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

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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

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:

\[
E + O_3 \rightarrow \text{products}
\]

\[
-\frac{dC_{o3}}{dt} = k_1C_{o3}C_E
\]

(1)

Heterogeneous reactions:

\[
E + OH \rightarrow \text{products}
\]

\[
-\frac{dC_{OH}}{dt} = k_4C_{OH}C_E
\]

(2)

E + AC \rightarrow \text{products}

\[
-\frac{dC_{AC}}{dt} = k_4C_{AC}C_E
\]

(3)

E + AC + O_3 \rightarrow \text{products}

\[
-\frac{dC_{AC+O3}}{dt} = k_4C_{AC+O3}C_E
\]

(4)

E + AC + OH \rightarrow \text{products}

\[
-\frac{dC_{AC+OH}}{dt} = k_4C_{AC+OH}C_E
\]

(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, \( r_{hom} \) calculated in the absence of activated carbon, and of endosulfan ozonation rates in heterogeneous reaction \( r_{hete} \) due to the presence of activated carbon (Valdes, 2006; Sanchez, 2005) or could be expressed as sum of (1)-(5) as follows:

\[
-\frac{dC_E}{dt} = r_{hom} + r_{hete} = (k_{hom} + k_{hete})C_E
\]

(6)

with,

\[
k_{Homogeneous} = k_{d}C_{d} + k_{h}C_{h}
\]

(7)

and

\[
k_{Heterogeneous} = k_{d}C_{d} + k_{h}C_{h}
\]

(8)

Integrating equation (6) with initial condition \( C_E = C_{E0} \), leads to:

\[
\ln \left( \frac{C_{E0}}{C_E} \right) = (k_{hom} + k_{hete})t = k_{Overall}t
\]

(9)

with,

\[
k_{Overall} = k_{Homogeneous} = k_{Heterogeneous}
\]

(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. \( C_{d} \), \( C_{h} \), and \( C_{hete} \), and \( k_{d} \) are pseudo-component concentration and represent the concentration of ozone, of hydroxyl radical, and the concentration of activated carbon, respectively. \( k_{hom} \) and \( k_{hete} \) 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, $k_{\text{overall}}^i$ 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 ($\delta_{\text{Homo}}$) is calculated from the experimental endosulfan removal rate with ozonation absence ($k_{\text{rem}}$) and presence activated of carbon ($k_{\text{rem}}^i$) at pH 7, as follows:

$$\frac{dC_{\text{rem}}}{dt} = -(k_{\text{rem}}C_0 + k_{\text{rem}}^iC_0)e^{-k_{\text{rem}}C_0} = k_{\text{rem}}^iC_0$$

(11)

$$\delta_{\text{Homo}} = \frac{k_{\text{rem}}^i}{k_{\text{rem}}^i} \times 100$$

(12)

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

$$\delta_{\text{Hete}} = 100 - \delta_{\text{Homo}}$$

(13)

3. Experimental

Endosulfan (1,2,3,4,7,7-hexachlorobicyclo-2,2,1heptane 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 Quantachrome Autosorb-6 with surface area 6.87x10$^2$ m$^2$/g and micropore volume 0.24 cm$^3$/g (with diameter of < 0.2 mm).

Ozone was produced by a type 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 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 (K1 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 x 10$^{-2}$ 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 duplicate 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$^{-1}$; $C_{in}$ 6.372 x 10$^{-5}$ O, mol/L, and $C_{in}$ 5.0 x 10$^{-3}$ 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 (○)](image)
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 ($\delta^{hew}$) held between 11 - 21% and of homogeneous reaction ($\delta^{homo}$) held between 79 - 89% to overall endosulfan removal by catalytic ozonation. Similar phenomenon also showed at activation energy (Ea). 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 Ea 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

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

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$k^E_{swatt}$</th>
<th>$\delta^{hew}$ (%)</th>
<th>$E_a$ (kcal/mol)</th>
<th>$R^2$</th>
<th>$k_{hom}$</th>
<th>$\delta^{homo}$ (%)</th>
<th>$E_a$ (kcal/mol)</th>
<th>$R^2$</th>
</tr>
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<tbody>
<tr>
<td>20</td>
<td>7.97x10^-2</td>
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<td>21</td>
<td>6.32x10^-2</td>
<td>0.98</td>
<td>79</td>
<td>6.586</td>
<td>0.99</td>
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<tr>
<td>25</td>
<td>9.61x10^-2</td>
<td>0.99</td>
<td>18</td>
<td>7.86x10^-2</td>
<td>0.99</td>
<td>82</td>
<td>8.631</td>
<td>0.97</td>
</tr>
<tr>
<td>30</td>
<td>11.54x10^-2</td>
<td>0.99</td>
<td>11</td>
<td>10.27x10^-2</td>
<td>0.98</td>
<td>89</td>
<td></td>
<td></td>
</tr>
</tbody>
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