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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

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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.

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 (Juraske, 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 (Juraske 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), yhung@uga.edu (Y.-C. Hung).

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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 ($MgSO_4$) 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