is a priority issue. Research has shown that they are persistent and their residues decrease very slowly (Nowacka A., 2009), so that the levels of benomyl, carbendazim, methyl thiophanate and thiabendazole residues were stable in apples stored at 0 - 2°C, and after 140–150 days the active ingredients were at 36– 60% of the initial level (Holland P. T. 1994).

The washing phase using various agents, a component of the technological flow of processing vegetables and fruits, achieves the reduction of impurities.

The efficiency of washing is influenced by several factors such as: the time elapsed since the last treatment and the location of the residue on the surface of the fruit, as well as the water solubility of a certain residue. The type of detergents as well as the temperature of the solution in which the washing is carried out, can considerably improve the efficiency of the process (Holland P. T. 1994).

The current trend to use "greener" food additives and the fact that regulatory authorities have approved and accepted that ozone can be used in green technologies, has led to the development of a number of ozone-based treatment solutions / systems.

Ozone (O3) acts against a wide spectrum of microorganisms, which makes it considered among the most powerful hygiene products. Ozone is found in the atmosphere and is the highly oxidizing allotropic form of oxygen (Eo = 2.07 V), so it can oxidize many organic compounds.

The way of generating ozone by passing air or gaseous oxygen through a high-voltage electric discharge, or by irradiating ultraviolet light, made it easy to use for sterilization, inactivation of viruses, deodorization, bleaching (discoloration), decomposition of organic matter, degradation of mycotoxins and others (Balawejder M. 2013). Due to the fact that ozone has the property of converting to oxygen through autolysis, it is recognized as safe for food contact applications.

Essentially, the reduction of chemical contaminants in food products with ozone is based on two different processes, i.e. washing with aqueous ozone solutions and gas phase ozone treatment. In current technologies fruits and vegetables, during the washing phase, can be sprayed/immersed in aqueous ozone solution.

MATERIALS AND METHODS

The research was carried out within the ADER 7.5.1 project, financed by the Ministry of Agriculture and Rural Development through the Sectoral Plan for research and development in the field of agriculture and rural development - ADER 2022, where ICDIMP-Horting and INMA Bucharest were partners.

In order to ensure the effective washing of fruits and vegetables to remove residues from the active ingredients of pesticides used in the treatments carried out in horticultural crops, the following requirements must be met: the source of obtaining ozone must be atmospheric air; achieving an optimal concentration of O3 in the washing water; adapting the flow of ozonated solution to the working capacity of the washing installation.

Taking into account these requirements, the research team designed and built a demonstrative laboratory installation shown schematically in figure 1.

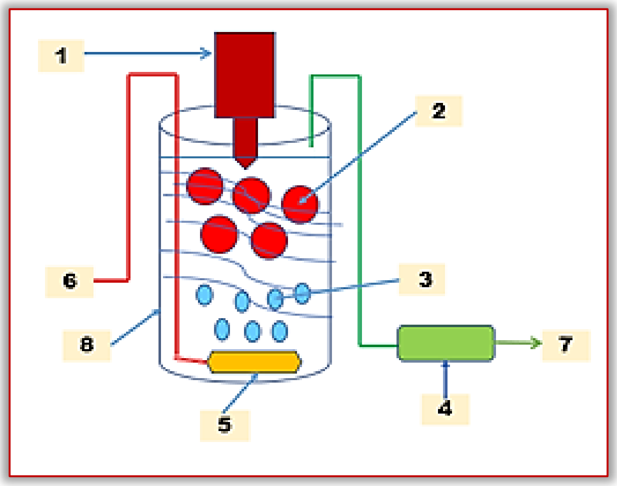

Figure 1 - Demonstrative installation for the use of ozone to remove pesticide residues
1 – O_3 concentration measuring device; 2 - Tomatoes treated with O_3 aqueous solution; 3 – Ozone; 4 - O_3 destruction unit; 5 – O_3 diffuser; 6 – Outlet from the ozone generator; 7 – Air outlet; 8 – Experimental vessel

The tomatoes were treated with the following substances:

— pyrethroid insecticide Cyperguard 25 EC, contains the active substance Cypermethrin 250g/l, is generally miscible with other fungicides, insecticides or foliar fertilizers and requires a pause time of 14 days;
— the systemic fungicide Topsin 70 WDG has Thiophanate methyl 70% as its active substance, and the pause time from the last treatment until harvesting is 3 days for vegetables and melons and 15 days for fruit trees and vines;
— contact fungicide, Dithane M-45 with active substance Mancozeb 80%, in which the pause time from the last treatment to harvesting is recommended to be 21 days for tomatoes treated to prevent brown spot and 14 days for the other diseases, 28 days when treating the trees (plum, apricot, peach), 28 days after treating the vine manna.

Starting from the scheme shown in figure 1, in order to carry out the laboratory determinations, the experimental installation shown in figure 2 was created.

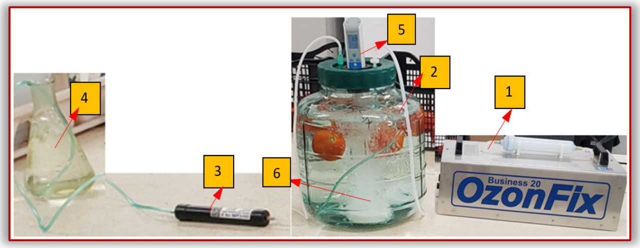

Figure 2 - Experimental installation
1- Ozone generator, 2- Wash vessel, 3- Residual ozone destruction unit, 4- Final residue collection vessel, 5- Apparatus for measuring the concentration of aqueous ozone solution, 6. Ozone diffuser (bubble stone)

The experiments were carried out on tomatoes, in order to establish the usefulness of ozone treatment for decontamination of the external surfaces of these fruits, before their use in processing technologies to obtain tomato juice or paste.

The variants and treatment parameters in the case of tomatoes are those presented in table 1.

Table 1. Variants and parameters of tomato treatment with ozonated water by bubbling

Treatment substances	Cyperguard 25 EC		Dithane M-45		Topsin 70 WDG	
Variants	V1	V2	V3	V5	V6	V7
No. fruits	8	8	8	8	8	8
Solution temperature (^{0}C)	15.00	15.00	15.00	15.00	15.00	15.00
Treatment duration (min)	5	10	5	10	5	10
O3 concentration (mg/l)	2.50	2.50	2.50	2.50	2.50	2.50
Control variants	M1		M2		M3	

During the experiments, the variable was the treatment duration of 5 and 10 minutes respectively. Aspects regarding the treatment method (bubble washing) can be found in figure 3.

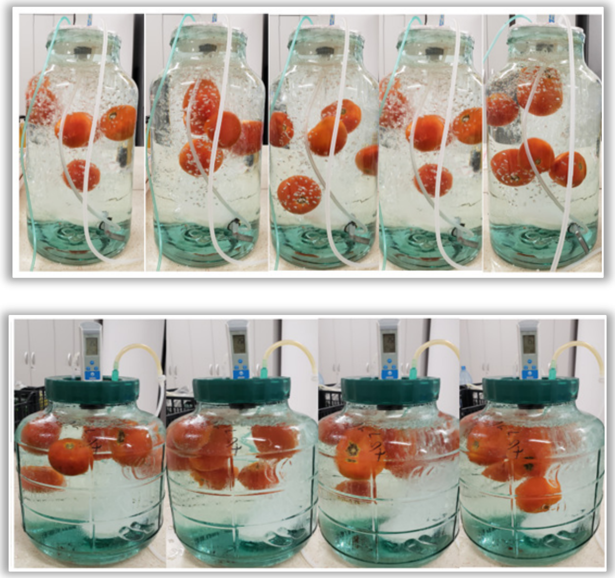

Figure 3 - Aspects of the washing process in O_3 solution

After performing these treatments, the samples were sent to the laboratory for residue determination using mass spectrometry.

The analyzes were carried out in the SC Holland Farming Agro SRL laboratory, on a GC-MSMS Thermo Scientific equipment, using the working procedure according to SR EN 15662:2018, for vegetable matter, with U% ≥ 80%.

RESULTS

In the tomato samples, pesticide residues were determined for the treatment with Cyperguard 25 EC pyrethroid insecticide (table 2).

Table 2. Pesticide residues after treatment with Cyperguard 25 EC

Pesticide residues	Concentration (mg/kg)	Maximum admissible limit (mg/kg)
M1 - control		
Cypermethrin 1	2.91	0.05
Cypermethrin 2	2.75	0.05
Cypermethrin 3	1.08	0.05
Cypermethrin 4	3.28	0.05
Treatment for 5 minutes – V1		
Cypermethrin 1	0.5	0.05
Cypermethrin 2	0.6	0.05
Cypermethrin 3	0.3	0.05
Cypermethrin 4	0.6	0.05
Treatment for 10 minutes V2		
Cypermethrin 1	0.2	0.05
Cypermethrin 2	0.2	0.05
Cypermethrin 3	0.1	0.05
Cypermethrin 4	0.2	0.05

In the treatments with Topsin 70 WDG and Dithane M-45 the concentration values determined for residues were < 0.01 (mg/kg) at a maximum allowed limit of 0.05 (mg/kg).

In the graph in figure 4, the values of the pesticide residues are represented comparatively, when the tomatoes were treated with Cyperguard 25 EC.

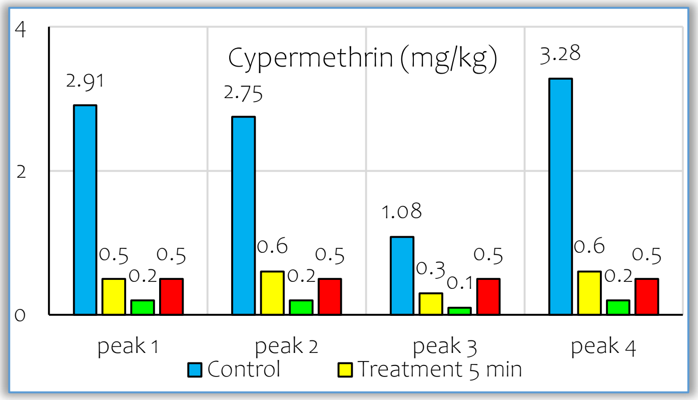

Figure 4 - Comparative values of the residues recorded when treated with Cyperguard 25 EC

Compared to the contamination values recorded in the control variant, when treated with ozonated water for 5 minutes, the determined values fluctuate around the allowed values (0.5 mg/kg), and the 10-minute treatment ensures that the determined values fall below the admissible limit.

CONCLUSIONS

The process of washing vegetables and fruits is mandatory before processing or consumption. This can be done by immersing in water or detergent solution, which removes a considerable part of the pesticides present in tomatoes. Washing tomatoes in water saturated with O_3, with or without bubbling, is an efficient and environmentally friendly method of removing residues. In addition to the process of removing residues from the surface of tomatoes, there is also the possibility of their degradation. The treatment with a concentration solution of 2.50 mg/l ozone carried out for 10 minutes ensured the effective removal of pesticide residues generated by the treatment with Cyperguard 25 EC carried out 24 hours before. The use of ozone in the technological phases of processing and/or storage increases the shelf life of the products; however, it is important to consider the concentration applied because a high concentration of O_3 can cause oxidation damage and changes in the color of the product.

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