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RESEARCH ARTICLE

Removal of pesticide residues from apple and tomato cuticle

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Abstract

Pesticide residues are always an unsolved problem in the world despite all kinds of prevention measures. The present research work is based on a scientific hypothesis, i.e., “The removal of average pesticide residue is inversely proportional to the thickness of cuticle.” The effects of boron-containing products and plant-based surfactants were tested for the removal of five pesticides (lambda-cyhalothrin, chlorpyrifos, diflubenzuron, metaflumizone, acetamiprid) on tomatoes and apples. Boron-containing products were able to remove the pesticide residues on average between 58.0 and 72.6% in tomatoes and 33.2–58.8% in an apple. While plant-based surfactants removed residues on average between 58.5 and 66.6% in tomatoes and 41.0–53.2% in an apple. The highest removal rate was 72% with etidot at 1%. The solution of 1% C8–C10 provided 66.6% average removal for tomatoes. Less removal was achieved in apples. For an apple, Log K_{ow} and molecular mass (independent variables) were significant with $p < 0.01$, and the coefficient of determination (R^2) was > 0.87. However, the multiple linear regression analysis for ground colemanite was significant with R^2 of 0.96. In tomatoes, neither Log K_{ow} nor molecular mass as significant. The correlation was found between the physical and chemical properties of pesticides, but it is estimated that the thickness of the cuticle is effective in removing pesticides.

Keywords Pesticides removal · Pesticide residue · Boron · Plant-based surfactant · Thickness of cuticle

Introduction

Sustainable agriculture is the basis of the economy, health, and, nutrition of the world. Modern agricultural practices are now used to feed 6000 million people worldwide (Tilman et al. 2002). Apple and tomatoes are commonly consumed fruits and vegetables in the EU and many countries. Apple is one of the most nutritious fruits containing many antioxidants, vitamins, and fibers that help in the maintenance of good health, in accordance with the well-known saying that “An Apple a Day Keeps Doctor Away.” The production of apples is 76 million tons in the world (United States Department of Agriculture 2021). However, tomato is a vegetable that is mostly preferred to be used in salads and meals and the production is 182 (VSS et al. 2020) million tons in the world (NEWSWIRE 2021). The farmers are extensively using pesticides in order to increase production and profitability (VSS et al. 2020). Intensive pesticide usage is carried out to control pests, diseases, and weeds to prevent crop loss. As a result, high concentrations of residues occur in fruits and vegetables, which directly or indirectly cause many diseases and related problems in human health (Carvalho 2006; Craven 2003; Medina et al. 2021; Tari and Patil 2014; VSS et al. 2020). The harmful chemical agents from pesticides are the main reason for the deterioration of the environment and human health as well. Pesticides have a tendency for being mobile in soil and are persistent (Tari et al. 2020). The chlorpyrifos residues were determined in several fruits, viz., oranges, peaches, tomatoes, wine, and table grapes. In this study, they found that oranges and peaches chlorpyrifos can be accumulated and it leads to the appearance of residues over the maximum residue limits (MRL) (Angioni et al. 2011).

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The study of the transfer of chlorpyrifos residues into lettuce (leafy vegetable), carried out by Hwang et al. (2018), found that the residues ranged from 0.66 to 13.26% of the initial concentration in soils. The degradation behavior of chlorpyrifos was analyzed in spinach and soil; however, it was found that the harvest interval should be more than 14 days for the safety of humans and the environment (Shukor et al. 2015; Yap and Jarroop 2018).

In another similar kind of study, lambda-cyhalothrin was detected in kales, tomatoes, and cabbages during the dry and wet seasons (Kithure et al. 2017). The dissipation behavior of lambda-cyhalothrin residues was studied which revealed that the pre-harvesting interval should be more than 6 days for safety (Shalaby 2017; Seenivasan and Muraleedharan 2009; Sreenivasa Rao et al. 2017). Lambda-cyhalothrin follows the first-order dissipation kinetics (Seenivasan and Muraleedharan 2009). The diflubenzuron (DFB) is proved to be highly stable in the environment, i.e., around 127 days (Levot et al. 2004; Nejmanová et al. 2006). The horse chestnut leaves were tested for the diflubenzuron pesticide residues; they found that residues were stable in respective leaves for more than 4 months (Nejmanová et al. 2006). The effect of penetration of the insecticide into the cuticular layer and the leaf mass (parenchymal tissues) was studied and they found that such penetration may lead to the persistence of the DFB. Since such penetration would become obstacles to the degradation of pesticides through UV light or washing treatments (Nejmanová et al. 2006), the metaflumizone is known to be a non-persistent pesticide and non-resistant (Niladri Sekhar Chatterjee and Suman 2012). They found that residues persisting beyond 5 days and dissipated with a half-life (T1/2) of 1.7–2.1 days. However, no residues were found in cabbage or the soil after 7 days of treatment. Therefore, metaflomizone can be safe to use (Niladri Sekhar Chatterjee and Suman 2012). The preharvest residue limit for metaflumizone was established by. The half-life values of acetamiprid in eggplant fruits, leaves, and soil were found to be 1.96, 2.31, and 10.47 days respectively. Therefore, the recommended dosage can be considered as safe as per as health hazards to consumers are concerned. However, 1-day waiting period before consumption and processing of eggplant fruits was suggested for reducing the risk (Romeh and Hendawi 2013). Despite training, practices, and regular controls in many countries, the residue problem has not been eliminated. Therefore, additional measures are needed to reduce pesticide residues. Many household treatments of fruit processing such as washing, peeling, blanching, pasteurization, refrigeration, microwave cooking, fermentation, ultrasonic cleaning, and sterilization are applied to reduce residue levels (El-sayed and Salman 2021; González-Rodríguez et al. 2011; Lozowicka et al. 2016; Soliman 2001; Medina et al. 2021). Although many studies are reported the removal of pesticides during cooking and blanching, this is not applicable for raw-consumed fruits and vegetables (Bonnechere et al. 2012; Lozowicka et al. 2016; Medina et al. 2021). The highest, medium, and lowest pesticide concentrations were reported to be in potato tubers, pommes fries, and chips, respectively, indicating that washing with water and/or food processing, e.g., cooking, plays an important role in pesticide residue mitigation (Soliman 2001). The addition of chemicals into the washing water was not able to yield complete residue elimination. Amqam et al. (2019) stated that the washing of tomatoes can significantly reduce amount of chlorpyrifos residues from 0.006 ppm to 0.050 ppm. Residues of lambda-cyhalothrin from sweet paper fruits can be reduced by washing with 1% sodium carbonate or by frying the fruits in boiling oil (Shalaby 2017; Kithure et al. 2017). For reducing lambda-cyhalothrin residue household material, e.g., 2% salt solution and 4% acetic acid/vinegar solution, is suggested by Sreenivasa Rao et al. (2017). The experiment was conducted to estimate effect of processing, viz., washing, grilling, and cooking in oil and water, on eggplant fruits, leaves, and soil. They found that higher residue was removed by boiling (56%) and grilling (99%) than in frying (46.24%) and washing (24.73%) after first day of treatment (Romeh and Hendawi 2013). The processing factor (PF), i.e., the ratio of the concentration of residues to the commodity, has been proposed to study their fate during processing and storage (El-sayed and Salman 2021). However, the dependence of PF on the crop and physicochemical properties of respective pesticides complicates its suitability (González-Rodríguez et al. 2011; Tomer 2013). Nevertheless, the large variation in the effectiveness of the available household methods limits their suitability. In consequence, new effective washing solutions are required to ensure food safety. One of the alternatives may be boron-containing detergents and natural surfactant compounds, which have not been investigated yet in the literature. It is known that boron-containing compounds have been used for centuries to clean pollutants from different environments. They are added to detergents and bleaches and used to remove contaminants. They can stabilize liquid formulations and can soften hard water and increase the performance of applied surfactants (Woods 1994).

This study aimed to investigate the removal efficiency of four different boron substances and three plant based surfactants in contaminated tomatoes and apples, and to determine their relationship with the physical and chemical properties of the investigated pesticides, i.e., chlorpyrifos, lambda-cyhalothrin, diflubenzuron, metaflumizone, and acetamiprid.

Material and methods

Chemicals and reagents

The standards of chlorpyrifos, lambda-cyhalothrin, diflubenzuron, metaflumizone, and acetamiprid were purchased from

Dr. Ehrenstorfer GmbH (Augsburg, Germany) and the pesticides formulations were supplied from pesticide retailers.

Properties of studied pesticides and removal compounds

The active substances studied belong to various pesticide classes and have different modes of action. Different pesticides were selected from different groups to obtain the removal effect of treatments. In the present work, the processing experiment was carried out on apples and tomatoes to investigate pesticide removal (post-harvest treatments) by using different boron substances and three vegetable surfactants. Physical and chemical properties are given in Table 1.

The first boron-containing compounds was etidot ($Na_2B_8O_{13}.4H_2O$) which contained 67% B_2O_3 with particle size 0.09 mm. Borax decahydrate ($Na_2B_4O_7.10H_2O$) was used technical grade as powder and contained 36.47 to 38.5% B_2O_3 with particle size 1.18 mm. The boric acid (H_3BO_3) was selected as technical grade as granular, normal sulphate. Its B_2O_3 amount was 56.25 to 56.90% with particle size 1.0 mm. Ground colemanite ($2CaO.3B_2O_3.5H_2O$) contained 40% B_2O_3 and particle size was 45 micron meter. All boron compounds were provided by Eti Maden, Turkey. C8–C10 is a plant based surfactants which is brown liquid. It has 68–72% active substances. Its water content is 28–32%, viscosity is 4800, pH value is between 6 and 8 and is biodegradable. C12–C14 is also plant-based surfactants which has light yellow color and is hazy paste It has 48–52% active substance, 42–48% water content, 18,000 viscosity, 11.55–12.5 pH value, and is biodegradable. C8–C14 is a plantbased surfactants and itis clear liquid. It has 48–52% active substance, 42–48% water content, 550 viscosity, 7–9.5 pH value, and is biodegradable.

Sample preparation and processing

Tomato and apple samples (organically cultivated) were purchased from the market, packed in polyethylene bags, and transported to the laboratory. Tomatoes and apples were sprayed by a pesticide sprayer at the laboratory separately for each pesticide. After spraying, the apples and tomatoes were kept under the fume up to the plant surface was dry. Then, tomatoes and apples were washed in a washing water solution containing boron and plant-based surfactants, and all apples and tomatoes were left to be dried at room temperature (25 °C) for 2 h, and then the extraction process was started. Some of the taken samples were left without spraying as the negative control.

Extraction and analysis

The QuEChERS (quick, easy, cheap, rugged, safe) method was used for pesticide extraction and validation of the extraction method (Anastassiades et al. 2003). Approximately 1 kg of tomato and apple samples was homogenized and 10 g from this sample was weighed and put into 50-mL tubes. Then, an acetonitrile:acetic acid mixture (99:1 v:v ratio) of 10 mL was inserted into the homogenized sample and shaken for 1 min followed by adding 4 g $MgSO_4$, 1 g NaCl, and 1 g trisodium citrate dehydrate ($C_6H_9Na_3O_9$) and then again they were shaken for 1 min. After that, the upper layer was transferred to a 15-mL tube containing 150 mg $MgSO_4$ and 25 mg primary secondary amine (PSA), and vortexed again. In the end, the 1 mL upper layer was filtered and stored until analysis (Anastassiades et al. 2003).

The pesticide solutions have been confirmed by the guidelines of the European Commission (Pihlström 2011). The LC–MS/MS analysis was carried out using a C18 column (Purospher® STAR RP-18). The injection turnover view is 20mu with 1 at a flow rate of 0.4 mL/min. The auto-sampler temperature was set to 5 °C and the column temperature was set to 40 °C.

The pesticide residue analysis was performed on a Schimadzu (LC/MS–MS) and (GC–MS). The residues of chlorpyrifos and lambda-cyhalothrin were determined using GC–MS with a BP5 column (30-m length, 0.25-mm diameter, and 0.25-µm film thickness) (Agilent, DB 5 MS) with an injector temperature of 270 °C. The oven temperature program; 70 °C for 2.0 min hold then increased by 30 °C min^{-1} up to 180 °C; and then was increased by

Table 1 Physical and chemical properties of pesticides

Pesticide	Group	Systemic	Log K_{ow}	Solubility in water mg/L	Boiling point	Molecular mass
Lambda-cyhalothrin (I)	Pyrethroid	No	7	0.005	498.9	449.9
Chlorpyrifos (I)	Organophosphate	No	4.7	1.4	> 400	350.6
Diflubenzuron (I)	Benzoylurea	Yes	3.89	0.08	–	310.7
Metaflumizone (I)	Semicarbazone	Yes	5.1	1.70×10^{-3}	–	506.4
Acetamiprid (I)	Neonicotinoids	Yes	0.80	4250	–	222.7

(I): Insecticides

10 °C $\min^{-1}$ to 290 °C and held for 15 min. The carrier gas was 1.0 mL $\min^{-1}$. The temperature of the detector and injector were 300 °C and 260 °C. The injection volume was 2 µL splitless mode and the split opened after 2.0 min. The temperature of the transfer line, ion source, and quadrupole was set at 280 °C, 230 °C, and 150 °C. Target peaks were accepted if the target/qualifying ion ratio was within 20% of standards. Calibration was based on the area given using external standards for MS calibration.

The limit of detection (LOD, mg/kg) and limit of quantification (LOQ, mg/kg) were used for method validation. The LOQs were determined via the S/N ratio = 10. The limit of quantification is the minimum concentration of the analyte that can be quantified with acceptable accuracy and precision (Sanco 2010).

The methods used for the analysis, extraction, and purification of selected pesticides were acceptable. The recoveries, LOD and LOQ are given in Table 2.

Statistical analyses

Percent removal data for the pesticides were averaged, and the differences were evaluated by statistically significant mean values ($P < 0.05$), which were calculated by using general linear model multivariate test and separated using Tukey in the SPSS statistical software package. Multiple linear regression (MLR) was performed to analyze the relationship between pesticide physicochemical properties and removal efficiency and ANOVA *F*-test was conducted with the significance level of $p < 0.001$.

Results and discussion

In the current study, washing of tomatoes with 0.1%, 1%, and 5% boric acid; 0.1%, 1%, and 5% borax decahydrate; 0.1%, 1%, and 5% ground colemanite; and 0.1%, 1%, and 5% etidot reduced the residue by (average %) 65.0, 69.2, 69.4, 69, 68.6, 58, 66.4, 72.4, 60, 64.2, 72.6, and 69.8 respectively (Table 3). However, washing of tomatoes with plant-based surfactant C8–C10 1% and 5%, C12–C14 1% and 5%, and C8–C14 1% and 5% reduced residue by (average %) 66.6, 60.8, 64.0, 58.5, 63.4, and 63.5 respectively (Table 3). Whereas, washing of apples with 0.1%, 1%, and 5% boric acid; 0.1%, 1%, and 5% borax decahydrate; 0.1%, 1%, and 5% ground colemanite; and 0.1%, 1%, and 5% etidot reduced the residue by (average %) 39.2, 45, 58.8, 53.6, 48.6, 33.2, 36, 37.4, 34.4, 34, 51.8, and 58.4 respectively (Table 4), while washing them with plant-based surfactant C8–C10 1% and 5%, C12–C14 1% and 5%, and C8–C14 1% and 5% reduced residue by (average %) 53.2, 50.3,41, 45, 47.6, and 48.8% respectively (Table 4).

Table 2 The recoveries, LOD, and LOQ of the studied pesticides

Selected Pesticides	LOD (mg/kg)	LOQ (mg/kg)	Recoveries (%)
Chlorpyrifos	0.001	0.003	80–92
Lambda-cyhalothrin	0.006	0.003	88–91
Metaflumizone	0.001	0.008	78–89
Diflubenzuron	0.005	0.008	77–85
Acetamiprid	0.001	0.004	82–95

Chlorpyrifos

Chlorpyrifos was easily removed from the apple surface with boron compounds. Etidot 1% was found to be the most effective (56%) in removing chlorpyrifos in tomatoes, but 1% boric acid was found to be 82% most effective on apple surfaces. Chlorpyrifos was removed at the highest with 56% with 1% etidot application ($P < 0.05$)and the lowest in the borax decahydrate application ($P > 0.05$) (Table 3). The borax decahydrate (1%) was able to remove 68% ($P < 0.05$) of chlorpyrifos from the plant surface of an apple. The chlorpyrifos removal efficiencies obtained in this study are higher than those reported by Ling et al. (2011) obtained with tap water, detergent, and sodium hypochlorite: 46.6, 40.8, and 37.5%, respectively.

Although plant-based surfactants removed chlorpyrifos residues between 51 and 68% from the apple surface, they were able to remove between 2 and 33% from the tomato surface. The highest removal effect was achieved with 5% C_{12}–C_{14} plant-based surfactant solution in apples, which on the other hand resulted in the lowest removal in tomatoes. Many researchers have studied the removal of chlorpyrifos residues in apples and tomatoes. Hao et al. (2011) and Ling et al. (2011) kept tomatoes in detergent solution for 10, 20, and 30 min and obtained a reduction of 4 to 52%. Soaking tomatoes in an ethanol solution for 3 min provided chlorpyrifos removal of 70 to 72% (Lizuka et al. 2014) while washing with sodium hypochlorite resulted in 37% removal (Ling et al. 2011a). A chlorpyrifos removal of 72 and 69% were reported by keeping the tomatoes in 2% salt solution and in 2% tamarind solution, respectively (Harinathareddy et al. 2014), while 0.1% sodium bicarbonate and 4% acetic acid solutions were provided 65 and 59% removal. There is a large variation in the removal of chlorpyrifos by washing with tap water in the literature, e.g., for tomatoes 30% (Han et al. 2013) to 74% (Velioglu et al. 2016). It could be increased to 45, 41, 39, 34, and 100% respectively by immersing in H_2O_2 (1%), baking soda (10%), and acetic acid (4%), added tap water, and sonicated for 60 min (Hassan et al. 2019). Acetic and citric acid applications on Capia

Table 3 Pesticide removed from tomatoes with different treatments (%) (mean ± SE)

	Chlorpyrifos	Lambda cyhalothrin	Diflubenzuron	Metaflumizone	Acetamiprid	Average
Boric acid % 0.1	17 ± 2.6de	46 ± 1.3 bcde	90 ± 1.2a	100 ± 0.0a	72 ± 0.3 bcd	65.0
Boric acid % 1	32 ± 1.2 abc	55 ± 3.7 abc	84 ± 12.1a	100 ± 0.0a	75 ± 0.2ab	69.2
Boric acid %5	26 ± 1.7bcd	57 ± 1.9 abc	89 ± 0.8a	100 ± 0.0a	75 ± 0.2 ab	69.4
Borax decahydrate % 0.1	37 ± 1.78 abc	47 ± 2.3 bcde	86 ± 2.0a	100 ± 0.0a	75 ± 0.1ab	69.0
Borax decahydrate % 1	24 ± 0.7 bcd	59 ± 2.2 ab	88 ± 0.7a	100 ± 0.0a	72 ± 0.7bc	68.6
Borax decahydrat % 5	0 ± 0.0 h	39 ± 1.8def	89 ± 8.6a	100 ± 0.0a	62 ± 0.1 g	58.0
Ground colemanite % 0.1	41 ± 5.7 ab	38 ± 1.5def	84 ± 2.8a	100 ± 0.0a	69 ± 0.7 def	66.4
Ground colemanite % 1	54 ± 3.2a	63 ± 3.1a	83 ± 0.9a	100 ± 0.0a	62 ± 1.7 g	72.4
Ground colemanite % 5	12 ± 1.1e	26 ± 1.7f	88 ± 0.7a	100 ± 0.0a	74 ± 0.3ab	60.0
Etidot % 0.1	21 ± 0.1cde	44 ± 2.3cde	87 ± 9.8a	100 ± 0.0a	69 ± 0.1 cde	64.2
Etidot % 1	56 ± 13.3a	50 ± 2.6 abcd	80 ± 6.9a	100 ± 0.0a	77 ± 0.2a	72.6
Etidot % 5	33 ± 5.0abc	61 ± 4.7 a	88 ± 1.0a	100 ± 0.0a	67 ± 0.6ef	69.8
Plant-based surfactants						
C8–C10% 1	31 ± 4.1abcd	50 ± 2.6 abcd	90 ± 0.5a	100 ± 0.0a	62 ± 0.5 g	66.6
C8–C10% 5	3 ± 0.0 g	45 ± 0.4cde	95 ± 6.5a	100 ± 0.0a	ND	60.8
C12–C14% 1	6 ± 0.4f	56 ± 3.5 abc	93 ± 1.2a	100 ± 0.0a	65 ± 0.2 fg	64.0
C12–C14% 5	2 ± 0.4gh	37 ± 0.8 def	95 ± 0.0a	100 ± 0.0a	ND	58.5
C8–C14% 1abc	33 ± 2.3de	40 ± 2.6 de	92 ± 19.3a	100 ± 0.0a	52 ± 0.5 h	63.4
C8–C14% 5bcd	25 ± 0.9ef	35 ± 1.9 ef	94 ± 8.3a	100 ± 0.0a	ND	63.5

$^{a–h}$Values with the different letters are significantly different ($P < 0.05$)

pepper, however, resulted in higher chlorpyrifos removals of 77.5 and 75.4%, respectively (Polat and Tiryaki 2020). Pugliese et al. (2004) stated that chlorpyrifos residue translocated into internal tissue may not be removed physically and chemically. The pesticides with low solubility and high Log Kow are retained in the fruit skin.

Table 4 Pesticide removed from apple with different treatments (%) (mean ± SE)

	Chlorpyrifos	Lambda cyhalothrin	Diflubenzuron	Metaflumizone	Acetamiprid	Average
Boric acid %0.1	46 ± 8.96abc	64 ± 5.81a	45 ± 0.88cde	13 ± 1.45 h	28 ± 0.56c	39.2
Boric acid % 1	82 ± 14.44a	3 ± 1.07 cd	31 ± 1.15 g	20 ± 0.58 g	89 ± 1.23a	45.0
Boric acid %5	68 ± 8.39ab	83 ± 6.50a	36 ± 1.45efg	13 ± 2.60 h	94 ± 0.58a	58.8
Borax decahydrate % 0.1	64 ± 6.94abc	33 ± 0.73ab	58 ± 0.34bc	26 ± 1.90efg	87 ± 0.66a	53.6
Borax decahydrate % 1	68 ± 4.33ab	20 ± 7.81b	47 ± 3.96cde	27 ± 4.37ef	81 ± 1.13a	48.6
Borax decahydrate % 5	0 ± 0.00d	0 ± 0.00d	56 ± 0.19bc	23 ± 0.58 fg	87 ± 1.20a	33.2
Ground colemanite % 0.1	40 ± 6.66abc	0 ± 0.00d	33 ± 0.52 fg	24 ± 0.11efg	83 ± 0.40a	36.0
Ground colemanite % 1	31 ± 6.08c	0 ± 0.00d	54 ± 0.49 cd	16 ± 0.76 h	86 ± 1.16a	37.4
Ground colemanite % 5	33 ± 8.08bc	4 ± 0.24c	34 ± 0.99 fg	13 ± 0.17 h	88 ± 1.79a	34.4
Etidot % 0.1	51 ± 9.24abc	55 ± 0.25a	41 ± 0.99def	23 ± 2.66 fg	0 ± 0.00d	34.0
Etidot % 1	61 ± 3.79abc	60 ± 2.40a	13 ± 0.17 h	33 ± 0.57 cd	92 ± 0.00a	51.8
Etidot % 5	52 ± 0.00abc	73 ± 4.65a	41 ± 0.22def	30 ± 0.33de	96 ± 0.00a	58.4
Plant-based surfactants						
C8–C10% 1	51 ± 9.34abc	0 ± 0.00d	80 ± 0.99a	46 ± 0.76b	89 ± 0.64a	53.2
C8–C10% 5	50 ± 10.64abc	0 ± 0.00d	88 ± 1.16a	63 ± 0.95a	ND	50.3
C12–C14% 1	66 ± 5.85abc	0 ± 0.00d	36 ± 3.63efg	40 ± 1.71bc	63 ± 11.55b	41.0
C12–C14% 5	68 ± 0.13ab	19 ± 0.33b	56 ± 1.32c	37 ± 2.66bcd	ND	45.0
C8–C14% 1	58 ± 10.77abc	0 ± 0.00d	43 ± 6.60def	47 ± 3.23b	90 ± 0.18a	47.6
C8–C14% 5	56 ± 0.41abc	0 ± 0.00d	74 ± 0.49ab	65 ± 0.96a	ND	48.8

$^{a–h}$Values s with the different letters are significantly different ($P < 0.05$)

Lambda-cyhalothrin

The average removal rate of lambda-cyhalothrin from tomatoes was between 26 and 63% by boron compounds. While the highest removal rate was found in the 1% ground colemanite application ($P < 0.05$), increasing the amount of colemanite harmed the removal, reducing it to the lowest level when its amount was increased to 5% (Table 3). Boron applications were found to be effective in removing lambda-cyhalothrin in apples, i.e., 5% boric acid application provided 83% removal, followed by 73% with 5% etidot application and 64% with 0.1% boric acid application. However, application of 5% borax decahydrate and 0.1%, 1% colemanite application showed no effect (Table 3).

Although plant-based surfactants showed a removal effect of lambda-cyhalothrin from the tomato between 35 and 56%, the solution of plant-based surfactant did not remove it from the apple surface except 5% C_{12}–C_{14} (Table 3). In a study on tomatoes, 2% tamarind application provided 37%, 1% lemon water application 59%, 0.1% sodium bicarbonate application 41%, and 4% acetic acid application provided 30% removal of pesticides (A. Harinathareddy et al. 2014). Tomatoes washed with running tap water removed chlorpyrifos 27% (Wanwimolruk et al. 2017).

Diflubenzuron

In the removal of diflubenzuron insecticide, boron compounds provided very good removal between 0–90%. Here, 0.1% boric acid treatment gave the best results, followed by 5% boric acid and 5% borax decahydrate application. Relatively lower removal was achieved from apples. Diflubenzuron from the apple surface was removed 58% in the application of borax decahydrate of 0.1% and followed by 56% in 5% borax decahydrate application, between 47 and 54% by 1% ground colemanite application, and 47% in 1% borax decahydrate and 45% in 0.1% boric acid application. Although plant-based surfactants were effective in removing diflubenzuron from tomatoes and apples, they showed a greater effect in tomatoes. Surfactants removed diflubenzuron from tomatoes between 90 and 95%. Here, the most effective surfactant was determined to be 5% C8–C10. Both in apples and tomatoes, 1% C8–C14 surfactants provided 43% removal from apple surface, while 5% C8–C10 surfactant removed diflubenzuron 88% with the highest efficiency (Table 3).

Metaflumizone

In the applications for the removal of metaflumizone in tomatoes, the insecticide was completely (100%) removed (Table 3). On the apple surface, metaflumizone residues were removed between 13 and 33% with boron compounds (Table 4). It was followed by 1% borax decahydrate with 27% and 1% borax decahydrate with 26% removal. Among the plant-based surfactants, the highest removal rate was obtained at 65% by 5% C8–C14 carbon application, whereas the lowest was achieved at 37% by 5% C12–C14 carbon application (Table 4).

Acetamiprid

Similar results were obtained in the removal of acetamiprid from tomatoes with boron applications. The removal rate was found to be between 62 and 77%. The application of 1%, 5% boric acid, and 0.1% borax decahydrate ($P < 0.05$) removed 75% of acetamiprid residues in tomatoes (Table 3). Plant-based surfactants removed acetamiprid residues between 52 and 65% from tomatoes.

In the removal of acetamiprid residues from the apple surface, 0.1% etidot application had no effect, while 0.1% boric acid removed 28% of acetamiprid residues. The highest removal effect was achieved at 96% with 5% etidot solution ($P < 0.05$), followed by 94% by 5% boric acid application. The application of 0.1% and 5% borax decahydrate solution removed acetamiprid 87%, 1% boric acid 89%, and 5% ground colemanite 88% from apple surfaces (Table 4). In apples, 1% C12–C14 carbon application removed 63% of acetamiprid residues, 1% C8–C10 application 89%, and 1% C8–C14 carbon contained plant-based surfactant application removed 90%. When the removal of all pesticides by boron applications, in general, was examined, it was determined that the removal of 1% etidot application was 72.6%, 1% ground colemanite was 72.4%, 5% etidot was 69.2%, and 0.1% borax decahydrate application was 69%.

It has been determined that the results of plant-based surfactant applications are slightly different from each other. In the study conducted with boron compounds on the apple surface, the most effective was found to be 5% boric acid application and followed by 5% etidot application, 0.1% borax decahydrate application, and 1% etidot application (Table 4).

The best result was obtained with 5% boric acid. In plant-based surfactants, the best removal from both apple and tomato surfaces was found in 1% C8–C10 carbon-containing surfactant (Tables 3 and 4).

Washing is considered an easy and practical way (post-harvesting process) to reduce pesticide residue from the surface of fruits and vegetables. The effectiveness of dishwashing liquids (detergents) for reducing pesticide residue was studied by Wang et al. (2013). They found that multiple washing, the addition of acetic acid, and increased washing temperature lead to boost the effectiveness of detergents. Interestingly, a combination of vinegar and hot water facilitated more residue removal. Whereas, NaCl solution leads to a lower effectiveness of dishwashing liquids (Wang et al. 2013). The effectiveness of both commercial and homemade washing agents to reduce pesticide residue from apples was investigated by Yang et al. (2017). It was observed that washing with $NaHCO_3$ solution was most effective to reduce residue from the surface of the apple. However, there are many limitations to diminishing residue completely through washing as residues penetrate deep into the fruit (Yang et al. 2017).

Qi et al. (2018) evaluated the effect of long treatment of electrolyzed oxidizing (EO) water (15 min) along with high available chlorine content, i.e., 120 mg/L for reducing pesticide residues from fruits and vegetables. They found that there is a significant reduction in residues with no color, texture, or produce quality deterioration after derived post-harvesting treatment (Qi et al. 2018). Washing was used for reducing chlorothalonil, oxazolyl, and thiophanate-methyl residues by 92%, 52%, and 84% respectively, from tomatoes (Kwon et al. 2015). Harinathareddy et al. (2014) reported pesticide removal from tomatoes with tap water, lemon water, tamarind solution (2%), salt solution (2%), baking soda, vinegar, and Bio-wash (commercial washing product) to be in the ranges of 37–73.2%, 42.5–72.3%, 26.1–69.1%, 44.3–78.7%, 24–65.1%, 17.1–58.5%, and 44.5–75.2%, respectively, followed by cooking leads to reduction of the residue by 42.9–83.2% (A. Harinathareddy et al. 2014). In conclusion, the literature agrees on the effect of washing treatment for significant reduction of pesticide residues (Wang et al. 2013; Zhang et al. 2007; Qi et al. 2018; Yang et al. 2017; Medina et al. 2021; Kwon et al. 2015; Marican and Durán-Lara 2018; Ling et al. 2011; Lozowicka et al. 2016; Harinathareddy et al. 2014; Soliman 2001).

Physicochemical properties of pesticides

Log K_{ow} and molecular mass (MM) were the independent variables. The criteria to enter and remove for an independent variable were $p < 0.05$ and < 0.10, respectively. MLR models for all chemicals for tomatoes were significant according to ANOVA F-test, in none of which the constant was significant. Therefore, models that were forced through the origin were constructed, for which both of the independent variables were significant ($p < 0.01$) and coefficients of determination (R^2) were > 0.87 (Table 5). For apple, on the other hand, only the MLR model for ground colemanite was significant with an R^2 of 0.96 (Table 5). Unlike tomatoes, the constant of the constructed model for apples was significant. Neither log K_{ow} nor MM was useful in explaining the observed variation in the removal efficiency for the remaining chemicals.

The behavior of pesticide residue is significantly dependent on the physicochemical properties of the compounds and the process used for removal (El-sayed and Salman 2021; Kwon et al. 2015). The pesticides are persistent in the ecosystem due to their elevated stability and water solubility (Marican and Durán-Lara 2018). Table 1 shows the physicochemical properties of five selected pesticides in the present study. Out of the five selected pesticides, lambda-cyhalothrin and chlorpyrifos are non-systemic whereas, diflubenzuron, metaflumizone, and acetamiprid are systemic. Therefore, these systemic insecticides can be absorbed by the plant and can be entered into the transport system (Hou et al. 2016).

The water solubility (Table 1) of acetamiprid is very high, i.e., 4250 with less Log K_{ow} 0.80 by which this pesticide residue can be transferred to juices of respected vegetables and fruits (El-sayed and Salman 2021). The lower value of the water partitioning coefficient, i.e., Log K_{ow} means more residue can be eliminated by washing (Chen et al. 2016; Huan et al. 2015). Whereas pesticide like metaflumizone has a very low water solubility (1.70×10^{-3}), and a high Log K_{ow} value of 5.1 (Table 1), therefore, it remains in the fruit skin and fibrous part of vegetables and fruits (Ling et al. 2011).

Here, it can be seen that there is a difference between performances of concentrations in the removal of average

Table 5 Results of multiple linear regression analysis

	ANOVA F-test p-value	Constant	log K_{ow}	MM	Adjusted R^2
Tomatoes					
Boric acid	< 0.001	NS	0.002	< 0.001	0.91[a]
Borax decahydrate	< 0.001	NS	0.005	< 0.001	0.88[a]
Ground colemanite	< 0.001	NS	0.002	< 0.001	0.91[a]
Etidot	< 0.001	NS	0.002	< 0.001	0.93[a]
Apple					
Boric acid	0.124	NS	NS	NS	0.18
Borax decahydrate	0.037	0.001	NS	NS	0.33
Ground colemanite	< 0.001	< 0.001	< 0.001	0.057	0.96
Etidot	NS	–	–	–	–

MM molecular mass, *NS* not significant ($p > 0.05$)

[b]The model forced to the origin

residues although there is a significant correlation found in the chemical and physical properties of pesticides; therefore, it can be concluded that the thickness of the cuticle is playing important role in the mechanism of pesticide residue removal. The experiment of endria residue removal on alfalfa hay (9% moisture) was unsuccessful when washed with hot or cold water; oven heated could remove 35% of residues, whereas 73% of residue removed when saturated with water and heated. Interestingly, residues were found in the wax-like cuticle. Hence, the residue was found to be correlated with the plant surface area/cuticle (Archer 1968; C. T. Lewis 1980). The effectiveness of commercial and homemade washing methods for removing systemic and non-systemic pesticides from the surface and inside apples using SERS mapping and LC–MS/MS methods; in their study, it was found that systemic pesticides penetrate deeper into the thick waxy cuticle of apples than non-systemic pesticide. Therefore, peeling of the cuticle can be preferred to reduce the respective health impacts of pesticide residues (Yang et al. 2017). Therefore, our study is in line with the previous literature.

Pesticide residues pose a significant risk to human health; therefore, it is important to avoid or reduce pesticide exposure. Post-harvesting treatments are shown to be effective. The application of boron and plant-based surfactants was more successful in tomatoes than in apples. The most important reason for this is the pesticides stay in the cuticle and the applied chemical does not remove the pesticides from the cuticle.

Conclusion

The present research work is based on a scientific hypothesis, i.e., “The removal of average pesticide residue is inversely proportional to the thickness of cuticle.” However, this research hypothesis can be well accepted, since the cuticle thickness of the apple is 2–8 times thicker than the tomato the average residue removed from the apple (according to the apple variety) was less than that of the tomato.

Author contribution All authors contributed to the study conception and design. Conceptualization: Nalan TURGUT, Cengiz GÖKBULUT; methodology: Melis YALÇIN, Cengiz GÖKBULUT, Cafer TURGUT; formal analysis and investigation: Melis YALÇIN, Nalan TURGUT, Serhan MERMER, Cafer TURGUT; writing—original draft preparation: Melis YALÇIN, Sait SOFUOĞLU, Cafer TURGUT; writing—review and editing: Sait SOFUOĞLU, Vinaya TARİ.

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Declarations

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