



# Kinetic modeling of wet peroxide oxidation with a carbon black catalyst



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## ABSTRACT

A kinetic model has been developed describing the rate of hydrogen peroxide consumption and target pollutant (phenol) degradation in CWPO with a commercial carbon black as catalyst. The model allows following the evolution of the oxidation by-products (up to 12) through a detailed reaction pathway. The kinetic parameters were obtained by fitting the experimental results in batch reactor runs at  $T=90\text{--}130\text{ }^{\circ}\text{C}$ ,  $P=4\text{ bar}$ ,  $[\text{Phenol}]_0=1\text{ g/L}$ ,  $[\text{catalyst}]=0\text{--}10\text{ g}_{\text{cat}}/\text{L}$  and the theoretical stoichiometric amount of hydrogen peroxide for complete mineralization of phenol (5 g/L). The results were subjected to the analysis of variance (ANOVA). The model includes a set of power-law expressions with different reaction orders which provides a complete description of the process and allows obtaining the efficiency of hydrogen peroxide consumption under giving operating conditions.

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## 1. Introduction

Catalytic wet peroxide oxidation (CWPO) relies on the treatment of wastewater by oxidation of the organic pollutants with hydroxyl and hydroperoxy radicals, produced by the catalytic decomposition of hydrogen peroxide under circumambient to more severe operating conditions ( $T=25\text{--}130\text{ }^{\circ}\text{C}$ ,  $P=1\text{--}5\text{ atm}$ ). It represents an emerging technology whose main challenge, currently limiting its industrial application, is the development of not only active but also stable solid catalysts capable of performing at efficient  $\text{H}_2\text{O}_2$  consumption.

Current trends are addressing the development of bare carbon-based materials as CWPO catalysts, thus avoiding the presence of metallic phase susceptible of leaching [1,2]. Activated carbons are the most studied, mainly tested for the treatment of organic dyes [3–10]. Also, graphites [9,11,12] and to a lesser extent, carbon nanotubes, nanofibers and xerogels [9,12–14] have been used for the CWPO of phenol and derivatives. The work of Dominguez et al., [15] introduced the use of carbon black, viz. the Chemviron carbon black ( $S_{\text{BET}}=A_{\text{ext}}=75\text{ m}^2/\text{g}$ ,  $C=99\%$  and negligible ash content), as novel potential catalyst for this process. Its relative low specific surface area determines a low adsorption capacity hindering the formation of adsorbed oligomeric by-products on the carbon surface, respect to what occurs with activated carbons, and con-

sequently preventing deactivation. Complete conversion of phenol and around 70% TOC abatement were achieved in 24 h reaction time at  $90\text{ }^{\circ}\text{C}$  and 5 g/L catalyst concentration using 1 g/L starting phenol concentration at initial pH 3.5. The remaining TOC corresponded to short-chain carboxylic acids. The efficiency of hydrogen peroxide consumption was maintained at 90–100% (ratio of TOC to  $\text{H}_2\text{O}_2$  conversion,  $X_{\text{TOC}}/X_{\text{H}_2\text{O}_2}$ , percent).

Research on CWPO has been mainly focused on the development of highly active, stable and efficient solid catalysts and the kinetic studies reported are in general based on pseudo-first order rate equations describing the disappearance of target pollutants [16–25]. So far only a few works have been reported where crucial issues such as catalyst deactivation [26], homogeneous contribution [27], the existence of radical parasitic reactions [28,29] or the amount of specific active sites [30] have been considered.

The current work deals with the kinetic modeling of CWPO with a commercial carbon black as catalyst using phenol as target compound. Temperatures in the range  $90\text{--}130\text{ }^{\circ}\text{C}$  were tested. A model has been developed to follow the rate of phenol disappearance, hydrogen peroxide consumption, the evolution of the individual aromatic intermediates and acid by-products on the basis of the reaction pathway derived from the experimental results. Also, TOC evolution was predicted from the model.

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## 2. Materials and methods

### 2.1. Materials and reagents

Carbon black was supplied in powder form by Chemviron (ref.:2156090). Hydrogen peroxide solution (30% w/v) was purchased from Sigma–Aldrich. Working standard solutions of phenol, hydroquinone, resorcinol, catechol, *p*-benzoquinone, acetic acid, formic acid, malonic acid, maleic acid all from Sigma–Aldrich and oxalic acid (Panreac) were prepared and used for High Performance Liquid Chromatography (HPLC) and Ionic Chromatography (IC) calibration. Other reagents used in the analyses were H<sub>2</sub>SO<sub>4</sub> (Panreac), Na<sub>2</sub>CO<sub>3</sub> (Panreac), NaHCO<sub>3</sub> (Merck), TiOSO<sub>4</sub> (Riedel-deHaën), HCl (Panreac) or NaOH (Panreac) were used to adjust the initial pH of the reaction media. All these reagents were of analytical grade and were used without further purification. All solutions were prepared with milli-Q water.

### 2.2. CWPO experiments

The experiments were carried out in a stoppered glass batch reactor (Büchi, inertclave Type I) equipped with a backpressure controller. The reaction volume was 400 mL and the starting concentrations of reactants were 1 g/L phenol and 5 g/L H<sub>2</sub>O<sub>2</sub> (which corresponds to the theoretical stoichiometric amount for mineralization of phenol). The catalyst was always the CWPO-second use carbon black. In a previous study [15], it was observed that the activity, tested in five consecutive runs of 24 h each, increased from the first to the second use and then remained almost unchanged. This increase was attributed to the higher hydrophilicity and electrochemical capacity of the use carbons as a consequence of the increased population of surface oxygen groups upon the first 24 h of CWPO reaction (mainly carboxylic acid and, in less extent, anhydride, ether and phenol moieties). Thus, the as-received catalyst in the current study was previously used in CWPO during 24 h under identical operating conditions to those used in the subsequent runs.

Initially, 370 mL of milli-Q water with the selected amount of carbon black was placed into the reactor and the mixture stirred. A N<sub>2</sub> flow rate of 100 mL/min was used to achieve the selected pressure and temperature. Then, 10 mL of 40 g/L phenol solution and 20 mL of an adjusted solution of hydrogen peroxide were injected, being this the starting time for the reaction. The pressure was maintained at 4 atm during the reaction by means of a back-pressure control valve. The temperature was tested within the 90–130 °C range and the catalyst concentration within 0–10 g/L. The initial pH value was ranged from 3.5 to 10.5 and not controlled along the process. Samples at different reaction times were taken from the reactor. The catalyst was separated by filtration (0.45 μm Nylon filter) and the sample was immediately cooled and analyzed.

### 2.3. Analytical methods

Phenol and aromatic intermediates were analyzed by HPLC (Varian, Mod. ProStar) using a 5 μm FORTIS C18 column (150 × 4.6 mm) with a mixture of 4 mM H<sub>2</sub>SO<sub>4</sub> aqueous solution at 1.3 mL/min as mobile phase. A diode array detector (PDA) at wavelengths of 210 and 246 nm was used. Short-chain organic acids were determined by ionic chromatography (Metrohm, mod. 883 BASIC IC Plus) with anionic chemical suppression using a conductivity detector. A Metrosep A supp 5–250 column (25 cm length, 4 mm diameter) was used as stationary phase and 0.7 mL/min of an aqueous solution 3.2 mM of Na<sub>2</sub>CO<sub>3</sub> and 1 mM of NaHCO<sub>3</sub> as mobile phase. Total Organic Carbon (TOC) was measured with a TOC analyzer (Shimadzu TOC VSCH). Hydrogen peroxide concentration was determined by colorimetric titration with a UV2100 Shimadzu

UV–vis spectrophotometer using the TiOSO<sub>4</sub> colorimetric method [31].

### 2.4. Kinetic modeling

The production rate of each given compound (*i*) in the reaction medium,  $R_i$  (mol·g<sub>cat</sub><sup>-1</sup>·s<sup>-1</sup>), is given by:

$$R_i = \frac{d[i]}{[W] \cdot dt} \quad (1)$$

where the terms in brackets refer to the concentrations of *i* (mol·L<sup>-1</sup>) and catalyst (W, g·L<sup>-1</sup>).  $R_i$  can be expressed as a function of the concentration of the species involved in the reaction according to the corresponding pathway.

The numerical integration of the rate equations in a batch reactor with the initial conditions [Phenol]=[Phenol]<sub>0</sub>, [H<sub>2</sub>O<sub>2</sub>]=[H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> and [reactor products]=0 at t=0 was solved by using the Microsoft Excel Solver (Microsoft Office 2010, Microsoft Corp.) based on the Generalized Reduced Gradient (GRG) algorithm for least squares minimization. The equations were solved at each temperature. The activation energy and the pre-exponential factor values were calculated using the Arrhenius equation.

Analysis of variance (ANOVA) was used for statistical model evaluation. The F-value and the critical F-value were calculated in order to compute the statistical significance of the regressions. The F-value is the ratio of the mean square due to regression to mean square due to error. The critical F-value was obtained from the F-distribution for a significance level of 0.05. The computed F-values should be several times greater than the critical F-value for good agreement with the experimental data. The coefficient of determination (R<sup>2</sup>) was also calculated by regression analysis of the experimental data.

## 3. Results and discussion

Kinetic control was verified under the operating conditions tested. Both, the catalyst in powder form (42 nm) and the appropriate stirring velocity (300 rpm) were used to avoid mass transfer limitations.

Neutral initial pH was selected since a slight effect was observed when this variable was varied within the range from 3.5 to 10.5 (see Fig. S1 of Supporting Information).

Fig. 1 depicts the time-course of hydrogen peroxide, phenol and TOC upon 6 h of reaction, at different temperatures and catalyst loadings. As expected, higher H<sub>2</sub>O<sub>2</sub>, phenol and TOC conversions were achieved at increasing catalyst concentration. The observed initial rates increased linearly with that concentration (see Fig. S2 of Supporting Information).

A higher temperature increases the rate of H<sub>2</sub>O<sub>2</sub> decomposition into active radical species (HO• and HOO•) [32], as the enhanced rate of phenol disappearance and mineralization indicate in the current study. Under 10 g/L catalyst and 130 °C, complete phenol disappearance and 80% TOC removal was achieved in 4 h reaction time. The trend in the TOC curve suggests the existence of some refractory by-products even under the most severe conditions.

### 3.1. Phenol oxidation route

The reaction by-products identified along the experiments of Fig. 1 were aromatic compounds, viz. resorcinol (RS), catechol (CTL), hydroquinone (HQ) and *p*-benzoquinone (BQ) and carboxylic acids, viz. maleic (MAL), fumaric (FUM), malonic (MLO), oxalic (OXA), acetic (ACE) and formic (FORM). The time-course of those species under the different conditions tested is shown in Figs. 2–4. The trend of the curves show that the aromatics and the C<sub>3</sub>–C<sub>4</sub> carboxylic acids were intermediate compounds whereas formic, acetic

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