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# Decontamination Techniques of Pesticide Residues before Food Processing or Consumption

Mehmet Fatih Cengiz, Muharrem Certel

Akdeniz University, Faculty of Engineering, Food Engineering Department, Antalya, Turkey

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✉ *Corresponding author (Yazışmalardan Sorumlu Yazar): fcengiz@akdeniz.edu.tr (M.F. Cengiz)*
✆ 0 246 311 66 61 ℻ 0 246 311 63 94

## ABSTRACT

Food is the basic necessity of life, and foods contaminated with toxic pesticides are associated with severe adverse effects on the human health. Therefore, there is a need of certain techniques for eliminating these pesticide residues on fresh produce for safe consumption. The washing of raw materials is the simplest way to reduce the pesticide residue in the final product. The more effective and convenient alternative could be used with dilute solutions of other chemicals such as chlorine, chlorine dioxide, hydrogen peroxide, ozone, acetic acid and sodium chloride depending upon the type of food. An important point to be considered is that these chemical may produce byproducts as a result of reactions between chemical and pesticides in raw material. Therefore, suitable chemicals and controlled dose should be considered when using these chemicals. The purpose of this review is to present recent research about the influence of some washing treatment on pesticide residues.

**Key Words:** Pesticide residue, Decontamination, Chemical agent, Food processing

## Gıda İşleme veya Tüketimi Öncesi Tarım İlacı Kalıntılarını Arındırma Teknikleri

Gıda hayatın temel ihtiyacıdır ve zehirli tarım ilaçları ile bulaşmış gıdalar insan sağlığı üzerine ciddi olumsuz etkiler ile ilişkilendirilmiştir. Dolayısıyla, taze ürünlerde bu tarım ilacı kalıntılarını gidermek amacıyla güvenli tüketim için bazı tekniklere ihtiyaç vardır. Hammaddelerin yıkanması son üründeki tarım ilacı kalıntısını azaltmak için en basit yoldur. Bununla birlikte klor, klor dioksit, hidrojen peroksit, ozon, asetik asit ve sodyum klorürün seyreltik çözeltileri gibi daha etkili ve uygun alternatifler gıdaya bağlı olarak kullanılabilmektedir. Bu kimyasallar kullanıldığı zaman göz önünde bulundurulması gereken önemli bir nokta, hammaddedeki kimyasallar ile tarım ilacı arasında gerçekleşen reaksiyonlar sonucu olarak ara ürünlerin oluşabilmesidir. Bu nedenle, bu kimyasallar kullanıldığı zaman uygun kimyasallar ve kontrol edilmiş dozlar dikkate alınmalıdır. Bu makalenin amacı bazı yıkama uygulamalarının tarım ilacı kalıntıları üzerine etkisini değerlendirmek için yakın zamandaki araştırmaları derlemektir.

**Anahtar Kelimeler:** Pestisit kalıntısı, Arındırma, Kimyasal ajan, Gıda işleme

## INTRODUCTION

Pesticides are chemical substances that are widely used against plant pests and diseases. The use of pesticides in commercial agriculture has led to an increase in farm productivity. Their residues in fruits and vegetables are a major concern to consumers due to their negative health effects. A substantial body of laboratory and epidemiological evidence suggests that certain pesticides are associated with carcinogenesis, immunotoxicity, neurotoxicity, behavioural impairment, reproductive dysfunction, endocrine disruption, developmental disabilities, skin conditions, and respiratory diseases such as asthma [1].

The main exposure to pesticides for humans is via food (especially by fruit and vegetables), contributing five times more than other routes, such as air and drinking water [2]. Food and health authorities around the world are continuously monitoring pesticide residues in fruits and vegetables. The maximum allowed concentrations of pesticide residues in food products can be explained in the term of MRL. Governments and international organizations are regulating the use of pesticides setting the acceptable MRLs in foods. When these compounds are applied according to good agricultural practices, MRLs are not exceeded, but their incorrect application may leave harmful residues, which involve possible health risk and environmental pollution.

Food processing techniques can have an important effect in reducing consumer exposure to pesticide residues in fruits and vegetables. Through these techniques, pesticides can be degraded to innocuous products, such as carbon dioxide, water and inorganic constituents. However, some intermediate products, by-products, degradation products and/or metabolites formed can be more toxic and persistent than the parent compounds. Therefore, the level of these toxic compounds formed as a result of pesticide degradation should be seriously taken into consideration in food commodities during food processing. An example of this is the degradation of ethylene-bis-dithiocarbamates (EBDCs) to ethylenethiourea (ETU) which is far more toxic than the parent compound [3]. ETU is classified by US NIOSH as a carcinogen for humans by IARC as group 2B on the basis of sufficient evidence of carcinogenicity in animals but not in humans [4]. Levels of ETU can increase when products are processed, especially during cooking [5, 6]. Therefore decontamination techniques before food processing or consumption have an important role, not only in the reduction of residues, but also the conversion of degradation products which pose a serious threat to human health.

Residual pesticides on food materials can decrease by various decontamination techniques prior to processing or consumption depending on the type and properties of the pesticides such as water solubility, hydrolytic rate constant, volatility and octanol-water partition coefficient. Washing is the most common form of decontamination techniques which is a preliminary step in both household and commercial preparation. The residues of contact pesticides that appear on the surface of the plant can be removed with reasonable efficiency by washing processes. Although washing with tap water has led to a significant reduction in residue concentrations for some pesticide classes, certain pesticide residues are not significantly lowered by rinsing with water alone. Krol and co-workers have reported that a reduction in levels associated with washing or rinsing also is impacted by whether the pesticide is a systemic or surface-acting pesticide [7]. The residues of surface acting pesticides can be removed with reasonable efficiency by washing processes. There are several studies that have examined the effects of washing on removing pesticide residues [8-11]. On the other hand, because systemic pesticides translocate throughout plants, removal of these pesticides via rinsing with water or other surface treatment is less effective [7].

The use of washing procedure has shown potential as an effective treatment in the reducing pesticides residue. However, the process may show less effect on removing more persistence pesticide residues. Therefore, there is a need certain techniques for eliminating these pesticide residues on fresh produce for safe consumption. Some chemical agents can be added to the wash water to improve the effectiveness of the washing procedure. Added agents to the washing water can cause a decrease in the pesticide residue much more than water by affecting the chemical bonds between pesticide and plant surface into the dipping solutions. There are great deals of dipping solutions for the reduction of pesticide residues in food commodities. The most commonly recommended chemical agents for residue removal purposes are chlorine, ozone, acetic acid, sodium chloride, chlorine dioxide and hydrogen peroxide. These agents have been employed historically for the oxidation of organic compounds at water treatment plants and have received a good deal of attention for their capacity to degrade organic pesticides.

Chlorine is a very potent disinfectant with powerful oxidizing properties. It is soluble in water, either by injection of chlorine gas or by the addition of hypochlorite salts. Chlorine as sodium, potassium, or calcium hypochlorite has been used for many years by the food industry and public water suppliers as their principal sanitizing and disinfecting agent [12]. Hypochlorites are powerful disinfectants which are active against a wide spectrum of organisms, and they are nontoxic to humans at low concentrations [13]. Many organic compounds present in foods and water treated with chlorine are subjected to chlorination reactions. When chlorine is applied onto organic molecules, their hydrophobicity or lipophilic nature increases. This in turn often increases the toxicity and bioaccumulation of these compounds. There are potential health hazards connected with the use of chlorine because reaction products that are formed have toxic activity such as mutagenicity, teratogenicity, or carcinogenicity [14].

The use of postharvest chlorine dips has shown potential as an effective postharvest treatment in the reducing pesticides residue. However, potential hazards have been associated with chlorine-based compounds. The use of ozonated water dips is an alternative postharvest treatment method [15]. Ozone (CAS No. 10028-15-16) is a gas at ambient and refrigerated temperatures. It is a powerful oxidant that can react with numerous organic chemicals. The oxidation potential of ozone (2.07V) is higher than HOCL and free chlorine. In 1997, an expert panel reviewed the safety and potential for food processing use of ozone and declared ozone to be Generally Recognized as Safe (GRAS) for food contact applications [16]. Their declaration of GRAS status for ozone was submitted to the Food and Drug Administration and its use on food products is legal in the United States [17]. Since that time, interest in developing ozone applications in the food industry has increased. Many applications appear in the food industry. Dissolved ozone has been used in water for sanitizing surfaces of vegetables, fruits and other agricultural products. Ozone can oxidize many organic compounds, particularly those with phenolic rings or unsaturated bonds in their structure and can have a role in reducing pesticide residues in process water [18, 19]. Ozone has one of the highest standard redox potentials, lower only than those of the fluorine atom, oxygen atom, and hydroxyl radical as shown in Table 1. Because of its high standard redox potential, the ozone molecule has a high capacity to react with numerous compounds by means of this reaction type [20].

Table 1. Standard redox potential of some oxidant species

| Oxidant Species | $E_o$ (Volts) | Relative Potential of Ozone |
|---|---|---|
| Fluorine | 3.06 | 1.48 |
| Hydroxyl radical | 2.80 | 1.35 |
| Atomic oxygen | 2.42 | 1.17 |
| Ozone | 2.07 | 1.00 |
| Hydrogen peroxide | 1.77 | 0.85 |
| Permanganate | 1.67 | 0.81 |
| Chlorine dioxide | 1.50 | 0.72 |
| Hypochlorous acid | 1.49 | 0.72 |
| Chlorine | 1.36 | 0.66 |
| Hydrogen peroxide | 0.87 | 0.42 |
| Oxygen | 0.40 | 0.19 |

Like ozone, chlorine dioxide is another good disinfectant and can kill a large number of microorganisms, including some that are resistant to treatment with chlorine [21]. Chlorine dioxide has been used since 1944 by the food industry as a sanitizing and disinfecting agent and for oxidizing organic compounds at water treatment plants. It has a greater oxidizing capacity than chlorine and does not react with ammonia or nitrogenous compounds like chlorine [22]. It has been reported that pesticides can be removed by chlorine dioxide, particularly aldrin and methoxychlor. Herbicides such as paraquat and diquat are eliminated within a few minutes at a pH higher than 8 [23].

Additionally it was reported that the hydrogen peroxide have been employed for the oxidation and degradation of some organic pesticides. Hydrogen peroxide ($H_2O_2$) is classified as generally recognised as safe (GRAS) for use in food products as a bleaching agent, oxidising and reducing agent and antimicrobial agent [24]. The antimicrobial properties of $H_2O_2$ have long been recognized. Dilute $H_2O_2$ is used as a topical disinfectant and available as a consumer product. $H_2O_2$ vapour shows promise as a sterilizing agent for medical equipment and supplies [25].

In addition, various agents such as sodium chloride, acetic acid, potassium permanganate and sodium carbonate have been used for the reduction of pesticide in food commodities. The summary of representative results of pesticide residue reductions by these applications are illustrated in Table 2.

## CONCLUSION

It can be concluded that, the pesticide residues in food can be affected in various levels by the washing solutions. This affection largely depends on the physicochemical properties of the pesticide and chemical agent as well as the type of food processing techniques. But peoples are not able to know beforehand these properties of pesticides in their consumed food in order to selection of chemical agents. Therefore, first and foremost the application of pesticides in farms should be in compliance with good agricultural practices, using only the required amounts. Further the processes such as controlled dose setting for the use of pesticides, controlled greenhouse treatments, harvest and storage processes, and applications before consumption have a crucial role in the reduction of residual pesticides which pose a serious threat to human health and the environment.

In addition, these chemical agents may produce byproducts as a result of reactions between agents and pesticides in raw material, and it has been reported that for some organophosphate pesticides, the degradation by-products have higher toxicity than the original pesticides themselves. Therefore suitable chemicals and controlled dose should be considered when using these chemicals. It has also been suggested that the fruit and vegetable may want repeated rinses or washes with water if the chemical washing technique is used.

Table 2. Effect of decontamination techniques on pesticide residue dissipation.

| Agent | Conc. | Duration (min) | Commodity | Pesticide | Initial Conc. (ppm) | Reduction% | Reference |
|---|---|---|---|---|---|---|---|
| Acetic acid | 0.1% | 15 | Chinese-Kale | Methomyl | 58.72 | 43.40 | [26] |
| | | | | Carbaryl | | 90.46 | |
| Acetic acid | 2% | 1 | Sweet Pepper | Profenofos | 0.31 | 85.48 | [27] |
| | | | Hot Pepper | | 0.66 | 60.61 | |
| | | | Eggplant | | 0.15 | 100 | |
| Acetic acid | 10% | 30 | Cucumber | Diazinon | | 69.0 | [28] |
| | | | | Profenofos | | 67.8 | |
| | | | | Quinalphos | | 63.4 | |
| | | | | Chlorpyrifos | | 61.9 | |
| | | | | Chlorothalonil | | 58.6 | |
| | | | | α-Endosulfan | | 58.3 | |
| | | | | β-Endosulfan | | 57.0 | |
| Acetic acid | 10% | 20 | Cabbage | Chlorpyrifos | 1.19 | 79.8 | [29] |
| | | | | *p,p*-DDT | 1.17 | 65.8 | |
| | | | | Cypermethrin | 1.31 | 74.0 | |
| | | | | Chlorothalonil | 1.12 | 75.0 | |
| Calciumhypochlorite | 50ppm | 5 | Apple | Mancozeb | 2 | 40 | [30] |
| | | 15 | | | | 70 | |
| | | 30 | | | | 80 | |
| Calciumhypochlorite | 250ppm | 5 | Apple | Mancozeb | 2 | 80 | [30] |
| | | 15 | | | | 90 | |
| | | 30 | | | | 99 | |
| Chlorinedioxide | 5ppm | 5 | Apple | Mancozeb | 2 | 43 | [30] |
| | | 15 | | | | 62 | |
| | | 30 | | | | 70 | |
| Chlorinedioxide | 10ppm | 5 | Apple | Mancozeb | 2 | 48 | [30] |
| | | 15 | | | | 68 | |
| | | 30 | | | | 78 | |
| Hydrogenperoxyacetic acid | 5ppm | 5 | Apple | Mancozeb | 2 | 55 | [6] |
| | | 15 | | | | 82 | |
| | | 30 | | | | 90 | |
| Hydrogenperoxyacetic acid | 50ppm | 5 | Apple | Mancozeb | 2 | 85 | [6] |
| | | 15 | | | | 99 | |
| | | 30 | | | | 100 | |
| Ozone | 1ppm | 5 | Apple | Mancozeb | 2 | 40 | [6] |
| | | 15 | | | | 73 | |
| | | 30 | | | | 95 | |
| Ozone | 3ppm | 5 | Apple | Mancozeb | 2 | 85 | [6] |
| | | 15 | | | | 90 | |
| | | 30 | | | | 99 | |
| Potassiumpermanganate | 0.001% | 15 | Chinese-Kale | Methomyl | 58.72 | 47.57 | [26] |
| | | | | Carbaryl | 363.82 | 93.50 | |
| Sodiumcarbonate | 0.1% | 15 | Chinese-Kale | Methomyl | 58.72 | 43.19 | [26] |
| | | | | Carbaryl | 363.82 | 91.24 | |
| Sodiumchloride | 0.9% | 15 | Chinese-Kale | Methomyl | 58.72 | 39.33 | [26] |
| | | | | Carbaryl | 363.82 | 91.18 | |
| Sodiumchloride | 1% | 1 | Sweet Pepper | Profenofos | 0.31 | 78.84 | [27] |
| | | | Hot Pepper | | 0.66 | 79.85 | |
| | | | Eggplant | | 0.15 | 97.41 | |
| Sodiumchloride | 10% | 20 | Cabbage | Chlorpyrifos | 1.19 | 67.2 | [29] |
| | | | | *p,p*-DDT | 1.17 | 65.0 | |
| | | | | Cypermethrin | 1.31 | 73.3 | |
| | | | | Chlorothalonil | 1.12 | 74.1 | |
| Sodiumhydroxide | 0.1% | 1 | Sweet Pepper | Profenofos | 0.31 | 79.35 | [27] |
| | | | Hot Pepper | | 0.66 | 65.15 | |
| | | | Eggplant | | 0.15 | 92.22 | |
| Water | | 0,25 (running tap water) | Cucumber | DDVP Diazinon | 1.74 | 22.4 | [9] |
| | | | | | 0.82 | 22.3 | |
| Water | | 0,25 (running tap water) | Tomato | Procymidone | 0.86 | 68 | [10] |
| | | | | Captan | 0.83 | 89 | |
| Water | | 0,5 | Bitter Gourds | Endosulfan | | 59.05 | [31] |
| Water | | 10 | Mango Fruit | Dimethoat | | 66-68 | [32] |
| | | | | Fenthion | | 66-68 | |
| | | | | Fenvelerat | | 21-27 | |
| | | | | Cypermethrin | | 21-27 | |
| Water | | 15 | Chinese-Kale | Methomyl | 58.72 | 37.90 | [26] |
| | | | | Carbaryl | 363.82 | 88.77 | |
| Water | | 20 | Cabbage | Chlorpyrifos | 1.19 | 17.6 | [29] |
| | | | | *p,p*-DDT | 1.17 | 17.1 | |
| | | | | Cypermethrin | 1.31 | 19.1 | |
| | | | | Chlorothalonil | 1.12 | 15.2 | |

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