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Potential mechanism involved in removal of hydrophobic pesticides from vegetables by hydrostatic pressure

Toshiaki Iizuka, Masayuki Yahata, Akio Shimizu *

Department of Environmental Engineering for Symbiosis, Soka University, 1-236 Tangi-cho, Hachioji-shi, Tokyo 192-8577, Japan

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ABSTRACT

In our previous study, we found that the removal rate of hydrophobic pesticide on cherry tomatoes shows the maximum by hydrostatic pressure treatment (HPT) around 75 MPa. The objective of this study was to investigate the causes of reduction in the removal rate above 75 MPa HPT. Separating cuticle from flesh of the cherry tomatoes after HPT and examining the pesticide residues in each part the following was found: the detectable pesticide amount in the flesh part showed little change from the non-treated samples. Ethanol was applied as the surrounding solution during pressurization so as to prevent the reattachment of pesticide and decrease water solubility, and removal efficiency declined little. The effect of HPT on removal rate time indicated no significant difference at 0.1 MPa, the optimum level to be at 75 MPa for a comparatively short time, and at 400 MPa removal rate increased with time.

1. Introduction

Recent agriculture methods with pesticides have enabled mass and stable food production. However, the food safety issue induced by food contamination with reference to pesticide residue is becoming more and more important. Cases of collective pesticide poisoning in Japan have been occasionally reported due to accidental consumption of pesticide-contaminated vegetables. Since agricultural products cannot be sold if they contain pesticides exceeding the residual limit, methods to effectively eliminate residual pesticides in crops need to be developed (Yamaguchi, 2006). Therefore, in addition to the control of the application of pesticides, effective ways for removal of pesticide residue on vegetables are being sought as a preventive measure to avoid adverse impact on human health.

There have been several reports of pesticide removal from the surfaces of vegetables and fruits, in which the concentration of the pesticide residue was found to be higher on the outside than the inside (Yoshida et al., 1992; Abou-Arab, 1999). Pesticides can be roughly classified into water-soluble and hydrophobic (water-insoluble); the latter exhibits higher residues in food production. Some researchers have demonstrated that a decrease in high water-soluble pesticides can be expected during the cooking process (Chavarri et al., 2005; Mukherjee et al., 2006; Nagayama, 1996; Zhang et al., 2007). Furthermore, 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 (Ong et al., 1996; Zohair, 2001; Pugliese et al., 2004; Wu et al., 2007; Ikeura et al., 2011). Additionally, the ultrasonic removal of hydrophobic pesticide residues in fruit has been studied (Kimura and Ogawa, 1976; TianLi et al., 2009; Yamashita et al., 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; Krol et al., 2000; Guardia-Rubio et al., 2007), and partition coefficients between cuticle and water correlated well with octanol/water partition coefficients, as reported by Baur et al. (1997). While the residue removal mechanism is complicated, the issue seems to be generally based on form, material structures and 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 per-

* Corresponding author. Tel./fax: +81 42 691 2317.
E-mail address: shimizu@soka.ac.jp (A. Shimizu).

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ishable 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 et al., 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 pressurization to cherry tomatoes with pesticide, and found HPT helped reduce the levels it in samples. In a previous study (Iizuka et al., 2013), we showed the optimum pressurization conditions to be around 75 MPa at 5 °C, resulting in a removal rate of about 75% from cherry tomatoes (Table 1). The pesticides migrated to the surrounding water of the samples after HPT. We also showed that above 75 MPa the removal rate decreased with increasing pressure. This mechanism had not been investigated before, since few reports have discussed the application of hydrostatic pressure for removal pesticide from vegetables and fruits. The objective of this study was to examine the causes of the reduced removal rate observed above 75 MPa HPT on cherry tomatoes.

In a previous study (Iizuka et al., 2013), we made two observations: (1) no toxic pesticide intermediates were detected in unprocessed samples or HPT samples, and (2) cherry tomatoes were softened at pressures higher than 200 MPa. The former result provided us with evidence that the pesticide remained in the cherry tomato without changing into other materials, while the latter result led to our presumption that the thick wall of the cherry tomato surface had broken under increasing pressure and the pesticide solution had penetrated inside, concomitant with a reduction in the apparent removal rate. Therefore, by separating the cuticle from the flesh of cherry tomatoes after HPT and examining the pesticide residues in each part, we could investigate this process. Another potential aspect of reduced removal rate is reattachment under decompression from high pressure or lower solubility under high pressure. Thus samples were pressurized while soaked into ethanol solution, which is hydrophobic compared to water, so that reattachment was blocked. Also the effect of HPT on the structure of cherry tomato and pressurization time 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).

Table 1
Chlorpyrifos (CP) concentration in cherry tomatoes, remaining 24 h after immersing in an aqueous mixture of CP, and after each hydrostatic pressure treatment for CP-loaded samples. All values are the mean ± standard error (n = 10).

CP concentration of nontreatment (mg/kg)	Pressure (MPa)	5 °C	25 °C
		CP residues (mg/kg)	CP residues (mg/kg)
7.6 ± 0.2	0.1	5.5 ± 0.1 a[a]A[b]	6.6 ± 0.2 a B
	25	3.7 ± 0.1 b A	4.3 ± 0.2 c B
	50	2.1 ± 0.1 c A	3.4 ± 0.4 d 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

[a] Different letters (a, b…) on the same row indicated significant difference between treatment groups ($P < 0.05$).
[b] Different letters (A and B) in the same column indicated significant difference between controlled temperatures (5 or 25 °C) on the treatments at the same pressurization ($P < 0.05$).

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 Ikeura et al. (2011).

Dursban™ 40 EC was 1000-fold diluted with tap water. Then, five cherry tomatoes were selected and steeped for 1 min in this solution. After that, the samples were left for 24 h at room temperature in a fume hood. The control sample was non-treated after pesticide coating.

2.4. Hydrostatic pressure treatment

Hydrostatic pressure treatments (HPTs) were performed in a custom-ordered and constructed laboratory-scale unit (capacity: 295 cm^3; maximum pressure: 500 MPa). Kerosene was used as the pressure-transmitting medium. The temperature of this high-pressure vessel was controlled by circulating water at constant temperature (Fig. 2).

Each cherry tomato was packed in a polyethylene terephthalate pouch (60 × 85 mm). Each pouch was filled with 20 mL water or 70% ethanol solution and sealed. This pouch was set in a pressure vessel filled with a pressurizing medium of water. The samples in pouches were pressurized at 25, 50, 75, 100, 200, 300 and 400 MPa at 5 or 25 °C for 30 min. Immediately after HPT, samples were spiked and rinsed for 15 s with tap water.

2.5. Extraction processing

Extraction of CP from cherry tomatoes was performed independently on whole tomato, the cuticle part and the flesh part. Firstly, for whole or flesh parts, five cherry tomatoes were homogenized using a home food-processer and stainless steel-armed blender. A 20 g portion of slurry sample was weighed in a 200 mL beaker. Then every sample was extracted in 100 mL acetone for 30 min. The extract was filtered with a glass filter (GF/A; 55 mm) under reduced pressure and then was poured into a Chem Elut diatomaceous column for clean-up. The column was washed twice with 10 mL acetone. The elution was concentrated to dryness in a vacuum rotary evaporator with a water bath at 60 °C, then reconstituted to 10 mL with a mixture of dichloromethane: hexane (1:4, v/v) for instrumental analysis, and 500 μL of 200 ppm DMTP was added as an internal standard.