

# Catalytic wet air oxidation of substituted phenols: Temperature and pressure effect on the pollutant removal, the catalyst preservation and the biodegradability enhancement

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## Abstract

The influence of temperature (140 and 160 °C) and oxygen partial pressure (2 and 9 bar) on the continuous catalytic wet air oxidation (CWAO) over activated carbon (AC) has been investigated for the removal of phenol, *o*-cresol and 2-chlorophenol in aqueous solutions. Seventy-two-hour tests were performed in a fixed bed reactor in trickle flow regime. A commercial AC was employed as catalyst. The pollutant elimination effectiveness, the distribution of major reaction products and the AC behaviour were studied for each compound. Also, respirometric screening tests were completed to the effluents before and after each CWAO experiment to assess the biodegradability enhancement. The results show that pollutant disappearance, chemical oxygen demand (COD) removal, total organic carbon (TOC) abatement and biodegradability enhancement (fraction of COD readily biodegradable, %COD<sub>RB</sub>) were very sensitive to temperature but rather independent of the oxygen partial pressure ( $P_{O_2}$ ). On the contrary, AC catalyst preservation was strongly influenced by both temperature and pressure. For instance, for phenol CWAO at 2 bar of  $P_{O_2}$ , as temperature increased from 140 to 160 °C, phenol conversion increased from 45% to 78%, COD removal from 33% to 65%, TOC abatement from 21% to 62% and %COD<sub>RB</sub> from 4% to 36%. Similar behaviour was found for the other model compounds tested, although the level of refractoriness was rather different.

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## 1. Introduction

The importance of phenolic industrial effluents, besides their potential toxicity, is outlined by the high quantities that are eventually disposed. For instance, phenol, *o*-cresol and 2-chlorophenol are recognised toxic substances listed in the 2000 OECD List of High Production Volume Chemicals [1].

Biological treatment of these compounds usually has low removal efficiency. For instance, microbial toxicity studies with *Daphnia magna* showed that these compounds are toxic [2,3]. Among many others, catalytic wet air oxidation (CWAO) is a

technique for treating this kind of hazardous wastewater that is not amenable to biological treatment. At the proper operating conditions, CWAO is able to generate an effluent suitable to be discharged into a municipal biological wastewater treatment plant (WWTP). However, the catalyst choice is indeed the core in the CWAO performance. Recently, several studies have demonstrated that activated carbon (AC) alone can successfully perform as a true catalyst [4] for several reactions, including CWAO of phenol, *o*-cresol, 2-chlorophenol and other bioxenotic organic compounds [5–8]. Nevertheless, the performance of different ACs can significantly differ [9], which strongly suggests that different characteristics of the ACs affect their behaviour as catalyst. Hence, a depth inspection of the CWAO performance is needed for each AC chosen as catalyst and for each substrate in order to properly design a successful treatment plant.

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This study deals with an integrated treatment of substituted phenols based on CWAO followed by biological treatment. The main objective is that the CWAO effluent becomes a regular fraction of the total influent to a municipal biological WWTP without causing adverse effects over the efficiency and operation of the conventional sewage sludge process. To design such integrated chemical–biological systems, the substrate degradation extent and the knowledge of physical, chemical and biological properties of the main reaction intermediates occurring in the CWAO step are key points [10]. Thus, the appropriate CWAO conditions for each specific case can be assessed.

Several CWAO tests were done using phenol, *o*-cresol and 2-chlorophenol as target pollutants. CWAO was continuously conducted in a trickle bed reactor using a commercial AC as catalyst. Two temperatures, 140 and 160 °C, and two oxygen partial pressures ( $P_{O_2}$ ), 2 and 9 bar, were studied. The aims are to determine the effect of varying temperature and pressure on the substrate removal and the biodegradability enhancement (i.e. fraction of chemical oxygen demand (COD) readily biodegradable (%COD<sub>RB</sub>) of the CWAO effluents) and on the AC preservation.

Another article presents a detailed study of the biodegradability, toxicity and inhibition characteristics of the main intermediates detected in the effluents coming from CWAO of a high-strength *o*-cresol wastewater. In addition, the results of a pilot scale study for an integrated CWAO-biological WWTP for the treatment of this wastewater are presented [11].

## 2. Experimental

### 2.1. Materials

Aldrich provided analytical grade phenol, *o*-cresol and 2-chlorophenol. Table S1 in supporting information summarises some physico-chemical characteristics of the model compounds. Feed concentration was always 5 g l<sup>-1</sup>. However, in terms of COD concentration, the initial concentrations were 10.8 g COD l<sup>-1</sup> for phenol, 9.5 g COD l<sup>-1</sup> for *o*-cresol and 7.5 g COD l<sup>-1</sup> for 2-chlorophenol. These concentrations were chosen to check the feasibility of using CWAO as an effective pre-treatment before a biological WWTP, according to the technology map drawn by Hancock [12].

The AC used as catalyst was supplied by Merck (reference #102518) in the form of 2.5 mm pellets. Prior to use, AC was crushed and sieved. Then, the chosen particle size was in the range 0.7–0.3 mm in order to minimise mass transfer limitations according to Stüber et al. [13]. The characteristics of this AC, prior to use, can be found elsewhere [6].

### 2.2. Experimental set-up and procedures for CWAO experiments

A complete scheme of the CWAO experimental apparatus as well as a more detailed description of the procedures can be found elsewhere [6,7,9].

CWAO experiments were done in a trickle bed reactor in down-flow co-current for 72 h. The experiments were run at 140

and 160 °C and synthetic air was used as oxidant to guarantee a  $P_{O_2}$  of 2 and 9 bar at each temperature. Typically, 7.0 g of AC was loaded into the reactor. In all the experiments, the liquid flow rate was set to give a space time of 0.12 h, i.e. a liquid weight hourly space velocity of 8.2 h<sup>-1</sup>, giving a value of 57.4 ml h<sup>-1</sup>. The air flow rate was kept constant at 2.4 STP ml s<sup>-1</sup> in all the experiments, which is well beyond the stoichiometric oxygen uptake needed. Liquid samples were periodically withdrawn and analysed to determine target compound destruction ( $X$ ), COD reduction ( $X_{COD}$ ), TOC abatement ( $X_{TOC}$ ), distribution of partial oxidation products, and biodegradability enhancement, measured as %COD<sub>RB</sub>.

Experiments were repeated to check reproducibility of results and the agreement (within ±5%) between successive experiments was excellent. The data reported in this work are the arithmetic average of the results derived from three repeated CWAO experiments.

According to the oxidation pathways proposed in the literature for each model compound [14–19], a set of reported oxidation intermediates was checked. Target compounds, quinone-like compounds, condensation products and organic acids were separated by HPLC. The analysis was done in a C18 reverse phase column (Hypersil ODS, Agilent Technologies) with a gradient mixture of ultra-pure water and methanol. A HPLC chromatogram from a standard calibration mixture is shown in the supporting information section (Figure S1). In addition, 4-hydroxybenzoic acid (4-HB), its isomer salicylic acid (2-HB) and resorcinol were also calibrated. Other possible intermediates such as methyl- and chlorinated-quinones were also checked. However, these latter intermediates were not detected in any CWAO sample, therefore, they were neither included in the sample chromatogram (Figure S1, supporting information section) nor in the results section.

COD and total organic carbon (TOC) analysis were measured following the standard methods 5220D and 5310B [20], respectively.

The AC used in each CWAO test was collected and dried overnight at 105 °C under N<sub>2</sub> atmosphere. Then, the used AC was subjected to several analysis such as thermogravimetric analysis (TGA), nitrogen adsorption isotherms at 77 K to determine its textural properties, and mass change estimation ( $M_{AC}$ ) by drying at 400 °C as described elsewhere [6,7].

### 2.3. Experimental set-up for respirometric experiments

The respirometer used for the biodegradability screening tests corresponds to a LFS type, in which dissolved oxygen concentration ( $S_O$ ) is measured in the liquid-phase ( $L$ ), which is static ( $S$ ) and continuously aerated ( $F$ ) [21]. The pH was maintained at 7.5 ± 0.5 and the temperature was set at 31 ± 0.5 °C. The biomass used as seed culture came from a municipal biological WWTP (Tarragona, Catalonia, Spain). The biomass was starved overnight to ensure endogenous conditions before each respirometric experiment. The presence of 20 mg l<sup>-1</sup> of 1-allyl-2-thiourea (ATU) avoided nitrification interference. The average concentration of volatile suspended solids (VSS) in the respirometric tests was 3400 ± 300 mg VSS l<sup>-1</sup>.

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