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# The critical role of the operating conditions on the Fenton oxidation of 2-chlorophenol: Assessment of PCDD/Fs formation

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## KEYWORDS

2-chlorophenol, Fenton oxidation, hydrogen peroxide dose, temperature effect, chloride influence, PCDD/Fs formation

## Highlights

- Oxidation byproducts were quantified when 2-CP s was treated by Fenton process.
- H<sub>2</sub>O<sub>2</sub> dose, T<sup>a</sup> and chloride show positive influence in the degradation of 2-CP.
- TOC balance was only closed with H<sub>2</sub>O<sub>2</sub> at 100% of the stoichiometric dose and 70°C.
- Besides, PCDD/Fs formation, promoted in presence of chloride, was quantified.

## ABSTRACT

This work assesses the influence of the operating conditions H<sub>2</sub>O<sub>2</sub> dose (20 or 100% of the stoichiometric amount), temperature (20 or 70°C), and the presence of chloride in

the oxidation medium in the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) during Fenton treatment of aqueous samples of 2-chlorophenol, 2-CP, one of the strongest precursor of PCDD/Fs. After 4 h of oxidation in the experiments carried out with 20% H<sub>2</sub>O<sub>2</sub> chlorinated phenoxyphenols and biphenyls, which are intermediates in PCDD/Fs formation, as well as PCDD/Fs were observed, resulting in concentrations 11 times higher than in the untreated sample. Additionally, when NaCl was also present in the reaction medium, PCDD/Fs were formed at higher extent, with a total concentration 74.4 times higher than in the untreated 2-CP solution. Results depicted a preferential formation of PCDFs over PCDDs, with dominance of lower chlorinated PCDD/Fs (tetra and penta-PCDD/Fs). Besides, the formation of the most toxic PCDD/Fs congeners (2,3,7,8-PCDD/Fs) was not favored under the operating conditions used in this work.

## 1. INTRODUCTION

Chlorophenols (CPs) are a family of organic compounds listed as priority pollutants by the U.S.EPA's Clean Water Act [1] and by the European Decision 2455/2001/CE [2] due their acute toxicity, resistance to biodegradation, tendency to bioaccumulate, and suspected carcinogenicity [3]. CPs have been applied as wood preservatives and disinfectants, and serve as intermediates in the synthesis of some insecticides, herbicides, pharmaceuticals and dyes [4]. CPs may be formed during waste incineration, pulp bleaching, and water disinfection [5]. As a result of their wide use and production for many years, and the past practice of chemical waste disposal in ordinary landfills, CPs have been detected in industrial wastewaters, surface waters, groundwater, soils and municipally treated drinking waters [6,7].

Wastewater treatment is necessary to remove CPs before their potential discharge into the environment. Biological processes are effective only when CPs are present in low

concentrations due to its inhibition of microbial growth, and physical/chemical treatments require post-treatment processes to remove the pollutants [7]. Alternatively, advanced oxidation processes (AOPs) offer many advantages to these aforementioned remediation techniques. They are based on the formation of very active species, typically hydroxyl radicals ( $\text{OH}^\cdot$ ), to remediate target organic compounds in wastewater. Fenton oxidation involves the generation of  $\text{OH}^\cdot$  from  $\text{H}_2\text{O}_2$  using  $\text{Fe}^{2+}$  as a catalyst at acidic pH [8]. The highly reactive  $\text{OH}^\cdot$  initiate the oxidative destruction of organic compounds leading to the formation of carbon-centered radicals,  $\text{R}^\cdot$ , which can be further oxidized by  $\text{Fe}^{3+}$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{OH}^\cdot$ , or other intermediates to form a stable and oxidized product [9,10].

Several studies emphasize the relative ease of use and efficacy of Fenton oxidation treatment for various industrial waters, and for the remediation of CPs [5,8,11,12]. One important limitation in the treatment of heavily polluted wastewaters by Fenton oxidation may be its high  $\text{H}_2\text{O}_2$  consumption. To maintain economic feasibility, lower oxidant concentrations have been proposed, but this may lead to the formation of stable, and potentially toxic, aromatic intermediates. One important consideration for Fenton oxidation, therefore, is the potential formation of byproducts that can be more dangerous than the target parent compounds. For example, the formation of coupling-reaction aromatic byproducts, such as chlorinated biphenyls, dibenzofurans and dibenzodioxins, have been addressed from a qualitative and/or semi-quantitative perspective during the treatment of CPs under nonstoichiometric Fenton system conditions [13-15]. CPs are potential precursors of the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and may also contain many chlorinated impurities, such as PCDD/Fs [16,17]. PCDD/Fs are a family of persistent

organic pollutants regulated internationally by the Stockholm Convention, characterized by their persistence, bioaccumulative behaviour and toxicity [18].

To date, a thorough understanding of PCDD/Fs and other related byproducts formation during the application of AOPs for the abatement of chlorinated organic compounds is lacking. This work, therefore, evaluates the reaction products, with especial and detailed quantitative assessment of PCDD/Fs, during Fenton treatment of solutions containing 2-chlorophenol (2-CP). The influence of H<sub>2</sub>O<sub>2</sub> dose, temperature and presence of chloride ions in the reaction media on the potential formation of PCDD/Fs has been evaluated. Furthermore, in order to provide a better understanding of the reaction mechanisms that are involved in their formation the distribution of intermediates oxidation products has been analyzed.

## **2. MATERIALS AND METHODS**

### **2.1. Fenton oxidation experiments**

All the chemicals used were analytical grade reagents. Fenton oxidation experiments consisted of 1L of 15.56 mM 2-CP, and were performed in batch mode in magnetically stirred (700 rpm) glass reactors. The initial pH was adjusted to 3.0 with HNO<sub>3</sub>. Excess H<sub>2</sub>O<sub>2</sub> was removed by NaHSO<sub>3</sub> when the oxidation time was reached. All experiments were done in duplicate under the operating conditions listed in Table 1. H<sub>2</sub>O<sub>2</sub> doses corresponding to 100% (202.28 mM) and 20% (40.44 mM) of the theoretical stoichiometric amount to oxidize 2-CP were used. Two different temperatures, 20°C and 70°C, were evaluated, and the presence of chloride (56.34 mM) in the reaction medium was tested.

Table 1. Experimental conditions of Fenton experiments.

<b>H<sub>2</sub>O<sub>2</sub> (mM)</b>	40.44	40.44	40.44	202.28	202.28	202.28
<b>Fe<sup>+2</sup> (mM)</b>	0.18	0.18	0.18	7.22	7.22	7.22
<b>T<sup>a</sup> (°C)</b>	20	20	70	20	70	70
<b>NaCl (mM)</b>	-	56.34	-	-	-	56.34

## 2.2. Analytical methods.

Total organic carbon (TOC) analysis was performed using a TOC-V CPH (Shimadzu). 2-CP and aromatic reaction intermediates were quantified using a HPLC (Waters 2690) equipped with a reversed-phase column LC-8 (Supelco) and a PDA detector, and using 4 mM H<sub>2</sub>SO<sub>4</sub> as the mobile phase at  $\lambda = 211$  nm.

Quantification of acetic, formic, maleic, fumaric and oxalic acids were made using ion chromatography with anionic suppression (Dionex ICS-1100) with a conductivity cell detector (ASR-ULTRA model). An IonPac AS9-HC (4 mm) column was used as the stationary phase with a mobile phase of 9 mM solution of Na<sub>2</sub>CO<sub>3</sub> at 1 mL min<sup>-1</sup>.

Samples were L-L extracted with dichloromethane, concentrated in a rotary evaporator (Buchi R-210) and analyzed by GC-MS (Shimadzu QP2010 Ultra) with a capillary column (HP-5ms, 30 m length, 0.25 mm internal diameter). Confirmation of all structural assignments for the identified compounds was made using the NIST08 spectra library.

## 2.3. PCDD/Fs analysis

Standard Method U.S.EPA 1613 (1994) for PCDD/Fs analysis was used in this study. Briefly, samples (0.45 L) were spiked with 10  $\mu$ L of a 15 <sup>13</sup>C-labeled PCDD/Fs solution (EPA 1613 LCS) dissolved in acetone. PCDD/Fs were extracted with dichloromethane in triplicate. The organic extract was concentrated in a rotary evaporator (Buchi R-210),

transferred to n-hexane, treated with H<sub>2</sub>SO<sub>4</sub> and extracted twice with n-hexane. The organic phase was then dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated in the rotary evaporator to approximately 1-2 mL. The extract was then filtered and further cleaned-up using an automated system (Power-Prep<sup>TM</sup>, Fluid Management Systems) through silica, alumina and PX-21 active carbon columns (Technospec). The purified extract was concentrated using a rotary evaporator, transferred into a vial and concentrated to dryness under N<sub>2</sub>. Before analysis, an internal standard (EPA 1613 ISS) was added to the sample.

Purified samples were analyzed by the SERCROM Service (University of Cantabria) using high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS), whereas it must be noticed that in previous works the formation of coupling reaction products during the Fenton oxidation of CPs was faced using low resolution MS. The HRGC system is comprised of a TRACE GC Ultra<sup>TM</sup> gas chromatograph equipped with a split/splitless injector (Thermo Electron S.p.A.) and a DB-5 MS fused silica capillary column (J&W Scientific). The column was connected through a heated transfer line (270°C) to a DFS high-resolution magnetic sector mass spectrometer with BE geometry (Thermo Fisher Scientific). Positive electron ionization (EI+) mode with ionization energy of 45 eV was used in the source at 270 °C. The mass spectrometer was operated in SIM mode at 10000 resolution power (10% valley definition).

Detection limits were calculated as the concentrations that gave instrumental responses within a signal-to-noise ratio of 3.

Quantitative analyses were performed using the isotopic dilution method. Relative response factors, obtained from the calibration curve by analyzing CS-1 to CS-5 standard solution mixtures, were used to determine the target compound's concentration in the samples. The recoveries of labeled standards were calculated using the ISS standard.

#### **2.4. Quality control.**

The reliability of the PCDD/Fs analytical methodology was assured by analyses of ultrapure water samples spiked with native PCDD/Fs standards (EPA 1613 PAR), blank samples and the EPA 1613 LCS standard. The average recoveries were in the range of 74.3 to 105.6% for  $^{13}\text{C}_{12}$ -labeled 2,3,7,8-PCDD/Fs congeners, and were within the ranges established by the EPA 1613 method. Blanks representing all sample preparation steps were analyzed and indicated that congeners were either not detected or below the detection limits.

### **3. RESULTS AND DISCUSSION**

#### **3.1. Effect of $\text{H}_2\text{O}_2$ dose on Fenton degradation of 2-CP**

The effect of two different concentrations of  $\text{H}_2\text{O}_2$  (20 and 100% of the stoichiometric  $\text{H}_2\text{O}_2$  dose) on the Fenton oxidation of 2-CP was investigated. Although oxidation was effective for both concentrations, it was faster with 100%  $\text{H}_2\text{O}_2$  due to a higher OH availability (Figure 1a).



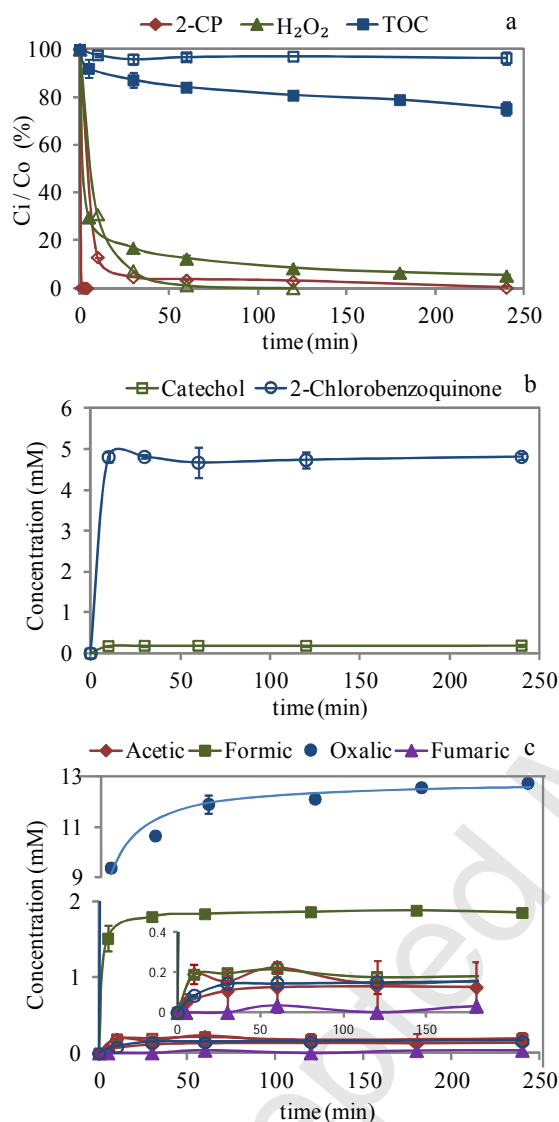


Figure 1. Effect of H<sub>2</sub>O<sub>2</sub> dose on: a) 2-CP, H<sub>2</sub>O<sub>2</sub> and TOC; b) aromatic intermediates; c).organic acids. Empty dots: 20% stoichiometric, solid dots: 100% stoichiometric.

However, even when 2-CP was completely degraded, the mineralization was far from complete at both H<sub>2</sub>O<sub>2</sub> initial concentrations. With H<sub>2</sub>O<sub>2</sub> at 20% of the stoichiometric value, TOC was reduced only by 4%, and remained constant after 30 min, whereas using the stoichiometric amount of H<sub>2</sub>O<sub>2</sub> (100%) higher TOC removal was achieved (22.9% after 4 h). This is likely due to both the low concentration of H<sub>2</sub>O<sub>2</sub> remaining in solution, and to the presence of organic compounds such as carboxylic acids that could

form complexes with Fe(III), deactivating its capacity to regenerate Fe(II) and diminishing OH<sup>·</sup> production [19].

Aromatic intermediate products were identified only in samples containing 20% H<sub>2</sub>O<sub>2</sub>. Concretely, 2-chlorobenzoquinone and catechol (Figure 1b), reached maximum concentrations at 5 min and remained at constant values after 30 min, coinciding with total H<sub>2</sub>O<sub>2</sub> consumption. The cleavage of the aromatic ring led to the formation of aliphatic carboxylic acids: acetic, formic, oxalic and fumaric acids. Although the same organic acids were identified with both H<sub>2</sub>O<sub>2</sub> dose (fumaric acid was not detected at 20% H<sub>2</sub>O<sub>2</sub>), higher concentrations were obtained with H<sub>2</sub>O<sub>2</sub> at 100% because of the higher OH<sup>·</sup> availability.

### **3.2. Effect of Temperature on Fenton degradation of 2-CP**

The analysis of 2-CP degradation was performed at two different temperatures, ambient (20°C) and 70°C, for both H<sub>2</sub>O<sub>2</sub> concentrations (20% and 100% of the stoichiometric dose). Faster degradation of 2-CP was observed at 70°C than at room temperature for both H<sub>2</sub>O<sub>2</sub> concentrations, as would be expected due to the increase in the kinetic constant of the oxidation reactions with temperature.

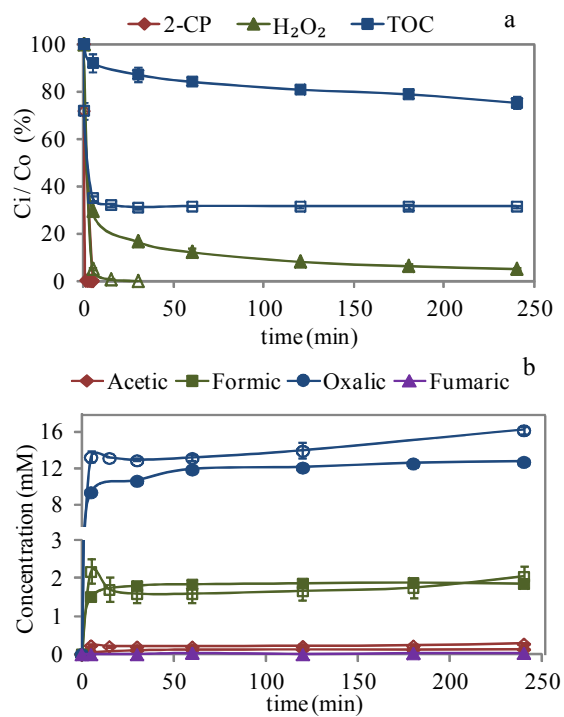


Figure 2. Effect of Temperature with H<sub>2</sub>O<sub>2</sub> at 100% in: a) 2-CP, H<sub>2</sub>O<sub>2</sub> and TOC; b) organic acids. Empty dots: 70°C, filled dots: 20°C.

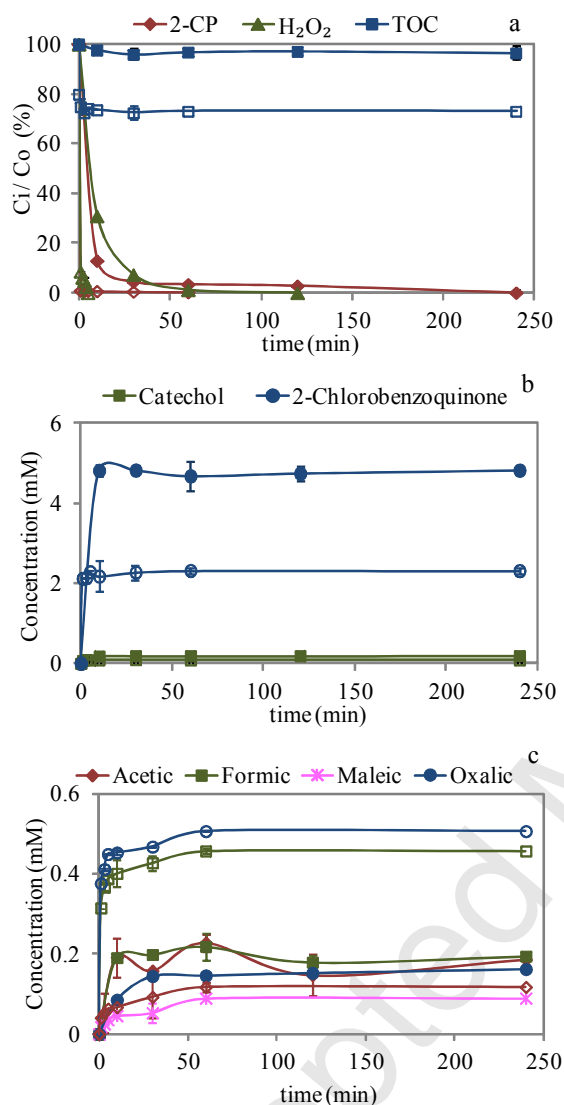


Figure 3. Effect of Temperature with H<sub>2</sub>O<sub>2</sub> at 20% in: a) 2-CP, H<sub>2</sub>O<sub>2</sub> and TOC; b) aromatic intermediates; c) organic acids. Empty dots: 70°C, filled dots: 20°C.

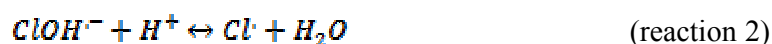
Although some authors claim that the thermal instability of H<sub>2</sub>O<sub>2</sub> is a limitation for the use of Fenton oxidation at high temperatures [20], Zazo et al. [21] found that increasing the temperature in the range 25 to 130°C enhanced mineralization rates. Accordingly, our results indicate that the overall mineralization was considerably more effective at 70°C (Figures 2a and 3a). The reduction in TOC increased from 3% at 20°C to 27% at 70°C (H<sub>2</sub>O<sub>2</sub> at 20%, 4h) and from 23% at 20°C to 69% at 70°C (H<sub>2</sub>O<sub>2</sub> at 100%, 4 h).

The concentration of the main aromatic intermediate products, 2-chlorobenzoquinone and catechol, which were only identified with 20% H<sub>2</sub>O<sub>2</sub>, was lower at 70°C than at 20°C in agreement with the enhancement in TOC mineralization. On the other hand, the temperature increase resulted in high concentrations for some organic acids, formic and oxalic at 20% H<sub>2</sub>O<sub>2</sub>, and oxalic acid with 100% H<sub>2</sub>O<sub>2</sub>. Although the temperature increment favored TOC degradation, a complete mineralization could not be achieved, accordingly to section 3.1, because of H<sub>2</sub>O<sub>2</sub> consumption and the resistance of some carboxylic acids, such as oxalic acid, to Fenton degradation.

### 3.3. Effect of chloride on Fenton degradation of 2-CP

Since chloride may be one product of 2-CP degradation and high concentrations of inorganic salts, especially NaCl, have been measured in wastewaters, such as those generated during the manufacture of pesticides, pharmaceuticals, dyes, and from landfill leachates [22-24], the effect of 2-CP was analyzed using two sets of experiments, differently favored in terms of TOC removal (H<sub>2</sub>O<sub>2</sub> at 100% and at 70°C; H<sub>2</sub>O<sub>2</sub> at 20% and 20°C) and in the presence of 2000 mg L<sup>-1</sup> (56.34 mM) of Cl<sup>-</sup>.

With 100% H<sub>2</sub>O<sub>2</sub> and 70°C, the presence of Cl<sup>-</sup> in the reaction medium did not affect the degradation of 2-CP, but increased the mineralization of TOC by 11% in comparison to samples without Cl<sup>-</sup> (Figure 4). As was shown by Micó and coworkers [25], this fact can be attributed to the formation of chloride radical anions (Cl<sup>•</sup>) from the reaction between OH<sup>•</sup> and Cl<sup>-</sup> (reactions 1 to 3), which contribute to the degradation of organic compounds.



Although  $\text{Cl}^-$  formation requires  $\text{OH}^-$  scavenging, and  $\text{Cl}^-$  are generally less reactive than  $\text{OH}^-$  with organic species, the magnitude of rate constants for  $\text{Cl}^-$  reactions with organic compounds are comparable to those for  $\text{OH}^-$  [25,26]. Additionally, Pignatello [27] found that the scavenging effect of  $\text{OH}^-$  by  $\text{Cl}^-$  is noticeable above 10 mM  $\text{Cl}^-$ ; we have, accordingly, used  $\text{Cl}^-$  concentrations higher than 10 mM.

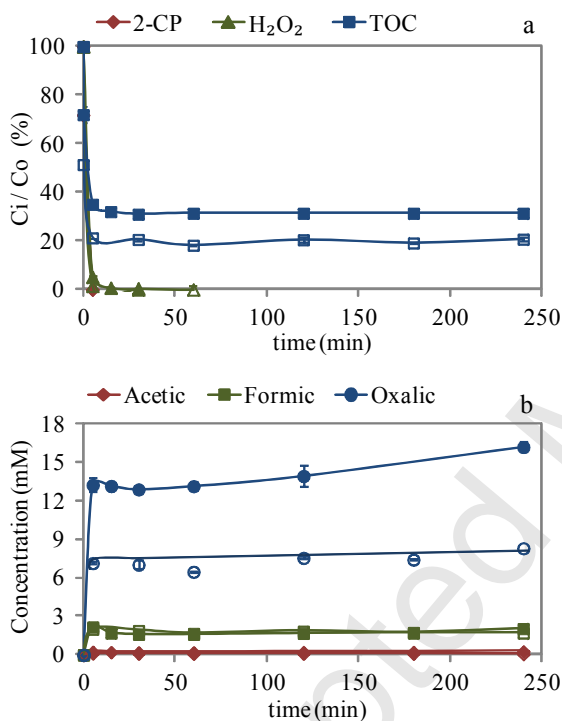


Figure 4. Effect of Chloride with  $\text{H}_2\text{O}_2$  at 100% and at  $70^\circ\text{C}$  in: a) 2-CP,  $\text{H}_2\text{O}_2$  and TOC; b) organic acids. Empty dots: with NaCl, filled dots: without NaCl.

These results were opposed to other studies where  $\text{Cl}^-$  significantly inhibited organic matter removal via  $\text{OH}^-$  scavenging, as well as ferric ion complexation [25].

Nevertheless, the formation of ferric chlorocomplexes that affect the regeneration of  $\text{Fe}^{2+}$ , can be overcome if  $\text{Cl}^-$  concentrations are less than 200 mM [28], as was also observed in this study. Alternatively, with 20%  $\text{H}_2\text{O}_2$  and at  $20^\circ\text{C}$ , the presence of  $\text{Cl}^-$  did not affect the degradation of 2-CP and the overall TOC removal (Figure 5). These results suggest that when using low concentrations of Fenton reagent, the lower

production of  $\text{OH}^\cdot$  leads to preferential degradation of the main organic contaminant, 2-CP.

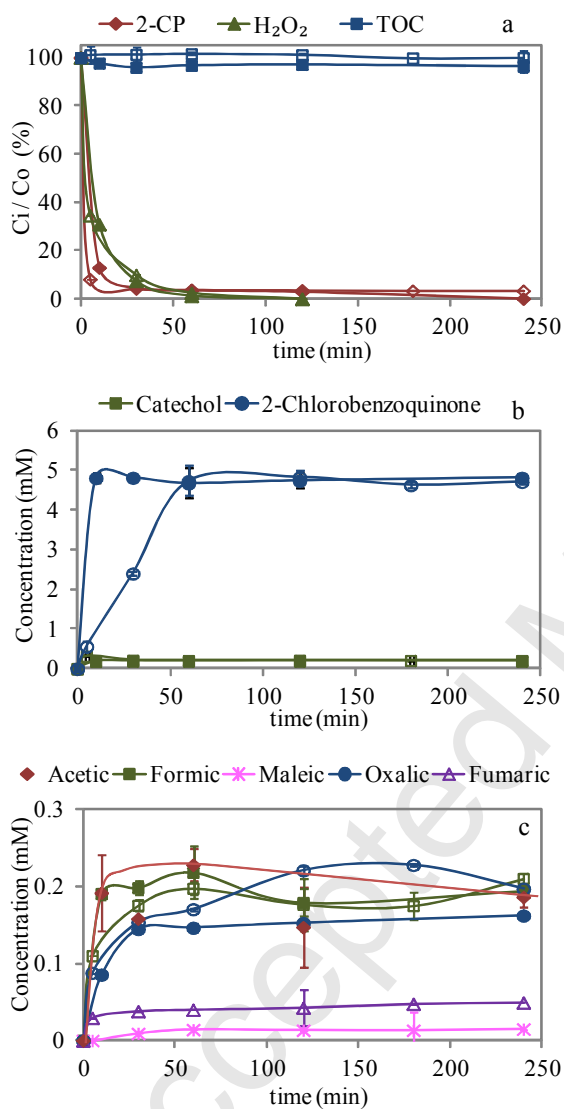


Figure 5. Effect of Chloride with  $\text{H}_2\text{O}_2$  at 20% and at  $20^\circ\text{C}$  in: a) 2-CP,  $\text{H}_2\text{O}_2$  and TOC; b) aromatic intermediates; c) organic acids. Empty dots: with NaCl, filled dots: without NaCl.

### 3.4. TOC and Cl<sup>-</sup> balance

Theoretical TOC values after 4 h of treatment were calculated in order to account for the detected intermediate products and compared to the experimentally measured TOC data (Figure 6).

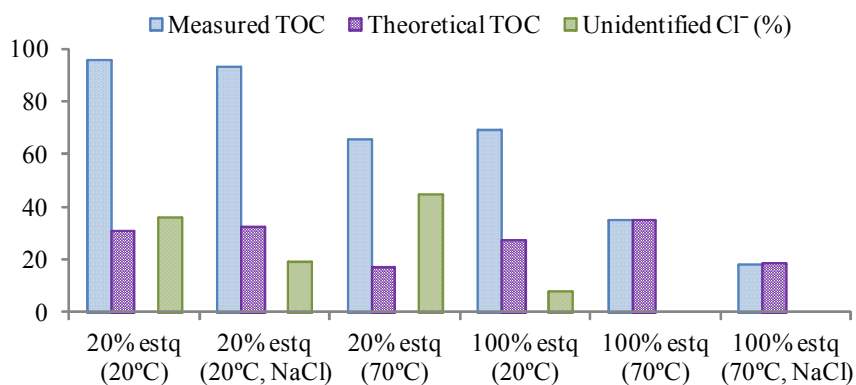


Figure 6. Differences between measured and calculated TOC (mM) and unidentified chloride (%) after 4h.

The difference between measured and theoretical TOC values decreased with increasing  $H_2O_2$  dose and temperature. After 4 h, the TOC balance was only 100% satisfied with 100%  $H_2O_2$  at 70°C. Under experimental conditions other than 100%  $H_2O_2$  and 70°C, a difference between the measured and quantified TOC was observed and attributed to the presence of unidentified oxidation intermediates, which may be aromatic condensation species [21]. In addition,  $Cl^-$  measurements were only balanced when the TOC was balanced. It is, therefore, likely that the aforementioned condensation byproducts included chlorinated organic compounds.

There are significant gaps in the understanding of the formation and identity of aromatic intermediates when using pronounced substoichiometric  $H_2O_2$  to  $CP_0$  molar ratios for Fenton oxidation [13]. In order to identify some of these unknown byproducts, samples were analyzed using GC-MS. Working with 20%  $H_2O_2$ , the main species identified at low retention times were chlorobenzenediols, mainly as 2-chlorohydroquinone, 4-chlorocatechol and 4-chloresorcinol (which were only detected by GC-MS, suggesting low yields). Compounds with higher molecular weights, such as condensation products formed by two-chlorinated aromatic rings, were detected at higher retention times. They



were primarily 4-chloro-3-(4-chlorophenoxy)phenol ( $m/z$ : 254, 184) and 4,4'-dichloro[1,1'-biphenyl]-3,3'-diol ( $m/z$ : 254, 155). The formation of coupling-reaction aromatic byproducts is supported by the development of a brownish reagent medium [29] and have also been reported during the treatment of chlorinated phenols under nonstoichiometric Fenton [13] and Fenton-like systems [14,15, 30]. Nevertheless, these compounds are present in low concentrations that do not balance the differences observed in the TOC. Therefore, it is likely that there were unknown analytes remaining in the solution. However, such compounds are susceptible to oxidation, as the organic carbon balance was closed by increasing  $H_2O_2$  dose and temperature. Similarly, Sedlak and Andren [29] identified the formation of colored aromatic polymers during the Fenton oxidation of chlorobenzenes that were further oxidized by subsequent  $OH^\cdot$  attack.

### **3.5. Formation of PCDD/Fs during the Fenton degradation of 2-CP**

Since 2-CP is a potent precursor of PCDD/Fs, and its Fenton oxidation byproducts (i.e., chlorinated hydroxybiphenyls and phenoxyphenols) are key intermediates in the formation of PCDD/Fs from chlorinated phenols [31,32], the assessment of the potential formation of PCDD/Fs as minor byproducts during Fenton oxidation of 2-CP is necessary. PCDD/Fs analyses were performed after 4 h of treatment under the operating conditions discussed in sections 3.1, 3.2 and 3.3. The homologue profiles of total PCDD/Fs and the congener profiles of 2,3,7,8-PCDD/Fs in untreated 2-CP solutions and in oxidized samples (4 h) are shown in Figure 7a and 7b, respectively.

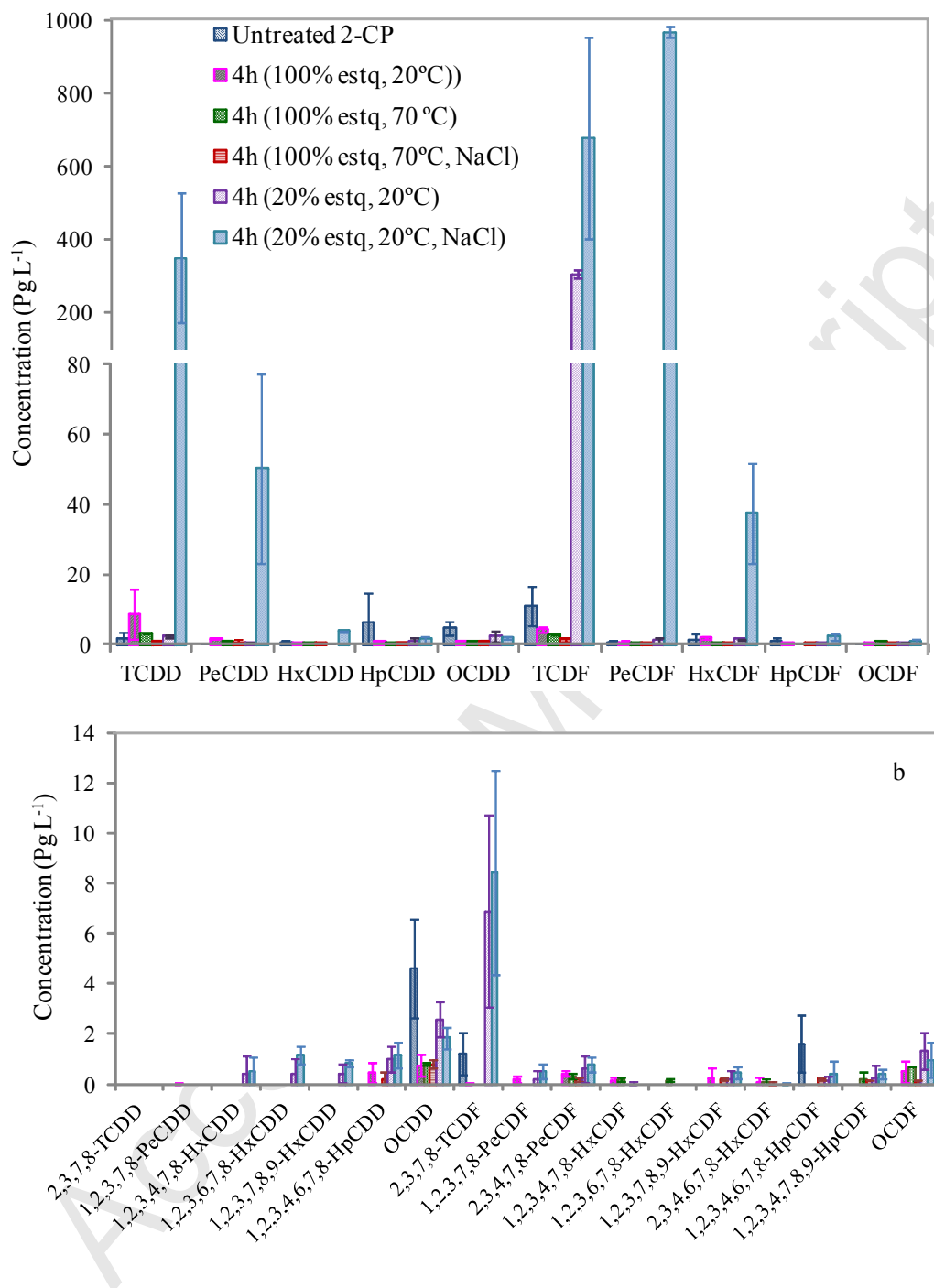


Figure 7. PCDD/Fs concentration: a) homologue profile of total PCDD/Fs; b) congener profile of 2,3,7,8-PCDD/Fs.

As can be observed in Figure 7a, three groups of homologues (HpCDD, OCDD, and TCDF) were detected at very low concentration (4.6-12.2 pg L<sup>-1</sup>) in the untreated water

solutions containing 2-CP. For 100% H<sub>2</sub>O<sub>2</sub>, although new groups of homologues appeared in the oxidized sample, in comparison to the untreated one, a significant PCDD/Fs formation was not observed. Besides, the concentration of some homologue groups, namely TCDD and TCDF, decreased when working at 70°C. On the other hand, after 4 h of treatment with 20% H<sub>2</sub>O<sub>2</sub>, relatively large quantities of PCDD/Fs were observed, resulting in concentrations (312.9 pg L<sup>-1</sup>, Table 1SI) 11 times higher than in the untreated sample. Results from figure 7a showed a preferential formation of PCDFs over PCDDs, so the formation of PCDFs intermediate products seemed to be favored over the corresponding for PCDDs. According to Duesterberg and Waite [33], the electrophilic addition of OH<sup>·</sup> to CPs followed by water elimination results in the formation of Cl-phenoxy radicals. These radicals have been identified as key intermediates in basically all suggested pathways for PCDD/Fs formation [34]. The oxidative coupling reactions of Cl-phenoxy radicals with other radicals and/or molecules give rise to bioaromatic intermediates such as biphenyls and phenoxyphenols and then to PCDD/Fs [35,36]. Since radical-molecule pathway requires chlorine and hydroxyl displacement, steps that are not energetically favored, the radical-radical pathway is considered the major pathway for the formation of PCDD/Fs [36].

Furthermore, when NaCl was present in the reaction medium, PCDD/Fs were formed at higher extent, with a total PCDD/Fs concentration (2092 pg L<sup>-1</sup> Table 1SI) 74.4 times higher than in the untreated 2-CP solution, highlighting the significance of ubiquitous Cl<sup>-</sup> in the reaction medium. Chlorine radicals (Cl<sup>·</sup>), formed from the reaction between OH<sup>·</sup> and Cl<sup>-</sup> as was described in section 3.3, could contribute to PCDD/Fs formation by chlorination of their precursors as well as of lower chlorinated PCDD/Fs. The dominance of lower chlorinated PCDD/Fs (tetra and penta derivatives) underscores the reactivity dynamics of the reaction medium where lower chlorinated compounds (2-CP

and its derivatives) predominate, progressing with time to PCDD/Fs by means of chlorination/condensation reactions.

Among total PCDD/Fs, congeners with chlorine at 2,3,7,8 positions (a total of 17 PCDD/Fs congeners) are of particular interest due to their high toxicity and potential effects on human health. Only two 2,3,7,8-PCDD/Fs, OCDD and 2,3,7,8-TCDF, were detected at very low concentrations ( $1.2\text{--}4.6\text{ pg L}^{-1}$ ) in the untreated 2-CP solution (Figure 7b). After 4 h of treatment using 20%  $\text{H}_2\text{O}_2$ , both congeners remained in the reaction medium although at low concentrations,  $2.6\text{ pg L}^{-1}$  for OCDD and  $6.9\text{ pg L}^{-1}$  for 2,3,7,8-TCDF (Table 2 SI). Similar values were obtained when NaCl was added to the reaction medium (20%  $\text{H}_2\text{O}_2$ ), with concentration values of  $1.8\text{ pg L}^{-1}$  for OCDD and  $8.4\text{ pg L}^{-1}$  for 2,3,7,8-TCDF (Table 2 SI). For both systems, the rest of the 2,3,7,8-PCDD/Fs were observed at negligible concentrations. Under the remaining operating conditions and taking into account the low PCDD/Fs concentrations and the experimental error, the formation of 2,3,7,8-PCDD/Fs could not be confirmed. Therefore, the formation of the less toxic PCDD/Fs congeners was favored under the operating conditions used in this work. Although PCDD/Fs have been shown to be formed in very small concentrations (i.e.  $2092\text{ pg L}^{-1}$ ), it must be emphasized that these low yields do not eliminate environmental threats, as many compounds, such as PCDD/Fs, are toxic even at very low concentrations. In fact, the maximum contaminant level established by the U.S. EPA is  $30\text{ pg L}^{-1}$  of the equivalent 2,3,7,8-TCDD. In addition, as PCDD/Fs are highly persistent in the environment and their lipophilic nature causes them to accumulate through food chains, there can be adverse effects for biota (including humans) from very low and continuous exposure to these compounds. The formation of PCDD/Fs has also been reported during the treatment of chlorinated phenols using other AOPs. Vollmuth et al. [37] found that the photolytic treatment of

pentachlorophenol (PCP) in water resulted in the formation of several congeners of PCDD/Fs. Hong et al. [38] observed the presence of 1,2,3,4,6,7,8-HpCDD and OCDD as a minor transformation product during the photolysis of PCP. Furthermore, photolytical and photocatalytical treatment of triclosan in water solutions have been shown to result in the formation of some PCDD congeners [39-41]. On the other hand, Holt et al. [42] found that the concentration of 93 PCDD/F congeners in two pesticide formulations increased between 3000 to 5600% after exposure to natural light. More recently, Vallejo et al. [43] assessed the formation of PCDD/Fs as a result of the electrochemical treatment of 2-CP as a function of the type of electrolyte used. When NaCl was used as electrolyte, the concentration of total PCDD/Fs increased by 26,800 times compared to the untreated sample (equivalent to the toxicity index of 220 pg-ITEQ L<sup>-1</sup>).

Regarding Fenton oxidation, Fukushima and Tatsumi [44] observed the formation of OCDD during the photo-Fenton treatment of PCP. Poerschmann et al. [13] observed the generation of chlorinated biphenyls, diphenyl ethers, benzofurans and related compounds during the Fenton oxidation of 2-CP under substoichiometric conditions. More recent studies report the formation of similar compounds, including dichlorodibenzodioxins, as a result of Fenton-like treatment of several CPs with substoichiometric doses of H<sub>2</sub>O<sub>2</sub> and low quantities of iron [14,15]. These observations, in combination with the results presented in this paper, serve to confirm our recent observations of increasing concentrations of PCDD/Fs congeners during the Fenton treatment of different leachate samples from a municipal waste landfill [45].

#### 4. CONCLUSIONS

This work reports the importance of understanding the effects of the operating conditions during the Fenton oxidation of 2-CP in regards to the formation of oxidation

byproducts (i.e., PCDD/Fs). Substoichiometric  $H_2O_2$  concentrations lead to the formation of PCDD/Fs, and PCDD/F concentrations increase when  $Cl^-$  is in the reaction medium. Our analyses represent a valuable contribution because they go beyond the previously published results, in which the formation of dioxins and related compounds was covered from a qualitative approach. Furthermore, these results provide evidence for the necessity of using proper operating conditions during the Fenton treatment of chlorinated pollutants, in particular when PCDD/Fs precursors and/or  $Cl^-$  are present, or may be formed, in the treated samples.

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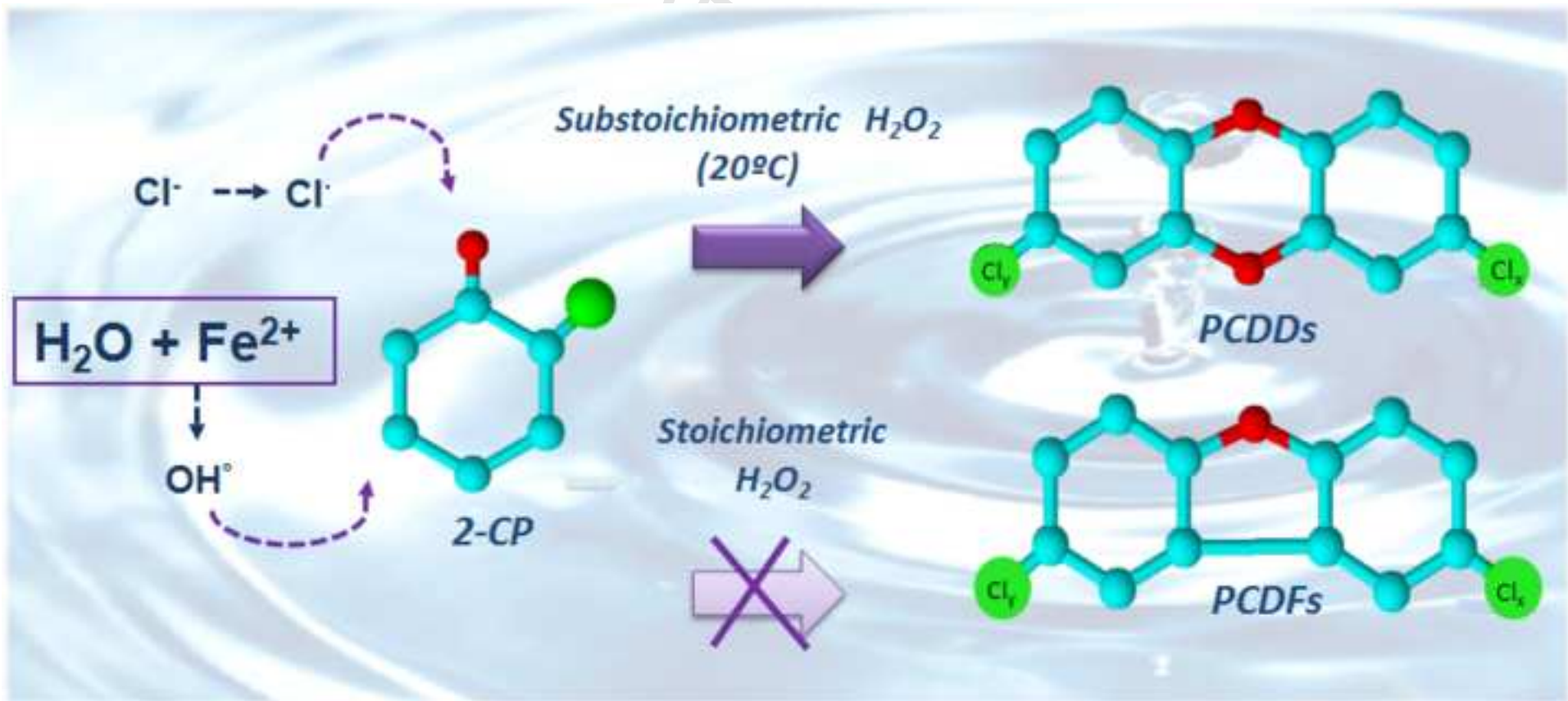


Figure 1

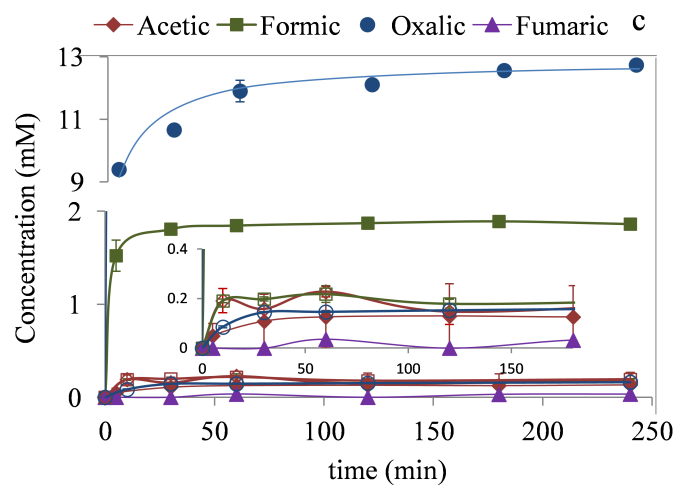
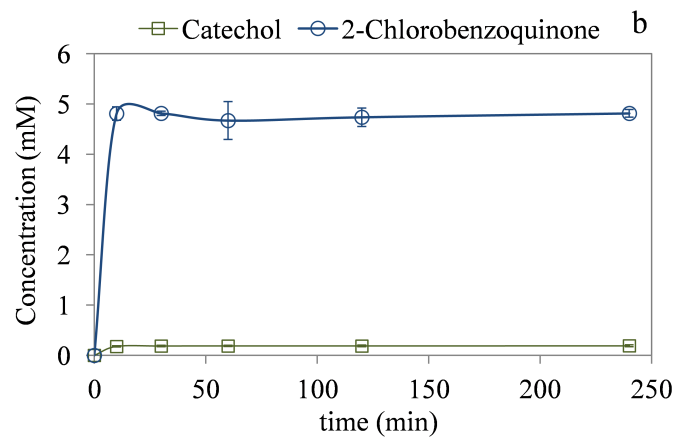
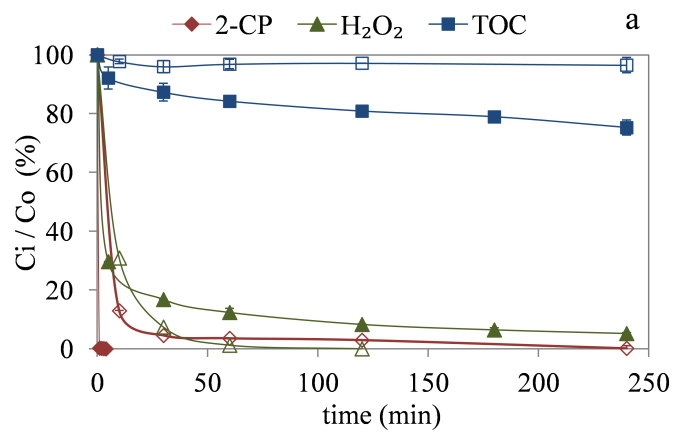


Figure 2

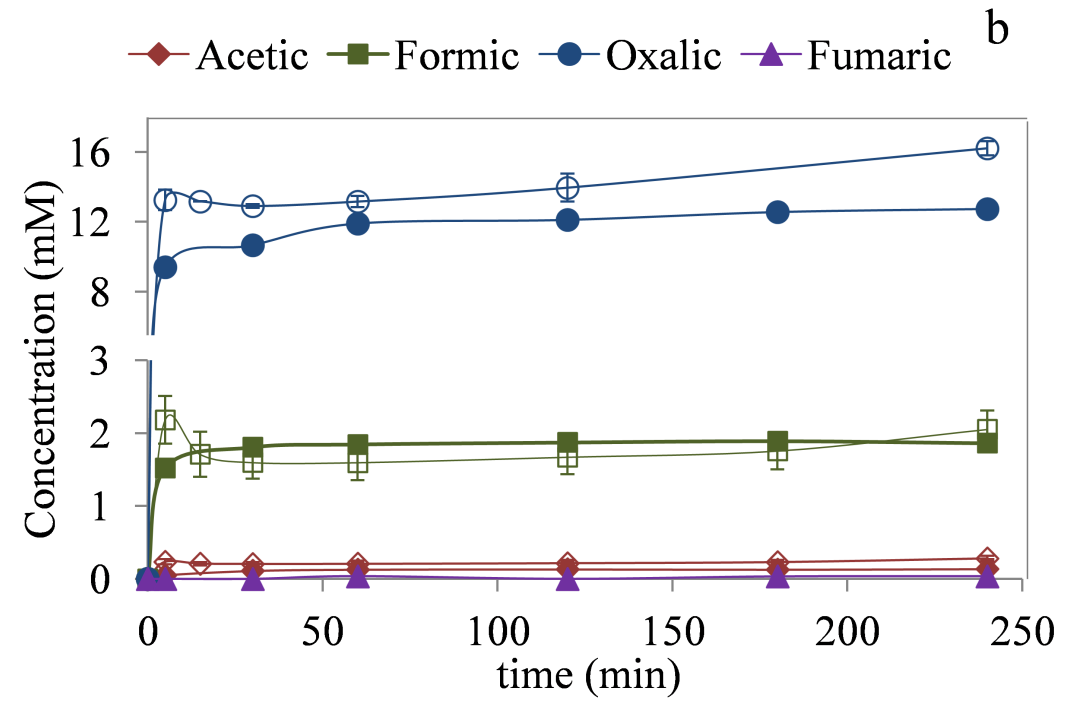
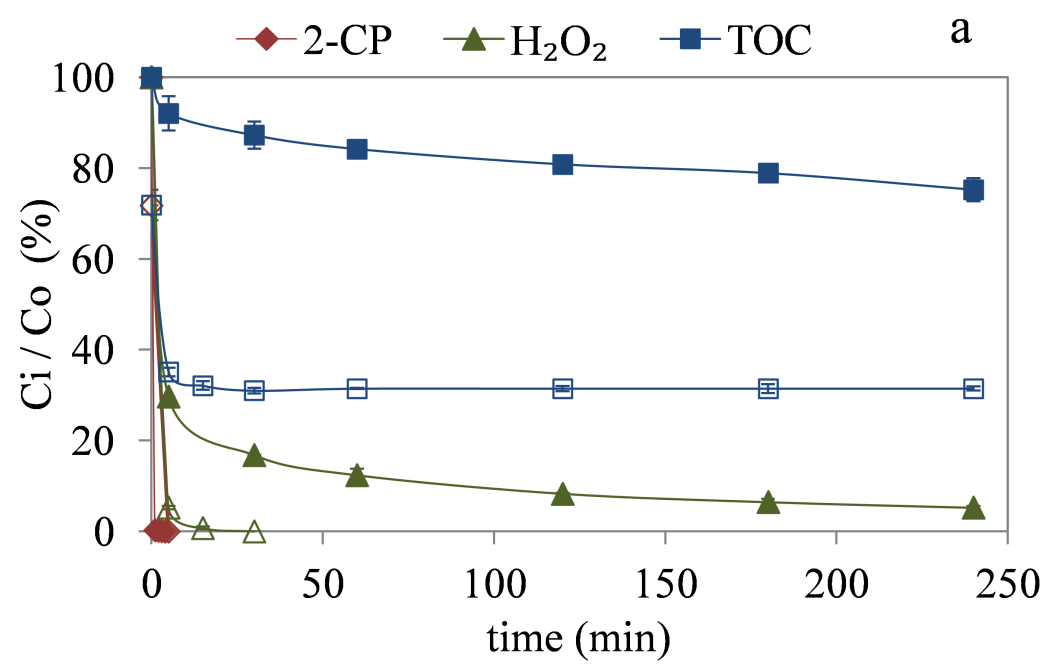


Figure 3

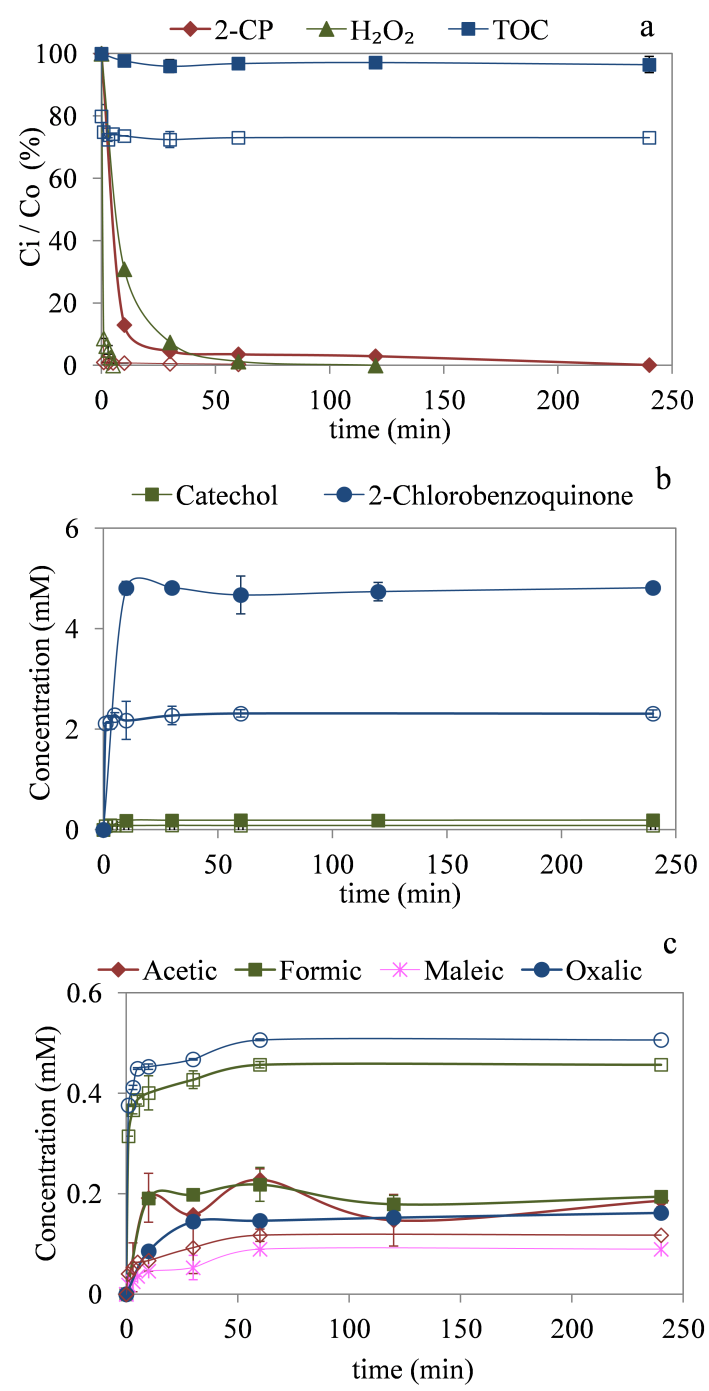




Figure 4

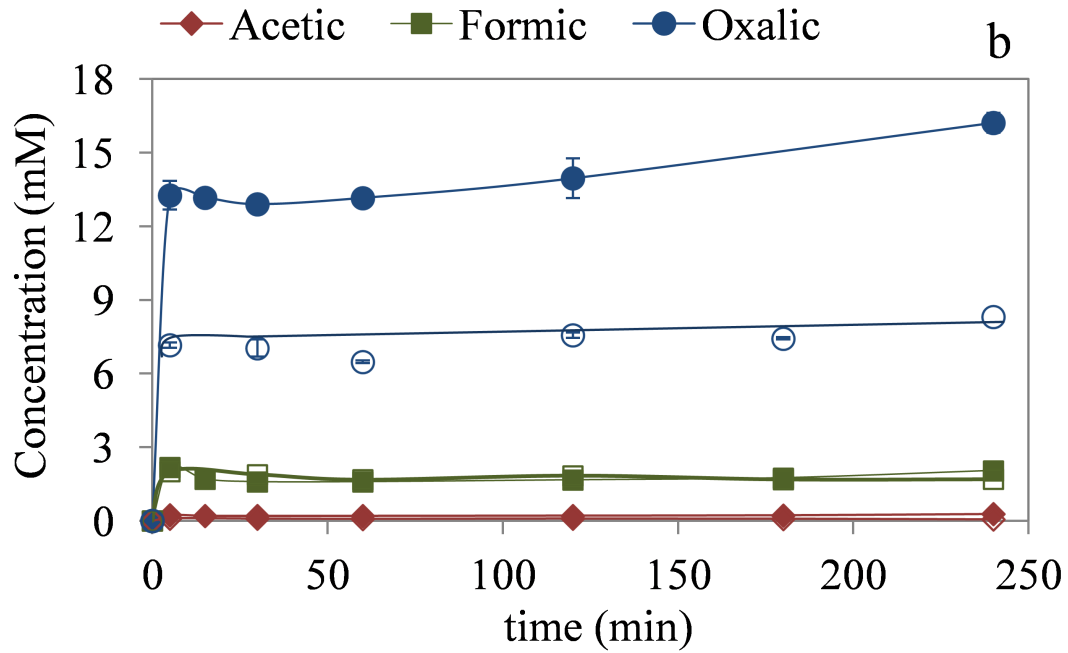
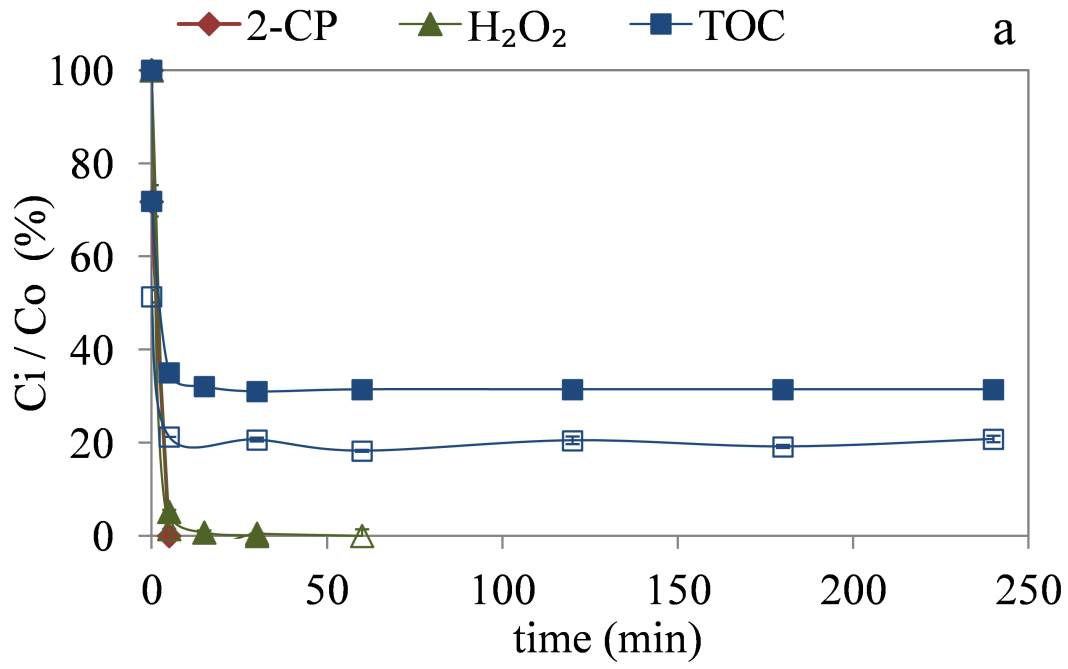


Figure 5

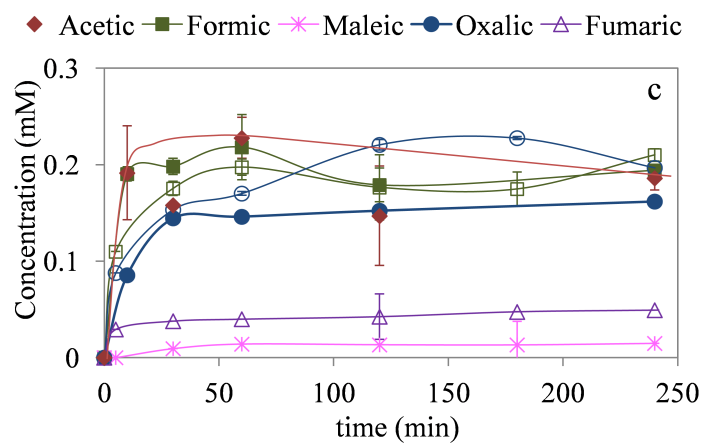
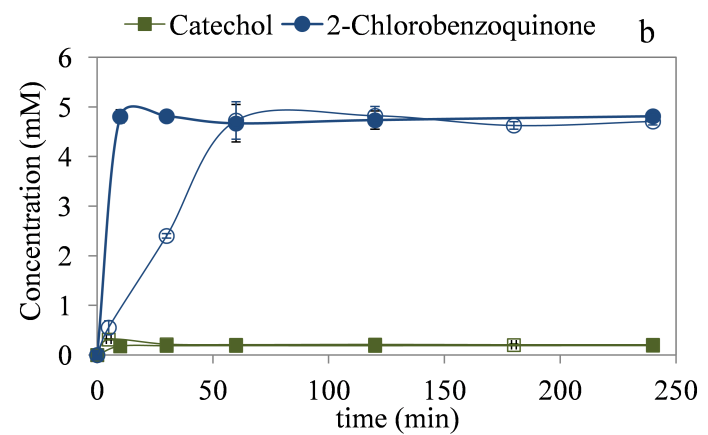
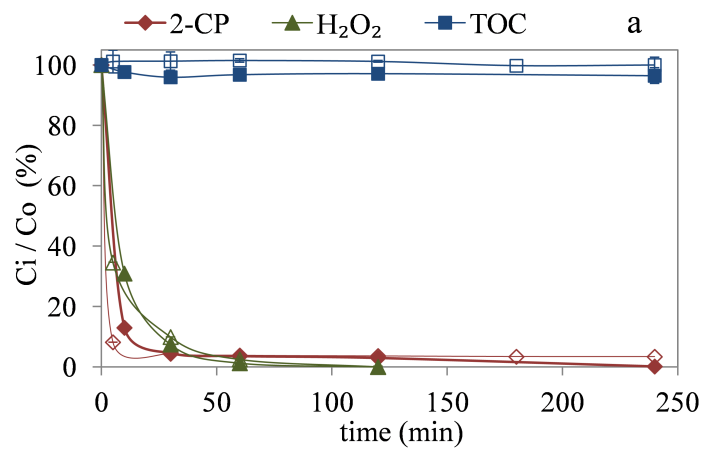


Figure 6

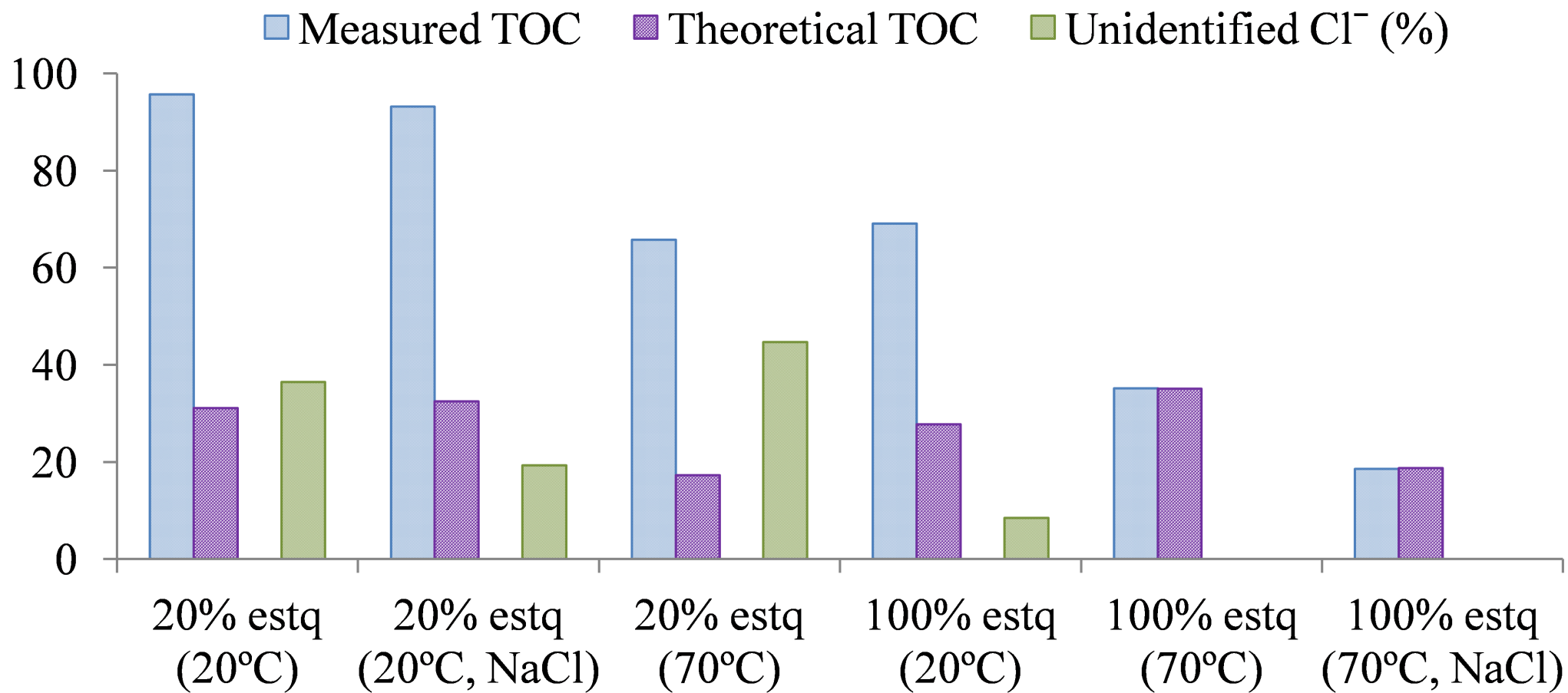


Figure 7

