



Kinetics of wet peroxide oxidation of phenol with a gold/activated carbon catalyst



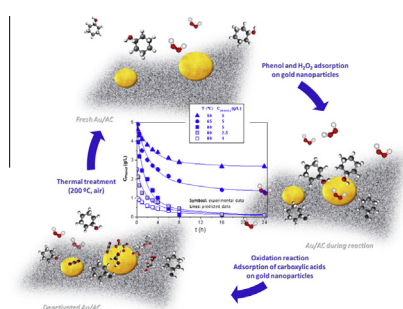
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HIGHLIGHTS

- Au/AC is an active and efficient catalyst for CWPO of phenol.
- The Au/AC catalyst provided a good performance within a wide pH range (from acidic to neutral).
- The activity of Au/AC can be recovered by a thermal treatment at 200 °C in air.
- A kinetic model including catalyst deactivation has been developed.

GRAPHICAL ABSTRACT



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ABSTRACT

Gold nanoparticles supported on activated carbon (Au/AC) have been tested in catalytic wet peroxide oxidation using phenol as target pollutant. In the current work, the effect of several operating conditions, including initial pH (3.5–10.5), catalyst load (0–6 g/L), initial phenol concentration (0.1–5 g/L), hydrogen peroxide dose (4–100% of the theoretical stoichiometric amount) and reaction temperature (50–80 °C) has been investigated. The results show that the Au/AC catalyst would be useful at relatively high pollutant to catalyst ratios (at least 0.4 w/w) and it can work efficiently within a wide range of pH (3.5–7.5). The catalyst suffers rapid deactivation but its activity can be completely restored by an oxidative thermal treatment at low temperature (200 °C). A kinetic model is presented, capable of describing the experimental results. This model is based on a rate equation of order one for hydrogen peroxide consumption and two for phenol oxidation and includes the catalyst deactivation and its temperature dependence.

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1. Introduction

Catalytic wet peroxide oxidation (CWPO) is a well-known process used for the abatement of water pollutants [1,2]. Like other advanced oxidation processes (AOPs), it is based on the action of hydroxyl and hydroperoxyl radicals produced, in this case, upon catalytic decomposition of hydrogen peroxide under relatively mild operating conditions (50–130 °C, 1–5 atm) in the presence of a solid catalyst. However, the difficulty of developing suitable

catalysts is pointed out in the literature [3–5], being currently the factor limiting the industrial application of CWPO. This still remains as an important challenge for research on the topic.

Current trends are addressed to the development of supported and un-supported metal nanoparticles, being the most studied iron, manganese and gold nanoparticles [5]. Recent studies on the catalytic applications of gold nanoparticles show that CWPO is a promising area in that respect [6–9]. So far, gold nanoparticles deposited on hydroxyapatite (Au/HAP) [6], diamond (Au/npD) [8] or activated carbon (Au/AC) [9] have shown fairly high activity. However, frankly different efficiencies of hydrogen peroxide consumption were observed with those catalysts, which are attributed to the nature of the support, crucial for the activity of gold [9].

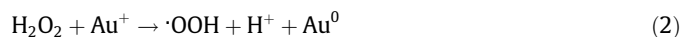
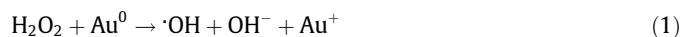
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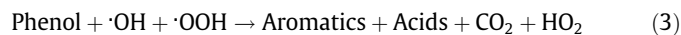
In our previous studies [9,10], a reaction mechanism and an oxidation pathway for phenol with Au/AC catalyst were proposed based on the experimental evidences. CWPO proceeds through a complex scheme of reactions involving a number of intermediates, such as aromatic compounds (mainly resorcinol, hydroquinone and p-benzoquinone) and low molecular weight carboxylic acids (maleic, malonic, oxalic, acetic and formic), according to the following steps: (i) adsorption of phenol and, preferentially, hydrogen peroxide on the gold-support interface, (ii) production of hydroxyl and hydroperoxyl radicals mainly on the gold surface though in some extension also occurs on the carbon surface and (iii) reaction between hydroxyl radicals and phenol molecules on the gold surface. The hydroxyl radicals are also released to the liquid phase where they react with phenol in solution. Parasitic reactions involving recombination of radical species, can take place yielding hydrogen peroxide as well as oxygen and water.

According to that mechanism, and considering only the main reactions for CWPO of phenol, the following reaction scheme is likely to occur:

- Hydrogen peroxide decomposition into hydroxyl and hydroperoxyl radicals in the presence of gold nanoparticles by a redox cycle:



- Phenol oxidation by radical species into aromatic compounds, low-molecular carboxylic acids, carbon dioxide and water can be described by:



In the current work, the attention is focused on the potential application of the Au/AC catalyst in CWPO. With this purpose, the effects of several operating conditions, viz. initial pH, catalyst load, initial phenol concentration, hydrogen peroxide dose and reaction temperature are investigated and the stability of the catalyst studied, as well as its regeneration. A kinetic model has been developed describing the rates of phenol oxidation and hydrogen peroxide decomposition which includes the catalyst deactivation and its temperature dependence.

2. Materials and methods

2.1. Catalyst

The 0.8 wt% Au/AC catalyst (Sample n°: 106C) was provided by World Gold Council and used as received. The characterization of the catalyst is summarized in Table 1, according to the data provided by the supplier with the exception of the BET surface area (S_{BET}), the external or non-microporous surface area (A_{ext}) and the elemental carbon analysis. The two former were obtained from the N_2 adsorption/desorption isotherms at 77 K using a Micromeritics Tristar apparatus on the sample previously outgassed overnight at 150 °C to a reduced pressure $<10^{-3}$ torr. Elemental analyses were carried out in a LECO Model CHNS-932 analyzer.

2.2. Oxidation experiments

The CWPO experiments were performed batch-wise in a magnetically stirred three-necked glass reactor equipped with a reflux condenser. In a typical experiment, 45 mL of phenol solution at the desired pH (adjusted with HCl or NaOH) were placed in the reactor with the catalyst and heated up to the reaction temperature. After

Table 1
Physico-chemical properties of Au/AC catalyst.

Support	Activated carbon	
Carbon type	Camel X40S	
	Vegetal	
	Specific surface area, S_{BET} (m^2/g)	934
	External area, A_{ext} (m^2/g)	56
	C (%)	76.6
	O (%)	20.6
Gold	Au content (wt.%)	0.8
	d_{Au} (nm)	10.5 ± 6.7
	Au^0 (at.%)	75
	Au^+ (at.%)	12.5
	Au^{3+} (at.%)	12.5

that, 5 mL of an adjusted concentration of hydrogen peroxide aqueous solution were added and the stirring at 1200 rpm started. Previous to the analysis of the reaction samples, the catalyst was separated by filtration (0.45 μm Nylon filter) and dried at 60 °C. All the experiments were performed by duplicate being the standard deviation always less than 5%.

The oxidation runs were performed at different initial pH (3.5–10.5), phenol concentration (0.1–5 g/L), temperature (50–80 °C), catalyst loading (0–6 g/L) and H_2O_2 dose (4–100% of the theoretical stoichiometric amount for complete phenol mineralization, namely $5 \text{ g}_{\text{H}_2\text{O}_2}/\text{g}_{\text{Phl}}$). Previous to the oxidation runs, the fresh catalyst was contacted with a phenol solution under the same experimental conditions as in the corresponding CWPO runs but in the absence of hydrogen peroxide for adsorption equilibration.

2.3. Analytical methods

Liquid samples from the reactor were analyzed by different procedures. Phenol and aromatic by-products were determined by high performance liquid chromatography, HPLC (Varian, mod. Pro-Star), low molecular weight acids by anionic suppression ionic chromatography, IC (Metrohm, mod. 761 Compact IC) and total organic carbon (TOC) using a TOC analyzer (O. I. Analytical, model 1010). Hydrogen peroxide was determined by colorimetric titration with a UV 2100 Shimadzu UV-VIS spectrophotometer using the titanium sulfate method [11]. A more detailed description of these analytical procedures can be found elsewhere [9].

3. Results and discussion

3.1. Mass transfer considerations

Experiments at different stirring velocities within the range of 200–1500 rpm showed the absence of limitation due to the external diffusion (see Fig. S1 of Supporting Information). The stirring velocity was set at 1200 rpm for all the following experiments. The Weisz-Prater criterion has been used to check whether internal diffusion could be rate-controlling:

$$\Phi = \eta \cdot \varphi^2 = \left(\frac{\text{observed rate}}{\text{diffusion rate}} \right) = \left(\frac{r_{\text{obs}} \cdot L_s^2}{D_{\text{eff}} \cdot C_s} \right) \cdot \left(\frac{n+1}{2} \right) < 0.15 \quad (4)$$

Assuming pseudo-second order kinetics ($n = 2$), as will be further demonstrated, the above expression is simplified to:

$$\Phi = \eta \cdot \varphi^2 = \left(\frac{k_{\text{obs}} \cdot C_{\text{phenol}} \cdot L_s^2}{D_{\text{eff}}} \right) \cdot \left(\frac{3}{2} \right) \quad (5)$$

The observed kinetic rate constant for phenol oxidation, $k_{\text{obs}} = 6 \cdot 10^{-5} \text{ L}/(\text{g}_{\text{Ph}} \text{ h})$, was calculated using a power-law pseudo-second order model at the highest temperature (80 °C) and catalyst

load (2.5 g/L). L_s is defined as a characteristic length of the catalyst particle ($d_p/6 = 1.33 \cdot 10^{-5}$ m). For the effective diffusivity (D_{eff}) of phenol into the activated carbon has been taken a value of $1.1 \cdot 10^{-9}$ m²/s [12]. By substituting in Eq. (5), the Wheeler-Weisz modulus results $4.82 \cdot 10^{-5}$, therefore internal diffusion limitation can be excluded.

3.2. Influence of the operating conditions

Efficient consumption of hydrogen peroxide is of main concern in CWPO processes [8,13–16]. It is crucial to establish the operating conditions allowing to minimize parasitic reactions that consume $\cdot\text{OH}$ and $\cdot\text{OOH}$ radicals to produce oxygen, a non-effective species under the range of working conditions commonly used in CWPO. This consideration is particularly important when using activated carbons [16]. In order to find those conditions with the Au/AC catalyst, the influence of different reaction variables has been studied.

3.2.1. Initial pH

It is well known that wet peroxide oxidation is sensitive to the pH and usually acid conditions are used [17]. However, with solid catalysts a wider range, covering up to neutral pH has been reported [18]. In our case, with the Au/AC catalyst, this variable has been explored within the range of 3.5–10.5. The starting pH was adjusted (but not buffered) with 1 M HCl or NaOH, as required. The evolution of phenol conversion, TOC removal and hydrogen peroxide efficiency (η , defined as the amount of TOC removed per hydrogen peroxide consumed) upon reaction time is depicted in Fig. 1. As can be seen, the initial pH does not show any effect within the acid to neutral range, whereas a significant decrease of phenol and TOC conversions was observed at frankly alkaline pH. With regard to the efficiency of H₂O₂ consumption, a favorable effect is observed at acidic pH. In these conditions the efficiency of hydrogen peroxide is maximum ($\eta \approx 1$) and decreases up to around 0.8, as mineralization proceeds within the 24 h of the experiment. At neutral pH, the efficiency of H₂O₂ is somewhat slower but fairly stable. On the other hand, at frankly alkaline pH (10.5), a dramatic decrease of the efficiency is observed, which is associated to a rapid decomposition of H₂O₂ ($X_{\text{H}_2\text{O}_2} = 99\%$ in 1 h reaction), evolving, in great part, to oxygen and water at that pH. However, under this alkaline condition, no by-products were detected since phenol and TOC conversions were coincident (Fig. 1). This might be due to the increase observed for adsorption contribution with pH.

The results obtained allow concluding that CWPO with Au/AC can be efficiently performed without necessarily working at acidic pH as it is most commonly claimed for Fenton-related processes.

3.2.2. Catalyst loading

The effect of catalyst loading was analyzed at 80 °C and initial phenol concentration of 1 g/L. Fig. 2 shows the dependence of the initial reaction rates of phenol and hydrogen peroxide disappearance on the catalyst load. Increasing the catalyst concentration in the range 0–6 g/L, the initial reaction rates increased linearly. Besides, homogeneous reaction in the absence of catalyst can be discarded, since very low conversions were obtained (5 and 9% for hydrogen peroxide and phenol, respectively, after 4 h reaction time), much below the achieved in the presence of catalyst.

3.2.3. Phenol concentration

Initial phenol concentrations up to 5 g/L were tested at 80 °C, 3.5 initial pH, 2.5 g/L catalyst and stoichiometric dose of H₂O₂. Fig. 3 shows the results obtained. As can be seen, phenol conversion and TOC removal increase with the initial concentration as the efficiency of hydrogen peroxide consumption does. Only at phenol concentrations as high as 5 g/L, efficiency values close to

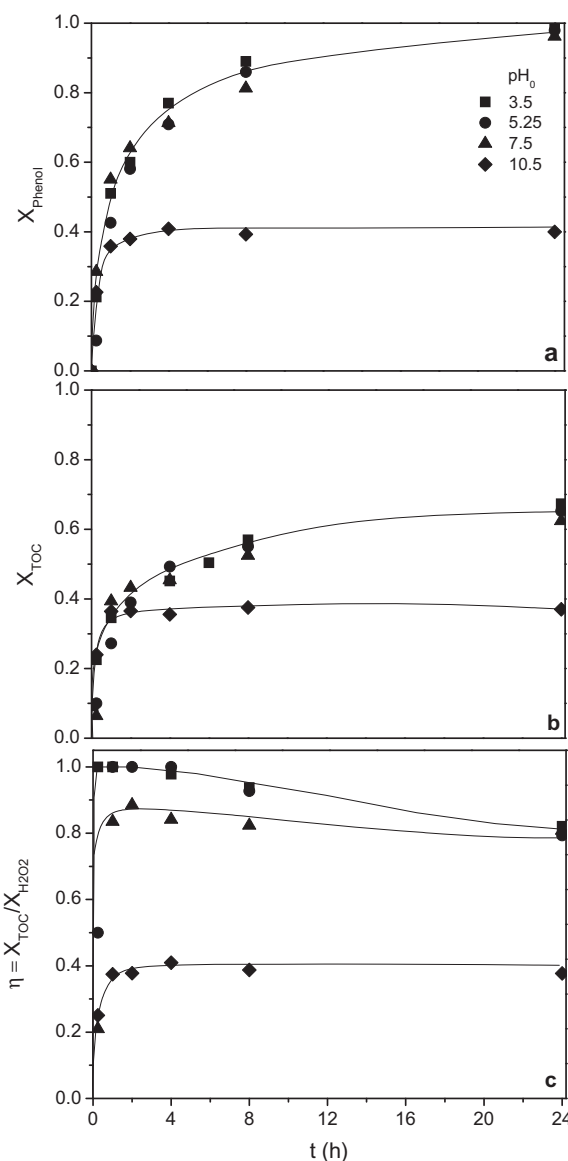


Fig. 1. Effect of initial pH on phenol conversion (a), TOC removal (b) and hydrogen peroxide efficiency (c). Operating conditions, $C_{\text{cat}} = 2.5$ g/L, $C_{\text{Ph},0} = 5$ g/L, $C_{\text{H}_2\text{O}_2,0} = 25$ g/L, $T = 80$ °C.

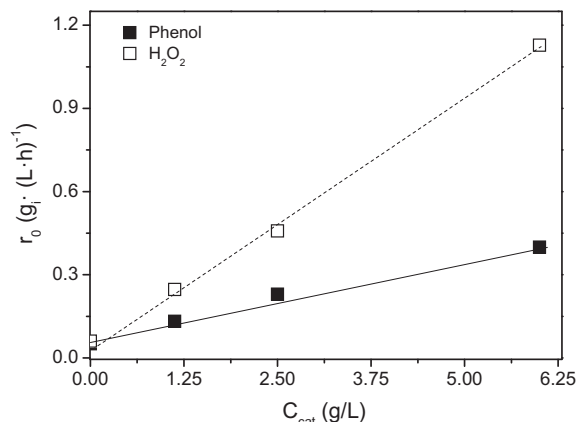


Fig. 2. Effect of the catalyst loading on the initial rates of disappearance of phenol and hydrogen peroxide decomposition. Operating conditions: $C_{\text{Ph},0} = 1$ g/L, $C_{\text{H}_2\text{O}_2,0} = 5$ g/L, $T = 80$ °C, $\text{pH}_0 = 3.5$.

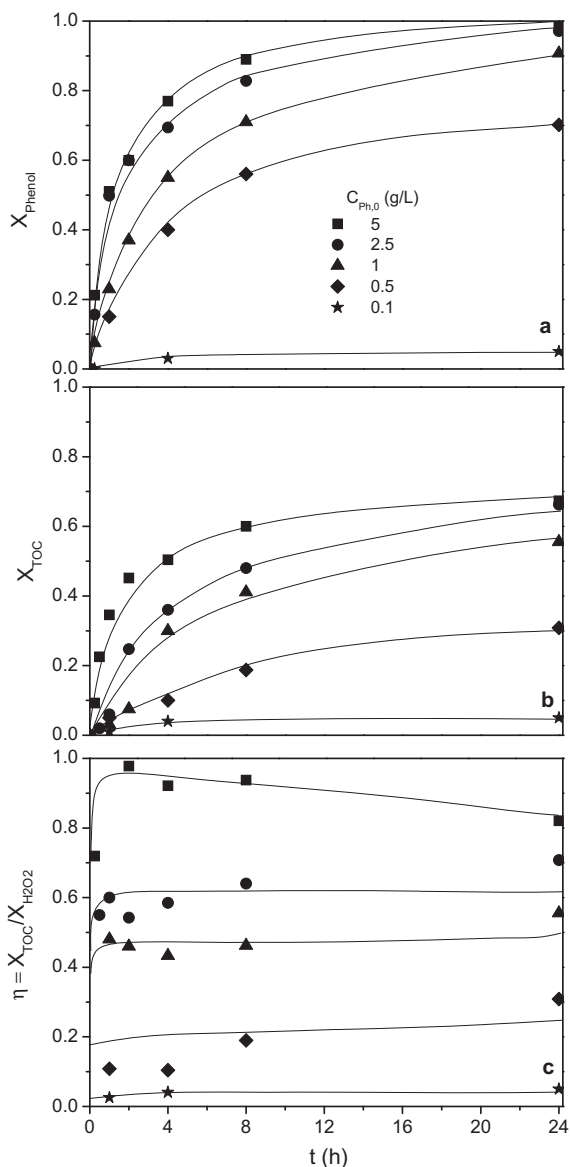


Fig. 3. Effect of the initial phenol concentration on phenol conversion (a), TOC removal (b) and hydrogen peroxide efficiency (c). Operating conditions: $C_{Ph,0} = 0.1$ – 5 g/L, $C_{H_2O_2,0}$ = stoichiometric dosage, $C_{cat} = 2.5$ g/L, $T = 80$ °C, $pH_0 = 3.5$.

one were observed, which decreased dramatically as the initial concentration was lowered. These findings are in good agreement with the results reported by Domínguez et al. [16] dealing with CWPO of phenol with activated carbons. Higher pollutant/carbon mass ratios, lead to higher occupancy of the surface active sites, with the consequent reduction of those available for hydrogen peroxide decomposition. This allows a more progressively generation of $\cdot OH$ and $\cdot OOH$ radicals, reducing the occurrence of parasitic autoscavenging reactions. On the other hand, the initial reaction rate within this inlet concentration range, given in Fig. 4, shows that the order of reaction with respect to phenol is 2.

3.2.4. Hydrogen peroxide dose

Different hydrogen peroxide doses were tested, corresponding to 4, 50 and 100% of the theoretical stoichiometric amount for complete oxidation of phenol to CO_2 and water. The results obtained at 80 °C, in terms of phenol conversion vs. reaction time are depicted in Fig. 5, showing the important dependence on the H_2O_2 dose. The initial reaction rate of hydrogen peroxide

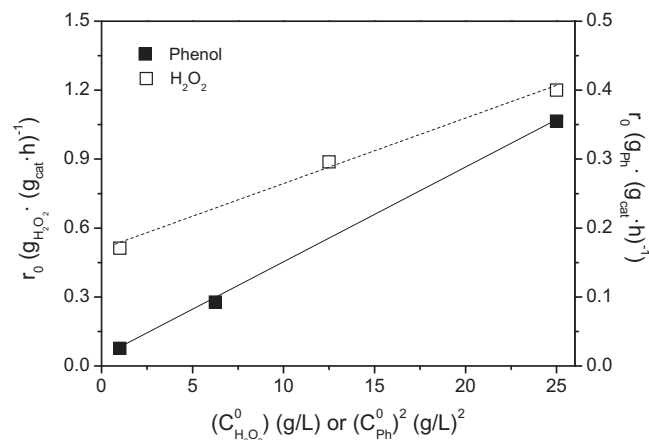


Fig. 4. Relationship between the initial rates of H_2O_2 decomposition and phenol disappearance with their respective initial concentrations. Operating conditions: $T = 50$ °C, $pH_0 = 3.5$.

decomposition increases linearly with its starting concentration (Fig. 4), and a reaction order of 1 with respect to hydrogen peroxide was obtained.

3.2.5. Effect of temperature

Fig. 6 presents phenol conversion upon reaction time at different temperatures, 50, 65 and 80 °C, working with 5 g/L of initial phenol concentration and the stoichiometric amount of hydrogen peroxide. As can be seen, the rate of phenol disappearance increases substantially with the temperature within the 30 °C range tested. Complete conversion of phenol was achieved at 80 °C after 24 h reaction versus about 40% at 50 °C. The observed activation energy, as obtained by the Arrhenius equation from the initial rate values was 47.2 kJ/mol.

3.3. Catalyst stability and regenerability

The Au/AC catalyst was tested in four successive runs in order to analyze its stability. In each cycle, the catalyst was used for 24 h, then separated by filtration and dried at 60 °C for 24 h without any further treatment. The values of the initial rate of phenol disappearance are given in Fig. 7. The one obtained with the bare activated carbon is also included for the sake of comparison. The gold catalyst undergoes an important deactivation after its first use and the remaining activity can be mostly attributed to the

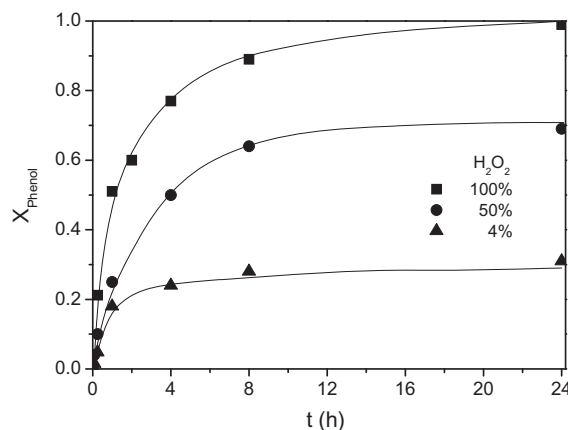


Fig. 5. Effect of hydrogen peroxide dosage on phenol disappearance. Operating conditions: $C_{cat} = 2.5$ g/L, $C_{Ph,0} = 5$ g/L, $T = 80$ °C, $pH_0 = 3.5$.

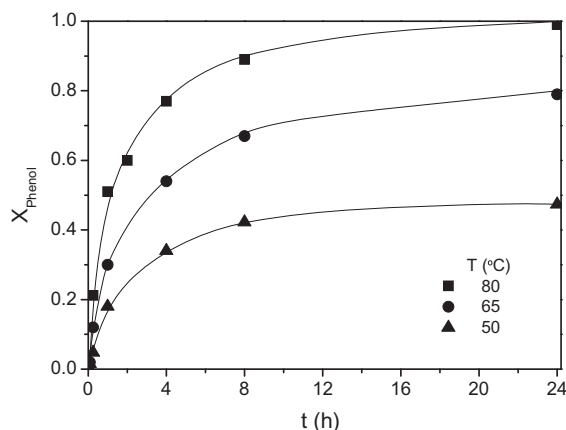


Fig. 6. Temperature effect on phenol disappearance. Operating conditions: $C_{\text{cat}} = 2.5 \text{ g/L}$, $C_{\text{Ph},0} = 5 \text{ g/L}$, $C_{\text{H}_2\text{O}_2,0} = 25 \text{ g/L}$, $\text{pH}_0 = 3.5$.

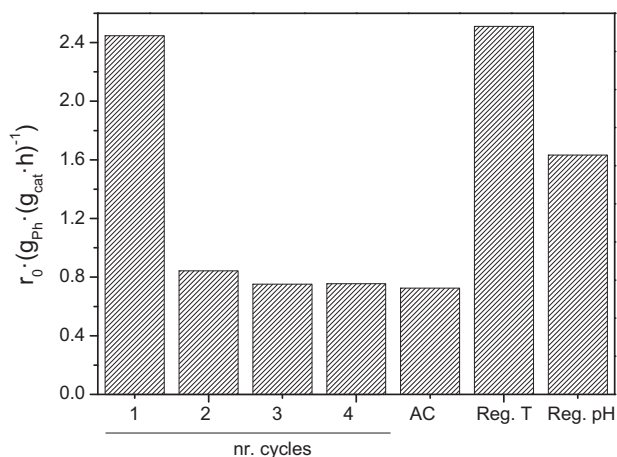


Fig. 7. Evolution of the initial rate of phenol disappearance upon successive reaction cycles with the Au/AC catalyst and after regeneration. Operating conditions: $C_{\text{Ph},0} = 5 \text{ g/L}$, $C_{\text{H}_2\text{O}_2,0} = 25 \text{ g/L}$, $T = 80 \text{ °C}$, $\text{pH}_0 = 3.5$.

carbon support. To learn on the causes of this rapid deactivation, some reactor effluents were analyzed and the first-used catalyst was characterized and submitted to different treatments addressed to its regeneration.

No traces of gold were detected in the liquid samples by TXRF, therefore, deactivation by gold leaching was discarded. On the other hand, it is well-known that carboxylate species [8,9,19,20] strongly adsorb on gold nanoparticles which ultimately lead to catalyst poisoning. In particular in CWPO, dicarboxylic acids, which are typical oxidation by-products, have been considered responsible of gold deactivation [8,21]. At the operating conditions of Fig. 7, almost 900 mg C/L of low-weight carboxylic acids were measured after 24 h reaction time, corresponding to maleic (184 mg C/L), malonic (239 mg C/L) and oxalic (49 mg C/L), in addition to acetic (332 mg C/L) and formic (70 mg C/L).

Alkaline washings of the spent catalyst are effective to dissolve those species, thus allowing removing this type of poison [20,21]. Hence, the recovery of the gold activity was first intended by washing the used Au/AC catalyst at room conditions in basic media (Na_2CO_3 , $\text{pH} = 14$, $C_{\text{cat}} = 2 \text{ g/L}$, $t = 3 \text{ h}$) followed by distilled water until neutral pH. Upon this treatment, 2 wt% of the initial gold in the catalyst was leached and the activity recovered in about 60% (see Fig. 7, Reg pH). Alternatively, the spent catalyst was submitted to an oxidative thermal treatment at 200 °C during 14 h in air

atmosphere in order to burn-off the adsorbed species. This treatment resulted in a 10% weight loss and the catalyst activity was completely restored (Fig. 7, Reg T).

3.4. Kinetic analysis

The mass balance of H_2O_2 and phenol in the stirred batch reactor can be expressed as:

$$-\frac{dC_{\text{H}_2\text{O}_2}}{dt} = (-r_{\text{H}_2\text{O}_2}) \cdot C_{\text{cat}} \quad (6)$$

$$-\frac{dC_{\text{Ph}}}{dt} = (-r_{\text{Ph}}) \cdot C_{\text{cat}} \quad (7)$$

with the first terms related to volume of the liquid phase.

From the values of the initial rates given in Fig. 2 and the reaction scheme proposed Eqs. ((1)–(3)), the following equation can be written for the reaction rate of H_2O_2 :

$$(-r_{\text{H}_2\text{O}_2}) = k_{\text{H}_2\text{O}_2} \cdot C_{\text{H}_2\text{O}_2} \quad (8)$$

From the results of Figs. 2 and 4 and the reaction scheme proposed Eqs. ((1)–(3)), the reaction rate of phenol can be expressed by:

$$(-r_{\text{Ph}}) = k_{\text{Ph}} \cdot C_{\text{OH}+\text{OOH}} \cdot C_{\text{Ph}}^2 \quad (9)$$

At steady state for radical species, their concentration can be included in the kinetic constant, resulting:

$$(-r_{\text{Ph}}) = k'_{\text{Ph}} \cdot C_{\text{Ph}}^2 \quad (10)$$

As discussed before, the Au/AC catalyst is deactivated upon reaction time due to gold poisoning by low-weight carboxylic acid by-products. Then, the active catalyst concentration can be described by a decreasing-time function:

$$C_{\text{cat}} = C_{\text{cat},0} \cdot e^{-k_d \cdot t} \quad (11)$$

Substituting Eqs. (8) and (11) in Eq. (6) and Eqs. (10) and (11) in Eq. (7), the following expressions can be written:

$$-\frac{dC_{\text{H}_2\text{O}_2}}{dt} = k_{\text{H}_2\text{O}_2} \cdot C_{\text{H}_2\text{O}_2} \cdot C_{\text{cat},0} \cdot e^{-k_d \cdot \text{H}_2\text{O}_2 \cdot t} \quad (12)$$

$$-\frac{dC_{\text{Ph}}}{dt} = k'_{\text{Ph}} \cdot C_{\text{Ph}}^2 \cdot C_{\text{cat},0} \cdot e^{-k_d \cdot \text{Ph} \cdot t} \quad (13)$$

Considering the first term in Eqs. (12) and (13) as the rate of H_2O_2 decomposition and phenol disappearance, respectively, they can be expressed as:

$$(-r'_{\text{H}_2\text{O}_2}) = -\frac{dC_{\text{H}_2\text{O}_2}}{dt} \quad (14)$$

$$(-r'_{\text{Ph}}) = -\frac{dC_{\text{Ph}}}{dt} \quad (15)$$

Thus, the modeling equations are:

$$(-r'_{\text{H}_2\text{O}_2}) = k_{\text{H}_2\text{O}_2} \cdot C_{\text{H}_2\text{O}_2} \cdot C_{\text{cat},0} \cdot e^{-k_d \cdot \text{H}_2\text{O}_2 \cdot t} \quad (16)$$

$$(-r'_{\text{Ph}}) = k'_{\text{Ph}} \cdot C_{\text{Ph}}^2 \cdot C_{\text{cat},0} \cdot e^{-k_d \cdot \text{Ph} \cdot t} \quad (17)$$

3.4.1. Modeling: parameter estimation

The numerical integration of these rate equations in a batch reactor with $C_{\text{Ph}} = C_{\text{Ph},0}$ and $C_{\text{H}_2\text{O}_2} = C_{\text{H}_2\text{O}_2,0}$ at $t = 0$, using the software package Scientist 3.0 (Runge–Kutta fourth order method with least squares minimization based on a modification of Powell's algorithm), led to:

Table 2

Values of the deactivation constants (h^{-1}) at different temperatures.

Parameter	Value
$k_{d,H_2O_2,80^\circ C}$	0.0903 ± 0.0068
$k_{d,H_2O_2,65^\circ C}$	0.1326 ± 0.0097
$k_{d,H_2O_2,50^\circ C}$	0.3060 ± 0.0420
$k_{d,Ph,80^\circ C}$	0.0555 ± 0.0071
$k_{d,Ph,65^\circ C}$	0.1663 ± 0.0531
$k_{d,Ph,50^\circ C}$	0.2567 ± 0.0877

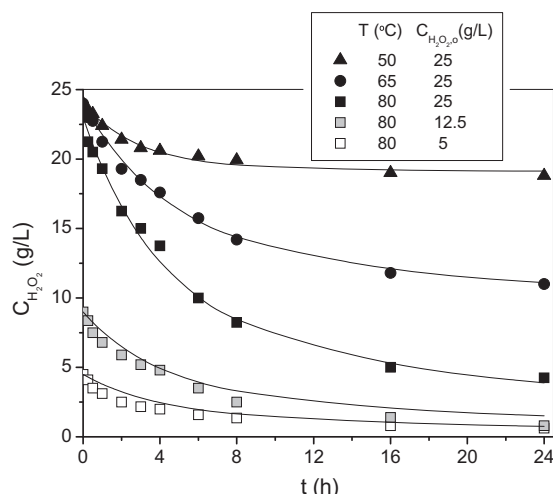


Fig. 8. Experimental data (symbols) and predicted values (curves) of H_2O_2 concentration at the different conditions tested.

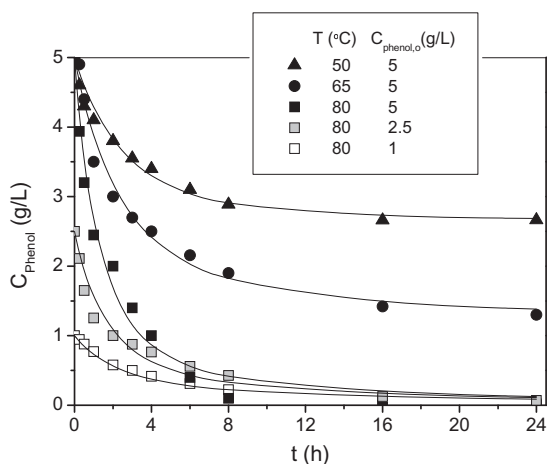


Fig. 9. Experimental data (symbols) and predicted values (curves) of phenol concentration at the different conditions tested.

$$(-r'_{H_2O_2}) \left(\frac{g_{H_2O_2}}{L \cdot h} \right) = 2,179 \pm 1.45 \cdot e^{-\frac{30,33+2,66}{RT}} \cdot C_{H_2O_2} \cdot C_{cat,0} \cdot e^{-k_{d,H_2O_2} \cdot t} \quad (18)$$

$$(-r'_{Ph}) \left(\frac{g_{Ph}}{L \cdot h} \right) = 24,654 \pm 19.23 \cdot e^{-\frac{45,78+9,14}{RT}} \cdot C_{Ph}^2 \cdot C_{cat,0} \cdot e^{-k_{d,Ph} \cdot t} \quad (19)$$

being the activation energy in kJ/mol.

The values of the deactivation constants corresponding to the different temperatures tested are collected in Table 2. As can be seen, the values decrease as temperature increases, consistently with a deactivation caused by adsorption of intermediate species, in particular, carboxylic acid by-products. Similar values were obtained for both H_2O_2 and phenol. Figs. 8 and 9 show the comparison of the experimental and predicted results which confirm the good agreement.

4. Conclusions

Au/AC can act as efficient catalysts in the wet peroxide oxidation of phenolic wastewater if high pollutant concentrations (>2.5 g/L) and pollutant/carbon mass ratios (≥ 0.4) are used. By this way, the active sites for hydrogen peroxide decomposition are highly covered by phenol molecules and the extension of parasitic reactions, consuming radical species, is minimized thus giving rise to improved efficiency (i.e. total phenol removal and 70% TOC conversions were achieved at 80°C and 22 h). Phenol solutions with acid or neutral pH can be treated in the presence of Au/AC, widening the pH range commonly used in CWPO processes.

A kinetic model based on a simplified reaction mechanism that considers partial orders of one and two for hydrogen peroxide and phenol, respectively, and takes into account the rapid catalyst deactivation with reaction time has been found to properly predict the hydrogen peroxide and phenol experimental concentrations in a wide range of temperatures (50 – 80°C) and initial phenol concentrations (1 – 5 g/L) and always at the stoichiometric dose of hydrogen peroxide. The Au/AC activity can be easily recovered by a thermal treatment at low temperature in air atmosphere (200°C , 14 h).

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Appendix A. Notation

C	concentration (g/L)
C_{cat}	catalyst load (g/L)
CS	reactant concentration on the catalyst surface (g/L)
k_d	catalyst deactivation rate constant (h^{-1})
$k_{H_2O_2}$	H_2O_2 rate constant ($\text{L}/(\text{g}_{cat} \cdot \text{h})$)
k_{Ph}	phenol rate constant ($\text{L}^2/(\text{g}_{cat} \cdot \text{g}_{OH} + \text{g}_{OH}) \cdot \text{g}_{Ph} \cdot \text{h})$)
k'_{Ph}	$k_{Ph} \cdot C_{(-OH+OOH)}$ ($\text{L}^2/(\text{g}_{cat} \cdot \text{g}_{Ph} \cdot \text{h})$)
$(-r'_i)$	reaction rate of the i reactant ($\text{g}_i/(\text{g}_{cat} \cdot \text{h})$)
$(-r'_i)$	disappearance rate of the i reactant ($\text{g}_i/(\text{L} \cdot \text{h})$)
r_{obs}	observed reaction rate related to volume of the liquid phase ($\text{g}/(\text{L} \cdot \text{h})$).
R	gas constant ($\text{J}/(\text{mol} \cdot \text{K})$)
t	reaction time (h)
T	temperature (K or $^\circ\text{C}$)
W	stirring velocity (rpm)
X	conversion
Subscripts	
0	initial
cat	catalyst
H_2O_2	hydrogen peroxide
Ph	phenol

Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2014.05.063>.

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