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Non-thermal plasma for elimination of pesticide residues in mango

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ABSTRACT

The effects of non-thermal plasma (NTP) on elimination of pesticide residues and on quality changes of mango (cv. Nam Dok Mai) were investigated. Varied flow rate of Ar gas (2, 5 and 8 L/min) and time dependent degradations of chlorpyrifos and cypermethrin as a result of NTP treatments using a gliding arc (GA) discharge for 5 or 10 min were studied. Results showed that the NTP treatment for 5 min at 5 L/min Ar flow rate successfully decreased the concentrations of chorpyrifos by 74.0% and cypermetrin by 62.9%. There were significant ($p \leq 0.05$) decreases in titratable acidity and total phenolic content and increases in carotenoid content for the treated mangoes. However, total soluble solid, color and texture parameters were not significantly different ($p > 0.05$). The emission signal of hydroxyl (OH•) radicals at 309 nm was also obtained to monitor that the system was working properly.

Industrial relevance: This study demonstrates the potential application of non-thermal plasma (NTP) as a way to eliminate pesticide residues and on quality changes in mango. A varied flow rate of Ar gas and time dependent degradation of chlorpyrifos and cypermethrin were studied for NTP treatments produced using a gliding arc (GA) discharge. Our results have proved that the GA discharge NTP has the potential to be an effective method to ensure chemical safety not only for mangoes, but also for other types of postharvest produce. This system can be adapted for the industrial up-scale.

1. Introduction

Thailand is the fourth ranked mango (*Mangifera indica* L.) producer in the world with a 27% share of the world market, and the Nam Dok Mai cultivar is used for export and for local consumption at the ripening stage (Schulze, Spreer, Keil, Ongprasert, & Müller, 2013). However, various insects, mites and microorganisms lead to quality deterioration reducing the market value of mangoes. To minimize the economic losses caused by these pests, farmers rely on pesticides (Singh et al., 2008), and when applied improperly, residues of some of these chemicals can remain and can become hazardous to human health (Sharma, Nagpal, Pakade, & Katnoria, 2010). The Thailand Pesticide Alert Network (Thai-PAN, 2016) suggested that 44% of mangoes contained pesticide residues. Chlorpyrifos, an organophosphorus (OP) and cypermethrin, a pyrethroid, are widely used insecticides for many crops including mango (Singh et al., 2008) with high detection percentages (~95%) in many fruit samples such as tangerine, guava, apple, dragon fruit and mango purchased from local markets in Thailand (Pakvilai et al., 2011). According to the Codex Alimentarius Commission (2016), the Maximum Residue Limits (MRL) for chlorpyrifos on spices, fruits and berries is 1 ppm, and for cypermethrin on mangoes is 0.7 ppm.

Several methods have been applied to eliminate pesticide residues in postharvest products. Chemical sanitizing methods, usually chlorine-based compounds, are commonly used. However, with increased public health concerns about the risk of carcinogenic by-products formation, these compounds have been prohibited in a number of countries (Baier et al., 2013; Schnabel, Niquet, Schlüter, Gniffke, & Ehlbeck, 2015). Thermal treatments may ensure a safe level, but they also affect the flavor, color and texture of products (Heo et al., 2014). Thus, new processes for the decontamination of chemical residues as well as maintaining nutritional and sensory qualities of fruits are required.

Non-thermal plasma (NTP) is one of the emerging novel technologies that could potentially decontaminate fresh food and food processing surfaces. It involves exposing food to ionizing radiation including

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charged particles, electric fields, photons and/or reactive species to disinfect products by removing microbes and hazards while ensuring the safety of products (Misra, Pankaj, et al., 2014; Phan, Phan, Brennan, & Phimolsiripol, 2017). The reactive agents mainly produced by common NTP sources include excited O_2 and nitrogen N_2, reactive oxygen species (ROS), reactive nitrogen species (RNS), and in the presence of humidity, H_2O^+, OH^- anion, OH· radical or hydrogen peroxide (H_2O_2) are also present (Scholtz, Pazlarova, Souskova, Khun, & Julak, 2015). Among ROS contained in plasmas, the OH· radical is considered as the highest oxidation potential species (Surowsky, Schlüter, & Knorr, 2014). NTP using a dielectric barrier discharge (DBD) has been successfully shown to degrade pesticide residues on strawberries (Misra, Pankaj, et al., 2014). The reduction of OP pesticides sprayed onto maize samples when treated with oxygen NTP was also studied by Bai, Chen, Mu, Zhang, and Li (2009). By applying NTP, harmful bacteria and toxins in fruits, vegetables, and meat products can be eliminated effectively while the fresh taste, aroma, texture, wholesomeness, and nutritional content are still preserved (Baier et al., 2013; Pankaj et al., 2014). Besides, the disinfecting ability of NTP, it offers the advantages of being free of sanitizing chemicals, a low temperature of operation, and can be used safely and continuously (Lacombe et al., 2015). However, studies are limited for fresh produce including mangoes. Therefore, this work aimed to investigate the potential of NTP produced by applying a gliding arc (GA) discharge for decontamination of pesticide residues on fresh Nam Dok Mai mangoes and to quantify the impact of plasma treatment on the physicochemical attributes of the fruit.

2. Materials and methods

2.1. Materials

Export grade Nam Dok Mai mangoes (90–100 days after full bloom) were purchased (Shine Forth Co. Ltd., Bangkok, Thailand). Fruits were packed in new, unused carton boxes (12 fruits per box) to avoid causing any external or internal damage to the fresh fruits, transported to the laboratory within 2 days at 28–30 °C and stored in a refrigerated chamber at 4–5 °C until used (maximum 3 days of storage). Mangoes which had uniform size and appearance without any mechanical injuries and disease symptoms were selected for the experiments. Analytical standard pesticides, chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate) and cypermethrin ((*RS*)-alpha-cyano-3 phenoxybenzyl (1*RS*)-cis-trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylate), were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). All chemicals and reagents used in this work were at least of analytical grade purchased from Sigma-Aldrich (St. Louis, MO, USA) and ACI Labscan (Bangkok, Thailand). Gases including He, H_2 and Ar was supplied by Lanna Industrial Gases Co. Ltd. (Chiang Mai, Thailand).

2.2. NTP system

In this study, the NTP system was slightly modified from Kim et al. (2013) using an GA discharge at the Agriculture and Bio Plasma Technology Laboratory, which is a part of the Thai-Korean Collaboration Center (TKRCC), Chiang Mai University. The system had four major parts including (1) a GA discharge system driven by a neutron generator and DC transformer (8 kV and 0.6 A) to generate plasma at 600 W; (2) a gas-transport system to provide controlled flows of Ar gas and vapor of micro-bubble distilled water generated using an electro-flotation method that went through the GA discharge system; (3) control devices; and (4) a reservoir tank containing distilled water as shown in Fig. 1. The basic approach with this NTP design was to have both the Ar gas and the micro-bubble vapor passing through the GA discharge system first and then introduce plasma-treated Ar gas and water vapor to the water in the reservoir to decontaminate the pesticide residues on mango's surface. The flow of Ar gas and water vapor inside the GA discharge leads to the production of non-equilibrium NTP. The arc discharge initially ignited the thermal plasma at the point of the smallest gap between the two electrodes, then, the arc was forced to move downstream by the gas flow and convectively cooled by a stream of gas which was at room temperature (32–35 °C) to become an NTP.

The NTP system was validated by measuring the OH· radical emission signal at 309 nm using an optical emission spectroscopy (OES) equipped with an AvaSpecULS2048CL-EVO spectrometer operating at a resolution of 1.2 nm and complementary metal-oxide-semiconductor (CMOS) linear image sensor detector (Avantes, Louisville, KY, USA). The light emitted from the NTP was obtained after passing through an SMA-905 optical fiber with the diameter of 2.5 mm, and the fiber-optic spectrometer was configured for the near UV-VIS range of 200–850 nm wavelength. The integration times were set to 300 ms. The emission spectra generated by NTP were qualitatively analyzed using the US National Institute of Standards and Technology atomic spectra database and published research (Misra, Pankaj, et al., 2014; Thana, Ngamjarurojana, & Boonyawan, 2016) for identification of active chemical species and the preliminary trails showed that all experimental conditions produced OH· radicals.

2.3. Exposure of mango to pesticides

Chlorpyrifos and cypermethrin solutions were prepared separately by adding 0.01 g of the standard pesticide powder into 100 mL of acetone nitrile (MeCN) containing Tween 20 (1%) as a surfactant which help to increase adhesion of pesticide to the smooth surface of mango skin. Then each pesticide solution (100 ppm) was sprayed 4 times onto both sides of mango fruits (10 mL per fruit) using glass sprayers under a fume hood and the fruits sprayed with pesticide solution were dried using an electric fan. The control was soaked in distilled water for 10 min. After that, the chlorpyrifos and cypermethrin contents on the surface of mango were measured.

2.4. NTP treatment

For each treatment, one mango fruit done in duplicate was put into the glass beaker (reservoir) containing 1 L of distilled water, then the vapor mixture of Ar gas and micro-bubble water was passed through the GA discharge. After that cold plasma-treated Ar gas and water vapor were transferred into the beaker. Temperature for all treatments was 28–30 °C. The flow rate of Ar gas was varied from 2 to 8 L/min for treatment times of 5 and 10 min, which had been optimized during preliminary studies. The effect of NTP on changes of physicochemical quality parameters were measured in triplicate for each sample.

2.5. Analysis of pesticides

AOAC Official Method 2007.01 was used to analyze the pesticide residues using MeCN extraction, partitioning with $MgSO_4$ and quantifying by gas chromatography (GC). The pesticide residue concentrations were expressed as mg pesticide per 1000 g of mango skin or ppm and the degradation efficiency of pesticides measured as the percentage of reduction rate (removal efficiency) according to the method described by Bai, Chen, Yang, Guo, and Zhang (2010), which was calculated using the following equation:

$$\text{Reduction rate }(\%) = [(C_o - C_t)/C_o] \times 100$$

where C_o was the initial concentration of pesticide on mango, and C_t was the concentration after time *t*.

An Agilent 6890A GC (Agilent Technologies, Palo Alto, CA, USA) coupled with an Agilent 7683B auto-sampler and a flame photometric detector (FPD) was used to analyze chlorpyrifos residues. A RTX®-OPP2 Restek column (30 m, 0.32 mm ID, 32 µm, Cat.#11241) (Restek Corp., Bellefonte, PA, USA) was used. The detector and injector temperatures