

CWAO of phenol over activated carbon catalysts with hydrogen peroxide as promoter

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Abstract

Catalytic wet air oxidation (CWAO) of phenol over activated carbon catalysts in presence of a typical promoter such as hydrogen peroxide has been studied. The experiments were carried out in a trickle-bed reactor at given operating conditions ($C_{inlet\ phenol} = 1\text{ g/L}$, $C_{inlet\ H_2O_2} = 5\text{ g/L}$, $T = 127\text{ }^\circ\text{C}$, $P_T = 8\text{ atm}$ and $W_{CAT} = 2.5\text{ g}$) in a wide range of space time values ($W/Q_L = 20\text{-}320\text{ g}_{CAT}\cdot\text{h/L}$). The effect of the addition of hydrogen peroxide was analyzed in terms of initial reaction rate, distribution of intermediates and toxicity of the effluent. To this purpose, the experimental profiles of phenol and TOC conversions vs. space time were obtained, intermediates were properly identified and the phenol oxidation pathway proposed. Toxicity of the effluents was also measured. The results showed that due to the employ of hydrogen peroxide which leads to the production of hydroxyl and hydroperoxy radicals to initiate the reaction, faster initial reaction rates of phenol and TOC were achieved (rates were increased around 90 and 60%, respectively). Phenol was fully hydroxylated to hydroquinone which was instantaneously oxidized to p-benzoquinone. This quinone was oxidized to CO_2 and low molecular weight acids such as maleic, oxalic, acetic and formic. Acetic acid was the only refractory specie at the operating conditions employed. Concentrations of the cyclic intermediates (hydroquinone and p-benzoquinone) were lower in presence of hydrogen peroxide; therefore, detoxification of the wastewater was significantly enhanced. Wet oxidation at space times above $160\text{ g}_{CAT}\cdot\text{h/L}$ should be enough for the disposal of the liquid effluent in a municipal wastewater treatment plant. These results present CWAO with activated carbon catalysts promoted by hydrogen peroxide as a promising technology to treat phenolic wastewaters. As far as toxicity of the effluent is concern, it is preferable to use a promoter than to work only with activated carbon as catalyst or support.

Keywords: wet air oxidation; hydrogen peroxide; activated carbon; wastewater; phenol

1. Introduction

Catalytic wet air oxidation (CWAO) is an effective technology to treat aqueous hazardous wastes, especially when these are too dilute to incinerate and too concentrated for a biological treatment (COD:10-100 g/L). It is used for the transformation of bioresistant pollutants into biodegradable intermediates and CO₂. This reaction occurs through a radical mechanism. CWAO uses molecular oxygen as oxidant and operates at $T < 250$ °C and $P < 100$ (Bhargava et al., 2006). The employ of catalysts allows reducing the operating conditions. Of course, an heterogeneous catalyst is desirable from an economical point of view, the issue is to find long term stable catalysts. Deactivation by deposition of carbonaceous material on the catalyst surface, in the case of the noble metal catalysts (Hamoudi et al., 1998; Pirkanniemi et al., 2002) and leaching of the active phase, due to the acidity of the reaction media, in the case of metal oxides catalysts (Njiribeako et al., 1978; Mantzavinos et al., 1997) can take place. Research efforts have been addressed to solve these problems like buffered the reaction media at basic pH (Santos et al., 2004a). Bare activated carbons have been successfully employed (Tukac and Hanika, 1998). The oxygenated surface groups, mainly the most acidic ones, are the active sites for the oxidation reaction (Quintanilla et al., 2007). However, restrictions in the operating conditions need to be considered ($T < 160$ °C and $P_T < 10$ atm) in order to avoid carbon combustion (Mundale et al., 1996).

There are different options to increase conversion and mineralization of a pollutant under these mild operating conditions: to increase the number of oxygenated surface groups, to incorporate a metal on the activated carbon, to use a free radical promoter to initiate the reaction and combinations of these options. The two former options were already studied in a previous work (Quintanilla et al., 2007a). Activated carbons after oxidative treatments of different degrees were tested in the CWAO of phenol according to their activity, selectivity and the detoxification achieved in the reactor effluent. These modified activated carbons were also employed as supports in home-made iron-activated carbon catalysts (Fe/AC). Fe/AC catalysts gave better results than their corresponding supports. Activated carbon without further oxidative treatment being the best choice to prepare the Fe/AC catalysts for the CWAO of phenol under mild conditions ($T = 127$ °C and $P_T = 8$ atm). This catalyst presented an appropriate stability. Fe leaching was negligible (< 2%) during the 216 h tested in which catalytic activity remained invariable.

In the non-catalytic WAO systems, the use of a promoter such as hydrogen peroxide enhances phenol oxidation rate (Lin and Wu 1996; Kolaczowski et al., 1997). The reactions that produce the initial free radicals are:



The presence of activated carbon favours hydrogen peroxide decomposition according to the following mechanism (Oliviera et al., 2004):

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In presence of organic compounds the decomposition is strongly inhibited due to the adsorption of the organic compounds on the active sites of the carbon and/or the reaction of the organic compounds with the radicals formed in the hydrogen peroxide decomposition.

The viability of the hydrogen peroxide promoted CWAO processes with activated carbon catalysts has been scarcely studied. Rubalcaba et al., (2007) studied the feasibility of this treatment from a biodegradability point of view. Oxidation of different phenolic compounds was carried out in a trickle-bed reactor at 140 °C and 2 atm of oxygen partial pressure. Under these conditions, higher conversions of the pollutants were achieved although effluents were not biodegradable (readily biodegradable fraction lower than 8%). However, biodegradability was increased comparing to the treatment in absence of hydrogen peroxide.

The objectives of this work were to demonstrate the beneficial effect of hydrogen peroxide in CWAO processes with activated carbons not only on the conversions but also on detoxification of phenolic wastewaters by using appropriate operating conditions. Toxicity is linked to intermediate species; therefore, reaction pathway was also elucidated. Stability of the activated carbon catalyst was also analyzed. The results were compared to those obtained with Fe/AC, a promising catalyst in the wet oxidation technology.

2. Experimental

2.1. Catalyst

A granular activated carbon commercialized by Merck (Ref.:102514) was used as received (particle size ranged from 0.5 to 1 mm). This catalyst presents the following properties: $S_{\text{BET}} = 974 \text{ m}^2/\text{g}$, $A_t = 85 \text{ m}^2/\text{g}$, $V_{\text{micropores}} = 0.420 \text{ cm}^3/\text{g}$ and $V_{\text{mesopores}} = 0.126 \text{ cm}^3/\text{g}$.

2.2. Experimental set-up and chemical analyses

Oxidation experiments were conducted in a standard wet oxidation unit at bench scale. The main component is a trickle-bed reactor consisting of a stainless steel tube of ½" of diameter with a steel porous plate at 100 mm from the entrance where the catalyst was placed. The temperature was measured by a thermocouple located into the catalytic bed. The liquid and gas phases were passed through the bed in cocurrent down-flow. Pure oxygen was used as oxidising agent. Detailed information about the

components and operation procedure of this unit has been reported elsewhere (Quintanilla et al., 2006).

An aqueous solution of 1 g/L of phenol at pH 3.5 (adjusted with H₂SO₄) was continuously fed to the reactors at different flow rates (0.125–2 mL/min) to cover the experimental range of space-time values ($W/Q_L = 20\text{--}320 \text{ g}_{\text{CAT}} \text{ h/L}$). A 91.6 NmL/min pure oxygen flow was continuously passed in all the experiments. The oxidation runs were performed at 65 and 127 °C and 8 atm of total pressure using 2.5 g of activated carbon. In all the experiments the stoichiometric amount of hydrogen peroxide (5 g/L) for the complete mineralization of a solution of 1 g/L of phenol was always employed.

The progress of the reaction was followed by taking periodically liquid samples from the reactor outlet. The steady state was reached after 4–8 h of operation, depending on the space time employed. The liquid samples were analysed by different procedures. Phenol and ring compounds were determined by HPLC (Varian, mod. ProStar), low molecular weight acids by anionic suppression IC (Metrohm, mod. 761 Compact IC) and total organic carbon (TOC) using a TOC analyzer (O.I. Analytical, model 1010). Hydrogen peroxide concentration was quantified by colorimetric titration using the Ti(SO₄)₂ method.

Toxicity of the liquid effluent, expressed as TU₅₀, was determined by a bioassay in a Microtox M500 Analyzer (Azur Environmental) following the standard Microtox test procedure (ISO 11348-3, 1998). This bioassay is based on the decrease of light emission by *Photobacterium phosphoreum* as the result of its exposure to a toxicant. The toxicity units of the sample are calculated as:

$$\text{TU}_{50} = \frac{100}{\text{IC}_{50}} \quad (6)$$

The parameter IC_{50} is defined as the dilution ratio of the wastewater sample that yields the 50% reduction of the light emitted by the microorganisms.

Before measuring the toxicity, the pH values of all the samples were readjusted between 6 and 7 to prevent the pH effect. The microorganisms were purchased from Microtox Acute Reagent supplied by I.O. Analytical. For further information about this assay and its application in CWAO effluents see (Santos et al., 2004b).

3. Results and discussion

3.1. CWAO promoted by H₂O₂

Evolution of phenol and TOC conversions vs. space time are shown in Figure 1. Higher phenol and TOC conversions were obtained in presence of hydrogen peroxide. Initial reaction rates for phenol are 3 and 42 g_{Phenol}/(kg_{CAT}·h) and for TOC 1.8 and 12

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$g_{\text{carbon}}/(\text{kg}_{\text{CAT}}\cdot\text{h})$ in absence and presence of hydrogen peroxide, respectively. As was expected, the employ of hydrogen peroxide significantly enhanced the oxidation and mineralization rates of phenol, above all the former one. To learn about the role of oxygen in the initiation of the reaction, some additional experiments were carried out under nitrogen atmosphere instead of oxygen. Figure 2 shows the initial rates corresponding to the oxidation of phenol and TOC. The lowest activity observed in the system $\text{AC}+\text{H}_2\text{O}_2+\text{N}_2$ clearly revealed that oxygen participated in the initial formation of radicals (eq. 2) for phenol oxidation. Initial TOC rates were affected by the presence of O_2 in far less extension which indicated that oxygen itself mainly participated in the propagation step.

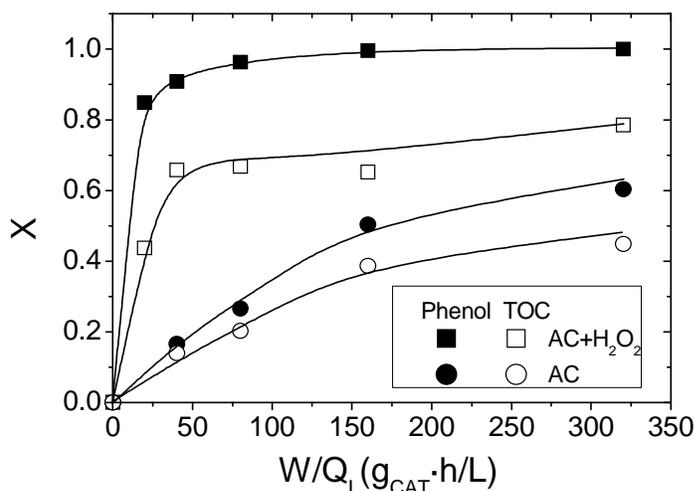


Figure 1. Influence of addition of hydrogen peroxide on phenol and TOC removal. Operating conditions $C_{\text{Phenol}_0} = 1 \text{ g/L}$, $C_{\text{H}_2\text{O}_2} = 5 \text{ g/L}$, $\text{pH}_0 = 3.5$, $P_T = 8 \text{ atm}$, $T = 127 \text{ }^\circ\text{C}$, $Q_{\text{O}_2} = 91.6 \text{ NmL/min}$ and $W = 2.5 \text{ g}$.

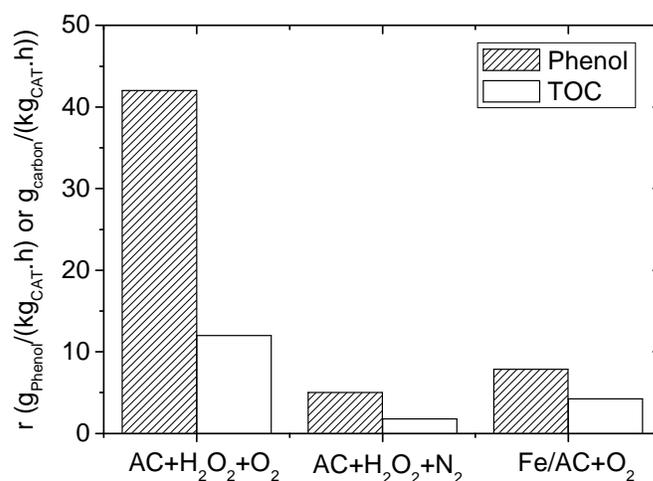


Figure 2. Influence of oxygen on initiation phenol and TOC removal. Operating conditions: $C_{\text{Phenol}_0} = 1 \text{ g/L}$, $C_{\text{H}_2\text{O}_2} = 5 \text{ g/L}$, $\text{pH}_0 = 3.5$, $P_T = 8 \text{ atm}$, $T = 65 \text{ }^\circ\text{C}$ and $W = 2.5 \text{ g}$.

In spite of the enhancement in the reaction rates, there are higher amounts of intermediate species in the reactor effluent in presence than in absence of hydrogen peroxide, as proved the difference between phenol and TOC conversion curves (Figure 1). The identified intermediate species were p-benzoquinone and low molecular weight acids such as maleic, acetic, oxalic and formic. In the oxidation route of carbon based catalysts in absence of a promoter, p-benzoquinone was mainly mineralized to CO_2 and H_2O through oxalic acid with Fe/AC catalysts (Quintanilla et al., 2006) or formic acid with AC catalysts (Eftaxias et al., 2006). In presence of hydrogen peroxide, the mineralization seems not to occur and higher concentration of low molecular weight acids remain in the effluent, as shows Figure 3, in which the normalized concentration of identified intermediates in mg/L of carbon (C_C/C_{C_0}) are plotted vs. space time. The oxidation of p-benzoquinone is faster in presence of hydrogen peroxide therefore it is detected in low amounts. Low molecular weight acids, in general, are quite refractory species (Figure 3) although only acetic acid is totally refractory to the oxidation at the conditions employed. The reaction pathway given in Figure 4 takes into account the concentration profiles observed for each intermediate specie through space time. According to this Figure 4, phenol is hydroxylated in *para* position to yield hydroquinone which is instantaneously oxidized to p-benzoquinone. p-Benzoquinone broke to yield CO_2 and low molecular weight acids. It is remarkable that in presence of hydrogen peroxide, phenol disappeared through only one route, oxidation to p-benzoquinone, whereas in absence of the radical promoter, also a second route due to carboxylation of phenol to p-hydroxybenzoic acid was observed (Santos et al., 2005; Eftaxias et al., 2006; Quintanilla et al., 2006). Therefore, the addition of hydrogen peroxide gives preference to phenol hydroxylation route, the most toxic one (Santos et al., 2004a).

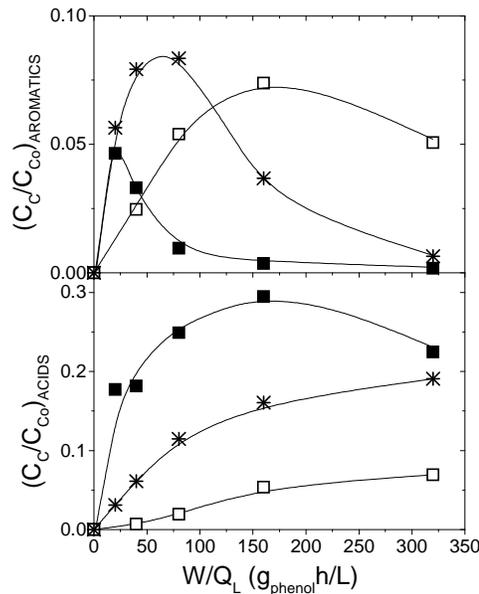


Figure 3. Influence of addition of hydrogen peroxide on the distribution of intermediates. Operating conditions $C_{\text{phenol}_0} = 1 \text{ g/L}$, $C_{\text{H}_2\text{O}_2} = 5 \text{ g/L}$, $\text{pH}_0 = 3.5$, $P_T = 8 \text{ atm}$, $T = 127 \text{ }^\circ\text{C}$, $Q_{\text{O}_2} = 91.6 \text{ NmL/min}$ and $W = 2.5 \text{ g}$.

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As a consequence of the different oxidation rates of phenol and intermediate species, distribution of intermediates was different in presence of hydrogen peroxide (Figure 3) and therefore toxicity of the effluent was also affected as can be observed in Figure 5. In presence of hydrogen peroxide, the maximum in the toxicity, expressed as TU_{50} , took place at shorter space time values and was significantly lower. The curves follow the same profile as the concentration of aromatic intermediates.

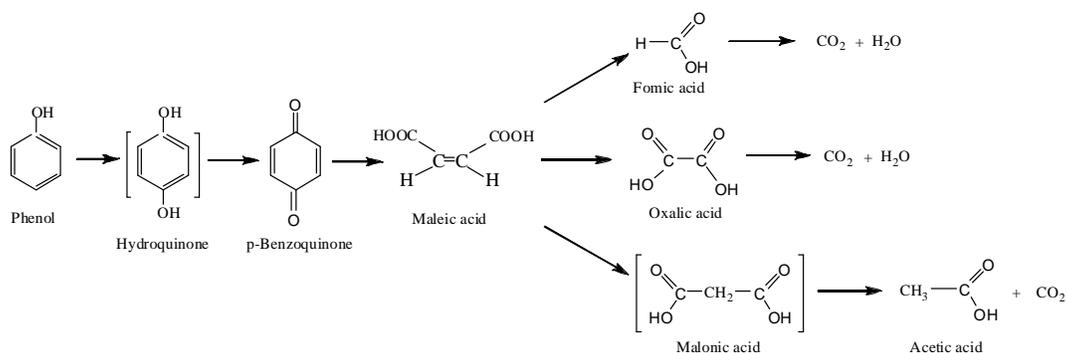


Figure 4. Reaction pathway for the wet oxidation of phenol with AC catalysts promoted by hydrogen peroxide.

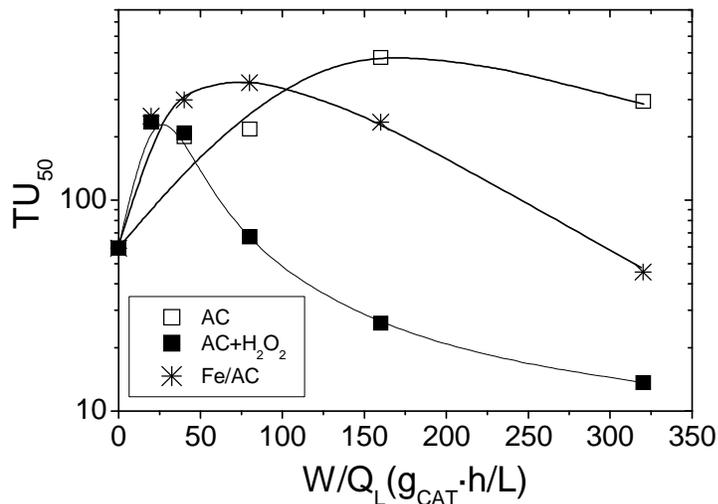


Figure 5. Influence of addition of hydrogen peroxide on toxicity of the effluent. Operating conditions $C_{\text{Phenol}_0} = 1$ g/L, $C_{\text{H}_2\text{O}_2} = 5$ g/L, $\text{pH}_0 = 3.5$, $P_T = 8$ atm, $T = 127$ °C, $Q_{\text{O}_2} = 91.6$ NmL/min and $W = 2.5$ g.

3.2. Stability and reproducibility of the catalyst

To learn about stability of the activated carbon catalyst, a long term experiment of 130 h was carried out at two space times values 40 and 80 $\text{g}_{\text{CAT}} \cdot \text{h}/\text{L}$. The results collected in Figure 6 showed the appropriate stability in phenol and TOC conversions.

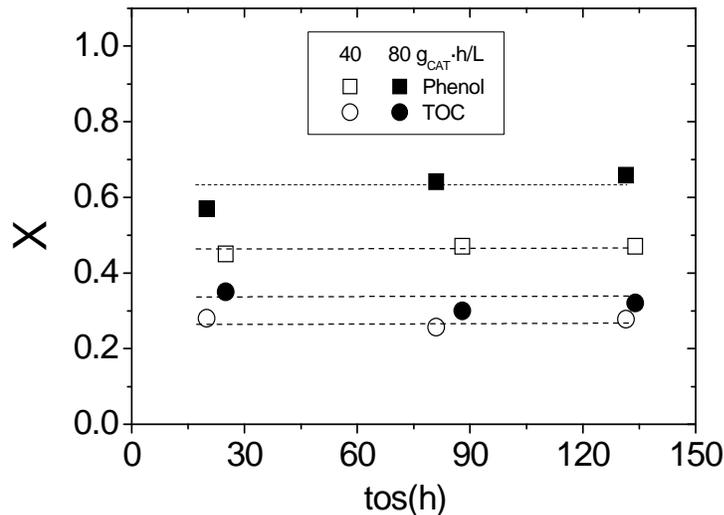


Figure 6. Long-term activity of the AC catalyst in presence of hydrogen peroxide. Operating conditions $C_{\text{Phenol}_0} = 1 \text{ g/L}$, $C_{\text{H}_2\text{O}_2} = 5 \text{ g/L}$, $\text{pH}_0 = 3.5$, $P_T = 8 \text{ atm}$, $T = 65 \text{ }^\circ\text{C}$ and $Q_{\text{O}_2} = 91.6 \text{ NmL/min}$.

3.3. CWAO with Fe/AC catalysts vs. CWAO with AC promoted by H_2O_2

We studied in previous works (Quintanilla et al., 2006 and 2007) that Fe/AC catalyst was a promising carbon-based catalyst for the CWAO of phenolic wastewaters. In this work, we present the CWAO with activated carbon catalysts promoted by hydrogen peroxide also as a very competitive treatment to decontaminate phenolic wastewater. To compare both different oxidation processes, results corresponding to CWAO with an Fe/AC catalyst have been included in Figures 2, 3 and 5. Higher initial reaction rates of phenol and TOC (Figure 2), lower concentration of aromatics species (Figure 3) and far lower toxicity of the effluents (Figure 5) were obtained when a radical promoter such as hydrogen peroxide was used at the operating conditions employed in this work ($T = 127 \text{ }^\circ\text{C}$ and $P_T = 8 \text{ atm}$). Therefore, it can be concluded that the use of hydrogen peroxide in the CWAO of phenol with activated carbon catalysts is more efficient from an environmental point of view than the use of Fe/AC catalysts. Further research should be focused now on the optimization of the required amount of hydrogen peroxide to minimize costs, the bottleneck for the scale-up of this process.

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4. Conclusions

CWAO with activated carbon catalysts in presence of a typical promoter such as hydrogen peroxide is a promising technology to treat phenolic wastewaters. Due to the addition of the promoter, detoxification of the wastewater was seriously enhanced. Wet oxidation at space times above 160 $g_{CAT}\cdot h/L$ should be enough for the disposal of the liquid effluent in a municipal wastewater treatment plant. This faster detoxification is due to the faster initial reaction rates of phenol and TOC triggered by the presence of hydroxyl and hydroperoxy radicals coming from hydrogen peroxide. Rates were increased around 60 and 90%, for phenol and TOC, respectively. These radicals are produced from the decomposition of hydrogen peroxide and the reaction of hydrogen peroxide with oxygen, respectively. The intermediate species detected were mainly p-benzoquinone and low molecular weight acids such as maleic, oxalic, acetic and formic. Acetic acid was the only refractory specie to the wet oxidation at the conditions employed. Further experiments are now in progress focused on the optimization of hydrogen peroxide in the feed stream in order to minimize costs.

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