HOMOGENEOUS AND HETEROGENEOUS CATALYTIC OZONATION OF ENDOSULFAN WITH ACTIVATED CARBON AS CATALYST

Enjarlis,^(1,2) Setijo Bismo,⁽¹⁾ Slamet,⁽²⁾ Roekmijati W. Soemantojo⁽¹⁾

⁽¹⁾Department of Chemical Engineering, University of Indonesia, Depok 16424 Tel. 7863515

⁽²⁾Department of Chemical Engineering, Institute Technology of Indonesia, Serpong

Tangerang 15311, Tel. 7561092

Email: en_jarlis@yahoo.com

Abstract

Catalytic ozonation of endosulfan with the presence of activated carbon as catalyst was investigated at neutral pH and different temperatures. The model kinetics was developed based on the mechanism of catalytic decomposition ozone, namely homogeneous and heterogeneous decomposition reaction. This study focuses on determining the contribution of homogeneous and heterogeneous reaction to endosulfan removal in catalytic ozonation with activated carbon as catalyst. Endosulfan was selected as a target of study because it is organic pollutant and organic chlorine pesticide (OCPs) groups that may cause a serious environmental concern. The use of activated carbon from Bogor Forest Centre actually provides a slightly contribution in enhancing endosulfan oxidation reaction with ozone. This is because endosulfan has sulfide group or sulfur element that is very reactive to ozone. Even though, the amount of OH increases because of ozonation with activated carbon use. The heterogeneous and homogeneous reaction contributions at neutral pH and temperature range of 20–30°C were 11–21% and 79–89% from overall endosulfan removal in catalytic ozonation with promoted by of activated carbon, respectively.

Keywords: Activated Carbon, Catalytic Ozonation, Endosulfan

Abstrak

Ozonasi katalitik endosulfan dengan adanya katalis karbon aktif dilakukan pada pH netral dan suhu yang berbeda-beda. Persamaan kinetika reaksi dikembangkan berdasarkan mekanisme reaksi dekomposisi ozon secara katalitik yaitu reaksi homogen dan heterogen. Penelitian ini ditujukan terutama untuk menentukan kontribusi reaksi homogen dan heterogen terhadap penyisihan endosulfan di dalam ozonasi katalitik dengan karbon aktif sebagai katalis. Endosulfan dipilih sebagai sasaran penelitian karena merupakan polutan organik dan kelompok pestisida organoklorida (OCPs) yang menjadi perhatian serius di lingkungan. Karbon aktif yang digunakan berasal dari Balai Hutan Bogor yang ternyata memberikan pengaruh kecil terhadap peningkatan reaksi oksidasi endosulfan dengan ozon. Hal ini disebabkan endosulfan mempunyai gugus sulfida atau sulfur yang sangat reaktif terhadap ozon. Meskipun, jumlah OH meningkat disebabkan penggunaan ozonasi dengan karbon aktif. Kontribusi reaksi homogen dan heterogen terhadap penyisihan endosulfan pada kondisi pH netral dan suhu 20–30°C masing-masing sebesar 79–89% dan 11–21% dari total penyisihan endosulfan dalam ozonasi katalitik dengan dipromosikan oleh karbon aktif.

Kata kunci: Endosulfan, Karbon Aktif, Ozonasi Katalitik

1. Introduction

Catalytic ozonation was found to be effective for the removal of several organic compounds from drinking and wastewater. Catalytic ozonation with activated carbon as catalyst can accelerate ozone decomposition to form OH radical (Jans, 1998; Beltran, 2002; Sanchez, 2005). These OH radicals are powerful, non-selective chemical oxidants, which act very rapidly with most organic compounds. 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 and even carbon dioxide (Benitez, 2001).

Beltran et al. (2002) reported that the mechanisms of catalytic ozone decomposition are homogeneous and heterogeneous ozone decomposition reactions. In such context, the model kinetic degradation of endosulfan was developed based on the mechanism of catalytic decomposition ozone, namely homogeneous and heterogeneous decomposition reactions. Endosulfan (E) was selected here as a target organic pollutant, because of its endocrine disruptors, stable chemical compound with long half-life under neutral and acidic condition. The organic chlorine pesticide (OCPs) may cause serious environmental concern and health problem in animals, including humans (Extoxnet, 2000).

The aim of this work is to study the effect of the addition of activated carbon on the degradation rate of endosulfan at pH neutral and different temperature, which focuses on determining the contribution of homogeneous and heterogeneous reactions to endosulfan removal in catalytic ozonation with the of granular activated carbon as catalyst.

2. Fundamental

The degradation of endosulfan in the presence of the activated carbon was a result of combination of competing homogeneous and heterogeneous reaction: direct reaction of molecular ozone, and an indirect reaction involving non selective free-radicals. Both reactions take place in the solution bulk and on activated carbon surface (Valdes, 2006). This can be described by a simplified and unbalanced mechanism as follows:

Homogeneous reactions:

$$-\frac{dC_{E2}}{dt} = k_2^E C_{OH} \cdot C_E \quad (2)$$

Heterogeneous reactions:

$$-\frac{dC_{E3}}{dt} = k_3^E C_{AC} \cdot C_E \quad (3)$$

$$-\frac{dC_{E4}}{dt} = k_4^E C_{AC} \cdot C_{O_3} \cdot C_E \quad (4)$$

$$-\frac{dC_{E5}}{dt} = k_5^E C_{AC} \cdot C_{OH} \cdot C_E \quad (5)$$

The overall ozonation rate of endosulfan in the presence of activated carbon can be defined as the sum of endosulfan ozonation rates in homogeneous reaction, (r_{Homo}^E) calculated in the absence of activated carbon, and of endosulfan ozonation rates in heterogeneous reaction (r_{Hete}^E) due to the presence of activated carbon (Valdes, 2006; Sanchez, 2005) or could be expressed as sum of (1) - (5) as follows:

$$-\frac{dC_{E(overall)}}{dt} = r_{Homo}^E + r_{Hete}^E = (k_{Homo}^E + k_{Hete}^E) C_E \quad (6)$$

with,

$$k_{Homogen}^E = k_1^E \cdot C_{O_3} + k_2^E \cdot C_{OH} \quad (7)$$

and

$$k_{Hete}^E = k_3^E \cdot C_{O_3} + k_4^E \cdot C_{OH} + k_5^E \cdot C_{AC} \quad (8)$$

Integrating equation (6) with initial condition $C_c = C_{c_0}$ leads to:

$$\ln \frac{C_{E0}}{C_E} = (k_{Homo}^E + k_{Hete}^E) t = k_{Overall}^E t \quad (9)$$

with,

$$k_{Overall}^E = k_{Homo}^E + k_{Hete}^E \quad (10)$$

AC represents the carbon active surface sites. C_E and C_{E0} are the concentrations of endosulfan at any time t and time zero, respectively. C_{O_3} , C_{OH} and C_{AC} , are pseudo-component concentration and represent the concentration of ozone, of hydroxyl radical and the concentration of activated carbon, respectively. $k_1^E, k_2^E, k_3^E, k_4^E, k_5^E, k_{Homo}^E$, and k_{Hete}^E represent the rate constants of endosulfan in homogeneous reaction with ozone, homogeneous reaction with hydroxyl radical, adsorption, heterogeneous reaction with ozone, heterogeneous reaction with hydroxyl radical, global homogeneous and heterogeneous reactions, respectively. The contribution of homogeneous and heterogeneous reactions on degradation of

activated carbon was established using Eq. (10). First, apparent pseudo first-order constants of endosulfan global reaction, $k_{Overall}^E$ were obtained from the line slopes shown in Fig. 2, at different temperature with correlation coefficient of 0.99.

The contribution of homogeneous reaction to the overall endosulfan removal (δ^{Homo}) is calculated from the experimental endosulfan removal rate with ozonation absence (k_{Homo}^E) and presence activated of activated carbon ($k_{Overall}^E$) at pH 7, as follows:

$$-\frac{dC_{Endosulfan}}{dt} = r_{Homo}^E = (k_1^E C_{CB} + k_2^E C_{OH}) C_E = k_{Homo}^E C_E \quad (11)$$

$$\delta^{Homo} = \frac{k_{Homo}^E}{k_{Overall}^E} \times 100 \quad (12)$$

The contribution of heterogeneous reaction and adsorption to the overall endosulfan removal due to ozonation in presence of activated carbon (δ^{Hete}) was obtained by difference:

$$\delta^{Hete} = 100 - \delta^{Homo} \quad (13)$$

3. Experimental

Endosulfan (1,2,3,4,7,7-hexachlorobicyclo-2,2,1 heptane 2,3-bis-hydroxy methane-5,6 sulfite) was obtained from Chem. Service West Chester with purity 95%. The endosulfan solution was prepared by deionizer 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 $6.87 \times 10^2 \text{ m}^2/\text{g}$ and microspore volume $0.24 \text{ cm}^3/\text{g}$ (with diameter of $< 0.2 \text{ mm}$). Ozone was produced by a type RS-09805 ozone generator with maximum ozone production capacity of $0.25 \text{ g of O}_3/\text{h}$. The experimental instrument consists of an ozone generator, a cylindrical glass column reactor with an external jacket surrounded and a water stream which was pumped from thermostatic bath to maintain the temperature at the selected value for each experiment. The dimension of the reactor is 450 mm high with ID 40 mm which is equipped by 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 the pH was adjusted to 7. The temperature was set for 20, 25, and 30°C , until a predetermined volume of water was saturated

with ozone in excess continuously by injecting ozone gas for 30 min. The process is followed by the addition 0.5 g of activated carbon (for the catalytic process) and $5.0 \times 10^{-5} \text{ mol/L}$ endosulfan solution. The concentration of endosulfan and ozone presence in the system was measured every 0, 3, 6, 10, and 15 min of treatment. The dissolved ozone concentration in aqueous solution was determined by iodometric methods, which endosulfan was analyzed by Gas Chromatograph type 4C, column silicone ov-17 3 meters, ECD (Electron Capture Detector), Shimadzu, solvent n-hexane and mobile gas-phase N_2 . All experiments were carried out in duple the presence and the absence of activated carbon.

4. Results and Discussion

Fig.1 shows the effect of temperature on degradation of endosulfan for catalytic ozonation at condition: pH 7; gas flow rate 0.1603 L.h^{-1} ; agitation speed 750 min^{-1} ; C_{O_3} $6.372 \times 10^{-3} \text{ O}_3 \text{ mol/L}$; and C_E $5.0 \times 10^{-5} \text{ mol/L}$. From that figure, it can be stated that the higher the temperature is, the higher the degradation rate of endosulfan is. This effect is due to an increase in the rate constant of the chemical reaction. Yazgan et al. (2004) reported that the change of temperature gave positive effect on the removal rate of the endosulfan. Although increasing the temperature causes the decrease of 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 efficient at higher temperature.

Figure 1. The degradation of endosulfan for catalytic ozonation at temperature 20°C (□), 25°C (△), 30°C (○)

Figure 2. Constant rate of endosulfan by catalytic ozonation temperature 20°C (), 25°C (Δ), 30°C (o)

Figure 2 shows the contribution of homogeneous and heterogeneous reaction mechanism to endosulfan removal in catalytic ozonation with activated carbon as catalyst. The results summarized in Table 1 indicate that the total constant rate (k_{overall}) degradation of endosulfan increased with the presence of activated carbon. This is because ozone and activated carbon surface interactions could account for the observed endosulfan removal rate enhancement. In the combined process, activated carbon does not only provide a contact surface where endosulfan and ozone are adsorbed, but it also participates in ozone aqueous decomposition (Kasprzyk-Hordern, 2003).

From Table 1 it can be seen the use of activated carbon in the degradation of endosulfan, provides a slightly contribution in enhancing endosulfan oxidation reaction with ozone. The heterogeneous and homogeneous reaction contribution at pH neutral and temperature range 20 – 30°C were 11 – 21% and 79 – 89% from overall endosulfan removal, respectively.

The contribution of heterogeneous reaction give a slight significance compared to homogeneous reaction. The heterogeneous and homogeneous reaction contribution at neutral pH and temperature range 20 – 30°C were 11 – 21% and 79 – 89% from overall endosulfan removal. Therefore, the contribution of heterogeneous reaction (δ^{Hete}) held between 11 – 21% and of homogeneous reaction (δ^{Homo}) held between 79 – 89% to overall endosulfan removal by catalytic ozonation. Similar phenomenon also showed at activation energy (E_a). This is because endosulfan has sulfide group or sulfur element that is very reactive to ozone (Ying, 2000; Langlais, 1991). Even though, the amount of OH increased because of ozonation with activated carbon use. Similar phenomenon also occurred at degradation of carbofuran by catalytic ozonation using the same activated carbon as catalyst (Enjarlis, 2007).

5. Conclusion

The use of the activated carbon from Bogor Forest Center as catalysts at degradation of endosulfan by ozonation processes is slightly significant in enhancing the degradation rate of endosulfan in aqueous solution. The contribution of heterogeneous reaction between 11 – 21% and homogeneous reaction between 79 – 89% from the overall endosulfan removal by ozonation with the presence of activated carbon as catalysts. Similar phenomenon also accounts for E_a namely 6.586 kcal/mol for catalytic and 8.631 kcal/mol for non catalytic ozonation. The contribution of activated carbon surface to endosulfan degradation can be increased by modifying the carbon chemical surface properties and subsequent initiating the decomposition of ozone in the aqueous phase into highly oxidized species.

References

- [1.] Jans, U., Hoigne, J., (1998), "Activated carbon and carbon black catalyzed transformation of aqueous ozone into OH-radicals", *Ozone Sci. Eng.*, vol 20, pp. 67-89.

Table 1. Contribution of homogeneous and heterogeneous reaction mechanism to endosulfan removal in catalytic ozonation with activated carbon as catalyst

T (°C)	Catalytic Ozonation (Homogeneous & Heterogeneous reaction)									
	$k^E_{\text{Overall}} \cdot 10^{-2} \text{ (min}^{-1}\text{)}$	R^2	δ^{Hete} (%)	E_a (kcal/mol)	R^2	$k_{\text{Homo}} \cdot 10^{-2} \text{ (min}^{-1}\text{)}$	R^2	δ^{Homo} (%)	E_a (kcal/mo)	R^2
20	7.97×10^{-2}	0,99	21			6.32×10^{-2}	0,98	79		
25	9.61×10^{-2}	0,99	18	6,586	0,99	7.86×10^{-2}	0,99	82	8,631	0,97
30	11.54×10^{-2}	0,99	11			10.27×10^{-2}	0,98	89		

- [2.] Beltran, F. J., Rivas, F. J., Alvarez, P., Fernando, L.A., Alfarez, P.M., and Montero-de Espinosa, R. (2002), "Kinetics of ozone decomposition catalyzed by activated carbon in water", *Ind. Eng. Chem. Res.*, vol 41, pp. 6510-6517.
- [3.] Sanchez Polo, M., Gunten, U.V., Rivera-Utrilla, J., (2005), "Efficiency of activated carbon to transform ozone into OH radicals: Influence of operational parameters", *Water Res.*, vol. 39, pp. 3189-3198.
- [4.] Benitez, F.J., Beltran-Heredia, J., Acero, J.L., and Rubio, F.J., (2001), "Oxidation of several chlorophenolic derivatives by UV irradiation and hydroxyl radicals", *J. Chem. Technol. Biotechnol.*, vol. 76, pp. 312-320.
- [5.] Beltran, F.J., Rivas, J., Alvarez, J., Montero-de-Espinosa, R., (2002), "Kinetics of heterogeneous catalytic ozone decomposition in water on an activated carbon", *Ozone Sci. Eng.*, vol 24, 227.
- [6.] Extoxnet, (2000), "Pesticide Information Profiles: Endosulfan", Extention Toxicology Network, Oregon State University (<http://ace.orst.edu/info/extoxnet/pips/carbofur.htm>)
- [7.] Valdes, H., Zaror, C.A., (2006), "Heterogeneous and homogeneous catalytic ozonation of benzothiazole promoted by activated carbon: Kinetic approach", *Chemosphere.*, vol. 65, pp. 1131-1136.
- [8.] Polo Sanchez, M., Ramos Leyva- Ramos, Rivera-Utrilla., (2005), "Kinetics of 1,3,6-naphthalenetrisulphonic acid Ozonation in presence of activated carbon", *Carbon* vol. 43, pp. 962-969.
- [9.] Yazgan, M. S., and Kinaci, C., (2004), "Beta-Endosulfan Removal from Water by Ozone Oxidation", *Water Science & Technology*, vol.48. (11), pp. 511-517.
- [10.] Kasprzyk-Hordern, B., Maria Ziolek, Jacek Nawrocki., (2003), "Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment", *Applied Catalysis B: Environmental.*, vol 46, pp. 639-669.
- [11.] Ying, H. J., Morita, T., Magara, Y. and Aizawa, T., (2000). "Evaluation of Reactivity of Pesticides with ozone in water using the energies of frontier molecular orbital", *Waters Res.*, vol. 34(8), pp. 2215 - 2222.
- [12.] Langlais, B., David A. R., Brink, D. R., (1991). "Ozone in Water Treatment Application Engineering", Cooperative Research Report, Florida, Lewis Publishing
- [13.] Enjarlis., Setijo Bismo, Slamet and Roekmijati W. Soematoyo., (2007), "Kinetics degradation of carbofuran by ozonation in the presence activated carbon", *Proceeding 14th Regional symposium Chemical engineering*, UGM Yogyakarta Indonesia.