

## *Elimination of Phenol Content in Baiji Refinery Waste Water Using Ash Supported Cupper*

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### Abstract

High level of phenolic compounds is realized in some refinery waste water; fly ash waste of electrical station is applied in a trickle bed reactor to eliminate phenolic compounds contents in that wastewater. The fly ash with a cupper added was applied at different operation conditions namely pressure (5, 10, and 15), solution pH (5, 7 and 9), and 2-3 hr<sup>-1</sup> liquid hourly space velocity. The fly ash catalyst exhibited an optimum performance in the reactor at 2 hrs<sup>-1</sup>, 150 °C and 15 bar with a pH of 5 with a phenol conversion of 93.43% within a time period of 3hrs.

**Key Words:** Wet oxidation, Wastewater, Catalyst, Phenolic compounds

تقليل نسبة الفينول في مياه فضلات المصافي باستخدام الرماد السائد للنحاس

### الخلاصة

لوحظ وجود نسب عالية من الفينول في مياه فضلات المصافي، و يوجد الرماد الملقى كفضلات من وحدة توليد الطاقة الكهربائية في المحطة الحرارية و الذي تم استخدامه في هذا البحث كعامل مساعد في مفاعل الطبقة المتقطرة لتقليل نسبة المركبات الفينولية في مياه الفضلات. تم استخدام هذا الرماد المضاف اليه نسبة من النحاس في ظروف مختبرية مختلفة و هي ضغط (5 و 10 و 15) جو، حامضية المحلول (5 و 7 و 9) و سرعة فراغية للسائل 2 و 3 ساعة<sup>-1</sup>. اظهر الرماد ظروفًا مثلى للتشغيل عند 2 سرعة فراغية، 150 درجة مئوية و 15 جو مع 5 دالة حامضية حيث كانت نسبة التحول 93.44% خلال اقصى زمن تشغيل داخل المفاعل و هو 3 ساعات.

**الكلمات الدالة:** أكسدة رطبة، مياه فضلات، عامل مساعد، مركبات فينولية

### Introduction

Phenol and its derivatives have a significant presence in many industrial wastewater streams. Due to their toxicities, a variety of treatment techniques have been studied, including biological degradation<sup>[1]</sup>, distillation<sup>[2]</sup>, adsorption<sup>[3]</sup>, membrane extraction<sup>[4]</sup>, photocatalysis<sup>[5]</sup> and supercritical water oxidation (SCWO)<sup>[6]</sup>. The process can be controlled by two steps; (i) transfer of oxygen to the liquid phase; and (ii) reaction between dissolved oxygen and organic<sup>[1]</sup>.

Catalytic wet air oxidation (CWAO) is notable, therefore, as an economically and

technologically viable physico-chemical method, the high performance of which has been demonstrated<sup>[7-9]</sup>. In studies of CWAO, phenol is often chosen as a model pollutant because it is particularly damaging and prevalent; being an important raw material widely used in dye, pharmaceutical, petrochemical and plasticizer industries. Metal oxides can be classified according to the physico-chemical properties. One of these properties is the stability of metal oxide. Metals with unstable high oxidation state oxides, such as Pt, Pd, Ru, Au, and Ag do not

perform stable bulk oxides at moderate temperatures. Most of the commonly used metal oxide catalysts (Ti, V, Cr, Mn, Zn, and Al) have stable high oxidation state oxides. Fe, Cu, Co, Ni, and Pb belong to group with intermediate stability of high oxidation state oxides<sup>[2]</sup>.

Zhao et. al. <sup>[10]</sup> showed that CuO/AC catalyst-sorbent (an activated carbon-supported copper oxide) is capable of adsorbing phenol from the water phase at room temperature and catalyzing phenol oxidation at temperature below 300 °C. Although its performance is much better than that of activated carbons reported in the literature, the phenol adsorption capacity of the CuO/AC was not determined, and changes in the capacity in consecutive cycles were not analyzed, and moreover the nature of the residue is not studied. AC is gaining popularity; because of its good performance that could be related to its high adsorption capacity and ability to generate oxygenated free radicals promote the oxidation reaction. Solid wastes are produced in large quantities from various industries each year. The most important solid wastes from industry include mixed fly ash produced from Baiji power plants. Currently, most of the fly ash is dumped of in landfills. However, fly ash contains silica, alumina and iron oxides, which are thermally stable and can be used as an adsorbent and catalyst supports <sup>[11-14]</sup>. Catalytic wet air oxidation using AC can be an alternative and cost effective way of wastewater treatment. Through this work, a modified type of Cu/Activated carbon was prepared and used as a catalyst to oxidize phenol in Baiji refinery wastewater which contains a dangerous level of 1000 ppm.

## Experimental work

### Materials

Phenol with 99.5% purity, molecular weight of 94.11 gm/mol with boiling range of 180-182°C, supplied by E-Merck was used in preparation of test solutions using deionized water as a dilution copper chloride salt was used with 99.5% purity from Sigma. Fly ash was obtained from a coal-based Baiji power station as shown in table (1); it was used without further treatment. 99.9% oxygen was supplied from Tikrit Teaching

Hospital. A stock solution of phenol at 1000 ppm was prepared using distilled water. For synthesis of Cu loaded catalysts, an impregnation method was used. Typically, 2.16 g of CuCl<sub>2</sub> was dissolved in 100 mL of distilled water. Then 6 g of fly ash was added followed by continuous stirring at 90 °C until total evaporation of H<sub>2</sub>O. Furthermore, the sample was dried at 130 °C overnight and calcined at 450 °C for 4 hrs in air. Then the catalyst was stored in a desiccator until use.

### Apparatus and procedure

The scheme of the experimental setup is shown in Figure (1). The continuous oxidation of phenol is carried out in a packed bed reactor in co-current down-flow mode with pure oxygen. The fixed trickle bed reactor was installed in postgraduate laboratory of Chemical Engineering Department in Tikrit University. It consists of SS-316 tubular reactor, 40 cm height and 15gm catalyst. At different liquid hourly space velocity, a waste water sample (5 mL) was withdrawn into a product vial, to be tested in HPLC DIONEX (UV (JYNKOTEK)/VIS160S). Determination of the intermediate components concentrations was achieved using C18 reverse phase column (Philips, 5µm 25 x 0.4 cm). A mixture of 65% / 35% vol. of methanol to water (slightly acidified) was used as a mobile phase. For all compounds the flow rate of the mobile phase is 1 ml/min. Detection of compounds was performed using UV absorbance at a wavelength of 254 nm.

### Characterizations of catalyst

#### 1. Catalyst Composition

The chemical analysis of the prepared catalyst was achieved using Atomic Absorption spectrophotometer Shimadzu AA6200). The particles were crushed, dipped in HCl and distilled water solution for 1 hour under stirring to dissolve the Cu and other elements in ash, few drops of H<sub>3</sub>PO<sub>4</sub> were added to ensure dissolving of those elements. The solution is diluted with distilled water then Cu and other elements concentrations were measured to ensure a concentration of 4.5% and other concentrations of constituents.

#### 2. Surface area measurements

Catalyst surface area was determined using BET Quanta Chrome Autosorb 6B apparatus system supplied by Quanta chrome Corporation (USA).

## Results and Discussion

### Surface properties

Some properties of as received fly ash are listed in Table (1). As it can be seen, fly ash predominantly composed of considerable quantities of alumina and silica with some iron oxide and calcium oxide, alumina with a fair surface area of 340.3 m<sup>2</sup>/gm and a good pore volume distribution in a range of 45-1000 Å.

Figure (2) shows the SEM image which shows that most Cu/FA particles are spherical with particle size of 0.1–0.3 µm. Some irregular particles are also evident. Elemental mapping shows good distribution of Cu in Cu/FA.

### Phenol conversion

From Figure (3), it is clear that most of the phenol was rapidly removed within 2.5 hrs at pH =7 and liquid hourly space velocity (LHSV) of 2 hr<sup>-1</sup> and it initially increases, up to a maximum, and then falls when time on stream increase to 3 hrs., indicating that some of the phenol was converted into other intermediate organic species rather than directly into inorganic carbon species (i.e., CO<sub>2</sub> and CO). This is the general trend of phenol conversion in the present study.

### Effect of operating pressure

Figure (4) depicts the effect of operating pressure at certain conditions of pH of 7 and 2 hr<sup>-1</sup> LHSV. As expected, this figure shows a proportional relationship between pressure and phenol conversion. The increase in phenol conversion may be attributed to the increases in oxygen solubility which leads to more efficient oxidation reaction. As indicated before from literatures<sup>[15-17]</sup> phenol conversion depends besides the bed characteristics on the velocity of liquid phase and on physiochemical properties of the flowing fluids, regarding the fluids physiochemical properties, mainly gas density is influenced by pressure. Thus for this situation a higher gas density produces a higher interfacial drag force equivalent to a higher pressure gradient hence the

conversion increases proportionally from 75.3% to 83.84% and then to 90.06% when pressure of 5 bar was doubled to 10 bar and then tripled to 15 bar. This result is attributed to the fact that elevated pressure results in higher density, which consequently produces a higher drag at gas-liquid interphase and lower inertia force of the gas phase.

### Effect of pH

The acidity of the reaction solution is an important factor in controlling the rate of the catalyzed oxidation (catalytic activity) of phenol over carbaneous catalyst, and the toxicity of the resulting effluents in wastewater<sup>[18]</sup>. This is evident in Figures (5) and (7), it is shown at a certain pressure of 15 bar (optimum operating pressure in this study) that the final conversion increases slightly from 90.06% to 93.43% when pH decreases from 7 to 5, and dramatically falls to 70.24% when pH increases to 9 at 2 hr<sup>-1</sup> LHSV and the corresponding values of increasing and decreasing are 86.83%, 87.74% and 64.24% at 3 hr<sup>-1</sup> LHSV. The initial oxygen surface groups present on the Cu/FA are responsible for functioning of this acidity. The surface groups that are desorbing as CO<sub>2</sub> seem to have a somewhat higher influence on the catalytic activity although all the oxygen surface groups show a beneficial effect<sup>[10]</sup>. This is similar to the rate change following the change of the solution acidity in the oxidation of phenol catalyzed by natural peroxidase. The optimum acidity of the system in the present study was pH 5.0 because the ionic state on the surface of fly ash is controlled by the acidity of the reaction system and, hence, the spatial conformation of the substrate is transformed and the catalyst activity is changed depending on the acidity of the reaction system. Moreover, the stability of the intermediate formed from the substrate and the active species would also be changed with changing acidity of the reaction system<sup>[8]</sup>. Therefore, the rate of the catalytic reaction is controlled by the acidity of the reaction system, which must be strictly controlled in the carbon catalysis reaction. This finding is consistent with those of Jin et

al<sup>[19]</sup>, Eugenia et al<sup>[20]</sup> and Quintanilla et al.<sup>[21]</sup>.

### Effect of LHSV

The effect of LHSV on phenol conversion is presented in figure (8) at pH = 7 and 15 bar. It was seen that increasing LHSV has an adverse impact on phenol conversion. It is clearly evident that a phenol conversion of 92.74 % is achieved at LHSV = 2 hr<sup>-1</sup>, but at 3 hr<sup>-1</sup> LHSV phenol conversion decrease to 88.43% at the maximum time on stream. So as liquid flow rate increases, phenol conversion decreases, this due to reduce the space time of reactant in the reactor (i.e. reducing the time required for phenol reaction with oxygen over the catalyst).

Moreover, higher liquid flow rates give greater liquid hold up which evidently decreases the contact of liquid and gas reactants at the catalyst active site, by increasing the film thickness. While at low liquid flow rate, the liquid resides in the column for a longer time. This behavior can be described under the light of residence time, where increasing liquid flow rate reduces the residence time of the reactant thus reducing the time of reaction of phenol with oxygen (reactant gas) which is proved by Devlin and Harris<sup>[22]</sup>. Moreover, higher liquid flow rates give greater liquid holdup which evidently decreases the contact of liquid and gas reactants at the catalyst active site by increasing film thickness. It is illustrate the effect of LHSV on intermediate compounds, where acetic acid, formic acid and malic acid concentration increase with increasing LHSV, this is due to reduce the time required to achieve complete oxidation. These results are in agreement with Singh et al, Guo and Al Dahan<sup>[15]</sup> and Sharma et.al<sup>[22]</sup>.

### Conclusions

Phenol that constitutes an important class of organic pollutant in industrial wastewaters can be removed to substantial extent by catalytic wet oxidation in a high pressure reactor.

With Cu as promoter (Cu/FA), CWAO of phenol was efficient at 150 °C. It is well-

dispersed and narrow size distribution ranging from 0.1 to 0.3 μm due to good impregnation method which was certified by different approaches such as BET, and SEM.

Elimination of phenol (93.43%) was achieved within time on stream similar to that of conventional setups (3 hrs). The elimination rate was increased significantly by decreasing the initial pH of the feed solution (up to 5) and increasing the operating pressure (up to 15 bar), while it decreases with increasing liquid hourly space velocity (up to 3 hr<sup>-1</sup>).

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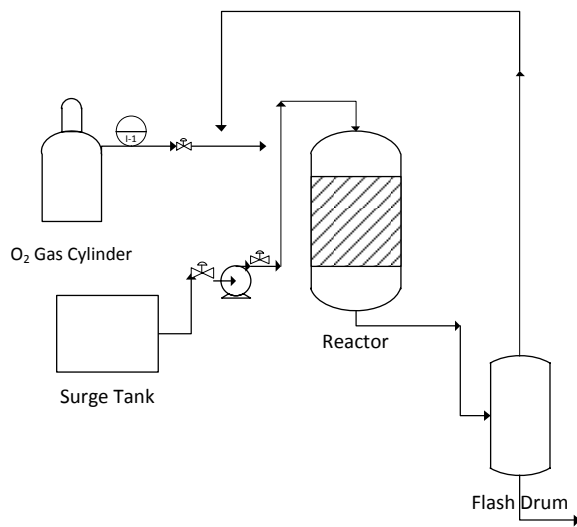


Figure (1) Experimental setup

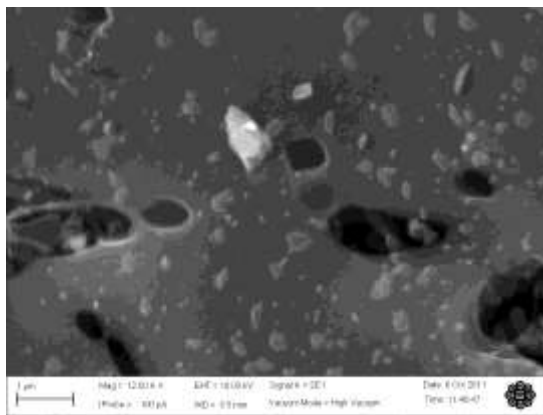


Figure (2) SEM image of Baiji fly ash

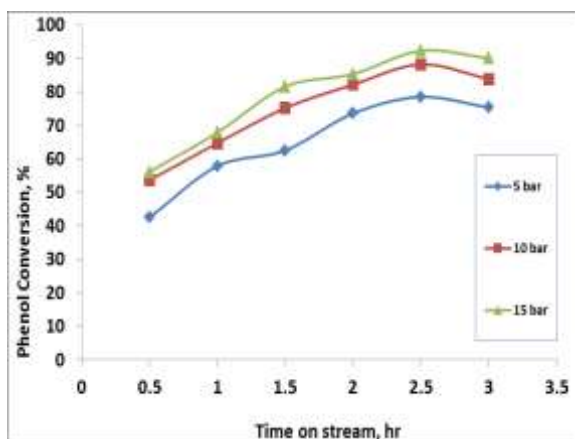


Figure (3) Phenol conversion at pH= 7 and LHSV= 2 hr<sup>-1</sup> and different operating pressure

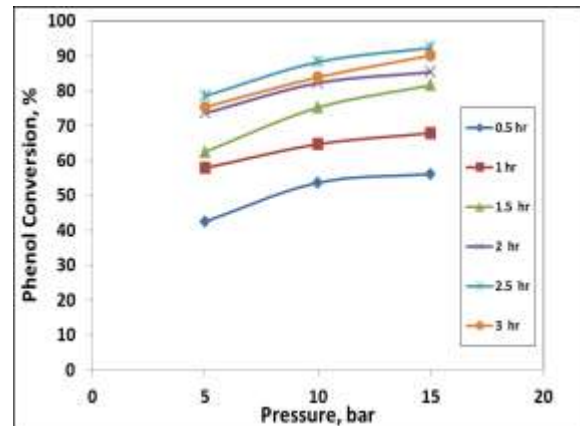


Figure (4) Effect of operating pressure on phenol conversion at pH= 7 and LHSV= 2 hr<sup>-1</sup>

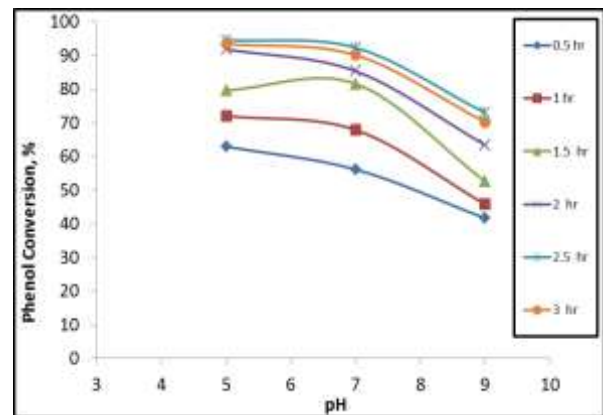


Figure (5) Effect of solution pH on phenol conversion at 15 bar and LHSV= 2 hr<sup>-1</sup>

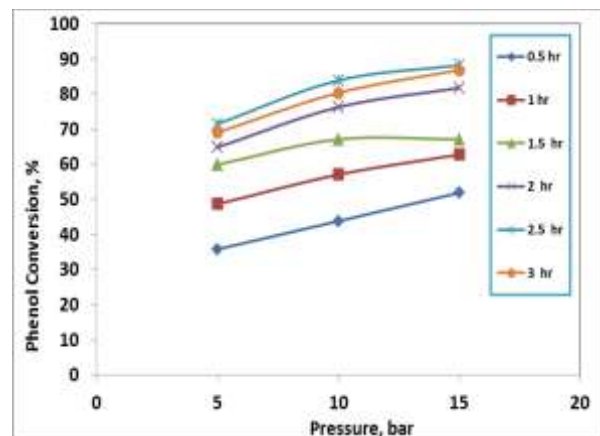
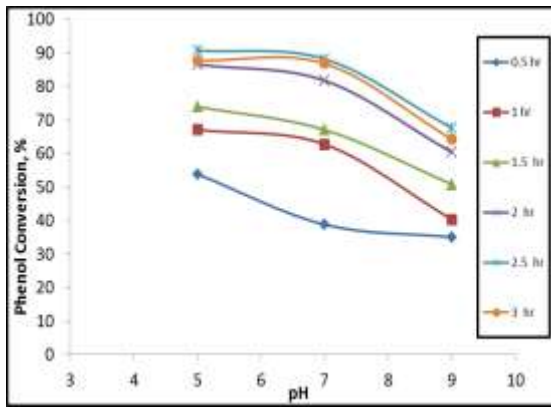
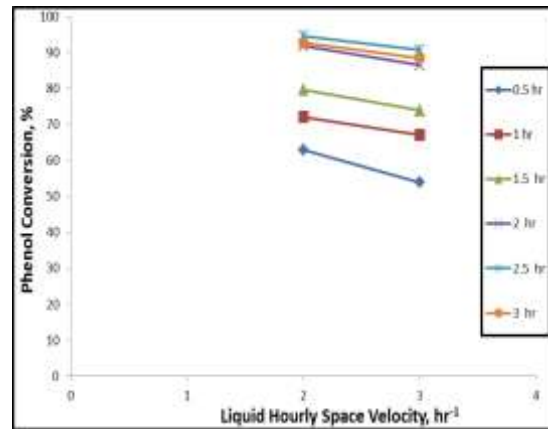


Figure (6) Effect of Operating pressure on phenol conversion at pH= 7 and LHSV= 3 hr<sup>-1</sup>



**Figure (7) Effect of pH on phenol conversion at 15 bar and LHSV= 3 hr<sup>-1</sup>**



**Figure (8) Effect of liquid hourly space velocity on phenol conversion at 15 bar and pH=5**