ABSTRACT

Kinetics degradation of carbofuran by ozonation in the presence of activated carbon was investigated at neutral pH and different temperatures. The aim of this work is to study the effect of the addition of activated carbon on the degradation rate of carbofuran through ozonation, focusing on the rate constant (k) and the activation energy (Ea). The presence of the activated carbon as catalyst is not significant in enhancing degradation rate of carbofuran compared to non catalytic ozonation, because the carbofuran is very reactive to ozone. The rate constant (k) of carbofuran were $14.99 \times 10^{-2} \text{min}^{-1}$ at $30^\circ C$ for catalytic ozonation, and $12.56 \times 10^{-2} \text{min}^{-1}$ for non catalytic ozonation. The activation energy for catalytic ozonation was 11.31 kcal/mol and for non catalytic ozonation was 11.91 kcal/mol.

Keywords: Carbofuran, Catalytic ozonation, Non-catalytic ozonation, Activated carbon.

I. INTRODUCTION

Insecticides such as carbofuran (2,3-dihydrido-2,2-dimethylbenzofuran-7-ylmethylcarbamate) is still being used mostly by farmers in Indonesia. The carbofuran has high persistence in water due to its chemical stability under acid and neutral condition [1, 2], consequently it is detected in water surface. In addition, carbofuran is a toxic character and it’s hazardous potential increases because of the possibility of generating organohalogen compounds through its reactions with chloro derivatives, which is commonly used as oxidation agent and disinfectant of surface waters and wastewaters [3]. Therefore, it is very important to develop the treatment processes for degradation of carbofuran urgently.

Hydrolysis and microbial degradation of carbofuran appear to be important pathways in the environment. However, these processes require long times for carbofuran in aqueous solutions. It is reported that the half-lives of the compound in water ranged from 690 days at pH 5 to one week at pH 8 [2]. A variety of effective treatment techniques for aqueous carbofuran have been studied by researchers namely: Fe (III) aquacomplexes as effective photocatalysts [3], UV irradiation in the presence of ozone or Fenton reagent [4], anodic Fenton treatment (AFT) [3] and UV radiation plus H$_2$O$_2$ [4]. Recently, it’s pointed out that presence of hydroxyl radicals is very crucial in organic compounds oxidation, as these radicals are known to be reactive species in the advanced oxidation processes. In most cases, It can cause the complete mineralization of the pollutants. It has been reported that hydroxyl radicals were generated by combinations of ozone plus UV radiation, UV radiation plus H$_2$O$_2$, UV radiation plus Fenton’s reagent (photo-Fenton system) [5]. These OH• radicals could also be obtained by mixing a few milligrams of activated carbon in ozone-containing water. [6]. The presence of activated carbon in ozonation processes does not really act as a catalyst, but rather than as an initiator and/or a promotor for ozone transformation into OH$^-$ [7].

This study was investigated the degradation of carbofuran in water by catalytic ozonation and non catalytic at neutral pH and at different temperatures, which is focused on (i) determining possible diffusion limitation (ii) determining the rate constants (k) and activation energy (Ea).
II. EXPERIMENTAL

The carbofuran (C₁₂H₁₅NO₃) were obtained from Chem. Service West Chester with purity 99%. The Carbofuran solution was prepared by deionized water obtained from Aquatron Auto Still Yamato Tipe W-182. The specific surface area of activated carbon were measured using the multipoint BET of N₂ adsorption in a Quantachrome Autosorb -6 with surface area 6.87×10⁻² m²/g. Ozone was produced by a RS 09805 ozone generator with maximum ozone production capacity of 0.25 g of O₃/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 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 or until the saturated ozone was reached. The process is followed by the addition of activated carbon (for the catalytic process) and 4.5×10⁻⁵ mol/L carbofuran solution. The concentration of carbofuran and ozone presence in the system was measured every 0, 3, 6, 10, 15 and 30 min of treatment. The dissolved ozone concentration in aqueous solution was determined by iodometric methods, which carbofuran was analyzed by Gas Chromatograph type 4C, colum silicone ov-17 3 meters, ECD (Electron Capture Detector), Shimadzu, solvent n-hexsane and mobile gas-phase N₂. All experiments were carried out in duplo the presence of (catalytic) and the absence of (non catalytic) activated carbon.

II. RESULTS AND DISCUSSION

The influence of variables on the degradation of carbofuran was first assessed. Non-catalytic and catalytic ozonation experiments were conducted for each experimental series. Since the catalytic ozonation process involves steps of external and internal diffusion, variables studied were: activated carbon particle size and agitation speed. A series of experiments were then carried out at different temperatures to determining k and Ea.

Influence of activated carbon particle size on carbofuran conversion

The influence of activated carbon particle size on carbofuran conversion is presented in Fig. 1 with process condition 30°C; pH 7; ozone gas concentration 6.372×10⁻³ O₃ mol/L; Cₒₙ 4.5×10⁻⁵ mol/L and gas flow rate 0.1603 L h⁻¹. Fig. 1 shows that the particle size of activated carbon which is equal to or lower than 0.2-0.3 mm, does not affect the process rate. These results indicate that the degradation rate of carbofuran in the presence of activated carbon is influenced by diffusion processes. Hence, internal mass transfer resistance is limited to particle sizes higher than 0.2-0.3 mm. As a consequence, the remaining experimental runs were carried out with a 0.2-0.3 mm catalyst particle size. Beltran et al [8] have obtained activated carbon particle size is equal to 1-1.6 mm, the discrepancy of this surface area was different. They used activated carbon with 789 m² g⁻¹ surface area in oxalic acid solution whereas in this experiment, it used activated carbon 687 m² g⁻¹ surface area in carbofuran solution.
Influence of agitation speed on carbofuran conversion

The influence of agitation speed on carbofuran conversion is presented on Fig. 2. It can be seen that the agitation speeds higher than 750 rpm does not influence in improving the carbofuran removal rate, thus the external mass transfer resistances (gas to liquid and liquid to solid mass transfer) are negligible for gas flow rate and agitation speed higher than at value above indicated. As a consequence, the remaining experimental runs were carried out at 750 rpm. If compared to Beltran et al [8], his result indicated that the speed agitation was equal to or large than 200 rpm, as the discrepancy of this agitator model was different. They used agitation impeller in oxalic acid solution whereas in this experimental used magnetic stirrer in carbofuran solution.

Influence of temperature on the degradation of carbofuran

Figures 3 and 4 show the influence of temperature on degradation rate of carbofuran in the catalytic and non-catalytic ozonation. From that figure, it can be stated that the bigger the temperature, the bigger the degradation rate. This effect is due to an increase in the rate constanta of the chemical reaction. Benitez et al [3] reported that the change of temperature gave positive effect on the removal rate of the carbofuran. 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 [9].

The reaction kinetics of carbofuran ozonation can be determined after the saturation of ozone is reached, and the resistance of the ozone transfer from the gas phase to the liquid phase becomes insignificant where the concentrations of ozone are uniform in the liquid (data are not shown). The overall degradation kinetics of carbofuran by single ozonation in terms of molecular ozone and hydroxyl radical that is produced by the decomposition of ozone at neutral pH can be formulated as follows [10]:

\[
\left( - \frac{dCc}{dt} \right)_{\text{Homogen}} = k_o Cc \cdot C_{O3} + k_{OH} \cdot Cc \cdot C_{OH}\cdot
\]

where \( Cc \) is the concentration of carbofuran in the solution, \( C_{O3} \) and \( C_{OH}\cdot \) are the concentrations of ozone and hydroxyl radicals, \( k_o \) and \( k_{OH} \) are the kinetic rate constants. In this study, since the ozone was offered in excess, the hydroxyl-free radicals and ozone concentration in the solution are presumably close to constant (i.e., at a steady state). Therefore, Eq. (1) can be rearranged to the pseudo-first-order equation in Eq. (2), as follows:

\[
\left( - \frac{dCc}{dt} \right)_{\text{Homogen}} = k_o Cc \cdot C_{O3} + k_{OH} \cdot Cc \cdot C_{OH}\cdot = k'_{\text{Homogen}} Cc
\]

where \( k'_{\text{Homogen}} \) represents the apparent pseudo-first-order rate constant for the non-catalytic ozonation process. After integration with the boundary conditions \( Cc = C_{co} \) for \( t = 0 \), and \( Cc = C_{c} \) for \( t = t \), this equation leads to

\[
\ln \frac{C_{co}}{Cc} = k'_{\text{Homogen}} t
\]

Thus, a plot of \( \ln(C_{co}/Cc) \) versus time \( t \) in every experiment must lead to straight lines which slopes are \( k'_{\text{Homogen}} \). Insert of Fig. 3 shows, as an example, this plot for experiments where the temperature was varied that can be seen, points lie satisfactorily around straight lines.

![Fig. 3 Degradation rate of carbofuran for non-catalytic ozonation at condition: pH 7; gas flow rate 0.1603 L h\(^{-1}\); agitation speed 750 min\(^{-1}\); \( C_{O3} \) 6.372.10\(^{-3}\) O\(_3\) mol/L; \( Cc\) 4.5.10\(^{-5}\) mol/L; temperature □ 20\(^\circ\)C, △ 25\(^\circ\)C, ○ 30\(^\circ\)C. Insert: Influence of temperature on degradation rate constants of carbofuran](image)

**Influence presence activated carbon in degradation carbofuran by ozonation**

Fig 4 shows the results degradation of carbofuran in the presence of activated carbon on ozonation processes. It can be seen that the degradation of carbofuran enhanced compared to the degradation of carbofuran at non catalytic ozonation. Therefore, the total carbofuran degradation rate in the presence of activated carbon can be defined as the sum of the homogeneous reaction rate, \((-rC)_{\text{homogen}}\), calculated in the absence of activated carbon, and the
heterogeneous reaction rate, \((-r_C)_{\text{hetero}}\), due to the presence of activated carbon [11]. As discussed earlier the activated carbon enhanced the oxidation rate of carbofuran by promoting the reduction of dissolved ozone into hydroxyl radicals that cause the carbofuran degradation, the rate of equation, given in Tabel 1. The total carbofuran degradation rate can be mathematically expressed as:

\[
R_{C,\text{Total}} = R_{C,\text{Homo}} + R_{C,\text{Hete}}
\]

Tabel 1. Rate of equation at degradation of carbofuran by ozonation in the presence activated carbon

<table>
<thead>
<tr>
<th>No</th>
<th>With activated carbon</th>
<th>Without activated carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>((-\frac{dC_c}{dt})<em>{\text{hete}} = f_1(C_c, C</em>{O3}, C_{\text{OH}•}, C_{AC}))</td>
<td>((-\frac{dC_c}{dt})<em>{\text{homo}} = f_2(C_c, C</em>{O3}, C_{\text{OH}•}, C_{AC}))</td>
</tr>
<tr>
<td>2</td>
<td>((-\frac{dC_{O3}}{dt})<em>{\text{hete}} = f_3(C_c, C</em>{O3}, C_{\text{OH}•}, C_{AC}))</td>
<td>((-\frac{dC_{O3}}{dt})<em>{\text{homo}} = f_4(C_c, C</em>{O3}, C_{\text{OH}•}, C_{AC}))</td>
</tr>
<tr>
<td>3</td>
<td>((-\frac{dC_{\text{OH}•}}{dt})<em>{\text{hete}} = f_5(C_c, C</em>{O3}, C_{\text{OH}•}, C_{AC}))</td>
<td>((-\frac{dC_{\text{OH}•}}{dt})<em>{\text{homo}} = f_6(C_c, C</em>{O3}, C_{\text{OH}•}, C_{AC}))</td>
</tr>
</tbody>
</table>

Recently, Jans and Hoigne [6] pointed out that catalytic ozone decomposition can be catalogued as another Advance Processes Oxidation (AOP) with a stoichiometric ratio (ozone decomposed/hydroxyl radical formed) equal to that of the other ozone involved in AOPs. Thus, since of ozone concentration in solution in excess at the constant amount of activated carbon, the amount of \(\text{OH}•\) and \(O_3\) stayed constant during the processes (i.e., at a steady state).

Therefore, Eq. (4) can be rearranged to the pseudo-first-order equation in Eq. (5) as follows:

\[
\left(-\frac{dC_c}{dt}\right)_{\text{Total}} = k'_{C,\text{Homo}} C_c + k'_{C,\text{Hete}} C_c = (k'_{C,\text{Homo}} + k'_{C,\text{Hete}}) C_c \quad \text{......... (5)}
\]

\[
\left(-\frac{dC_c}{dt}\right)_{\text{Total}} = k''_{C,\text{Total}} C_c \quad \text{......... (6)}
\]

where \(k''_{C,\text{Total}}\) represents the apparent pseudo-first-order total rate constant for the ozonation process in presence activated carbon. After integration with the boundary conditions \(C_c = C_{co}\) for \(t = 0\), and \(C_c = C_c\) for \(t = t\), the last equation leads to

\[
\ln \left(\frac{C_{co}}{C_c}\right) = k''_{C,\text{Total}} t \quad \text{......... (7)}
\]

Thus, a plot of \(\ln(C_{co}/C_c)\) versus \(t\) in every experiment must lead to straight lines which slopes are \(k''_{C,\text{Total}}\). Insert of Fig. 4 shows, as an example, this plot for experiments where the temperature was varied: as can be seen, points lie satisfactorily around straight lines. The presence of the activated carbon as catalyst is not significant in enhancing degradation rate of carbofuran compared to a non-catalytic ozonation. This is caused the carbofurans have amino group that is very reactive to ozone [12], thus amount increasing of \(\text{OH}•\) gives slightly effect to degradation rate of carbofuran.

\[\text{Fig. 4 Degradation rate of carbofuran for catalytic ozonation at condition: pH 7; gas flow rate 0.1603 L h}^{-1}\]
agitation speed 750 min$^{-1}$; catalyst concentration 1.67 g L$^{-1}$; particle size 0.2-0.3 mm; CO$_3$ 6.372.10$^{-3}$ mol/L; Cc$_o$ 4.5.10$^{-3}$mol/L; temperature $\square$ 20°C, $\Delta$ 25°C, $\circ$ 30°C. Insert: Influence of temperature on degradation rate constants of carbofuran

Fig 5 shows a typical Arrhenius plot for $\ln k'$ against $1/T$ to carbofuran in the absence and presence of activated carbon on ozonation processes, with a mean value for Ea are 11.91 kcal/mol and 11.31 kcal/mol, respectively. These results have small difference for Ea at catalytic and non-catalytic ozonation in carbofuran degradation. This is caused the carbofuran is very reactive to ozone [12]. In addition, the presence of activated carbon in ozonation processes does not really act as a catalyst, but rather than as an initiator and/or a promotor for ozone transformation into OH$^•$ [7]. Finally, from the rate constants and activation energy given in Table 2 corresponded to the experiments completed at different temperatures in the range of 20-30°C.

Table 2 Pseudo-first order constant ($k$), correlation coefficient ($R^2$), activation energy of carbofuran degradation by catalytic ozonation and non-catalytic ozonation

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>Catalytic Ozonation</th>
<th>Non-catalytic ozonation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k. 10$^{-2}$ (min$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>20</td>
<td>14.99</td>
<td>0.99</td>
</tr>
<tr>
<td>25</td>
<td>11.32</td>
<td>0.99</td>
</tr>
<tr>
<td>30</td>
<td>7.94</td>
<td>0.99</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

The presence of the activated carbon (catalytic ozonation) is not significant in enhancing the degradation rate of carbofuran in aqueous solution compared to non-catalytic ozonation processes. The rate constant ($k$) of carbofuran were 14.99 x 10$^{-2}$min$^{-1}$ at 30°C for catalytic ozonation, and 12.56x10$^{-2}$min$^{-1}$ for non catalytic ozonation. The activation energy (Ea) for catalytic ozonation was 11.31kcal/mol and for non catalytic ozonation was 11.91kcal/mol.

5. REFERENCES