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Oxidation of phenol in aqueous solution with copper catalysts

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Abstract

The oxidation of phenol in aqueous phase over four different catalysts based on copper has been studied in a basket stirred tank reactor. Runs have been carried out at 140°C and 16 bar of oxygen pressure, with a catalyst loading of 60 g/l and at an initial acidic pH. Phenol, total organic carbon and some intermediates have been measured with the reaction time. The improvement achieved with the catalyst is established by comparison with a blank (reaction without catalyst). The commercial catalyst Engelhard Cu-0203T (CuO, 67–77%, Cu chromite, 20–30%, graphite sint., 1–3%) was found to be the most active catalyst with an acceptable mechanical and chemical stability. Copper leaches from the catalyst are higher when the mineralization of the acid intermediates does not occur (lower values of pH are obtained). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oxidation; Engelhard Cu-0203T; Cu chromite; Phenol

1. Introduction

Aqueous effluents from industries such as pharmaceutical, chemical, petrochemical, etc. contain refractory organic pollutants in a concentration too small to make their recovery profitable but too high to be treated through conventional processes of biological oxidation. The oxidation of these refractory compounds using oxygen over a solid catalyst [3,6,7] offers an interesting alternative to other more conventional processes such as non-catalytic wet oxidation, supercritical oxidation, adsorption, etc. The heterogeneous catalytic oxidation allows a significant reduction of the temperature and the necessary pressure employed by the non-catalytic oxidation techniques [5,13] and avoids the problem of the adsorbent regeneration in the adsorption process [2], thus improving the economy of the process.

In this work, four catalysts with copper as active component have been tested for the phenol oxidation. The comparison of the proposed catalysts is based not only on their activity on phenol and TOC conversion but also on their mechanical and chemical stability under reaction conditions. As it is described in literature, the catalyst activity may be significantly reduced in short times (minutes or hours) due to abrasion or metal leaches produced during the oxidation process [9–11]. The catalyst selected should not only be the most active as possible but to keep its activity for longer time, thus being mechanically and chemically stable for a larger period of time.

2. Experimental

2.1. Catalysts

In this work, four catalysts based on copper have been employed, three are commercial in an extruded form and the fourth is a self-manufactured monolithic catalyst, supplied by the Instituto de Catálisis y Petroleoquímica (CSIC, Spain). The properties of the catalysts are given in Table 1.

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Table 1
Properties of the catalysts

Catalyst	Composition (wt.%)	Physical properties			
		ρ (g cm^{-3})	S_g (m^2 g^{-1})	V_p (cm^3 g^{-1})	Size
C1, Engelhard Cu-0203T	CuO, 67–77%; Cu chromite, 20–30%; Graphite sint., 1–3%	2.0	10	0.10	$d_p = \frac{1}{8}$ in.
C2, Engelhard Cu-1152T	CuO, 18%; Cu chromite, 53%; CrO_4Ba, 13%; $CaSiO_4$, 11%	1.4	70	0.25	$d_p = \frac{3}{16}$ in., $l = \frac{1}{8}$ in.
C3, Engelhard Cu-1230	CuO, 15%; $(2CuO)Cr_2O_3$, 44%; CrO_4Ba, 12%; Al_2O_3, 29%	1.05	120	0.36	$d_p = 1.6$ mm
C4, Monolith H-23M CSIC	$Cu(NO_3)_2$, 9%; $Ni(NO_3)_2$, 1%; γ-Al_2O_3/silicate, 90%	1.18	124	0.52	Square channel wall thickness 0.9 mm

2.2. Experimental set-up and procedure

Catalysts were *pretreated* by boiling for 4 h in distillated water. Metal leaches and weight losses were measured at this step.

Preliminary experiments were performed to stabilize the catalyst because the bonding of phenol on the surface of the fresh catalyst takes place before the oxidation. This event was studied under nitrogen atmosphere under the reaction conditions described below. This effect was observed in a previous work using Engelhard 1230 catalyst for the phenol oxidation [12].

Reaction runs to select the catalyst have been carried out in a basket stirred tank reactor (BSTR) from Autoclave Engineers (500 ml Spectrum Reactor). The liquid phase was in batch operation while the oxygen flow was continuously fed to the reactor. In order to compare the results obtained using the different catalysts, the experimental runs were performed with the same conditions of temperature ($T = 140°C$), oxygen pressure ($P_{O_2} = 16$ bar), initial pH value ($pH_0 = 3.5$), catalyst loading ($C_{cat} = 60$ g/l) and initial phenol concentration ($C_{0,Ph} = 1200$ ppm). A blank run without catalyst was also carried out to appreciate the effect of the catalyst in the phenol oxidation. In a typical experiment 15 g of catalyst, after pretreatment and stabilization, was placed in the basket. A volume of 250 ml of water was introduced in the reactor, previously setting the pH to an initial value (pH_0). The reactor was pressurized with an oxygen stream (0.15 l/min, STP). Constant flow rate and pressure values were achieved by means of a mass flow controller and a back-pressure control valve, respectively. The reactor was heated up to the reaction temperature, this one being measured and controlled in the liquid phase, holding its value within a ±0.5 K range. The rotating speed of the magnetic stirrer was fixed at 700 rpm. No external mass transfer limitation were found at this condition. When steady state conditions for temperature and pressure were achieved, the phenol was introduced at the reactor by injecting a loop of concentrated phenol solution. Thus, at zero time, the liquid phase was saturated with oxygen and the initial phenol concentration was about 1200 ppm. A scheme of the experimental set-up is given in Fig. 1. Mechanical and chemical stability were determined under reaction conditions ($P = 16$ bar, $T = 140°C$) for the four catalysts tested by measuring the weight losses and metal leaches, respectively. The influence of the particle size was tested for the two catalysts C1 and C3 by using the particle size in Table 1 and crushed catalysts to 1 mm in diameter, and no differences were found. Therefore, the particle diameter selected was the commercial one in Table 2 because this is the diameter at which the mechanical stability must be analyzed.

The *catalyst selected for further studies* on its chemical stability (metal leaches and deactivation) were accomplished. Also, since it was observed that the pH has a significant effect on the reaction rate, runs at a basic initial pH were carried out. To analyze the metal leaches, two different set-ups have been used, the BSTR of Fig. 1 and a fixed bed reactor (FBR) as shown in Fig. 2. In the FBR set-up 5 g of catalyst was placed in an stainless steel tubular reactor (0.9 cm internal diameter and 25.0 cm in length). A solution 1000 ppm in phenol at pH_0 of 3.5, liquid flow rate of 45 ml/h and an oxygen flow rate of 150 ml/min (STP) were fed to the reactor. The reactor was kept at 140°C

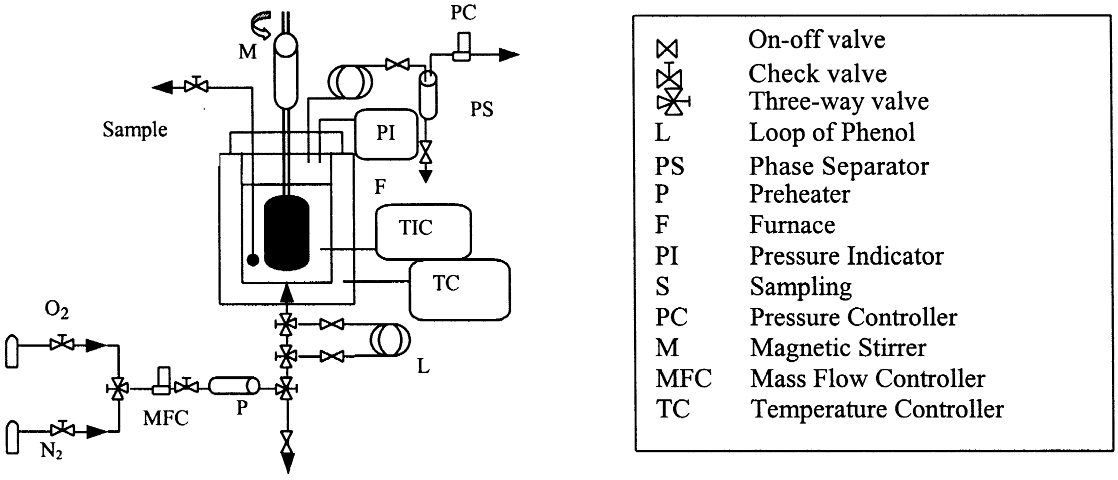

Fig. 1. Experimental set-up for the basket stirrer tank reactor (BSTR).

Table 2
Metal leaches under pretreatment and reaction conditions

Catalyst	Pretreatment (240 min in boiling water)		Reaction (8 h, $T = 140^{\circ}\mathrm{C}$, $p = 16\,\mathrm{bar}$)	
	Cu	Cr	Cu	Cr
C1	0.068 mg/g catalyst, 0.011% $\mathrm{Cu_0}$	0.597 mg/g catalyst, 0.60% $\mathrm{Cr_0}$	2.254 mg/g catalyst, 0.376% $\mathrm{Cu_0}$	9.3×10^{-4} mg/g catalyst, 9×10^{-4}% $\mathrm{Cr_0}$
C2	0.0036 mg/g catalyst, 0.0012% $\mathrm{Cu_0}$	7.72 mg/g catalyst, 2.97% $\mathrm{Cr_0}$	0.0328 mg/g catalyst, 0.0115% $\mathrm{Cu_0}$	0.103 mg/g catalyst, 0.048% $\mathrm{Cr_0}$
C3	0.694 mg/g catalyst, 0.230% $\mathrm{Cu_0}$	2.37 mg/g catalyst, 1.39% $\mathrm{Cr_0}$	0.4424 mg/g catalyst, 0.155% $\mathrm{Cu_0}$	0.00016 mg/g catalyst, 5.3×10^{-3}% $\mathrm{Cr_0}$
C4	0.0016 mg/g catalyst, 0.002% $\mathrm{Cu_0}$	–	0.0278 mg/g catalyst, 0.03% $\mathrm{Cu_0}$	–

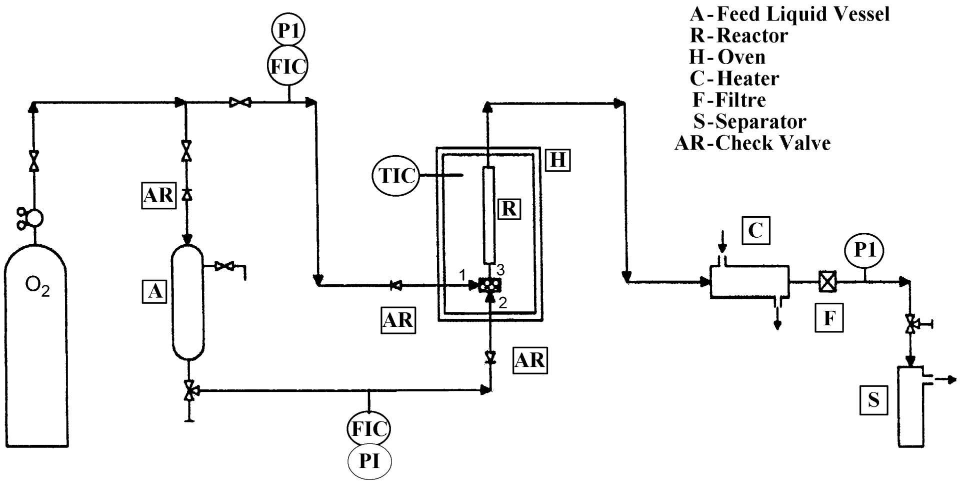

Fig. 2. Experimental set-up for the fixed bed reactor (FBR).

and 16 bar. The deactivation of the catalyst was studied in the BSTR comparing the results obtained after consecutive runs with the same catalyst loading.

2.2.1. Analytical methods

Liquid samples were periodically taken from the reactor and analyzed. The extent of the reaction was determined based on the results of the analysis of the liquid phase. Phenol and some intermediates concentrations were determined by HPLC with a diode array detector (HP G1315A), using a Nucleosil C_{18} column (RP-185 μm, 25 cm long, 4.5 mm diameter) as stationary phase and a mixture formed by acetonitrile and water (1:1) as mobile phase. Flow rate of the mobile phase was set at 0.5 l/min and the UV detector was used at a 210 nm wavelength. Main intermediate compounds identified at acidic pH were catechol, hydroquinone, benzoquinone and C_2–C_4 acids, such as acetic and maleic acids. Total organic carbon (TOC) values in the liquid phase were obtained in an SGE analyzer. Copper and chromium leaches from catalysts were determined using a fotometer (Aqualytic AL282). The pH values of the liquid samples were also measured with time.

3. Results and discussion

From the experiments carried out at reaction conditions under nitrogen atmosphere, the amount of phenol irreversibly quimisorbed on the fresh catalyst surface was 6.4, 1.7, 35 and 6 mg phenol/g catalyst for the catalysts C1, C2, C3 and C4, respectively. Thereby, the highest bonding of phenol to the catalyst surface takes place when the catalyst C3 is used. The rest of the catalyst offers an almost negligible quimisorption of phenol, the lowest corresponding to the catalyst C2.

3.1. Comparison of catalytic activity

Some of the results obtained for the phenol (Ph) and total organic carbon (TOC) conversion and the pH with time are shown in Fig. 3a, b and c, respectively. In all these runs, the initial pH of the water in the reactor was set at 3.5. It can be seen from Fig. 3c that the catalysts have different effects on the pH of the liquid phase. This effect on the pH was noticed even before the phenol was injected from the loop and can be explained if some components of the catalyst were dissolved in the liquid phase. If the catalyst increases the initial pH of the liquid phase, the phenol disappearing rate becomes slower. A significant increase of the initial pH was observed with the catalyst C2, and a smaller increase was found with C3 and C4 catalysts. The catalyst C1 had a negligible effect on the initial pH. Consequently, the faster phenol disappearance rate was obtained with the catalysts C1 and C3 and the lowest with the catalyst C2. Regarding the intermediates formed, it was found that with the C1 catalyst the dihydroxyphenolic intermediates (hydroquinone and catechol) were oxidized at higher rate yielding the higher benzoquinone concentration for small phenol conversion values, as can be seen in Fig. 4c. The progress of mineralization with phenol conversion increase is shown in Fig. 5. The mineralization of phenol is more effective for the catalyst C2 (no intermediates were detected, and phenol and TOC

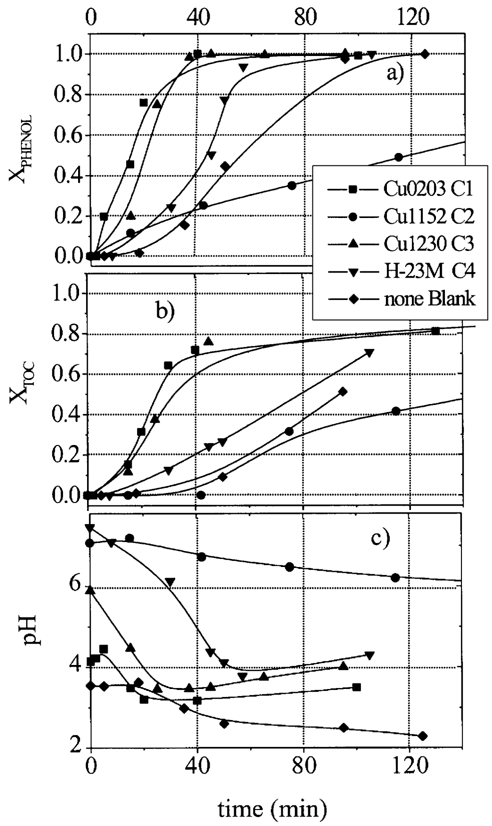

Fig. 3. Comparison of catalyst activity: (a) X_{Ph}, (b) X_{TOC}, (c) pH vs. time.

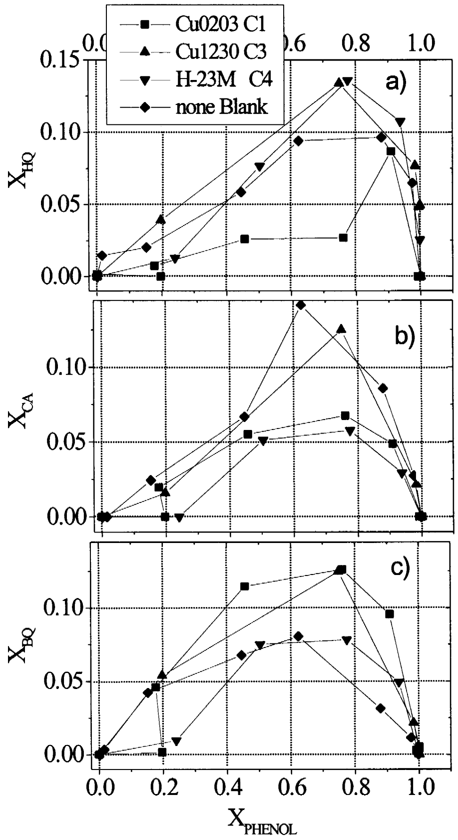

Fig. 4. Intermediates of phenol oxidation: (a) hydroquinone, (b) catechol, (c) benzoquinone.

conversions were very close as shown in Fig. 4), but this catalyst has the lower rate for phenol and TOC disappearance rate. Thus, from the point of view of activity the best catalysts were C1 and C3.

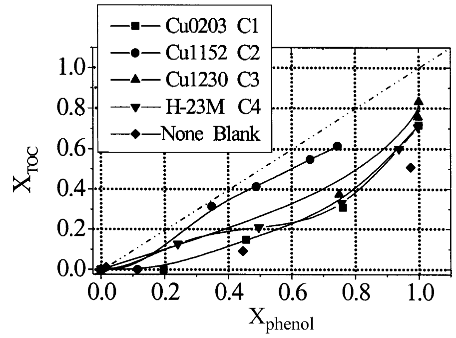

Fig. 5. Comparison of phenol mineralization.

3.2. Comparison of mechanical and chemical stability

The weight of catalyst lost by abrasion after 4 h in boiling distilled water was about 0.65, 4.3, 4.2 and 0% for the catalysts C1, C2, C3 and C4, respectively. After 16 h in the BSTR under reaction conditions, these weight losses were 1, 0, 12, and 7%, for C1, C2, C3 and C4, respectively. Thus, the catalysts C1 and C2 offer the best mechanical stability. Regarding the metal leaches, the main results found are summarized in Table 2. As can be seen in Table 2, the leaches of chromium are almost negligible in two of the three catalysts containing this element (C1 and C3). The copper in the solution after pretreatment and 8 h of reaction is in all the cases under 0.5% of the initial copper of each catalyst. Under reaction conditions, the lowest leaches of copper are obtained with the catalyst C2, and this could be explained because of the pH_0 (3.5) raises around 6–7 when this catalyst is employed.

Taking into account the results of catalyst activity and stability above the quoted catalyst C1 (Cu-0203T) was selected because it has the optimal activity–stability relationship.

3.3. Catalyst Cu-0203T (C1)

Because a significant influence of the pH was observed, two additional runs at initial basic pH were carried out, with and without the previous selected catalyst C1. Results obtained are shown in Fig. 6. As can be seen, the phenol conversion is much slower at basic pH. Regarding the mineralization of phenol to CO_2, similar curves with and without catalyst were obtained at each pH. However, at basic pH the mineralization achieved for a given phenol conversion is slightly higher than that obtained at acidic pH.

The chromium leaches measured at basic pH are significantly higher than that obtained at acidic pH. After 8 h of reaction, at pH 9 the catalyst lost 0.28 mg Cr/g catalyst (0.28% of the initial chromium) and copper leaches about 0.957 mg Cu/g catalyst (0.16% of the initial copper). Because the oxidation of phenol takes place quickly at acidic pH, leaches of metals have been determined in hot acid solutions for longer time than 8 h with this catalyst, results from consecutive

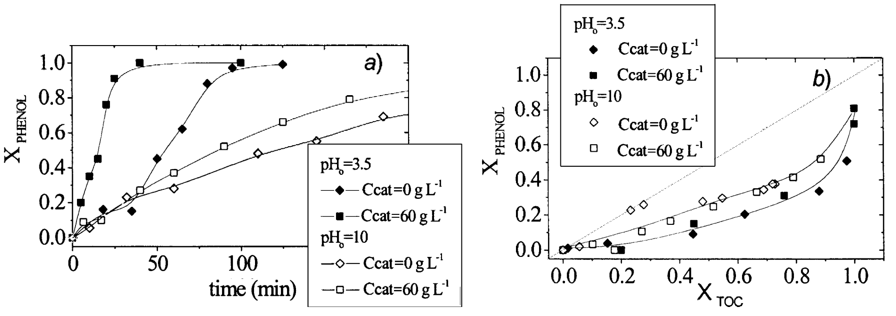

Fig. 6. pH influence with C1 catalyst: (a) phenol conversion, (b) phenol mineralization.

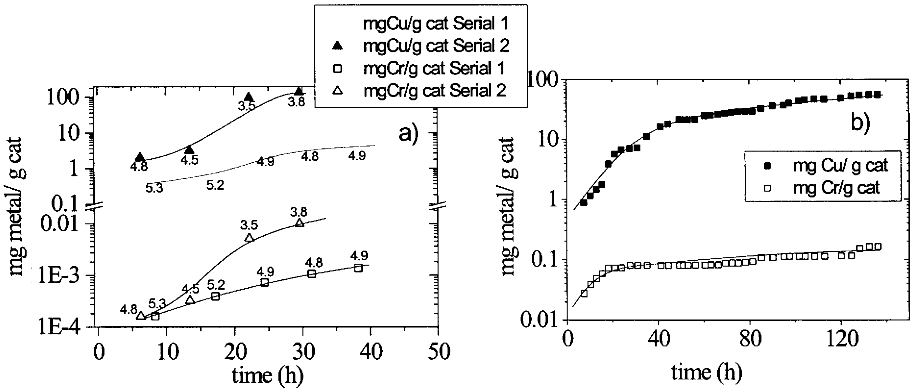

Fig. 7. Accumulated metal leaches of Cu-0203T catalyst with time of operation. $T = 140°C$, $P_{O_2} = 16\,bar$, $pH_0 = 3.5$. (a) BSTR, (b) FBR.

runs carried out in the BSTR and FBR at initial pH of 3.5 are shown in Fig. 7a and b, respectively. In the BSTR, the catalyst loading was in the range 4–120 g/l. For the low catalyst loading (4 g/l) the final pH was around 3 (lower mineralization of the acid intermediates) while at higher catalyst loading (120 g/l) the final pH was around 5. The final pH of the liquid phase is indicated in Fig. 7a. As can be deduced from Fig. 7a, the copper elutes from the catalyst at higher rate when the pH of the solution decreases to a lower value. The copper leaches measured in the FBR are similar to those observed in BSTR for the highest catalyst loading (higher values of residual pH). A run carried out in the FBR without solid catalyst by using 20 ppm of Cu^{2+} in solution yielded a negligible conversion compared with that obtained with catalyst C1, so that the catalytic effect of the copper leaches can be neglected.

To analyze the catalyst deactivation several consecutive runs were performed under the same operational conditions. Results are shown in Fig. 8, as can be seen, no deactivation occurs at least after 20 h of operation.

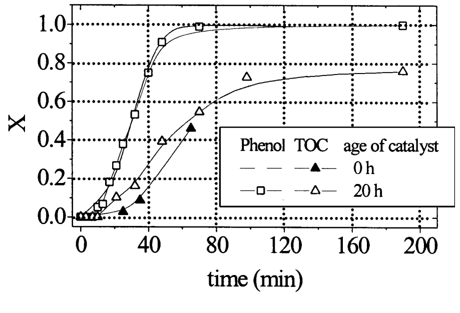

Fig. 8. Activity of Cu-0203T (C1) catalyst with time of operation. $T = 140°C$, $P_{O_2} = 16\,bar$, $pH_0 = 3.5$, $C_{cat} = 4\,g/l$.

4. Conclusion

The phenol disappearance rate becomes slower when the catalyst tested increases the initial pH of the liquid phase. The faster phenol conversion was obtained with C1 (CuO, 67–77%; Cu chromite, 20–30%; Graphite sint., 1–3%) and C3 (CuO, 18%; Cu chromite, 53%; CrO_4Ba, 13%; $CaSiO_4$, 11%) catalysts (in 40 min, total phenol conversion and 30% mineralization to CO_2 is achieved). The C1 catalyst (Engelhard Cu-0203T) was finally selected due to its better mechanical and chemical stability under reaction conditions. This catalyst shows similar or better catalytic activity than those found in other works [1,4,8].

For the selected catalyst the quimisorption of phenol to the catalysts surface before reaction is not significant. The phenol oxidation takes place at higher rate when the initial pH of the solution is acidic (3.5). When a low catalyst loading (4 g/l) is employed in the BSTR, the copper leaches are higher because the acid intermediates do not mineralize to CO_2 and the catalyst remains at lower pH for a long period of time. However, when the catalyst concentration in the reactor increases, the copper leaches measured are much lower (10% of the initial copper after 140 h of operation) than those found in other works (Ohta et al., 1980) [9–11] using other catalysts based on copper.

Some authors [9] have noticed a significant catalyst deactivation in the first hours of the reaction because a “free” copper oxide is easily dissolved. This effect has not been observed in this work and no deactivation occurs at least after 20 h of operation. At this time, the dissolved copper of catalyst C1 is about 1% of the initial content of the catalyst.

Regarding the chromium leaches, these were found to be lower than 0.1% after 140 h of operation when the initial pH is acidic.

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