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Catalytic wet oxidation of phenol on active carbon: stability, phenol conversion and mineralization

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Abstract

Catalytic wet oxidation (CWO) of phenol as model pollutant has been studied by using three commercial active carbons (AC) as catalysts. Runs were carried out in a fixed bed reactor, at 160 °C of temperature and 16 bar of oxygen pressure. All the AC tested showed high catalytic activity in both phenol conversion and mineralization. Small amounts of intermediates were found in phenol oxidation being the main compounds detected hydroquinone, *p*-benzoquinone, *p*-hydroxybenzoic acid, catechol and short chain acids (SCA) C_2–C_4, mainly maleic, acetic and formic acids. Only small amounts of oxalic acid were found in the liquid phase. These SCA were the most refractory compounds to catalytic oxidation.

Keywords: Catalytic wet oxidation; Phenol; Active carbon; Oxidation route; Stability

1. Introduction

The removal of refractory pollutants in industrial wastewaters is nowadays an environmental and economic problem. If it is not possible to remove these pollutants employing the standard biological treatments, the organic compounds in these effluents must be removed by alternative methods.

By now, one of the well-established technologies is the adsorption of the pollutant onto active carbon (AC). The economy of the process makes necessary the regeneration of the spent carbon being the thermal and the wet air oxidation (WAO), the most common procedures for this purpose. If the oxidation of the adsorbed compounds is carried out at high temperature, a significant burning of the carbon can take place [1].

Moreover, if the pollutant concentration is high enough, the oxidation of organic pollutants is preferred to the adsorption process [2]. Among the methods employed to oxidize refractory pollutants, the advance oxidation processes (AOPs) [3] and the WAO processes [4–7] can be cited. These techniques allow oxidizing refractory organic pollutants to CO_2 and short chain acids (SCA) which are more amenable to biodegradation.

The use of heterogeneous catalyst in WAO is a promising alternative [8] which permits to decrease temperature and pressure, being the catalyst stability under operation conditions the main problem to solve. The loss of activity of the catalyst with the time on stream is usually related to the leaching of the catalytic species under reaction conditions [9–11]. Moreover, the original pollutant is not directly oxidized to CO_2 but different intermediates are produced in serial reactions. The amount and nature of these intermediates must be determined because in many cases some of these compounds can be more toxic than the initial pollutant [12].

The active carbon is not only an excellent adsorbent but also has appropriate catalytic properties because of its different oxygen surface complexes [13,14]. Carbon catalysts have a large number of applications as catalyst support because they are relatively cheap and stable in both acidic and alkaline environments. Active carbon has been recently used as catalyst with impregnation of different metals [15,16] or even as catalyst itself [17–19]. Because the AC can be regenerated by WAO, an interesting possibility

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for high enough pollutant concentration in the wastewater is to accomplish both the adsorption and the oxidation steps on the AC surface simultaneously. The chemical and mechanical stability of the active carbon with the time on stream must be checked for the industrial application of the catalytic wet oxidation (CWO) by using active carbon as catalyst. In this work, the CWO of phenol, as model pollutant, in aqueous phase has been carried out by employing three commercial carbons as catalysts. Not only have the phenol disappearance and mineralization been studied but also the oxidation route.

2. Experimental

Three active carbons have been used in this work: RTA-180 (R), Centaur (C) and Industrial React (IR), all kindly supplied by Molecular Products (R) and Chemviron Carbon (C, IR). The main physical properties of these commercial active carbons are summarized in Table 1. The BET area, micropore and mesopore (2–8 nm in size) pore volume was measured by N_2 adsorption at 77 K with a Quantachrome Autosorb-1. The mesopore pore volume (8–50 nm in size) was measured by mercury porosimetry in a Carlo Erba Porosimeter 4000.

The catalytic activity was studied in an integral fixed-bed reactor with co-current up-flow of gas and liquid phases. An amount between 1 and 3.5 g of the active carbon was placed in the stainless steel tubular reactor (internal diameter = 0.75 cm; length = 25 cm). Different aqueous solutions were fed to the reactor containing phenol or the cyclic intermediates detected in the phenol oxidation runs: dihydroxylbenzenes (catechol (CTL) and hydroquinone (HQ)), *p*-benzoquinone (BQ) and *p*-hydroxybenzoic acid (HBZO). The initial pH was set to 3.5 and different liquid flow rates were used in order to change the ratio W/Q_L between 0.2 and 10.5 g_{cat} min mL^{-1}. The oxygen gas flow rate was set to 90 mL min^{-1} (STP). Temperature and oxygen pressure in the reactor were fixed to 160 °C and 16 bar, respectively.

Phenol and organic intermediates were identified and quantified by HPLC (Hewlett-Packard, mod. 1100) using a diode array detector (HP G1315A). A Chromolith performance column (monolithic silica in rod form, RP-18e 100–4.6 mm) was used as stationary phase and a mixture of acetonitrile, water and a solution of 3.6 mM H_2SO_4 in the ratio 5/90/5 (v/v) were used as mobile phase. Flow rate of the mobile phase was 1 mL min^{-1} and de UV detector was used at wavelengths of 192, 210 and 244 nm. Organic acids were analyzed by ionic chromatography (Metrohm, mod. 761 Compact IC) using a conductivity detector. A column of anion suppression Metrosep ASUPP5 (25 cm long, 4 cm diameter) was used as the stationary phase and an aqueous solution of 3.2 mM Na_2CO_3 and 1 mM $NaHCO_3$ as the mobile phase, at a constant flow rate of 0.7 mL min^{-1}. Total organic carbon (TOC) values in the liquid phase were determined with a Shimadzu TOC-V CSH analyser by oxidative combustion at 680 °C, using an infrared detector.

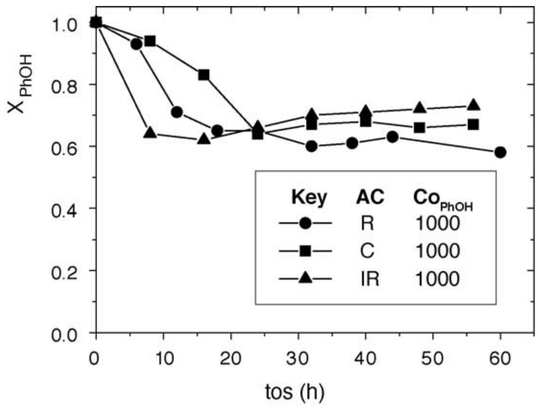

Fig. 1. Phenol conversion as a function of time on stream: $T = 160$ °C, $W/Q_L = 2.3$ g_{cat} min mL^{-1}, $P_{O_2} = 16$ bar, $Q_G = 90$ mL min^{-1}, $C_0 = 1000$ mg L^{-1} and pH_0 3.5.

3. Results and discussion

The stability of the three active carbons under reaction conditions was checked by analyzing the phenol (PhOH) conversion with time on stream at $W/Q_L = 2.33$ g_{cat} min mL^{-1}. The results are displayed in Fig. 1. It shows that after 20 h of operation, the steady state is reached and the phenol conversion keeps constant with time on stream at least during the 60 h studied. Thus, the phenol adsorption and oxidation on the carbon surface occur at the same rates. After 60 h of operation, the catalyst was taken out from the bed reactor, weighted and the BET area and pore volume was measured. Values obtained are also summarized in Table 1. As can be seen, the BET area decreases significantly after reaction and this effect is more remarkable for the IR active

Table 1
Physical properties of the active carbons employed, fresh and after 60 h of time on stream

Carbon	tos (h)	Weight loss (%)	S_g BET (m^2/g)	$V_{p\ mesopores}$, 20–500 Å $cm^3\ g^{-1}$	$V_{micropores}$, $d_p < 20$ Å $cm^3\ g^{-1}$
Sonofcarb RTA 180	0		1333	0.162	0.604
Centaur FE80127H	0		931	0.035	0.407
IndReact FE01606A	0		745	0.120	0.322
Sonofcarb RTA 180	60	−2	372	0.027	0.176
Centaur FE80127H	60	3.68	361	0.026	0.170
IndReact FE01606A	60	−5	111	0.025	0.032

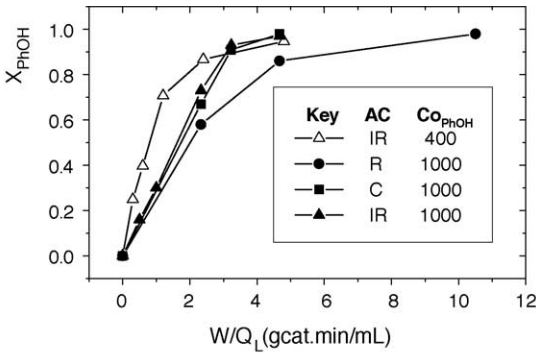

Fig. 2. Phenol conversion vs. W/Q_L, $T = 160\ ^\circ C$, $W/Q_L = 0.2–10.5\ g_{cat}$ min mL^{-1}, $P_{O_2} = 16$ bar, $Q_G = 90\ mL\ min^{-1}$, $C_0 = 1000\ mg\ L^{-1}$ and 400 mg L^{-1} and pH_0 3.5.

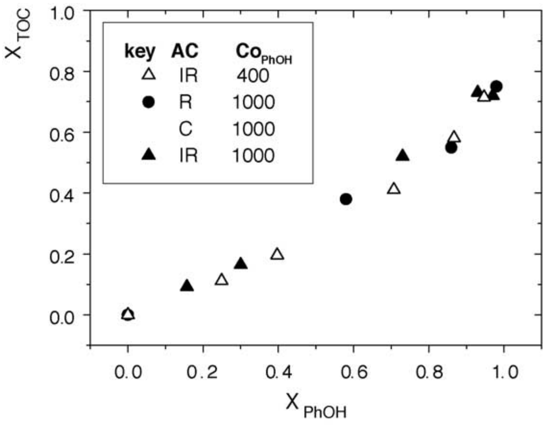

Fig. 3. Phenol mineralization as a function of the phenol conversion, $T = 160\ ^\circ C$, $W/Q_L = 0.2–10.5\ g_{cat}$ min mL^{-1}, $P_{O_2} = 16$ bar, $Q_G = 90$ mL min^{-1}, $C_0 = 1000\ mg\ L^{-1}$ and 400 mg L^{-1} and pH 3.5.

carbon. The micropore volume is also drastically reduced. The mesopore volume decreases significantly for the R and IR active carbons that showed the higher initial values for this parameter. The changes on both surface area and pore volumes can be also related to the initial non-steady state (see Fig. 1). The changes on the active carbon weight after 60 h under reaction conditions is lower than 5%, as can be seen in Table 1. For the Industrial React and RTA-180 active carbons, a small increase in the weight is noticed, probably due to a polymer formation in the pores. This increase corresponds to the decrease in the mesopore volume detected for IR and R active carbons.

Phenol conversion obtained at steady-state conditions in the phenol oxidation runs carried out at different W/Q_L values are shown in Fig. 2. Two different initial phenol concentrations were fed to the reactor, 1000 and 400 mg L^{-1}, in order to analyze the effect of this variable on the phenol conversion. As can be seen in Fig. 2, the highest phenol conversion is obtained with the IR and C active carbons. It can be also noticed that the conversion obtained at the same W/Q_L value increases when the initial phenol concentration decreases. This fact indicates that there is a significant adsorption term in the denominator of the kinetic equation of the phenol oxidation. As can be also seen in Fig. 2, phenol is almost totally converted at relatively low W/Q_L values. The phenol conversion obtained with AC is higher than that obtained in the WCO with typical WCO catalyst based on copper oxides under similar operation conditions [20].

In Fig. 3, the TOC conversion values obtained in the phenol oxidation runs are plotted against the phenol conversions, shown in Fig. 2. As can be seen, total mineralization of phenol has not been achieved but some intermediates are detected, mainly hydroquinone, benzoquinone, *p*-hydroxybenzoic acid and short chain acids as maleic, acetic and formic acids. Only traces of catechol were detected and a small quantity of oxalic acid was produced by using active carbon as catalyst while significant amounts of both compounds were found with catalyst based on copper oxides as described in previous works [21]. The three active carbons tested show no significant differences in phenol mineralization in relation to phenol conversion. The initial concentration of phenol has also no influence on this relationship.

However, only small amounts of intermediates are obtained by using AC as catalyst being the TOC conversion quite closed to the phenol conversion for the three catalysts employed.

The product distribution obtained in the phenol oxidation runs is shown in Fig. 4. Because of the higher phenol mineralization reached with active carbon, lower concentrations of CTL + HQ + BQ are detected in the liquid phase comparing to those previously found by using copper oxide catalysts [21]. Furthermore, it can be pointed out that the R active carbon yields the lowest concentration to cyclic intermediates in the phenol oxidation runs. The slight differences between TOC and phenol conversion are mainly due to the refractory SCA formed (Fig. 4c).

As can be seen in Fig. 4a and b, the cyclic intermediate concentrations show a maximum with the phenol conversion increasing, thus with the increase of the W/Q_L values. This fact indicates that these compounds are directly produced from phenol being further oxidized according to a serial reaction scheme. On the other hand, the short chain acids accumulate in the media are the final refractory intermediates of this serial scheme. Moreover, carbon dioxide must be produced simultaneously to these acids because of a high mineralization of the phenol reacted is also achieved at low phenol conversion values.

While the maximum in the first oxidation intermediates HQ + CTL + BQ is obtained at phenol conversion values lower than the unity (between 0.6 and 0.7), it can be supposed that these intermediates show a high oxidation rate. This is attractive from an environmental point of view because these compounds are more toxic than phenol. Effective nominal concentration of catechol, hydroquinone and benzoquinone measured by Mictrotox® after 15 min of contact were 8.32, 0.041 and 0.1 mg L^{-1}, respectively [12].

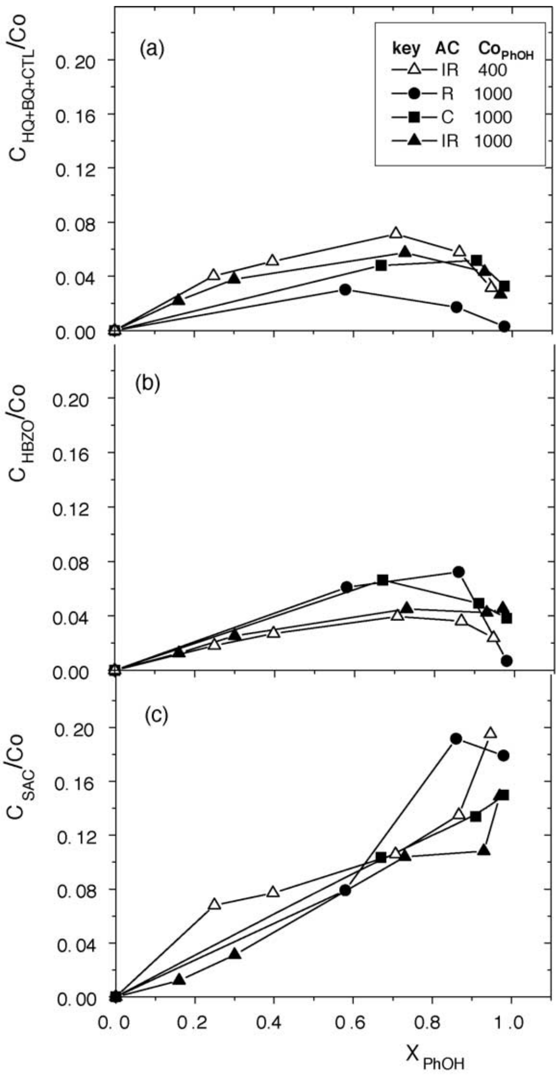

Fig. 4. Results obtained in the catalytic oxidation of phenol. (a) HQ + BQ + CTL, (b) HBZO and (c) SCA as a function of phenol conversion: $T = 160\,^{\circ}\mathrm{C}$, $W/Q_L = 0.2\text{–}2.4\ \mathrm{g_{cat}\ min\ mL^{-1}}$, $P_{O_2} = 16$ bar, $Q_G = 90\ \mathrm{mL\ min^{-1}}$, $C_0 = 1000$ and $400\ \mathrm{mg\ L^{-1}}$ and pH = 3.5.

In order to elucidate better the phenol oxidation route, the first intermediates in the phenol oxidation have been fed to the reactor by changing the W/Q_L. A solution of $400\ \mathrm{mg\ L^{-1}}$ of each hydroquinone, benzoquinone and catechol were fed to the reactor. To check if the *p*-hydroxybenzoic acid oxidation yields dihydroxylbenzenes, a solution of 400 ppm of this compound was also fed to the reactor. The IR active carbon was chosen for these runs because of its high activity in the phenol oxidation, as shown in Fig. 2.

Results obtained for hydroquinone, *p*-benzoquinone, catechol and *p*-hydroxybenzoic acid oxidation runs are shown in Fig. 5a–d.

As can be seen in Fig. 5a and c, both hydroquinone and catechol are much faster oxidized than phenol. On the contrary, when $400\ \mathrm{mg\ L^{-1}}$ of *p*-benzoquinone are fed to the reactor, a slower oxidation rate is obtained, similar to the oxidation rate found in runs carried out by feeding

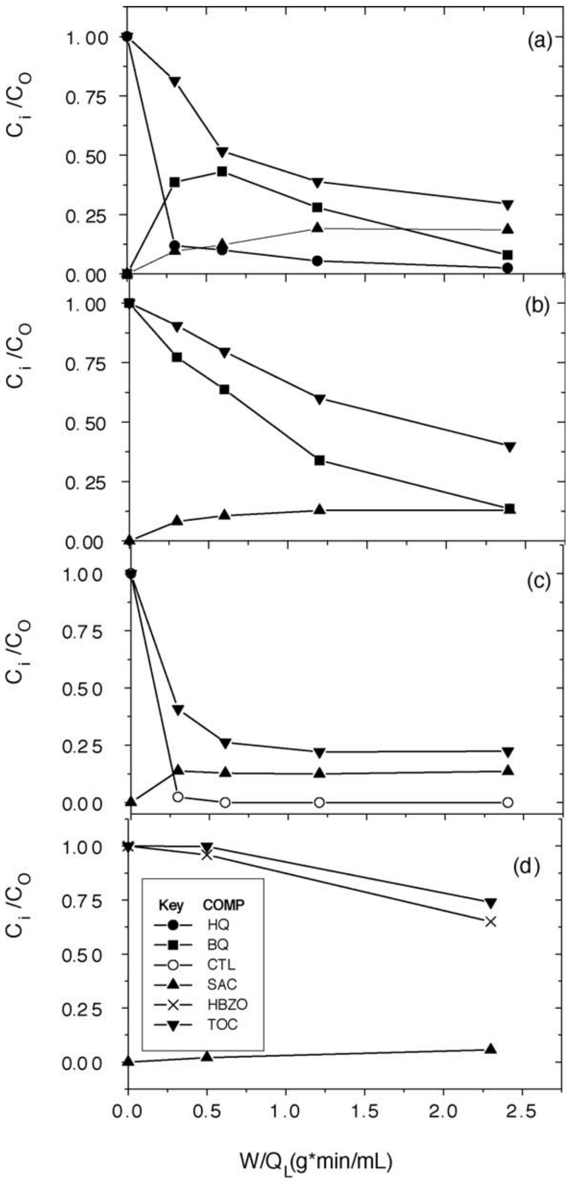

Fig. 5. Experimental results obtained for catalytic oxidation of (a) $400\ \mathrm{mg\ L^{-1}}$ HQ, (b) $400\ \mathrm{mg\ L^{-1}}$ BQ, (c) $400\ \mathrm{mg\ L^{-1}}$ CTL and (d) $400\ \mathrm{mg\ L^{-1}}$ HBZCO: $T = 160\,^{\circ}\mathrm{C}$, $W/Q_L = 0.2\text{–}2.3\ \mathrm{g_{cat}\ min\ mL^{-1}}$, $P_{O_2} = 16$ bar, $Q_G = 90\ \mathrm{mL\ min^{-1}}$, $C_0 = 400\ \mathrm{mg\ L^{-1}}$ and pH = 3.5, AC: Industrial React.

$400\ \mathrm{mg\ L^{-1}}$ of phenol. As can be seen in Fig. 5a, the first intermediate in the hydroquinone oxidation is *p*-benzoquinone, being this compound responsible of the lower increase obtained in the TOC conversion in the hydroquinone oxidation runs. Benzoquinone is further oxidized to short chain acids and CO_2. On the contrary, *o*-benzoquinone was not formed from catechol and the mineralization conversion was closer to the catechol conversion than the mineralization achieved by using hydroquinone as reactant. The small differences in catechol conversion and mineralization must be due to the refractory SCA remaining in the media. The oxidation of *p*-hydroxybenzoic acid takes place at the

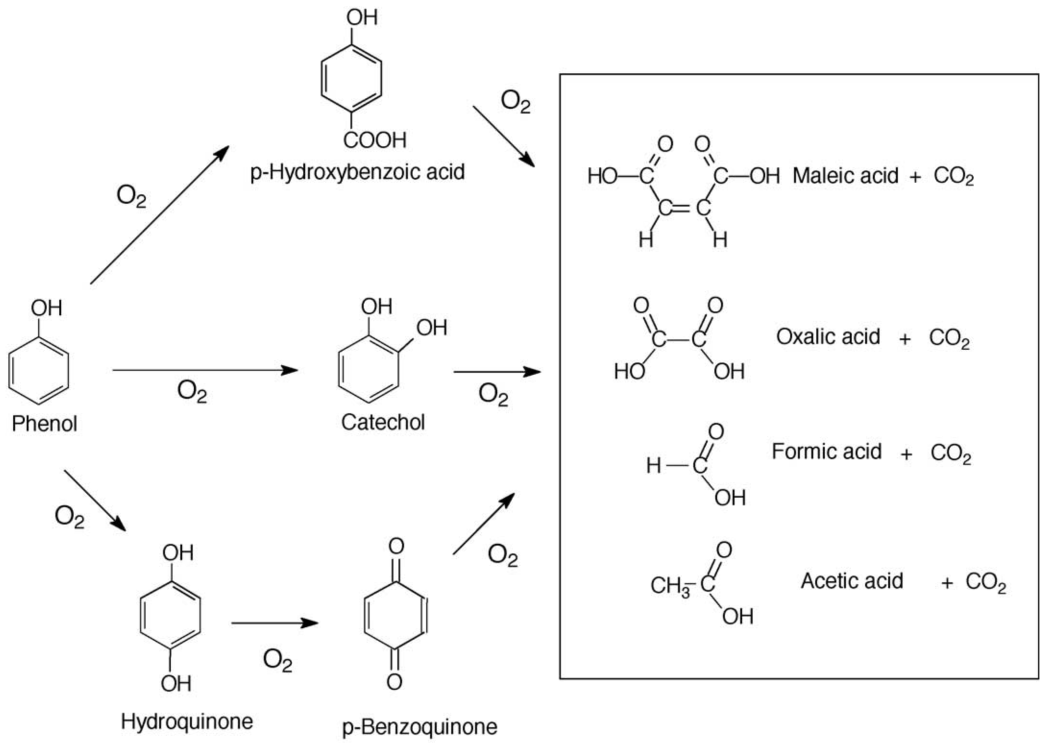

Fig. 6. Scheme proposed for the CWO of phenol by using active carbon as catalyst.

lowest rate and either dihydroxylbenzenes or benzoquinones are not detected as intermediates, as can be seen in Fig. 5d.

From the results above described, the scheme in Fig. 6 has been proposed as reaction scheme. Phenol is oxidized to hydroquinone and catechol as first intermediates and these dyhydroxylbenzenes follow different oxidation routes producing or not benzoquinones, respectively. The *p*-hydroxybenzoic acid is an intermediate not found under acid conditions when copper catalyst was used in the CWO of phenol [21]. This compound can be formed from phenol on the catalytic active carbon surface. The slow oxidation rate observed for the HBZO could be explained either by the inductive effect produced by the carboxylic group on the aromatic skeet or by desorption of this compound on the catalyst surface.

4. Conclusions

Active carbon can be a competent catalyst in the catalytic wet oxidation of refractory organic compounds, such as phenol. After the time required achieving the same rates for the pollutant adsorption and oxidation on the carbon surface, a steady-state operation is achieved. The stability on the phenol conversion is kept for long periods at the medium temperature value used in this work. A main advantage of the active carbon as catalyst in the CWO is the poor selectivity in the oxidation, yielding higher mineralization of the pollutants in comparison to the values obtained with other catalyst based on copper oxides. Moreover, the leaching of the active phase is also avoided while the metal impregnation is not required to obtain high catalytic activity.

The first oxidation intermediates in phenol oxidation are hydroquinone, *p*-hydroxybenzoic acid and traces of catechol. On the other hand, the TOC curve in the hydroquinone oxidation decreases more slowly than in the case of catechol oxidation because both dihydroxylbenzenes are oxidized through different pathways. The first intermediate in hydroquinone oxidation is *p*-benzoquinone that is further oxidized to C_4–C_2 acids and CO_2 while the catechol oxidation yields directly short chain acids and carbon dioxide.

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