

# INFLUENCE OF ELECTROLYTE TYPE ON THE FORMATION OF PCDD/Fs DURING THE ELECTROCHEMICAL OXIDATION OF 2-CHLOROPHENOL

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## Introduction

Chlorophenols (CPs) comprise a group of organic compounds that have been largely applied as intermediates in the synthesis of pesticides, pharmaceuticals, dyes and wood preservatives. Therefore, due to their extensive use, CPs have been detected in the aquatic environment, including surface and ground waters, wastewaters, and even finished drinking waters.<sup>1</sup> Since some CPs have been listed as priority pollutants by the U.S. EPA and by the European Commission because they are highly toxic and hardly biodegradable, their removal from contaminated waters is required. Advanced oxidation processes (AOPs), which are based on the formation of very active hydroxyl radicals (OH<sup>•</sup>) have been applied successfully in wastewater treatment to degrade many organic contaminants, including phenolic compounds.<sup>2</sup> Amongst different AOPs, electrochemical oxidation has shown high mineralization degrees during the remediation of aqueous solutions containing CPs.<sup>3,4</sup> However, beyond the degradation of main contaminants, the potential formation of toxic byproducts is an important issue to be considered in the assessment of treatment technologies. CPs are known to contain many chlorinated impurities such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs)<sup>5</sup> and are thought to be the most important and direct precursors of PCDD/Fs.<sup>6</sup> The formation of PCDD/Fs during the application of AOPs for the treatment of aqueous solutions containing chlorinated organic compounds has been reported in the literature.<sup>7,8</sup> In addition, the concomitant presence of chloride in the reaction medium could favor the formation of PCDD/Fs. Since chloride has been detected in a wide variety of wastewaters,<sup>9</sup> it has been commonly used as the electrolyte in the electrochemical oxidation of polluted waters. This work aims to study the potential formation of PCDD/Fs during the electrochemical treatment of aqueous solutions containing 2-chlorophenol (2-CP), paying special attention to the influence of two frequently used electrolytes, NaCl and Na<sub>2</sub>SO<sub>4</sub>.

## Materials and methods

### *Electrochemical oxidation experiments*

Electrooxidation experiments of aqueous solutions (1L) containing 2-CP (15.56 mM) were performed in batch mode in a laboratory DiaCell system comprised of two circular electrodes, boron doped diamond (BDD) on silicon anode and stainless steel cathode, with surface area of 0.007 m<sup>2</sup> each and an electrode gap of 5 mm. The working current density was set at 900 A m<sup>-2</sup> and the operational flowrate was 9 L min<sup>-1</sup>. Two commonly applied supporting electrolytes were used, NaCl (34.2 mM) and Na<sub>2</sub>SO<sub>4</sub> (21.1 mM) resulting in an initial conductivity of 7.5 mS cm<sup>-1</sup>.

### *2-CP, TOC, COD analysis*

2-CP was measured in a high-pressure liquid chromatograph (HPLC) Agilent Series 1100, using a Supelco reversed-phase column LC-8 and H<sub>2</sub>SO<sub>4</sub> 4 mM as mobile phase. 2-CP was measured at  $\lambda = 210$  nm with a photo diode array (PDA) detector. TOC analysis was performed using a TOC-V CPH (Shimadzu) and COD was determined by the open reflux method following the analytical procedure 5220B from Standard Methods.

### *PCDD/Fs analysis*

#### Samples preparation

Standard Method U.S.EPA 1613 (1994) for PCDD/Fs analysis was applied in this study. Samples (0.45 L) were spiked with 10  $\mu$ L of a mixture of <sup>13</sup>C-labelled solution of PCDD/Fs (Wellington Laboratories) dissolved in acetone and then extracted with three portions of 60 mL aliquots of dichloromethane. Afterwards, the organic extract was concentrated in a Buchi R-210 rotatory evaporator, transferred to n-hexane and treated with H<sub>2</sub>SO<sub>4</sub>. Later, the organic phase (n-hexane) was L-L extracted, dried with sodium sulphate and concentrated in the rotatory evaporator to approximately 1 to 2 mL. At that point, the extract was filtered through a 0.45  $\mu$ m PTFE

filter and cleaned-up by liquid-solid adsorption in the Power-Prep<sup>TM</sup> system using silica, alumina and carbon columns. The final purified extract was concentrated in the rotatory evaporator and then transferred into a vial to be concentrated to dryness under nitrogen.

#### Instrumental Analysis

The purified extracts were analyzed by the Chromatography Service (SERCROM) of the University of Cantabria. Before the analysis, the internal standards (EPA 1613 ISS) were added to the sample. The analysis was carried out on a TRACE GC Ultra<sup>TM</sup> gas chromatograph (Thermo Electron S.p.A.) using a DB-5 MS fused silica capillary column (J&W Scientific). The initial temperature of the column, 120 °C, was kept constant for 2 min and then it was increased sequentially in 3 steps to 210, 230 and 310 °C at 15, 1 and 3 °C min<sup>-1</sup> respectively. The column was connected through a heated transfer line kept at 270 °C to a DFS high-resolution magnetic sector mass spectrometer with a BE geometry (Thermo Fisher Scientific). Positive electron ionization (EI+) mode with ionization energy of 45 eV was used in the source and its temperature was set at 270 °C. The mass spectrometer was operated in SIM mode at 10000 resolution power (10% valley definition). Detection limits were calculated as the concentration values that gave instrumental responses within a signal-to-noise ratio of 3.

#### **Results and discussion**

The change of normalized 2-CP concentration with treatment time for both electrolytes, NaCl and Na<sub>2</sub>SO<sub>4</sub>, is displayed in Figure 1a. On the other hand, the mineralization efficiency expressed in terms of TOC abatement and COD removal versus treatment time was shown in Figure 1b. Experimental data are depicted together with error bars obtained after replication of the experiments.

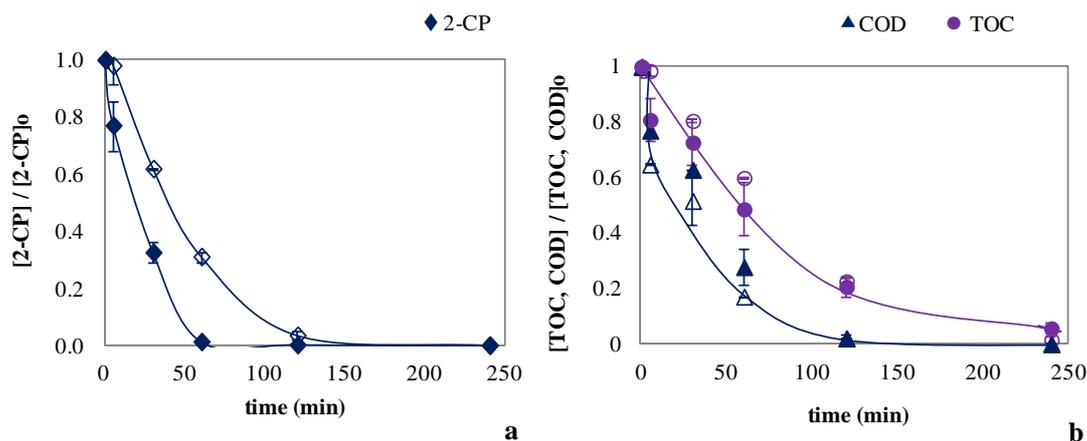


Figure 1. Change in normalized concentration with time, a) 2-CP, b) TOC and COD. (Solid dots: NaCl; empty dots: Na<sub>2</sub>SO<sub>4</sub>).

According to the results from Figure 1a, 2-CP was completely degraded after 60 min using NaCl as electrolyte, whereas in the case of Na<sub>2</sub>SO<sub>4</sub>, higher treatment times were necessary to achieve a complete depletion of 2-CP. Therefore, these results depict a positive contribution to the main oxidation mechanism by OH<sup>•</sup> of the indirect oxidation by active chlorine electrogenerated at the anode surface.<sup>10</sup> On the other hand, as shown in Figure 1b, taking into account the experimental error bars, there is no clear influence of the electrolyte type on the kinetic change of either TOC or COD. The experimental data showed that complete mineralization (decrease in TOC) required higher times than the reduction of both COD and 2-CP. This fact could be explained by the formation of oxidation byproducts that need longer times to be mineralized. After 4 h of treatment, 5% of TOC remained in the solution, suggesting the presence of organic minor byproducts in the reaction medium. Since CPs are direct precursors of PCDD/Fs,<sup>6</sup> their potential formation in the electrochemical oxidation of 2-CP was assessed. The concentrations of PCDD/Fs in the untreated 2-CP solutions as well as after 4 h of electrochemical oxidation using both electrolytes are shown in Figure 2. All PCDD/Fs concentrations depicted in this Figure were previously blank corrected.

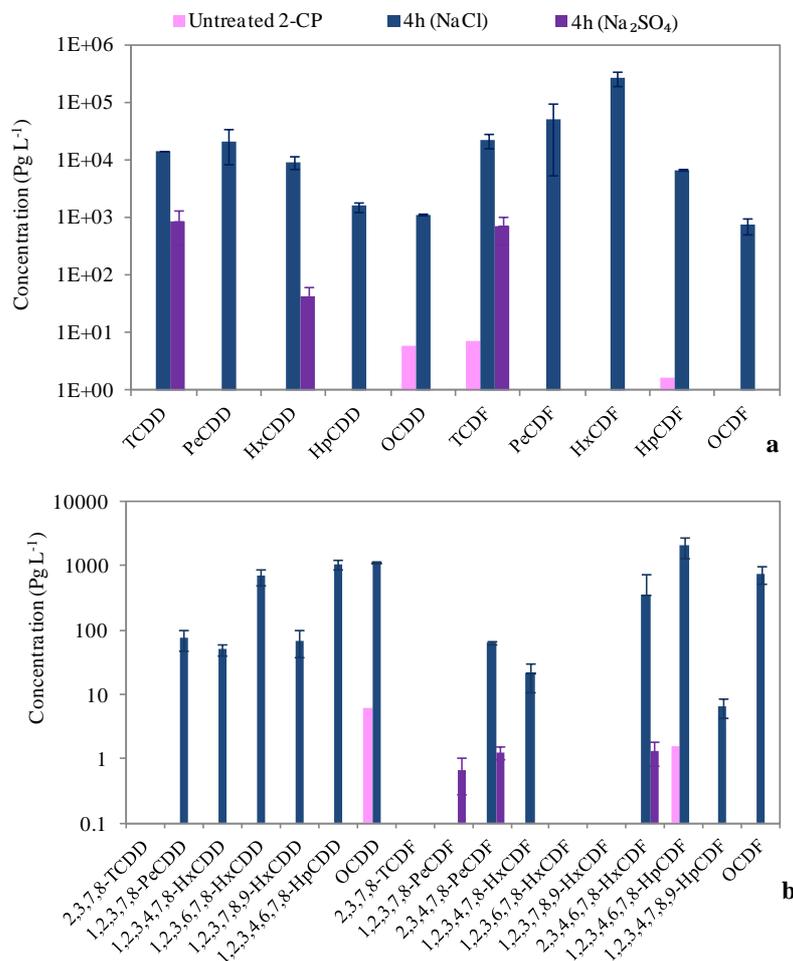


Figure 2. PCDD/Fs concentration: a) homologue profile of total PCDD/Fs; b) congener profile of 2,3,7,8-PCDD/Fs.

Regarding total PCDD/Fs (Figure 2a), three groups of homologues, OCDD, TCDF and HpCDF, were detected at very low concentration ( $1.6\text{--}7\text{ pg L}^{-1}$ ) in the untreated 2-CP solution. According to data reported in Figure 2a, significant formation of PCDD/Fs could be observed after 4 h of treatment with NaCl as electrolyte. The total PCDD/Fs concentration in the oxidized samples was  $2.68 \times 10^4$  times higher than in the untreated solution. The homologue profile was dominated by PCDFs, which accounted for 88% of the total PCDD/Fs concentration. Among PCDFs, HxCDF was the prevailing group accounting for 68% of the total PCDD/Fs concentration. On the other hand, when Na<sub>2</sub>SO<sub>4</sub> was used as electrolyte, the concentration of PCDD/Fs increased by 200 times relative to the untreated sample, but such increase was 134 times lower than in the presence of NaCl. TCDD, HxCDD and TCDF, which contribute over 51.6%, 2.5% and 39.8% to the total concentration, were the only groups that showed an increase in their concentration after 4 h of treatment.

With respect to the most toxic congeners, 2,3,7,8-PCDD/Fs (Figure 2b), only two congeners, OCDD and 1,2,3,4,6,7,8-HpCDF, were detected at very low concentration ( $1.6\text{--}6\text{ pg L}^{-1}$ ) in the untreated solution of 2-CP. When Na<sub>2</sub>SO<sub>4</sub> was used as electrolyte, a negligible formation of 2,3,7,8-PCDD/Fs was observed. On the other hand, when NaCl was present in the reaction medium a remarkable formation of 2,3,7,8-PCDD/Fs was shown. The total 2,3,7,8-PCDD/Fs concentration increased by 828 times in comparison with the untreated solution. The total concentration of 2,3,7,8-PCDD/Fs represented the 1.6% of the total PCDD/Fs concentration, depicting the

preferential formation of non 2,3,7,8-PCDD/Fs. The congener profile of 2,3,7,8-PCDD/Fs was dominated by 1,2,3,4,6,7,8-HpCDF (32.6%), followed by OCDD (17.7%), 1,2,3,4,6,7,8-HpCDD (17%) and OCDF (12%). Talking in terms of Toxic Equivalents (TEQ) and using the International Toxic Factors (I-TEF), TEQ levels increased from values close to zero for the untreated solution to 220 page-ITEQ L<sup>-1</sup> after 4 h of treatment in the presence of NaCl. This value is far higher than the maximum contaminant level, 30 pg L<sup>-1</sup> of 2,3,7,8-TCDD, established by the U.S. EPA based on potential health effects from ingestion of water. The obtained results evidenced the role and relevance of the chloride concentration in the formation of highly substituted chlorinated byproducts, PCDD/Fs, in the oxidation medium. Whereas the use of Na<sub>2</sub>SO<sub>4</sub> did not lead to a significant formation of 2,3,7,8-PCDD/Fs, NaCl, which exerted a positive kinetic influence in the removal of 2-CP, showed a strong influence on the formation of PCDD/Fs during its electrochemical oxidation. Therefore, the selection of the appropriate electrolyte in the electrochemical oxidation of CPs must go beyond the removal of the primary pollutant and/or major parameters such as TOC or COD in order to assess the potential formation of harmful reaction byproducts. A detailed description of the results reported in this abstract is included in Vallejo et al., 2013.<sup>11</sup>

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