



Original Article

## Oxidation of phenol by a laboratory scale three-phase fluidized bed reactor with Fe on activated carbon catalyst and/or ozone

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### Abstract

Metal oxide catalysts can be used in several applications requiring rapid oxidation of an organic compound. This research describes the catalytic effects of Fe on activated carbon (Fe/Ac) oxidation in an attempt to maximize oxidation rates by a laboratory scale three-phase fluidized bed reactor. Four different conditions have investigated: (a) employing O<sub>3</sub> only, (b) employing Ac only, (c) employing Ac enhanced with O<sub>3</sub>, and (d) employing Fe/Ac enhanced with O<sub>3</sub>. The Fe/Ac was prepared by using the wetness impregnation method. Phenol 10 mg/l and O<sub>3</sub> 300 mg/h were used as tested and oxidizing agents that were continuously fed to the effective volume 272 ml reactor at constant flow rate 1 and 2 l/min with co-current and up-flow, respectively. The removal of phenol was identified and quantified by HPLC. From the experimental results, it was found that the phenolic removal using Ac enhanced with O<sub>3</sub> provides the best result.

**Keywords:** phenol, activated carbon, Fe/Ac catalyst, three-phase fluidized bed reactor, ozone

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### 1. Introduction

Phenols and phenolic compounds are starting and/or intermediate chemicals in various industrial processes, such as petrochemical, synthetic chemical, pesticide, and pharmaceutical industries. Phenol is known or suspected to be carcinogens, it is well known for its high toxicity and high stability, and it has been declared to be a hazardous pollutant (Zazo *et al.*, 2006). Moreover, phenols are toxic even at low concentrations. Therefore, the treatment of phenolic pollutants will be of considerable importance in environmental protection.

Many technologies have been conventional attempted for phenolic wastewater treatment, for example biological treatment, advanced oxidation process (AOP), and adsorption. Biological treatment is the conventional process such as activated sludge and sequence batch reactor. The disadvantage of this process is caused by the resistance to common microorganisms. High concentrated phenolic wastewater cannot be treated by a biological treatment that requires a large treatment area. The examples of AOP are chemical oxidation, ozone oxidation, UV enhanced oxidation, wet air oxidation (WAO), and catalytic wet air oxidation (CWAO). WAO and CWAO technologies are required to operate at high pressure and temperature conditions (Santos *et al.*, 2002; Quintanilla *et al.*, 2006a; Quintanilla *et al.*, 2006b; Quintanilla *et al.*, 2007). Homogeneous catalysts using in the WAO are necessary to remove and recover metal ions in the effluents after the treatment (Yang *et al.*, 2005). Thus, the

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treatment costs are increasing both for WAO and CWAO. In case of adsorption by adsorbents such as activated carbon (Ac), phenol is adsorbed in the pore of Ac. When adsorption reached its equilibrium the regeneration of Ac is necessary thus increasing the treatment cost. Due to the above disadvantages of the three technologies, this research studied an alternative technology to solve these problems.

The three-phase fluidized bed reactor has received considerable attention and wide utilization in wastewater treatment due to several advantages. For example, first, this reactor has a more intensive contact between gas, liquid, and solid phase causing high mass transfer, high reaction, and small external mass transfer resistance between solid and liquid phase. Second, it could eliminate the operating problems such as bed clogging and high pressure drop, which occur in packed-bed operations. Third, it is a high efficient, simple, stable and economical operation compared to other reactor configurations (Mowla and Ahmadi, 2007).

The catalytic oxidation method offers the prospect of non-toxicity, high stability and high activity of decomposing pollutants. Therefore, the catalytic oxidation method for removal of phenolic compounds has attracted a great deal of attention. Transition metal oxides have proved to be active in the catalytic reactions of complete degradation of phenol and its derivatives in wastewater. Fe, Co, Ni, and Pb belong to the group with intermediate stability of high oxidation state oxides. It is a well-known fact that metal oxides are usually less active catalysts than noble metals (Pt, Pd, Ru, Au, and Ag). Nevertheless, for the majority of applications metal oxides are more suitable since they are more resistant to poisoning.

There are several advantages of the three-phase fluidized bed reactor using catalytic oxidation with  $O_3$ . First, the system can convert organic pollutants into products that cannot be eliminated by biological treatment. Second, it was operated under atmospheric pressure and room temperature; and under continuous state without removal of the metal ions

in the effluents. Finally, it is a more economic alternative technology when compared with the other technology for the treatment of phenols and phenolic compounds. In this research the removal of phenol was investigated under the ozonation, catalytic oxidation, and ozonation combined with catalytic oxidation by using a three-phase fluidized bed reactor.

## 2. Materials and Methods

### 2.1 Catalyst preparation

The microporous activated carbon (Ac) supplied by Carbokarn Co., Ltd. (Thailand) was used as catalytic support after sieving a fraction of 0.4 to 1.7 mm particle diameter. Ac was pretreated at 200°C for 4 hrs before impregnation. The Ac impreged with iron catalyst (Fe/Ac) prepared by using incipient wetness impregnation method. An aqueous solution of  $Fe(NO_3)_3 \cdot 9H_2O$  is slowly dropped on Ac and continuously stirred by a glass rod in a water bath with constant temperature control at 80°C. After impregnation, Fe/Ac was dried in the oven at 100°C for 24 hrs then calcined under nitrogen flow at 0.8 l/min at 500°C for 5 hrs. The concentration of Fe on the catalyst is controlled at 5% Fe (w/w) by using  $Fe(NO_3)_3 \cdot 9H_2O$  0.5 ml per gram of catalyst, which equaled to the pore volume of Ac.

### 2.2 Experiments

The laboratory scale three-phase fluidized bed reactor is used as a test system. The schematic diagram and a picture of the equipment are shown in Figure 1 and 2, respectively. The reactor with an effective volume of 272 ml is made from transparent acrylic that allows to observe the phenomena occurring inside. The outside diameter and height of the reactor are 40 and 300 mm, respectively. Phenol 10 mg/l and  $O_3$  300 mg/h were used as tested and oxidizing agents that

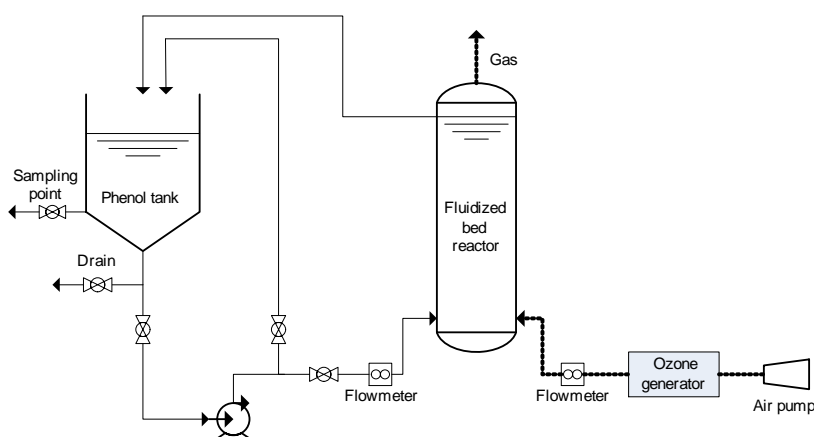


Figure 1. Schematic diagram of the lab scale fluidized bed reactor.



Figure 2. Lab scale fluidized bed reactor

were continuously fed to the reactor at a constant flow rate of 1 and 2 l/min with co-current and up-flow, respectively. The 6 liters of phenol was tested with a catalyst concentration of  $0.83 \text{ g}_{\text{cat}}/\text{l}_{\text{phenol}}$ . The aqueous temperature in the tank was constantly measured and controlled at  $30^\circ\text{C}$  using a thermocouple and a cooler. Four different conditions have been investigated: (a) employing  $\text{O}_3$  only, (b) employing Ac only, (c) employing Ac enhanced with  $\text{O}_3$ , and (d) employing Fe/Ac enhanced with  $\text{O}_3$ .

### 2.3 Chemical analysis

The progress of the reaction was followed by taking periodically liquid samples from the reactor and immediately analyzed after filtration through 0.45 mm nylon filter. Phenol was identified and quantified by high performance liquid chromatography (HPLC, Shimadzu, LC-20A Series) with a diode array detector at wavelengths of 210 and 254 nm. The 5 mm column of  $\text{C}_{18}$  column (Inertsil ODS-3, 25 cm long, 4.6 mm diameter) was used as a stationary phase. The mixture of 4 mM aqueous sulfuric and acetonitrile (4:1, v/v) was used as a mobile phase at 1 ml/min.

### 3. Results and Discussion

The degradation of phenol from the initial concentration of 10 ppm by treatment with lab scale fluidized bed reactor under four different conditions: (a) employing  $\text{O}_3$  only, (b) employing Ac only, (c) employing Ac enhanced with  $\text{O}_3$ , and (d) employing Fe/Ac enhanced with  $\text{O}_3$  are presented in Figure 3. The presented information represents the average value at each experimental condition that repeated at least three times and the results showed the same trend.

The efficiency of phenolic degradation was revealed in terms of  $-\ln(C/C_0)$  to express the rate constant ( $k$ ). Initial rate constants were determined from the slope of  $-\ln(C/C_0)$

vs.  $t$  (min) by fitting data at 0-60 minutes as shown in Figure 4, when  $C_0$  and  $C$  are the phenol concentration at initial and at time,  $t$ , respectively. The experimental results of the degradation of phenol solution revealed that using only  $\text{O}_3$  gave the worst result ( $k = 0.0037 \text{ min}^{-1}$ ). However, the result was better when employed only Ac ( $k = 0.0313 \text{ min}^{-1}$ ) and employed Fe/Ac enhanced with  $\text{O}_3$  ( $k = 0.0474 \text{ min}^{-1}$ ). In the case of using Ac enhanced with  $\text{O}_3$ , it provided the best result ( $k = 0.0653 \text{ min}^{-1}$ ). In the best case, the complete degradation of phenol can be essentially achieved within 75 min. The disappearance of phenol in all cases followed pseudo first order kinetics because the plot of  $-\ln(C/C_0)$  vs.  $t$  presented a straight line. In case (b), the degradation of phenol comes only from the adsorption process, while case (c) comes from both, adsorption process and chemical reaction.

There are many steps of phenol degradation by using Ac enhanced with  $\text{O}_3$  for example: diffusion of phenol to the surface, adsorption of phenol on the surface, chemical re-

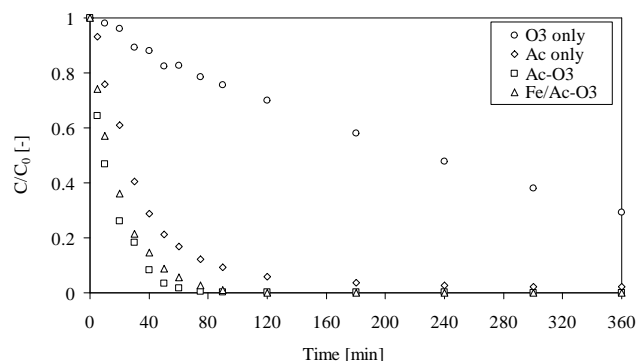


Figure 3 Concentration removal of phenol under 4 different conditions: (a) employing  $\text{O}_3$  only, (b) employing Ac only, (c) employing Ac enhanced with  $\text{O}_3$ , and (d) employing Fe/Ac enhanced with  $\text{O}_3$  at  $C_0=10 \text{ ppm}$ ,  $C_{\text{O}_3}=300 \text{ mg/h}$ ,  $Q_{\text{O}_3}=2 \text{ l/min}$ ,  $Q_{\text{phenol}}=1 \text{ l/min}$ ,  $C_{\text{cat}}=0.83 \text{ g}_{\text{cat}}/\text{l}_{\text{phenol}}$  and  $30^\circ\text{C}$ .

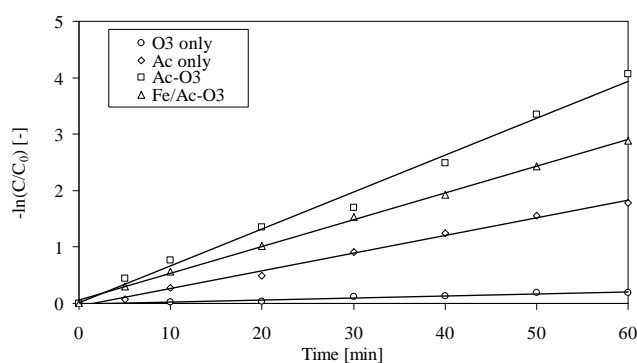


Figure 4. Phenol removal rate under 4 different conditions: (a) employing Ac only (b) employing  $\text{O}_3$  only, (c) employing Ac enhanced with  $\text{O}_3$  and (d) employing Fe/Ac enhanced with  $\text{O}_3$  at  $C_0=10 \text{ ppm}$ ,  $C_{\text{O}_3}=300 \text{ mg/h}$ ,  $Q_{\text{O}_3}=2 \text{ l/min}$ ,  $Q_{\text{phenol}}=1 \text{ l/min}$ ,  $C_{\text{cat}}=0.83 \text{ g}_{\text{cat}}/\text{l}_{\text{phenol}}$  and  $30^\circ\text{C}$ .

action on the surface, oxidation of phenol to its intermediates, desorption of intermediates to the surface and diffusion of intermediates from the surface. The steps of phenol degradation of Fe/Ac enhanced with O<sub>3</sub> are similar to the steps of phenol degradation of Ac enhanced with O<sub>3</sub>, except the quantity of intermediates. The amount of intermediates when using Fe/Ac are higher than when using Ac, because the Fe on the surface of the Fe/Ac catalyst directly activated the phenol while there are no active species on the surface of Ac.

From (a) and (b), it can be seen that effect of adsorption by activated carbon is stronger than the effect of chemical reaction by ozone. Activated carbon directly adsorbed phenolic compounds in aqueous solution until it reached its equilibrium. Interestingly, when comparing the results of phenol degradation between Ac enhanced with O<sub>3</sub> and Fe/Ac enhanced with O<sub>3</sub>, we found that case (c) removed phenol faster and better than case (d). As a result, Fe molecule may be adsorbed to the pores of the activated carbon that decreased in both pore volume and adsorption performance. Fresh activated carbon has higher adsorption ability than doped activated carbon. However, in actual waste treatment, using fresh activated carbon in each batch of waste treatment is not practical. The phenol removal from ozone by ozonation is an alternative due to the lower cost. In the past batch after using fresh activated carbon, the efficiency of the adsorption kinetic decreases while the effect of ozonation increases. Ozonation exhibits a stronger effect when activated carbon enhanced with a noble metal, i.e. Fe in this research. The choice is between the fast removal in a short period, case (c), or slightly fast removal during a long period, case (d). Table 1 shows the removal rate constants and R-square values of phenol removal in four different conditions.

Table 1. Initial rate constants and R-square values of phenol removal.

Condition	Phenol	
	k[ $\text{min}^{-1}$ ]	R <sup>2</sup>
(a) O <sub>3</sub>	0.0037	0.9577
(b) Ac only	0.0313	0.9952
(c) Ac-O <sub>3</sub>	0.0653	0.9908
(d) Fe/Ac-O <sub>3</sub>	0.0474	0.9989

#### 4. Conclusions

Oxidation of phenol by a laboratory scale three-phase fluidized bed reactor with Fe on activated carbon catalyst and/or ozone has been examined. The conclusions are as following:

1. The phenolic degradation using only O<sub>3</sub> give the worst result compared with the other cases using activated carbon.

2. The phenolic degradation using Ac enhanced with O<sub>3</sub> provides the best result.

3. The effect of adsorption by activated carbon, case (b), is stronger than the effect of chemical reaction by ozone, case (a), to treat phenol.

4. Case (c), Ac enhanced with O<sub>3</sub>, removed phenol faster and better than case (d), Fe/Ac enhanced with O<sub>3</sub>, because fresh activated carbon has a higher adsorption ability than doped activated carbon.

5. The alternative is between fast removal in a short period, case (c), or slightly fast removal during a long period, case (d).

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