Simultaneous Degradation of Carbofuran-Endosulfan Mixtures by Ozonation in the Presence of Activated Carbon

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Abstract: Carbofuran and endosulfan are chemical of high toxicity and still being used mostly by farmer in Indonesia. The simultaneous degradation of carbofuran-endosulfan mixture by ozonation in the presence of activated carbon was investigated to study the effect of activated carbon to degradation rate and by-products species. The presence of the activated carbon is slightly in enhancing degradation rate of carbofuran and endosulfan compared to absence of activated carbon. However, the degradation of carbofuran and endosulfan by ozonation in the presence of activated carbon generated some by-products which are generally environmentally friendly. Therefore, the ozonation in the presence of activated carbon can be one of detoxification processes of carbofuran and endosulfan individually. Furthermore, based on chromatography-mass spectrometry (GC/MS) analysis, it showed that ozonation in the presence of activated carbon generated eight by-products and ozonation in the absence of activated carbon generated five products after 15 minutes process.

Key words: Simultaneous degradation · carbofuran · endosulfan · ozonation · activated carbon

INTRODUCTION

Insecticides such as carbofuran (2, 3-dihidro-2, 2-dimethylenzofuran-7-ylmethylcarbamate) and endosulfan (1,2,3,4,7,7-hexachlorobicyclo-2,2,1 heptene-2,3-bis-hydroxy methane-5,6 sulfite) are still being used mostly by farmers in Indonesia simultaneously on the same farm land. Even though the carbofuran has high persistence in water due to its chemical stability under acid and neutral condition [1], it is consequently detected in water surface. Besides, endosulfan is a stable chemical compound with long half-life under neutral and acidic condition and is highly toxic for fishes and aquatic invertebrates [2]. Therefore, it is very important to develop specific treatments which are effectively degradation and generating environmentally friendly by-products.

The ozonation in the presence of activated carbon can accelerate ozone decomposition to form •OH [3-6]. •OH are known to be reactive species in the advanced oxidation processes (AOP), powerful, non-selective chemical oxidant, which acts very rapidly with most organic compounds [7]. It was demonstrated that incorporated metal centers, electrons of the graphenic layers (basal plane electrons) and basic surface group of the activated carbon, are main factors responsible for decomposition of ozone at the activated carbon surface [8].

Ozonation is the most effective process for degradation of carbofuran or endosulfan [9-11], but the simultaneous degradation of carbofuran and endosulfan mixture by ozonation especially with addition of the activated carbon is rarely carried out. Ozonation process always involves two molecules, ozone and OH-radicals [12]. The OH-radicals (•OH) are generated by the decomposition of ozone in aqueous solution and are especially by hydroxide ion (OH⁻). Ozone is a selective oxidant and reacts quickly with some organic moieties whereas other are only oxidized very slowly [13, 14], but leads to partially oxidized products [15].

The objective of this research is to investigate the effects of activated carbon to the simultaneous degradation of carbofuran and endosulfan mixture by ozonation which focuses on the degradation rate and identifies the by-products species. Furthermore, the degradation pathway of carbofuran and endosulfan is proposed.

MATERIALS AND METHODS

The endosulfan ($C_9Cl_6H_6O_3S$) and carbofuran ($C_{12}H_{15}NO_3$) were obtained from Chem. Service West Chester with purity of 95 and 99%, respectively. The mixed carbofuran and endosulfan 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 RS 09805 ozone generator with maximum ozone production capacity of 0.25 g of O_3/h. The experimental instrument consists of an ozone generator, a cylindrical glass column reactor with an external jacket surrounded and 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 and consists of an inlet diffuser for bubbling the 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 300 ml demineralized-water and then the pH was adjusted at 7. The temperature was set for 20, 25 and 30°C. When a predetermined volume of water was saturated with ozone in excess continuously by injecting ozone gas for 30 minutes finished, the process was followed by the addition 0.5 g of activated carbon (for the catalytic process) and carbofuran-endosulfan, so its concentration reached 4.5×10^{-5} M. The concentration of carbofuran, endosulfan and ozone presence in the system was measured at the minutes of 0, 3, 6, 10 and 15. The dissolved ozone concentration in aqueous solution was determined by iodo metric methods. The carbofuran and endosulfan were 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 250 kPa in helium carrier gas (1.2 ml min^{-1}) and with split less injection system.

RESULTS AND DISCUSSION

The degradation rate of carbofuran and endosulfan: The simultaneous degradation of carbofuran-endosulfan mixture by ozonation experiment was undertaken at excessive ozone concentration in solution, at constant of activated carbon and at the same initial concentration of carbofuran and endosulfan. Furthermore, from GC/MS analisys, it can be seen that there is no by-products generated from carbofuran and endosulfan interaction. Therefore, degradation rate of carbofuran and endosulfan respectively were assumed with a pseudo first-order kinetic law and estimated with the equation below,

$$-\frac{dC}{dt} = k_{obs} C \qquad (1)$$

C is the concentration of carbofuran or endosulfan in the solution, k_{obs} is the observed first-order rate constant. In order to confirm the $ln (Co/C)$ was plotted as a function of the reaction time with slope as k_{obs}, where C_O is initial concentrations carbofuran or endosulfan. The Ea as slope obtained from Arrhenius plot $ln k$ as a function of the 1/T with linear regression indicates $R^2 = 0.99$, it is not presented but the values k and Ea are presented in Table 1.

From that Table 1, it can be stated that the higher the temperature is, the higher the degradation rate of carbofuran and endosulfan. This effect is due to an increase in the constants rate of the chemical reaction. Benitez et al. [9] and Yaszan et al. [10] reported that the change of temperature gave positive effect on the removal rate of the carbofuran and endosulfan. Although increasing temperature causes decreasing in dissolved ozone concentration (data are not shown), a higher oxidation rate was obtained at higher temperatures. This phenomenon can be explained by the increasing diffusion coefficient at higher temperature.

As seen in Table 1 that ozonation in the presence of the activated carbon slightly enhanced degradation rate of carbofuran and endosulfan compared to ozonation without activated carbon. This is because carbofuran has amine group or nitrogen element and endosulfan has sulfide group or sulfur element that is very reactive to ozone [16, 17]. Even though, the amount of OH• increased because of ozonation with activated carbon use, it only affected slightly to the degradation rate. The •OH was assumed by decomposition reaction of O_3 with hydroxide ion (OH^-) and H_2O_2 as initiators on activated carbon surface and in the solution bulk [9]. On the other hand, simultaneous degradation of carbofuran and endosulfan in the mixture by ozonation with activated carbon decreased the Ea slightly compared to ozonation without activated carbon. Thus, the presence of activated carbon in ozonation processes to degrade simultaneously carbofuran and endosulfan does not really act as a catalyst. This phenomenon is also similar to a study that was carried out by Sanchezs at al [6] about ozonation with activated carbon of *p*-chlorobenzoic acid.
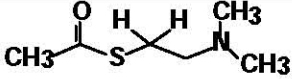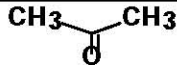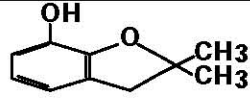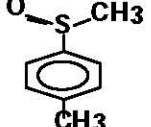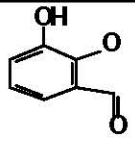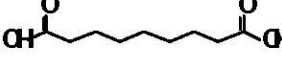
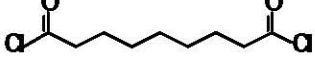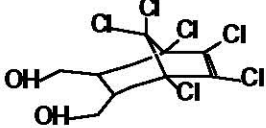**The identification of products and degradation mechanism:** The ozonation products formed in the presence and absence of activated carbon on degradation of carbofuran and endosulfan in the mixture for 15 min were investigated by GC/MS

Table 1: Pseudo-first order constant (k) and activation energy *(Ea)* of carbofuran and endosulfan degradation in mixture by ozonation with and without activated carbon

T (°C)	Ozonation with of activated carbon				Ozonation without of activated carbon			
	k_E 10^{-2}(min^{-1})	Ea^E (kkal/mol)	k_C 10^{-2} (min^{-1})	Ea^C (kkal/mol)	k_E 10^{-2} (min^{-1})	Ea^E (kkal/mol)	k_C 10^{-2} (min^{-1})	Ea^C (kkal/mol)
20	10.15		9.47		7.23		7.47	
25	12.18	5	12.26	9	9.03	8	10.37	10
30	13.24		15.16		11.33		12.89	

Note: k_E and k_C are rate constant of endosulfan and carbofuran, Ea^E and Ea^C are activation energy of endosulfan and carbofuran

Table 2: Ozonation products obtained by simultaneous of degradation carbofuran and endosulfan in the mixture by ozonation with and without activated carbon

Product No.	Retention time (min)	Molecular weight (*m/z*)	Product	Ozonation
1	2.617	99		With activated carbon
2	2.648	58		With activated carbon
3	3.425	164		With and without activated carbon
4	3.522	168		With and without activated carbon
5	4.750	152		With activated carbon
6	6.055	188		With and without activated carbon
7	7.725	224		With and without activated carbon
8	9.763	358		With and without activated carbon

analysis. Eight products were identified from ozonation in the presence of activated carbon and five products from without activated carbon by the molecular ion and mass fragment ions and also through the comparison with NIST library data. Table 2 summarizes the molecular weight obtained for these ozonation products. The similarities of these compounds to the NIST library data were more 80%.

Based on intermediate products listed in Table 2 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 2 it can be seen that ozonation product number 2, 3 and 5 identified as *aceton* (A), *2,2-dimethyl-2, 3-dihydro-benzofuran-7-ol* (CF) and

4-hydroxy-2-methoxy benzaldehyde (HMB) respectively from degradation result of carbofuran (C) in the mixture by ozonation in the presence of activated carbon, whereas for ozonation without activated carbon only product number 3 identifed as the degradation result of carbofuran. The CF generated by cleavaging carbamate group from carbofuran, was main ozonation product from degradation result of carbofuran by ozonation with activated carbon and without activated carbon. This product was also detected in the hydrolysis [18], AFT treatment [19] and photodegradation by exitation of iron (III) aquacomplexes under UV iradiation [11]. Whereas, the A and HMB were formed by further oxidizing CF on the furan ring by •OH.
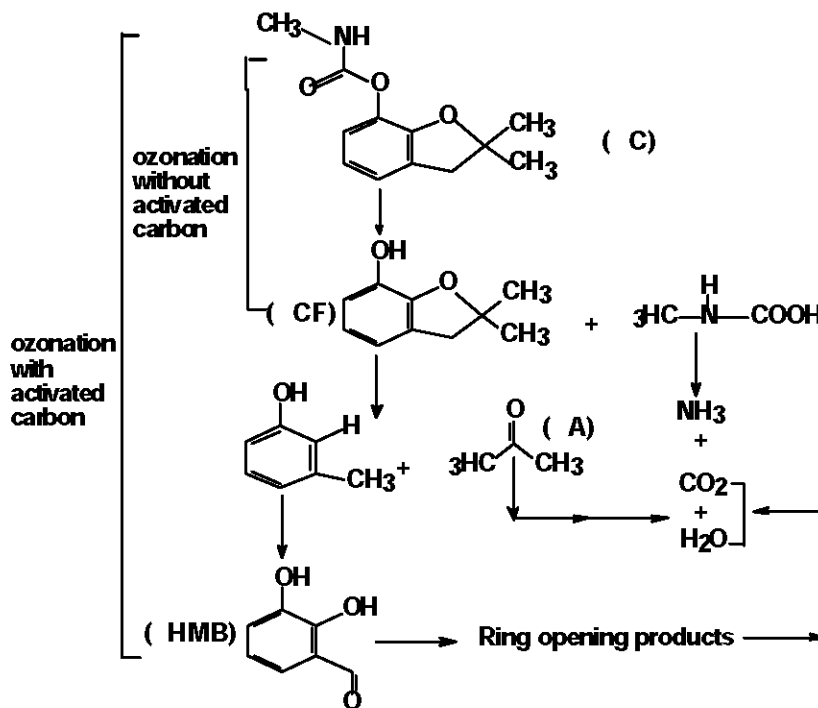
The ozonation product number 6, 7 and 8 were identified as *1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-5-heptene-2* (HCH) *or endodiol, azelaic acid* (AA) and *azelaoyl chloride* (AC) from the degradation result of endosulfan (E) in the mixture by ozonation in the presence and absence of activated carbon. The HCH was main ozonation product and detected by the hydrolysis as well as photolisis [20]. Whereas, the AA and AC were formed by further oxidizing HCH by OH• and O_3.

Moreover, ozonation product number 1 was identified as *S-[2-(di methyl amino) ester]* (SDAE) from the interaction result of the degradation between intermediate of carbofur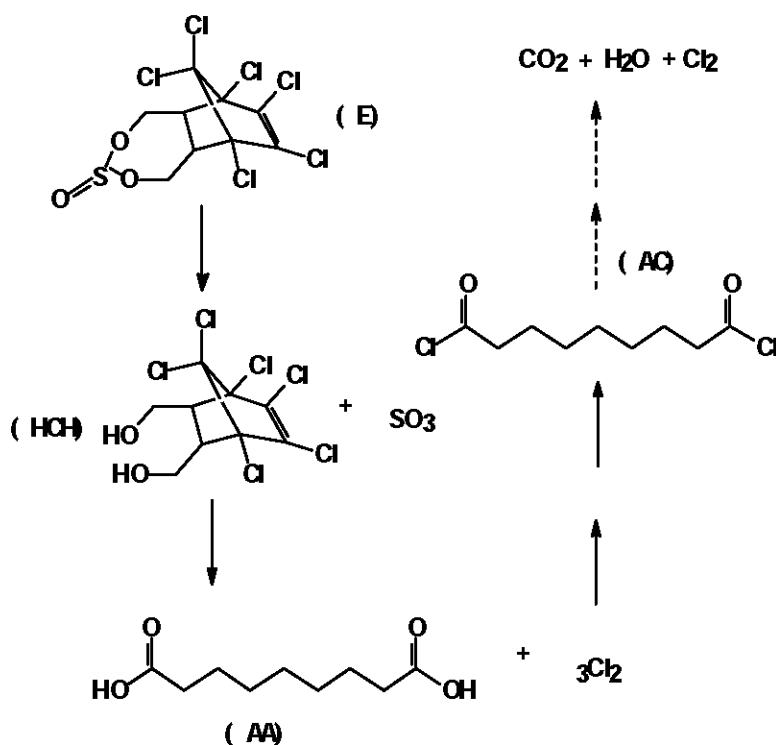an and endosulfan by ozonation in the presence of activated carbon. The ozonation product number 4 was identified as methyl 4-methylphenylsulfoxide (MMPS) from the interaction result between intermediate of carbofuran and endosulfan by ozonation in the presence and absence of activated carbon, respectively.

The proposed degradation pathway of carbofuran and endosulfan in the mixture by ozonation based on our experimental results GC/MS analysis and literature. The possible degradation pathway for carbofuran and endosulfan in the mixture are proposed in scheme 1 and scheme 2 by ozonation with of activated carbon as well as without activated carbon. From the scheme 1 it can be seen the degradation pathway of carbofuran in the mixture from CF, then A and to HMB by ozonation in the presence of activated carbon. Whereas, the degradation pathway of carbofuran in the mixture by ozonation without activated carbon only untill CF formation as the process run in 15 minutes and ozone is more selective to carbofuran.

The first step of the cleavage of the carbamate group from carbofuran was most likely due to the activating effect of O_3 attacking on carbamat group by insertion of O_3 (CF formed at this stage). At the same time carbamic acid was formed but undetectable, probable because of its rapid reaction with O_3 and/or •OH formed CO_2, H_2O and NH_3. On the other hand, the ozonation with presence of activated carbon can

Scheme 1: Proposed degradation mechanism of carbofuran in mixture by ozonation with and without activated carbon

Scheme 2: Proposed degradation mechanism of endosulfan in mixture by ozonation with and without activated carbon

increase amount of •OH in solution. Moreover, the •OH are non-selective chemical oxidant and it may react with carbofuran and/or intermediates. In addition, the •OH has oxidation potential much higher than that of the ozone molecule in order to act very rapidly with most organic compounds [4], furthermore ultimately oxidized to CO_2 and H_2O. Katsumata *et al.* [11] reported that degradation pathway of single carbofuran by photodegradation with exitation of iron (III) aquacomplexes under UV iradiation obtained through CF, 2,2-dimethyl-2,3-dihydro-benzofuran-3,7-diol (DDBF) and 7-hydroxy-2,2-dimethyl-benzofuran-3-one (HDBF).

From the scheme 2 it can be seen that the degradation pathway of endosulfan in the mixture by ozonation with of activated carbon and without activated carbon were equal to HCH or endodiol as major metabolites followed by the production of AA and AC. However, the difference between ozonation with activated carbon and without activated carbon to degrade endosulfan in the mixture is only on the degradation rate. This is because the degradation of endosulfan by ozonation in the presence of activated carbon was influenced dominantly by •OH as oxidant compared to the degradation of endosulfan by ozonation without activated carbon. According to free radical reaction theory, •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 •OH to final products; organic acid, ion chloride and even carbon dioxide [21].

From the scheme 2 it also can be seen that degradation pathway of endosulfan in the mixture by ozonation in the presence of activated carbon although absence of activated carbon does not likely generate endosulfan sulfate first but it forms endodiol directly. On the other hand, the biodegradation pathway of endosulfan by fungi *M.thermo-hyalospora* produced endosulfan sulfate [22]. According to an earlier report, endosulfan sulfate is toxic and persistent [23]. Moreover, these results show that simultaneous degradation of carbofuran and endosulfan by ozonation in the presence of activated carbon can be used as detoxification process.

CONCLUSION

The simultaneous degradation of carbofuran and endosulfan mixture by ozonation in the presence of activated carbon slightly enhances the degradation rate of carbofuran and endosulfan compared to by ozonation absence of activated carbon. It is shown by the rate

constant (k) increased slightly and activation energy (Ea) has a bit decreased value; however, the mixture by ozonation with activated carbon can generate eight intermediate products that are environmentally friendly and it can be used as a detoxification process.

ACKNOWLEDGEMENT

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