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Removal of pesticide residue from cherry tomatoes by hydrostatic pressure (Part 2)

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ABSTRACT

The food safety for polluted products has ignited more considerable interest in recent years. Internal penetrated and insoluble materials possess high persistence, and removing them is desired in the process of producing food. Hydrostatic pressure is a potential technology to efficiently inactivate the vegetative microorganisms, to extract internal substance and to remove hydrophobic matter from products as pressure level is controlled. Here we applied hydrostatic pressure to remove hydrophobic pesticide from cherry tomato loaded with close to maximum residue limits. Removing insoluble pesticide from products with several processing was reported, but so far complete removal has not been achieved. Taking these results into consideration, hydrostatic pressure with ethanol solution as the surrounding medium were performed, and led to complete removal at comparatively low pressure. Under these conditions, visual changes did not occur, toxic intermediates from pesticide were not detected, and nutrients from the samples were identified in the surrounding medium.

Industrial Relevance: This article demonstrates that hydrostatic pressure treatment with 10% ethanol solution can be a potential washing technology from the perspective of safety and harmless: can remove pollutant from cherry tomatoes and collect it from surrounding medium of them, without bringing about pollutant breakdown into more toxic materials. We believe that the existence of this treatment will be known as one of the safety food washing process among readers of your journal, and may eventually be used for food safety in the process of producing food.

1. Introduction

The safety and quality of food products are among the most important factors influencing consumer choices in modern times, as well as being the most important considerations of food manufacturers and distributors (Cardello, Schutz, & Lesber, 2007; Ohlsson, 1994). Indeed, following the 2008 frozen dumpling scandal and the 2011 Fukushima Daiichi nuclear plant accident in Japan, these concerns are now at unprecedented levels. Food safety associated problems include illnesses, deaths, product recalls, industry bankruptcies, job losses, overall economic losses, and tension in international relations. It is therefore of utmost importance for the food industry to continue to seek out more effective methods to remove pollutants from products and reduce undesirable changes in foods associated with food processing. The pollutions may include chemicals that cause acute or long-term toxicity, biological agents such as pathogenic bacteria, viruses, parasites and abnormal prions causing transmissible spongiform encephalopathies, or physical objects, but we focus on chemicals. It is well known that the soluble pollutant on products surface is washed with water easily, while insoluble one has high persistence on food and followed by the potential to threaten human health (Chavarri, Herrera, & Arino, 2005; Mukherjee, Kole, Bhattacharyya, & Banerjee, 2006; Nagayama, 1996; Zhang, Liu, & Hong, 2007). In addition, the substance infiltrated into food products also possesses high persistence.

There have been several reports of washing method for food products, in which pesticides were employed as pollutants. Pesticides can also be roughly classified into water-soluble and hydrophobic (water-insoluble); the latter exhibits higher residual levels in food production. Several washing solutions such as chlorine solution, ozonated water and strong acid have been proven to successfully remove even hydrophobic pesticide residues during the commercial crop process (Ikeura, Kobayashi, & Tamaki, 2011a, 2011b; Ong, Cash, Zabik, Siddig, & Jones, 1996; Pugliese et al., 2004; Wu, Luan, Lan, Lo, & Chan, 2007; Zohair, 2001). Additionally, the ultrasonic removal of hydrophobic pesticide residues in fruit has been studied (Kimura & Ogawa, 1976; TianLi, ZhengKun, YaHong, ZhenPeng, & XiaoRong, 2009; Yamashita, Noma, & Honda, 2009). Other reports have concluded that the water solubility of pesticides does not play a significant role in their reducibility in different commodities by washing (Cabras et al., 1997; Guardia-Rubio, Ayora-Cañada, & Ruiz-Medina, 2007; Krol, Arsenault, Pylypiw, & Incorvia Mattina, 2000), and partition coefficients between cuticle and water were found to correlate well with octanol/water partition coefficients, as reported by Baur, Marzouk, Achönherr, and Grayson (1997). While the residue removal mechanism is complicated, the issue seems to be generally based on form, material structures and

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Table 1
Chlorpyrifos (CP) concentration for cherry tomato, remaining 24 h after immersing into aqueous mixture of CP, and after each hydrostatic pressure treatments for CP loading samples. All values are the mean ± standard error ($n = 10$).

CP conc of non treatment (mg/kg)	Water		High hydrostatic pressure		
	Processing	CP residues (mg/kg)	Pressure (MPa)	5 °C	25 °C
				CP residues (mg/kg)	CP residues (mg/kg)
7.6 ± 0.2	Rinsing	6.1 ± 0.6 ab*	25	3.7 ± 0.1 b A**	4.3 ± 0.2 c B
	0.1 MPa 5 °C	5.5 ± 0.1 a	50	2.1 ± 0.1 c A	3.4 ± 0.4 d B
	0.1 MPa 25 °C	6.6 ± 0.2 b	75	1.9 ± 0.1 c A	2.2 ± 0.1 e A
			100	2.3 ± 0.1 c A	4.8 ± 0.2 c B
			200	4.2 ± 0.1 b A	5.4 ± 0.2 b B
			300	5.3 ± 0.4 a A	5.7 ± 0.1 b A
			400	5.4 ± 0.3 a A	6.5 ± 0.3 a B

* Different letters (a, b, c…) on the same row indicated significant difference between treatment groups ($P < 0.05$).

** Different letters (A, B) indicated significant difference between controlled temperatures (5 or 25 °C) on the treatments at the same pressurization ($P < 0.05$).

chemical composition of the individual residue; the main factor probably being intermolecular interactions, so that store should be set by weakening the hydrophobic bonds.

Hydrostatic pressure treatment (HPT) in excess of 100 MPa is effective for the inactivation of most vegetative pathogens and spoilage bacteria that are commonly found in foods. The same pressure processing is among the emerging technologies that have been investigated to enhance the safety and shelf-life of many perishable foods (Knorr, 2002). Furthermore, this treatment is expected to be less detrimental than thermal processes to low molecular weight food compounds such as flavoring agents, pigments and vitamins, as covalent bonds are not affected by pressure (Hayashi, 1992; Tauscher, 1995). Water molecules at high pressure are stabilized by not being present as free-water but by combining with ions, non-polar groups and polar groups (Hayashi, 1991). Consequently, hydrophobic bonds/interactions are weakened at high pressure.

We applied the pressurization technique to cherry tomatoes with pesticide, and found that HPT helped to reduce levels in samples. In a previous work, we showed that the optimum pressurization conditions of around 75 MPa at 5 °C resulted in a removal rate of about 75% from cherry tomatoes with high concentrations of pesticide (Iizuka, Maeda, & Shimizu, 2013; Table 1). The pesticides migrated to the surrounding water of samples after HPT. However, the initial amount of adhesion Chlorpyrifos (CP) on the cherry tomatoes, which is a hydrophobic organophosphorus pesticide, was as high as 7.6 mg/kg, which is much higher than the national maximum residue limit (MRL). For example, 0.01 mg/kg is the national MRL for CP in cherry tomatoes, and 0.5 mg/kg is the MRL in the EU, EPA (USA) and China. In that previous work, we followed the method of Ikeura et al. (2011a) and aimed to remove high concentration CP from samples using the maximum removal rate. However, removal rate at the practical and low-level adhesion levels has not been investigated to date, and few reports have discussed applications of hydrostatic pressure for removal of pesticide from vegetables and fruits. The objective of the present study was to examine whether high efficiency removal of pesticide at practical and low-level adhesion is achievable, and whether complete removal is possible.

In a previous study (Iizuka et al., 2013), we also compared other treatments such as soaking in ethanol solution and ultrasonic treatment and showed that HPT can potentially rank with other applications. Considering that result, therefore, we set up the hypothesis that applying ethanol solution, which is hydrophobic compared to water, as the surrounding solution during pressurization leads to a higher efficiency of hydrophobic pesticide removal. In addition, the effect of repeating the HPT cycle on raising the removal ratio was studied.

2. Experimental

2.1. Cherry tomatoes

Cherry tomatoes (species: coco) were purchased from a supermarket in Hachioji City. The samples utilized for all assays contain no pesticide residue according to GC/MS analysis. After purchase, the commodity was maintained at approximately 4 °C until use (maximum of 1 day).

2.2. Chemicals

The pesticide standard Chlorpyrifos (CP), with purity up to 98% was purchased from Sigma-Aldrich (Steinheim, Germany). Dursban ™ 40 EC containing 40% (w/v) CP for preparation of pesticide coating the vegetable samples was obtained from Dow Agrosciences (Indiana, USA). The structural formula is given in Fig. 1. Physical–chemical properties of CP are as follows: water solubility (25 °C) is 1.4 mg/L, water half-life (pH 7, 25 °C) is 72 days and log P, which is the octanol–water partition coefficient, is 4.7.

Methidathion (DMTP) used as an internal standard for GC/MS was from Supelco Ltd. (Pennsylvania, USA). Analytical grade acetone, dichloromethane, hexane and ethanol were from Wako Pure Chemical Industries (Osaka, Japan).

2.3. Pesticide coating on cherry tomatoes

Firstly, we sprayed CP on the cherry tomatoes. However, as reported elsewhere, the amount of pesticide residue varies widely with this approach (Yamashita et al., 2009). For the reasons mentioned above, we adopted the method of immersion in the pesticide solution. This treatment was in accordance with the model of Pugliese et al. (2004).

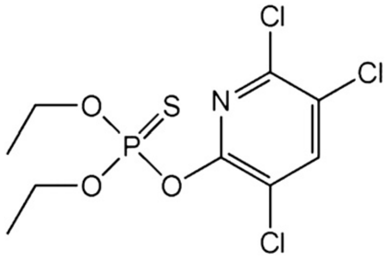

Fig. 1. Structural formula of Chlorpyrifos.