Phenol oxidation by a sequential CWPO–CWAO treatment with a Fe/AC catalyst

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Abstract

Catalytic wet peroxide oxidation (CWPO) of phenol with a homemade Fe/activated carbon (Fe/AC) catalyst has been studied in a stainless steel fixed-bed reactor at different operating conditions ($T = 23$–$100\,^{\circ}$C, $P_T = 1$–8 atm, $W = 0$–2.5 g, and $\tau = 20$–$320\,g_{CAT}\,h/g_{Phenol}$). The results show that, thanks to the incorporation of Fe on the activated carbon, phenol conversion improved dramatically, reaching a 90% at 65 °C, 2 atm, and $40\,g_{CAT}\,h/g_{Phenol}$. However, TOC conversion values remain fairly low, (around 5% at $40\,g_{CAT}\,h/g_{Phenol}$), and no improvement was obtained with the inclusion of Fe. The presence of Fe seems to promote the nondesirable coupling reactions that take place in CWPO of phenol due to the condensation of the ring intermediates (the primary phenol oxidation products). These condensation products are quite refractory to CWPO at the conditions employed. Taking advantage of the high phenol conversions in CWPO and the high phenol mineralization in CWAO, along with the good stability of the Fe/AC catalyst, a CWPO–CWAO sequential treatment has been successfully performed by using a fixed-bed and trickle-bed reactor in series. A CWPO treatment at ambient conditions followed by a CWAO treatment at mild conditions (100 °C and 8 atm) is presented as high efficiency process for the decontamination of phenolic wastewaters.
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Keywords: Phenol; Hydrogen peroxide; Iron on activated carbon catalyst; Wet oxidation

1. Introduction

Population growth, increasing industrialization, and in general, the present development model of our societies cause an important pressure on natural resources. In particular, aqueous resources support discharges of wastewaters coming from a wide number of different industries, which imply the necessity for developing and improving technologies to remove pollutants in order to minimize their environmental negative effects.

Conventional biological processes represent an environmentally friendly way of treatment with reasonable costs but are not adequate to treat nonbiodegradable wastewaters. In this case, alternative technologies are available such as adsorption, advanced oxidation processes (AOP), wet air oxidation (WAO), incineration, etc. To choose the most appropriate technology some aspects, such as the concentration and nature of the pollutants, and the volume of wastewater, must be considered.

Suitable options to treat wastewaters containing medium concentrations of organic pollutants are the AOP and WAO. A complete removal of the organic matter by these treatments is not economically feasible in most cases, since the end oxidation products are low molecular weight acids, which are refractory to the chemical oxidation, but not to conventional biological processes. Therefore, integrated processes consisting of a partial chemical oxidation followed by a biological treatment offer a feasible solution to obtain a clean effluent [1].
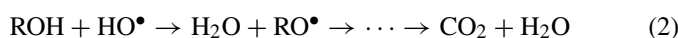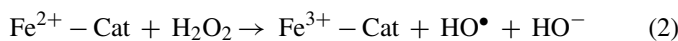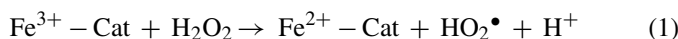
The AOP that employs hydrogen peroxide as oxidant in presence of a catalyst, is known as catalytic wet peroxide oxidation (CWPO). The redox properties of the transition metals used as catalysts (generally, Fe^{2+} and Cu^{2+}) generate hydroxyl radicals in presence of hydrogen peroxide at mild conditions ($T \leq 120\,^{\circ}$C and $P \leq 3$–5 atm) [2]. The main limitation of this process is that the homogeneous catalyst cannot be retained in the process, and therefore, additional water pollution is caused. Important efforts have been focused on finding heterogeneous catalysts with adequate catalytic activity and a convenient stability, taking into account the acidic conditions at which the reaction takes place. Alumina supported Fe and Fe–Cu [3], Fe containing zeolites [4–7], mesostructured materials [8], or pillared clays [9–11] are

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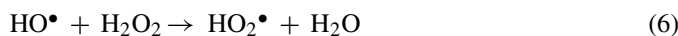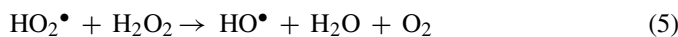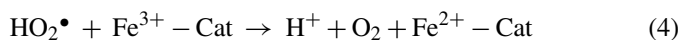*E-mail address:* asun.quintanilla@uam.es (A. Quintanilla).

Nomenclature

C_{ci}/C_{c0} concentration of species i relative to the initial concentration of phenol, as equivalent of carbon

Q_L liquid flow rate (L/h)

Q_{O_2} oxygen flow rate (NmL/min)

t_R residence time of the liquid in the reactor (min), calculated as V_L/Q_L

W mass of catalyst (g)

X conversion

τ space-time (g_{CAT} h/g_{Phenol}), calculated as $W/(Q_L\, C_{Phenol\ initial})$

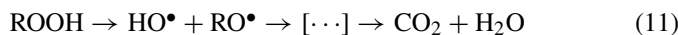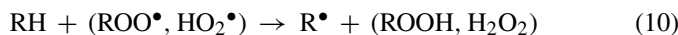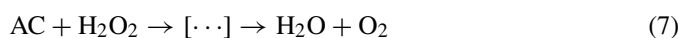
the most common catalysts tested for the CWPO of phenol. The following mechanism can be described in these catalytic systems:

$$Fe^{3+} - Cat + H_2O_2 \rightarrow Fe^{2+} - Cat + HO_2^\bullet + H^+ \qquad (1)$$

$$Fe^{2+} - Cat + H_2O_2 \rightarrow Fe^{3+} - Cat + HO^\bullet + HO^- \qquad (2)$$

$$ROH + HO^\bullet \rightarrow H_2O + RO^\bullet \rightarrow \cdots \rightarrow CO_2 + H_2O \qquad (2)$$

Also side reactions occur such as,

$$HO_2^\bullet + Fe^{3+} - Cat \rightarrow H^+ + O_2 + Fe^{2+} - Cat \qquad (4)$$

$$HO_2^\bullet + H_2O_2 \rightarrow HO^\bullet + H_2O + O_2 \qquad (5)$$

$$HO^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \qquad (6)$$

Leaching of Fe was in most cases detected. For this reason, new catalysts, such as activated carbon without metal impregnation, have started to be used in the CWPO of phenol and derivatives [12], although lower conversions of the refractory pollutants have been achieved. This is related to the preferential decomposition of hydrogen peroxide on the activated carbon into oxygen and water, instead of giving rise to hydroxyl radicals as has been reported in literature [13–15]:

$$AC + H_2O_2 \rightarrow [\cdots] \rightarrow H_2O + O_2 \qquad (7)$$

$$RH + O_2 \rightarrow R^\bullet + HO_2^\bullet \qquad (8)$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet \qquad (9)$$

$$RH + (ROO^\bullet, HO_2^\bullet) \rightarrow R^\bullet + (ROOH, H_2O_2) \qquad (10)$$

$$ROOH \rightarrow HO^\bullet + RO^\bullet \rightarrow [\cdots] \rightarrow CO_2 + H_2O \qquad (11)$$

In this work, a homemade Fe/activated carbon (Fe/AC) catalyst has been used in the CWPO of phenol in a continuous fixed-bed reactor. This catalyst was successfully tested in the catalytic wet air oxidation (CWAO) of phenol at mild conditions (100–127 °C and 8 atm of total pressure) in previous studies [16,17]. The results obtained in this work have been analyzed in terms of phenol and TOC conversions, and hydrogen peroxide consumption. The efficient use of the oxidant has been also assessed along with the catalysts stability. Moreover, identification of the intermediate species was attempted. Special attention has been paid to this aspect since total mineralization of phenol

does not occur and the species formed at short reaction times can be more toxic than the starting pollutant [18].

The results obtained in the CWPO of phenol with the Fe/AC catalyst have been compared to those found in the CWAO process. After analyzing the main features of both processes with the Fe/AC catalyst, a CWPO–CWAO sequential treatment was performed.

2. Experimental

2.1. Catalyst preparation

A granular activated carbon (AC) supplied by Merck (Ref.: 102514) was used as catalyst and catalytic support after sieving a fraction of 0.5–1 mm particle diameter. The following properties were measured: $S_{BET} = 974\ m^2/g$, $V_{micropores} = 0.341\ cm^3/g$, $V_{mesopores} = 0.190\ cm^3/g$, and $V_{macropores} = 0.222\ cm^3/g$. A homemade Fe/AC catalyst has been prepared by introduction of Fe (2.5% wt) in the AC using the incipient-wetness impregnation method as described elsewhere [17]. This catalyst presents the following textural properties: $S_{BET} = 890\ m^2/g$, $V_{micropores} = 0.393\ cm^3/g$, $V_{mesopores} = 0.168\ cm^3/g$, and $V_{macropores} = 0.212\ cm^3/g$.

2.2. Experimental setup and chemical analyses

Phenol CWPO runs were carried out in a fixed-bed reactor consisting of a stainless steel tube of 8.5 mm internal diameter and 170 mm length. Phenol and hydrogen peroxide aqueous solution was continuously fed to the reactor in upflow. The catalyst particles were mixed with glass beads in order to avoid fluidization of the catalytic bed. The phenol CWAO runs were conducted in a standard wet oxidation unit, also at bench scale. The main component is a trickle-bed reactor. 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 have been reported elsewhere [16]. In both processes the reactor was placed in an oven, and the temperature was always measured by a thermocouple located into the catalytic bed. Blank experiments (in absence of catalysts) were carried out with 1 mm inert beads. In the CWPO–CWAO sequential treatment, both reactors were placed in series.

An aqueous solution of 1 g/L of phenol at pH 3.5 (adjusted with H_2SO_4) was continuously fed to the reactors at different flow rates (0.125–2 mL/min) to cover the experimental range of space-time values ($\tau = 20$–$320\ g_{CAT}$ h/g_{Phenol}). The operational window tested was: 23–100 °C, 1–8 atm, and 0–2.5 g of catalyst. 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. In the CWAO runs, a 91.6 NmL/min pure oxygen flow was used in all the experiments. The operating conditions were 65 and 100 °C, 8 atm, and 2.5 g

The progress of the reaction was followed by taking periodically liquid samples from the reactor outlet. The liquid samples were analyzed by different procedures. Phenol and ring compounds were determined by HPLC (Varian, mod. ProStar), low

molecular weight acids were analyzed by anionic suppression IC (Metrohm, mod. 761 Compact IC), and total organic carbon (TOC) measurements were accomplished with a TOC analyzer (O.I. Analytical, model 1010). Iron in the reactor effluent was analyzed by total reflection X-ray fluorescence (TXRF). More detailed description of these chemical analyses can be consulted elsewhere [16,17]. Hydrogen peroxide concentration was quantified by colorimetric titration using the $Ti(SO_4)_2$ method.

3. Results and discussion

3.1. Preliminary experiments

Before using the Fe/AC catalyst in the CWPO experiments, some preliminary runs were carried out to analyze separately the contribution of hydrogen peroxide and activated carbon in the abatement of phenol and TOC.

3.1.1. Effect of H_2O_2 in the WPO

In order to examine the effect of hydrogen peroxide in the oxidation of phenol, a set of experiments were carried out in absence of catalyst at different operating conditions (65 °C and 2 atm and 100 °C and 8 atm). The results obtained, which have been analyzed in terms of phenol and TOC conversions, and H_2O_2 consumption *versus* residence time, are shown in Fig. 1. Concentrations of Fe detected in the reactor effluent collected from the beginning of the reaction until the stationary stage was achieved have been also included in the figure. As can be seen, complete phenol conversion can be reached at 100 °C and 8 atm. This can be due to the catalytic effect of Fe. This Fe is present in the media as metallic Fe (in the pipes and reactor walls), and as

cation Fe^{3+} (in solution, due to both the leaching of the metallic Fe and the oxidant conditions). Increasing the temperature led to higher Fe leaching consistently with higher phenol conversion and H_2O_2 consumption values.

The Fe is leached due to the hot acidic aqueous media. These acidic conditions are enhanced by the low molecular weight carboxylic acids (mainly formic, oxalic, acetic, and maleic acid) formed upon phenol oxidation. The presence of H_2O_2 does not favor the leaching, as was proved by feeding a hydrogen peroxide solution in absence of phenol to the reactor, and comparing the data to those obtained when distilled water at the same pH was used to wash the reactor. The influence of the residence time on the Fe leached is difficult to predict due to the formation of Fe-organic complexes that can take place upon reaction between the Fe leached and the intermediate species formed in the media. For instance, the formation of Fe-catechol [19] and Fe-oxalic [20] has been reported in Fenton and CWPO process, respectively. This phenomenon, which makes the Fe measurement more difficult, could explain the decrease in the concentration of Fe with residence time at 65 °C and 2 atm. In fact, at the highest residence time, the highest amount of catechol was detected in the effluent, more that 200 mg/L (higher than at 100 °C and 8 atm).

To reduce Fe leaching, it seems convenient to conduct the CWPO process under operating conditions milder than 100 °C and 8 atm.

3.1.2. Effect of the activated carbon support in CWPO of phenol

Fig. 2 shows the results obtained in CWPO of phenol at two different loads of activated carbon. By comparing Figs. 1 and 2, the beneficial effect of the activated carbon can be observed. For instance, at a residence time of 14 min, phenol, and TOC conversions in presence of activated carbon (Fig. 2) are 75 and 25%, respectively, whereas in absence of activated carbon (Fig. 1), they are 48 and 10%.

In spite of the fact that phenol and TOC conversions in presence of activated carbon are higher than those obtained in the corresponding experiments in absence of activated carbon, increasing the load of activated carbon in the reactor from 1 to 2.5 g did not affect the evolution of phenol and TOC. This indicates that phenol and TOC conversions depend on the residence time but not on space-time, which means that oxidation of phenol proceeds essentially through homogeneous reaction.

In contrast, hydrogen peroxide consumption was also dependent on activated carbon loading. There is a homogeneous and heterogeneous contribution in the decomposition of hydrogen peroxide because it takes place mainly through two routes: decomposition into oxygen and water on the activated carbon surface (Eqs. (7)–(10)) and production of hydroxyl radicals in the liquid phase due to Fe (as a Fenton-like system). In fact, concentrations of Fe ranging from 0 to 2 mg/L were measured in the reactor effluents. The former route seems to predominate in the range of residence time values tested, as can be deduced by comparing the data of hydrogen peroxide consumption in Fig. 1 (pure homogeneous contribution) and in Fig. 2 at the same residence time.
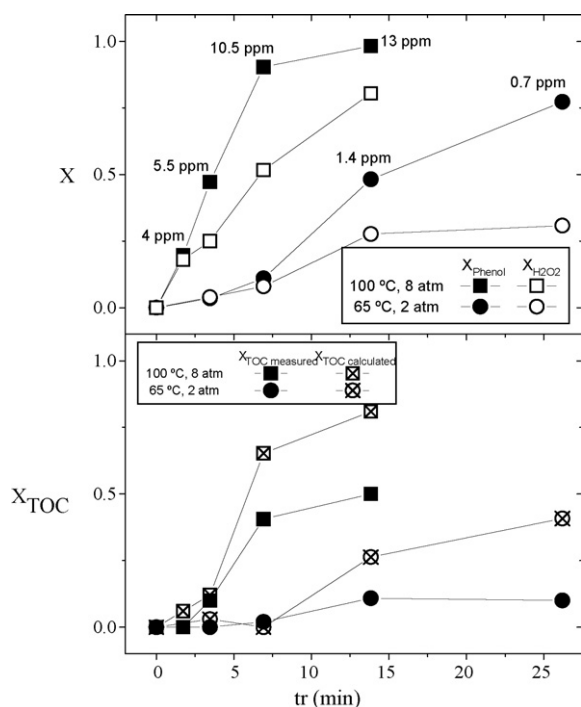

Fig. 1. Results from WPO of phenol in absence of catalyst at different operating conditions. $C_{Phenol\ initial} = 1$ g/L, $C_{H_2O_2\ initial} = 5$ g/L, and $pH_{initial}$ 3.5.

To explain why increasing the load of activated carbon does not increase the phenol and TOC conversions, in spite of the fact that there is more O_2 available due to a higher decomposition of hydrogen peroxide, some additional experiments were carried out. CWPO reaction was performed at residence times of 3.5 and 7 min and at 65 °C and 8 atm, and no influence of the pressure was observed on phenol and TOC conversions. This observation suggests that the liquid phase is already saturated in oxygen at 2 atm. Therefore, the extra oxygen produced when the load of activated carbon is increased from 1 to 2.5 g is not used in the oxidation and mineralization of phenol. The presence of activated carbon in CWPO simply enhances the rate of oxygen production from H_2O_2 decomposition.

The oxidation intermediates identified were ring species and low molecular weight carboxylic acids, such as maleic, malonic, oxalic, formic, and acetic. Among the aromatic intermediates *p*-benzoquinone was the main compound and hydroquinone, catechol, and resorcinol were also analyzed in much lower amounts. The evolution of the concentration of both groups of intermediates is shown in Fig. 2 in terms of normalized concentration expressed in mg/L of carbon (C_{Ci}/C_{C0}). The TOC conversion values calculated from these intermediates have been also included in Fig. 2. As can be seen, important amounts of
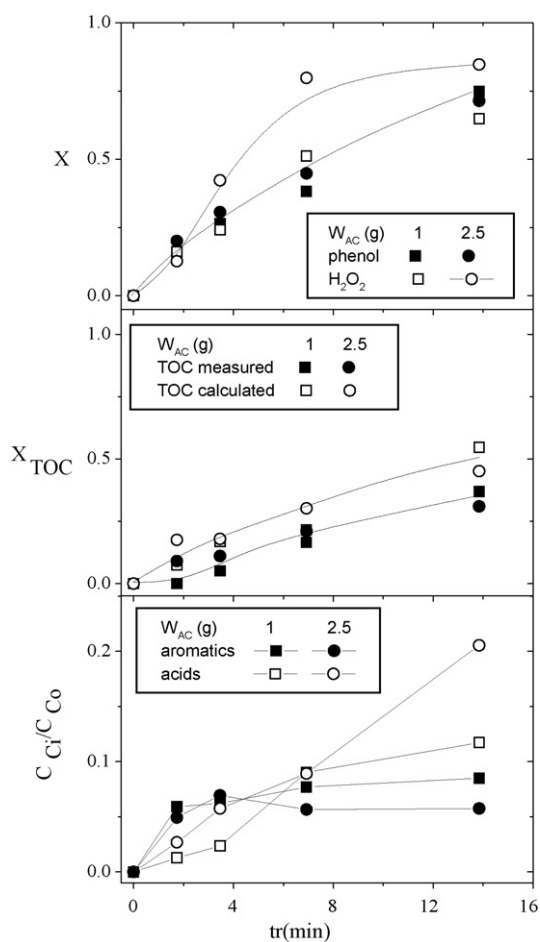
carbon remain unidentified since the measured TOC values are not coincident with the calculated ones. Most probably unidentified intermediates formed in the first stages of the oxidation process along with condensation products formed from the ring intermediates are the main responsible of the differences formed in TOC, and also of the deep brown color of the reactor effluents. This color was already observed in the oxidation of phenol by Fenton reaction with a Fe concentration of 1 mg/L [22], comparable to those detected in the reactor effluent. The toxicity of the afore mentioned compounds is higher than that of phenol [18], and therefore it is important to reduce their presence in the reactor effluent as much as possible.

3.2. CWPO of phenol with the Fe/AC catalyst

A set of experiments was carried out with the Fe/AC catalyst at different loadings and at 65 °C and 2 atm. The results are shown in Fig. 3 as a function of the space-time. As can be observed, by comparing the data with those of Fig. 2 at the same residence time (for instance 1.7 and 3.5 min, which are collected in Fig. 3), phenol conversion and hydrogen peroxide consump-
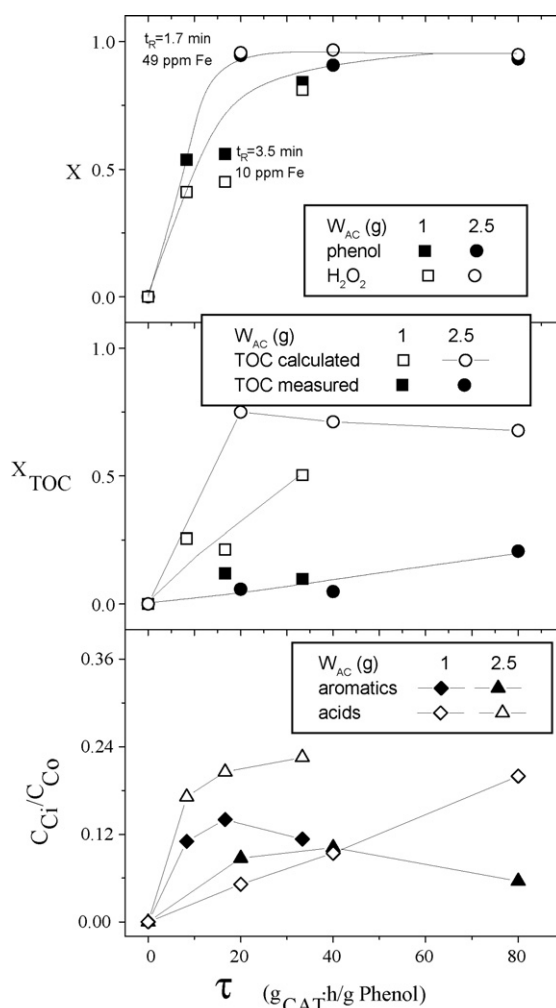

Fig. 2. Results from CWPO of phenol at two different loads of activated carbon. $T = 65$ °C, $P_T = 2$ atm, $C_{Phenol\ initial} = 1$ g/L, $C_{H_2O_2\ initial} = 5$ g/L, and $pH_{initial}$ 3.5.

Fig. 3. Results from CWPO of phenol at two different loads of Fe/AC catalyst. $T = 65$ °C, $P_T = 2$ atm, $C_{Phenol\ initial} = 1$ g/L, $C_{H_2O_2\ initial} = 5$ g/L, and $pH_{initial}$ 3.5.
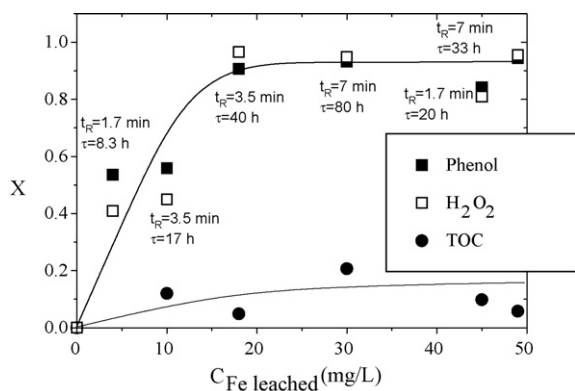
Fig. 4. Results from CWPO of phenol with Fe/AC catalyst as a function of Fe leached. $T = 65\,°C$, $P_T = 2$ atm, $C_{Phenol\ initial} = 1$ g/L, $C_{H_2O_2\ initial} = 5$ g/L, $W = 1$ and 2.5 g, and $pH_{initial}$ 3.5.

tion are enhanced with the incorporation of Fe on the activated carbon. But this fact does not mean that oxidation takes place on the catalyst surface since as much as 71% of Fe was leached out from the catalyst after 42 h of time on stream. As can be seen in Fig. 3, a higher residence time does not lead to a higher conversion at a constant space-time because the concentration of Fe in the liquid phase is smaller. Fig. 4 shows clearly the dependence of phenol, and TOC conversions, and hydrogen peroxide consumption with the Fe leached. This indicates that the main route of consumption of hydrogen peroxide is the production of hydroxyl radicals in the liquid phase by the Fe dissolved and these radicals oxidize phenol. These observations also reveal the low stability of the Fe/AC. Apart from the hot acidic aqueous media, the leaching of Fe from the catalyst must be also promoted by the intermediates formed in the phenol oxidation that interact with Fe [8]. Same intermediates as those identified with the carbon support were detected. Among all the intermediates, oxalic acid deserved special attention. Previous studies have reported that the amount of leached Fe could be related to the amount of oxalic acid in solution [20,21].

It is also noteworthy that in spite of the higher phenol conversions obtained with the Fe/AC catalysts, the TOC conversions were similar to those obtained with the carbon support alone. Moreover, the differences between the calculated and the measured TOC values are higher with the Fe/AC catalyst and increase with the catalyst load, that is, with the amount of Fe in the liquid phase. Therefore a higher amount of nonidentified intermediates are produced with the Fe/AC catalyst, and it seems that the presence of Fe in the reaction media favors the coupling reactions of ring intermediates in the phenol oxidation route, which is in agreement with the results reported by other authors [23,24].

With the aim of reducing the Fe leaching, the oxidation process was also investigated at ambient conditions. The results are shown in Fig. 5, along with those obtained at 65 °C and 2 atm for the sake of comparison. It can be seen that although the phenol conversions are lower, relatively high values can be reached at high enough space-time. TOC conversions of no more than 20% were achieved, and the presence of nonidentified intermediates persists.
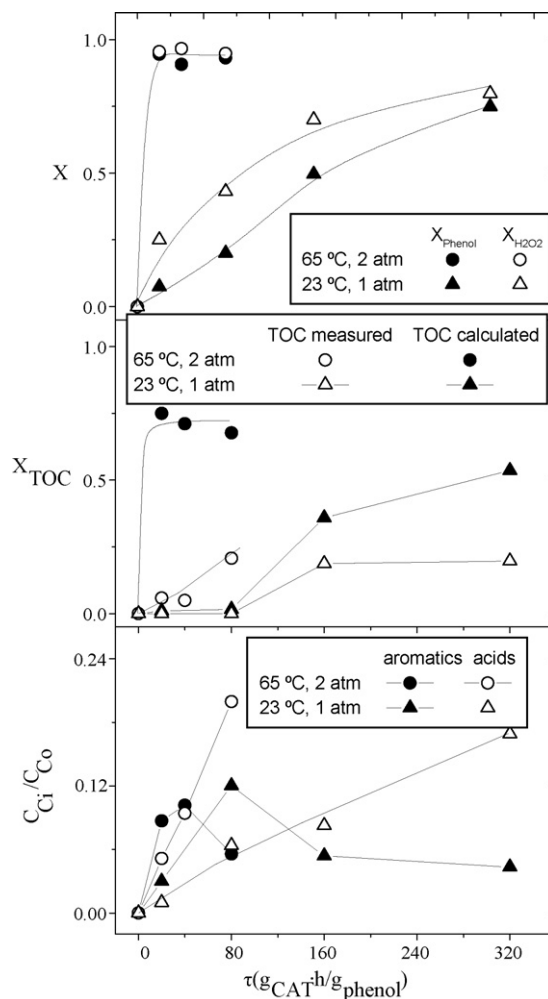

Fig. 5. Results from CWPO of phenol with Fe/AC catalyst at different temperature and pressures. $C_{Phenol\ initial} = 1$ g/L, $C_{H_2O_2\ initial} = 5$ g/L, $pH_{initial}$ 3.5, and $W_{CAT} = 2.5$ g.

Fig. 6 compares the results obtained in a trickled-bed reactor at 100 °C and 8 atm with the Fe/AC catalyst in CWAO [17] and CWPO of phenol. It can be concluded that although higher phenol conversions can be achieved in the CWPO a higher accumulation of intermediates takes place, as proves the higher differences between the TOC and phenol conversion curves. These intermediates are refractory low molecular weight carboxylic acids and condensation products, both remain in the media even after complete H_2O_2 consumption. On the opposite, in CWAO, condensation products were only detected at short space-times being completely oxidized to refractory low molecular weight acids (mainly acetic and formic) at space-times beyond 160 g_{CAT} h/g_{Phenol}. In this point the calculated and measured TOC conversion curves begins to coincide. Moreover, negligible leaching of Fe was observed (less than 2% in 216 h of time on stream) [17].

Looking at the main advantages of both processes, the high phenol conversion in CWPO and the high mineralization in CWAO, an efficient treatment can be designed consisting in a sequential CWPO–CWAO process.
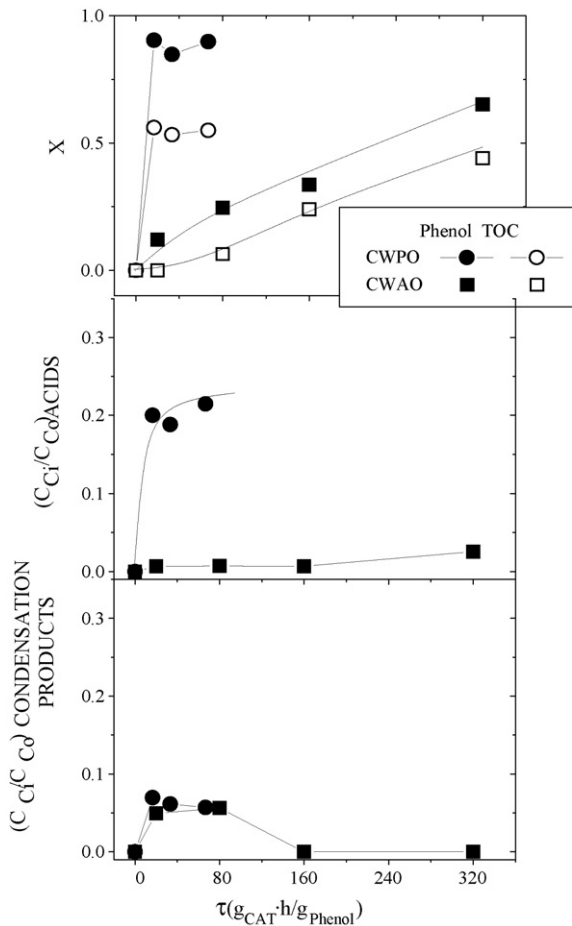
Fig. 6. Comparison of the results obtained in the CWPO and CWAO processes with the Fe/AC catalyst. $T = 100\,°C$, $P_T = 8\,atm$, $C_{Phenol\ initial} = 1\,g/L$, $C_{H_2O_2\ initial} = 5\,g/L$, Q_{O_2} for CWAO = 91.6 NmL/min, Q_{N_2} for CWPO = 91.6 NmL/min, $pH_{initial}$ 3.5, and $W_{CAT} = 2.5\,g$.

Table 1
Experimental conditions of the sequential CWPO–CWAO treatment

	CWPO		CWAO		Fig. 7
	$T\,(°C)$	P_T (atm)	$T\,(°C)$	P_T (atm)	
P23-A100	23	8	100	8	a
P65-A65	65	2	65	2	b
P65-A100	65	2	100	8	c

$C_{Phenol\ initial} = 1\,g/L$, $C_{H_2O_2\ initial}$ for CWPO = 5 g/L, Q_{O_2} for CWAO = 91.6 NmL/min, $pH_{initial}$ 3.5, $W = 2.5\,g_{CAT}$ in each reactor.

3.3. Sequential CWPO–CWAO treatment with the Fe/AC catalyst

A set of experiments was carried out using two reactors in series. The operating conditions employed in these experiments (P23-A100, P65-A65, and P65-A100) are summarized in Table 1. The results are reported in Fig. 7a–c, respectively. These figures also include the results obtained in each individual treatment under similar operating conditions. Total consumption of H_2O_2 was reached in all the experiments. As can be seen from the phenol conversion values, the sequential treatment significantly improves the results obtained from CWPO and CWAO separately, except when complete phenol conversion was already reached in the individual CWPO treatment (Fig. 6b and c). On the other hand, a significant enhancement of mineralization can be always observed, reaching the TOC reduction an asymptotic value around 75% in the P23-A100 and P65-A100 run, and 65% in the case of P65-A65. The residual TOC corresponds to low molecular weight acids refractory at these operating conditions, in fact their concentration curves (not shown) exhibit also asymptotic values.

An important decrease of the concentrations of ring intermediates occurred when the CWAO reaction in the sequential
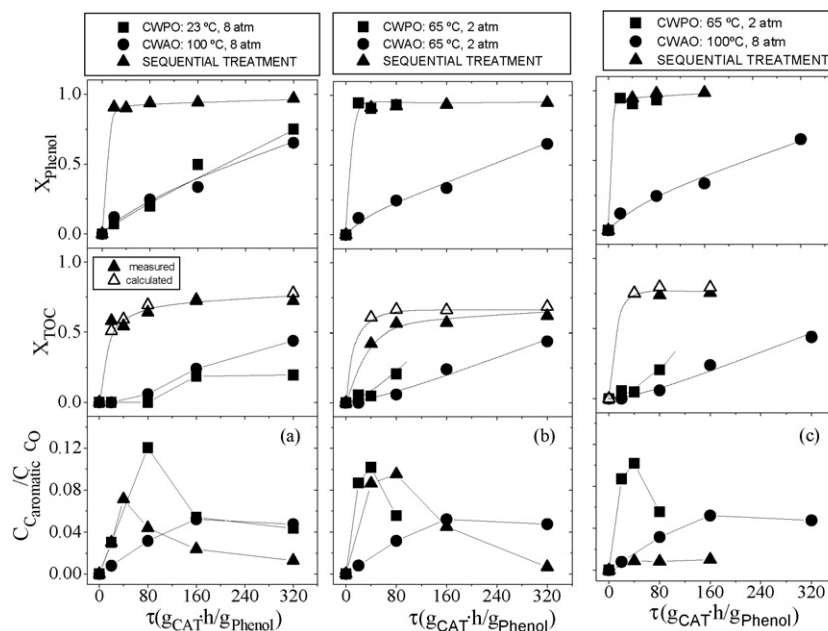

Fig. 7. Results from phenol sequential CWPO–CWAO treatment with the Fe/AC catalyst. (a) P23-A100, (b) P65-A65, and (c) P65-A100 experiments. Operating conditions summarized in Table 1.

treatment was conducted at 100 °C and 8 atm. However, when the CWAO is performed at milder conditions (65 °C and 2 atm) space-times higher than 160 g_{CAT} h/g_{Phenol} must be used to avoid the presence of condensation.

Another important advantage of the sequential CWPO–CWAO treatment is derived from the fact that Fe leaching is substantially reduced in comparison with CWPO.

Taking into account the TOC abatement, the residual concentration of ring intermediates and the stability of the catalyst a sequential treatment consisting of CWPO at 23 °C and 8 atm followed by CWAO at 100 °C and 8 atm seems to be the most convenient arrangement. As the pressure does not appear to be a determining factor in CWPO, this step can be performed in practice at ambient conditions.

4. Conclusion

A homemade Fe and activated carbon catalyst has proved to be effective in a sequential CWPO–CWAO process for phenol oxidation. CWPO proceeds at higher initial rates than CWAO but most of the intermediates produced are refractory to further oxidation. These refractory compounds are condensation products from ring intermediates and short chain acids, which remain even after complete disappearance of hydrogen peroxide. On the opposite, CWAO at mild conditions (100 °C and 8 atm) leads to the oxidation of most of the intermediates, including the condensation products detected at short space-times values. The final products are only acetic and formic acids.

A sequential treatment consisting of CWPO at ambient conditions followed by CWAO at mild conditions (100 °C and 8 atm), both using a homemade Fe/AC catalyst, allows to obtain phenol conversions up to 90% at short space-times (20 g_{CAT} h/g_{Phenol}) from a starting phenol concentration of 1 g/L. This sequential treatment reduces TOC as much as the CWAO process does, leading to a complete oxidation of ring intermediates, and avoiding the presence of condensation by-products in the reactor effluent when appropriate space-times are used. Further studies must be focused on the stability of the catalyst, trying to minimize Fe leaching in the CWPO step.

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