Decontamination of pesticide residues on tangerine fruit using non-thermal plasma technology

C Sawangrat¹, K Leksakul¹, D Bonyawan², T Anantana¹ and S Jomjunyong¹

¹Industrial Engineering Department, Faculty of Engineering, Chiang Mai University, Thailand
²Physic Department, Faculty of Science, Chiang Mai University, Thailand

Abstract. Plasma Technology is a well-known approach to decontaminated not only pesticide residues but also fungus on fruits and vegetables. In the present paper, Non-Thermal Plasma (NTP) were successful generated via plasma activated water technique, pin hole. NTP were applied to decontaminated pesticide residues named, cypermethrin, on “Sai Num Pueng”, tangerine fruit. A electrical power 125 watt and air flow rate 15L/min has been used. It was observed that cypermethrin concentration is significantly reduce from 1 ppm to 0.25 ppm which meet international food standard requirment (Codex standard). In particular, the NTP tangerine orange exhibits longer shelf-life as compared to the conventional tangerine orange. There are no significantly different related to appearance, acid flavor, sweetness and smell as also compared to conventional products.

1. Introduction

In 2050 world population would increasing up to 10 billion and effecting to world food demand [1]. The conventional agriculture process was innovatively transitioned to chemical agriculture process. Such a chemical agriculture process leads to higher productivity as compared to conventional process. However, chemical agriculture results in pesticide contamination and leads to customer health and reliable. In Thailand, there are several class of vegetables and fruits have been reported contaminate pesticide exceeds maximum international standard see in Fig. 1. In addition, it was found that cypermethrin and chlorpyrifos are most pesticide residues which contaminated in agriculture product in Thailand see in Fig. 2. Both of them lead to human health by nausea, vomiting, abdominal cramps, fatigue, fatigue, headache, dizziness if given in large doses [2]. Customer are now under risk of health.

![Most famous vegetables in Thailand](image1)

![Most famous fruits in Thailand](image2)

Figure 1. Results amount of pesticide residue in vegetables and fruits from local market in Thailand. [3]
Figure 2. Percent of each pesticide residues sampling from local market in Thailand [3]

Non-thermal plasma (NTP) are an important class of plasma technology which are wieldy used for agriculture and food industry due to improved productivity and food safety standard [4-5]. NTP are suitable for decontaminated pesticides residues on blueberries and strawberries up to 60-80% by packaging without any significantly change on physical properties [6-7]. A similar trend has also been reported in cherry tomatoes using NTP [8-9]. Therefore, the present work is aim to decontaminate pesticide residue, cypermethrin, on “Sai Num Pueng”, tangerine fruit. The NTP were successful generated by pin-hole method, tornado discharge technique. The effect of NTP on reducing cypermethrin compound have been investigated. Finally, results related with sensory evaluation of NTP product are presented and compared to understand mechanism of NTP.

2. Materials and methods

2.1. Tangerine fruit samples and inoculation.
Commercial tangerine fruit and cypermethrin compound were obtained randomly from local market in Chiang Mai province, Thailand. A Cypermethrin contains 20-40% of α-cypermethrin were used in this study. Each experiment was prepared using cypermethrin stock solution 10%(w/v). First concentration cypermethrin was adjusted to 10 ppm and inoculated to product by spraying process.

2.2. Non-thermal plasma preparation
NTP was prepared using pin-hole plasma technique, operating at atmospheric pressure, in acrylic container (410x290x90 mm) (Fig3). The actuator was made of tungsten electrode. The DC power supply 15kV and electric power 125 watt were used for decontaminated pesticide residues on tangerine fruit. NTP was treat for 20, 30, 40, 50 and 60 min by air flow rate 15L/min. Finally, optical emission spectroscopy (OES) was employed to record emission between wavelengths 200nm to 800nm.
2.3. Pesticide residue, shelf life and sensory evaluation.
Inoculated samples were plasma treated and determined pesticide residues through Gas chromatography method (GC). Control and 60 min plasma discharge samples were stored under cold conditions (4°C) for 10 days. Finally sensory evaluation was performed in term of appearance, smell, acid flavor and sweetness with 30 consumers.

3. Results and discussion

3.1. Optical emission spectroscopy results
Fig. 4 shows representative light emission intensity spectrum of tornado discharge. It can be clearly observed that there are several main peaks presented consist of Oxygen (O) and Nitrogen (N) molecules. In particular, Reactive Oxygen Species (ROS) was found at wavelength 309 nm and 777.53 nm. Since intensity of peaks at 315.93, 337.13, 357.69 and 380.49 nm corresponding to Reactive Nitrogen Species (RNS). Both ROS and RNS are well-known important players to not only decontaminated pesticide residues but also sterilized harmful bacteria in agriculture product [4, 8-9]. These results clearly indicate that formation of ROS and RNS would be active players to decontaminate cypermethrin on commercial tangerine fruit.

![Figure 4](image)

Figure 4. The emission intensity spectra of atmospheric pressure tornado discharge.

3.2. Cypermethrin concentration results
Fig. 5 shows the variation of cypermethrin concentration with increasing discharge time on samples, as estimated using GC results. It can be noted that the amount of cypermethrin concentration decreased significantly with increasing discharge time. Especially, discharge time 60 min significantly reduced concentration to 0.25 ppm which meet basic requirement of international food standard (Codex standard). Previous work mentioned that ROS, OH- radical act as a key role to generate chemical
reaction together with cypermethrin compound and results in other non toxic chemical compound and finally precipitated in water only [7-9]. These evidences suggest that NTP is suitable technology to decontaminated pesticide residues and possible extend to other valuable agriculture products.

![Figure 5](image)

**Figure 5.** The reduction of cypermethrin concentration with increased discharge time

### 3.3. Preliminary storage results

Table 1 illustrates the surface evolution of tangerine fruit during storage process. It is interesting to noted that there are no evidence of difference between surface of control and NTP product at early stage of storage (1st day). While, it appears some amount of fungal located on product surface especially in control sample (red circle) at middle stage of storage (5th day). Furthermore, in final stage of storage (10th day), it can be noticed that control sample had significantly amount of fungal located on surface (red circle) since there are no any fungal was founded on surface of NTP products. Generally, it is well known that ROS in NTP provide chemical interaction with microbial cells. Such reactive species in NTP directly contact on microbial cells and leads to damage cell membrane [9]. As a result, microbial have been sterilized and led to extend shelf life of agriculture product. These results are in conformity with previous reported [11-12].

| Storage day | Tangerine fruit (Sai Num Pueng) |
|-------------|---------------------------------|
|             | NTP (60 min discharge) | Control |
| **1st day** | ![Side-view](image) ![Top-view](image) | ![Side-view](image) ![Top-view](image) |
| **5th day** | ![Side-view](image) ![Top-view](image) | ![Side-view](image) ![Top-view](image) |

### 3.4. Sensory evaluation results

The results of 30 consumers acceptability study are presented in table 2. It has been observed that there are no significantly difference (P-value<0.05) were founded in term of appearance (6.97 vs 6.83), smell (7.03 vs 6.97), acid flavor (6.77 vs 6.63), sweetness (6.70 vs 6.60) and total acceptability (6.97 vs 6.80).
In addition, most consumers mentioned that flavor characteristics and total acceptability was more or less similar for both code samples. These evidences suggest that NTP did not affect any kind of basic sensory. However, further work is request to compare other characteristic such as texture and moisture between control and NTP product.

Table 2. Statistical analysis results between control and NTP samples.

| Characteristics    | Variable | N  | Mean | StDev | SE | Mean | 95% CI for difference | P-value |
|--------------------|----------|----|------|-------|----|------|------------------------|---------|
|                    | code 145 | 30 | 6.97 | 1.03  | 0.19 | 6.77 | (-0.431, 0.636)       | 0.64    |
| Appearance         | code 208 | 30 | 6.83 | 1.15  | 0.21 | 6.63 | (-0.460, 0.660)       | 0.72    |
| Smell              | code 145 | 30 | 7.03 | 0.93  | 0.17 | 6.77 | (-0.395, 0.662)       | 0.62    |
|                    | code 208 | 30 | 6.97 | 1.00  | 0.18 | 6.63 | (-0.400, 0.664)       | 0.72    |
| Acid flavor        | Code 145 | 30 | 6.77 | 0.82  | 0.15 | 6.70 | (-0.303, 0.636)       | 0.48    |
|                    | Code 208 | 30 | 6.60 | 1.20  | 0.23 | 6.80 | (-0.431, 0.698)       | 0.64    |
| Sweetness          | Code 145 | 30 | 6.97 | 0.89  | 0.16 | 6.70 | (-0.303, 0.636)       | 0.48    |
| Total acceptability| Code 208 | 30 | 6.80 | 0.93  | 0.17 | 6.63 | (-0.431, 0.698)       | 0.64    |

4. Conclusions
Non-thermal plasma were successfully generated via plasma pin-hole technique. The NTP consisted of both Reactive Oxygen Species (ROS) and Reactive Nitrogen Species (RNS) which play important role to decontaminated cypermethrin located on surface of tangerine fruits and results in satisfy with international food standard (Codex standard). NTP are promising technology not only increased food safety international standard level but also extend shelf life without any affect to physical characteristics of agriculture product.

References
[1] UN (2017). The future of food and agriculture Trends and challenges.
[2] http://www.healthandtrend.com/healthy/what-the-health/orange-is-dominating-the-fruit-is-very-toxic 2018
[3] www.thaipan.org 2018
[4] Phumon S, Sittidet Y, Jenjira D, Jaruwan J, Dheerawan B and Sugunya M 2014 J. food and nutrition research. 2 12 946-951
[5] http://www.fao.org/fao­who­codexalimentarius /standards/pestres/pesticide-detail/en Codex Alimentarius, 2016.
[6] Harinathreddy A, Prasad N.B.L. and Devi L.K. 2014 J.Biological Chemistry Research 31 1005–1015.
[7] Chaitanya S, Grainne O, P.J. Cullen and Paula B 2017 Innovative Food Science and Emerging Technologies 44 235-241.
[8] N.N. Misa 2014 J. Hazardous Materials 271. 33-40.
[9] Nrusimha N M 2014 J. Bioscience and Bioengineering 118 2 177-182.
[10] Rohit T, Chaitanya S, Uday S A 2014 J. food biophysic 10 1 11-11.
[11] Monica M, R.Sirbu, Daniela D and Mihai G 2018 Plasma chemistry and plasma processing. 38 989-1001.
[12] Chiara L P, Dana Z, Agata L, Daniela B, Fabio P, Pietro F, Brijesh T, Paula B and Patrick J C 2018 Innovative food science&emerging technologies. 49 13-19