

CHAPTER 5

Toxicity of Degraded Ethion and Wastewater after Washed Tangerine by Titanium Dioxide Photocatalysis

5.1 Introduction

The toxicity of the by-products from pesticide degradation using titanium dioxide photocatalysis should be evaluated. Bioassay can be used in a laboratory in order to determine toxicity by the estimation of the median lethal concentration fifty (LC_{50}) which have been reported for a series of toxins, pesticides and other contaminants (Kanwar, 2007).

Environmental pollution is an undesirable spinoff of human activities and represents a problem of repeated occurrences. Indubitably, pesticides attract public concern due to their potential transport from one environmental compartment to another and their effects on non-target biota (Desouky *et al.*, 2013).

Organophosphorus insecticides (OPIs) are widely used in Thailand. They were applied in large quantities and repeatedly because of their rapid breakdown in the environment. These compounds are quickly degraded in aquatic environments where the alkaline water accelerates their degradation (Desouky *et al.*, 2013). However, the effects of these contaminants on aquatic crustaceans include a widespread disturbance in general physiological processes (Chang *et al.*, 2006). Agricultural run off are the sources of pesticides in environment and the waste water causing the high threat for aquatic systems (Rajeswari and Kanmani, 2009).

Ethion [O,O,O',O'-tetraethyl S,S'-methylene bis (phosphorodithioate) or $C_9H_{22}O_4P_2S_4$] is one of the extensively applied organophosphorus insecticides (OPIs), which have been recognized as contaminated substances in many components of the environment. It was applied in order to control aphids, spiders, mites and insects for various crops. Among

pollutants, agricultural residues discharged to environment regarded a major environmental concern, as chemical substances are extensively used as diseases and pests control in a wide variety of products, such as pesticides, acaricides, herbicides,

fungicide, bacteriocides etc. During the photocatalytic processes, complex chain reactions occur that may lead to the formation of non-toxic intermediates, sometimes more toxic than the initial pollutant (Lomoră *et al.*, 2011)

5.2 Materials and methods

5.2.1 Toxicity of degraded ethion solution after TiO₂ photocatalysis by bioassay method

Toxicity assessment becomes a significant method to evaluate the treatment competency. Toxicity of degraded ethion after TiO₂ photocatalysis was conducted against brine shrimp (*Artemia salina* L.) as shown in Figure 5.1. Brine shrimp eggs were hatched in synthetic sea water (3% marine salt of water), oxygenated with bubbles from air pump. The adults brine shrimps (3 weeks after sowing) were accessible for the brine shrimp lethality test based on Kanwar (2007). The 10 adults of brine shrimps were placed into a vial with 5 mL of the degraded ethion concentrations at 0, 0.1, 1, 10 and 100 mg L⁻¹ after using TiO₂ photocatalysis treatment, with marine salt 1.5 mg / 5 ml of the solution. The experiment was determined from 5 replications. Temperature of solutions during experiment was in the ranged from 25 - 30°C. Mortality of adult brine shrimps has been checked every 6 h eventually after 18 h. LC₅₀ of the ethion solution was computed. Brine shrimp mortality in each concentration was calculated using following formula:

$$M_{mct} = \frac{N_{Mm} \times 100}{N_0}$$

where: M_{mct} is the mortality of individuals in time t (%)

N_{Mm} is the average number of died individuals

N_0 is the initial number of living individuals placed into each concentration at the test start

Brine shrimp mortality percentage was plotted against log concentration of ethion and from this graph the LC₅₀ values were evaluated by linear regression analysis.



Figure 5.1 Materials and method of brine shrimp hatching: marine salt (A), eggs of brine shrimp (B), hatching set-up (C) and adult brine shrimp (D).

5.2.2 Ethion concentration of wastewater washing from tangerine after TiO₂ photocatalysis for 60 min

Tangerine washed water was collected in order to compare the differences among the direct discharged washed water and the treated washed water by TiO₂ photocatalysis. The tangerine washed water was prepared followed the steps explained in Chapter 3. TiO₂ used in this experiment was solely at the concentration of 60 mg mL⁻¹, then exposed to UV illumination for 15, 30, 45 and 60 min. Samples were taken out periodically and each ethion concentration of ethion was monitored. Thereafter, the washed water at TiO₂ concentration of 60 mg mL⁻¹ was drained into a new container, then the samples of washed water were collected each week for 4 weeks to assess the ethion concentration left inside. Concentrations of ethion were determined using GC-FPD (Agilent Technologies Model 6890). The wastewater was analyzed in three replications.

Statistical analysis

The statistical analysis was carried out using a statistical program Statistic version released 8.0 and Least Significant Different Test at 95% was used to determine significant difference among the treatment

5.3 Results and discussion

5.3.1 Toxicity of degraded standard ethion solution after TiO₂ photocatalysis by bioassay method

The logarithm plots of ethion concentration and the mortality percentage of brine shrimp were presented in Figure 5.2 and the calculated LC₅₀ values at 18 h of brine shrimps with different treatments were shown in Table 5.1. Toxicity was slightly reduced after TiO₂ photocatalysis treatment as revealed by the LC₅₀ values which increased from 1.01 to 765.8 mg L⁻¹.

Titanium dioxide photocatalysis could effectively reduce the yields of toxic intermediate ethion. According to Desouky *et al.* (2011), initial ethion was reduced and change to the other intermediates. Figure 5.3 (Appendix : Table A 22) and 5.4 were shown the mortality percentage of brine shrimps after treated ethion solution with titanium dioxide photocatalysis, various standard ethion concentrations at 0, 0.1, 1.0, 10 and 100 mg L⁻¹. At the initial time, the brine shrimps of all treatments were still alive, whereas almost all of brine shrimps died in 100 mg/l of standard ethion after 6 h. Every 6 h eventually till 18 h, the percentage of brine shrimp mortality were increased with increasing contact time. It may be due to degradation of ethion concentration by titanium dioxide photocatalysis were less toxicity than the initial ethion was observed.

Treatment reduced toxicity as evidenced by the increasing LC₅₀ value with increasing time (Table 5.1). The highest value was 765.8 mg mL⁻¹ after treatment with TiO₂ for 60 min, compared with the control (1.01 mg mL⁻¹). Toxicity evaluation indicated the toxicity of ethion decreased after treatments. Ethion concentration may be degraded by TiO₂ photocatalysis process. In order to establish brine shrimp tolerance limits to

ethion, a preliminary short-term lethal concentration (LC_{50}) toxicity test was carried out according to the methods described by the American Public Health Association (1985). Probit method was used to calculate LC_{50} . Adult brine shrimp were put into the glass vial (5 drams) containing concentrations of ethion solutions (0, 0.1, 1, 10, 100 $mg L^{-1}$). Each vial contained ten brine shrimps. Water temperature was maintained at room temperature. The results were observed at 24 h intervals up to 96 h. Death was assumed when brine shrimps were immobile and nonresponded to the touch. According to Konstantinou and Albanis (2002), the titanium dioxide photocatalysis is a cost effective treatment to complete pesticide mineralization. It is usually not feasible and by-products generation appears to be unavoidable with photocatalytic degradation process. Kinetics of formation and decomposition of the intermediates are needed and identification of these by-products needs to be established in order to 1) determine which specific compounds will appear in the effluent 2) increase our knowledge on the degradation pathways in order to reveal which step is crucial for the global reaction of the process. Identification of by-products is the key to maximizing the overall process efficiency. Since hydroxyl radicals react non-selectively, various by-products are formed at low concentration levels. Toxicity analyses of the phototreated solutions of pesticides indicate the toxicity of the sum of compounds formed and not only those that have been identified (Desouky *et al.*, 2013). The parameter is very important for the treatment operation. If only partial degradation is considered, toxicity assessment of treated water becomes necessary. The toxicity of all temporary intermediates was compared to that observed for the initial compound.

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According to Herrmann and Guillard (2000), in the toxicity test of insecticide was found that the toxicity of the medium initially increased because of the formation of initial intermediates which is more toxic than the initial compounds (Tsuda *et al.*, 1997). Fortunately, all these products were punctually eliminated by photocatalysis.

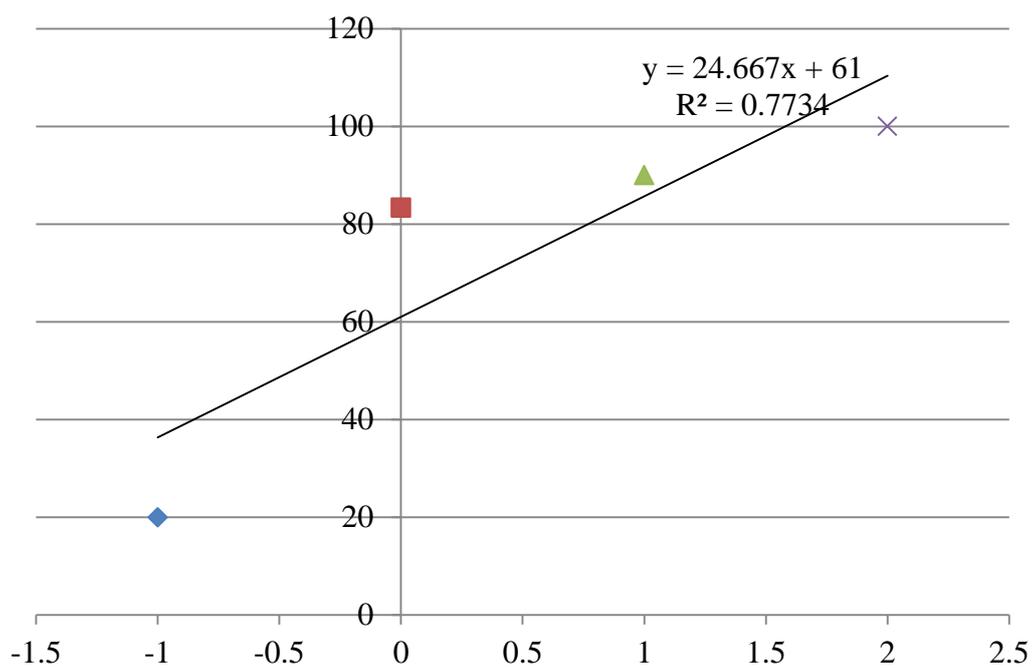


Figure 5.2 Linear regression of the brine shrimp (*Artemia salina* L.) in treated standard ethion solution

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Table 5.1 Bioassay toxicity test at 18 h with brine shrimp (*Artemia salina* L.) of standard ethion solution (1 mg L^{-1}) after TiO_2 photocatalysis treatment

Concentrations of TiO_2 (mg mL^{-1})	Total mortality at 18 h (mg L^{-1})	LC_{50} value (mg L^{-1})
Control (0)	44.82a	1.01e
TiO_2 15 mg mL^{-1}	27.56b	8.21d
TiO_2 30 mg mL^{-1}	18.56c	30.25c
TiO_2 45 mg mL^{-1}	12.50d	312.50b
TiO_2 60 mg mL^{-1}	7.16e	765.80a

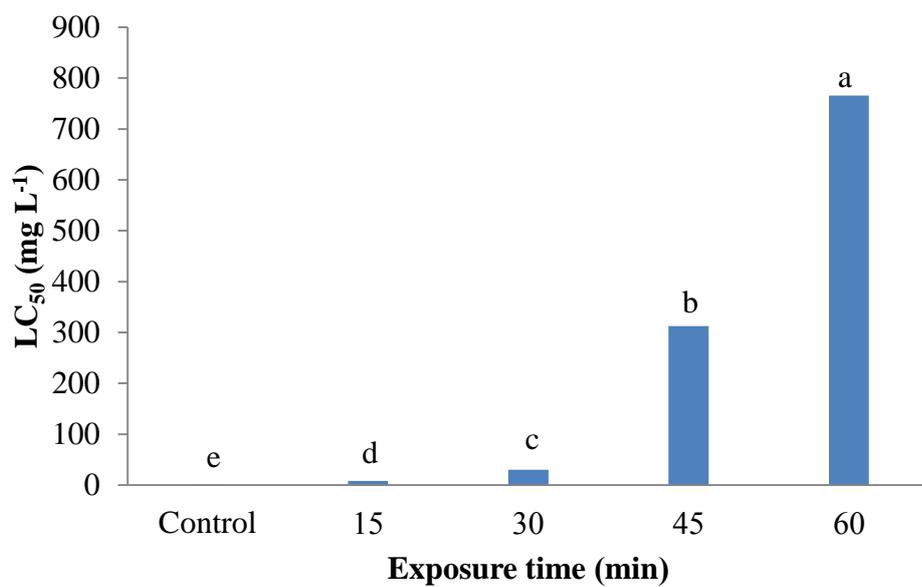


Figure 5.3 LC₅₀ value to the brine shrimp (*Artemia salina* L.) toxicity of ethion after treated by TiO₂ photocatalysis for 15, 30, 45 and 60 min

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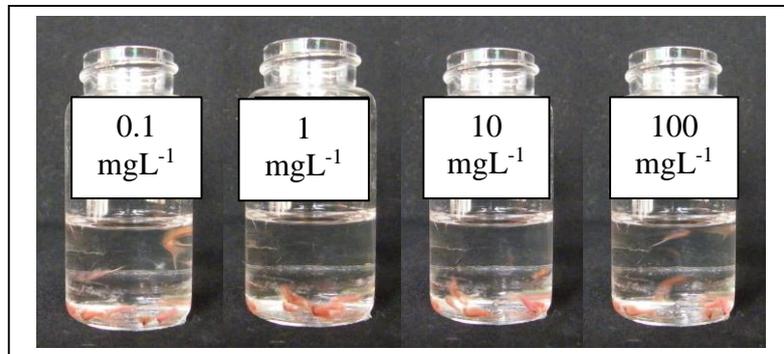


Figure 5.4 The brine shrimps (*Artemia salina* L.) at 18 h in various standard ethion concentrations (0.1, 1.0, 10 and 100 mg L⁻¹)

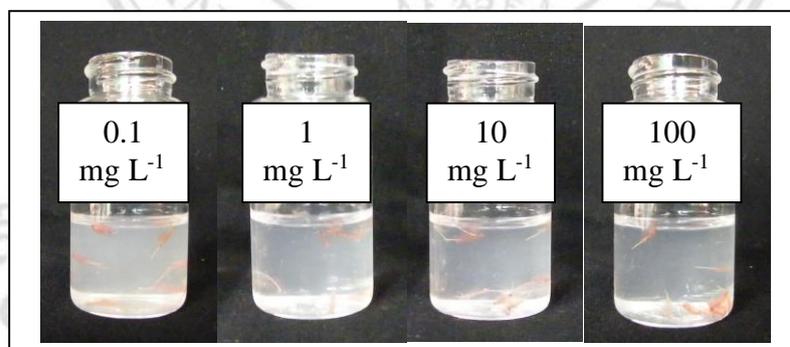


Figure 5.5 The brine shrimps (*Artemia salina* L.) at 18 h in treated ethion solutions with TiO₂ photocatalysis

5.3.2 Ethion concentration of wastewater washing from tangerine after TiO₂ photocatalysis for 15, 30, 45 and 60 min

In this experiment, ethion residues in wastewater was increased with increasing contact time, correspond to the increase of ethion degradation, and cause the wastewater more toxic than initial time. As the results shown in Figure 3.2 and Figure 4.19, the ethion concentration after treated by TiO₂ photocatalysis was reduced while increase the exposure time. Thereafter, the ethion contaminated tangerines which were treated with 60 mg mL⁻¹ TiO₂ photocatalysis for 60 min and stored for 45 days, showed the markedly reduction of ethion concentration. Thus, it could be explained that the contaminated ethion was ruptured from tangerine fruits (Hassarangsee *et al.*,2015b). Likewise, Miguel *et al.* (2012) and Verma *et al.* (2013) found that the contaminated aqueous phase could be degraded by the titanium dioxide photocatalysis treatment.

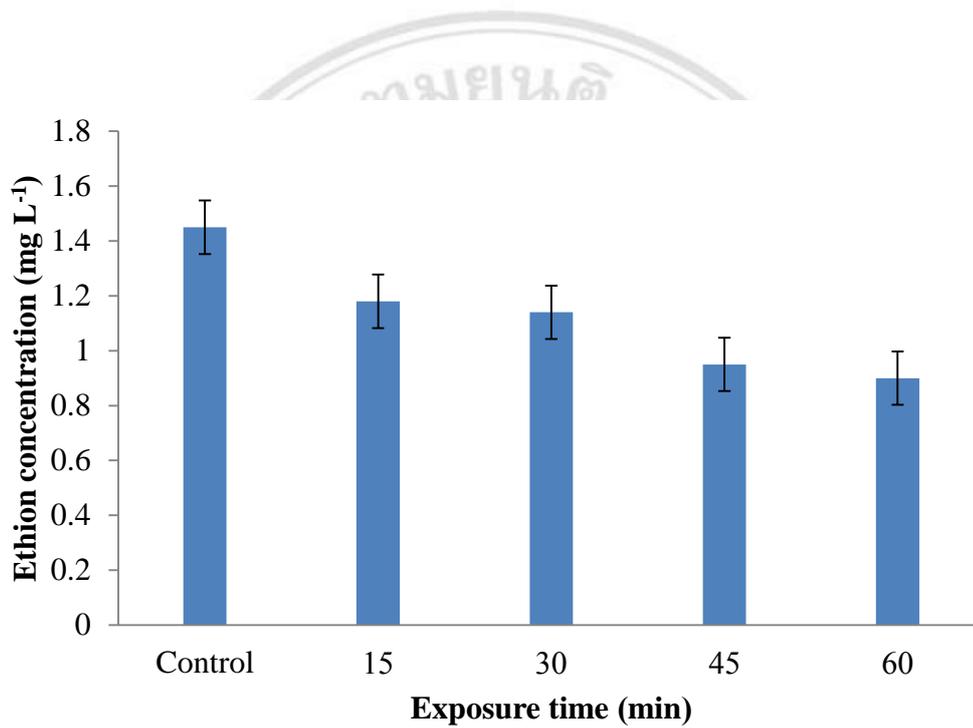
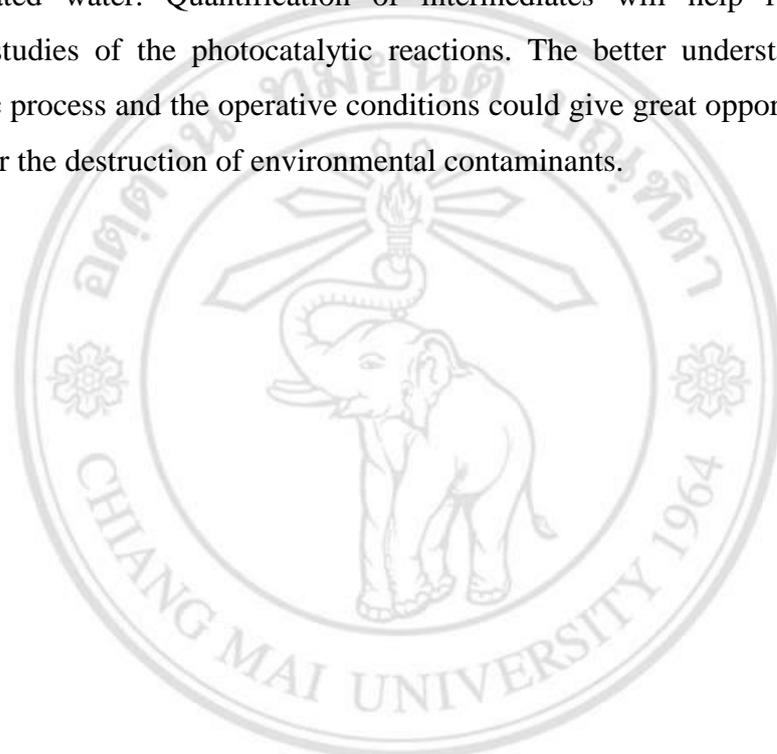


Figure 5.6 Ethion concentration of wastewater from tangerine washing by TiO₂ photocatalysis for 15, 30, 45 and 60 min

5.4 Conclusion

TiO₂ photocatalysis increases reduction the standard ethion toxicity in solution. The washing water of tangerine fruit treated with TiO₂ photocatalysis for 60 min was significantly reduced brine shrimp mortality, compared to control. Since the formation of temporary intermediates are important, some being more toxic than the initial compounds even at low concentrations, should be monitored for the realistic assessment of contaminated water. Quantification of intermediates will help further in the mechanistic studies of the photocatalytic reactions. The better understanding of the photocatalytic process and the operative conditions could give great opportunities for its application for the destruction of environmental contaminants.



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