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## Degradability of Treated Ethion Insecticide by TiO<sub>2</sub> Photocatalysis

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### ABSTRACT

Ethion, an insecticide, is widely used with fruit and vegetable crops. This research studied the reduction and oxidative degradation of standard ethion by TiO<sub>2</sub> photocatalysis. A standard ethion solution (1 mg L<sup>-1</sup>) was treated with different concentrations of TiO<sub>2</sub> powder (5, 10, 20, 40 and 60 mg mL<sup>-1</sup>) for 0, 15, 30, 45 and 60 min. The amount of ethion residue was detected by gas chromatography with flame photometric detection (GC-FPD) and the concentration of anions produced as major degradation products was determined by Ion Chromatography (IC). The TiO<sub>2</sub> photocatalysis efficiently reduced ethion concentrations, with the highest degradation rate occurring within the first 15 min of reaction. The reaction produced sulphate and phosphate anions. The TiO<sub>2</sub> photocatalysis reduced 1 mg L<sup>-1</sup> ethion to 0.18 mg L<sup>-1</sup> when treated with 60 mg mL<sup>-1</sup> TiO<sub>2</sub> powder for 60 min. The lethal concentration (LC<sub>50</sub>) of standard ethion was also estimated and compared to the treated ethion. All treatments, especially 60 mg mL<sup>-1</sup> TiO<sub>2</sub> powder, markedly detoxified ethion, as tested with brine shrimp (*Artemia salina* L.), with an LC<sub>50</sub> value of 765.8 mg mL<sup>-1</sup>, compared to the control of 1.01 mg mL<sup>-1</sup>.

**Key words:** Ethion, degradation, titanium dioxide, photocatalysis

### INTRODUCTION

Ethion (O,O,O',O'-tetraethyl S,S'-methylene bisphosphorodithioate) is an organophosphate pesticide widely used as an insecticide and acaricide to control aphids, spiders, mites and insects in fruit and vegetable production (Desouky *et al.*, 2013). Organophosphorus insecticides (OPIs), including ethion, contaminate many components in environment. It accumulates in biological systems and its presence in agricultural products and aquatic environments is potentially harmful to humans and other organisms. Ethion is highly toxic to freshwater and marine fish. The half-life of ethion in soil is range from 1.3-49 weeks depending on soil conditions and repeated usage of ethion (Extonet, 1996).

Titanium dioxide (TiO<sub>2</sub>) belongs to the family of transition metal oxides (Jian, 1997; Hashimoto *et al.*, 2005). Four commonly known polymorphs of TiO<sub>2</sub> are found in

nature: Anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal) and TiO<sub>2</sub> (B) (monoclinic) (Gupta and Tripathi, 2011; Florencio *et al.*, 2004). This study reports on TiO<sub>2</sub> powder only. The TiO<sub>2</sub> is relatively economical, photostable in solution, highly stable chemically, nontoxic, redox selective and strongly oxidizing (Fujishima *et al.*, 2000; Gupta and Tripathi, 2011). TiO<sub>2</sub> powder is highly photocatalytic due to its high specific surface area. When TiO<sub>2</sub> absorbs Ultra Violet (UV) radiation from sunlight or an illuminated light source (fluorescent lamps), pairs of electrons and holes are produced (Philippopoulos and Nikolai, 2010). The positive-hole of TiO<sub>2</sub> breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with the oxygen molecule to form a super oxide anion. This cycle continues when light exists. Hydroxyl radicals have been reported as extremely powerful oxidizing agents due to their oxidizing strength (Stasinakis, 2008). Environmentally, this mechanism

has been utilized to oxidize hazardous organic pollutants into nontoxic materials (Ravelli *et al.*, 2010). Many studies have reported TiO<sub>2</sub>'s ability to remove toxic substances (Konstantinou and Albanis, 2004), such as malathion, methamidophos, chlorfenapyr, phoxim, dichlofenghion, bromophos ethyl, bromophos methyl, atrazine, cyanazine, irgarol, prometryne, propazine, chlorotoluron, metobromuron, isoproturon, isosulfuron, triasulfuron (Gupta and Tripathi, 2011), fenamiphos (Gupta and Tripathi, 2011), pirimiphos-methyl (Herrmann and Guillard, 2000), diquat, paraquat (Tariq *et al.*, 2007), triclopyr, daminozid (Lomoră *et al.*, 2011), parathion (Carp *et al.*, 2004), 4-bromoaniline, 3-nitroaniline, pentachlorophenol, 1,2,3-trichlorobenzene and diphenylamine (Rahman and Muneer, 2005). However, the potential and appropriate applications of TiO<sub>2</sub> need further study, including oxidative degradation. Currently, the use of TiO<sub>2</sub> photocatalysis as an oxidation process for water treatment is increasing. The advantage of photocatalysis is that the photogeneration of <sup>•</sup>OH radicals are not harmful to the environment. This study was conducted to determine the oxidative degradation of ethion by TiO<sub>2</sub> photocatalysis.

## MATERIALS AND METHODS

### Chemical standard and preparation

**Preparation of ethion standard:** Ethion (Fig. 1) of analytical standard and 98.7% purity, was purchased from Sigma-Aldrich Pte Ltd. (Singapore, Fluka®). Ethion stock solution (1,000 mg L<sup>-1</sup>) was prepared by dissolving standard ethion in 99.8% acetone. The solution was diluted with distilled water to the appropriate concentrations.

**Photocatalyst:** Commercial titanium dioxide (TiO<sub>2</sub>) powder was purchased from Ajax Finechem®.

**Photoreactor and light source:** Photocatalytic experiments (Fig. 2) were all carried out in a dark acrylic box (30×30×60 cm) with the upper cover at room temperature. Two UV lamps at 10 W each supplied the UV radiation.

**Reduction of standard ethion solution by TiO<sub>2</sub> photocatalysis:** A standard ethion solution (25 mL, 1 mg L<sup>-1</sup>) was subjected to TiO<sub>2</sub> photocatalysis using different concentrations of TiO<sub>2</sub> powder (5, 10, 20, 40 and 60 mg mL<sup>-1</sup>). The titanium dioxide particles and ethion solution were adequately mixed using an air pump throughout the experiment. Samples were taken at 15 min intervals for 1 h. Three replicates of ethion samples for each treatment were conducted. Ethion concentrations were determined by gas chromatography. The analysis was performed in an Agilent Technologies (Wilmington, DE) model 6890 gas chromatograph equipped with a flame photometric detector (GC-FPD). The GC column was a fused silica capillary column HP-5, 5% phenylmethylsiloxane, with the dimensions

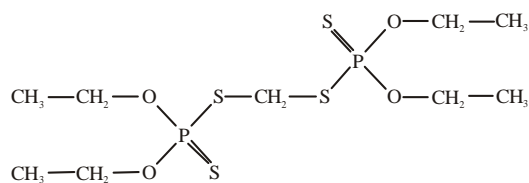


Fig. 1: Chemical structure of ethion

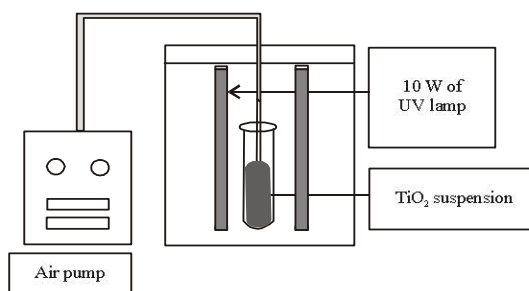


Fig. 2: Schematic diagram of the TiO<sub>2</sub> photocatalysis for ethion reduction *in vitro*

of 30 m×0.32 mm i.d. and a 0.25 μm film thickness (Agilent Technologies). The temperature was programmed to increase at 10°C min<sup>-1</sup> from an initial 100–200°C and then at 4°C min<sup>-1</sup> until the final temperature of 220°C was reached. A purified helium carrier gas was used at a flow rate of 3.6 mL min<sup>-1</sup>. The detector temperature was set at 250°C. Sample solution (1.0 μL) was injected in splitless mode. Quantification of ethion was performed using an ethion standard as reference.

**Oxidative degradation of treated ethion by TiO<sub>2</sub> photocatalysis:** Concentrations of sulphate and phosphate anions of treated ethion solutions by TiO<sub>2</sub> photocatalysis were determined. Anions, released from the decomposition of ethion, were analyzed at 60 min by Ion Chromatography (IC). The amount of these ions corresponded to the degradation of ethion in this study. The analysis was performed using an ion chromatograph equipped with a Metrosep A Supp 5 250/4.0. Eluent composition was A Supp 5 eluent 3.2 mM Na<sub>2</sub>CO<sub>3</sub> and 1.0 mM NaHCO<sub>3</sub>. Samples were filtered by syringe filters of size 13 mm, 0.45 μm (Vertical®). A 10.0 μL sample was automatically injected in conductivity mode and ethion was quantified using calibration curves with external standards at a flow rate of 0.70 mL min<sup>-1</sup>, pressure of 12.71 MPa and recording time of 28 min.

**Toxicity test by bioassay method:** Toxicity was estimated using brine shrimp (*Artemia salina* L.). Brine shrimp eggs were hatched in artificial sea water (3% marine salt in water) oxygenated by air pump and sown for three weeks to reach adult stage. Ten adult brine shrimps were put into a vial containing 5 mL of TiO<sub>2</sub> of 60 mg mL<sup>-1</sup> with ethion



concentration at 1.0 mg L<sup>-1</sup> and then subjected to photocatalysis as described in experiment 1. The experiments were conducted in five replications. Mortality of adult brine shrimp was checked every 6 h. The LC<sub>50</sub> of the ethion solution was calculated.

**Statistical analysis:** All experiments were evaluated with a regression procedure, using SPSS version 17 while the differences among various treatments were calculated using one-way analysis of variance followed by Duncan's New Multiple Range test (p<0.05).

### RESULTS

**Reduction of standard ethion solution by TiO<sub>2</sub> photocatalysis:** Reduction of standard ethion by TiO<sub>2</sub> photocatalysis is shown in Fig. 3. The concentration of ethion solution decreased as the amount of TiO<sub>2</sub> powder and time of exposure increased. Within the first 15 min, a rapid reduction in ethion concentration was observed for all treatments. However, the most effective method of reducing the amount of ethion was observed using 60 mg mL<sup>-1</sup> TiO<sub>2</sub> powder for 60 min; it was able to reduce 1-0.28 mg L<sup>-1</sup>.

Ethion treated with TiO<sub>2</sub> photocatalysis resulted in increased anion concentrations. As shown in Fig. 4a the amount of phosphate ions increased abruptly for the first 15 min but slowed down from 30-60 min. During TiO<sub>2</sub> photocatalysis, the phosphate concentration increased from 5.73-7.01 ppm.

Table 1: Bioassay toxicity test with brine shrimp (*Artemia salina* L.) of ethion solution after TiO<sub>2</sub> photocatalysis treatment for 60 min

Treatments	Total mortality at 18 h	LC <sub>50</sub> value (mg mL <sup>-1</sup> )
Control	44.82 <sup>a</sup>	1.01 <sup>d</sup>
TiO <sub>2</sub> 15 min	27.56 <sup>b</sup>	8.21 <sup>d</sup>
TiO <sub>2</sub> 30 min	18.56 <sup>c</sup>	30.25 <sup>c</sup>
TiO <sub>2</sub> 45 min	12.50 <sup>cd</sup>	312.50 <sup>b</sup>
TiO <sub>2</sub> 60 min	7.16 <sup>d</sup>	765.80 <sup>a</sup>

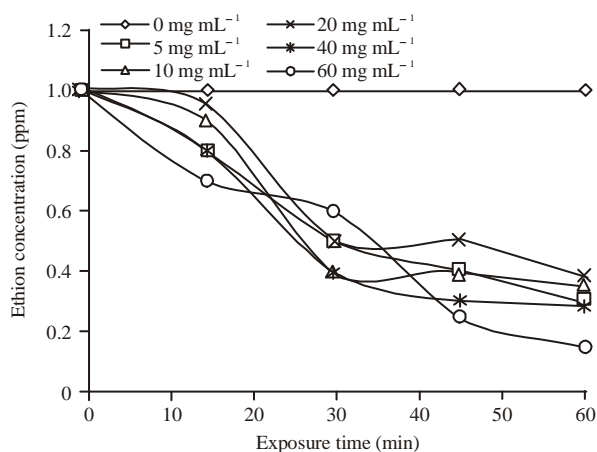


Fig. 3: Concentration of ethion after treatment with TiO<sub>2</sub> photocatalysis

TiO<sub>2</sub> photocatalysis also induced the release of sulphate anion from ethion. The sulphate anion increased during the first 15 min of reaction time, then stabilized from 30 min until 60 min of reaction (Fig. 4b).

Treatment reduced toxicity as evidenced by the increasing LC<sub>50</sub> value with increasing time (Table 1). The highest value was 765.8 mg mL<sup>-1</sup> after treatment with TiO<sub>2</sub> for 60 min, compared with the control (1.01 mg mL<sup>-1</sup>). Toxicity evaluation indicated the toxicity of ethion decreased after treatments. Ethion concentration may be degraded by TiO<sub>2</sub> photocatalysis process.

### DISCUSSION

Results obtained from this study conformed to the one where an organophosphate pesticide decomposes better the longer it is exposed to UV light (Mountacer *et al.*, 2013). This is because as irradiation time of the UV lamp increases lots of

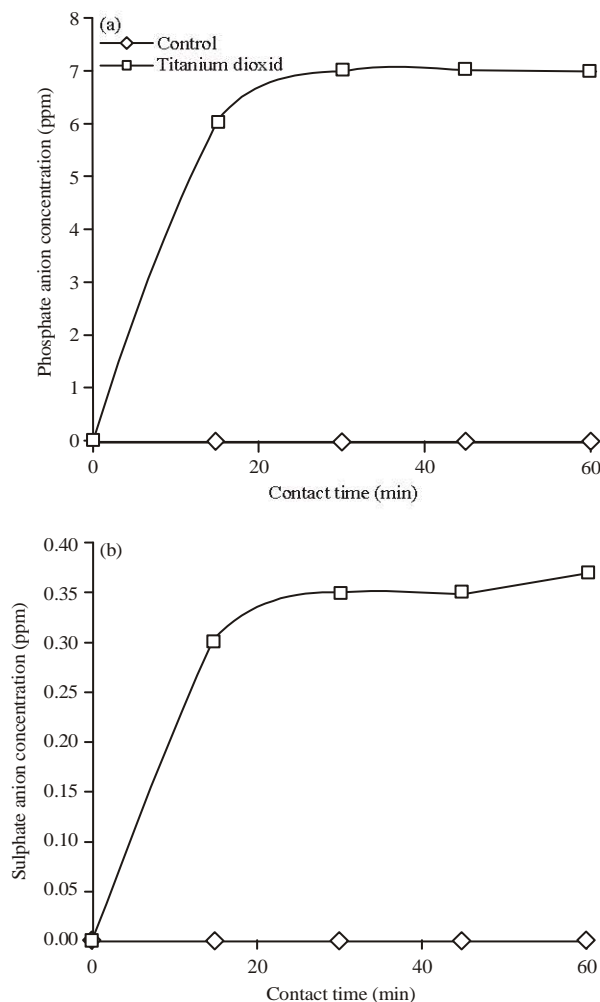


Fig. 4(a-b): (a) Phosphate and (b) Sulphate anion released from ethion solution during TiO<sub>2</sub> photocatalysis using 60 mg mL<sup>-1</sup> TiO<sub>2</sub> powder

free radicals had formed in the liquid, causing much decomposition on the pesticides (Konstantinou and Albanis, 2002; Shayeghi *et al.*, 2012).

During the reaction while the formation of sulphate from the stoichiometric concentration is achieved, the remaining amount is still linked to the parent molecule (Calza *et al.*, 2004; Rajeswari and Kanmani, 2009).

Many previous studies have shown several intermediates of photocatalytic degradation that have been identified corresponding to the reaction that taking place to break apart the ethion molecules (Herrmann *et al.*, 1999). Oxidant attack of OH on the P = S bond occurred first, resulting in the formation of oxon derivatives. The continuous attack of OH, followed by the rupture of the P-O bond, resulted in the formation of corresponding phenols and different alkyls or phosphate esters (Mountacer *et al.*, 2013; Konstantinou and Albanis, 2004).

The result of toxicity tested against brine shrimp (*Artemia salina* L.) in this research was also confirmed by Tsuda *et al.* (1997) that the contamination of fish and other aquatic organisms by the oxidation products in the environment is very low.

## CONCLUSION

TiO<sub>2</sub> photocatalysis applied to ethion solution reduced ethion concentration. Most of the decomposition appeared within the first 15 min. The best condition for reducing ethion was to use 60 mg mL<sup>-1</sup> TiO<sub>2</sub> powder exposed for 60 min. During degradation, sulphate and phosphate anions were released from the ethion structure, due to the TiO<sub>2</sub> photocatalysis that generated <sup>•</sup>OH. The treatment of TiO<sub>2</sub> photocatalysis significantly lowered the toxicity of ethion. The results proved that TiO<sub>2</sub> photocatalysis offers potential to chemically reduce residues and by-products also have low toxicity tested while tested against *Artemia salina* L. However, continuous efforts to improve the photocatalytic properties should be considered.

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