

Abatement of phenolic mixtures by catalytic wet oxidation enhanced by Fenton's pretreatment: Effect of H₂O₂ dosage and temperature

A. Santos*, P. Yustos, S. Rodriguez, E. Simon, F. Garcia-Ochoa

Dpto Ingeniería Química, University Complutense Madrid, Ciudad Universitaria S/N, 28040 Madrid, Spain

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Abstract

Catalytic wet oxidation (CWO) of a phenolic mixture containing phenol, o-cresol and p-cresol (500 mg/L on each pollutant) has been carried out using a commercial activated carbon (AC) as catalyst, placed in a continuous three-phase reactor. Total pressure was 16 bar and temperature was 127 °C. Pollutant conversion, mineralization, intermediate distribution, and toxicity were measured at the reactor outlet. Under these conditions no detoxification of the inlet effluent was found even at the highest catalyst weight (W) to liquid flow rate (Q_L) ratio used. On the other hand, some Fenton Runs (FR) have been carried out in a batch way using the same phenolic aqueous mixture previously cited. The concentration of Fe²⁺ was set to 10 mg/L. The influence of the H₂O₂ amount (between 10 and 100% of the stoichiometric dose) and temperature (30, 50, and 70 °C) on phenols conversion, mineralization, and detoxification have been analyzed. Phenols conversion was near unity at low hydrogen peroxide dosage but mineralization and detoxification achieved an asymptotic value at each temperature conditions. The integration of Fenton reagent as pretreatment of the CWO process remarkably improves the efficiency of the CWO reactor and allows to obtain detoxified effluents at mild temperature conditions and relatively low W/Q_L values. For a given phenolic mixture a temperature range of 30–50 °C in the Fenton pretreatment with a H₂O₂ dosage between 20 and 40% of the stoichiometric amount required can be proposed.

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1. Introduction

The effective removal of refractory pollutants in industrial wastewater is currently an environmental and economic problem [1–3], because these effluents do not allow the use of conventional biological treatment due to their poor biodegradability and toxicity [2]. Among these residual aqueous streams the wastewaters containing phenol and cresols could be a typical example of effluent that requires an advanced treatment technology. These effluents are obtained mainly in petrochemical and coal processing industries [4–15].

Treatment technologies available for handling phenolic waste are physical, chemical, biological, and electrochemical processes [16–18]. Among these, oxidation has a great potential to eliminate those pollutants. Under the adequate conditions this technology converts the refractory pollutants into CO₂, water, and biodegradable short chain acids. The oxidant agents most frequently used have been oxygen, in wet air oxidation technolo-

gies, catalytic or not, called here catalytic wet oxidation (CWO) and WAO, respectively [19], and the hydroxyl radical generated in the advanced oxidation processes (AOPs) [20].

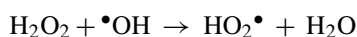
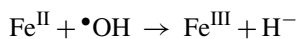
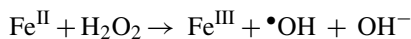
Although the WAO process has demonstrated high effectiveness in the abatement of the organic pollutants, it may be prohibitively expensive due to the high temperatures and pressures required, 150–325 °C and 20–200 bar [21]. Therefore, the use of catalysts in the wet oxidation process is an attractive possibility, as it allows a significant reduction of the pressure and temperature [22]. The heterogeneous catalysis would be preferred to the homogeneous one if a stable and active catalyst under operation conditions is found. Recently, activated carbon without impregnation of metals has been used as a catalyst with success [23–26]. To keep the catalyst stability for longer times on stream the temperature and oxygen pressure must be controlled, avoiding the burning of the catalyst. By using activated carbon the catalytic activity is attributed to the oxygenated groups at the catalyst surface [27].

In relation to AOPs, one of the most studied processes for generating the OH• radical is the Fenton system, which employs iron salts and hydrogen peroxide as source of hydroxyl radicals [28–31]. The main reactions involved in the Fenton process are

* Corresponding author.

E-mail address: aurusan@quim.ucm.es (A. Santos).

as follows:



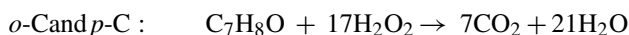
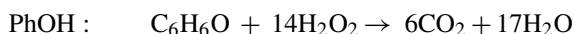
Although some pilot-plant and full-scale applications have been undertaken, Fenton processes have been studied mainly at laboratory scales [32]. The necessary high dosages of iron and hydrogen peroxide to obtain a high mineralization of the pollutants are the major disadvantage of wastewater treatment by Fenton reagent. Iron must be removed from the water after treatment in order to recover the metal and comply with regulatory limits for aqueous effluent discharge. Large volumes of sludge containing iron are formed if pH is increased in order to precipitate the iron in solution. Moreover, low mineralization is usually achieved by Fenton reagent and improvement by UV light irradiation, photo-Fenton processes, has been proposed in the last years [20,33].

In the case of phenolic pollutants, it has been deduced from results in literature that higher mineralization of phenols is obtained in the CWO [34–36] than that obtained by using the Fenton reagents [15,37]. On the contrary, the abatement of the initial phenolic pollutants is quicker if the Fenton reagent is used, even at low dosages of hydrogen peroxide. Therefore, an integrated process combining a Fenton reaction and a CWO process can be proposed to enhance the efficiency of the CWO reactor, diminishing the temperature required in this last step. An aqueous mixture of phenol and cresols will be used to evaluate the advantages of a Fenton pretreatment. The influence of variables as temperature and hydrogen peroxide dosage in the Fenton reactions on the improvement of the efficiency obtained in the CWO reactor will be analyzed. Conversion, mineralization, and detoxification of the initial phenolic solutions obtained will be the parameters selected to analyze the process.

2. Methods

Fenton's reactions have been carried out by adding different amounts of hydrogen peroxide to an aqueous solution of 1500 mg/L on a mixture of phenol (PhOH), *o*-cresol (*o*-C) and *p*-cresol (*p*-C) containing 500 mg/L of each phenolic pollutant. Taking into account the maximum concentration of iron cation permitted for the discharge of industrial wastewater in the region of Madrid (Spain), 10 mg/L of Fe^{2+} was the amount selected to carry out the Fenton Runs (FR). This avoids having to add a further step for iron elimination and/or recovery. FeSO_4 from Fluka was used as iron source. The concentration of H_2O_2 was in the range of 750 to 7500 mg/L, corresponding to 10 to 100% approximately of the stoichiometric dose required for the total mineralization of the mixture of phenolic pollutants. The H_2O_2 reagent was a solution 30% in weight provided by Riedel-Haën. The stoichiometric amount of H_2O_2 was calculated

according to the following reactions:



Reaction has been carried out in a batch way at three different temperature values, 30, 50, and 70 °C. Temperature was controlled along the experiments with a temperature controller. The pH and oxidation-reduction potential were measured during the runs by means of pH and ORP electrodes, respectively, during a period of 180 min, assuring that the reaction was ending.

CWO has been studied in a three-phase Fixed Bed Reactor (FBR) by feeding either an aqueous solution 1500 mg L⁻¹ on the mixture of phenol, *o*-cresol and *p*-cresol, or the effluent after Fenton reaction (carried out a 10, 20, and 40% of the stoichiometric H_2O_2 amount), concurrently with a gaseous oxygen flow (90 mL/min at STP conditions). The FBR reactor is made of a stainless steel tube 0.75 cm in internal diameter and 25 cm in length. The catalyst employed was a commercial activated carbon (Industrial React FE01606A) kindly supplied by Chemviron Carbon, selected in previous work [25]. Temperature and pressure at the reactor were set to 127 °C and 16 bar, respectively. The catalyst weight to liquid flow rate ratio (W/Q_L) was varied from 1.8 to 15 g_{AC} min/mL. A scheme of the experimental set-up is given elsewhere [34]. At the operational conditions employed, a steady state for the outlet composition of the reactor was achieved in the first 40 h of operation when fresh catalyst is placed in the reactor. For consecutive runs the time required to reach the steady state is about 10–20 h.

The BET area was measured by N₂ adsorption at 77 K with a Quantachrome Autosorb-1.

Liquid samples were periodically drawn and analyzed. Phenol, cresols, and organic intermediates were identified and quantified by HPLC (Hewlett-Packard, mod. 1100) using a Diode Array detector (HP G1315A); a Chromolith Performance column (monolithic silica in rod form, RP-18e 100-4.6 mm) was used as the stationary phase; a mixture of acetonitrile, water and a solution of 3.6 mM H_2SO_4 in the ratio 5/90/5 (v/v/v) was used as mobile phase. Flow rate of the mobile phase was 1 mL min⁻¹ and a UV detector was used at wavelengths of 192, 210, and 244 nm. The remaining organic content (TOC) was measured with a Shimadzu TOC-V CSH analyzer by oxidative combustion at 680 °C, using an infrared detector. Organic acids were analyzed by ionic chromatography (Metrohm, mod. 761 Compact IC) using a conductivity detector; a column of anion suppression Metrosep ASUPP5 (25 cm long, 4 mm diameter) was used as the stationary phase and an aqueous solution of 3.2 mM Na_2CO_3 and 1 mM NaHCO_3 as the mobile phase, at a constant flow rate of 0.7 mL min⁻¹. The toxicity of the liquid samples after treatment was determined by means of a bioassay following the standard Microtox test procedure (ISO 11348-3, 1998) using a Microtox[®] M500 Analyzer (Azur Environmental) based on the decrease of light emission by *Photobacterium phosphoreum* resulting from its exposure to a toxicant. The inhibition of the light emitted by the bacteria was measured after 15 min contact time. Before measuring the toxicity, the pH values of all the samples were

re-adjusted to between 6 and 7, in order to prevent the pH effect. More details for toxicity measurements are given elsewhere [36].

Hydrogen peroxide degradation was measured using a Shimadzu UV-1603 spectrophotometer, after colour development with titanium sulphate technique [38].

All the chemicals used were purchased from Sigma-Aldrich, and the microorganisms were Microtox[®] Acute Reagent supplied by I.O. Analytical.

3. Results and discussion

3.1. FR

The results obtained at 50 °C for pollutant and TOC conversion, intermediates distribution and Toxicity Units (TUs) by using different hydrogen peroxide dosage (10, 20, 40, and 100% of the stoichiometric amounts) are shown in Fig. 1a. Cyclic organic intermediates detected were for *p*-C as pollutant 4-hydroxybenzyl alcohol (4-BZOL), 4-hydroxybenzaldehyde (4-BZAL), 4-methylcatechol (4-MeCTL), *p*-hydroxybenzoic acid (4-HBZO). The *o*-C oxidation produces as cyclic intermediates methylhydroquinone (MeHQ), and 3-methylcatechol (3-MeCTL). The phenol oxidation produces as cyclic intermediates hydroquinone (HQ), and catechol (CTL). No benzoquinones are detected with the analytical method used but a strong brown color is obtained at low H₂O₂ dosages that could be due to quinone condensation. The cyclic intermediates are produced in a serial reaction scheme and can be further oxidized to the short chain acids (acetic, formic, maleic, and oxalic acid) and to CO₂. Hydroquinone type compounds have been lumped in A species, which include HQ, MeHQ, and methylbenzoquinone (MeBQ). Catechol type compounds were lumped in B species, which include CTL, 3-MeCTL, 4-MeCTL and also 4-BZOL and 4-BZAL. The *p*-hydroxybenzoic acid is plotted as C. Maleic, manolic, oxalic, acetic, and formic acids were measured and quantified by ionic chromatography, as described in Section 2. The pK_a of these acids (for the first dissociation in the case of dicarboxylic acids) are: 2 for maleic acid, 2.85 for malonic acid, 1.27 for oxalic acid, 4.76 for acetic acid, and 3.75 for formic acid). Therefore, their formation can be related to the detected pH decrease. Other acids as muconic, etc. could be present but were not detected by the analytical method here used. An example of this pH change is given in Fig. 1b. As can be seen in Fig. 1b, the pH has reached an asymptotic value at times lower than 30 min. The pH and TOC profiles versus time are in agreement achieving the corresponding asymptotic values at the same reaction time. Therefore, the time required in the FR for the operation conditions used is much more lower than the maximum value here used (180 min).

As can be seen in Fig. 1a, the phenolic pollutants disappear almost completely at low H₂O₂ dosage (between 10 and 20% of the stoichiometric amount) while the TOC conversion shows firstly a linear increase reaching an asymptotic value for H₂O₂ doses higher than 40% of the stoichiometric amount, approximately. This asymptotic mineralization could be due to the complexation of iron cation with the intermediates [39], decreasing the availability of iron and stopping the radical OH[•]

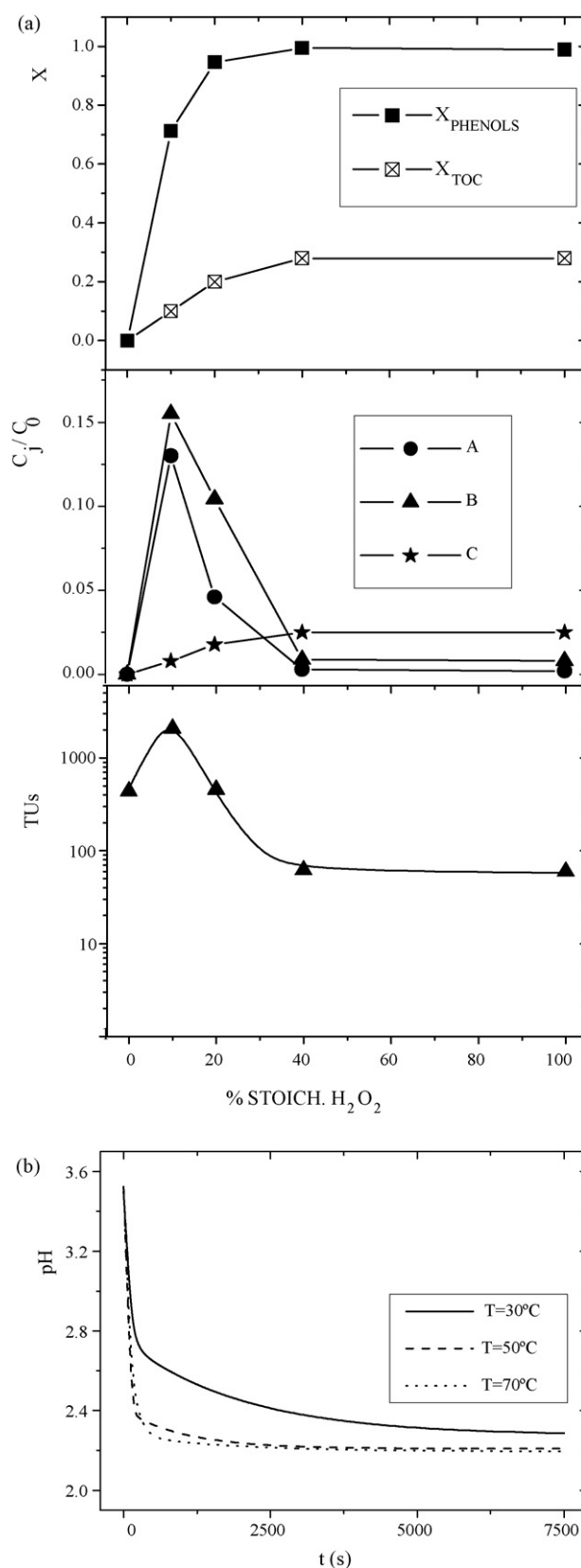


Fig. 1. Results obtained with the FR applied to a phenolic aqueous mixture. $C_0 = 500$ mg/L phenol, 500 mg/L *o*-cresol, 500 mg/L *p*-cresol. $T = 50$ °C. $t = 180$ min. (a) Conversion, intermediate distribution and TU's versus H₂O₂ dosage. (b) Typical pH evolution with time (H₂O₂ = 20% of the stoich. dosage).

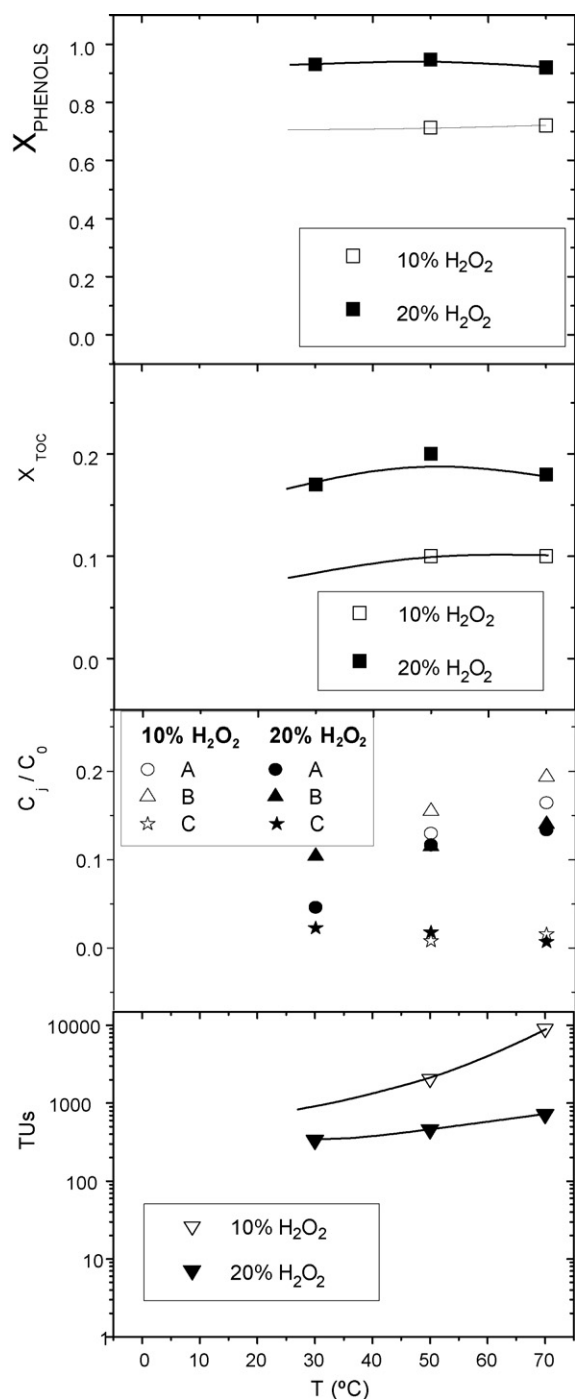


Fig. 2. Temperature effect on FR of an aqueous phenolic mixture. $C_0 = 500$ mg/L.

generation by H_2O_2 . Because of this, the excess of H_2O_2 (over 40%) is not effective in the oxidation of these organic intermediates.

The influence of temperature for a given H_2O_2 dosage is shown in Fig. 2. As can be seen, the higher the temperature is, the more toxic effluents are obtained. To explain this fact, the H_2O_2 decomposition with temperature has been analyzed and results are shown in Fig. 3.

As can be seen in Fig. 3, the stability of the hydrogen peroxide is greatly influenced by temperature. At 70 °C the thermal

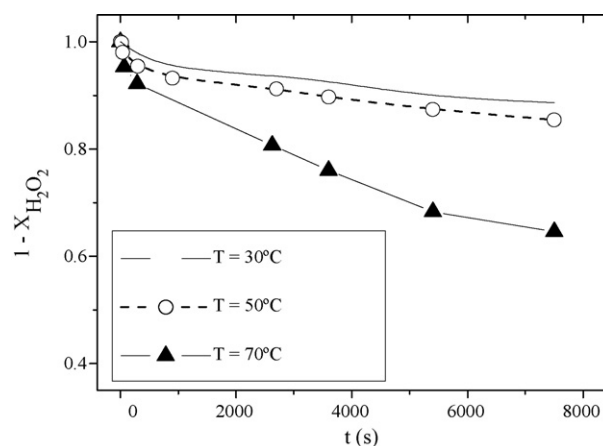


Fig. 3. Influence of temperature in the H_2O_2 stability. pH 3.5. $C_{0H_2O_2} = 1500$ mg/L.

decomposition of this reactant is about 25% for the first 60 min. On the other hand, the H_2O_2 decomposed at 30 and 50 °C is almost negligible at this time. Thus, for an initial H_2O_2 dosage the oxidant available for the oxidation of the first cyclic intermediates produced is lower if the temperature increases. While these cyclic intermediates are the most toxic of the oxidation route the higher toxicity obtained at the reactor exit when temperature increase is explained.

At the conditions used in the FR, pH 2–3 and 10 mg/L of iron cation, no precipitates were observed and it is assumed that iron cation remains in solution.

The remaining H_2O_2 in runs carried out at hydrogen peroxide concentration equal or less than 40% of the stoichiometric amount was almost negligible. The runs carried out at 100% of stoichiometric H_2O_2 were neutralized and kept for a time of 24 h at room conditions. After this treatment a negligible H_2O_2 amount was remaining while TOC amount did not change in comparison with values shown in Fig. 1. Therefore, the samples used in the Microtox test were free of H_2O_2 .

CWO of the aqueous phenolic mixture (500 mg/L on each PhOH, *o*-C and *p*-C) was carried out at temperature of 127 °C. Total pressure was 16 bar and pure oxygen was fed to the reactor. After the steady state was reached, phenols and TOC conversion, the distribution of organic intermediates and the TU of the reactor effluent were determined at each value of the ratio catalyst weight in the reactor (W) to the liquid flow rate (Q_L). Results obtained are shown in Fig. 4a.

As can be seen, higher pollutant and TOC conversions are obtained at higher W/Q_L values. In the CWO besides the cyclic intermediates above quoted, identified in the FR, some benzoquinone intermediates are detected as MeBQ and benzoquinone (BQ) produced in the oxidation of *o*-C and PhOH, respectively. These compounds are lumped in the A specie. The cyclic compounds A and B, produced as first intermediates, are the more toxic of the oxidation route. While these compounds are further oxidized to the short chain acids (acetic, formic, maleic, and oxalic acid) and to CO_2 , a maximum is noticed for the concentration of these cyclic compounds versus W/Q_L .

The TUs of the reactor effluent are in agreement with the organic intermediate profiles detected and their corresponding

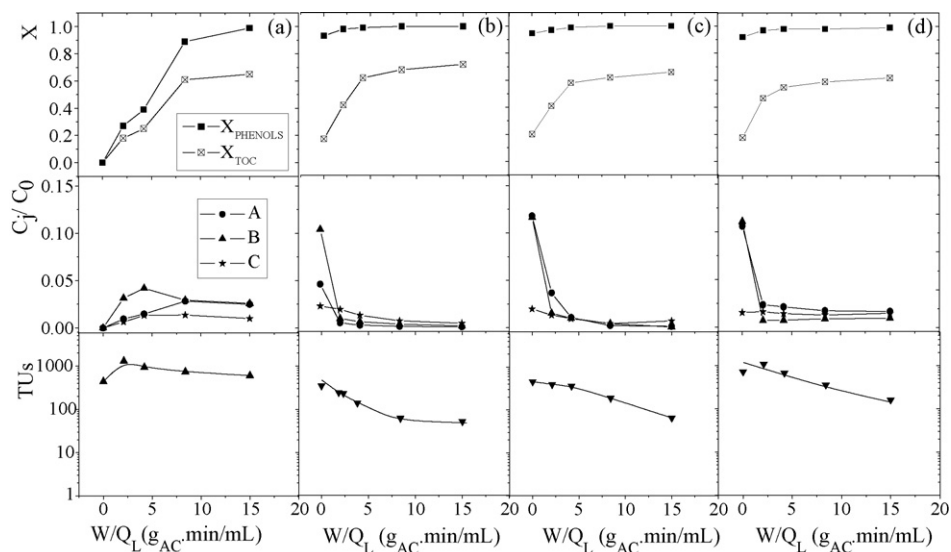


Fig. 4. Results obtained in the catalytic wet oxidation of aqueous phenol mixture with AC. $P = 16$ bar, $T = 127$. $C_0 = 500$ mg/L phenol, 500 mg/L *o*-cresol, 500 mg/L *p*-cresol. (a) No Fenton pretreatment, (b) Fenton pretreatment: 20% H_2O_2 $T = 30$ °C, (c) Fenton pretreatment: 20% H_2O_2 $T = 50$ °C, (d) Fenton pretreatment: 20% H_2O_2 $T = 70$ °C.

EC₅₀ values [36]. As can be seen in Fig. 4a the TUs of the effluent are higher than those fed to the reactor ($TU_0 = 458$) even at high W/Q_L values.

The catalyst was stable at least up to 500 h. After a time on stream (TOS) of about 10–40 h, the catalyst surface area achieved a steady state, with the pollutant conversion and mineralization values keeping stable in the time range studied. A remarkable BET area reduction of the activated carbon was found elsewhere [36] after the phenol and cresols catalytic wet oxidation runs were carried out at 160 °C. It was also noticed that after a TOS of about 40–10 h, depending mainly on whether the reactor is filled with fresh catalyst or not, the catalyst surface area achieved a steady state, with the pollutant conversion and mineralization values keeping stable in the time range studied. The decrease in the surface area was about 2/3 of the original value, diminishing from 745 m²/g of the fresh AC to approximately 250 m²/g of the used one. In this paper, similar values have been obtained at the temperatures of 140 and 127 °C, with S_g values measured after oxidation reaction randomly between 220 and 300 m²/g.

3.2. Integrated Fenton and CWO treatment

In order to improve the efficiency of the CWO, the effect of a Fenton pretreatment has been analyzed. Thus, the samples obtained after treatment of aqueous solution of the phenolic mixture (500 mg/L on each PhOH, *o*-C and *p*-C) with the FR using 20% of the stoichiometric H_2O_2 amount at temperatures of 30, 50, and 70 °C were fed to the three-phase catalytic reactor. Temperature and total pressure in the CWO process were set to 127 °C and 16 bar, respectively, and different W/Q_L values were employed. The influence of the Fenton pretreatment placed before the CWO reactor can be deduced from results in Fig. 4b (FR at 30 °C), c (FR at 50 °C) and d (FR at 70 °C). In these figures, the phenols and TOC conversion, the distribution

of organic intermediates A, B and C, and the TUs are plotted versus W/Q_L . All conversions are related to the values before the Fenton step ($C_0 = 1500$ mg/L of phenols and 1158 mg/L of TOC). As can be seen, the cyclic intermediates A and B are fed to the reactor at a higher concentration than that obtained without Fenton pretreatment but these compounds are quickly oxidized in the CWO reactor with the corresponding decrease in the toxicity in the reactor effluent. Therefore, it can be supposed that these intermediates A and B are more quickly oxidized than the initial phenolic pollutants, making the Fenton pretreatment proposed useful. As can be seen in Fig. 4b–d, as the temperature of the Fenton step increases also builds up the TUs of the sample fed to the CWO reactor and therefore the toxicity of the CWO reactor effluent.

To analyze the influence of the H_2O_2 dosage used in the FR on efficiency improvement obtained in the CWO reactor, another set of runs has been carried out. Aqueous solutions obtained after the treatment of the phenolic mixture with the FR using 10, 20, and 40% of the stoichiometric H_2O_2 amount, at a temperature of 50 °C, were fed to the three-phase catalytic reactor. Results are shown in Fig. 5. As can be seen in Fig. 5a, complete detoxification is not achieved with Fenton pretreatment at 10% H_2O_2 even at high values of the ratio W/Q_L due to the high concentration of A and B species fed to the reactor from the FR. When the H_2O_2 dosage in FR is increased from 10 to 20% (Fig. 5b), concentration of phenols, A and B species obtained after Fenton pretreatment are significantly lower and higher detoxification is achieved in the subsequent CWO step. Feeding the reactor with the same aqueous phenol mixture but pretreated with FR using 40% of H_2O_2 non-toxic effluents are obtained. Also, an almost transparent color is observed in the effluent of CWO reactor, even at low W/Q_L .

The Fenton pretreatment of the phenolic aqueous mixture is carried out at H_2O_2 concentration 40% or less of the stoichiometric amount. The concentration of the remaining H_2O_2 that

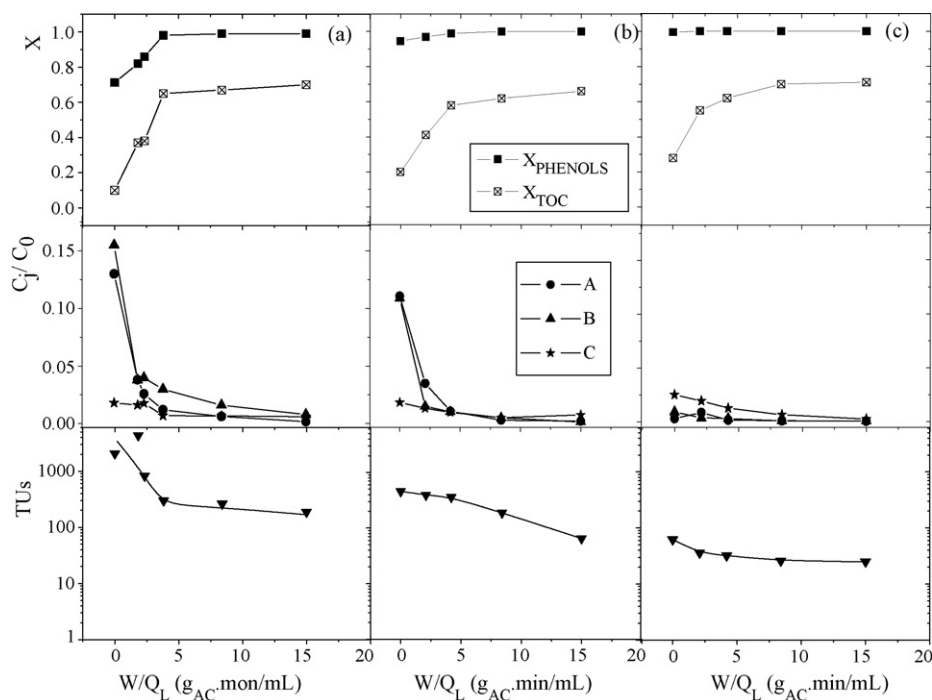


Fig. 5. Results obtained in the catalytic wet oxidation of aqueous phenol mixture with AC. $P = 16$ bar, $T = 127$. $C_o = 500$ mg/L phenol, 500 mg/L *o*-cresol, 500 mg/L *p*-cresol. (a) Fenton pretreatment: 10% H_2O_2 $T = 50$ °C, (b) Fenton pretreatment: 20% H_2O_2 $T = 50$ °C, (c) Fenton pretreatment: 40% H_2O_2 $T = 50$ °C.

is fed to the CWO reactor was almost zero and, consequently, does not affect the results shown in Figs. 4 and 5.

Besides, it was found that an amount of 10 mg/L of Fe^{2+} added to the phenolic stream fed to the CWO, without Fenton pretreatment, does not modify the results obtained in Fig. 4a.

Therefore, the toxicity of the final effluent is reduced due to Fenton pretreatment, not by the effect of the remaining H_2O_2 and Fe^{2+} after Fenton pretreatment fed to the CWO reactor.

4. Conclusions

FR and CWO applied in serial steps are proposed for the treatment of phenolic wastewaters in order to eliminate the initial pollutants and achieve higher mineralization and detoxified effluents.

By using this FR as previous step, with relatively low hydrogen peroxide dosage –under 40% of the stoichiometric amount and iron cation concentration under legislation limits for discharge–, the CWO can be accomplished efficiently at a milder temperature and short residence times. In this study, the tested value of 127 °C –a quite low temperature for this type of technology– gives a relative high TOC conversion and decreases the CWO reactor effluent toxicity to much lower values than those fed. Moreover, the residence times required (reactor volume to liquid flow ratio, V_R/Q_L) are lower than 30 min, being these values also low in comparison to the usually employed in wet oxidation processes.

This improvement is due both to the almost total abatement of phenols that takes place in the Fenton pretreatment at low dosages of hydrogen peroxide and iron concentration, and that,

in the CWO reactor, the oxidation of the dihydroxyphenols-benzoquinone and their condensation intermediates is faster than that of the initial phenols. The remaining TOC is due to the refractory organic compounds obtained which are short chain acids readily biodegradable.

The temperature used in the Fenton pretreatment clearly affects the final detoxification achieved. Higher temperatures (70 °C) in this pretreatment step produce a faster thermal decomposition of the hydrogen peroxide diminishing the available reactant. The increasing of H_2O_2 peroxide in Fenton pretreatment from 10 to 40% of the stoichiometric amount produces a remarkable increment on the detoxification obtained in the effluent from the CWO reactor.

Acknowledgements

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