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# Degradation Kinetics of Diazinon and Triazophos Pesticides in Dried Chili under Gaseous Ozone Fumigation

**Panlop Sintuya[1,2], Kanjana Narkprasom[1], Jaturapatr Varith[1]*, Somkiat Jaturonglumlert[1], Niwooti Whangchai[3], Danuwat Peng-ont[2] and Chanawat Nitatwichit[1]**

*[1]Graduate Program in Food Engineering, Faculty of Engineering and Agro-industry, Maejo University, Chiang Mai, 50290, Thailand*
*[2]Institute of Product Quality and Standardization, Maejo University, Chiang Mai, 50290, Thailand*
*[3]Faculty of Fisheries Technology and Aquatic Resources, Maejo University, Chiang Mai, 50290, Thailand*

## ABSTRACT

Dried chili is normally contaminated with pesticide residue as a result from the excessive uses of pesticide in the field. The objective of this study was to determine the degradation kinetics of diazinon and triazophos pesticides in dried chili due to the oxidative potential of gaseous ozone fumigation. Both pesticides were spray-coated on dried chili and later fumigated with gaseous ozone at concentration rate of 5.5 g/hr for 30 min. Results showed that the degradation kinetic of diazinon and triazophos pesticides were presented on the first-order kinetic reaction. After 30 min of ozone fumigation, diazinon and triazophos residues were decreased by 69% and 47% with the half-life ($t_{1/2}$) of 17.9 and 32.1 min, respectively. Scanning electron microscopy (SEM) images indicated that ozonated chili exhibited more rough surface morphology than unozoned chili. Ozone fumigation can be further developed as pesticide scrubber on agri-foods due to it high efficiency in term of shortening of half-life period and rapid pesticide decay rate.

*Keywords*: Degradation kinetics, diazinon, dried chili, half-life period, ozone, triazophos

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*E-mail addresses*:
panlop062@gmail.com (Panlop Sintuya)
varithj@gmaejo.mju.ac.th (Jaturapatr Varith)
aoihighso@hotmail.com (Kanjana Narkprasom)
yaidragon@mju.ac.th (Somkiat Jaturonglumlert)
niwooti@hotmail.co.th (Niwooti Whangchai)
danuwat_2493@hotmail.com (Danuwat Peng-ont)
n_chanawat@hotmail.com (Chanawat Nitatwichit)
* Corresponding author

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## INTRODUCTION

Dried chili is a popular spice product that is commonly used as ingredient for food flavoring and coloring (Jitbunjerdkul & Kijroongrojana, 2007; Toontom et al., 2012). Conventionally, dried chili is obtained by natural sun drying which takes about 7-20 days until moisture content decreased to 10-15% (Condorí et al., 2001; Öztekin et al., 1999; Toontom et al., 2012). The persistence problem remains as dried chili product in current market contains high level of pesticide residues (Pérez-Olvera et al., 2011). The pesticide contamination in chili product is due to the use of pesticide to increase crop production during agriculture of farmers (Ormad et al., 2010; Popp et al., 2013). Even if the drying process can help to degrade pesticide residue, it takes a long period (Özbey et al., 2017). A previous work reported that 59.3% of vegetables from farms and 13.2% of vegetables from markets contained organophosphorus pesticide residues at or above the maximum residue limits of the European Union (Sapbamrer & Hongsibsong, 2014). Despite the fact that organophosphates pesticides residue can be naturally degraded, Rasmusssen et al. (2003) mentioned that organophosphates chlorpyrifos, diazinon and fenitrothion could be reduced only 25–69% during storage for 79 days. In order to create a safe dried chili product, pesticide residues degradation prior to export is a proper approach.

Gaseous ozone utilization is one of the most prominent technique to reduce pesticide efficiently. It is able to be applied by either ozonated water or gaseous ozone (Mezzanotte et al., 2005; Smilanick et al., 2002; Whangchai et al., 2011). However, a study indicated that gaseous ozone exhibited higher degradation activity than ozonated water (Whangchai et al., 2011). This study aimed to study the degradation kinetic of diazinon and triazophos pesticide residues using gaseous ozone fumigation treatment. The effect of ozone treatment to chili surface, total phenolic compounds and antioxidant properties were also conducted to ensure the product qualities after ozone treatment.

## MATERIALS AND METHODS

### Dried Chili Sample Preparation

Pesticide-free red dried chili samples used in this study were purchased from USDA Certified farm. Ten kg of dried chili samples were coated with 20 mL of pesticide solution containing 1,000 mg/L of diazinon and 1,000 mg/L of triazophos (Dr.ehrenstorfer GmbH., Germany). The pesticide coated chillies were then allowed to dry at room temperature for 10 h.

### Ozone Fumigation Treatment

Red dried chili samples were treated with ozone by loading of 500 g of red dried chili samples into a fumigation chamber (Figure 1). The chamber was filled with gaseous ozone with a flow rate of 5.5 g/hr. Corona discharger with $O_2$ flow rate of 7.5 L/min and back pressure of 12 kPa was used to generate ozone (Changchai et al., 2015). The pesticide coated dried chilies were treated with gaseous ozone for 0, 5, 10,15, 20, 25 and 30 min. Pesticide coated chili without ozone treatment was used as a control. After the fumigation process, dried chili samples were kept in low density polyethylene (LDPE) bags at 25ºC prior to evaluating the chemical, physical properties and kinetics degradation of pesticides.

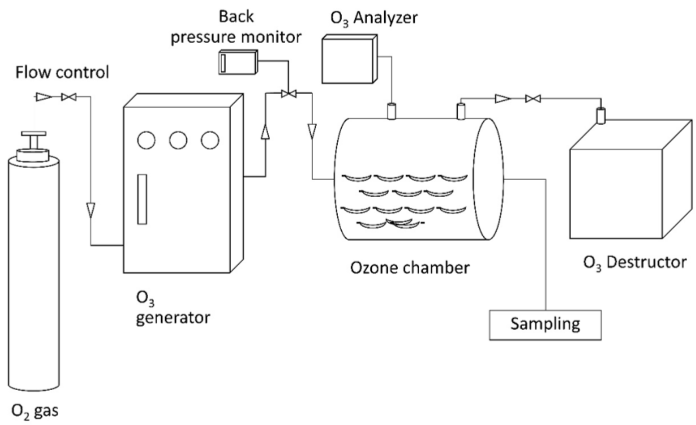


*Figure 1*. Gaseous ozone fumigation experimental setup

### Diazinon and Triazophos Pesticide Residue Determination

The extraction of dried chili samples for the determination of diazinon and triazophos pesticide residue was achieved by QuEChERS technique using dispersive solid phase extraction (Grimalt & Dehouck, 2016). Pesticide residue determination was carried out using gas chromatograph equipped with flame photometric detector (GC/FPD, 6890N, Agilent Technologies Canada Inc.) using HP-5 capillary column (0.25 µm particle size, 30 m x 0.32 mm i.d., Agilent Technologies Canada Inc.,). Helium gas with a flow rate of 1.5 $mL.min^{-1}$ was used as a carrier gas. The oven temperature was set up at 80°C for 2 min, then it was increased to 150°C at the rate of 25°$C.min^{-1}$ and was held for 5 min. After that it was increased to 190°C at the rate of 5°$C.min^{-1}$, held for 5 min, ramped up to 220°C at the rate of 10°C $min^{-1}$, held for 5 min, and finally ramped up to 250°C at the rate of 10°$C.min^{-1}$, respectively.

### Evaluation of Diazinon and Triazophos Pesticides Degradation Kinetic

The rate constant of diazinon and triazophos degradation and half-life period of pesticide degradation were evaluated using Equations 1 and 2, respectively.

$$\ln \frac{[C]}{[C_0]} = -kt \quad [1]$$

$C_0$ is initial concentration of pesticide at treatment time = 0 (mg/kg), C is concentration of pesticide at treatment time = t (mg/kg), k is rate constant of the pesticide degradation, t is treatment time (min). In order to obtain the half-life period ($t=t_{1/2}$) of each pesticide, a pesticide with concentration at half-life period is determined by $[C] = [C_0]/2$. Therefore, half-life period could be calculated as shown in Equation 2 (Alighourchi & Barzegar, 2009).

$$t_{1/2} = \frac{0.693}{k} \quad [2]$$

**Determination of Total Phenolic Content (TPC)**

The content of total phenolic compound (TPC) was studied using the Folin-Ciocalteu assay (Kovacova & MaliNoVá, 2007), with slight modification. Firstly, methanolic extract solution was prepared by mixing 5 g of sample with 20 ml of 70% methanol. The mixture was kept overnight at -20˚C. Then the sample was adjusted final volume to 50 ml and was centrifuged at 2,500 rpm, 4˚C for 10 min. The mixture of 0.5 ml of 50% Folin-Ciocalteu, 1 ml of 95% ethanol, 1 ml of methanolic extract, and 5 ml of reverse osmosis water was mixed and was kept at room temperature (25± 5˚C) for 5 min. After that, 1ml of 5% (w/v) of sodium carbonate solution was added. The mixture was homogenized and was kept at room temperature for 60 min. TPC was analyzed using a NICOLET evolution 300 (Thermo Electron Eorporation, USA) spectrophotometer at 725 nm. The standard calibration curve was plotted using gallic acid at the concentration of 10 – 200 mg/L. The TPC was presented as gallic acid equivalent (GAE) mg/100g.

**Determination of Free Radical Scavenging Activity**

The determination of scavenging activity of dried chili extract was carried out based on 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical scavenging assay (Milardović et al., 2006). The 2 ml of chili extract was mixed with 1 mL of 100 µM DPPH solution which was dissolved in 80% methanol. The mixture was then shaken vigorously and was kept in a dark room for 30 min at room temperature. The absorbance was evaluated using a spectrophotometer (Thermo Electron Corporation, NICOLET evolution 300, USA). The detection was determined at 515 nm of wavelength using methanol as a blank solution. Triplicate analysis was done and their activity was expressed as Trolox equivalent (TEAE) in mg/100g.

### Scanning Electron Microscopy (SEM) Analysis

SEM technique was used to examine microstructure of chili surface without and with ozone fumigation for 30 min. Dried chili peel (5x5 mm) sample was cut into a small piece. The sample was coated with gold with 20 nm thickness in an ion sputter coater model JFC-1200 (JEOL, Japan). The microstructure of chili surface was observed by SEM JSM-5410LV (JEOL, Japan) at 10 kV.

### Statistical Analysis

In this experiment, the obtained data were statistically examined using the Statistics Package for the Social Sciences (SPSS, IBM Corp., USA) by one-way analysis of variance (ANOVA). Duncan's test is commonly used in agricultural research. It has a great power for statistical analysis. The significant difference of responses was determined at $p<0.05$ using Duncan's method.

## RESULTS AND DISCUSSION

### Diazinon and Triazophos Pesticide Residue Analysis

In this study, diazinon and triazophos pesticide residues of dried chili after ozone fumigation treatment were studied. They were compared with those of dried chili stored in a polyethylene bag without any fumigation. Figure 2 shows that after 30 min of ozone fumigation, diazinon and triazophos could be degraded 69 and 47%, respectively. For untreated dried chili sample, diazinon and triazophos could be degraded 40 and 42% after being stored in a polyethylene bag for 8 weeks. The reason behind this is that ozone is a strong oxidizing agent that can allow pesticide degradation (Ikehata & El-Din, 2006; Ikeura et al., 2011; Tiwari et al., 2010). Therefore, the degradation of pesticide with ozone fumigation exhibited higher efficiency than the degradation without ozone fumigation.

### Determination of Diazinon and Triazopho Pesticides Degradation Kinetic

Kinetics parameters for degradation of diazinon and triazophos during storage at 25°C (without ozone fumigation) and with ozone fumigation were shown in Table 1. Degradation kinetics of diazinon and triazophos are considered to be the first-order reaction. The degradation rate constants (*k*) of diazinon and triazophos on ozone treated chili were $3.8 \times 10^{-2}$ and $2.2 \times 10^{-2}$ mg/kg/min, respectively. Meanwhile, the degradation rate constants (*k*) of diazinon and triazophos on untreated chili were $7.0 \times 10^{-6}$ and $6.0 \times 10^{-6}$ mg/kg/min, which were approximately 5,400 and 3,700 folds different in order of magnitude. The greater degradation rate constant revealed the shorter time for pesticide residue to decline. The results corresponded well with previous work by Bourgin et al. (2013) who reported that the degradation of pesticide by ozonation fumigation was the first-order reaction. For the degradation half-life period ($t_{1/2}$), untreated chili revealed the $t_{1/2}$ for diazinon and triazophos of 68.8 and 80.2 days, respectively. However, chilies with ozone fumigation exhibited $t_{1/2}$ value for the degradation of diazinon and triazophos of 17.9 and 32.1 min.

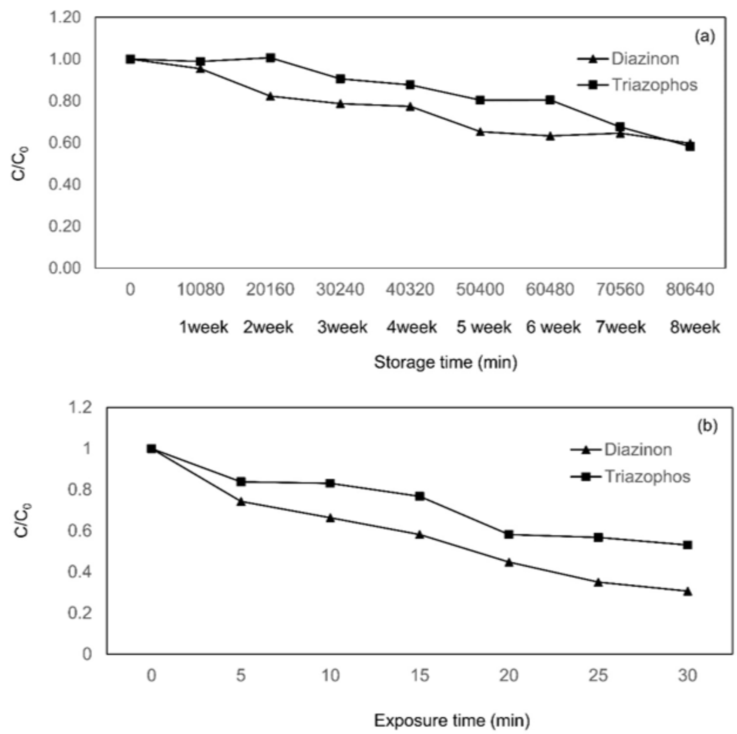


*Figure 2.* Diazinon and triazophos degradation by (a) self-degradation during storage at 25°C without ozone fumigation, and (b) accelerated degradation with ozone exposure.

Table 1

*Kinetics study for degradation of the diazinon and triazophos during storage at 25°C (non-ozone fumigation) and with ozone fumigation*

| Pesticide | Non-ozone fumigation | | | Ozone fumigation | | | Half-life time difference (%) |
|---|---|---|---|---|---|---|---|
| | $k$ (mg/kg/min) | $R^2$ | $t_{1/2}$ (day) | $k$ (mg/kg/min) | $R^2$ | $t_{1/2}$ (min) | |
| Diazinon | $7.0 \times 10^{-6}$ | 0.94 | 68.8 | $3.8 \times 10^{-2}$ | 0.99 | 17.9 | 99.9% |
| Triazophos | $6.0 \times 10^{-6}$ | 0.88 | 80.2 | $2.2 \times 10^{-2}$ | 0.94 | 32.1 | 99.9% |

## Determination of Total Phenolic Content (TPC) and Free Radicals Scavenging Activity

The TPC and free radicals scavenging activity represent the quality of dried chili. The result of TPC in dried chili sample after fumigation for 30 min is shown in Table 2. The TPC tended to decrease due to fumigation time at 0, 5, 10, 15, 20 and 25 min but not significantly different ($p \geq 0.05$). However, after fumigation for 30 min, the TPC was significantly different ($p < 0.05$) from the others. This phenomenon occurred due to reaction of ozone and free radical (Misra et al., 2015; Sarangapani et al., 2017). For the free radical scavenging activity, there was not significantly different on fumigation 0 to 30 min as shown in Table 2. The results from this experiment corresponded to the previous reports (Alwi, 2017; Torres et al., 2011). It was found that total phenolic compound could be reduced by increasing of ozone concentration or time of fumigation.

Table 2

*Total phenolic content and free radical scavenging activity in chili sample with ozone fumigation for 30 min.*

| Exposure time (min) | Total phenolic content (mgGAE/100g) | Free radical scavenging activity (mgTEAE/100g)$^{n.s.}$ |
|---|---|---|
| 0 | $150.27^a \pm 8.62$ | $51.01 \pm 5.57$ |
| 5 | $145.28^a \pm 2.98$ | $43.94 \pm 0.61$ |
| 10 | $147.81^a \pm 6.86$ | $51.69 \pm 3.68$ |
| 15 | $150.93^a \pm 6.28$ | $44.30 \pm 0.81$ |
| 20 | $150.83^a \pm 5.01$ | $51.73 \pm 0.85$ |
| 25 | $145.53^a \pm 9.77$ | $44.33 \pm 5.34$ |
| 30 | $130.00^b \pm 5.64$ | $49.10 \pm 1.22$ |

*n.s. = not significantly different ($p \geq 0.05$).
*Values followed by the different letter within the same row are significantly different from each other ($p < 0.05$).

## Scanning Electron Microscopy (SEM) Analysis

SEM image of chili surface without ozone fumigation was compared to chili surface with ozone fumigation for 30 min as shown in Figure 3. It was found that ozone affected surface of chili. The increasing of roughness structure of chili surface was observed after ozone treatment. This phenomenon cannot be clearly explained but it is possible that the ozone fumigation at high concentration may have oxidative reaction with some substance at surface causing the distort morphological changes as a rougher or corrosive surface of the chili (Alwi, 2017; O'Donnell et al., 2012).

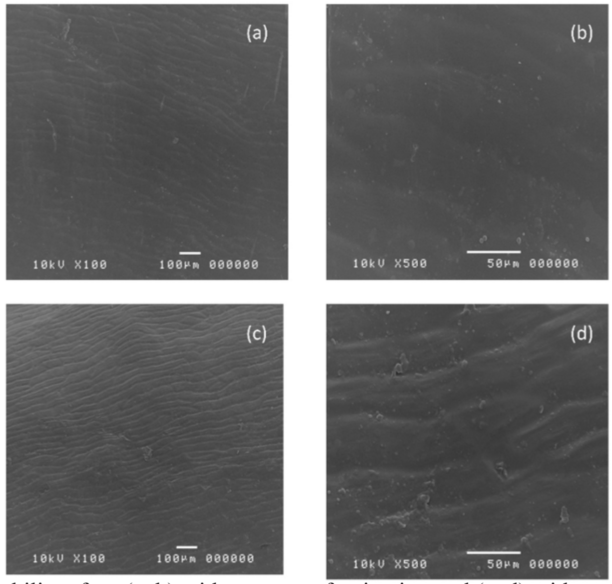


*Figure 3*. SEM image of chili surface (a, b) without ozone fumigation and (c, d) with ozone fumigation for 30 min.

## CONCLUSIONS

Gaseous ozone treatment was succesfully used to degrade diazinon and triazophos in dried chili. The kinetic study revealed that first-order reaction of diazinon and triazophos degradation on ozone treated chili showed rate constants ($k$) of 3.8 x $10^{-2}$ and 2.2 x $10^{-2}$ mg/kg/min, respectively, which were approximately 5,400 and 3,700 folds different in order of magnitude compared to untreated chili. For the degradation half-life period ($t_{1/2}$), the untreated chili revealed the $t_{1/2}$ for diazinon and triazophos of 68.8 and 80.2 days, respectively. However, chili with ozone fumigation exhibited $t_{1/2}$ value for the degradation of diazinon and triazophos of 17.9 and 32.1 min. TPC was significantly different ($p<0.05$) after 30 min of ozone treatment. For the result of free radical scavenging activity, there was no significant difference on fumigation from 0 to 30 min. SEM image showed that roughness structure of chili surface was observed after ozone treatment, possibly due to the ozone corrosive effect. Since ozone fumigation shortens the $t_{1/2}$ diazinon and triazophos by 69 and 47%, it exhibits a promising protential to be applied for reducing the pesticide residues in dried chilli without significant changes in physical and chemical properties. Therefore, gaseous ozone fumigation can be an alternative to effectively reduce pesticide residue in chilli and other agricultural products in order to improve food qualities and safety.

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