Phenols removal using ozonation-adsorption with granular activated carbon (GAC) in rotating packed bed reactor

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Abstract. Synthetic wastewater containing phenols was treated using combination method of ozonation-adsorption with GAC (Granular Activated Carbon) in a packed bed rotating reactor. Ozone reacts quickly with phenol and activated carbon increases the oxidation process by producing hydroxyl radicals. Performance parameters evaluated are phenol removal percentage, the quantity of hydroxyl radical formed, changes in pH and ozone utilization, dissolved ozone concentration and ozone concentration in off gas. The performance of the combination method was compared with single ozonation and single adsorption. The influence of GAC dose and initial pH of phenols were evaluated in ozonation-adsorption method. The results show that ozonation-adsorption method generates more OH radicals than a single ozonation. Quantity of OH radical formation increases with increasing pH and quantity of the GAC. The combination method prove better performance in removing phenols. At the same operation condition, ozonation-adsorption method is capable of removing of 78.62% phenols as compared with single ozonation (53.15%) and single adsorption (36.67%). The increasing percentage of phenol removal in ozonation-adsorption method is proportional to the addition of GAC dose, solution pH, and packed bed rotator speed. Maximum percentage of phenol removal is obtained under alkaline conditions (pH 10) and 125 g of GAC.

1. Introduction
Industri al development brings benefits and negative impacts of waste generated. Phenol is an important and main waste material in a many industries. Phenol compounds have high toxicity and are carcinogenic. United States Environmental Protection Agency (EPA) put phenol to the list of priority substances in the wastewater that must be eliminated [1]. Indonesian Environmental Minister by Decree No. KEP-51/MENLH/10/1995 stated that phenol in water safe for the environment within concentration range 0.5-1.0 mg/L and the threshold phenol in drinking water is 0.002 mg/L. Phenol wastes generated from the pharmaceutical industry and hospitals can reach 100-150 mg/L because of its extensive use to synthesize drugs and antiseptics.

Biological methods can only deal with the phenol concentration below 100 mg/L [2]. Other methods include such as, the activated carbon adsorption [3], wet air oxidation method [4], photocatalytic oxidation [5], supercritical water oxidation [6], as well as ozonation method [7]. Phenol degradation studies using ozonation-adsorption technique conclude that GAC could increase phenol removal percentage, and ozonation can oxidize heavy metals dissolved in water, organic compounds, as well as remove color, odor, and taste [8,9]. The addition of activated carbon not only as an adsorbent, but also as a catalyst in supporting ozone oxidation [9]. Ozone reacts quickly with phenol and activated carbon increases the oxidation process by producing hydroxyl radicals which are capable to mineralize substituents of wastewater [10].
In this study, phenol was removed by ozonation-adsorption techniques with GAC in rotating packed bed reactor. The reactor used is a modification from Lin and Wang study [11]. Rotator in packed bed serves to enlarge the mass transfer of ozone gas into the waste solution and GAC. Performance parameters evaluated are phenol removal percentage, the quantity of hydroxyl radical formed, changes in pH and ozone utilization, dissolved ozone concentration and ozone concentration in off gas. To evaluate the significance of combination method, the method configuration was varied (single adsorption, single ozonation, and combination of ozonation-adsorption). The variation of initial pH, stirrer speed in the reactor bed, and the quantity of GAC on ozonation-adsorption technique was conducted to evaluate the influence of these parameters to the phenol removal.

2. Experimental
Rotating packed bed reactor is used to minimize the damage and immobilizing the GAC particles, easy to control, and produce extensive contact between the gas phase and the solid or liquid so that the mass transfer and diffusion between adsorbate and adsorbent is faster. Bed reactor is connected to the rotor arms on stationary vessel with a diameter of 2.5 cm, and 28 cm axial height. Rotator connected to the rotor arms are also connected to the motor speed regulator. The reactor was made of acrylic material with a thickness of 0.5 cm, ID of 8 cm, 8 cm bed height, total reactor height of 35 cm, and a total reactor volume of 1.51 L. Figure 1 shows the scheme of the reactors.

![Figure 1. Scheme of Rotating Packed Bed Reactor](image)

Before conducting phenol removal, quantity of OH radicals was measured for each configuration process, using iodometry. In addition, the productivity of ozonator was also tested by bubbling outlet gas from ozonator in a KI solution for a certain time. All of the experiment was conducted in a constant temperature of 20°C to prevent the decomposition of ozone into oxygen.

Phenol removal process was conducted in a series of research equipment as can be seen in Figure 2. The initial phenol concentration was 100 mg/L. Granular activated carbon (GAC) was dried at 100°C for 1-2 hours. The parameter variables in this experiment includes: initial solution pH (pH ≈4 acidic, alkaline pH ≈ 10, and phenol without pH adjustment), GAC quantity used as packed bed (75 g, 100 g and 125 g) and the rotator speed (150 rpm, 225 rpm, and 300 rpm).

The phenol removal process was conducted in the equipment as can be seen in the experimental set-up in Figure 2. Five liter of phenol solution in reservoir was circulated in a flow rate of 1.5 L/min and ozone gas as much as 3.31 mg/min supplied to the reactor. The process was carried out for 60 minutes and sampling was conducted every 15 minutes.
3. Results and Discussion

3.1. Quantification of OH radical
This quantification test aims to determine the effect of variations in configuration and operating conditions on OH radical (OH•) generated, using permanganometry. The following reactions occur during the test:

\[ 3\text{H}_2\text{O} + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow 4\text{O}_2 + 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 6\text{H}_2\text{O} \]
\[ \text{H}_2\text{O}_2 \rightarrow 2\text{OH}^• \]

Figure 3 shows the results of quantification of OH radical for configurations of ozonation and its combination with adsorption. This figure shows that the amount of OH radical formed from ozonation-adsorption method is higher. This is because the existence of GAC with active site that allows the adsorption and surface reaction with ozone, thus accelerating the formation of the radical component when it reacts with ozone to form OH radical. However, starting from 15 minute to 45 minute, number of OH radical on single ozonation increased significantly. This is due to adjusting the pH of distilled water in accordance with phenol pH (pH ≈ 6) so that ozone can react directly and indirectly to form OH radical which needs longer time for its formation.

Figure 4 shows the effect of GAC dose on the number of OH radical. This figure shows that higher dosage of GAC produces higher number of OH radical. This can occur because the ozone molecule is adsorbed on activated carbon hereinafter increasing residence time of ozone in the solution which will
further increasing ozone decomposition into radicals. The steady state of amount of OH radical starting from minute of 45 to 60 may be caused by saturation of activated carbon used. The addition of more GAC causes higher pressure drop in the bed so that the GAC can not be fluidized optimally. This reduces the mass transfer between ozone, solution, and activated carbon. Hence OH radical generated also decreased. Figure 5 explains that OH radical produced is higher in higher pH solution. The ozon decomposition reaction into OH radical is triggered by the existence of OH− ions. The more number of OH− ions in the solution, the more number of OH radical produced. In the acidic pH, direct ozone reaction dominates. While at pH ≈ 6, the direct (with ozon) and indirect (with OH radical) reactions occur.

![Effect of GAC quantity on production of OH radical](image1)

**Figure 4.** Effect of GAC quantity on production of OH radical (rotator speed 225 rpm, pH ≈ 6).

![Effect of initial pH on production of OH radical](image2)

**Figure 5.** Effect of initial pH on production of OH radical (rotator speed 225 rpm, pH ≈ 6) (GAC 75 gr, rotator speed 225 rpm).

### 3.2. The percentage of Phenol Removal

Percentage of phenol removal for variation of process configurations and operating conditions are presented in Figures 6-9. Figure 6 and Figure 7 show that the removal of phenol achieves highest result in ozonation-adsorption method (78.62%), followed by single ozonation (53.15%) and single adsorption (36.87%). The difference of phenol percentage in these variety of configurations is influenced by the number of OH radical formed for each configuration as has been discussed in the previous sub-section.
Figure 6. Effect of process configuration on Phenol Concentration (GAC 75 gr, rotator speed 225 rpm, pH ≈ 6).

Figure 7. Phenol removal percentage for each configuration.

In the absence of GAC, ozonation of phenol tends to proceed directly through electrophilic reaction at the ortho- and para- position. In the single adsorption, degradation occurs physically involving intermolecular force between GAC and phenol. Through physical adsorption, phenol is not strongly bound to the surface of the GAC because of the absence of surface reactions between the active site GAC with phenol. In ozonation-adsorption method, GAC not only act as an adsorbent, but also as a catalyst to increase the decomposition of ozone to radical component via the following reactions [12].

\[
\begin{align*}
O_3 + OH & \rightarrow O_2^* + HO_2^* \\
O_3 + O_2^* & \rightarrow O_3^* + O_2 \\
HO_2^* & \leftrightarrow O_3^* + H^* \\
HO_2^* & \rightarrow OH^* + O_2 
\end{align*}
\]

Ozonation-adsorption mechanism consists of adsorption, surface reaction, desorption and other chemical reactions in solution of phenol [13]. Microporous GAC is able to minimize the diffusion limitations and accelerate the rate of adsorption and desorption that ozone molecules adsorbed to the GAC and transformed into active molecular radicals components and forming OH radical. In addition, phenol compounds intermediates with molecular size of 0.5-0.6 nm are also adsorbed on microporous GAC so that assist lowering the concentration of phenol in the solution [11].

Figure 8 shows the influence of GAC quantity (dose) on the percentage of phenol removal. It shows that the GAC quantity is directly proportional to the phenol removal percentage. The existence of GAC increases contact between the ozone and the active site to form the active radical.
Figure 8. The influence of GAC quantity on the percentage of phenol removal (pH 6, 225 rpm).

Figure 9. The influence of pH on the percentage of phenol removal (GAC 100 g, 225 rpm).

Figure 9 shows that the pH condition influences the performance of phenol removal in combination of ozonation and adsorption process. The highest removal achievement is obtained at the alkaline pH while the lowest at acidic pH. High levels of degradation under alkaline conditions due to the highest quantity of OH radical which enhances the indirect ozone reaction. OH radical reacts with phenols in non-selective oxidation fashion with higher reaction rate \( k = 10^8 \text{–} 10^{10} \text{M}^{-1}\text{s}^{-1} \) and then the ozone \( k \approx 10^3 \text{M}^{-1}\text{s}^{-1} \). The decrease in phenol concentration on normal and acidic pH shows only a slight difference. This is due to a stable GAC adsorption process in a solution of pH < pKa (phenol pKa ≈ 10) [13]. At acidic pH, the degradation process begins with the adsorption of phenol by GAC lead up to an increase pH system. Increasing pH allows the indirect ozonation.

4. Conclusion
Ozonation-adsorption method generates more OH radicals than a single ozonation. Quantity of OH radical formation increases with increasing pH and quantity of the GAC. The presence of stirrer in bed reactor has an influence to increasing diffusion and mass transfer between the activated carbon, ozone molecules, and phenol solution. The increase of phenol removal percentage by ozonation-adsorption method is proportional to the increase in pH of the solution, GAC quantity, and rotator speed. Maximum percentage of phenol removal is obtained under alkaline conditions (pH 10), 125 grams of GAC quantity and the stirrer speed of 300 rpm.
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