CHAPTER 4

Reduction of Ethion in Tangerine Fruits Using Titanium Dioxide Photocatalysis

4.1 Introduction

The increasingly widespread application of pesticides substances with different physical and chemical properties means that ever larger amounts of these compounds are getting into the environment. As a result of the various processes to which they are subject in the environment, they may be converted to even more toxic compounds. They are currently regarded as some of the most dangerous environmental contaminants because of their stability, mobility and long-term effects on living organisms. Pesticides can be absorbed and stored by plants, and their metabolites can likewise be accumulated. As crops are an essential part of the human diet, the quality of these products is extremely important and is often a factor determining whether or not consumers would like to them. The intensive development of agriculture means that more and more toxic organic and inorganic compounds are entering the environment. Because of their widespread use, stability, selective toxicity and dangerous bioaccumulation, pesticides are among the most toxic substances contaminating the environment. They are particularly dangerous in fruit and vegetables.

Ethion is often used as crop protection specifically in tangerine production by to control insect pests. However, the Thai Agricultural Commodity and Food Standard (2006) reported that imported countries detected ethion in tangerines over the maximum residue limits, MRLs (1 mg L^{-1}). The present strategies to reduce residual pesticides include washing with water, potassium permanganate and detergents, but these methods cause water pollution and high cost with limited effectiveness. Nowadays, everyone is looking for clean technology, which is technology without requiring chemical inputs. Titanium dioxide photocatalysis is one promising process among the alternative methods to degrade toxic pesticides.

Titanium dioxide photocatalysis has been reported to be effective in reducing a variety of organic and inorganic contaminants in water (Hoffmann *et al*., 1996; Weavers *et al.*, 1998) . Titanium dioxide photocatalysis was a promising method for the pesticide reduction of several fresh produce (Whangchai *et al.*, 2004).

Thus, this study was conducted to determine the capability of titanium dioxide photocatalysis as alternative methods for washing to reduce if not destroy the chemical structure of ethion in tangerine fruits. Also changes in the quality of treated tangerine fruits were investigated.

4.2 Materials and Methods

Titanium dioxide powder and photocatalytic reactor

Titanium dioxide suspension at varying concentrations of 0, 15, 30, 45 and 60 mg mL^{-1} (as mentioned in Chapter 3) were illuminated with two UV lamps at 10 W each in the photocatalytic chamber for 60 min.

Tangerine samples

Tangerine fruits were freshly harvested from the organic orchard in Chiang Mai, Thailand then transported immediately to the laboratory in Chiang Mai University. All experiments were carried out right away.

4.2.1 Ethion degradation of tangerine fruits after washing by TiO_2 photocatalysis

1) Ethion degradation in tangerine fruits after washing by TiO_2 photocatalysis

Tangerine fruits 10 kg were immersed in 20 L distilled water and subjected to washing using TiO_2 photocatalysis with different concentrations (0, 15, 30 and 60 mg mL^{-1}). Tangerine fruit samples were extracted after washing 15 min eventually. All treatments were conducted in three replications. Ethion residual in tangerine fruits was extracted

based on Steinwandter (1985) (Appendix A; Figure A4). Tangerine fruit samples (25 g) were extracted with 50 mL of acetone, homogenized for 1 min. Then the following step was adding 40 mL of dichloromethane and NaCl 10 g, homogenized at 13,000 rpm for 1 min, and then dried using rotary vacuum evaporator at 340 mbar. The samples were analyzed using GC-FPD with acetone (HPLC grade) as the final solvent. Degradation percentage of ethion residue in stored tangerines was monitored every week for 4 weeks after storage at 13°C and 95% relative humidity (RH).

GC-FPD instrument set up

The GC-FPD analysis was performed with an Agilent Technologies (Wilmington, DE) model 6890 gas chromatograph equipped with a flame photometric detector. The GC was carried out using a fused silica capillary column HP-5, 5% Phenyl Methyl Siloxane, with dimensions of 30 m × 0.32 mm i.d. and a 0.25 μm film thickness (Agilent Technologies). The temperature was programmed at 10 min from the initial temperature at 100°C to 200°C. And then at 4°C $\cdot min^{-1}$, it increased to the final temperature of 220°C. A purified He carrier gas was used with the flow rate of 3.6 $mL \cdot min^{-1}$. The detector temperature was set at 250°C. Those sample solutions (1.0 μL) were injected in splitless mode, and the quanti-fication of ethion was performed using ethion standard as a reference .

Statistical Analysis

The Statistical Package for the Social Science (SPSS version 16) software for Windows was used for the Analysis of Variance (ANOVA) and least-significant difference (LSD) at the 95% confidence level of each variable value under completely randomized design (CRD).

4.2.2 Effects of TiO_2 photocatalysis on postharvest qualities of tangerine fruits

The washed tangerine fruits (distilled water, titanium dioxide) were put in the plastic basket, covered the whole basket with polyethylene plastic bag and stored in refrigerator at 5°C and 95% RH for 45 days. Qualities of stored tangerine fruits such as fruit firmness, total soluble solids (TSS), titratable acidity (TA), total ascorbic acid content,

peel color changes, weight loss, total count microorganisms and ethion residue in tangerine fruits were assessed before storage and 45-day of the storage. All treatments were conducted in three replications.

1) Fruit firmness

Texture analyzer (TA-XT 21/50) with the diameter of pressing probe 100 mm P100 (100 mm Compression platen) was set 15 mm from samples. The velocity of the probe was set at 1.0 mm sec^{-1}. The force was set at 8 N. The samples were analysed 3 replications per treatment.

2) Total soluble solids (TSS)

The tangerine juice was measured for TSS with a digital refractometer (Model PR-101), Atago, Tokyo, Japan) at room temperature (AOAC, 2005 method No.940.31). The TSS had triplicate measurement for each replication and averaged. The values were expressed in percentage (%) of TSS.

3) Titratable acidity (TA)

The TA was determined by titration of 5 mL of tangerine juice with 0.1 M NaOH (Sodium hydroxide, MERCK, Darmstadt, Germany) until pH 8.1, using autotitrator (Titroline easy, Schott, Mainz, Germany). Standardize pH electrode of autotitrator with pH 4, 7 and 10 buffers. The TA was expressed as percent of citric acid per 100 g juice, using the following equation (AOAC, 2005 method No. 942.15). The TA was measured in three replications.

$$\% \text{ TA} = \frac{\text{normality of NaOH (0.1 N)} \times \text{equi. wt. of citric acid (0.070)} \times \text{vol. NaOH} \times 100}{\text{volume of sample}}$$

4) Total ascorbic acid content

The tangerine juice (25 g) was homogenized with 25 mL of 4.5% (w/v) metaphosphoric acid solution (Merck, Darmstadt, Germany). The liquid was centrifuged at 6,000 × *g* (MIKRO 22R, Hettich Zentrifugen GmbH& Co. KG, Tuttlingen, Germany) for 10 min at 4°C. The supernatant was then filtered through a 0.45 μm pore size nylon membrane filter (Fisher Scientific, Fair Lawn, New Jersey, USA).The filtrate was analyzed for organic acids by high-performance liquid chromatography (HPLC) (Hewlet-Packard series 1100, Agilent Technologies, Waldbrom, Germany). Organic acids were separated by an ultra aqueous C18 (4.6 × 250 mm, 5 μm) column (Restek Corporation, Germany). Detection was done by visible wavelength detector (VWD) at 210 nm. Temperature of the column oven was set at 35°C. Mobile phase was 50 mM *ortho*-phosphoric acid (v/v) (Merck, Darmstadt, Germany) at a flow rate 0.5 mL min^{-1} for 30 min. A 20 μL of each sample was put into an injection loop with automatic system. HPLC samples were run in three replications.

Authentic standard of ascorbic acid was prepared in 0.05% (w/v) metaphosphoric acid. This standard was used to obtain the calibration curves for quantification of the ascorbic acid contents. Ascorbic acid (L-ascorbic acid, Merck, Darmstadt, Germany) was prepared with 0.1, 0.5, 1.5, 2.5, 4 and 5 g L^{-1}. Standard were analyzed in three replications.

5) **Peel color changes**

The exocarp colors of tangerine fruits in all treatments were measured using colorimeter (MINISCAN XE PLUS, Hunter Associates Laboratory, Inc., USA). The chromaticity of each treatment was measured as L* (the lightness factor value), a* (the chromaticity coordinates; hue) and b* (the chromaticity coordinates; chroma) values. The L* value measured the darkness or brightness of exocarp color which had value 0 to 100. A low L* value corresponded to a low brightness and a higher L* value meant a brighter fruit. The a* value measured the greenness and redness on a scale of -60 to +60. A minus a* value meant a green color and a positive value of a* meant red color. The b* value measured the blueness and yellowness on a scale of -60 to +60. A minus b* value meant

a blue color and a positive value of b* meant yellow color. The results were expressed as a mean value from three replications of the 6 measured samples

6) Weight loss (%)

Weight loss of tangerine fruits during storage was determined with samples of five fruits per replication. The fruit stored at 13°C and 95% RH were weighed on day 0 and 45 of storage. Each fruit was weighted using an electronic analytical balance. The percentage of weight loss was calculated from the difference between the initial and final weight, followed the equation:

$$\text{Weight loss (\%)} = \frac{\text{Initial fruit weight - Current fruit weight} \times 100}{\text{Initial fruit weight}}$$

7) Total microorganism count

Tangerine washed water from the treatments were used for serial dilution. Serial dilution were conducted by adding 1 mL of different water samples to the sterile distilled water 9 mL to get the 10^{-1} dilution. Then the 10^{-2} - 10^{-5} dilution were prepared followed the 10^{-1} dilution direction. In the meantime, the potato dextrose agar were prepared in sterile petridish. The 0.1 mL of sample solution with different dilution were then pore on the top of potato dextrose agar on each petridish. Each dilution were performed in 3 replications. Thereafter, all petridishes were incubated at 35-37 °C for 18-24 h. Count the colonies on PDA (30-300 colonies). The data was calculated by the following equation:

$$\text{CFU} = \frac{(\text{No. of colonies/amount of samples} \times \text{dilution})}{\text{weight of samples}}$$

8) Ethion residue on tangerine fruits after 45-Day storage

Tangerine samples washed with TiO_2 photocatalysis treatments were stored in refrigerator at 5°C and 95% RH. On Day-0 and Day-45 of storage, ethion residue from tangerine samples were extracted based on the methods mentioned in 4.2.1. Then, quantitative determination of ethion was done by GC-FPD.

Statistical analysis

The Statistical Package for the Social Science (SPSS version 16) software for Windows was used for the Analysis of Variance (ANOVA) and least-significant difference (LSD) at the 95% confidence level of each variable value under completely randomized design (CRD).

4.3 Results and discussion

4.3.1 Ethion degradation of tangerine fruits after washing by TiO_2 photocatalysis

1) Ethion degradation in tangerine fruits after washing by TiO_2 Photocatalysis

Tangerine fruits were washed in TiO_2 photocatalysis reactor with different illumination times to reduce ethion residue. It was indicated that titanium dioxide (60 mg mL^{-1}) photocatalysis could increase the percentage of ethion in fresh tangerine fruits from 1 ppm to 0.23 mg L^{-1}. The degradation tends to stable with increasing exposure time, TiO_2 photocatalysis at 60 mg mL^{-1} increased ethion degradation percentage to 77.2% for 15 min when compared with control which immersed in distilled water , the degradation was 15% (Figure 4.1,Appendix : Table A 11). The result was suggested by which indicated that advanced oxidation process could effectively reduce pesticides residue in agricultural products such as methyl-parathion, parathion, diazinon and cypermethrin on Pak Choi (*Brassica rapa*) surface (Wu *et al*., 2014) ; azinphos-methyl residue on apples dipped in titanium dioxide photocatalysis water were reduced by about 75% and chlorpyrifos in bird chilli (Chutidumrong, 2010; Pengphol, 2013); ethion reduction in tangerine fruits (Wongsirisak *et al*., 2011).

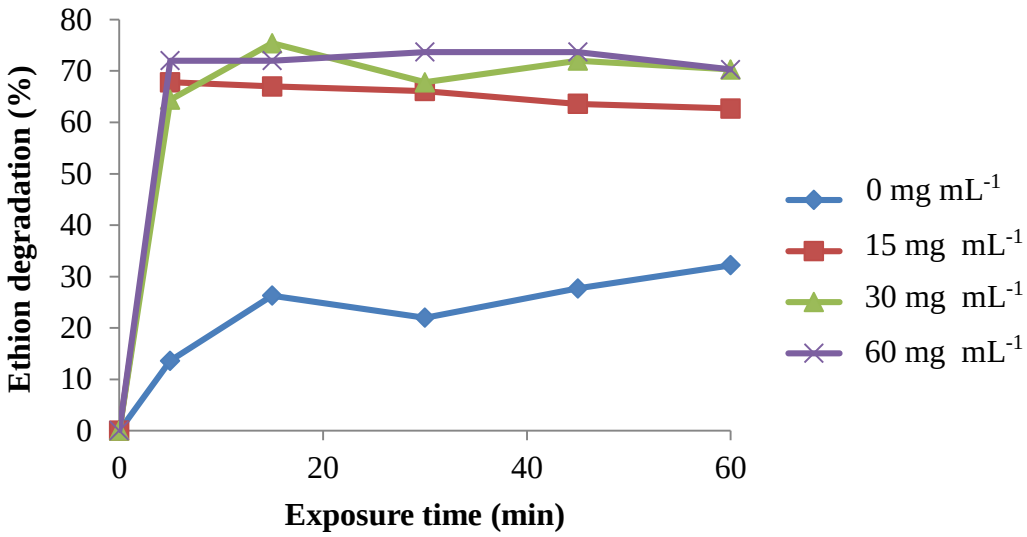

Figure 4.1 Ethion degradation in tangerine fruits after treated by TiO_2 photocatalysis for 60 min.

4.3.2 Effects of TiO_2 photocatalysis on postharvest qualities of tangerine fruits

1) Fruit firmness

The fruit firmness of tangerines varied between 4.72 and 5.49 N/mm before storage. While the firmness of the fruits of after storage for 45 days were decrease in every treatments. Similar results were found by Boonkorn (2012), the oxidative reaction could increase fruit firmness during storage of tangerines. The oxidative reaction also induced a delay of fruit softening in strawberry (Erkan *et al*., 2008), red raspberries (Giuggioli *et al*., 2015), tomato (Aguayo *et al*., 2014) during the storage. TiO_2 could directly maintained tangerine firmness by lower amount of fungi, resulted in delaying the invaded fungi on tangerine peel (Figure 4.2, Appendix : A 12).

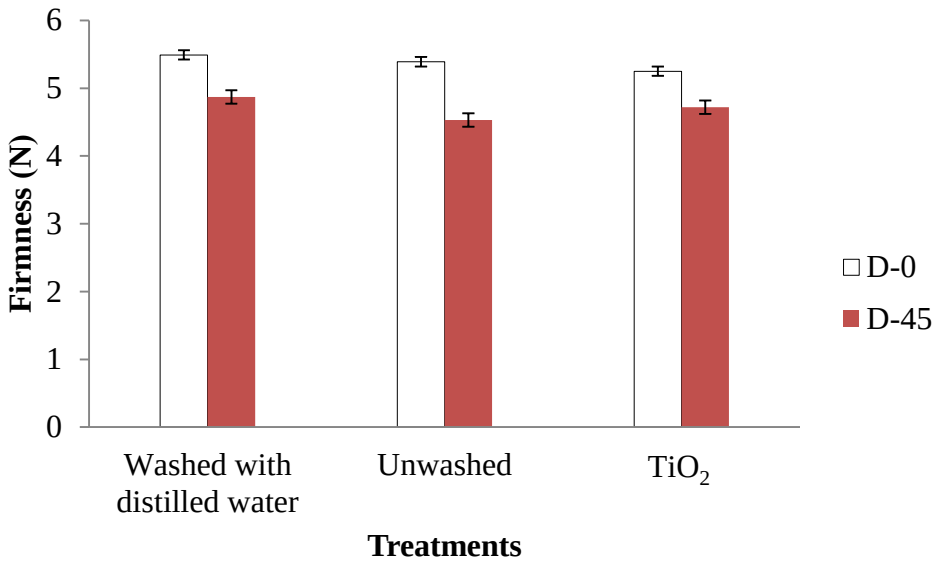

Figure 4.2 Changes in fruit firmness after washing with TiO_2 photocatalysis for 60 min and storage at 5°C for 45 days

Table 4.1 Postharvest qualities of tangerine fruits after washing with TiO_2 photocatalysis and storage at 5°C for 0 day

Postharvest qualities	Treatments	Exposure time (min)				
		0	15	30	45	60
Total soluble solids (TSS)	Control	9.38a	9.58a	8.16a	9.79a	8.97a
	TiO_2 60 mg mL^{-1}	8.77a	9.38a	9.38a	9.58a	9.18a
Titratable acidity (TA)	Control	0.50b	0.49b	0.50b	0.57b	0.50b
	TiO_2 60 mg mL^{-1}	0.49b	0.54b	0.49b	0.55b	0.44b
Ascorbic acid content	Control	12.0c	11.56c	11.4c	10.94c	10.5c
	TiO_2 60 mg mL^{-1}	10.5d	10.00d	10.0d	10.00d	9.71d
Peel L value	Control	28.0e	26.44e	21.51e	22.94e	25.1e
	TiO_2 60 mg mL^{-1}	20.08f	26.44e	24.38f	22.94e	22.2f
Peel a*value	Control	-5.49g	-4.86g	-5.17g	-5.49g	-4.8g
	TiO_2 60 mg mL^{-1}	-6.59h	-5.80h	-6.27h	-3.45h	-4.5g
Peel b*value	Control	22.30i	22.36i	21.23i	21.63i	20.1i
	TiO_2 60 mg mL^{-1}	21.63i	22.9i	21.27i	20.45i	20.1i

Mean ± SD within the same column followed by the same letter do not differ significantly at p=0.05 using the least significant difference test

Table 4.2 Postharvest qualities of tangerine fruits after washing with TiO_2 photocatalysis and storage at 5°C for 45 days

Postharvest qualities	Treatments	Exposure time (min)				
		0	15	30	45	60
Total soluble solids (TSS)	Control	1.08a	11.0a	11.52a	11.5a	9.78a
	TiO_2 60 mg mL^{-1}	9.56b	11.9a	11.95a	10.65	10.5a
Titratable acidity (TA)	Control	0.28c	0.2c	0.20c	0.22c	0.1c
	TiO_2 60 mg mL^{-1}	0.16d	0.1d	0.17c	0.20c	0.2b
Ascorbic acid content	Control	4.23e	4.2e	2.86e	4.09e	3.5e
	TiO_2 60 mg mL^{-1}	3.68f	4.6c	3.00e	3.82e	3.14e
Peel L value	Control	29.40g	32.2g	25.67g	28.0g	27.22g
	TiO_2 60 mg mL^{-1}	25.67h	29.4h	25.67g	24.8h	24.11h
Peel a*value	Control	-2.6i	2.0i	-2.9i	-2.7i	-2.2j
	TiO_2 60 mg mL^{-1}	-3.5j	-2.8j	-3.1j	-1.7j	-2.4bj
Peel b*value	Control	13.0k	14.6k	12.3k	11.2k	11.7k
	TiO_2 60 mg mL^{-1}	12.0l	13.8k	13.5l	13.8l	12.7l

Mean ± SD within the same column followed by the same letter do not differ significantly at p=0.05 using the least significant difference test

2) Total soluble solids (TSS)

Total soluble solids (TSS) of tangerines before storage and after 45 days of storage, increased as the increasing of exposure time. Before storage, the TSS of tangerine treated with TiO_2 at various exposure times were not significantly different as well as control treatment (Figure 4.3, Table 4.1, Appendix : A 13) . Total soluble solids of tangerine stored for 45 days increase from day 0 in every concentrations treatment of TiO_2 and control were not significantly different in every exposure time (Figure 4.4, Table 4.2, Appendix : A 14). Similarly to the previous research in tangerine treated with AOPs by Singkamanee (2008), Boonkorn (2012) and Wongsirisak (2012) showed the unchanged firmness of tangerine after treated to the untreated one.

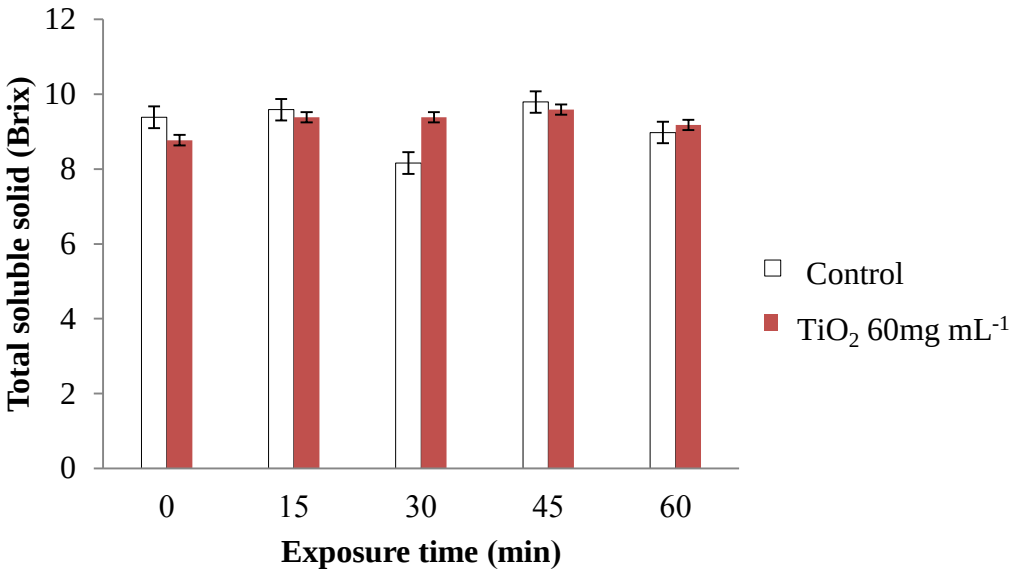

Figure 4.3 Changes in total soluble solids after washing with TiO_2 photocatalysis for 60 min and storage at 5°C for 0 day

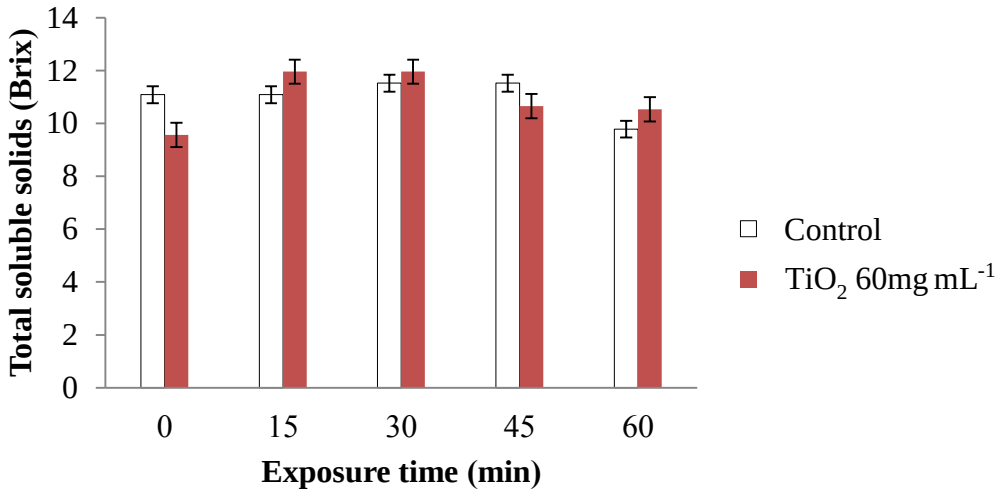

Figure 4.4 Changes in total soluble solids after washing with TiO_2 photocatalysis for 60 min and storage at 5°C for 45 days

3) Titratable acidity (TA)

Titratable acidity (TA) of tangerines before storage and 45 days after storage, decreased as the increasing of exposure time. Before storage, the TA of tangerine treated with TiO_2 at different exposure times quite fluctuated but it were not significantly with control treatment. The majority of TiO_2 treatment was at exposure time 45 min as well as control treatment whereas the minority was 0 min and 15 min (Figure 4.5, Table 4.1, Appendix : Table A 14). When tangerines stored for 45 days, found that both control and TiO_2 treatment at every exposure time decrease and nonsignificant from control (Figure 4.6, Table 4.2, Appendix : Table A14).

This experiment has the agreement in the TA result in the study of Singkamanee (2008), Boonkorn (2012) and Wongsirisak (2013) which study on the TA changes of tangerine under the AOPs treatment that tangerine fruits with no treatment and under the treatment of AOPs process causing no differences in TA during storage.

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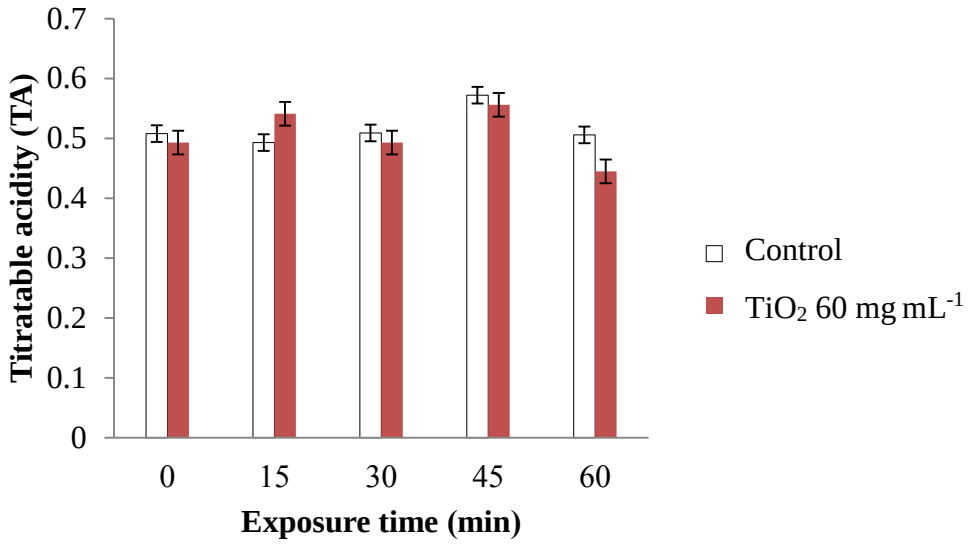

Figure 4.5 Changes in titratable acidity after washing with TiO_2 photocatalysis for 60 min and storage at 5°C for 0 day

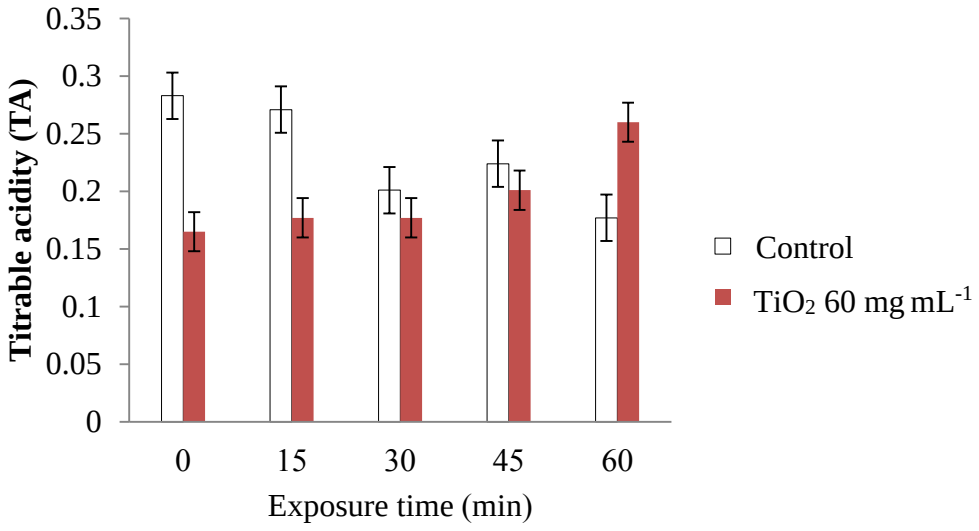

Figure 4.6 Changes in titratable acidity after washing with TiO_2 photocatalysis for 60 min and storage at 5°C for 45 days

4) Ascorbic acid content

Ascorbic acid content of tangerines before storage and 45 days of storage, decreased as the increasing of exposure time. Before storage, the ascorbic acid content of tangerine treated with TiO_2 at different exposure times were not significantly different from control (Figure 4.7, Table 4.1, Appendix : Table A 15). After storage during 45 days the ascorbic acid content of tangerine in both TiO_2 and control treatment decrease in every exposure time. Nevertheless, it was not significantly different at 15, 30, 45 and 60 min without 0 min (Figure 4.8, Table 4.2, Appendix : Table A15).

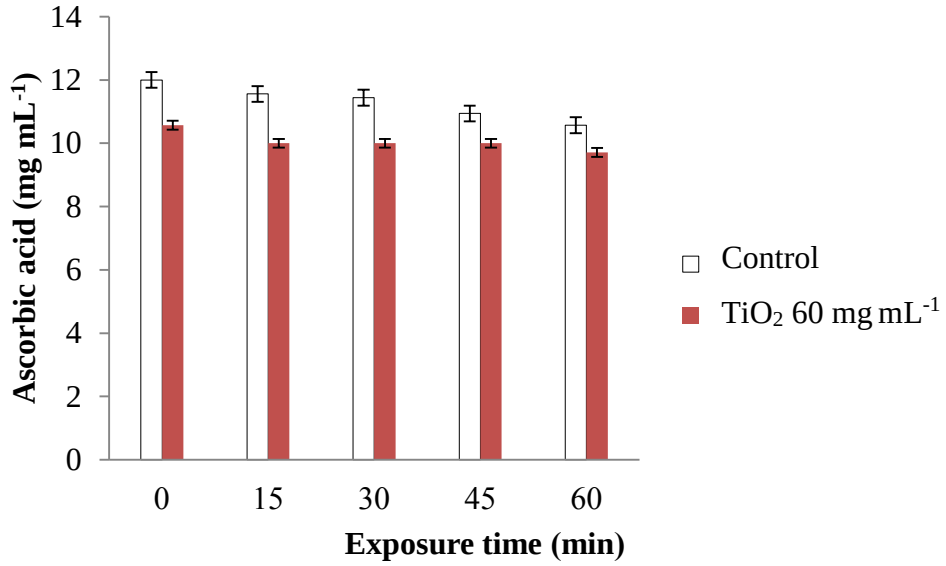

Figure 4.7 Changes in ascorbic acid content after washing with TiO_2 photocatalysis for 60 min and storage at 5°C for 0 day

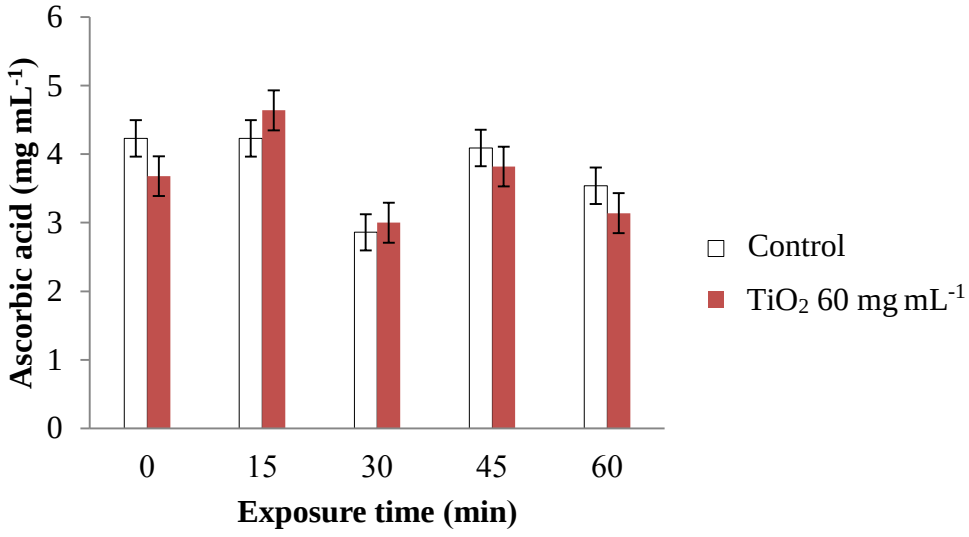

Figure 4.8 Changes in ascorbic acid content after washing with TiO_2 photocatalysis for 60 min and storage at 5°C for 45 days

5) Color changes of peel

The results showed that the color of tangerine in control and TiO_2 treatments were not significantly different in some exposure time which report in term of L*, a* and b* value (Figure 4.9, Figure 4.11, Figure 4.13, Table 4.1, Appendix : Table A 16, A 17, A 18). Found that in 0 day the value of L*,a* and b* fluctuated in follow exposure time. After the tangerine storage for 45 days, the tangerine peel color slightly became dark in both control and TiO_2 treatments. Likewise L *value (Figure 4.10, Table 4.2, Appendix : Table A16) increase while a*(Figure 4.12, Table 4.2, Appendix : Table A17) and b* value (Figure 4.14, Table 4.2, Appendix : Table A18) decrease from the first day of storage.

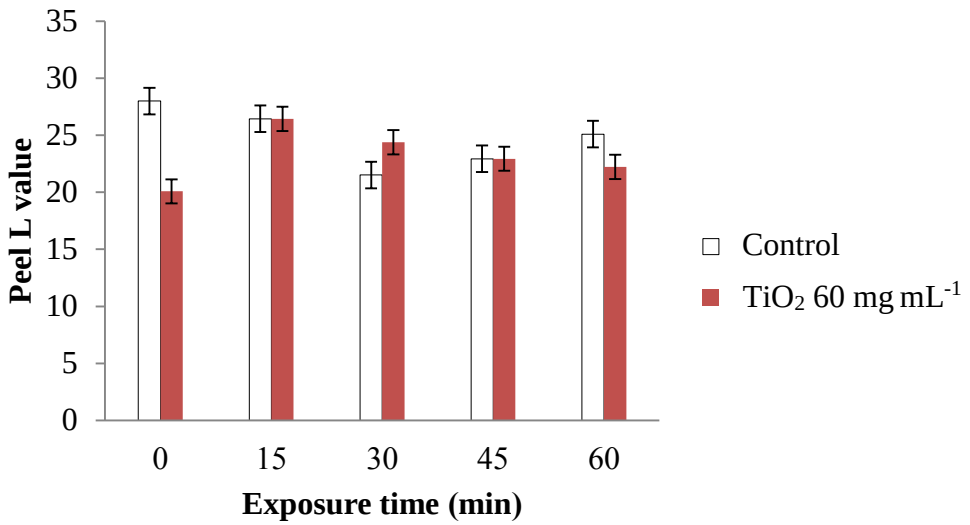

Figure 4.9 Changes in peel L value after washing with TiO_2 photocatalysis for 60 min and storage at 5°C for 0 day

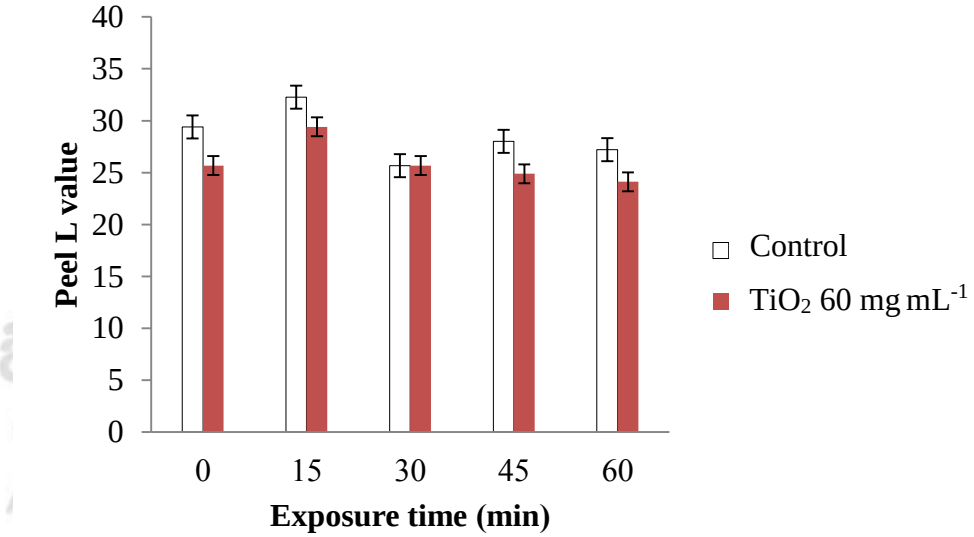

Figure 4.10 Changes in peel L value after washing with TiO_2 photocatalysis for 60 min and storage at 5°C for 45 days

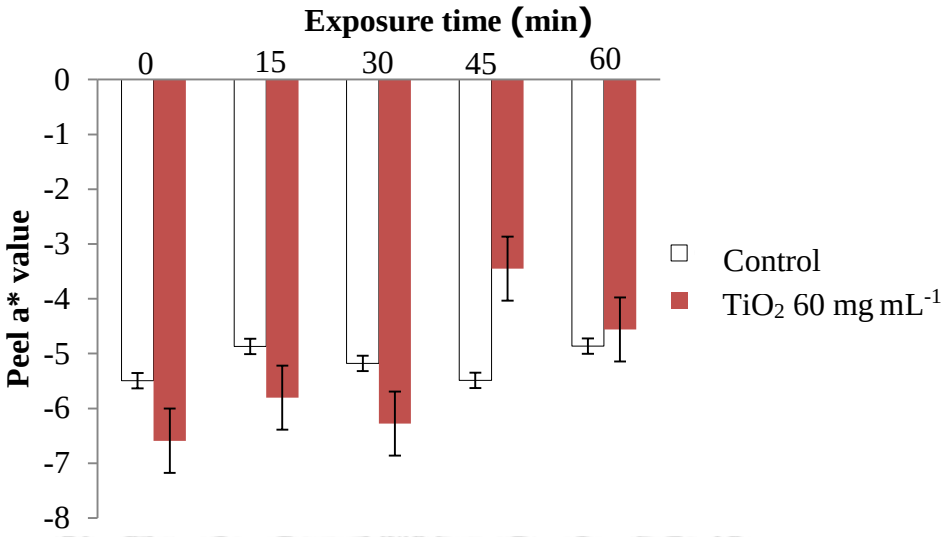

Figure 4.11 Changes in chroma values (a*) after washing with TiO_2 photocatalysis for 60 min and storage at 5°C for 0 day

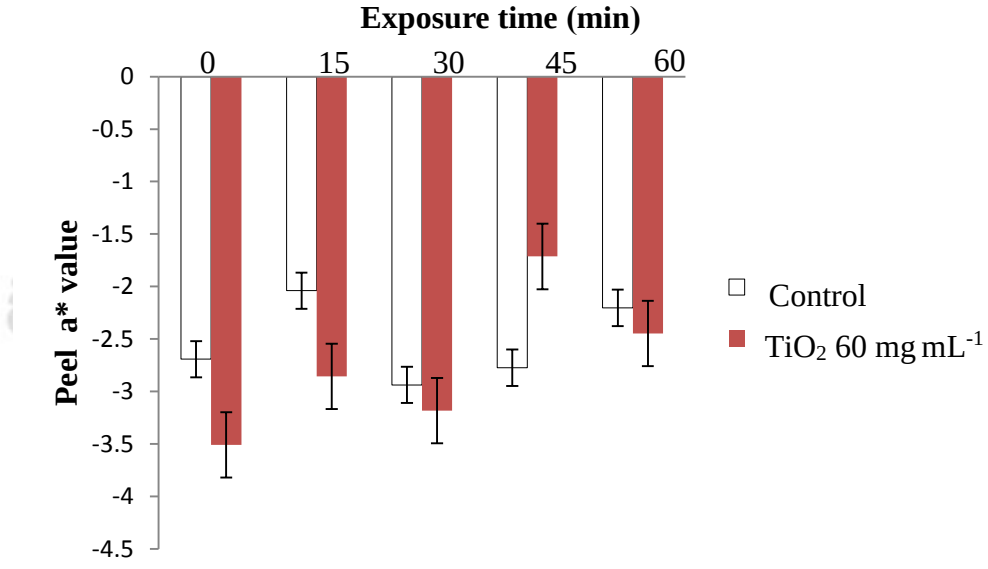

Figure 4.12 Changes in chroma values (a*) after washing with TiO_2 photocatalysis for 60 min and storage at 5°C for 45 days

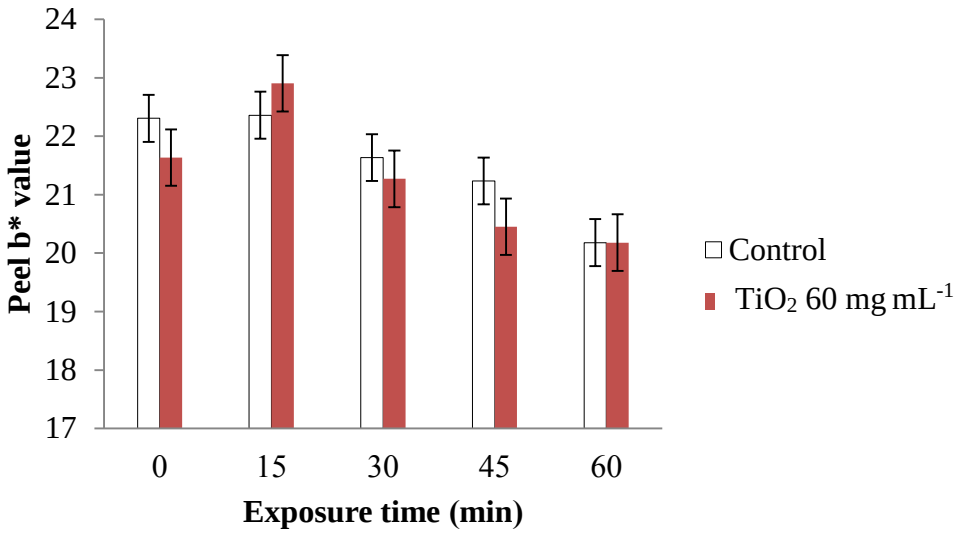

Figure 4.13 Changes in hue angle value (b*) after washing with TiO_2 photocatalysis for 60 min and storage at 5°C for 0 day

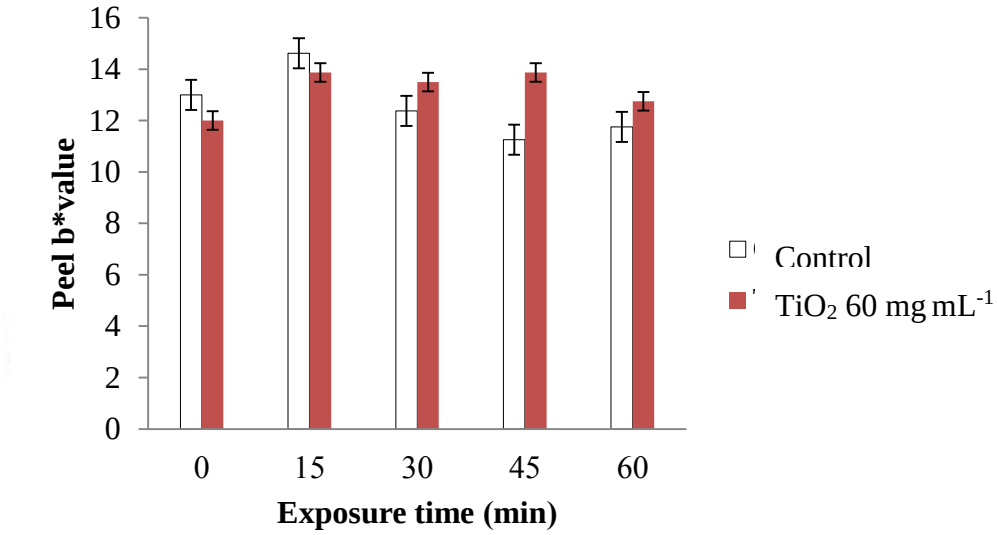

Figure 4.14 Changes in hue angle value (b*) after washing with TiO_2 photocatalysis for 60 min and storage at 5°C for 45 days

Figure 4.15 Tangerine fruits appearance after washing with TiO_2 photocatalysis for 60 min at day 0

Figure 4.16 Tangerine fruits appearance after washing with TiO_2 photocatalysis for 60 min and storage at 5°C for 45 days

6) **Weight loss (%)**

The weight loss of tangerine after washing with TiO_2 photocatalysis increased with increasing exposure time. The control and TiO_2 treatment were not significantly different at 0, 15, 30, 45, and 60 min. The highest percent weight loss was at exposure time 0 min of both 2 treatment while the lowest percent weight loss was exposure time 60 min of both treatment as well (Figure 4.17, Appendix : Table A 19). The TiO_2 photocatalysis treatment had no effect to weight loss of the tangerine fruits. Similarly, Whangchai *et al*. (2010a) and Wongsirisak (2013) reported that the potential of ozone had no effect on the quality changes of tangerine cv. 'Sai Nam Pung' fruits such as percent weight loss and peel color. Fruit water loss is the result of fruit respiration and diffusion through the fruit cuticle. Water loss by diffusion controlled by the water potential gradient from inside to outside the fruit and by the resistances to diffusion (Lownds *et al*., 1994). Usually, weight loss was 5 - 10% of agricultural products, that wilt (Peleg, 1985).

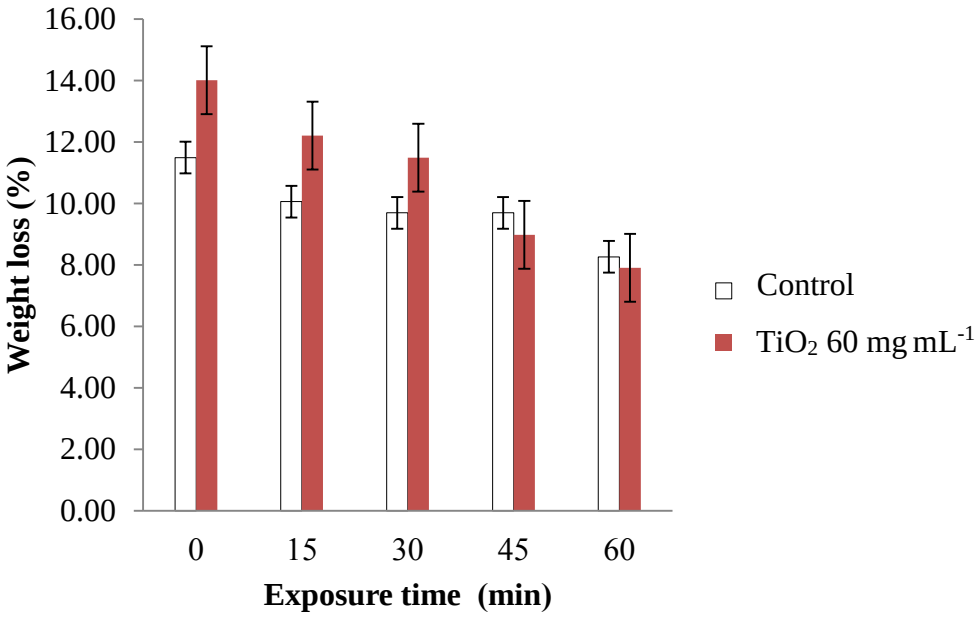

Figure 4.17 Weight loss of tangerine fruits after washing with TiO_2 photocatalysis for 60 min and storage at 5ºC for 45 days

7) Total microorganism count

Since fungi, especially *Penicillium digitatum* were the serious microorganisms that eliminate the quality of tangerine fruits during postharvest. Thus, this experiment emphasized to investigate amount of contaminated fungi on tangerine peel. It was found that, among the treatments of unwashed tangerines, washing with distilled water, and washing with TiO_2 photocatalysis, tangerine fruits washed with TiO_2 photocatalysis showed the lowest number of contaminated fungi both the begin day (106 CFU) and after storage 45 days (112 CFU) (Figure 4.18, Appendix : Table A 22). Similarly to the foundings of Cho *et al*. (2007) that carrots could be disinfected by TiO_2 photocatalysis. However, all treatments presented the lower number of fungi while increase the storage time. It was in agreement to Blake *et al*. (1999) that when TiO_2 was irradiated under UV light, the electrons could be excitation and produce hydroxyl radicals. Hydroxyl radical which have a strong oxidizing ability that induces the oxidative damage to the cell membrane or cell wall of microorganisms, resulted in the reduction of pathogen. Many previous research has reported on the effect of TiO_2 against microorganisms. Research on reduction of postharvest lost from fungi were shown in *Diaporthe actinidiae*, a major fungal pathogen of kiwifruit (*Actinidia deliciosa*) (Hur *et al*., 2005); *Penicillium expansum*, one of the most important fungal postharvest rots in fruits and vegetables (Maneerat and Hayata, 2005). Research on reduction of plant pathogens and severity of plan disease in the field could be shown in *Sclerotinia homoeocarpa* causing dollar spot disease of turfgrass (Hu, 2013); cercospora leaf spot and brown blotch of cowpea (*Vigna unguiculata* Walp) (Owolade and Ogunleti, 2008). Mechanism of TiO_2 photocatalysis in reduction of contaminated organisms (Thakaewet *al*., 2011) were explained according to Hu (2013) that when the reaction was going on, the oxidative species and UV radiation can react and cause cellular damage to microorganisms, which may reduce pathogen growth and help to control development. Some further research has found that the reactive oxygen species (ROS) which produced by TiO_2 photocatalytic reaction, can cause the peroxidation of the polyunsaturated phospholipids, thus inducing a major disorder in the *E. coli* cell membrane (Maness *et al.* 1999). KÜhn *et al*. (2003) used both light and scanning electron microscopy to observe that the microbial damage occurs through direct damage to cell walls caused by the hydroxyl radical (OH·).

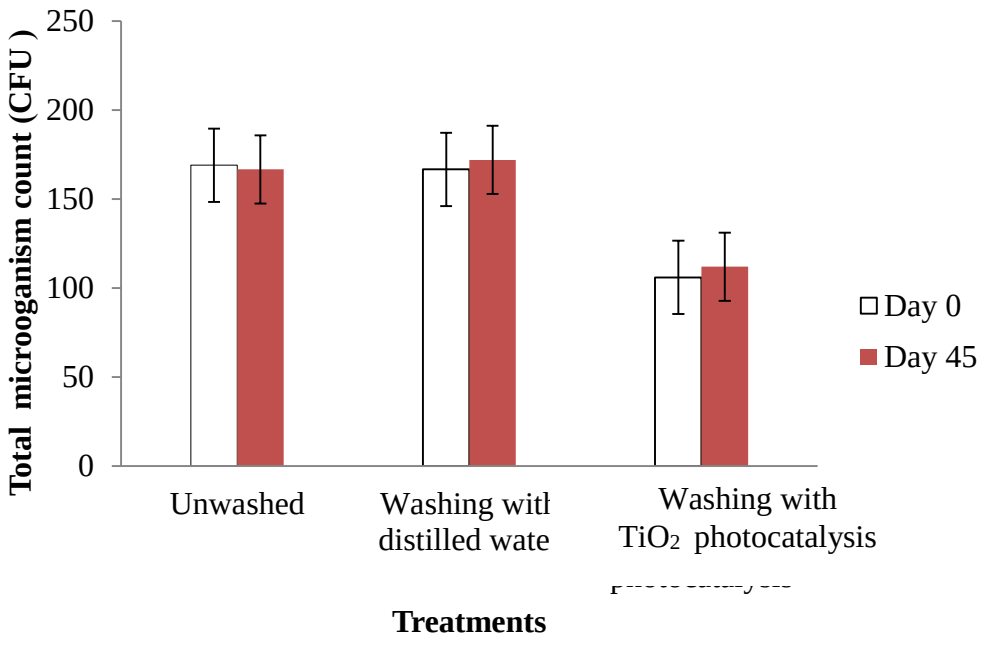

Figure 4.18 Total microorganism count of tangerine fruits after washing with TiO_2 photocatalysis for 60 min and storage at 5°C for 45 days

8) Ethion residue on tangerine fruits during storage

Ethion concentration residue on tangerine fruits at the initial time were positively reduced in all treatments when compared to the control (distilled water washing. The application of TiO_2 photocatalysis effect to significantly reduce residue ethion on tangerine fruits, compared to control, since initial time and during storage time. Moreover, at 45 days of storage period, residue ethion concentration was reduced to 0.05 mg L^{-1}, while ethion residue of the control was 0.30 mg L^{-1} (Figure 4.19, Appendix : Table A 21). Ordinarily, ethion residues on plant foliage dissipate with half-lives of less than 1 to 7 days. The dislodgeable residues on plant foliage dissipate even faster with half-lives of 0.1 to 3.4 days (Ware *et al*., 1993). Thus, residue ethion concentration was reduced from initial concentration when prolong time. The synergistic effect between using advance oxidation techniques and storage long time positively reduce pesticides on plant surface. Whangchai *et al*. (2010b) observed after storage at 10°C for 21 days that chlorpyrifos residue degradation in baby corn was increased from 12.38% to 21.88% and 65.81% to 77.92% after which exposed to ozone gas and dipping in ozonated water for 60 min, respectively.

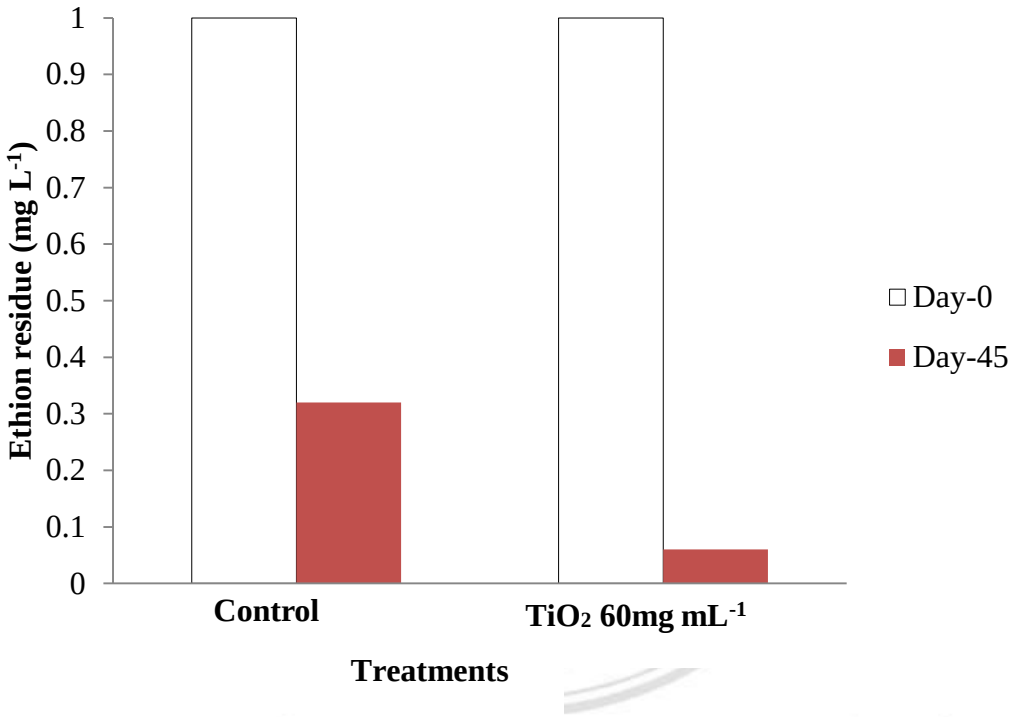

Figure 4.19 Ethion residue in tangerine fruits after washing with TiO_2 photocatalysis for 60 min and storage at 5ºC for 45 days

4.4 Conclusion

Ethion residue removal using TiO_2 photocatalysis on tangerine fruits was positively correlated to contact time. TiO_2 photocatalysis reduced fungi during storage of tangerine fruits comparing to the control. Therefore, further studies to confirm toxicity of ethion solution and wastewater of different tangerine washing by TiO_2 photocatalysis are also required.