

Kinetics and Identification of Products Degradation of Endosulfan in a Solution of Carbofuran by Hydrolysis, Ozonation with and Without Activated Carbon

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Abstract—Degradation of endosulfan in the solution carbofuran by hydrolysis, ozonation with and without activated carbon is investigated at fixed initial concentration, temperature and neutral pH. The objectives of this research were to study the effect of hydrolysis, ozonation with and without activated carbon on degradation rate of single endosulfan and endosulfan in the carbofuran solution as well as to identify products by ozonation. The hydrolysis process slightly influences in enhancing degradation rate of endosulfan compared to ozonation processes without and with of activated carbon. The ozonation with activated carbon for endosulfan in carbofuran solution significantly influences in enhancing degradation rate compared to single endosulfan. From gas chromatography-mass spectrometry (GC/MS) analysis showed that the four products obtain from the degradation of endosulfan in carbofuran solution by ozonation without activated carbon are carbofuran-phenol, endodiol, 4,5,6,7,8,8-hexachloro-1, 3, 3a, 4,7,7 a-hexahydro-alloxa and Azelaoyl Chloride. Whereas, products ozonation with activated carbon generate 1,4,5,6,7,-hexachlorobicyclo [2,2,1-5-heptene-2, 3-dimethanol (HBH), azelaic acid (AA), azelaoyl chloride (AC), S-[2-(dimethyl amino) ester (SDAE) and methyl 4-methylphenylsulfoxide (MMPs) after 15 minute process.

Index Terms—Activated carbon, Degradation rate, hydrolysis, Ozonation.

I. INTRODUCTION

Endosulfan (1,2,3,4,7,7-hexachlorobicyclo-2,2,1 heptene-2,3-bis-hydroxy methane-5,6 sulfite) and carbofuran(2,3-dihidro-2,2-dimethylenzofuran-7-ylmethylcarbamate) are pesticide that still being used mostly by farmers in Indonesia simultaneously on the same farm land. Whereas, the endosulfan and carbofuran are a stable chemical compound with long half-life under neutral and acidic condition, it is consequently detected in water surface. On the other hand, endosulfan and carbofuran are highly toxic for fishes and aquatic invertebrates. World Health Organization drinking water quality standards permits a maximum 20 $\mu\text{g/L}$ for endosulfan and 0.04 mg/L for carbofuran [1] and [2]. Therefore, effective methods of pesticide degradation in waters are urgently needed.

A variety of effective methods for endosulfan degradation have been studied namely through on biological processes with different groups of microorganisms [3], [4] and [5], hydrolysis [6], and photo catalysis with $(\text{FeCl}_3/\text{H}_2\text{O}_2)/(\text{TiO}_2/\text{H}_2\text{O}_2)$ [7]. Recently, ozonation of single endosulfan has been conducted in non-catalytic process [8] and catalytic ozonation [9], but the degradation of endosulfan in solution carbofuran by hidrolysis, adsorption with activated carbon, ozonation with and without activated carbon are rarely carried out.

Hydrolysis is one of the most important reactions in a water environment for organic contaminants. Hydrolysis on pesticide is the reaction of pesticides in water (as a nucleophile or Lewis base) on the abiotic or biotic media. Most of the hydrolysis, occurs through the mechanism of nucleophilic substitution by the nucleophile on the electrophile (eg P and S) or the elimination reaction (Leaving group) by a nucleophile and produces a smaller molecule, produce material that easily soluble in water and form a new bond of C-OH or CH [10].

The mechanism of endosulfan degradation through hydrolysis reactions similar to bond of alkyl halides (RX), where X will be destroy and replaced by OH^- or H^+ form a new bond C-OH or CH which more soluble in water [11]. The degradation rate of pesticide through the hydrolysis reaction depends on the type of pesticides and other factors such as pH, temperature and metal ions or other substances as a catalyst [10], [12].

The ozonation process always involves two molecules namely ozone and OH radicals [13]. OH radical ($\bullet\text{OH}$) is known as reactive molecule in the advanced oxidation processes (AOPs), powerful, compound oxidant non-selective which acts very rapidly with most organic compounds [14]. Activated carbon acts not only as the adsorbent but also as a catalyst in promoting oxidation [15]. The ozonation with activated carbon as catalyst can accelerate ozone decomposition to form OH radical [16] - [20]. Combination of ozonation with adsorption used activated carbon can strongly gives synergetic effects on the removal organic contaminan. Thus, ozonation with activated carbon included in the heterogeneous system with three mechanisms that occur followed [15]:

- 1) chemisorption of ozone on the catalyst surface leading to the formation of active species which reacts with non-chemisorbed organic molecule;

- 2) chemisorption of organic molecule (associative or dissociative) on the catalytic surface and its further reacts with gaseous or aqueous ozone;
- 3) chemisorption of both ozone and organic molecules and the subsequent interaction between chemisorbed species.

The objectives of this research were to study the effect of hydrolysis, ozonation with and without activated carbon on degradation rate of single endosulfan and endosulfan in the carbofuran solution as well as to identify products by ozonation. Furthermore, the degradation pathway of endosulfan in solution of carbofuran by ozonation with and without activated carbon is proposed.

II. MATERIAL AND METHODS

The endosulfan ($C_9Cl_6H_6O_3S$) and carbofuran ($C_{12}H_{15}NO_3$) were obtained from Chemical Service West Chester with purity of 95 % and 99 %, respectively. The endosulfan and carbofuran solution was prepared by de-ionized water obtained from Aquatron Auto Still Yamato Type W-182. The specific surface area of activated carbon were measured using the multipoint BET of N_2 adsorption in a Quanta chrome Autosorb-6 with surface area of 687 m^2/g . Ozone was produced by a type RS-09805 ozone generator with maximum ozone production capacity of 0.25 g of O_3/h .

Hydrolysis experiments carried out in 250 ml sized reactor containing demineralized water with pH adjusted at 7,0 and the temperature set at room temperature ($\pm 30^\circ C$). The process was performed by adding endosulfan and carbofuran in the reactor and then stirred until the concentration reached 4.5×10^{-5} M. Concentrations of carbofuran, endosulfan and the reaction products in the system were measured at 0, 3, 6, 9 and 15 minutes.

The experimental ozonation instruments consist of an ozone generator, a cylindrical glass column reactor with an external jacket, where a water stream was pumped from thermostatic bath in order to maintain the temperature at the selected value for each experiment. The reactor dimension is 450 mm in height and 40 mm ID with consists of an inlet diffuser for bubble gas mixture, outlet gas, sampling port and magnetic stirrer. Once the experiment was started, the air-ozone mixture was fed into the flasks (KI solution) in order to determine the ozone concentration in the gas form.

The reactor was filled with 250 ml demineralized water and then the pH was adjusted at 7. The temperature was set at room temperature ($\pm 30^\circ C$). After a predetermined volume of water was saturated with excess ozone by injecting ozone gas for 15 minutes, the process was followed by adding 0.5 g of activated carbon (for activated carbon process), carbofuran and endosulfan until the concentration reached 4.5×10^{-5} M. The concentration of carbofuran, endosulfan and ozone presence in the system was measured at 0, 3, 6, 9 and 15 minutes.

The dissolved ozone concentration in aqueous solution was determined by iodometrically methods. The endosulfan was then analyzed by Gas Chromatograph type 4C, column silicone ov-17, 3 meters, ECD (Electron Capture Detector), Shimadzu with *n*-hexsane as solvent and N_2 as mobile gas. GC/MS (Shimadzu GC/MS-QP2010) was used for the

separation and detection of the intermediate products. The GC/MS was equipped with a HP injection pressure of 250 kPa, a helium carrier gas (1.2 ml min^{-1}) and a split less injection system.

III. RESULTS AND DISCUSSION

A. The Kinetics of Degradation

Degradation of pesticides in water through hydrolysis by La Grega et al., (2001), ozonasi with and without activated carbon are set to follow the first order at constant pH and temperature. The degradation of endosulfan in the solution of carbofuran by ozonation was conducted in an excessive concentration of ozone in the solution, at constant amount of activated carbon, and at the same initial concentration of carbofuran and endosulfan. Subsequently, the GC/MS analysis can be used to identify the products.

The rate of degradation of endosulfan in a solution of carbofuran by hydrolysis, ozonation with and without activated carbon is assumed each with a pseudo first-order kinetic law and is estimated by the equation below,

$$-\frac{dC_E}{dt} = k_E \cdot C_E \quad (1)$$

C_E is the concentration of endosulfan, k_E is first-order rate constant of endosulfan. In order to get k_E value, the $\ln(C_{E0}/C_E)$ was plotted as a function of the reaction time, therefore the slope was k_E , and C_{E0} is the initial concentrations of endosulfan as seen in Table 1.

B. Hydrolysis

Figure 1 presents the pseudo-first order degradation rate of single endosulfan and endosulfan in carbofuran solution by hydrolysis with the plotted of $\ln(C_{E0}/C_E)$ versus time (t) with a slope of k_E . From this Figure it can be seen that the degradation rate of endosulfan in carbofuran solution was higher than degradation of single endosulfan. The k_E value for endosulfan in the carbofuran solution at pH 9.0 and $29^\circ C$ was $4.45 \times 10^{-2} \text{ min}^{-1}$ and for single endosulfan was $1.09 \times 10^{-2} \text{ min}^{-1}$. This phenomenon is caused by the interaction of an active group of carbofuran and endosulfan during the hydrolysis process so that the molecular structure of each insecticide in solution changed [10].

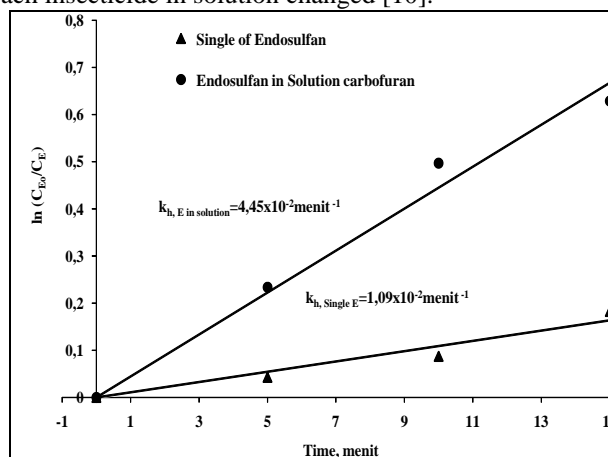


Figure 1. The pseudo-first order degradation rate of single endosulfan and endosulfan in solution by hydrolysis at temperature $\pm 30^\circ C$.

C. Ozonation Without Activated carbon

Figure 2 and Table 1 present the pseudo-first order degradation rate of single endosulfan and endosulfan in carbofuran solution by ozonation without activated carbon. From these Figures it can be seen that the degradation rate of endosulfan in carbofuran solution was slightly enhance compared to degradation of single endosulfan with $k_{h,E}$ at pH 9.0 and 30°C were $11.33 \times 10^{-2} \text{min}^{-1}$ and $10.27 \times 10^{-2} \text{min}^{-1}$, respectively. This is because endosulfan has sulfide group or sulfur element and carbofuran has amine group or nitrogen element which are very reactive to ozone [21], [22]. Therefore, interaction of both functional groups of carbofuran and endosulfan was slightly influenced and it can also be seen that there is no byproducts direct generated by carbofuran and endosulfan interaction.

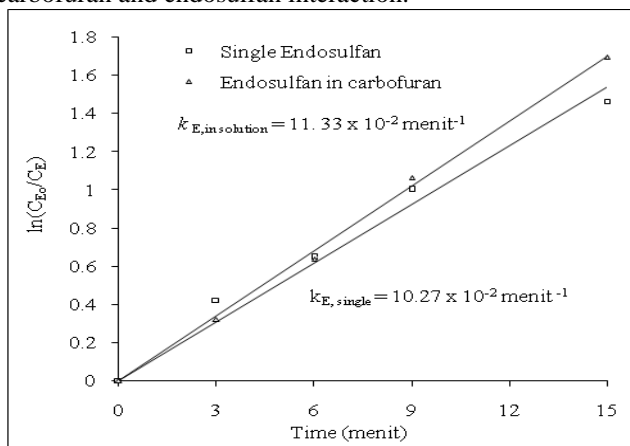


Figure 2: The pseudo-first order degradation rate of single endosulfan and endosulfan in mixture by non catalytic ozonation at temperature 30°C

D. Ozonation With Activated Carbon

Figure 2 shows the pseudo-first order degradation rate of single endosulfan and endosulfan in carbofuran solution by ozonation with activated carbon. From those Figures it can be seen that the degradation rate of endosulfan in carbofuran solution was higher than degradation of single endosulfan. k_E value for endosulfan in the carbofuran solution at 30°C was $13.24 \times 10^{-2} \text{min}^{-1}$ and for single endosulfan was $11.54 \times 10^{-2} \text{min}^{-1}$ by ozonation with activated carbon. Those results above were caused by endosulfan that very reactive to ozone [21], [22] and $\cdot\text{OH}$. Even though the amount of $\cdot\text{OH}$ increased because of ozonation with activated carbon used, it affected the degradation rate but did not influence the interaction of both functional groups of endosulfan and carbofuran. It can also be seen that there is no by-products generated from carbofuran and endosulfan interaction by catalytic ozonation.

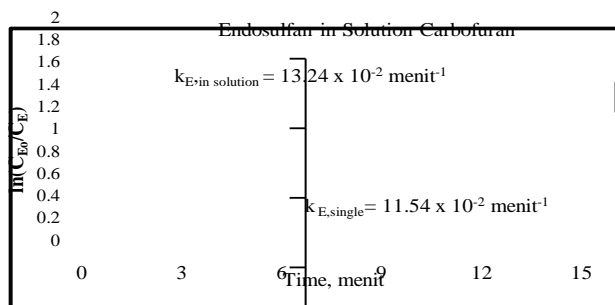


Figure 3: The pseudo-first order degradation rate of single endosulfan and endosulfan in solution carbofuran by catalytic at room temperature. The

influence of hydrolysis, ozonation with and without of activated carbon at removal endosulfan in carbofuran solution

Figure 4 shows the influence of hydrolysis, adsorption with activated carbon, ozonation with and without activated carbon at removal of endosulfan in carbofuran solution. From that Figure it can be concluded that the removal of endosulfan in carbofuran solution by ozonation with activated carbon was higher than ozonation, hydrolysis and adsorption with activated carbon. This is due to the combination of ozone with activated carbon that can be acts not only as the adsorbent but also as a catalyst in promoting oxidation. Thus, ozonation with activated carbon included in the heterogeneous system with three of chemisorption mechanisms [14].

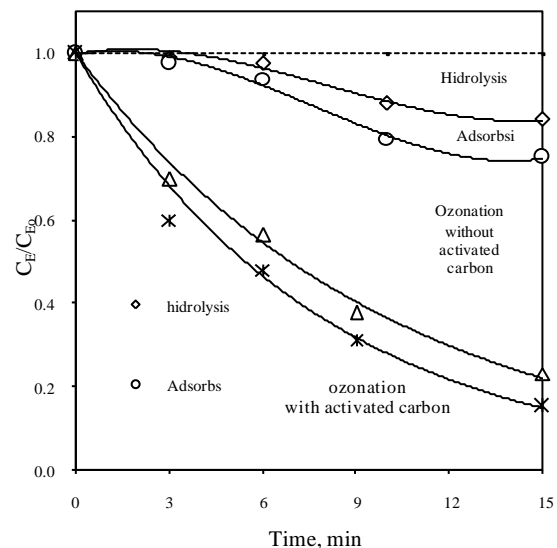


Figure 4: The influence of hydrolysis, adsorption with activated carbon, ozonation with and without activated carbon at allowance of endosulfan in carbofuran solution

Futhermore, the endosulfan removal in carbofuran solution at ozonation with activated carbon at pH > 6 is caused by reaction of endosulfan with $\cdot\text{OH}$, O_3^- , O_2^- and O^- [23]. Whereas in hidrolysis only caused by nucleophilic substitution reaction or the elimination reaction and in the adsorption process, endosulfan only accumulate on the surface of activated carbon.

E. The identification of products degradation mechanism of endosulfan in solution of carbofuran by ozonation with and without activated carbon.

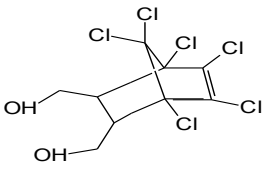
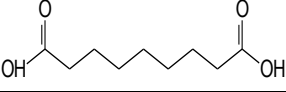
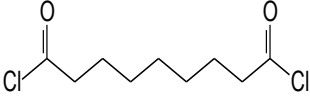
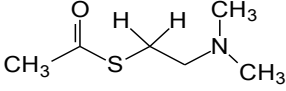
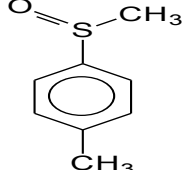
The ozonation products formed in the non catalytic and catalytic ozonation with activated carbon as catalyst on degradation of endosulfan in the mixture for 15 min were investigated by GC/MS analysis. Five products were identified from catalytic ozonation and four products from non catalytic ozonation by the molecular ion and mass fragment ions, and also through the comparison with NIST library data. Table 1 summarizes the molecular weight obtained for these ozonation products.

The similarities of these compounds to the NIST library data were more than 80 %. Based on intermediate products listed in Table 1 and other degradation products still possibly exist in the ozonation system but were not detected because

of their low concentration, extraction efficiency and limited sensitivity in GC/MS. From the Table 1, it can be seen that ozonation product number 1, 2 and 3 identified as *endodiol* or *1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-5-heptene-2* (HCH), *azelaic acid* (AA) and *azelaoyl chloride* (AC) resulted from the degradation of endosulfan (E) in the mixture by catalytic and non catalytic ozonation. HCH was the main ozonation product and also detected by biology process [4] and [5], whereas the AA and AC were formed by further oxidizing

HCH by OH^\bullet and O_3 . Moreover, ozonation product number 4 was identified as *S-[2-(di methyl amino) ester]* (SDAE) resulted from the interaction of the degradation between intermediate of carbofuran with endosulfan by catalytic ozonation. The ozonation product number 5 was identified as *methyl 4-methylphenylsulfoxide* (MMPS) obtained from the interaction result between intermediate of carbofuran and endosulfan by catalytic and non catalytic ozonation.

TABLE 1. OZONATION PRODUCTS OBTAINED OF DEGRADATION OF ENDOSULFAN IN THE MIXTURE

Product no	Retention time (min)	Molecular weight (<i>m/z</i>)	Intermediate product	Reaction
1	9.763	358		Catalytic and non-catalytic ozonation
2	6.055	188		Catalytic and non-catalytic
3	7.725	224		Catalytic and non-catalytic ozonation
4	2.617	99		Catalytic ozonation
5	3.522	168		Catalytic and non-catalytic

From the scheme 1 it can be reported that the degradation pathway of endosulfan in carbofuran solution by ozonation with activated carbon and without activated carbon produced HCH or endodiol which is major metabolite. Then it is followed by the production of AA and AC. However, the difference between ozonation with and without activated carbon in the degradation of endosulfan in carbofuran solution is only on the degradation rate. This is because the degradation of endosulfan by ozonation in the presence of activated carbon was dominantly influenced by $\bullet\text{OH}$ as oxidant compared to the degradation of endosulfan by ozonation without activated carbon. According to the free radical reaction theory, $\bullet\text{OH}$ will attack chlorinated organic compounds by hydrogen abstraction or electron transfer. Then, the organic radical will decompose further to chlorinated intermediates. These intermediates are eventually oxidized by $\bullet\text{OH}$ to final products: organics acid, ion chloride and even carbon dioxide [24].

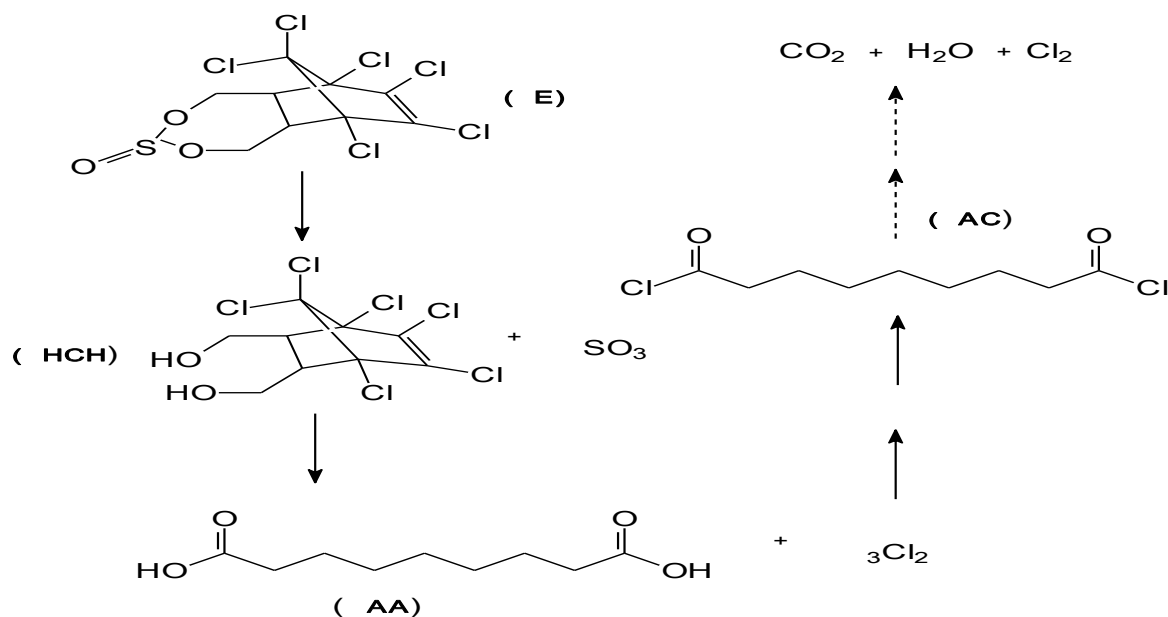
IV. CONCLUSION

The ozonation of endosulfan in carbofuran solution with activated carbon significantly effect in enhancing the

degradation rate compared to single endosulfan by ozonation without activated carbon, hydrolysis and absorption with activated carbon. It is shown by the increasing of the rate constant value (k_E) and the removal of endosulfan (C_E/C_{E0}). The degradation of endosulfan in carbofuran solution by ozonation can generate intermediate products that are generally environmental friendly, and ozonation with activated carbon can also be used to increase a detoxification process of endosulfan in water.

ACKNOWLEDGMENTS

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Scheme 1. Proposed degradation mechanism of endosulfan in of carbofuran solution by ozonation with and without activated carbon

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