Catalytic Wet Air Oxidation of Phenol in a Pilot Plant Scale Trickle Bed Reactor

Qiang Wu, Po Lock Yue and Xijun Hu*
Department of Chemical Engineering, Hong Kong University of Science and Technology, Clear water Bay, Kowloon, Hong Kong, China

Abstract

The catalytic oxidation of phenol was studied in a pilot plant scale “trickle bed reactor” (TBR). The TBR should be easy to scale up, design and optimize for large-scale treatment of industrial wastewater. In the TBR, wastewater flowing down the reactor that is packed with a bed of catalyst particles comes into intimate contact with the upcoming air. This type of reactor allows for efficient mass transfer between the gas, liquid and solid phases. The catalyst particles remain intact and do not suffer from attrition, a problem that is inherent with reactors (bubble column or slurry reactor) in which agitation is used for enhancing mass transfer. The TBR can be readily modeled for the purpose of scale-up, design and optimization. The performance of a copper catalyst supported on activated carbon for the oxidation of phenol was first evaluated in a batch reactor and subsequently in the pilot plant scale trickle bed reactor. Results on the treatment of a simulated phenol waste show extremely good performance. The temperature required for COD removal is only 150°C at a pressure of 1 MPa, which is considerably lower than that used in conventional Wet Air Oxidation (WAO) processes. The reactor is ideal for industrial WAO and large-scale applications.

* Author to whom all correspondences should be addressed. Email: kexhu@ust.hk; Tel: +852 2358 7134; Fax: +852 2358 0054.
Introduction

Wet air oxidation (WAO) has had a fairly long history of application in the treatment of municipal sludge and wastewater since the Zimpro Process developed in the 50s but has not yet received widespread use. The method is particularly suited for wastewater with high COD, as the energy released from the oxidation reactions can render the process self-sufficient in terms of thermal energy requirements. However, the pressures required are high and the efficiency in the use of oxygen or air is usually not optimized. By applying a suitable catalyst, the process becomes that of catalytic wet air oxidation (CWAO). In CWAO the reaction temperature and pressure could be significantly reduced (e.g. 1, 2).

The “bubble column”, in which air is injected into a pressurized column containing the wastewater to be treated, has been a favorite reactor configuration used in many WAO studies. In large-scale operations, the reactor size and inefficient oxygen mass transfer could impose severe limitations on the process. The bubble column type of reactor is not particularly suited for CWAO as the catalyst may suffer from severe attrition caused by vigorous agitation. Laboratory studies usually use a slurry type of reactor in which the oxygen supply either comes from dissolved oxygen or is sparged into the reactor. The results obtained from these laboratory studies may not be directly applicable for scale-up and design, especially when the mass transfer of oxygen in the full-scale plant is considerably different from that in the laboratory reactor. There are therefore incentives to develop new reactor designs and test alternative reactor configurations that can overcome these shortcomings.

The trickle bed reactor (TBR) provides an attractive alternative. A typical TBR has the following advantages:

- it can be operated at elevated temperatures and pressures;
- the range of allowable operating conditions for a TBR is sufficiently wide for a continuous process with high throughput;
- a “plug flow” pattern and a high liquid-solid interfacial area can be obtained, thus improving the effectiveness of mass transfer and reaction;
- catalyst supports can be in the form of suitably-sized particles with high surface area for reaction; and
• catalyst attrition is negligible relative to that which may be expected in a agitated slurry-type of reactor.

Several recent reports (3-6) in the literature have shown that the trickle bed reactor is suitable for CWAO. These studies were conducted in relatively small-size reactors. The present study was conducted in a pilot plant scale trickle bed reactor with the view of assessing its suitability for use in large-scale treatment plants. Copper supported on activated carbon was used as the catalyst. This catalyst has previously been shown to work well with organic containing wastewater (7). Experiments were first conducted in a slurry reactor with agitation to establish the suitability of the catalyst for use in the pilot plant TBR.

Experimental

Preparation and Characterization of Catalysts

Activated carbon was selected as the catalyst support and was impregnated with copper. The activated carbon was pre-treated by HCl (5 wt%) solution, and then soaked in copper nitrate solution (5 wt % in copper) for 24 hours. The impregnated carbon was calcined at 550°C for 18 hours. Details of the impregnation method have previously been reported (8).

To determine the amount of copper adsorbed on the activated carbon, a certain amount of catalysts was soaked in a known quantity of 65% nitric acid for 24 hours. The solution was then separated and the copper concentration determined by Inductively Coupled Plasma (ICP).

Evaluation of Catalyst Performance in a Batch Reactor

The performance of the catalyst was evaluated in a two-liter high temperature, high pressure reactor, equipped with a stirrer for mixing, an electric heating-jacket and an internal cooling coil for temperature control. The reactor was operated in the batch mode. The amount of catalyst added was 1g for 1.4 l of wastewater, which corresponds to a copper concentration of 58.7 mg/l. The detailed experimental procedures were similar to that reported in references 2 and 7.
Control experiments were performed using activated carbon without the impregnation of copper. The reaction temperature was 150°C and the reactor pressure 1 MPa. These conditions are much milder than that used in conventional WAO processes. The initial phenol concentration was 1,300 mg/l. Samples were withdrawn from the reactor at regular time intervals for the determination of COD and TOC.

The Trickle Bed Reactor

Fig. 1 shows a schematic diagram of the TBR equipment system. The reactor has an internal diameter of 96 mm and a catalyst bed height of 0.79 m. It is designed to be able to withstand a temperature of 300°C and a pressure of 10 MPa. 3.49 kg of Cu/AC were packed into the reactor. Pure oxygen was introduced into the reactor and the whole system allowed to reach the desired pressure. The heaters were switched on to heat the system until it rose to the required temperature. During the heating process some oxygen in the reactor was vented to balance the increase in pressure with temperature. After the pressure and temperature had been stabilized on pre-set values, the phenol containing wastewater was pumped into the reactor at a chosen flow rate. The phenol solution was mixed with oxygen in the static mixer and then enters the reactor via a shower head distributor. Flow rates were controlled to ensure that the flow is trickle. The reactor temperature and total pressure were fixed at 150°C and 1 MPa respectively.

The initial phenol concentration, liquid and gas flow rate were varied. Samples were withdrawn from the separator at the outlet of the reactor at equal time intervals of 30 minutes to establish steady state. The phenol concentration was determined by a UV-spectrophotometer and TOC by a Shimazu TOC analyzer.
Fig. 1. Schematic diagram of the trickle bed reactor

Results and Discussion

Catalyst Characterization

From the measurements of copper by ICP the amount of adsorbed copper on the catalyst was 8.2% of the total mass of catalyst. The physical properties of the activated carbon (Blank AC) and the catalyst (Cu/AC) are summarized as in Table 1.

**Table 1. Comparison of Physical Properties of Blank AC and Cu/AC**

<table>
<thead>
<tr>
<th>Property</th>
<th>Blank AC</th>
<th>Cu/AC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Density, g/ml</td>
<td>0.5956</td>
<td>0.6120</td>
</tr>
<tr>
<td>Macropore (d_p &gt; 60 Å) Volume, ml/g</td>
<td>0.7661</td>
<td>0.6843</td>
</tr>
<tr>
<td>Mesopore (20 Å &lt; d_p &lt; 60 Å) Volume, ml/g</td>
<td>0.1448</td>
<td>0.1305</td>
</tr>
<tr>
<td>Micropore (d_p &lt; 20 Å) Volume, ml/g</td>
<td>0.4747</td>
<td>0.4152</td>
</tr>
<tr>
<td>Total Pore Volume, ml/g</td>
<td>1.3856</td>
<td>1.2300</td>
</tr>
<tr>
<td>BET surface area, m²/g</td>
<td>1052.4</td>
<td>919.55</td>
</tr>
<tr>
<td>Distribution Peak Position</td>
<td>R=4.7A</td>
<td>R=5.1A</td>
</tr>
</tbody>
</table>


Table 1 shows the effects of calcination on the physical properties of activated carbon. There is about 10% loss of pore volume, but greater fractional loss was found in micropores than in meso- and macropores. This has also made the pore distribution peak position moved upward. The copper-activated carbon still has a high surface area and pore volume.

Catalyst Evaluation in a Batch CWAO Reactor

Figs. 2 and 3 show the removal of phenol and TOC in the batch reactor under three different conditions: without catalyst or carbon, with blank AC and with Cu/AC. The blank AC shows some catalytic activity in the removal of phenol and TOC, as compared with the case without any catalyst. This is consistent with results obtained by Fortuny et al. (4). However, the rate of phenol removal is considerably lower than that with Cu/AC. In the former case, 86.4% of phenol removal was obtained in 80 minutes. When Cu/AC was used, 87.8% of phenol removal was achieved within 20 minutes. Using the blank AC, the final TOC removal was 35.2% as against almost 60% TOC removal by Cu/AC.

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**Fig. 2 Phenol Removal by Cu/AC and Blank AC at 150 °C**

**Fig. 3 TOC Removal by Cu/AC and Blank AC at 150 °C**
Catalytic Oxidation of Phenol in the Pilot Plant TBR

The catalytic oxidation of phenol was studied in the pilot plant TBR under different liquid and gas flow rates at 150°C and 1 MPa. Results of phenol and TOC removal at steady state are shown in Table 2.

Table 2. Experimental Parameters and Results

<table>
<thead>
<tr>
<th>Experimental Run No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operation Pressure, MPa</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Operation Temperature, °C</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Liquid Flow Rate, L/min</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Liquid Superficial Velocity, mm/s</td>
<td>0.23</td>
<td>0.23</td>
<td>0.46</td>
</tr>
<tr>
<td>Liquid Residual Time, min</td>
<td>15.6</td>
<td>15.6</td>
<td>7.8</td>
</tr>
<tr>
<td>Liquid Reynolds Number, Re_L a</td>
<td>0.7</td>
<td>0.7</td>
<td>1.4</td>
</tr>
<tr>
<td>Gas Flow Rate, L(STP)/min</td>
<td>0.2</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Initial Phenol Concentration, mg/L</td>
<td>841.5</td>
<td>1512.5</td>
<td>875.3</td>
</tr>
<tr>
<td>Average Outlet Phenol Concentration, mg/L</td>
<td>38.1</td>
<td>25.1</td>
<td>14.9</td>
</tr>
<tr>
<td>Average Phenol Removal Rate, %</td>
<td>95.5</td>
<td>98.3</td>
<td>98.3</td>
</tr>
<tr>
<td>Initial TOC Concentration, mg/L</td>
<td>761.0</td>
<td>1449.5</td>
<td>752.5</td>
</tr>
<tr>
<td>Average Outlet TOC Concentration, mg/L</td>
<td>106.2</td>
<td>31.9</td>
<td>36.1</td>
</tr>
<tr>
<td>Average TOC Removal Rate, %</td>
<td>86.0</td>
<td>97.8</td>
<td>95.2</td>
</tr>
</tbody>
</table>

\[ a: \quad Re_L = \frac{\rho_L u_L d_p}{\mu_L (1 - \varepsilon_B)} \]

The results show that the TBR can effectively remove >90% of the phenol and TOC in the feed under different operating conditions. These results indicate that a TBR should be suitable for use in large-scale treatment plants.
Further experiments will be conducted to establish the limitations of the TBR and identify the optimal operating conditions. The TBR will be studied under a comprehensive range of conditions. A model will be developed and validated by further experimental results. A validated model can then be used as the basis for scale-up and design of a full scale TBR for a CWAO treatment plant.

Conclusions

The present study has demonstrated that activated carbon impregnated with copper is an effective catalyst for the oxidation of phenol. The catalyst has a high surface area and good catalytic activity. When the catalyst is used in a pilot plant trickle bed reactor, >90% removal of phenol and TOC were obtained. Since UV absorbance was used to monitor remaining phenol, the stated phenol removal is a lower bound to the actual removal. Furthermore, the TOC data showed that not only phenol but also the (perhaps more refractory) by-products were removed, indicating a usefulness for a wider variety of contaminants than just phenol. To conclude, the trickle bed reactor is suitable for use in large-scale plants for the treatment of wastewater containing high concentrations of organics.

Acknowledgments

The work described in this paper was supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. HKUST6232/00P).

Nomenclature

\( \text{Re}_L = \) Reynolds Number of liquid  
\( \rho_L = \) liquid density, kg/m\(^3\)  
\( u_L = \) superficial velocity of liquid, m/s  
\( d_p = \) diameter of catalyst particle, m  
\( \mu_L = \) viscosity of liquid, N/m\(^2\)-s  
\( \varepsilon_B = \) bed porosity
References:


