



Effectiveness of electrolyzed oxidizing water treatment in removing pesticide residues and its effect on produce quality



Hang Qi^a, Qingguo Huang^b, Yen-Con Hung^{a,*}

^a Department of Food Science and Technology, University of Georgia, 1109 Experiment Street, Griffin, GA 30223, USA

^b Department of Crop and Soil Sciences, University of Georgia, 1109 Experiment Street, Griffin, GA 30223, USA

ARTICLE INFO

Article history:

Received 16 March 2017

Received in revised form 31 May 2017

Accepted 27 June 2017

Available online 28 June 2017

Chemical compounds studied in this article:

Diazinon (PubChemCID: 3017)

Cyprodinil (PubChemCID: 86367)

Phosmet (PubChemCID: 12901)

Keywords:

Electrolyzed water

Chlorine

Pesticide residue

Fresh produce

Produce quality

ABSTRACT

This study evaluated the effects of electrolyzed oxidizing (EO) water treatment on the removal of pesticide residues (diazinon, cyprodinil and phosmet) from spinach, snap beans and grapes, and the effect on produce quality. High available chlorine content (ACC) and long treatment time of EO water resulted in high pesticide removals. Up to 59.2, 66.5 and 37.1% of diazinon; 43.8, 50.0 and 31.5% of cyprodinil; 85.7, 73.0 and 49.4% of phosmet; were removed from spinach, snap beans and grapes, respectively, after 15 min EO water treatment at 120 mg/l ACC. EO water was also more effective than electrolyzed reduced water, bleach, VegWash and DI water on pesticide removal. In addition, no significant colour or texture deterioration were found on produce samples treated with EO water. It was concluded, EO water can be very effective in pesticide residue removal from fresh produce without affecting the produce quality.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Pesticides have been widely applied in traditional agriculture to ensure high yielding and high quality crop production. The main purpose of pesticides is to control the competition from weeds and the losses from insects and fungi (Bonnechère et al., 2012). In 2007, about 857 million pounds of active pesticide ingredients were applied in the U.S. (Arduini, Cinti, Scognamiglio, & Moscone, 2016). As pesticides are biologically active, they can be extremely toxic even when present in minimal amounts (Pooja & Latika, 2014). Symptoms caused by pesticides can be both short-term, such as headache and nausea, and chronic, such as cancer and reproductive system damage (Berrada et al., 2010). Although the U.S. and many other countries have established comprehensive regulations to control pesticides, pesticide residues are still a big concern for consumers. From 2006 to 2010, there were 130,136 phone calls received annually associated with pesticide poisonings with about 23 death cases (Langley & Mort, 2012). More importantly, 95.8% of the reported poisonings were unintentional.

Pesticide exposure through food is five orders of magnitude higher than other routes, such as drinking water (Juraskie, Mutel, Stoessel, & Hellweg, 2009). Fresh fruits and vegetables are the major food source for pesticide exposure because fresh produce account for about 30% of an individual diet by mass and are assumed to contain more residual pesticides as they are usually minimally processed and consumed raw (Juraskie et al., 2009).

Processed foods made from fresh produce are also concerns due to pesticide contamination. Food processing could have a concentration effect that increases the pesticide residue level in the final processed food products (González-Rodríguez, Rial-Otero, Cancho-Grande, Gonzalez-Barreiro, & Simal-Gándara, 2011). The concentration effect can be from water loss (e.g. ketchup production from fresh tomatoes) or lipophilic materials accumulation (e.g. vegetable oil production) (González-Rodríguez et al., 2011). For instance, Lentza-Rizos, Avramides, and Kokkinaki (2006) found an increase of azoxystrobin residue level in raisins made from fresh grapes and Cabras et al. (1997) observed elevated insecticide levels in olive oil produced from olives. The residual pesticides can also be transformed into metabolite products during food processing, which could be more toxic than the parent pesticide compounds (González-Rodríguez et al., 2011). Furthermore, the presence of pesticide residues on fresh produce can significantly affect the food fermentation process and the food sensory quality, such as the

* Corresponding author at: Department of Food Science and Technology, University of Georgia, 1109 Experiment Street, Griffin, GA 30223-1797, USA.

E-mail addresses: qihang@uga.edu (H. Qi), qhuang@uga.edu (Q. Huang), hung@uga.edu (Y.-C. Hung).

polyphenolic content and aromatic profile (Regueiro, López-Fernández, Rial-Otero, Cancho-Grande, & Simal-Gándara, 2015). For example, Regueiro et al. (2015) found certain pesticide residues had significant influence on the polyphenol content in young lager beers. Therefore, fresh produce harvested from the fields must be thoroughly cleaned before putting into the market or processing and techniques that are effective in removing pesticide residues from fresh produce need to be developed and evaluated.

After harvest, fresh produce are often washed with tap water to remove dirt and debris. But the regular tap water wash has limited effect on pesticide residue removal because many pesticides are hydrophobic (Iizuka & Shimizu, 2014). Washing solutions added with strong oxidizing agents, such as ozone (Wu, Luan, Lan, Lo, & Chan, 2007) and chlorine dioxide (Chen, Wang, Chen, Zhang, & Liao, 2014) have shown to be effective in removing residual pesticides from produce samples. Amongst the common oxidizing agents, chlorine is the most widely used for water and produce disinfections due to its low cost, high effectiveness, and stability (Tian, Qiang, Liu, & Ling, 2013). Several studies have demonstrated the efficacy of chlorine in degrading pesticides (Acero, Benítez, Real, & González, 2008; Duirk, Desetto, & Davis, 2009; Pugliese et al., 2004). Therefore, water with dissolved chlorine could be effective in degrading and removing pesticide residues from fresh produce.

Electrolyzed oxidizing (EO) water generated from electrolysis of diluted salt solution (usually NaCl) has gained attention in the food industry as an effective sanitizer. During electrolysis, the anode side of the electrolytic cell generates EO water and the cathode side generates electrolyzed reduced (ER) water. EO water has strong oxidizing potential due to the presence of available chlorine with pH below 3.0 and oxidation-reduction potential (ORP) above +1000 mV, while ER water has reducing potential with pH above 11.0 and ORP below –800 mV (Huang, Hung, Hsu, Huang, & Hwang, 2008). The available chlorine in EO water usually presents in the form of hypochlorous acid, which is the most reactive chlorine species for inactivating microorganisms and oxidizing organic compounds (Deborde & von Gunten, 2008; Huang et al., 2008). The efficacy of electrolyzed water in inactivating foodborne pathogens has been extensively studied (Huang et al., 2008), but its efficacy in degrading chemical pollutants, such as pesticides, was not fully examined.

In addition to the concern on pesticide residues, produce colour and texture also need to be considered as they are key quality factors in fresh produce (Greve, McArdle, Gohlke, & Labavitch, 1994). Many studies indicated EO water treatment has no effect on the colour and appearance of fresh fruits and vegetables (Izumi, 1999; Park, Hung, Doyle, Ezeike, & Kim, 2001; Tian et al., 2015). However, in these studies, the available chlorine content (ACC) and treatment time were relatively low (ACC < 60 mg/l, treatment time < 10 min). Due to the strong oxidizing potential of chlorine, EO water at high ACC with long treatment time may cause discoloration and texture damage on produce samples.

In this study, the objective was to evaluate the effectiveness of EO water in removing pesticides diazinon, cyprodinil, and phosmet (Fig. S1) from fresh spinach, snap beans, and grapes. The effect of EO water treatment on produce colour and texture was also determined.

2. Materials and methods

2.1. Chemicals

Standard diazinon (purity 98.5%), cyprodinil (purity 99.9%), and phosmet (purity 99.7%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). LC/MS grade formic acid (purity 99.5%) was from Fisher Scientific (Fair Lawn, NJ, USA). Primary secondary amine

(PSA) was from Agilent Technologies (Santa Clara, CA, USA). ACS grade sodium chloride (NaCl) and USP grade magnesium sulfate anhydrous (MgSO₄) were from Amresco (Solon, OH, USA). HPLC grade acetonitrile was from EMD Millipore Corporation (Billerica, MA, USA). Concentrated bleach solution was from Clorox (Oakland, CA, USA). A commercial fresh produce washing solution was from VegWash (Irvine, CA, USA). Standard stock solutions (1000 mg/l) of each pesticide were prepared in acetonitrile and stored in amber glass bottles at 4 °C. Pesticide working solutions were prepared by diluting the standard stock solutions with deionized (DI) water.

2.2. Preparation of EO water and other washing solutions

EO and ER water were generated by electrolyzing a 0.03% NaCl solution with an electrolyzed water generator (Model #P30HST44T, EAU Technologies, GA, USA). EO and ER water were freshly made and used within 3 h. The pH and ORP were measured using an Accumet pH meter (AR50, Fisher Scientific, Pittsburgh, PA, USA) with pH and ORP electrodes. The ACC of EO water was measured using a DPD-FEAS titrimetric method (Hach Co., Loveland, Colo., USA). DI water was used to dilute EO water when ACC was higher than the targeted values. Drops of 1 M HCl and 1 M NaOH were used for adjusting the pH. EO water at pH 2.8 with 20, 70, and 120 mg/l ACC and ER water at pH 11.5 were collected into 10 L plastic bottles and sealed with plastic caps to prevent chlorine loss. Concentrated bleach solution was diluted with DI water to reach 120 mg/l ACC with pH around 7.5. VegWash solution was diluted according to its label: 8 ml VegWash in 1000 ml DI water.

2.3. Inoculation of produce with pesticides

Fresh organic spinach, organic snap beans and red seedless grapes (imported from Mexico) were purchased from a local grocery store and kept at 4 °C until use (within 72 h). All three produce did not contain the pesticides to be tested. To inoculate spinach and snap beans with pesticides, 3 or 1.6 ml of working solution with mixed diazinon, cyprodinil and phosmet (each at 20 mg/l or 40 mg/l, respectively) were deposited onto 15 g spinach leaves at the adaxial-side or 50 g snap beans at one side using a 200 µl micropipette, respectively. The inoculated spinach and snap beans were air dried for 3 h in a fume hood at 20 °C and then kept in a refrigerator at 4 °C for about 14 h to allow pesticide attachment. For grapes (5–7 g per grape), a working solution containing diazinon, cyprodinil, and phosmet each at 12 mg/l was prepared, and all grape samples were soaked in the working solution for 10 min followed by air-drying under a fume hood at 20 °C overnight (about 14 h).

2.4. Washing treatment

Treatment times of 1, 8, and 15 min with EO water at 20, 70, and 120 mg/l ACC were applied. A total of 9 treatment combinations were therefore conducted. Each inoculated produce samples were completely submerged in EO water to start the treatment. The ratios between produce samples to EO water were 15 g spinach: 1000 ml; 50 g snap beans: 500 ml; 200 g grapes: 500 ml. A plastic wire mesh was used to cover spinach and snap beans to prevent floating. All treatments were conducted in 2000 ml glass beakers placed on a reciprocal shaking bath (Model 2870, Thermo Fisher Scientific, Waltham, MA, USA) set at 100 rpm. After the EO water treatment, all produce samples were immediately transferred into 1000 ml tap water and soaked for about 15 s to remove the residual chlorine. ER water, diluted bleach (at 120 mg/l ACC), VegWash, and DI water were also used to treat the inoculated produce for 15 min as a comparison. After the treatment, all produce

samples were air dried for about 1 h at 20 °C before pesticide extraction.

2.5. Pesticide extraction

The pesticides on produce samples were extracted using the QuEChERS method (Anastassiades, Lehotay, Stajnbaher, & Schenck, 2003).

2.6. Pesticide analysis

Diazinon, cyprodinil and phosmet were determined with an ultra-performance liquid chromatography-tandem mass spectrometer (UPLC-MS/MS). An Acquity UPLC I-Class System (Waters Corp., Milford, MA, USA) was used for liquid chromatography. Chromatographic separation was carried out with an Acquity UPLC Bridged Ethylene Hybrid C18 reverse-phase column (2.1 × 50 mm, 1.7 μm particle size, Waters Corp., Milford, MA, USA). A TQD triple-quadrupole mass spectrometer (Waters Corp., Milford, MA, USA) with an ESI source operated in positive ion mode was used for mass spectrometry. The mobile phase of UPLC and spectrometer settings were the same as described in the work of Liang et al. (2013). The MRM transitions, limit of detection and limit of quantification are shown in Table S1. Quantification of each pesticide was based on five-point external standard curves prepared in matrix matched acetonitrile. Recoveries of each pesticide (Text S1) with the current extraction and analysis method are shown in Table S2.

2.7. Colour measurement

A Hunter Lab[®] Miniscan XETM colorimeter (Model 45/0-L, Hunter Associates Laboratory, Reston, VA, USA) using the CIE colour coordinates (L^* , a^* , b^*) was used to measure the colour of spinach and snap beans. Calibration of the colorimeter was performed at the start of each experiment day against a standard white tile and a black tile. Approximately 10 g spinach or 35 g snap beans were cut into small pieces and placed in a plastic petri-dish (9 cm diameter and 1 cm deep). Beneath the petri-dish, a dark background was placed to avoid diffraction. Three readings were taken from above for each sample with 120° rotation after each reading. The three readings were averaged to give representative values of L^* , a^* , b^* . Hue angle was calculated as $\tan^{-1}(b^*/a^*)$. Chroma was calculated as $(a^{*2} + b^{*2})^{1/2}$.

For grapes, a different colour measurement approach was performed as the colour of each grape was not uniform. A Minolta colorimeter (Model CR200b, Minolta CO., Japan) was used for colour measurement. The colorimeter was calibrated at the start of each experiment day against a standard white tile. Ten grapes were randomly selected before the washing treatment. Each grape was then numbered from 1 to 10 using a black marker. For each grape, colour measurements were conducted at three locations around the equatorial belt. The colour readings of the three locations on the same grape were averaged to give representative values of L^* , a^* , b^* . Each site used for the colour measurement was circled with a black marker. After the washing treatment, colour measurement was conducted again on the same site of each grape. Then, the total colour difference (ΔE) between the colour before and after the washing treatment for each grape was calculated using the equation $(\Delta a^{*2} + \Delta b^{*2} + \Delta L^{*2})^{1/2}$.

2.8. Texture measurement

Puncture and compression tests were conducted on grapes to measure the skin hardness and the overall firmness, respectively, using an Instron Universal Testing Machine (Mode 5544, Instron

Corporation, Canton, MA, USA). Ten grapes were used for each test. For puncture tests, individual grapes were placed with the equatorial side on a flat plastic washer (105 × 98 mm, 12 mm thick, with a 6.2 mm hole in the center) centered under the load cell and punctured with a probe (1.37 mm diameter) at 50 mm/min speed. The skin hardness was expressed as the peak force required to penetrate the skin in Newton (N). For compression tests, each grape was placed with the equatorial side on a stainless steel base (125 mm diameter and 25 mm thick). A 36 mm diameter cylindrical probe was used to compress each grape sample at a speed of 50 mm/min until the cylindrical probe reached 2 mm from the base plate. The energy (mJ) required to reach the peak force during compression test for each grape sample was used to represent firmness.

2.9. Statistical analysis

The entire experiment was replicated three times. Means and standard deviations were calculated using Excel (Micro software, USA). SAS software 9.4 (SAS Institute Inc., Cary, NC, USA) was used for statistical analysis. One-way analysis of variance was conducted followed by Duncan's multiple range test with proc anova procedure. A $P < 0.05$ was considered to be significantly different.

3. Results and discussion

3.1. Properties of EO water and other treatment solutions

EO water used was at pH 2.80 ± 0.05 with 20, 70, and 120 mg/l ACC and ORP of 1126.0 ± 7.0 , 1144.0 ± 10.0 , and 1151.5 ± 11.7 mV, respectively. ER water was at pH 11.50 ± 0.05 and ORP -878.1 ± 0.2 mV. Bleach was diluted to 120 mg/l ACC with pH 7.44 ± 0.08 and ORP 867.9 ± 8.8 mV.

3.2. Effect of EO water treatment on pesticide degradation in aqueous solution

The degradation of diazinon, cyprodinil, and phosmet under EO water treatment was conducted in aqueous solution first to evaluate its potential in pesticide degradation (Text S2). The results (Table S3) showed the efficacy of EO water in degrading the tested pesticides was affected by pH. When pH was reduced from 6.0 to 2.8, the degradations of all three pesticides increased significantly ($P < 0.05$). This pH effect may be attributed to the increase of ORP as EO water has a higher ORP at acidic pH (ORP > 1100 mV) while a lower ORP at neutral pH (ORP around 900 mV). Also, the available chlorine in EO water mainly exist in the form of hypochlorous acid at pH 3 to 6.5 (Huang et al., 2008). Hypochlorous acid is a strong oxidizing agent and its reaction with organic chemicals, such as pesticides, is strongly pH dependent (Deborde & von Gunten, 2008). At acidic conditions, EO water was highly effective in pesticide degradation with low ACC and short treatment time (Tables S4 and 5), and its efficacy was not significantly affected by the presence of multiple pesticides (Table S6). The kinetics study (Text S3) showed the reaction between EO water and the three pesticides followed pseudo-first-order kinetics at neutral pH while the reaction rate was too high to be observed at acidic pH (Fig. S2), demonstrating the higher pesticide degradation potential of EO water at acidic pH. In addition, the reductions of cyprodinil were always lower than diazinon and phosmet. Such difference might be explained by their chemical structures as hypochlorous acid is more prone to react with reduced sulfur moieties (Deborde & von Gunten, 2008). Both diazinon and phosmet contain the P=S double bond (Fig. S1) and are easy to be oxidized by hypochlorous acid. Based on the data of the aqueous study, the subsequent

washing experiments on produce samples were conducted with EO water at acidic pH, and the effect of ACC and treatment time was further investigated.

3.3. Effect of EO water treatment for pesticide removal on spinach

The reductions of diazinon, cyprodinil and phosmet residues from spinach after EO water treatment are shown in Table 1. The effect of EO water ACC and treatment time was studied with a total of 9 treatment combinations. The results showed both ACC and treatment time are important factors in pesticide removal using EO water. A maximum of 59.2% reduction of diazinon was achieved on spinach after treatment with EO water at 120 mg/l ACC for 15 min. The increase of ACC resulted in higher diazinon reductions. Significant ($P < 0.05$) differences of diazinon reductions were observed between 20 and 120 mg/l ACC at all three treatment times, while no significant difference was found between 70 and 120 mg/l ACC. The increase of treatment time also led to higher diazinon removals. This treatment time effect was more pronounced at the beginning (about 3 times more diazinon removal was achieved after extending the EO water (at 20 mg/l ACC) treatment from 1 to 8 min). However, further increase of treatment time from 8 to 15 min did not achieve additional reductions at 20 mg/l ACC.

The reductions of cyprodinil and phosmet followed the similar trend as diazinon. Both ACC and treatment time showed significant effects. A 43.8% and 85.7% reduction was achieved after 15 min EO water treatment at 120 mg/l ACC for cyprodinil and phosmet, respectively. The treatment time effect was more pronounced in the first 8 min and the ACC effect was observed between 20 and 120 mg/l. All treatment showed much higher overall reductions on phosmet than diazinon and cyprodinil. This is in accordance with our aqueous solution study (Section 3.2) (Tables S3–5) that phosmet was more sensitive towards EO water treatment.

There have been only two published studies investigating the effect of EO water on pesticide removal from fresh produce. Hao et al. (2011) reported that EO water with 70 mg/l ACC removed 74% acephate, 62% omethoate, and 59% dimethyl dichlorovinyl phosphate from spinach surface in 30 min. Another study by Lin, Tsai, Wu, Yeh, and Saalia (2006) found 67.5% reduction was achieved for both methamidophos and dimethoate on spinach in 9 min with constant refreshing of 50 mg/l ACC EO water and a 3-min follow-up wash with ER water. Their findings are close to the results achieved for diazinon and phosmet in the current study. Both diazinon and phosmet are organophosphorus pesticides as are the pesticides used in the two previous studies. Organophosphorus pesticides contain P=S double bonds and P-S or P-O single bonds and are easily attacked by chlorine (Deborde & von Gunten,

2008) and hence can be degraded by the available chlorine in EO water. Other sanitizing solutions, such as ozonated water and chlorine dioxide water, have also been reported for pesticide removal. About 35% and 44.5% diazinon were removed from vegetables leaves by chlorine dioxide solution (20 mg/l) (Chen et al., 2014) and ozonated water (2.0 mg/l) (Wu et al., 2007) in 15 min, which are both lower than the high reduction of diazinon (59.2%) achieved by the current study. Considering the relatively safe to handle and low toxicity of EO water, our study demonstrated the great potential of EO water for pesticide residue removal from spinach and other vegetables leaves.

3.4. Effect of EO water treatment for pesticide removal on snap beans

The removal of diazinon, cyprodinil and phosmet from snap beans are shown in Table 2. The overall reductions on snap beans were similar to the reductions on spinach. The increase of ACC and treatment time both resulted in higher pesticide reductions. The highest reduction of diazinon was 66.5%, which is higher than the maximum reduction (59.2%) achieved on spinach. This is probably because the surface of snap beans is smoother than spinach surface and therefore the residual pesticides are more easily washed off. The ACC effect was not significant in the first minute while significant ($P < 0.05$) ACC effect on diazinon reduction was found after 8 min washing treatment, where the diazinon removal (55.8%) achieved by EO water at ACC 120 mg/l was 2.5 times higher than that (20.4%) achieved by EO water at 20 mg/l ACC. Diazinon removal due to further increase of treatment from 8 to 15 min was more significant at 20 and 70 mg/l ACC and an addition of 115% (20.4–43.9%) and 80% (35.7–64.0%) reduction was observed, respectively.

For cyprodinil and phosmet, the maximum reductions were 50.0 and 73.0%, respectively. Same effect of ACC and treatment time was also observed. No significant difference in reduction was shown across different ACC levels until the treatment time reached 8 min. Also, for all three pesticides, the reductions achieved at 70 and 120 mg/l ACC after 15 min were very similar, from 64.0 to 66.5%, 49.6 to 50.0%, and 66.5 to 73.0% for diazinon, cyprodinil, and phosmet, respectively. These indicated longer treatment time is required to remove pesticide residues from snap beans while an ACC of 70 mg/l would be sufficient as further increase of ACC may not result in significantly high reductions. In addition, for both spinach and snap beans, the reductions of cyprodinil were lower than diazinon and phosmet at most of the treatment conditions. This might be explained by the relatively lower reactivity of cyprodinil with EO water shown in Fig. S2 and the different affinity of cyprodinil with produce surface due to its chemical structure and polarity.

Table 1
Mean reductions of diazinon, cyprodinil, and phosmet on spinach after EO water treatment.

Treatment time (min)	ACC (mg/l)	Percentage Reduction (%)		
		Diazinon	Cyprodinil	Phosmet
1	20	8.8 ± 5.9 ^E	9.7 ± 3.1 ^E	56.6 ± 2.1 ^E
	70	19.3 ± 5.4 ^{DE}	17.2 ± 2.7 ^D	57.8 ± 5.5 ^E
	120	29.8 ± 8.4 ^{CD}	19.4 ± 0.3 ^D	64.3 ± 7.9 ^{DE}
8	20	33.2 ± 3.5 ^C	21.9 ± 6.4 ^D	70.9 ± 4.5 ^{CD}
	70	40.3 ± 8.5 ^{BC}	32.3 ± 2.9 ^C	72.3 ± 6.2 ^{CD}
	120	47.0 ± 6.1 ^B	34.3 ± 0.3 ^{BC}	82.0 ± 4.0 ^{AB}
15	20	33.0 ± 6.7 ^C	30.5 ± 6.3 ^{BC}	74.7 ± 0.3 ^{BC}
	70	49.5 ± 6.7 ^{AB}	38.3 ± 1.8 ^B	83.5 ± 5.7 ^{AB}
	120	59.2 ± 5.5 ^A	43.8 ± 2.9 ^A	85.7 ± 4.8 ^A

The initial concentrations were 1.742 ± 0.461, 4.020 ± 0.393, and 3.727 ± 0.754 mg/kg for diazinon, cyprodinil, and phosmet, respectively. Mean values ($n = 3$) in the same column with the same superscript letters are not significantly different ($P \geq 0.05$).

Table 2
Mean reductions of diazinon, cyprodinil, and phosmet on snap beans after EO water treatment.

Treatment time (min)	ACC (mg/l)	Percentage reduction (%)		
		Diazinon	Cyprodinil	Phosmet
1	20	12.0 ± 5.2 ^D	12.0 ± 2.9 ^F	37.7 ± 6.7 ^F
	70	11.2 ± 7.0 ^D	12.9 ± 1.0 ^F	46.0 ± 4.4 ^{EF}
	120	18.5 ± 8.2 ^D	18.0 ± 4.0 ^{EF}	45.1 ± 8.9 ^{EF}
8	20	20.4 ± 2.5 ^D	25.8 ± 4.7 ^{DE}	43.2 ± 2.5 ^F
	70	35.7 ± 6.1 ^C	26.9 ± 1.0 ^{CD}	55.9 ± 3.5 ^{CD}
	120	55.8 ± 5.5 ^B	40.4 ± 6.9 ^B	63.5 ± 2.5 ^{BC}
15	20	43.9 ± 7.9 ^C	34.7 ± 2.3 ^{BC}	52.1 ± 0.1 ^{DE}
	70	64.0 ± 3.1 ^{AB}	49.6 ± 6.5 ^A	66.5 ± 2.8 ^{AB}
	120	66.5 ± 2.5 ^A	50.0 ± 8.2 ^A	73.0 ± 2.7 ^A

The initial concentrations were 0.306 ± 0.080, 1.207 ± 0.034, and 0.916 ± 0.125 mg/kg for diazinon, cyprodinil, and phosmet, respectively. Mean values ($n = 3$) in the same column with the same superscript letters are not significantly different ($P \geq 0.05$).

The studies on the effect of EO water on pesticide removal from snap beans are limited. But there have been studies about using sodium hypochlorite to remove pesticide residue from fresh produce with smooth surface. Pugliese et al. (2004) demonstrated that sodium hypochlorite had similar pesticide removal efficiency compared with tap water on nectarines. Similar results were also reported in the study of Al-Taher, Yang, Wylie, and Cappozzo (2013), that sodium hypochlorite (at 80 mg/l ACC) achieved the lowest reduction of seven pesticide residues on tomatoes compared to other washing solutions, such as tap water and peroxy-acetic acid. Ong, Cash, Zabik, Siddiq, and Jones (1996) achieved high reductions of pesticide formetanated-HCl with chlorine wash on apples, but the chlorine content was at 500 mg/l which is much higher than generally recommended for produce washing (Suslow, 1997). Therefore, EO water, as an advanced chlorine-based solution, is more superior than regular sodium hypochlorite-based sanitizers in removing pesticide residues from fresh produce.

3.5. Effect of EO water treatment for pesticide removal on grapes

The reductions of diazinon, cyprodinil, and phosmet on grapes after EO water treatment are shown in Table 3. Although the pesticide reduction trend on grapes was the same as on spinach and snap beans, the effect of ACC and treatment time were not significant due to the low overall reductions. As the ACC and treatment time increased, the pesticide reductions increased slowly. Additional reductions when EO water ACC was increased from 20 to 120 mg/l were achieved for diazinon (from 10.2–27.4% to 22.3–37.1%), cyprodinil (from 9.2–21.0% to 17.8–31.5%), and phosmet (from 21.4–35.2% to 34.2–49.4%). Similar additional reductions were also achieved when treatment time increased from 1 to

15 min for all three pesticides. The maximum reduction of diazinon and cyprodinil was only 37.1 and 31.5%, respectively. Although a 49.4% reduction of phosmet was achieved, it is still much lower than the high phosmet reductions achieved on spinach and snap beans (Tables 1 and 2).

The surface texture of grape may explain its low overall pesticide reductions. Fruits like grapes can form epicuticular waxes on their surface to prevent moisture loss (Rustioni, Maghradze, & Failla, 2012). López-Fernández, Rial-Otero, and Simal-Gándara (2013) argued that many pesticides have tendencies to migrate into the wax layer on fruit surfaces which makes pesticides less likely to contact with the dissolved oxidizing compounds in washing solutions. Because of the high liposolubility of many pesticides, they tend to strongly bond to the wax layer on fruit skins and become less likely to be washed off by washing treatment. Mourad, Aguilera, Camacho, Mohamed, and Valverde (2005) found that an intensive washing treatment on tomatoes only showed very limited reductions of pesticides (pyrifenoxy, pyridaben and tralometrin). Thus, it is highly possible that most of the pesticide residues will migrate and bond to the surface wax layer on grapes, and hence limit the effectiveness of EO water treatment.

3.6. Comparison between EO water and other solutions on pesticide removal

The reductions of diazinon, cyprodinil and phosmet from spinach, snap beans and grapes after EO water, ER water, bleach solution, VegWash and DI water treatment are compared and shown in Fig. 1. EO water at 120 mg/l ACC was used. Bleach was diluted to ACC of 120 mg/l. VegWash is a commercial produce wash solution. The results showed EO water was significantly ($P < 0.05$) more

Table 3
Mean reductions of diazinon, cyprodinil, and phosmet on grapes after EO water treatment.

Treatment time (min)	ACC (mg/l)	Percentage reduction (%)		
		Diazinon	Cyprodinil	Phosmet
1	20	10.2 ± 1.8 ^D	9.2 ± 3.6 ^E	21.4 ± 9.7 ^F
	70	18.4 ± 7.4 ^{CD}	14.9 ± 2.1 ^{DE}	28.3 ± 4.6 ^{EF}
	120	22.3 ± 4.2 ^{BC}	17.8 ± 1.2 ^{CD}	34.2 ± 5.1 ^{DE}
8	20	21.7 ± 1.8 ^{BC}	21.5 ± 3.4 ^{BCD}	28.7 ± 7.1 ^{EF}
	70	25.5 ± 5.7 ^{BC}	22.2 ± 3.8 ^{BC}	38.5 ± 5.6 ^{BCD}
	120	29.5 ± 9.9 ^{AB}	26.3 ± 6.3 ^{AB}	44.1 ± 3.2 ^{ABC}
15	20	27.4 ± 5.3 ^{ABC}	21.0 ± 4.9 ^{BCD}	35.2 ± 3.8 ^{CDE}
	70	31.9 ± 5.3 ^{AB}	25.2 ± 3.6 ^{AB}	45.3 ± 1.4 ^{AB}
	120	37.1 ± 4.1 ^A	31.5 ± 2.6 ^A	49.4 ± 1.3 ^A

The initial concentrations were 0.083 ± 0.014, 0.774 ± 0.091, and 0.133 ± 0.011 mg/kg for diazinon, cyprodinil, and phosmet, respectively. Mean values ($n = 3$) in the same column with the same superscript letters are not significantly different ($P \geq 0.05$).

effective than ER water, bleach, VegWash and DI water in removing diazinon, cyprodinil and phosmet from the three produce samples. The only exception was for cyprodinil on grapes that no significant ($P \geq 0.05$) difference was found between bleach and EO water treatment. However, the reductions achieved by bleach were mostly the lowest and not significantly different compared with the reductions achieved by DI water treatment. This demonstrated that EO water is much more effective than regular chlorine-based bleach solutions for pesticide residue removal from fresh produce.

ER water was shown to be equally effective as EO water in degrading phosmet in aqueous solution (Table S3). But its effect in removing phosmet from produce surface was not as significant

as EO water. This is different than the study of Hao et al. (2011) where they found ER water was more effective than EO water in removing acephate and omethoate residues from spinach surface. This is probably due to the low ACC (70 mg/l) of EO water they tested. As shown in Tables 1–3, the efficacy of EO water in removing pesticide residues can be enhanced by increasing the ACC, while the efficacy of ER water cannot be improved. In addition, VegWash generally achieved the second-best pesticide removals on all three tested produce. Its effect is probably due to the presence of saponified organic oils, such as coconut oil and olive oil that have cleaning functionalities.

3.7. Effect of EO water treatment on produce colour and texture

The colour change of spinach, snap beans and grapes after EO water treatment at different conditions are shown in Table 4. EO water at 120 and 70 mg/l ACC with 15 min treatment were selected because they achieved the highest pesticide reductions (Tables 1–3). EO water at 120 mg/l ACC with 8 min treatment and DI water treatment for 15 min were selected as comparisons. Unwashed produce samples were used as the control. No significant ($P \geq 0.05$) colour difference was found between spinach and snap beans treated with different solutions and the unwashed control in terms of L^* , Chroma and hue angle. This indicated the luminosity, colour intensity, and colour quality (greenish) of spinach and snap beans were not significantly affected. For grapes, although no statistical difference ($P \geq 0.05$) was found in hue angle, the mean hue angle values varied (from 18.2 to 13.9) a lot. This was mainly because the colour on grapes was not uniform. Therefore, total colour difference (ΔE^*) was measured for each individual grape. ΔE^* indicates the magnitude of colour difference between control and treated samples and the difference is classified as very distinct ($\Delta E^* > 3$), distinct ($1.5 < \Delta E^* < 3$), and small difference ($\Delta E^* < 1.5$) (Pathare, Opara, & Al-Said, 2013). The calculated ΔE^* values for both EO water and DI water treated grapes were around 1.4–1.7, indicating medium colour changes. This might be because the surface wax on grapes was washed off during the washing treatment. In addition, DI water washing caused 1.6 ΔE^* on colour change which was even higher than that of EO water treatment at 120 mg/l ACC (1.4 ΔE^*). This suggested that EO water within the current ACC and treatment time range studied would not cause significant discoloration on grapes.

Although the effect of EO water treatment on fresh produce colour quality have been well documented, most studies only applied EO water at low ACC and short treatment time. For example, Park et al. (2001) washed fresh lettuce with EO and acidified chlorinated water at 45 mg/l ACC for 3 min and found no significant discoloration compared to the tap water washed and unwashed lettuce. Our study showed EO water at 120 mg/l ACC with 15 min treatment time would also not cause significant colour deterioration. Based on our pesticide reduction results (Tables 1–3), it can be assumed that the efficacy of EO water on pesticide residue removal can be further improved by increasing ACC without causing significant appearance damage. This could be one major advantage of EO water against other potential sanitizers, such as ozonated water, because 15 min of 13 mg/l ozone treatment can cause significant pigment oxidation (Chu et al., 2007) whereas no colour effect was found on vegetable leaves after treated with ozonated water at 2 mg/l (Ikeura, Hamasaki, & Tamaki, 2013).

The texture changes of grapes after EO water treatment are shown in Table 5. Compression and puncture tests were conducted to measure the overall firmness and skin hardness, respectively. No significant texture difference was found between the treated and unwashed grape samples. The results indicated EO water at high ACC and long treatment time does not significantly affect the texture of grapes. Hung, Bailly, Kim, Zhao, and Wang (2010) reported

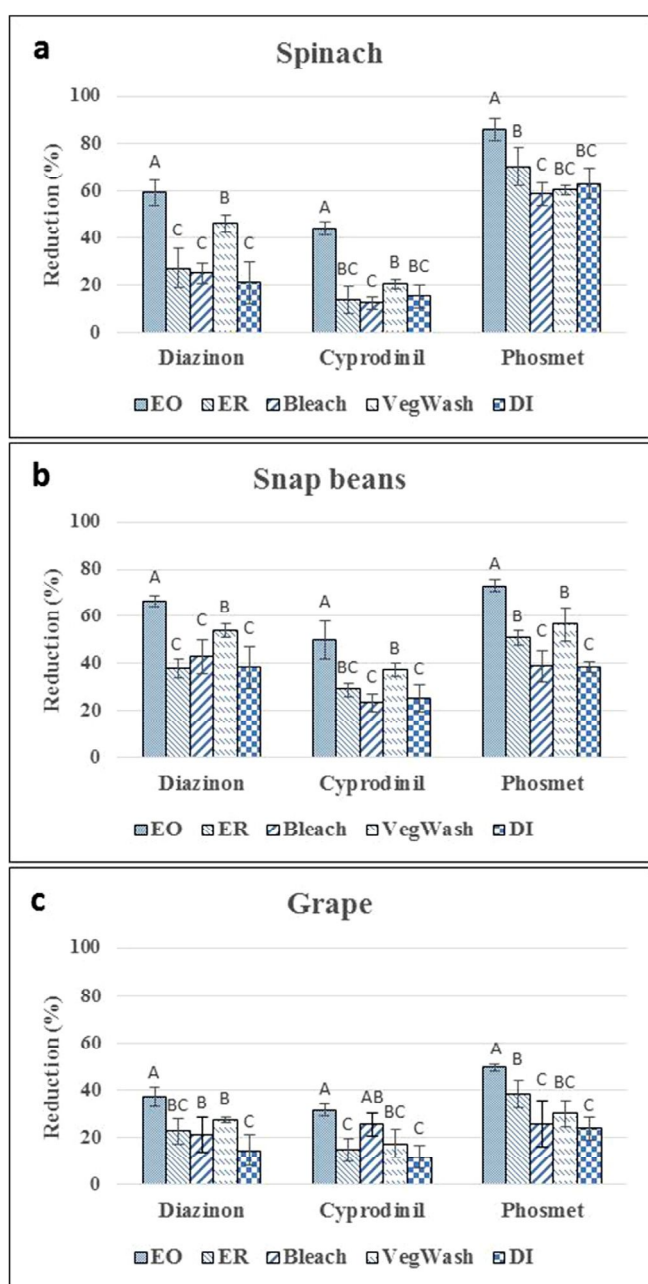


Fig. 1. Comparison of EO water and other washing solutions in removing pesticide residues from (a) spinach, (b) snap beans, and (c) grapes. Columns in each figure represent the mean ($n = 3$) pesticide reductions (%). Vertical bars represent the standard deviations. Columns with the same letters are not significantly ($P \geq 0.05$) different. EO water was at 120 mg/l ACC and pH 2.8. Bleach was at 120 mg/l ACC and pH 7.5. ER water was at pH 11.5. All produce were treated for 15 min.

Table 4
Results of produce colour before and after the washing treatment.

Produce	Treatment	L^*	Chroma (C^*)	Hue angle (h^*)	ΔE^*
Grapes	EO ₁	32.6 ± 1.2 ^A	8.9 ± 0.9 ^A	16.9 ± 6.1 ^A	1.4 ± 0.4 ^A
	EO ₂	32.9 ± 1.0 ^A	9.0 ± 0.7 ^A	18.2 ± 6.3 ^A	1.7 ± 0.3 ^A
	EO ₃	32.3 ± 0.8 ^A	8.5 ± 0.1 ^A	16.6 ± 5.1 ^A	1.5 ± 0.4 ^A
	DI	32.3 ± 0.8 ^A	9.0 ± 0.8 ^A	15.4 ± 4.2 ^A	1.6 ± 0.1 ^A
	Unwashed	32.7 ± 0.9 ^A	10.1 ± 0.4 ^A	13.9 ± 6.6 ^A	
Spinach	EO ₁	29.54 ± 3.00 ^A	16.06 ± 1.94 ^A	114.35 ± 1.55 ^A	
	EO ₂	30.32 ± 3.44 ^A	16.11 ± 2.44 ^A	114.06 ± 1.88 ^A	
	EO ₃	29.86 ± 3.36 ^A	16.96 ± 2.64 ^A	114.46 ± 1.53 ^A	
	DI	30.95 ± 3.48 ^A	17.62 ± 2.88 ^A	114.10 ± 1.63 ^A	
	Unwashed	29.49 ± 2.24 ^A	17.28 ± 2.73 ^A	113.53 ± 0.80 ^A	
Snap beans	EO ₁	36.35 ± 2.02 ^A	24.62 ± 1.34 ^A	107.74 ± 0.64 ^A	
	EO ₂	36.01 ± 0.98 ^A	23.22 ± 0.34 ^A	108.31 ± 0.71 ^A	
	EO ₃	35.95 ± 0.99 ^A	22.44 ± 0.78 ^A	107.83 ± 1.16 ^A	
	DI	36.92 ± 2.30 ^A	24.21 ± 2.14 ^A	109.06 ± 1.26 ^A	
	Unwashed	35.98 ± 0.74 ^A	23.43 ± 1.08 ^A	109.17 ± 0.87 ^A	

Means ($n = 30$ for grapes and $n = 3$ for spinach and snap beans) in the same column within each produce followed by the same superscript letters are not significantly different ($P \geq 0.05$). EO₁ = Washed by EO water at 120 mg/l ACC for 15 min; EO₂ = Washed by EO water at 70 mg/l ACC for 15 min; EO₃ = Washed by EO water at 120 mg/l ACC for 8 min; DI = Washed by DI water for 15 min.

Table 5
Results of compression and puncture tests for grapes before and after the washing treatment.

Treatment	Compression energy (mj)	Puncture force (N)
EO ₁	652.20 ± 61.66 ^A	2.56 ± 0.33 ^A
EO ₂	632.30 ± 75.95 ^A	2.38 ± 0.19 ^A
EO ₃	641.67 ± 40.11 ^A	2.45 ± 0.27 ^A
DI	655.29 ± 23.32 ^A	2.59 ± 0.12 ^A
Unwashed	651.51 ± 22.61 ^A	2.53 ± 0.13 ^A

Means ($n = 30$) in the same column with the same superscript letters are not significantly different ($P \geq 0.05$). EO₁ = Washed by EO water at 120 mg/l ACC for 15 min; EO₂ = Washed by EO water at 70 mg/l ACC for 15 min; EO₃ = Washed by EO water at 120 mg/l ACC for 8 min; DI = Washed by DI water for 15 min.

both EO and chlorinated water (55 and 100 mg/l ACC) treatment for 5 min did not cause significant texture change on strawberries and broccoli compared to tap water washed and unwashed samples during a 13-day storage. Laureano et al. (2016) also revealed that there was no significant difference of skin hardness on grapes after treated with EO at 400 mg/l ACC and DI water for 10 min. Thus, the overall results of the current study suggested that EO water with high ACC (120 mg/l) and long treatment time (15 min) would not cause a significant detrimental effect on the colour and texture of fresh produce.

4. Conclusions

Our study demonstrated that EO water can effectively remove diazinon, cyprodinil and phosmet residues from fresh spinach, snap beans and grapes. High ACC and long treatment time can lead to high pesticide removals. Within the current ACC (20–120 mg/l) and treatment time (1–15 min) range, EO water would not significantly affect the colour and the texture of the tested produce. Thus, EO water is suitable to wash produce for pesticide residue removal. Further studies are also needed to investigate the pesticide degradation mechanism and possible disinfection by-products after the EO water treatment.

Conflict of interest statement

The authors whose names are listed immediately below certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership,

employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

Acknowledgements

This research was supported by the State and Hatch funds allocated to the University of Georgia Agricultural Experiment Station, Griffin Campus. The authors would like to thank Qi Luo from the Department of Crop and Soil Sciences of the University of Georgia for her technical help on UPLC–MS/MS.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.foodchem.2017.06.144>.

References

- Acero, J. L., Benítez, F. J., Real, F. J., & González, M. (2008). Chlorination of organophosphorus pesticides in natural waters. *Journal of Hazardous Materials*, *153*, 320–328.
- Al-Tajer, F., Yang, C., Wylie, P., & Cappozzo, J. (2013). Reduction of pesticide residues in tomatoes and other produce. *Journal of Food Protection*, *76*, 510–515.
- Anastassiades, M., Lehotay, S. J., Stajnbaher, D., & Schenck, F. J. (2003). Fast and easy multiresidue method employing acetonitrile extraction/partitioning and “dispersive solid-phase extraction” for the determination of pesticide residues in produce. *Journal of AOAC International*, *86*, 412–431.
- Arduini, F., Cinti, S., Scognamiglio, V., & Moscone, D. (2016). Nanomaterials in electrochemical biosensors for pesticide detection: Advances and challenges in food analysis. *Microchimica Acta*, *183*, 2063–2083.
- Berrada, H., Fernandez, M., Ruiz, M. J., Molto, J. C., Manes, J., & Font, G. (2010). Surveillance of pesticide residues in fruits from Valencia during twenty months (2004/05). *Food Control*, *21*, 36–44.
- Bonnechère, A., Hanot, V., Jolie, R., Hendrickx, M., Bragard, C., Bedoret, T., & Van Looc, J. (2012). Effect of household and industrial processing on levels of five pesticide residues and two degradation products in spinach. *Food Control*, *25*, 397–406.
- Cabras, P., Angioni, A., Garau, V. L., Melis, M., Pirisi, F. M., Karim, M., & Minelli, E. V. (1997). Persistence of insecticide residues in olives and olive oil. *Journal of Agricultural and Food Chemistry*, *45*, 2244–2247.
- Chen, Q., Wang, Y., Chen, F., Zhang, Y., & Liao, X. (2014). Chlorine dioxide treatment for the removal of pesticide residues on fresh lettuce and in aqueous solution. *Food Control*, *40*, 106–112.
- Chu, L.-B., Xing, X.-H., Yu, A.-F., Zhou, Y.-N., Sun, X.-L., & Jurcik, B. (2007). Enhanced ozonation of simulated dyestuff wastewater by microbubbles. *Chemosphere*, *68*, 1854–1860.

- Deborde, M., & von Gunten, U. (2008). Reactions of chlorine with inorganic and organic compounds during water treatment—Kinetics and mechanisms: A critical review. *Water Research*, 42, 13–51.
- Duirk, S. E., Desetto, L. M., & Davis, G. M. (2009). Transformation of organophosphorus pesticides in the presence of aqueous chlorine: Kinetics, pathways, and structure-activity relationships. *Environmental Science & Technology*, 43, 2335–2340.
- Greve, L. C., McArdle, R. N., Gohlke, J. R., & Labavitch, J. M. (1994). Impact of heating on carrot firmness: Changes in cell wall components. *Journal of Agricultural and Food Chemistry*, 42, 2900–2906.
- González-Rodríguez, R. M., Rial-Otero, R., Cancho-Grande, B., Gonzalez-Barreiro, C., & Simal-Gándara, J. (2011). A review on the fate of pesticides during the processes within the food-production chain. *Critical Reviews in Food Science and Nutrition*, 51, 99–114.
- Hao, J., Wuyundalai Liu, H. J., Chen, T. P., Zhou, Y. X., Su, Y. C., & Li, L. T. (2011). Reduction of pesticide residues on fresh vegetables with electrolyzed water treatment. *Journal of Food Science*, 76, C520–C524.
- Huang, Y.-R., Hung, Y.-C., Hsu, S.-Y., Huang, Y.-W., & Hwang, D.-F. (2008). Application of electrolyzed water in the food industry. *Food Control*, 19, 329–345.
- Hung, Y.-C., Bailly, D., Kim, C., Zhao, Y., & Wang, X. (2010). Effect of electrolyzed oxidizing water and chlorinated water treatments on strawberry and broccoli quality. *Journal of Food Quality*, 33, 578–598.
- Iizuka, T., & Shimizu, A. (2014). Removal of pesticide residue from Brussels sprouts by hydrostatic pressure. *Innovative Food Science and Emerging Technologies*, 22, 70–75.
- Ikeura, H., Hamasaki, S., & Tamaki, M. (2013). Effects of ozone microbubble treatment on removal of residual pesticides and quality of persimmon leaves. *Food Chemistry*, 138, 366–371.
- Izumi, H. (1999). Electrolyzed water as a disinfectant for fresh-cut vegetables. *Journal of Food Science*, 64, 536–539.
- Juraske, R., Mutel, C. L., Stoessel, F., & Hellweg, S. (2009). Life cycle human toxicity assessment of pesticides: Comparing fruit and vegetable diets in Switzerland and the United States. *Chemosphere*, 77, 939–945.
- Langley, R. L., & Mort, S. A. (2012). Human exposures to pesticides in the United States. *Journal of Agromedicine*, 17, 300–315.
- Laureano, J., Giacosa, S., Segade, S. R., Torchio, F., Cravero, F., Gerbi, V., & Rolle, L. (2016). Effects of continuous exposure to ozone gas and electrolyzed water on the skin hardness of table and wine grape varieties. *Journal of Texture Studies*, 47, 40–48.
- Lentza-Rizos, C., Avramides, E. J., & Kokkinaki, K. (2006). Residues of azoxystrobin from grapes to raisins. *Journal of Agricultural and Food Chemistry*, 54, 138–141.
- Liang, X. Y., Liu, X. G., Dong, F. S., Xu, J., Qin, D. M., Li, Y. B., & Zheng, Y. Q. (2013). Simultaneous determination of pyrimethanil, cyprodinil, mepanipyrim and its metabolite in fresh and home-processed fruit and vegetables by a QuEChERS method coupled with UPLC–MS/MS. *Food Additives & Contaminants: Part A*, 30, 713–721.
- Lin, C.-S., Tsai, P.-J., Wu, C., Yeh, J.-Y., & Saalia, F. K. (2006). Evaluation of electrolysed water as an agent for reducing methamidophos and dimethoate concentrations in vegetables. *International Journal of Food Science & Technology*, 41, 1099–1104.
- López-Fernández, O., Rial-Otero, R., & Simal-Gándara, J. (2013). Factors governing the removal of mancozeb residues from lettuces with washing solutions. *Food Control*, 34, 530–538.
- Mourad, B., Aguilera, A., Camacho, F., Mohamed, S., & Valverde, A. (2005). Effect of household processing and unit-to-unit variability of pyrifenoxy, pyridaben, and tralomethrin residues in tomatoes. *Journal of Agricultural and Food Chemistry*, 53, 4054–4058.
- Ong, K. C., Cash, J. N., Zabik, M. J., Siddiq, M., & Jones, A. L. (1996). Chlorine and ozone washes for pesticide removal from apples and processed apple sauce. *Food Chemistry*, 55, 153–160.
- Park, C. M., Hung, Y.-C., Doyle, M. P., Ezeike, G. O. I., & Kim, C. (2001). Pathogen reduction and quality of lettuce treated with electrolyzed oxidizing and acidified chlorinated water. *Journal of Food Science*, 66, 1368–1372.
- Pathare, P. B., Opara, U. L., & Al-Said, F. A. (2013). Colour measurement and analysis in fresh and processed foods: A review. *Food and Bioprocess Technology*, 6, 36–60.
- Pooja, M., & Latika, Y. (2014). Uses of pesticide in foods: Curse for health. *Asian Journal of Bio Science*, 9, 123–128.
- Pugliese, P., Moltó, J. C., Damiani, P., Marín, R., Cossignani, L., & Mañes, J. (2004). Gas chromatographic evaluation of pesticide residue contents in nectarines after non-toxic washing treatments. *Journal of Chromatography A*, 1050, 185–191.
- Regueiro, J., López-Fernández, O., Rial-Otero, R., Cancho-Grande, B., & Simal-Gándara, J. (2015). A review on the fermentation of foods and the residues of pesticides-biotransformation of pesticides and effects on fermentation and food quality. *Critical reviews in Food Science and Nutrition*, 55, 839–863.
- Rustioni, L., Maghradze, D., & Failla, O. (2012). Optical properties of berry epicuticular waxes in four Georgian grape cultivars (*Vitis vinifera* L.). *South African Journal of Enology and Viticulture*, 33, 138–143.
- Suslow, T. (1997). *Postharvest chlorination: Basic properties and key points for effective disinfection*. Davis: University of California. ISBN 978-1-60107-183-5. URL <<http://anrcatalog.ucanr.edu/pdf/8003.pdf>> Accessed 15.03.2017.
- Tian, D., Zhi, G., John, S., Xu, Y.-T., Jones, C. I., & Liu, D.-H. (2015). Impact of slightly acidic electrolyzed water (SAEW) and ultrasound on microbial loads and quality of fresh fruits. *LWT – Food Science and Technology*, 60, 1195–1199.
- Tian, F., Qiang, Z., Liu, W., & Ling, W. (2013). Methiocarb degradation by free chlorine in water treatment: Kinetics and pathways. *Chemical Engineering Journal*, 232, 10–16.
- Wu, J., Luan, T., Lan, C., Lo, W., & Chan, Y. (2007). Removal of residual pesticides on vegetable using ozonated water. *Food Control*, 18, 466–472.