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EFFECT OF TiO_2-COATED SUBSTRATE PHOTOCATALYSIS ON CHLOPYRIFOS INSECTICIDE DEGRADATION

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ABSTRACT: The efficiencies of photocatalysis using TiO_2-coated substrates to reduce chlorpyrifos insecticides was evaluated. Three different glass substrates (glass ball, glass slide and glass bead) were prepared and tested with KI solution for efficiency of oxidation test. It was found that TiO_2-coated glass beads at 45 mg/ml for 60 min had the highest iodine liberation rate. A 1 mgL^{-1} standard chlorpyrifos was subjected to those TiO_2-coated substrates photocatalysis for 15, 30, 45 and 60 minutes. The percentage reduction of chlorpyrifos was calculated. It was shown that TiO_2-coated glass bead photocatalysis had high reduction rate of chlorpyrifos concentration within 15 minutes, which correlated with an increase in iodine liberation rate. The effectiveness of TiO_2 in photocatalysis to reduce contaminated chlorpyrifos in Chinese kale was determined by treatments with different TiO2-coated substrate photocatalysis and sampled every 15 minutes for 60 minutes. It was found that TiO_2-coated glass bead reduced chlorpyrifos concentration to 53% when compared with the control. In addition, in the quality of Chinese kale after treatment withTiO_2 in photocatalysis and stored for 12 days at 5 $^{\circ}C$ was also investigated. There was no significant difference in the quality of Chinese kale in weight loss, leaf color, total soluble solids and ascorbic acid content.

Keywords: Chlorpyrifos, Degradation, Titanium Dioxide, Photocatalysis

1. INTRODUCTION

Exporting countries are concerned with increasing crop production with constraints on available agricultural land. Increasing the use of pesticides in the future is one way to achieve this goal. Thai Agricultural Commodity and Food Standard in 2006 reported that the residual pesticides is the detected at higher concentration than the Maximum Residue Limit (MRL by importers). Among vegetables, chlorpyrifos residue was the most commonly found in Chinese kale. [Chlorpyrifos is an organophosphate insecticide and is widely used for pest control on vegetable crops [1]. The most common method for reducing chemical residues is by washing with detergent, sodium hypochlorite or potassium permanganate. However, this method creates chemically polluted water as a byproduct and has a high cost and limited effectiveness. The Good Agricultural Practices (GAPs) certification program has been a strategy for limiting pesticide residue on crops. However, chlorpyrifos contamination of chilli is still a critical problem to be solved because of over usage by growers. Titanium dioxide (TiO_2) belongs to the family of transition metal oxides [2, 12]. There are four commonly known polymorphs of TiO_2 found in nature, namely: anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal) and TiO_2 (B) (monoclinic) [5, 15]. Only TiO_2 powder was stated in this report. TiO_2 powder has high photocatalytic activity due to their higher specific surface area. It is relatively economical, photostable in solution, highly stable chemical, nontoxic, redox selective and strong oxidizing power [1, 5] and can be as a photocatalyst. When TiO_2 absorbs ultraviolet (UV) radiation from sunlight or illuminated light source (fluorescent lamps), pairs of electrons and holes will be produced [3]. The positive-hole of TiO_2 breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion. This cycle continues when light is available. Hydroxyl radicals were claimed to the extremely powerful oxidation agent due to their oxidizing strength. In the environmental aspect, this mechanism was utilized to oxidize hazardous organic pollutant into nontoxic materials [4]. TiO_2 has been proved for its advantages in removing toxic substances [7] such as malathion[17], methamidophos, chlorfenapyr, phoxim, dichlofenghion, bromophos ethyl, bromophos methyl, atrazine, cyanazine, irgarol, prometryne, propazine, chlorotoluron, metobromuron, isoproturon cinosulfuron, triasulfuron [5], fenamiphos [5], pirimiphos-methyl [10], dichlorvos and phosphamidon [13],diquat, paraquat [14], triclopyr, daminozid [16], parathion [19], 4-bromoaniline, 3-nitroaniline, pentachlorophenol, 1,2,3-trichlorobenzene and diphenylamine. However, the potential and appropriate applications of TiO_2 including oxidative degradation should be further studied. Currently, utilization of TiO_2 photocatalysis as an oxidation process for water treatment increases. The advantage of photocatalysis is that, the photogeneration of •OH radical is not harmful to the environment. This study was conducted to determine the degradation of chlorpyrifos in Chinese Kale by washing with various TiO_2-coated with substrate photocatalyst.

2. MATERIALS AND METHODS

2.1 Photocatalyst

Commercial TiO_2 powder was purchased from Ajax Finecham®, Australia)

2.2 Photoreactor and Light Source

All photocatalytic experiments were carried out in dark acrylic box of (30× 50 × 40 cm) operated with two UVA lamps with light intensity 10 watt each. The TiO_2-coated glass substrates were packed between the lamp and tube. Two reaction tubes were placed on the bottom of the reactor. A schematic diagram of the experimental set up is shown in Fig. 1

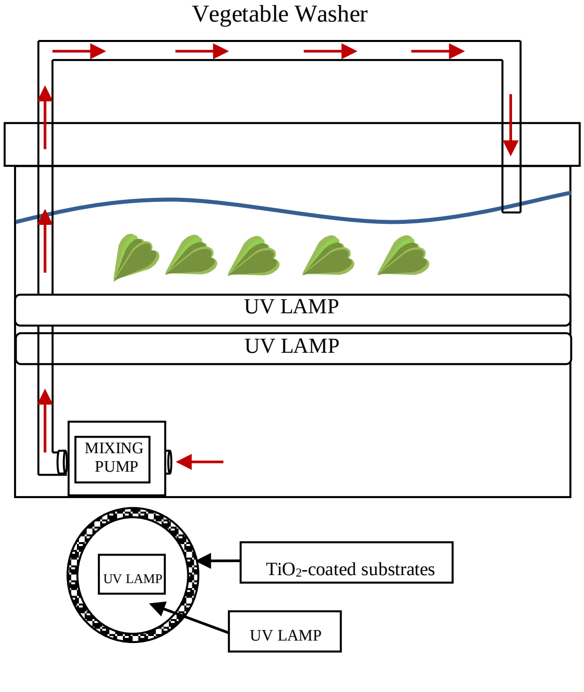

Fig. 1 Schematic of reaction system of TiO_2 coated substrate combined with photocatalysis in degradation of chlorpyrifos residue in Chinese Kale

2.3 Study of Various TiO_2-Coated Substrates Photocatalysis for Oxidative degradation activity and Reducing Standard Chlopyrifos Solution

Standard chlopyrifos at the concentration of 1 mg L^{-1} or 2% KI solution was prepared in a flask and then placed inside different types of glass substrates coated with TiO_2 (glass ball: 1 cm in diameter, glass slide (2.5 x 7.5 cm) and glass bead: 1 mm in diameter prepared by coating with TiO_2 powder at 45 mg mL^{-1} (with almost the same surface area) by FCVAD (Filterred Cathodic Vacuum Arc Deposition) at oxygen 10^{-2} Torr and 250 volt. Each TiO_2 coated substrate was put in photocatalysis reactor for 15, 30, 45 and 60 minutes. The concentration of iodine liberation from 2% potassium iodine was measured at 354nm using digital spectrophotometer. Finally, triplicates of chlopyrifos samples were analyzed. Using a gas chromatograph equipped with a flame photometric detector (GC-FPD). The percent removal of chlopyrifos was calculated at each collection time. Chlopyrifos concentrations were determined by gas chromatography. The analysis was performed using Agilent Technologies (Wilmington, DE) with 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 of 30 m × 0.32 mm i.d. and a 0.25 µm film thickness (Agilent Technologies). The temperature was programmed to increase at 10ºC min^{-1} from an initial 100ºC to 200ºC and then at 4ºC increase to the final temperature of 220ºC. A purified helium gas carrier was used at a flow rate of 3.6 mL min^{-1}. The detector temperature was 250ºC. Sample solution (1.0 µL) was injected in splitless mode. Quantification of chlopyrifos was performed using chlopyrifos standard as reference.

2.4 TiO_2-Coated substrates Photocatalysis on the Reduction of Chlorpyrifos Insecticide in Chinese Kale and Its Quality Changes During Storage

Chinese Kale were purchased from an organic agriculture farm in MaeTaeng district, Chiang Mai, Thailand. They were cleaned with distilled water and those with uniform shape and lesion free were selected. Each sample was dipped into 10 mgL^{-1} chlorpyrifos solution for 30 minute. and left to dry at room temperature. Then washed in photocatalysis reactor (Fig. 1). For 15, 30, 45 and 60 minute the reduction in percentage of pesticide residue was then determined by gas chromatography.

2.4.1 Quality Changes during Storage

Chinese Kale were washed in the reactor for 15, 30, 45 and 60 minute in the previous experiment and then kept in sealed PE bags. All the treated samples were stored at 5°C for 12 days and were selected to measure the quality changes at the end of storage. The percentage of weight loss, leaf color change, total soluble solids (TSS) content and ascorbic acid content (AOAC) were determined.

2.4.2 Statistic Analysis

All the experiments were done in triplicates and evaluated with regression procedure, using SPSS version 17. The differences between the treatments were analyzed, using Duncan's multiple range test (*$P < 0.05$).

3. RESULTS AND DISCUSSION

3.1 Study of Various TiO_2-Coated substrates Photocatalysis for Oxidative Degradation Activity and Reducing Standard of Chlorpyrifos Solution

Iodine liberation by 2 % KI increased in of all TiO_2-coated treatments (Fig. 2). The increase in iodine liberation promoted oxidation efficiency by the reaction time.The active hydroxyl free radical which generated from the reaction react with potassium iodide which resulting in iodine liberation[9]. Reduction in standard chlorpyrifos by different TiO_2-coated glass substrates with photocatalysis is shown in Fig. 3. The concentration of chlorpyrifos solution decreased and time of exposure increased. Within the first 15-minnute, a rapid reduction in chlorpyrifos concentration was obvious in all treatments. However, most effective method of reducing the amount of chlorpyrifos was observed when TiO_2-coated glass bead was used and treated for 15-min. It was able to reduce significantly almost 50% of chlorpyrifos from 1.0 mgL^{-1} to4.6 mgL^{-1} while the concentration of other treatments slightly decreased with increasing time. The increase in iodine liberation promoted oxidation efficiency by the reaction time. It's hypothesized that high density and surface area of TiO_2-coated glass bead as determined by BET (BRunaver Emmett-Teller) analysis (data not shown) are able to increase the photocatalytic efficiency by increasing reactive species generation. These confirmed with a study of an organophosphate pesticide exposed longer to UV decomposed better [6]. This is because when the irradiation time by UV lamp increases, lots of free radicals and formed in the liquid, causing much decomposition of the pesticides [8, 18].

Previous studies had shown many intermediates of the photocatalytic degradation identified according to the reaction [11]. Oxidant attack of the OH^- on the P=S bond occurred first, resulting in the formation of oxon derivatives. Continuous attack of OH^- followed by the rupture of P-O bond resulted in the formation of corresponding phenols and different alkyls or phosphate esters [6, 7].

3.2 TiO_2-Coated Glass Substrates Photocatalysis on the Reduction of Chlorpyrifos Insecticide in Chinese Kale and its Quality Changes During Storage

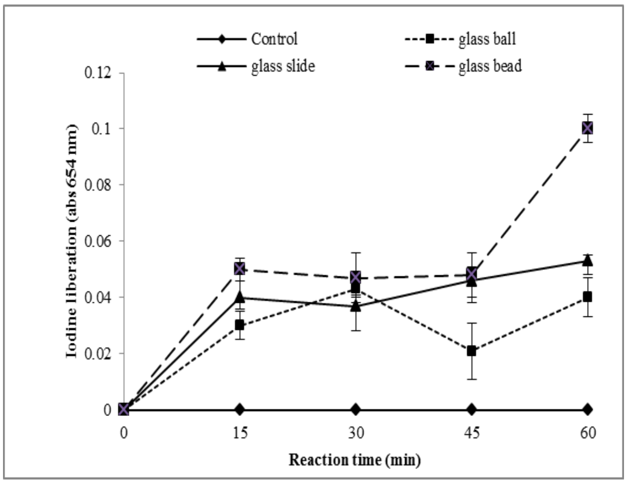

Fig. 2 Oxidative degradation activity (Iodine liberation) after treatment with different TiO_2- coated glass substrates

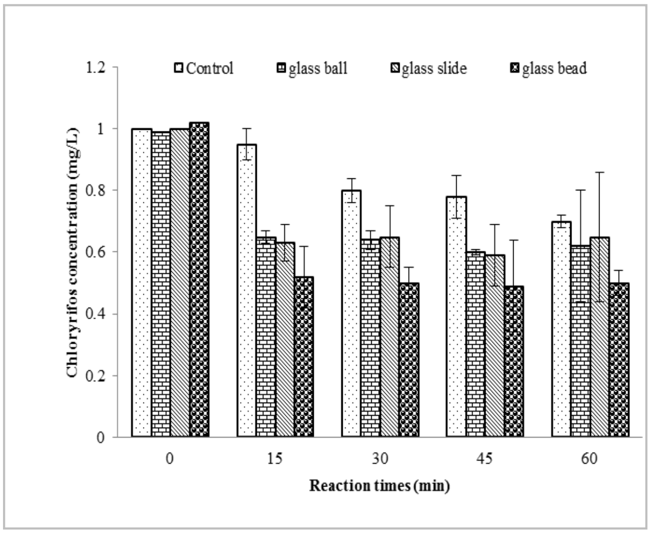

Fig. 3 Degradation efficiency of chlorpyrifos under different TiO_2-coated glass substrates

Chinese kale were washed in different TiO_2-coated substrate to remove residual chlorpyrifos. It was found that degradation percentage of chlorpyrifos in Chinese kale when washed in TiO_2-coated glass bead increased with increasing time. The highest rate of reduction occurred in 60 minutes when compare with the control, which was immersed in distilled water. It was found that the TiO_2 photocatalysis reduced chlorpyrifos concentration to 53 % when compared with the control which was 11.5 % (Fig. 4). Similarly, the decomposition rate of 17-β-oestradiol treated by immobilized TiO_2 was 98% in 3.5 h. [20]. In addition, two organophosphorus insecticides, dimethyl-2,2-dichlorovinyl phosphate (DDVP) and dimethyl-2,2,2-trichloro-hydroxy ethyl phosphonate (DEP), were photocatalytic degraded by illumination with a super-high pressure mercury lamp or by exposure to sun light[21]. All of these treatments were observed to have no effect on fruit quality, as determined by on weight loss, leaf color, total soluble solids and ascorbic acid (Table 1)

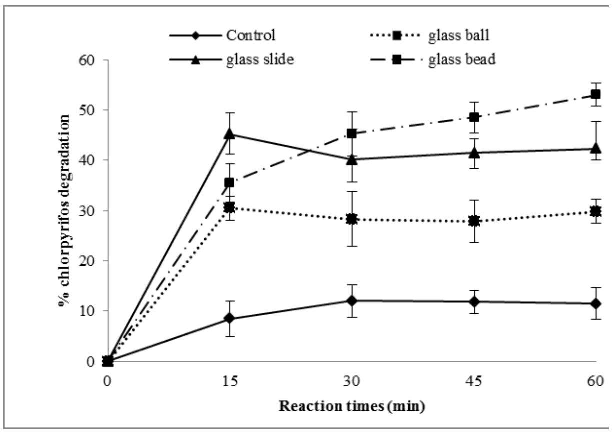

Fig. 4: Chlorpyrifos degradation in Chinese kale when treated with various TiO_2-coated substrates for 60 minutes

Table 1 Effect of TiO_2-coated substrates phytocatalysis on quality of Chinese Kale after Storage at 5°C for 12 days Columns with different letter of each parameter indicate significant differences by Duncan's multiple range test (*$P < 0.05$)

Treatment	Weight loss (%)	TSS (% brix)	Peel color L*	Peel color a*	Peel color b*	Ascorbic acid mg/100 g
Control	6.5 ab	8.8 a	23 a	-4.5 a	3.5 be	40.5 ab
glass ball	6.1 ab	9.0 ab	22.5 ab	-3.9 ab	4.2 ab	39.0 bc
glass slide	5.9 bc	7.8 ab	21.0 ab	-3.83 bc	4.3 ab	37.5 c
glass bead	6.3 ab	9.0 ac	23.7 a	-4.12 ab	4.9 a	42.8 a

4. CONCLUSION

Photocatalysis using TiO_2-coated glass bead had high performance on the degradation of chlorpyrifos insecticide. In addition, it was confirmed that this technique could improve vegetable quality with no adverse effects on quality of Chinese kale in weight loss, leaf color, total soluble solids and ascorbic acid content.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

[1] Fujishima A, Rao TN and Tryk DA, "Titanium dioxide photocatalysis", Journal of Photochemistry and Photobiology C: Photochemistry Reviews, Vol. 1, 2000, pp.1-21.

[2] Jian C, "Advanced oxidation technologies: Photocatalytic treatment of wastewater", PhD Thesis, 1997, Wageningen, Netherlands.

[3] Philippopoulos CJ. and Nikolai M D, "Photocatalytic processes on the oxidation of organic compounds in water", 2013, http://www.intechopen.com (Access: July 2013)

[4] Ravelli D, Dondi D, Fagnoni M and Albini A, "Titanium dioxide photocatalysis: An assessment of the environmental compatibility for the case of the functionalization of heterocyclics", Applied Catalysis B: Environmental, Vol., 99, 2010, pp.442–447.

[5] Mital GS and Manoj T, "A review of TiO_2 nanoparticles", Chinese Science Bulletin, Vol. 16, 2011, 56, pp. 1639-1657.

[6] Mountacer H, Nemmaoui SM, Rafqah S, Voyard G and Sarakha M, "TiO_2 Photocatalysis of the Organophosphorus Fenamiphos: Insight into the Degradation Mechanism", ISRN Environmental Chemistry, Article ID 319178, 2013, pp. 1-8.

[7] Konstantinou IK and Albanis TA, "Degradation pathways and intermediates of photocatalytic transformation of major pesticide groups in aqueous TiO_2 suspensions using artificial and solar light: A review", 3rd European Conference on Pesticides and Related Organic Micropollutants in the Environment, Halkidiki, Greece, 2004, pp.320-324.

[8] Konstantinou I K. and Albanis TA, "Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways", Applied Catalysis B: Environmental, Vol. 1310, 2002, pp. 1-17.

[9] Hart E.J. and Henglein A, "Free radical and free atom reaction in the solnolysis of aqueous iodine and formate solutions",Journal of Physical Chemistry,Vol.89,1985,pp 4342-4347.

[10] Herrmann JM, Guillard C, "Photocatalytic degradation of pesticides in agricultural used waters", Chemistry, Vol. 3, No. 23, 2000, pp. 417–422.

[11] Herrmann JM, Guillard C, Arguello M, Agüera A, Tejedor A, Piedra L and Fernández-Alba A, "Photocatalytic degradation of pesticide

pirimiphos-methyl: Determination of the reaction pathway and identification of intermediate products by various analytical methods", Catalysis Today, 1999, 54, 353–367.
[12] Hashimoto K, Irie H and Fujishima A, "TiO_2 photocatalysis: A Historical overview and future prospects", Japanese Journal of Applied Physics, Vol. 44, No. 12, 2005, pp. 8269-8285 (Part 1).
[13] Rahman MA and Muneer M, "Photocatalysed degradation of two selected pesticide derivatives, dichlorvos and phosphamidon, in aqueous suspensions of titanium dioxide", Desalination, Vol. 181, 2005, pp. 161-172.
[14] Tariq MA, Faisal M, Muneer M and Bahnemann D, "Photochemical reactions of a few selected pesticide derivatives and other priority organic pollutants in aqueous suspensions of titanium dioxide", Journal of Molecular Catalysis A: Chemical, Vol. 265, 2007, pp. 231–236.
[15] Florencio MH, Pires E, Castro AL, Nunes MR, Borges C and Costa F M, "Photodegradation of Diquat and Paraquat in aqueous solutions by titanium dioxide: evolution of degradation reactions and characterisation of intermediates", Chemosphere, Vol. 55, 2004, pp. 345–355.
[16] Lomora M, Draghici C and Enesca Al., "Intermediary compounds in advanced oxidation processes for wastewater treatment", in " Bulletin of the Translvania University of Brasov, Series K: Engineering Sciences Vol. 4 (53) No. 1-2011, 2011, pp. 51-58.
[17] Shayeghi M, Dehghani MH, Alimohammadi M and Goodini K, "Using ultraviolet irradiation for removal of malathion pesticide in water", Journal of Arthropod-Borne Diseases, Vol.6, No.1, 2012, pp. 45–53.
[18] Carp O, Huisman C L and Reller A, "Photoinduced reactivity of titanium dioxide", Progress in Solid State Chemistry, Vol. 32, 2004, pp. 33–177.
[19] Calza P, Medana C, Pazzi M, Baiocchi C and Pelizzetti E, "Photocatalytic transformations of sulphonamides on titanium dioxide", Applied Catalysis B: Environmental, Vol. 53, 2004, pp.63–69.
[20] Harada K, Hisanaga T and Tanaka K, “Photocatalytic degradation of organophosphorous insecticides in aqueous semiconductor suspensions”, Water Research, Vol. 24, 1990, pp. 1415-1417.
[21] Evgenidou E., Konstantinou I., Fytianos K. and Albanis T. “Study of the removal of dichlorvos and dimethoate in a titanium dioxide mediated photocatalytic process through the examination of intermediates and the reaction mechanism”, Journal of Hazardous Materials. Vol. B137, 2006, pp. 1056-1064.

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