



Strategies for enhanced CWPO of phenol solutions

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ABSTRACT

The performance of a commercial CuO/alumina catalyst used in the catalytic wet peroxide oxidation (CWPO) of 1 g/l phenol solutions is investigated in a batch reactor. The effect of temperature, catalyst load, hydrogen peroxide concentration and dosage strategies on phenol mineralization, hydrogen peroxide consumption efficiencies and catalyst stability was studied. Experiments were performed at 298, 323 and 343 K, using catalyst loads of 1 g/l or 25 g/l and concentrations of hydrogen peroxide 1.3, 2.6 and 3.9 times the stoichiometric requirement added at once or in distributed doses. The critical goal of the CWPO in terms of Process Intensification is to achieve total phenol mineralization working at optimal hydrogen peroxide consumption efficiencies while retaining catalyst stability. The present work highlights the complexity of this objective and shows viable working alternatives.

Results indicate that high temperatures and concentrations of catalyst and hydrogen peroxide (added at once) can be employed when fast mineralization and high pH values are required in order to prevent catalyst leaching, although oxidant consumption efficiencies are then low. However, simultaneous high mineralization and hydrogen peroxide consumption efficiencies are obtained with a proper oxidant dosage strategy at high temperature, using high catalyst load. Then, hydrogen peroxide degradation into non-oxidising (parasitic) species is minimized with final TOC conversions close to 90%. The drawback of this strategy is that the rate of reaction is lower because of the limited amount of oxidant available.

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1. Introduction

Heterogeneous catalysts based on low-valence transition metals appear as a promising alternative for the catalytic wet peroxide oxidation (CWPO) of organic pollutants since oxidation efficiencies are relatively high and pH sensitivity is lower, compared with homogeneous catalysis at the same operating conditions. Moreover, solid catalysts could be recuperated by means of a simple separation step and reused.

A wide variety of catalysts containing iron, copper or other transition metal precursors supported on different materials have been tested for CWPO of phenol compounds [1–15]. Main results from these previous studies are summarized in Table 1. A disadvantage of using iron precursors is that the reaction should be carried out at pH values around 3. In turn, copper has a similar role as iron in catalysing hydrogen peroxide to produce hydroxyl radical, with the advantage that this reaction still retains a high efficiency at a higher pH range. However, the use of Cu-based catalysts in the CWPO process is incipient [1,4,8,9,13,16,17].

It has been generally observed that the efficiency for CWPO strongly depends on the concentration of hydroxyl radicals (HO•) produced through a redox process once the H₂O₂ is contacted with the catalyst. For a given H₂O₂ concentration and pH, the production of hydroxyl radicals mainly depends on catalyst concentration and reaction temperature. Once the radical is formed, it can react either with an organic, leading to oxidized species; with unreacted hydrogen peroxide, leading in this case to inactive molecular oxygen; with other radicals or with the metal itself, both being undesired scavenger reactions. The first reaction is favoured when the organic is present at high concentrations and leads to a high degree of mineralization (wanted reaction). The second possibility is favoured when the H₂O₂ is present in large amounts (with respect to the organics) according to the following reactions [18]:



The hydroperoxyl radicals (HO₂•) are much less reactive and do not significantly contribute to the oxidative degradation of organic substrates, which mainly occur by reaction with HO•. In addition, HO₂• acts as radical scavenger. These parasitic reactions, probably occurring at low catalyst loads or small organics concentration, affect the overall degradation efficiency and can result in significant increase of operational costs [18]. The second reaction between

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Table 1
Catalytic wet peroxide oxidation of phenol by copper or iron heterogeneous catalysts.

Catalyst	Phenol conversion and/or TOC or COD removal (%)	Conditions	Ref.
CuO impregnated activated carbon	98% phenol, 90% COD	Phenol 1000 mg/l, multiple step H ₂ O ₂ addition: total dosage 0,1 M, 2 g/l catalyst, 180 min, 80 °C, 4,6–38,9% wt of active metal	[8]
Cu/ZSM-5 by hydrothermal synthesis	36, 68, 85, 92% phenol (50, 60, 70, 80 °C)	Phenol 0,01 mol/l, H ₂ O ₂ 0,1 mol/l, catalyst 0,1 g/l, 180 min, 50–80 °C, 1,62% wt of active metal	[9]
Cu/ZSM-5 by ion-exchanged synthesis	20, 56, 81, 96% phenol (50, 60, 70, 80 °C)	Phenol 0,01 mol/l, H ₂ O ₂ 0,1 mol/l, catalyst 0,1 g/l, 180 min, 50–80 °C, 2,53% wt of active metal	[9]
MFI-type metallosilicates (M = Al, Ga, Zn, Cu...)	78% phenol, 61% TOC	Phenol 0,00005 mol/l, H ₂ O ₂ 0,5–0,1 N, 0,5 g/l catalyst, 240 min, 20 °C, 1 atm, pH 4–5	[10]
Cu/α-Al ₂ O ₃	100% phenol, 48% TOC	Phenol 0,01 mol/l, H ₂ O ₂ 0,1 mol/l, 5 g/l catalyst, 180 min, 90 °C, 1 atm, 1% wt active metal	[11]
Cu-Y-5	50, 70, 80, 80% phenol (50, 60, 70 and 80 °C)	Phenol 0,01 mol/l, H ₂ O ₂ 0,03 mol/l, catalyst 0,1 g/l, 180 min, 50, 60, 70 and 80 °C, pH 3.5–4, 4,09 wt% of active metal	[1]
Polymer-supported copper complexes: polybenzimidazole loaded with copper	72% phenol, 54% TOC	Phenol 1000 mg/l, Phenol/H ₂ O ₂ molar ratio of 1:14, 50 mg/l Cu ²⁺ , 240 min, 30 °C	[4]
Fe/active carbon catalyst	100% phenol, 85% TOC	Phenol 100 mg/l, H ₂ O ₂ stoichiometric amount, catalyst 0,5 g/l, 240 min, 50 °C, pH 3, 4% wt of active metal	[12]
Fe(III) supported on resin, M1 Fe-resin	10, 100, 100% phenol and 23, 79, 75% COD (40, 60, 80 °C)	Phenol 1000 mg/l, H ₂ O ₂ 0,1 M, catalyst 5 g/l, 40, 60, 80 °C, 120 min	[6]
Iron containing silicates, catalyst B	100% phenol, 81% TOC	Phenol 180 mg/l, 1,5 stoichiometric amount of H ₂ O ₂ , catalyst 0,5 g/l, 180 min, 80 °C initial pH 3.5.	[7]
Fe-ZSM-5 zeolite	100% phenol, 46% TOC	TOC _[phenol] 0,069 mol/l, 1,5 stoichiometric amount of H ₂ O ₂ , catalyst 1,5 g/l (2% wt Fe), 180 min, 70 °C initial pH 3.5.	[15]

radicals will predominate when a large amount of catalyst is used. Then, an enhanced hydrogen peroxide decomposition into HO• radicals may occur. These radicals can react with the organics or can promote other competitive scavenger reactions when the amount of organics present is small. Therefore, there is a complex interaction between catalyst, H₂O₂ and organics, which can affect the overall mineralization achieved.

The effect of temperature in the generation of radicals has been extensively studied and the idea of thermal decomposition of H₂O₂ into O₂ and H₂O seems to be widely accepted as a serious drawback [5,6,19,20], but results presented by Zazo et al. [21] contradict this concept and are worth to mention. The authors studied the homogeneous Fenton oxidation of phenol solutions with Fe²⁺ at temperatures between 25 and 130 °C. Higher temperatures lead to a more efficient use of H₂O₂ upon enhanced generation of HO• radicals at low Fe²⁺ concentration. Therefore, the increase of the temperature was considered as an intensification way of the conventional Fenton process.

In the last years, the influence of H₂O₂ dosage has also been studied [8,22,23]. Liou and Chen [8] studied the removal of phenol with activated carbon-supported copper (CuAC) catalysts at 80 °C. When multiple doses were used, COD removal decreased slowly when compared with one-step H₂O₂ addition. However, the final COD removal was enhanced. Therefore, the residual H₂O₂ dominated the final COD and phenol removal and maintaining residual hydrogen peroxide in solution was helpful to generate more free radicals. Martins et al. [22] studied the homogeneous Fenton's oxidation of a mixture of six phenolic acids at room temperature. Oxidation efficiency and TOC conversions were improved when hydrogen peroxide was added in several doses. These results were related to the radical scavenger effect of hydrogen peroxide excess. Zazo et al. [23] studied the homogeneous CWPO of phenol at 25 °C, in a semicontinuous reactor. The overall amount of H₂O₂ was distributed as a continuous feed upon the reaction time. Results showed lower oxidation rates for phenol and intermediates when the H₂O₂ was added continuously. Nevertheless, a higher final TOC conversion was reached, in spite of a similar overall H₂O₂ consumption. This means that the HO•

generation was more efficient throughout the semicontinuous process, favouring the reaction with the organic species and reducing the occurrence of competitive scavenging reactions involving Fe²⁺, H₂O₂ and HO•. According to these outcomes, not only the load of hydrogen peroxide should be adjusted to ensure its efficient utilization but also addition strategies must be strongly considered.

In this study we investigate the performance of a commercial CuO/alumina catalyst in the CWPO of phenol solutions. While copper oxides exhibit a great activity for the catalytic oxidation of organic water pollutants with air or oxygen [24–26], few articles reported its use in CWPO [1,4,8,9,13,16,17]. Deactivation by leaching was observed in the catalytic wet air oxidation of phenol solutions [25,26]. This phenomenon was related to the low pH originated by the generation of carboxylic acids through the reaction mechanism as stated by Santos et al. [26] who observed an increase in the leaching of copper when the pH went under about 4. The authors observed that the metal leaching could be promoted by both the pH decrease due to the acid intermediates formed through the oxidation and the copper take-off from the surface during the redox reaction of the oxidizable organic compounds. On the other hand, Álvarez et al. [25] studied the stability of a catalyst of copper oxide mounted on activated carbon in the CWAO of phenol solutions. Copper leaching was not attributed to the acidic reaction medium (as H⁺) resulting from the accumulation of acids during the oxidation but to the actual CWAO mechanism and resulting reaction intermediates. The hot aqueous solution could leach copper from the surface of the catalyst because of the reaction of carboxylic acids (i.e., acetic acid) with copper oxide to give organometallic compounds [25].

According to these studies, the operating conditions should contemplate the rapid mineralization of carboxylic acids in order to avoid their accumulation and low pH values, so the catalyst stability is maintained.

In this context, experiments were performed addressing the effect of catalyst concentration, temperature, hydrogen peroxide concentration and dosification strategies on phenol conversion and mineralization. Therefore, process intensification of Fenton's

treatment was achieved through efficient use of reagents, lower reaction times and enhanced catalyst stability.

2. Experimental

Phenol CWPO was carried out in a 250 ml thermostated batch reactor provided with vigorous agitation (800 rpm). Experiments were performed at 298, 323 and 343 K, a temperature range investigated by several authors [1,6,9,12,20,27,28]. Catalyst concentration was fixed at 1 g/l or 25 g/l (125 and 3125 mg/l of Cu^{2+}). Most authors performed studies using a much lower catalyst to phenol mass ratio respect to the maximum ratio used in this study (3.12 g Cu^{2+} /g Phenol) [1,4,8,9,11,13]. However, others state that increasing the catalyst load (until some level) may have a beneficial effect on oxidation performance due to the increasing amount of active sites for H_2O_2 decomposition and for organic compounds adsorption [19]. The increase of copper sites should induce a better use of oxidant for the promotion of free radicals, avoiding its thermal decomposition into O_2 [5].

Finally, the effect of hydrogen peroxide was analyzed by varying its concentration between 1.3 and 3.9 times the stoichiometric demand. Most authors use concentrations between 0.7 and 1.3 [4,8,9,12] and only a few have studied concentrations between 3.5 and 4 of the stoichiometric requirement [10,28,29]. Such large range of catalyst and hydrogen peroxide concentrations were selected to analyze the different competing effects in the mineralization process.

The commercial catalyst (BASF Cu-0226 S) is a highly dispersed copper oxide (12.5%) impregnated on a high surface alumina used primarily for removing traces of O_2 in inert gases. Catalyst was used without previous treatment. In a typical experiment, a mass of fresh catalyst (average particle diameter 0.9 mm) was put into 170 ml of 1 g/l of phenol (p.a., JT Baker) aqueous solution under continuous stirring at 800 rpm. When the reaction temperature was reached, a given volume of 30% wt. hydrogen peroxide (Cicarelli, 30%) was added into the system and the reaction started. In order to compare reaction performance obtained at different operating conditions, final reaction time was fixed at 180 min. Accordingly, liquid samples were withdrawn at different time intervals up to 180 min and analyzed to determine phenol, hydrogen peroxide and total organic carbon (TOC) conversions. Also pH was followed. Phenol was detected and measured by UV absorbance at 508 nm wavelength with a standard colorimetric method [30]. Hydrogen peroxide was analyzed by an iodometric titration method [30], TOC was measured using a TOC analyzer (Shimadzu, model TOC- V_{CPN}). Values reported here are the averages of at least two measurements. Preliminary identification of reaction intermediates was performed in a HPLC (Agilent Technologies, model 1100) with a C18 reverse phase column (Agilent Technologies, Hypersil ODS) following the procedure reported by Castro et al. [4]. Copper leached from the catalyst was measured using atomic absorption spectroscopy (AA) in an ANALYST 300 Perkin-Elmer spectrophotometer.

The selectivity towards mineralization (σ) is described by the ratio between actual TOC and theoretical TOC if phenol consumed at a given reaction time is totally mineralized, expressed as:

$$\sigma = \frac{\text{TOC consumption (mg)}}{\text{phenol TOC consumption (mg)}} \times 100 \quad (3)$$

The efficiencies of hydrogen peroxide consumption described by Zazo et al. [21] as the ratio between TOC consumed and hydrogen peroxide decomposed at a given reaction time (η) and the amount of TOC consumed per unit weight of hydrogen peroxide fed (ε) were defined as:

$$\eta = \frac{\text{TOC consumption (mg)}}{\text{H}_2\text{O}_2 \text{ consumption (g)}} \quad (4)$$

$$\varepsilon = \frac{\text{TOC consumption (mg)}}{\text{H}_2\text{O}_2 \text{ fed (g)}} \quad (5)$$

3. Results and discussion

3.1. Preliminary experiments

In first place, phenol was oxidized with hydrogen peroxide without catalyst, but its conversion was very low (less than 5% after 3 h), indicating its negligible contribution to observed phenol concentration decay. Additionally, a previous set of experiments using catalysts without H_2O_2 was performed to discriminate the effect of adsorption and a maximum phenol disappearance of 6% after 3 h was recorded, which also is considered marginal.

Catalyst ability to decompose H_2O_2 in the absence of phenol was evaluated at three different temperatures (298, 323 and 343 K) using a catalyst concentration of 25 g/l. Initial H_2O_2 decomposition rates increase with temperature and, for instance, complete conversion of the oxidant is achieved in 15 min when working at 343 K.

The experimental data were contrasted against a kinetic model in which the rate of peroxide decomposition was assumed to be first order with respect to the hydrogen peroxide concentration. The apparent activation energy for hydrogen peroxide decomposition was evaluated as 44.9 kJ/mol ($r^2 = 0.9991$), value in agreement with previously reported data from Ariafad et al. [31].

3.2. Temperature and catalyst concentration effect

The catalytic oxidation of phenol solutions was tested at 298, 323 and 343 K using a H_2O_2 :phenol molar ratio of 18, a value 30% higher than the stoichiometric one, and catalyst concentrations of 1 and 25 g/l. Initial H_2O_2 decomposition rates are slower in the presence of phenol but still increase with temperature. At 343 K, complete conversion of the oxidant is achieved in 30 min.

The experimental data for hydrogen peroxide decomposition in the presence of phenol was fitted with a first order kinetic model and the apparent activation energy obtained was now 74 kJ/mol ($r^2 = 0.9985$). This value is higher than that calculated in the absence of phenol (44.9 kJ/mol).

In summary, hydrogen peroxide decomposition rates are higher when no phenol is present. These results were also observed by Bach et al. [32]. In the absence of organics, the hydroxyl radicals react mainly with unreacted hydrogen peroxide and copper ions. In presence of phenol, the radicals additionally react with it (and its derived oxidation intermediates), and these competition reactions partially suppress radical consumption through reaction with hydrogen peroxide, being responsible for the slower decomposition of the hydrogen peroxide observed.

Figs. 1–4 show phenol, H_2O_2 and TOC conversions as well as pH evolution as a function of time using 1 and 25 g/l of catalyst at different temperatures. When working with 25 g/l of catalyst, at 298 K and 180 min, phenol conversion and TOC abatement were of 27 and 18%, respectively, although H_2O_2 conversion was quite high (83%). The pH remained close to the initial value (7.5).

At 323 K and 180 min, conversion of phenol and TOC reduction were of 71% and 48%, respectively, while hydrogen peroxide was completely consumed. Reaction colour changed from transparent to dark brown (between 30 and 60 min) due to the occurrence of benzoquinones. The pH evolution exhibits a minimum value (5.8) at approximately 60 min. Although complete identification of intermediate compounds was not feasible, results suggest that a fraction of the initial phenol is gradually oxidized through aromatic intermediates like catechol, detected until 60 min, and dark coloured intermediates products such as p-benzoquinone detected until 90 min. Short chain organic acids are formed almost immediately

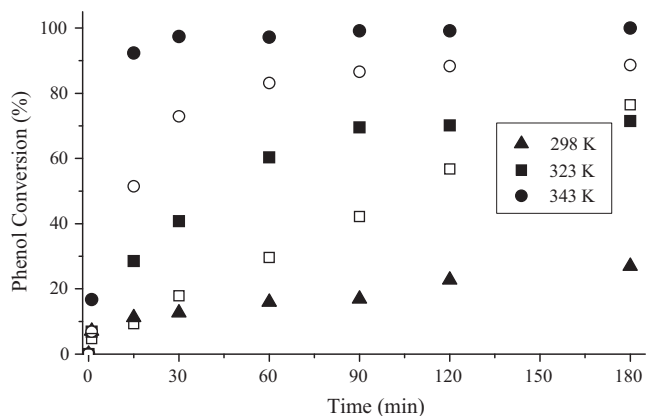


Fig. 1. Phenol conversion against time, at different reaction temperatures (▲: 298 K; ■, □: 323 K; ●, ○: 343 K). Full and open symbols represent results with 25 g/l and 1 g/l of catalyst.

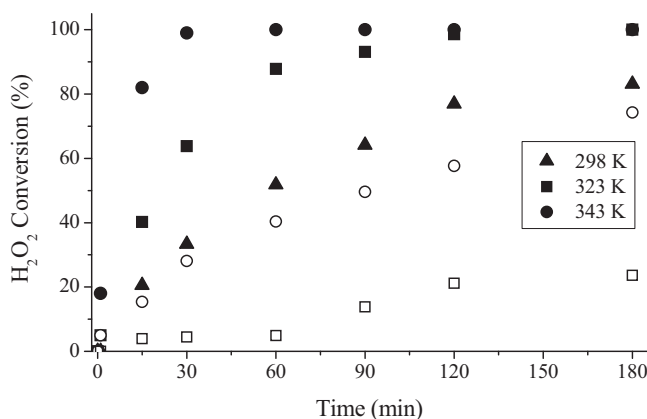


Fig. 2. Hydrogen peroxide consumption against time, at different reaction temperatures (▲: 298 K; ■, □: 323 K; ●, ○: 343 K). Full and open symbols represent results with 25 g/l and 1 g/l of catalyst.

(succinic, fumaric, malonic and maleic) and then are progressively mineralized by the hydroxyl radicals.

At 343 K, phenol and hydrogen peroxide conversions are almost complete at 30 min. However, a TOC conversion of 76% is still found at 180 min. A minimum value of pH of 3.3 was detected after approximately 15–20 min. This low pH value agrees well with

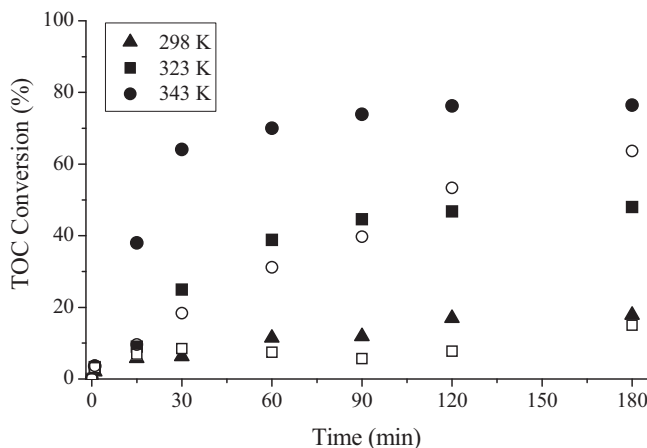


Fig. 3. TOC conversion against time, at different reaction temperatures (▲: 298 K; ■, □: 323 K; ●, ○: 343 K). Full and open symbols represent results with 25 g/l and 1 g/l of catalyst.

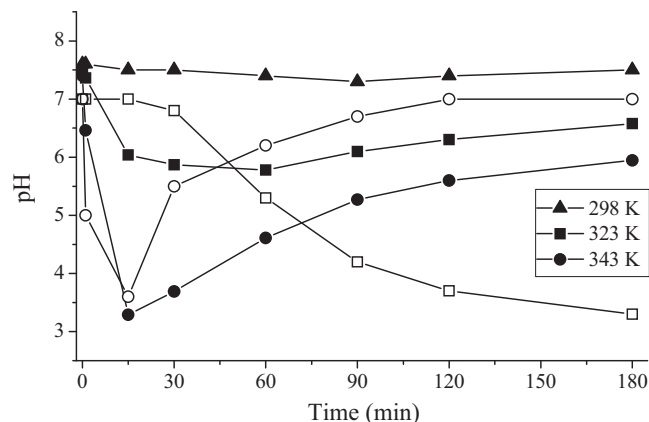


Fig. 4. pH evolution against time, at different reaction temperatures (▲: 298 K; ■, □: 323 K; ●, ○: 343 K). Full and open symbols represent results with 25 g/l and 1 g/l of catalyst.

the maximum concentration of detected organic acids (malonic, maleic, succinic and fumaric acids) produced during the initial step of phenol oxidation. Then, as phenol is exhausted, pH increased due to the enhanced oxidation of intermediate products. Reaction mixture turned from transparent to dark brown at 15 min and then remained in that colour, probably due to the presence of some benzoquinones. This product distribution is not desirable, not only because of the aesthetic effect but mainly owing to its ecotoxicity. The residual TOC reflects the presence of these partial oxidation products, which were incompletely oxidized. In addition, the pH dropped below the admissible value in terms of copper leaching.

Results clearly show that the rate and degree of phenol, TOC, H₂O₂ conversions increase as temperature increases but results are more marked for H₂O₂ decomposition. The increase of the temperature from 298 to 323 K promotes higher decomposition of H₂O₂ but not a significantly improved removal of TOC. This is probably related to the influence of temperature on the free radicals formation, as pointed out by Sotelo et al. [5], and to the fact that the rate of phenol disappearance is slower than the rate of HO• radical formation [6]. Therefore it was necessary to raise the temperature up to 343 K to improve significantly both phenol and TOC conversions. However, the faster decomposition of H₂O₂ at 343 K subsequently reduces the radicals available for the oxidation of the first aromatic intermediates produced, then increasing the toxicity of the effluent [33].

Higher mineralization rates are observed at short reaction times since the reaction between hydroxyl radicals and organic compounds becomes progressively less important when TOC concentration decreases. At extended reaction times, hydrogen peroxide concentration is already small and, if there is an excess of catalyst, there is a fast rate of radicals generation. As the TOC concentration is small too, the recombination reactions between these hydroxyl radicals becomes predominant with a prevalent scavenger effect. Moreover, the hydroxyl radicals could also react to produce less active HO₂•. Both effects could explain the decline in mineralization rate at the end of the reaction, when the TOC concentration is rather low [32]. Besides, the final compounds are mostly refractory acids.

For simplicity, results obtained with 1 g/l of catalysts are only presented at 323 and 343 K in Figs. 1–4. Outcomes obtained with 1 g/l of catalyst show similar trends but lower conversions were achieved. As described by several authors [5,6,19], when a small ratio of catalyst to target compound is used, phenol and TOC elimination rates decrease, due to the reduced amount of active sites for the H₂O₂ decomposition and for the adsorption of organic compounds over the catalyst. Furthermore, at both temperatures the

reaction media colour indicated the presence of p-benzoquinones. At 323 K, the pH reached a value of 3.3 at the end of the reaction. At 343 K, the pH reached a minimum value of 3.6 at 15 min and then it increased up to 7 at the end of reaction. The achievement of pH values below 4 could promote the leaching of the catalyst.

3.3. H_2O_2 concentration effect

Experiments were performed increasing the molar ratio peroxide/phenol using concentrations of hydrogen peroxide 1.3, 2.6 and 3.9 times the stoichiometric requirement. Final TOC conversions and initial TOC conversion rates, peroxide efficiencies (η , ε) and selectivity (σ) results for 1 and 25 g/l of catalyst and 323 and 343 K, are presented in Table 2.

When 1 g/l of catalyst is used at 323 and 343 K, initial TOC rates are almost independent of hydrogen peroxide concentration, because the small amount of active centres limits their availability to decompose it. The appearance of a maximum value in final TOC conversions is observed, at the intermediate ratio, when the amount of H_2O_2 increases. When the load of catalyst is small, an increase on H_2O_2 concentration beyond a critical value does not bring any benefit or even leads to a decrease on TOC removal due to the hydrogen peroxide scavenger effect, according to reactions (1) and (2) previously presented [18,19,22]. Additionally, for the three experiments at 323 K and for experiments performed using 2.6 and 3.9 times the stoichiometric hydrogen peroxide at 343 K, pH values decrease up to 3 and then remain in that value.

When 25 g/l of catalyst are used, initial TOC conversion rate and final TOC removal are enhanced as the amount of hydrogen peroxide is increased at the two temperatures investigated. The improvement of TOC conversion is more evident at lower initial dose. This could be due to the well-known hydroxyl radical scavenging effect. At 323 K, as the initial dose of hydrogen peroxide increases, the minimum pH decreases and appears earlier; from a minimum of 5.8 at 60 min at the lowest dose to a pH of 3.8 at 30 min at the highest dose. The increase of the H_2O_2 dose at 323 K with 25 g/l of catalyst improves conversions but has a detrimental effect in the pH values reached during the reaction, which leads to higher copper leaching. On the other hand, an increment of the initial H_2O_2 dose at 343 K has a positive effect on the pH evolution. At 343 K, the minimum pH value is reached at the beginning of the reaction (less than 15 min) and it increases from 3.3 to 4.7 when the hydrogen peroxide dose increases.

3.4. H_2O_2 dosage strategy effect

Several assays were performed by supplying the peroxide in sequential applications using 25 g/l of catalyst. Multiple dose experiments were designed so that, after first addition, H_2O_2 concentration was monitored and once its value was negligible, an additional quantity of H_2O_2 was added into the reactor. Thus, overall doses for experiments previously performed at the different temperatures were now distributed and added at different times.

Experiments were performed at 323 K and 343 K in which 1.3 times the stoichiometric H_2O_2 was added in multiple steps (3 doses of one-third each). Results are presented in Fig. 5 for 323 K. It is noteworthy to compare the outcomes with those obtained feeding the same quantity of oxidant at once (Figs. 1–4). The addition of the same total amount of oxidant using three doses is clearly a more effective method for phenol removal and mineralization. With the multiple step procedure, 87% of phenol removal and 60% TOC conversion are achieved at the same elapsed time (180 min). These values are much higher than those obtained with a single peroxide dose (71% and 48% of phenol and TOC conversions, respectively). The pH values decrease from an initial value of 7 to 6.1 at

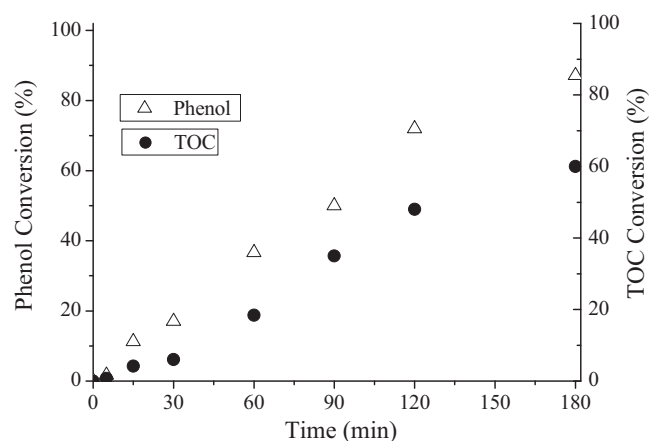


Fig. 5. Phenol (Δ) and TOC (\bullet) conversion against time, for three one-third doses of 1.3 times the stoichiometric H_2O_2 , at 323 K.

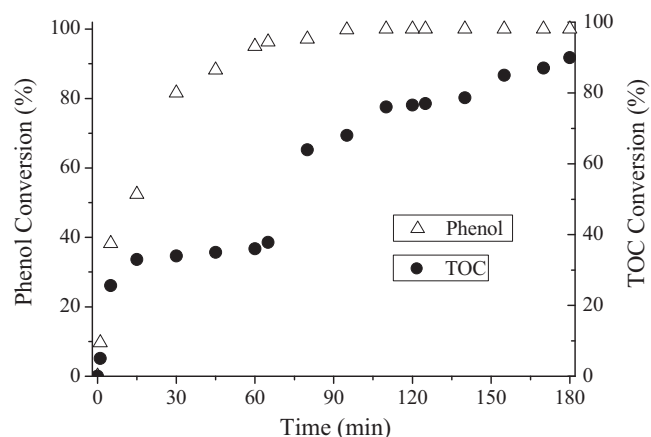


Fig. 6. Phenol (Δ) and TOC (\bullet) conversion against time, for three one-third doses of 1.3 times the stoichiometric H_2O_2 , at 343 K.

180 min. In any case, reaction colours change from transparent to dark brown and remain dark at the end of the reaction due to the presence of benzoquinones. Although phenol conversion and TOC removal are clearly enhanced, the selectivity towards mineralization is not good enough and the presence of quinones are not yet satisfactory.

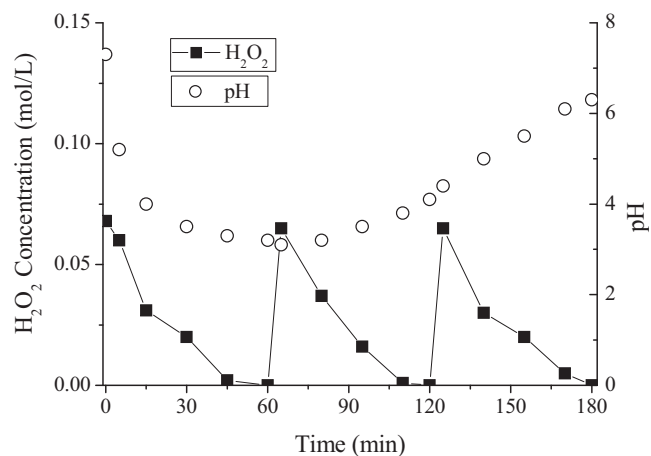


Fig. 7. Hydrogen peroxide consumption (\blacksquare) and pH evolution (\circ) against time, for three one-third doses of 1.3 times the stoichiometric H_2O_2 , at 343 K.

Table 2
Selectivity towards mineralization and H₂O₂ efficiencies at different experimental conditions.

Experimental conditions			Efficiency parameters				
T (K)	Catalyst load (g/l)	H ₂ O ₂ dosage ^{a,b}	Final TOC conversion (%)	Initial TOC conversion rate (min ⁻¹)	σ	ε	η
298	25	1 dose of 3.3 ml	18	–	67	21	25
323	25	1 dose of 3.3 ml	48	0.6	67	56	56
343	25	1 dose of 3.3 ml	76	2.53	76	90	90
323	25	1 dose of 6.6 ml	81	0.8	81	48	48
343	25	1 dose of 6.6 ml	89	4.18	90	53	53
323	25	1 dose of 9.9 ml	90	1.67	90	36	35
343	25	1 dose of 9.9 ml	94	5.12	95	37	37
323	1	1 dose of 3.3 ml	15	0.39	20	18	74
343	1	1 dose of 3.3 ml	64	0.6	72	75	101
323	1	1 dose of 6.6 ml	22	0.4	29	13	46
343	1	1 dose of 6.6 ml	70	0.64	70	42	60
323	1	1 dose of 9.9 ml	20	0.4	26	8	28
343	1	1 dose of 9.9 ml	51	0.67	51	20	31
323	25	3 doses of 1.1 ml	60	–	69	71	71
343	25	3 doses of 1.1 ml	90	–	90	107	102
323	25	3 doses of 3.3 ml	86	–	86	34	32
343	25	3 doses of 3.3 ml	91	–	91	36	34

^a 30% (w/w) H₂O₂ was used in all the cases.

^b 1.3 times the stoichiometric ratio requires 3.3 ml addition.

Results obtained at 343 K are shown in Figs. 6 and 7. At 180 min, complete phenol conversion and a TOC reduction of 90% are obtained with the step by step addition of peroxide. Reaction mixture colours change from transparent to dark brown (at 90 min) and then turn back to transparent at the end of the reaction. Identification of intermediate products at 180 min indicates the presence of succinic acid and only traces of acrylic, benzoic and salicylic acids, responsible for the remaining TOC. Although the pH rises to 6.3 at the end of the reaction, it reaches values below 4 during approximately 70 min of reaction, which could promote copper leaching from the catalyst.

To further investigate this concept, controlled step wise addition of 3 doses of 1.3 times the stoichiometric H₂O₂ each one was tested, using 25 g/l of catalyst, at 323 and 343 K. Results are presented in Table 3. Under these conditions (high catalyst and high hydrogen peroxide doses) the amount of radicals present in the reaction media is large, especially at the highest temperature studied. Most of these radicals will react with phenol and intermediates, enhancing the rate of phenol and TOC conversion. The net effect is that the mineralization takes place at shorter times. However, the drawback is that part of hydrogen peroxide is consumed in parasitic reactions. At 323 K, reaction colours change from transparent to dark brown and then turn clearer and finally transparent as the peroxide doses were added. Results in terms of phenol conversion and mineralization are quite satisfactory (100 and 86%), although the amount of hydrogen peroxide consumed is quite excessive (almost 4 times the stoichiometric one).

Results obtained at 343 K follow a similar trend, although rates are higher. Complete phenol conversion is obtained at 60 min while 91% TOC reduction is obtained at 120 min and remains constant up to 180 min. Reaction mixture colours change from transparent to dark brown at 15 min and then become transparent at 120 min.

Comparison with outcomes obtained with a single dose of 3.9 times the stoichiometric hydrogen peroxide shows that there is no benefit in dosification when such large ratios of hydrogen peroxide are used. Results obtained with the single dose are already satisfactory in terms of mineralization, pH and leaching. Anyway, the pH and colour evolution change when dosage is applied, which clearly evidences that a different intermediate distribution is obtained. When three doses of 1.3 times the stoichiometric each one are used, the pH reaches lower values for longer periods (especially at higher temperatures), so it is not recommendable in terms of metal leaching.

3.5. Effect of operating conditions on the selectivity and hydrogen peroxide efficiencies

Hydrogen peroxide efficiencies (η and ε) and selectivity towards mineralization (σ) were calculated with Eqs. (3)–(5) using data obtained at the different experimental conditions tested. Results are presented in Table 2. The η considers not only the TOC conversion but the H₂O₂ consumption as well. Therefore, it takes into account the amount of H₂O₂ that was consumed by different reactions (scavengers too) to obtain a final TOC removal. The ε considers the total H₂O₂ that was fed into the system. Both efficiencies are equal when the oxidant is completely consumed. The selectivity towards mineralization (σ) represents the part of TOC from phenol that is actually mineralized to CO₂ and H₂O.

3.5.1. Single dose experiments

Here, the effect of temperature, oxidant and catalyst concentration on efficiencies and selectivity will be discussed when the H₂O₂ is added at once at the beginning of the experiments. The value of η increases as temperature increases. A high temperature accelerates H₂O₂ conversion into hydroxyl radicals, thus minimizing the hydrogen peroxide available to scavenge these radicals, and enhancing TOC conversion [22]. As the initial dose of H₂O₂ increases, the η obtained at different conditions approaches.

For all experiments, ε increases with higher temperatures due to enhanced generation of HO• and TOC conversion [21]. When the H₂O₂ initial dose increases, the differences between ε values at different temperatures decrease.

The selectivity towards mineralization (σ) increases with temperature due to the enhanced generation of radicals and mineralization achieved. As the oxidant dose grows, the differences between σ values at different temperatures decreases. In general, at all conditions studied, an increment on the initial H₂O₂ dose reduces ε and η . This is due to the excess of hydrogen peroxide and promotion of scavenging reactions.

As expected, the maximum selectivity is found at 343 K. At low concentrations of catalyst, σ remains constant or even decreases when higher doses of oxidant are applied. Phenol conversion is enhanced but, due to scavenging effects, there are not significant changes on TOC conversions. Instead, when a high concentration of catalyst is used, σ increases as the oxidant dose is larger.

When the concentration of catalyst increases, the amount of active sites for the generation of radicals is greater. Therefore, the mineralization is enhanced and σ and ε are consequently improved.

Table 3
Reaction outcomes for different dosification strategies.

Experimental conditions			Reaction parameters		
T (K)	H ₂ O ₂ dosage ^{a,b}	Final TOC conversion (%)	Final phenol conversion (%)	Minimal pH	Final pH
323	3 doses of 1.1 ml	60	87	6.1	6.1
343	3 doses of 1.1 ml	90	100	3.1	6.3
323	3 doses of 3.3 ml	86	100	3.6	6.1
343	3 doses of 3.3 ml	91	100	2.4	7.2

^a 30% (w/w) H₂O₂ was used in all the cases.

^b 1.3 times the stoichiometric ratio requires 3.3 ml addition.

However, the increments decrease at higher temperatures mostly due to synergic effects.

According to these results, mineralization and selectivity are favoured at high temperatures, large doses of oxidant and great catalyst loads. In terms of η , better results are obtained with a small load of catalyst and low doses of H₂O₂. A further increment of the peroxide dose should be accompanied by a higher catalyst concentration to maintain the η . Finally, ε is favoured by high concentrations of catalyst and small doses of H₂O₂.

3.5.2. Multiple dose experiments

The multiple step addition of 1.3 times the stoichiometric results in a more efficient H₂O₂ utilization, with greater TOC removal being achieved. The applied strategy was adding three one-third doses as opposed to one single dose as previously done. Good conversions and H₂O₂ consumption efficiencies are obtained, but at lower rates.

Results clearly indicate that hydrogen peroxide is one of the most important factors to control the mineralization of phenol. It is evident that keeping residual hydrogen peroxide in solution with enough mass of catalyst allows generating more free radicals, which are efficient in the mineralization process.

When the 3.9 times dose is distributed in three additions of one-third each, only slightly lower phenol and TOC conversions are obtained but at longer time. These small differences in the final TOC removal explain the slight reductions of the selectivity and efficiencies. When the second one-third dose of hydrogen peroxide is added, the TOC concentration is already low, so the reaction between hydroxyl radicals and the excess of H₂O₂ added becomes more dominant as the TOC decreases.

In any case, proper dosage strategically designed is clearly beneficial when small doses of hydrogen peroxide are distributed throughout the time in the presence of sufficient catalyst at high temperature. Under these conditions, the scavenging effects are better avoided and good phenol conversions, TOC reductions and hydrogen peroxide consumption efficiencies are obtained. The drawback is that the oxidation rate is lower because of the limited amount of oxidant present at any time.

3.6. Catalyst stability

For all the experiments performed, liquid samples were withdrawn at the end of the reaction and copper concentration was measured to determine the degree of leaching. When the pH reached values below 4 during long reaction times, a leaching of about 0.6% (17 mg/l of copper in solution) was measured. When the operating conditions favoured pH values above 4, the leaching was diminished to values close to 0.2% (4 mg/l of copper in solution).

In order to discriminate between heterogeneous and homogeneous contribution, the results obtained from the heterogeneous reaction at 323 K, with a catalyst concentration of 25 g/l and a single initial dose of 1.3 times the stoichiometric H₂O₂, were compared with the activity of a homogeneous test with a concentration of Cu²⁺ equivalent to the leaching of the commercial catalyst after

3 h operation (4 mg/l). The reaction was performed under the same reaction conditions as the heterogeneous experiment.

Although this approach is used by several authors, the experiment may overestimate the homogeneous contribution since, as stated by Hudgins and Silveston [34] the homogeneous catalytic component due to the leached cupric ion in batch reaction varies with time as well as reaction conditions (Cu ions can form mostly inactive quelates with organic dicarboxylic acids). In our experiments, the release of Cu ions is gradual and, when 4 mg/l of Cu are present in solution, the peroxide concentration is actually very small and phenol is mostly oxidized.

Hydrogen peroxide and TOC conversions were found to be quite low, 20 and 9% respectively. The radicals generated from the H₂O₂ decomposition oxidized 75% of phenol, but only 9% of TOC was mineralized. The final colour of the solution was dark brown, which indicates the presence of toxic intermediates. The pH drop to 4 at the beginning of the reaction and maintained a value of 2.5 during the last two hours, suggesting the presence of refractory acids. The complexation of homogeneously dissolved copper ions by oxalic acid could inhibit further TOC removal [35].

Phenol conversion (75%) was slightly higher than the value obtained in the heterogeneous system (71%). Santos et al. [26] suggested a homogeneous contribution for the catalytic wet air oxidation of phenol (according to a free radical mechanism), while the oxidation of the intermediates would be mainly due to a heterogeneous reaction. This is because phenol is oxidized while homogeneous copper exits, but later is sequestered by dicarboxylic acids and loses its activity.

The global activity obtained under the heterogeneous conditions was higher than the activity shown in the homogeneous reaction. Therefore, the activity of the commercial catalyst mainly owns to a heterogeneous phenomenon and the contribution of the leached copper must be taken as minimal.

With respect to homogeneous experiments using 17 mg/l, results follow a similar trend but TOC conversions are higher. The homogeneous contribution may be slightly important in this case, although its quantification is not accurate following Hudgins and Silveston comments [34].

Overall, to minimize the amount of leaching, the operating conditions should be severe enough as to prevent the accumulation of carboxylic acids (responsible of the low pH values attained in some conditions). For the experimental conditions tested in the present work, better results are achieved with higher catalyst load, hydrogen peroxide concentration and temperature. Dosage strategies should be tuned up (i.e., higher temperatures) to avoid the lasting presence of organic acids.

4. Conclusions

The performance of a commercial catalyst (BASF Cu-0226 S) for the CWPO of phenol solutions was tested addressing the effect of temperature, catalyst load and hydrogen peroxide dosage on phenol mineralization and hydrogen peroxide consumption efficiency. Under proper reaction conditions, this catalyst is characterized by

a high rate of hydrogen peroxide decomposition and generation of radicals, which enables the application of dosage strategies. Also, the leaching measured under extreme conditions (pH below 4) was relatively low (0.6%) and could be reduced under adequate operating conditions.

The ultimate goal of the CWPO is to attain complete phenol mineralization working at optimal hydrogen peroxide consumption efficiency. The present work highlights the complexity of this objective and presents viable alternatives. Several competing effects may contribute to obtain an optimal rate of mineralization. If a high concentration of catalyst is used, more hydroxyl radicals are produced and are therefore available for phenol mineralization. However, the mineralization could be affected by two factors. First, there are several side reactions which produces less active HO₂[•] radicals. Second, the high concentration of radicals also promotes the recombination reaction between them (scavenging effect). Third, if there is an excess of hydrogen peroxide, hydroxyl radical will react with it, producing inactive species, such as H₂O and O₂. Additionally, it should be noticed the effect of TOC concentration. When the amount of organic species is low, the side reactions of hydroxyl radicals with the excess of H₂O₂ or catalyst become more important, and the scavenging effect enhances.

Phenol, TOC, H₂O₂ conversions and hydrogen peroxide consumption efficiencies rise with temperature. Increments in catalyst load (i.e., active sites) result in higher generation of radicals and in a reduction of scavenging effects due to peroxide excess, because they are consumed by the organic compounds rather than in side reactions. This results in higher values of σ and ε , but η decreases because of the accelerated decomposition of the oxidant. As the concentration of oxidant is increased, the consumption efficiencies are reduced and reaction rates improved. However, at small catalyst loads, when H₂O₂ is enlarged, a maximum in TOC conversion is observed. Results are attributed to scavenging effects that arise when there is a reduced amount of active sites competing for H₂O₂ decomposition and organic compound adsorption.

To reduce catalyst leaching, minimum pH values should be kept above 4. This condition is never fulfilled for small catalyst loads. To obtain high pH values and TOC conversions, high concentrations of catalyst and hydrogen peroxide should be employed. Also, at higher temperatures, the pH increases.

In terms of Process Intensification concepts, higher temperatures and concentrations of catalyst and hydrogen peroxide added at once may be employed when a faster mineralization rate and high pH values are required. On the other hand, high hydrogen peroxide consumption efficiencies and conversions could be obtained with a dosage strategy at high temperatures, with sufficient catalyst load and small doses of H₂O₂. Hydrogen peroxide degradation into non-oxidising (parasitic) species is then minimized with acceptable final TOC conversions.

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