

Transformation of 2,4-dichlorophenol by H₂O₂/UV-C, Fenton and photo-Fenton processes: Oxidation products and toxicity evolution

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ABSTRACT

In the present study, H₂O₂/UV-C, Fenton and photo-Fenton treatment of 2,4-dichlorophenol was compared in terms of oxidation products and acute toxicity. The oxidation products were identified by gas chromatography–mass spectroscopy, high performance liquid chromatography and ion chromatography, whereas changes in acute toxicity were evaluated by the *Vibrio fischeri* luminescence inhibition assay. H₂O₂/UV-C and photo-Fenton processes ensured complete 2,4-dichlorophenol removal, detoxification and significant mineralization. Hydroquinone and formic acid were identified as the common oxidation products of the studied advanced oxidation processes investigated. 3,5-dichloro-2-hydroxybenzaldehyde, phenol, 4-chlorophenol and 2,5-dichlorohydroquinone were identified as the additional H₂O₂/UV-C oxidation products of 2,4-dichlorophenol. Acute toxicity decreased with decreasing 2,4-dichlorophenol and increasing chloride release.

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1. Introduction

Chlorophenols (CPs) are being employed as disinfectants and preservatives in wood, dyes, vegetable fibers and leather due to their broad-spectrum antimicrobial properties. They constitute an important group of aromatic chemicals, which have an annual world market share of about 10⁸ kg [1]. The large scale production and heavy consumption of CPs and their derivatives generate wastewaters that contain these substances at high concentrations. Most CPs are highly toxic to microorganisms including activated sludge bacteria and their removal with biological treatment processes is rather problematic due to their inhibitory properties and resistance to biodegradation, making the efficient removal of these substances from wastewaters in a conventional WWTP very difficult if not impossible [2]. When wastewaters containing CPs are being discharged into natural water bodies they may cause serious environmental as well as ecotoxicological problems since many of them are suspected of being carcinogenic and mutagenic [3,4]. Because of the abovementioned issues, CPs have been listed as priority toxic substances in the US Clean Water Act as well as EU Directive 2455/2001/EC [1].

For the alternative efficient treatment of CPs and other hazardous and/or toxic pollutants, advanced oxidation processes (AOPs) based on the formation of reactive species including hydroxyl radicals (HO[•]) have been developed and investigated. AOPs have been employed for the treatment of organic and inorganic pollutants found in air, soil and water at acceptable rates and operating costs, most of the time without creating secondary waste problems [5–8]. Major limitations of their full-scale application, however, have not been overcome yet; their capital and operating costs are still relatively high, and in some cases the oxidation products are more biotoxic than the mother compound(s) [9–11]. Consequently, the control and optimization of AOPs remains a serious challenge, in particular for industrial wastewater treatment applications. In light of this, CPs acting as model pollutants found in different kinds of industrial effluents, seem to be very good candidates to examine the correlation between the type of oxidation products and their toxicity evolution.

Among the AOPs, H₂O₂/UV, Fenton (Fe²⁺/H₂O₂), and photo-Fenton (Fe²⁺/H₂O₂/UV) processes have been extensively studied in the scientific literature for the degradation of CPs due to the efficient elimination of these substances during the application of these processes [12–15]. However, these treatability studies rather focused on process efficiency evaluated by means of monitoring the changes in parent pollutant concentration, as well as collective environmental parameters such as chemical oxygen demand (COD) and total organic carbon (TOC). In most cases, AOPs do not achieve

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Nomenclature

List of abbreviations and symbols

| | |
|-----------------------|--|
| 2,4 DCP | 2,4-dichlorophenol |
| AcOH | acetic acid |
| AOPs | advanced oxidation processes |
| BQ | <i>p</i> -benzoquinone |
| CHQ | chlorohydroquinone |
| COD | chemical oxygen demand (mg L^{-1}) |
| CPs | chlorophenols |
| DAD | diode-array detector |
| FoOH | formic acid |
| GC–MS | gas chromatography–mass spectrometry |
| HO• | hydroxyl radical |
| HPLC | high performance liquid chromatography |
| HQ | hydroquinone |
| IC | ion chromatography |
| IT | luminescence intensity (relative luminescence units; RLU) |
| $k_{2,4 \text{ DCP}}$ | pseudo-first-order 2,4 DCP removal rate constant (min^{-1}) |
| k_{TOC} | pseudo-first-order TOC removal rate constant (min^{-1}) |
| LLE | liquid–liquid extraction |
| OxOH | oxalic acid |
| SPE | solid phase extraction |
| TOC | total organic carbon (mg L^{-1}) |
| WWTP | wastewater treatment plant |

total mineralization of industrial pollutants, and hence the toxicity of oxidation products should be a critical point when establishing the benefits of any applied technology. Until now, the effect of different AOP types including $\text{H}_2\text{O}_2/\text{UV}$, Fenton and photo-Fenton processes, on the changes in toxicity and oxidation products of CPs has been scarcely documented in scientific literature [16–18]. This information has to be established to transform pollutants to more biodegradable, less toxic degradation products during the application of AOPs.

Considering the above facts, the main objective of this research was to investigate the oxidation products and acute toxicity evolved during the application of $\text{H}_2\text{O}_2/\text{UV-C}$, Fenton, and photo-Fenton processes to remove the priority pollutant 2,4-dichlorophenol (2,4 DCP) in aqueous solution. In the first part of the study baseline experiments were conducted to comparatively elucidate 2,4 DCP and TOC removal efficiencies and kinetics during application of different AOPs. In the second part, the transformation of 2,4 DCP into aromatic and aliphatic oxidation products was investigated under selected treatment conditions. In parallel, acute toxicity changes and dechlorination patterns were also monitored for the same AOPs by using the marine photobacterium *Vibrio fischeri* as the test organism. Among the organisms used in toxicity assays, *V. fischeri* has been the most often employed one because of its high sensitivity towards a wide range of pollutants [11]. The relationship between the oxidation product formation and acute toxicity evolution was examined to scrutinize the effective application of AOPs for industrial pollutant degradation.

2. Experimental

2.1. Materials

2,4 DCP ($\text{C}_6\text{H}_4\text{Cl}_2\text{O}$), hydroquinone (HQ, $\text{C}_6\text{H}_4(\text{OH})_2$), *p*-benzoquinone (BQ, $\text{C}_6\text{H}_4\text{O}_2$), phenol ($\text{C}_6\text{H}_6\text{O}$), oxalic acid dihydrate ($\text{C}_2\text{O}_4\text{H}_2 \cdot 2\text{H}_2\text{O}$), formic acid (FoOH, CH_2O_2), and acetic acid (AcOH,

$\text{C}_2\text{H}_4\text{O}_2$) were all purchased from Merck (Germany). Chlorohydroquinone (CHQ, $\text{C}_6\text{H}_3(\text{OH})_2\text{Cl}$) and catechol ($\text{C}_6\text{H}_6\text{O}_2$) were obtained from Fluka (Sweden) and Acros Organics (Belgium), respectively. Methanol (CH_3OH , Merck, Germany), orthophosphoric acid (H_3PO_4 , 85–88%, Merck, Germany), AcOH, sodium sulphate anhydrous (Na_2SO_4 , Merck, Germany), and methanesulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$, Sigma–Aldrich, USA) were used to prepare HPLC mobile phases. Methanol was also used for the conditioning of the Oasis hydrophilic–lipophilic balance (HLB) (6 mL/200 mg, Waters, USA) solid phase extraction (SPE) cartridges. For the liquid–liquid extraction (LLE) of the parent compound and oxidation products prior to GC–MS analysis, dichloromethane (CH_2Cl_2) purchased from Merck (Germany) was employed. All other chemicals required for analytical and experimental procedures were at least of analytical grade and purchased from Merck (Germany) or Riedel-de Haën (Germany). Aqueous 2,4 DCP solutions were prepared with distilled water, whereas for mobile phases, stock and standard solutions doubly distilled water with a conductivity of $0.055 \mu\text{S cm}^{-1}$ was used (Arium 611UV, Sartorius AG, Germany).

2.2. Photoreactor and UV-C light source

All experiments were conducted in a 3250 mL capacity, cylindrical stainless steel photoreactor (length: 84.5 cm; diameter: 8.0 cm). The UV-C light source was a 40 W low pressure mercury vapour lamp being located in a quartz sleeve in the centre of the photoreactor. The batch-operated photoreactor was mixed by means of a peristaltic pump at a flow rate of 25 mL min^{-1} . The photon flux at 253.7 nm was determined by means of H_2O_2 actinometry [19] as $0.066 \mu\text{einstein cm}^{-2} \text{ s}^{-1}$.

2.3. Experimental procedures

Aqueous 2,4 DCP solutions were prepared at a concentration of 0.15 mM except for oxidation product and acute toxicity analyses where a concentration of 0.46 mM 2,4 DCP was selected. At the beginning of all experiments, the initial pH of the 2,4 DCP solutions was adjusted to pre-determined values by using H_2SO_4 and NaOH solutions at varying concentrations. Thus, no attempt was made to control pH throughout the experiments. H_2O_2 (35%, w/w) was added to pH-adjusted 2,4 DCP solutions at a concentration range of 2 mM to 40 mM H_2O_2 . Thereafter, the photoreactor was filled with the reaction solution by means of a peristaltic pump. Prior to Fenton and photo-Fenton experiments, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ from a 10%, w/v (0.36 M) stock solution was also added once the photoreactor was completely filled with the reaction solution.

2.4. Analytical procedures

30 mL of untreated or photochemically treated sample aliquots were withdrawn from the reactor at pre-determined time intervals from the sampling valve. The Fenton and photo-Fenton reactions were quenched with the addition of a few drops of 10 N NaOH solution to increase the pH to above 11 and in this way to remove iron catalyst in the form of $\text{Fe}(\text{OH})_3$ from the solution by filtering the sample through $0.45 \mu\text{m}$ PVDF syringes (Millipore Corp., USA).

2,4 DCP and its aromatic (phenol, catechol, HQ, BQ, and CHQ) and aliphatic oxidation products (FoOH, AcOH, and oxalic acid (OxOH)) were monitored by HPLC (Agilent 1100 Series, Agilent Technologies, USA) equipped with a diode array detector (DAD). Operating conditions of the HPLC for the selected target compounds are presented in Table 1. 2,4 DCP analysis was performed according to [20], while the analysis of phenol, catechol, HQ, and BQ was largely based on the method described by [21]. CHQ was separately analyzed applying a method proposed by [22]. HPLC analysis of carboxylic

Table 1
HPLC methods for target compounds.

| Compound | Column | Mobile phase | Flow rate (mL min ⁻¹) | Column temperature (°C) | Injection volume (μL) | Detection wavelength (nm) | |
|----------|---|--|-----------------------------------|-------------------------|-----------------------|---------------------------|-----|
| 2,4 DCP | Novapack C18 (150 mm × 3.9 mm, Waters, USA) | Methanol:0.1% H ₃ PO ₄ in water (65:35, v/v) Water:methanol:AcOH (79.2:19.8:1, v/v/v) | 1 | 20 | 100 | 280 | |
| Phenol | | | 0.8 | 40 | 40 | 270 | |
| Catechol | | | | | | | 276 |
| HQ | | | | | | | 290 |
| BQ | | | | | | | 245 |
| CHQ | | | 1 | 20 | 50 | 283 | |
| FoOH | Acclaim OA (250 mm × 4 mm, Dionex, USA) | Methanol:AcOH:water (60:2.5:37.5, v/v/v) 100 mM Na ₂ SO ₄ adjusted to pH 2.65 with methanesulfonic acid | 0.6 | 30 | 50 | 210 | |
| AcOH | | | | | | | |
| OxOH | | | | | | | |

acids was performed according to the instructions of the manufacturer of Acclaim OA organic acid column. Analyte concentrations in the samples were determined according to the calculation of peak areas by external calibration. The detection limits were determined as the signal-to-noise ratio (S/N) of 3 and individually found as 0.42, 0.67, 1.3, 0.48, 1.8, 0.51, 54 and 23 μM for 2,4 DCP, phenol, catechol, HQ, BQ, CHQ, FoOH and AcOH, respectively.

GC–MS analysis was also performed to identify oxidation products of 2,4 DCP and to monitor their evolution during H₂O₂/UV-C, Fenton, and photo-Fenton treatment. Prior to GC–MS analysis, oxidation products were extracted from samples being previously acidified to pH 2 with 20% H₂SO₄ solution using SPE according to [23] as well as LLE. Samples were extracted three times with 5 mL dichloromethane and the combined extract was directly injected into GC–MS. The oxidation products were analyzed via GC–MS (The Agilent 5975C Series GC/MSD, Agilent Technologies, USA) according to [20]. The chromatographic separation was achieved by means of an HP-5MS (5% phenyl methyl silox) 30 m × 250 μm × 0.25 μm film capillary column. He was used as the carrier gas at a constant flow rate of 1.0 mL min⁻¹. The oven temperature was programmed to start under isothermal conditions at 80 °C for 6 min, then rise to 180 at a rate of 4 °C min⁻¹ and remain constant at 180 °C for 10 min. The injection port and ion source temperatures were held at 280 and 230 °C, respectively. The MSD scan range was 50–700 amu. Oxidation products were identified comparing the obtained spectra with those provided by the ChemStation (Agilent Technologies, USA) mass spectral library and their evolution was determined by tracking the changes in peak areas of the individual oxidation products with respect to treatment time.

Chloride release was monitored on a Dionex ICS-1500 Ion Chromatography (IC) unit (Dionex Corporation, USA) equipped with a conductivity detector, a DionexlonPac AG14A (4 × 50 mm) guard column and a DionexlonPac AS14A (4 × 250 mm) analytical column. The IC was operated in auto-suppression mode with 1 mM NaHCO₃/8 mM Na₂CO₃ eluent at a flow rate of 1 mL min⁻¹.

The TOC of the samples was monitored on a ShimadzuV_{PCN} carbon analyzer (Japan) equipped with an autosampler. An Orion (USA) 720+ model pH-meter was used for pH measurements. Residual H₂O₂ in the treated samples was traced by employing the molybdate-catalyzed iodometric method [24].

Acute toxicity changes during the application of UV-C only, H₂O₂/UV-C, Fenton and photo-Fenton treatment processes were measured by using a commercial assay kit marketed as BioTox™ (Finland). The reagent was a lyophilized preparation of the marine photobacterium *V. fischeri* (NRRL B-11177). The assay is based on the decrease in light emission of *V. fischeri* resulting from its exposure to the toxicant. Prior to the assay the pH of all samples was adjusted to 7.0 ± 0.2 with NaOH or H₂SO₄ solutions. NaCl was added to obtain a final chloride concentration of 2%, w/v in the samples. Prior to analysis, the sample solutions were oxygenated by stirring and solid particles were removed via 0.45 μm filtration. In

order to eliminate its positive effect on the toxicity test results, any unreacted H₂O₂ remaining in the samples was catalytically decomposed with catalase made from *Micrococcus lysodeikticus* (200181 AU mL⁻¹, Fluka, Sweden). After mixing 0.5 mL of raw and treated 2,4 DCP solutions with 0.5 mL luminescent bacterial suspension (dilution ratio = 50%, v/v), the relative inhibition of light emitted by the photobacteria was measured after 15 min contact time at 15 °C and the percent relative inhibition (INH, %) was calculated relative to a control by the help of Eq. (1):

$$\text{INH\%} = 100 - 100 \times \left(\frac{IT_{15}}{KF} \right) T_0 \quad (1)$$

where IT₀ and IT₁₅ are the luminescence intensities (relative luminescence units; RLU) of the sample at the beginning and after 15 min contact time, respectively, and KF is the correction factor (dimensionless) for the control:

$$KF = \frac{IC_{15}}{IC_0} \quad (2)$$

where IC₀ and IC₁₅ are the luminescence intensities (RLU) of the control after 0 min and 15 min contact time, respectively. The effective concentration EC₅₀ (in mM) of aqueous 2,4 DCP was also determined.

3. Results and discussion

3.1. H₂O₂/UV-C, Fenton and photo-Fenton baseline experiments

In the first part of the study, H₂O₂/UV-C, Fenton and photo-Fenton processes were compared in terms of 2,4 DCP and TOC removal as well as H₂O₂ consumption rates. In addition, several control experiments were conducted to verify the combined effects of oxidant, catalyst and UV-C light. It could be demonstrated that the reaction of 2,4 DCP with 40 mM H₂O₂ at pH 7 in the absence of UV-C light irradiation resulted in only 15% removal of 2,4 DCP in 90 min, whereas no mineralization occurred under these experimental conditions (data not shown). Although 91% 2,4 DCP removal could be achieved via UV-C photolysis in 90 min (Fig. 1a), mineralization efficiency at the end of treatment was only 16% (Fig. 1b), indicating that the use of UV-C treatment alone was not sufficient in the effective degradation of 2,4 DCP intermediate photolysis products. The degradation of 2,4 DCP with H₂O₂/UV-C, Fenton, and photo-Fenton processes followed pseudo-first-order kinetics ($R^2 \geq 0.91$) with respect to parent compound and TOC concentrations. The experimental results revealed that the parent pollutant was most rapidly degraded by the photo-Fenton process ($k_{2,4 \text{ DCP}} = 0.65 \text{ min}^{-1}$) followed by H₂O₂/UV-C ($k_{2,4 \text{ DCP}} = 0.48 \text{ min}^{-1}$) and Fenton ($k_{2,4 \text{ DCP}} = 0.10 \text{ min}^{-1}$) processes (Fig. 1a). During the application of photo-Fenton treatment, 2,4 DCP disappeared to non-detectable levels after 8 min treatment, while it took up to 40 min with the Fenton's reagent. The enhancement of

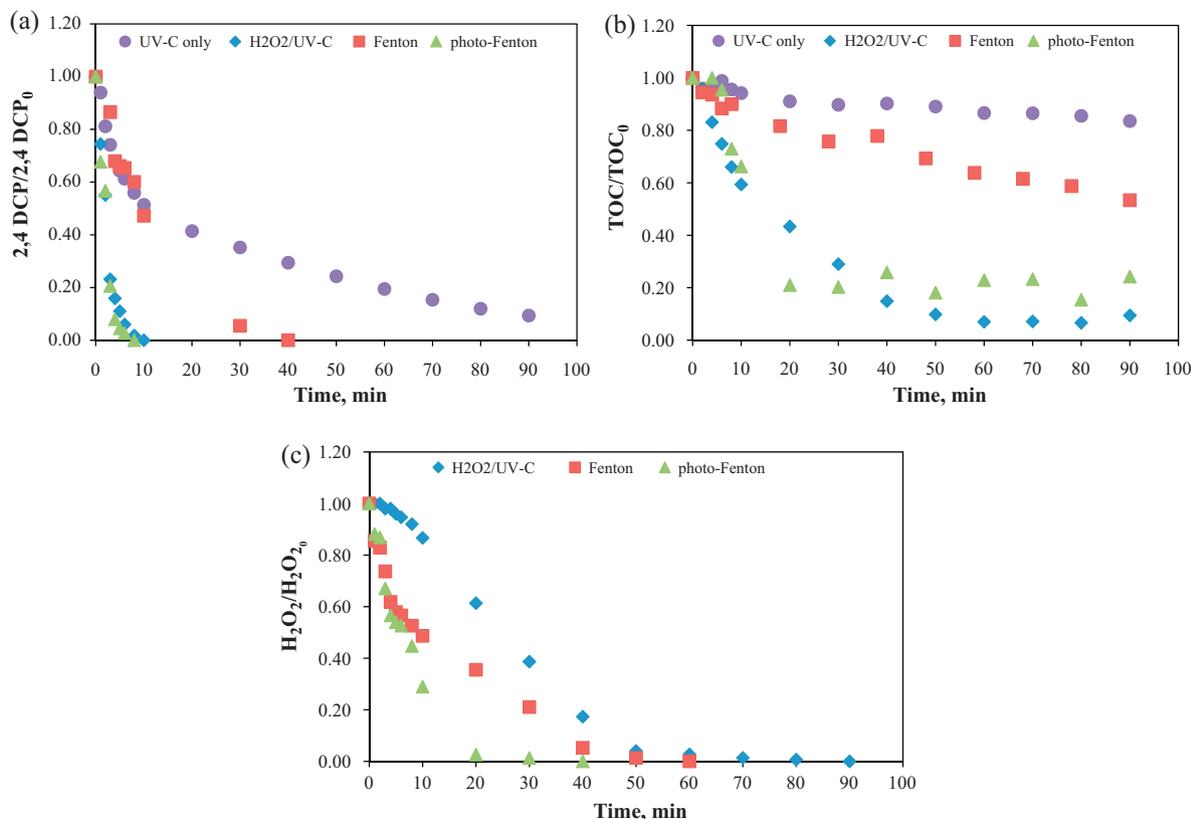


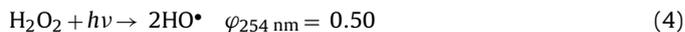
Fig. 1. Comparison of the decay of 2,4 DCP (a), TOC (b), and H₂O₂ (c) for UV-C only, H₂O₂/UV-C, Fenton and photo-Fenton processes. UV-C only: [2,4 DCP]₀ = 0.15 mM, pH₀ = 7; H₂O₂/UV-C: [2,4 DCP]₀ = 0.15 mM, [H₂O₂]₀ = 10 mM, pH₀ = 7; Fenton and photo-Fenton: [2,4 DCP]₀ = 0.15 mM, [H₂O₂]₀ = 10 mM, [Fe²⁺]₀ = 0.2 mM, pH₀ = 3.

2,4 DCP removal rate in the photo-Fenton process was most probably caused by the generation of additional HO• via photoreduction of Fe³⁺ to Fe²⁺ according to reaction (3) [25];

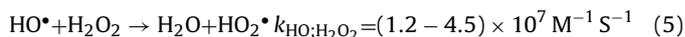


where $\varphi_{254\text{nm}}$ is the quantum yield of photochemical Fe³⁺ reduction at 254 nm. Despite complete degradation of 2,4 DCP during application of the dark Fenton's process, 53% of the initial TOC remained in the reaction solution after 90 min of treatment (Fig. 1b), indicating that Fenton's reagent was not effective in 2,4 DCP mineralization; a major limitation of this process as also observed in relevant studies [26,27]. Although the TOC removal obtained during the first 20 min of the photo-Fenton process was higher as compared with the TOC removal achieved by applying H₂O₂/UV-C oxidation, it practically stopped after this treatment time, an outcome most probably caused by the complete consumption of H₂O₂ during the first 20 min of Fenton's reaction. This observation is strongly supported by the experimental findings given in Fig. 1b and c, which clearly indicate that the residual H₂O₂ concentration is the major limiting factor for all the three photochemical treatment processes under study. The obtained findings also revealed that UV-C photoreduction of Fe³⁺ was not sufficient to continue significant HO• generation after complete exhaustion of H₂O₂ in the photo-Fenton process. The inefficiency of the Fe³⁺/UV-C process combination for the mineralization of 2,4 DCP was confirmed by a control experiment conducted with 0.2 mM of Fe³⁺ and UV-C light irradiation. In this experiment TOC removal obtained after 70 min was insignificant (only 4%; data not shown). Considering the above experimental findings as a whole, the application of H₂O₂/UV-C and photo-Fenton treatment processes resulted in higher removals both in terms of 2,4 DCP and TOC.

Prior to oxidation product and toxicity assessment, preliminary baseline experiments were also performed to determine the most appropriate reaction conditions for effective treatment of aqueous 2,4 DCP. Fig. 2 depicts the effect of initial H₂O₂ and Fe²⁺ concentrations on the pseudo-first-order 2,4 DCP and TOC removal rate constants ($k_{2,4\text{ DCP}}$ and k_{TOC} , respectively; in min⁻¹) for the H₂O₂/UV-C and photo-Fenton treatment processes. From Fig. 2a it can be seen that H₂O₂ addition greatly enhanced the oxidation and mineralization rates of 2,4 DCP as compared to UV-C photolysis alone ($k_{2,4\text{ DCP}}$ and $k_{\text{TOC}} = 0.08$ and 0.004 min⁻¹, respectively). This profound increase in the pseudo-first-order rate constants is mainly caused by the increasing concentration of HO• in the reaction solution being generated by UV-C photolysis of H₂O₂ [28];



From the experimental results it became evident that $k_{2,4\text{ DCP}}$ and k_{TOC} values both increased with increasing H₂O₂ concentration and peaked at 15 mM ($k_{2,4\text{ DCP}} = 0.52$ min⁻¹) and 5 mM of H₂O₂ ($k_{\text{TOC}} = 0.060$ min⁻¹), respectively, after which H₂O₂ started to inhibit the degradation and mineralization of 2,4 DCP. This is a well known phenomenon from the scientific literature [14,29] and known as HO• scavenging by H₂O₂ beyond a certain case-specific concentration according to the reaction shown below in Eq. (5);



The reduction potential of HO₂• is much lower (1.0 V; [30]) than that of HO• (2.8 V) and this is most probably the reason for the observed decrease in degradation and mineralization rates.

Considering the effect of initial Fe²⁺ concentration on 2,4 DCP and TOC removal rates in the photo-Fenton process (Fig. 2b) indicated that k_{TOC} peaked at 0.10 min⁻¹ at an initial Fe²⁺ concentration of 0.2 mM. A further increase in Fe²⁺ concentration decreased TOC

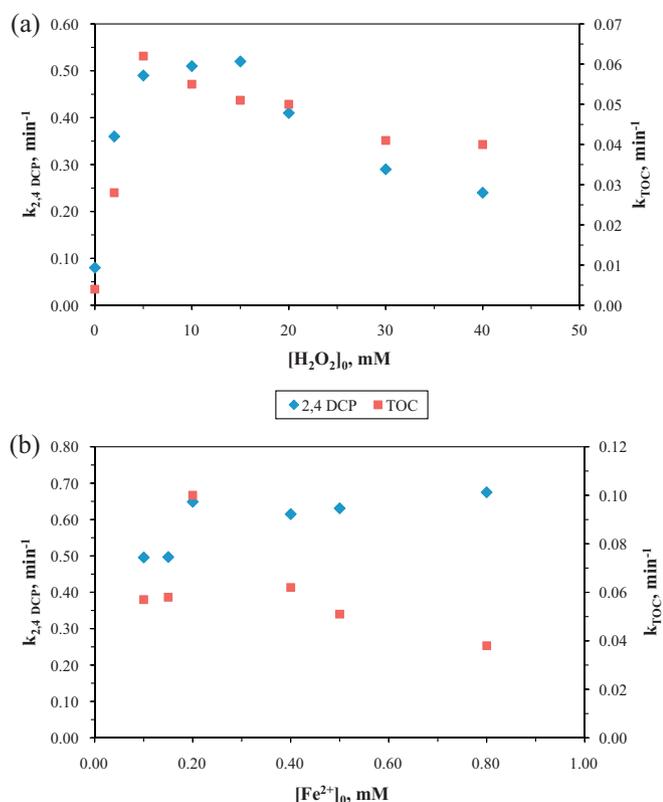
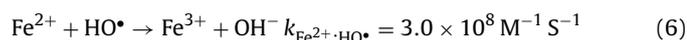


Fig. 2. Pseudo-first-order rate constants of 2,4 DCP and TOC removals as a function of initial H_2O_2 concentration ($[2,4 \text{ DCP}]_0 = 0.15 \text{ mM}$, $\text{pH}_0 = 7$) for $\text{H}_2\text{O}_2/\text{UV-C}$ oxidation (a) and initial Fe^{2+} concentration ($[2,4 \text{ DCP}]_0 = 0.15 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$, $\text{pH}_0 = 3$) in photo-Fenton reaction (b).

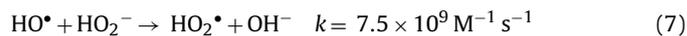
removal rates due to the fact that HO^\bullet -scavenging reactions became more and more dominant at excessive Fe^{2+} concentrations [31] according to reaction (6);



However, the effect of initial Fe^{2+} concentration on 2,4 DCP removal was less significant than its effect on TOC removal. Experimental results demonstrated that 2,4 DCP degradation kinetics increased until an initial Fe^{2+} concentration of 0.2 mM was applied ($k_{2,4 \text{ DCP}} = 0.65 \text{ min}^{-1}$). After this concentration no significant change was observed in the reaction rate constants. As a consequence 0.2 mM Fe^{2+} was chosen for the forthcoming $\text{H}_2\text{O}_2/\text{UV-C}$, Fenton, and photo-Fenton treatment processes.

A series of $\text{H}_2\text{O}_2/\text{UV-C}$ and photo-Fenton experiments was also performed to assess the effect of pH on degradation and mineralization of aqueous 2,4 DCP. $\text{H}_2\text{O}_2/\text{UV-C}$ oxidation of 2,4 DCP was accompanied by a rapid pH drop within the first 10 min of reaction followed by a slight increase in pH due to the formation of carboxylic acids and their subsequent mineralization to CO_2 , respectively [6]. During photochemical treatment, the reaction pH which was initially adjusted to 4.0, 7.0 and 11.0 decreased to 3.3, 3.8, and 5.8, respectively, while practically no pH change was observed when the reaction was initiated at pH 12. It could be demonstrated that the pseudo-first-order rate constants only marginally changed in the pH range of 4.0–7.0 ($k_{2,4 \text{ DCP}} = 0.51 \text{ min}^{-1}$ for both initial pH's; $k_{\text{TOC}} = 0.050 \text{ min}^{-1}$ for pH 4.0 and 0.045 min^{-1} for and initial pH of 7.0), but drastically decreased with a further increase, reaching minimum values at pH 12.0 ($k_{2,4 \text{ DCP}}$ and $k_{\text{TOC}} = 0.19$ and 0.011 min^{-1} , respectively) when approaching the pK_a of H_2O_2 ($=11.70$; [32]). Removal rates decreasing at elevated pH's during photochemical treatment with the $\text{H}_2\text{O}_2/\text{UV-C}$ process

it an expected consequence of H_2O_2 dissociation to its conjugate base HO_2^- becoming more intense at pH values > 10 . HO_2^- reacts two orders of magnitude faster with HO^\bullet [33] than H_2O_2 ;



The decrease in the parent pollutant and TOC elimination rates during $\text{H}_2\text{O}_2/\text{UV}$ treatment under alkaline pH conditions has already been observed by former studies [28,34].

Reaction pH is one of the most important process parameters in the Fenton and photo-Fenton processes, since iron speciation which in turn determines the UV absorption, complexation, and dissolution properties of the catalyst, is strongly affected by pH [35]. The most suitable pH range for the removal of organic pollutants with the Fenton and photo-Fenton processes has already been established as 2–5 [5,36]. However, in the present study 2,4 DCP removal rates were not affected at all by changing the initial reaction pH from 3 to 4 and 5 ($k_{2,4 \text{ DCP}} = 0.65 \text{ min}^{-1}$ at all studied pH's). It is thought that the rapid drop in pH down to values (pH = 2.5–2.8) at which Fe^{2+} efficiently catalyzes the photo-Fenton reaction likely compensated the difference in the initially adjusted pH values. On the other hand, photo-Fenton treatment of 2,4 DCP initiated at pH 3 resulted in an appreciably higher mineralization rate ($k_{\text{TOC}} = 0.10 \text{ min}^{-1}$) as compared to experiments that were started at pH 4 and 5 ($k_{\text{TOC}} = 0.058$ and 0.076 min^{-1} , respectively). As a whole, it could be postulated that overall treatment results obtained for 2,4 DCP degradation and mineralization were still encouragingly for photo-Fenton treatment initiated at pH 5. The experimental results delineated that relatively high pH values could be effectively used for the oxidation of 2,4 DCP by the photo-Fenton process. This issue has some practical importance since decreasing pH causes inevitable consumption of high amounts of acids and creates a major obstacle for the real-scale application of the photo-Fenton treatment process.

3.2. Chloride release

It has already been reported in the scientific literature that reactions involving $\text{H}_2\text{O}_2/\text{UV}$, Fenton and photo-Fenton oxidation of CPs are associated with the release of organically bound Cl atoms in the form of free Cl^- ions [14,37]. Fig. 3 displays Cl^- release versus treatment time profiles during $\text{H}_2\text{O}_2/\text{UV}$, Fenton and photo-Fenton treatment of aqueous 2,4 DCP. As is evident in Fig. 3, the $\text{H}_2\text{O}_2/\text{UV-C}$ process ultimately resulted in a slightly lower Cl^- release than the photo-Fenton process. For both photochemical oxidation processes, dechlorination was practically complete within 20 min such that Cl^- concentrations reached asymptotic values beyond this treatment time. Obtained findings indicated that

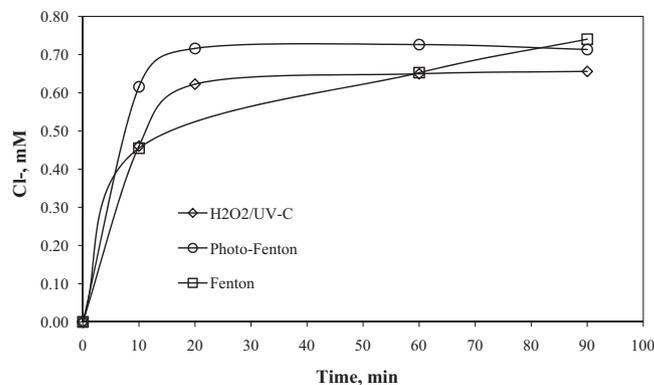


Fig. 3. Chloride release during $\text{H}_2\text{O}_2/\text{UV-C}$, Fenton, and photo-Fenton treatment of 2,4 DCP. $[2,4 \text{ DCP}]_0 = 0.46 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$, $[\text{Fe}^{2+}]_0 = 0.2 \text{ mM}$, $\text{pH}_0 = 7$ in $\text{H}_2\text{O}_2/\text{UV-C}$ and 3 in Fenton and photo-Fenton processes.

2,4 DCP degradation and dechlorination proceeded simultaneously, since 0.46 mM aqueous 2,4 DCP was completely removed after 20 min and 30 min for the photo-Fenton and $\text{H}_2\text{O}_2/\text{UV-C}$ treatment processes, respectively. These results also revealed that dechlorination is one of the initial stages of photochemical 2,4 DCP oxidation as has also been evidenced in former related work [10]. The dechlorination trend observed during the Fenton process was somewhat different; it proceeded at a relatively slow rate during the first 10 min of the reaction, but continued until the end of the treatment process, reaching levels similar to those obtained for the photo-Fenton experiment after around 80 min. The parallel trend between 2,4 DCP removal and Cl^- release was also evident for the Fenton's reaction. During UV-C photolysis of 2,4 DCP chloride release was also observed (data not shown) but at a relatively slow rate as compared to the studied AOPs. At the end of treatment, 0.74 mM, 0.74 mM, 0.66 mM and 0.37 mM Cl^- were obtained for photo-Fenton, Fenton, $\text{H}_2\text{O}_2/\text{UV-C}$ and UV-C only processes, respectively.

3.3. Evolution of oxidation products

3.3.1. Aromatics

Generally speaking, the following route has been reported in the scientific literature for the degradation of CPs by AOPs; C–Cl bond scission and subsequent HO^\bullet attack at ortho- and para positions corresponding to the formation of dechlorinated and hydroxylated oxidation products [22,38,39]. Further oxidation has been documented to result in the formation of quinones [33,39]. Based on these literature data, the potential formation of five selected aromatic compounds, namely (1) phenol, (2) catechol, (3) HQ, (4) BQ and (5) CHQ was investigated and compared during 2,4 DCP oxidation via $\text{H}_2\text{O}_2/\text{UV-C}$, Fenton and photo-Fenton processes.

For experiments where oxidation product identification was targeted, an initial 2,4 DCP concentration of 0.46 mM was selected instead of 0.15 mM 2,4 DCP that was chosen for the preliminary baseline (treatability) runs in order to improve the analytical conditions for the detection of intermediates. The 2,4 DCP solution exhibited colour changes during $\text{H}_2\text{O}_2/\text{UV-C}$ treatment, from colourless to a light brownish colour after 10 min, fading to yellow and ultimately to colourless after 20 min treatment. The yellow colour generated during the oxidation of phenol is believed to be caused by BQ, while the formation of HQ usually does not lead to coloured reaction solutions [40]. Nevertheless, neither BQ nor CHQ could be detected during application of the selected AOPs. Phenol and catechol could only be measured in samples treated with the $\text{H}_2\text{O}_2/\text{UV-C}$ process, reaching highest concentrations of 7.5 μM and 3.2 μM , respectively, after 6–8 min treatment and disappeared after approximately 10 min. HQ was found to be the only common aromatic oxidation product generated in all the three AOPs studied. For comparative purposes, HQ evolution was demonstrated on the same graph for $\text{H}_2\text{O}_2/\text{UV-C}$, Fenton and photo-Fenton processes (Fig. 4). As is obvious from Fig. 4, the highest HQ formation being 14 μM was found during $\text{H}_2\text{O}_2/\text{UV-C}$ treatment of 2,4 DCP, while the lowest HQ generation was observed during the photo-Fenton process (4.5 μM). During the $\text{H}_2\text{O}_2/\text{UV-C}$ process, HQ concentration increased very rapidly during the first 5 min of the reaction, peaked after about 10 min and completely disappeared after 30 min treatment. On the other hand, dark Fenton's reaction of 2,4 DCP resulted in a maximum HQ formation of 6.7 μM after 20 min treatment. In conclusion, obtained experimental findings delineated that HQ did not accumulate in the reaction solution and during all studied AOPs HQ could be further degraded, although $\text{H}_2\text{O}_2/\text{UV-C}$ and Fenton processes required longer treatment times. Considering the appreciably low EC_{50} value of HQ reported in the scientific literature (0.041 mg L^{-1} corresponding to 0.37 μM ; [41]) and its slow reaction rate, the oxidation of 2,4 DCP via $\text{H}_2\text{O}_2/\text{UV-C}$ treatment

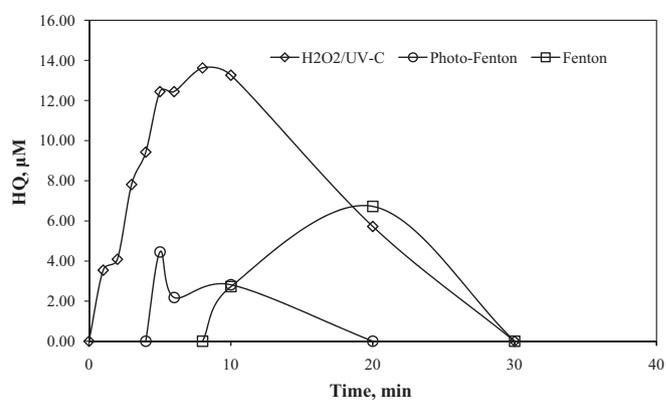


Fig. 4. Evolution of HQ during $\text{H}_2\text{O}_2/\text{UV-C}$, Fenton, and photo-Fenton treatment of 2,4 DCP. $[\text{2,4 DCP}]_0 = 0.46 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$, $[\text{Fe}^{2+}]_0 = 0.2 \text{ mM}$, $\text{pH}_0 = 7$ for $\text{H}_2\text{O}_2/\text{UV-C}$ and 3 for Fenton and photo-Fenton processes.

process appeared to be ecotoxicologically less safe than the other two AOPs.

GC–MS analyses were also performed on samples being subjected to $\text{H}_2\text{O}_2/\text{UV-C}$, Fenton and photo-Fenton treatment. According to the obtained GC–MS data presented in Fig. 5, the only identified oxidation product of Fenton and photo-Fenton oxidation was CHQ, which was detected at the initial treatment stages (10 min) and disappeared after 30 min treatment. Considering these findings and those shown in Fig. 4, one may suggest that the disappearance of CHQ during Fenton and photo-Fenton processes proceeds via a dechlorination pathway, speculatively transforming CHC into HQ. On the other hand, several degradation products, namely 3,5-dichloro-2-hydroxybenzaldehyde, 4-CP, CHQ, phenol and 2,5-dichlorohydroquinone could be identified during $\text{H}_2\text{O}_2/\text{UV-C}$ oxi-

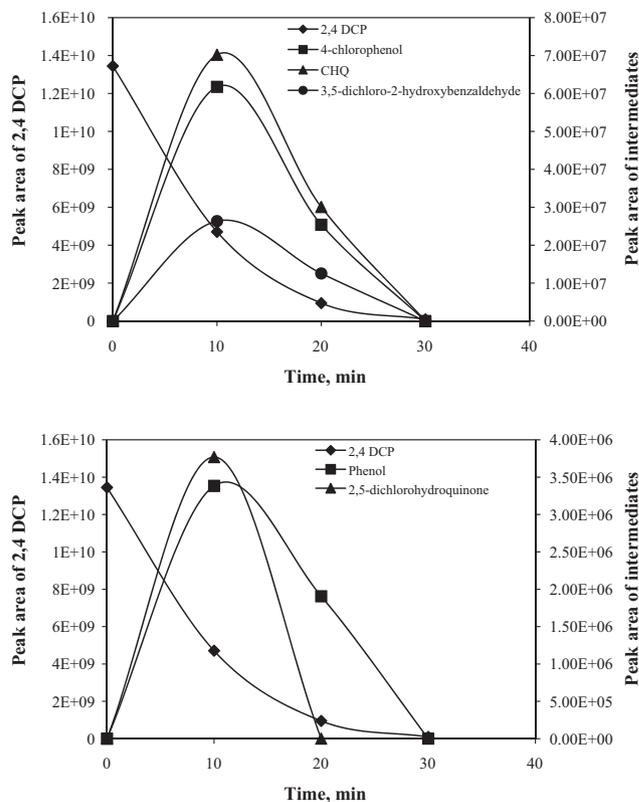


Fig. 5. Evolution of oxidation products of 2,4 DCP identified by GC–MS analysis during $\text{H}_2\text{O}_2/\text{UV-C}$ treatment of 2,4 DCP. $[\text{2,4 DCP}]_0 = 0.46 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$, $\text{pH}_0 = 7$.

dation of 2,4 DCP (Fig. 5). In fact, CHO• evolution has been suggested during TiO₂-mediated heterogeneous photocatalytic treatment of phenol, playing a role in the formation of 2-hydroxybenzaldehyde as a consequence of phenol attack by CHO• at the *ortho* position [42]. The same mechanism could also be responsible for the transformation of 2,4 DCP into 3,5-dichloro-2-hydroxybenzaldehyde during H₂O₂/UV-C treatment in the present study. The identification of 4-CP, CHQ, phenol, and 2,5-dichlorohydroquinone during 2,4 DCP oxidation via H₂O₂/UV-C process supports a treatment mechanism involving HO• addition and subsequent dechlorination. From Fig. 5 it is evident that all 2,4 DCP oxidation products being identified via GC-MS reached their maximum concentration after 10 min and disappeared to non-detectable levels after 30 min treatment, except 2,5-dichlorohydroquinone which was completely degraded after 20 min treatment.

3.3.2. Carboxylic acids

Aliphatic carboxylic acids have generally been reported as the final organic degradation products prior to mineralization of CPs during the application of AOPs [43,44]. The most common carboxylic acids generated in H₂O₂/UV-C, Fenton and photo-Fenton oxidation of CPs have been identified as FoOH, AcOH and OxOH in former related work [45,46]. For this reason, the analysis of FoOH, AcOH, and OxOH was also performed in 2,4 DCP samples being subjected to H₂O₂/UV-C, Fenton and photo-Fenton processes. According to the analytical results, OxOH could not be detected in the treated samples, although the anionic form of OxOH was identified as an oxidation product of CPs and its degradation intermediate HQ, particularly in iron-based advanced oxidation processes [47]. Evolution of FoOH and AcOH during treatment of 2,4 DCP via H₂O₂/UV-C, Fenton and photo-Fenton processes is displayed in Fig. 6. According to the obtained experimental results, FoOH was found to be a common aliphatic oxidation product for all studied processes, whereas AcOH was not detected in 2,4 DCP solutions treated with the H₂O₂/UV-C process. The AcOH evolution pattern was different for Fenton and photo-Fenton treatment of 2,4 DCP; more AcOH was generated during the Fenton process (0.68 mM) than in the photo-Fenton process (0.42 mM). During application of Fenton treatment, AcOH formation started immediately and its concentration continued to increase up to 40 min treatment at a slower rate than in the photo-Fenton process. AcOH disappeared to non-detectable levels at the end of the treatment. Unlike AcOH, FoOH remained almost unchanged throughout the Fenton's reaction. These findings imply that FoOH could not be further oxidized via dark Fenton process and the introduction of UV-C light was necessary to enable its further oxidation. Among the studied treatment processes, the highest FoOH formation (0.43 mM) was observed during H₂O₂/UV-C oxidation of 2,4 DCP and its degradation was complete after 40 min treatment, which was twice the time required for FoOH removal with the Photo-Fenton process.

3.4. Changes in acute toxicity during H₂O₂/UV-C, Fenton, and photo-Fenton treatment of 2,4 DCP

Table 2 shows the changes in acute toxicity towards *V. fischeri* photo bacteria in terms of percent relative inhibition of the luminescence intensities (INH%) during H₂O₂/UV-C, Fenton and photo-Fenton treatment of 0.46 mM 2,4 DCP for different treatment times. Acute toxicity changes during the application of UV-C only were also included in this table. As can be seen from Table 2, during UV-C photolysis, the acute toxicity of 2,4 DCP originally being 82% first diminished, attaining a value somewhat smaller (78%) than that of untreated 2,4 DCP solution. Thereafter, the inhibitory effect slightly re-increased, reaching 84% after 40 min UV photolysis. The observed trend in the acute toxicity changes in the early stages of UV-C treatment may be attributed to the formation and

Table 2

Acute toxicity results (INH% values) and 2,4 DCP removals obtained for 2,4 DCP treatment with UV-C only, H₂O₂/UV-C, Fenton and photo-Fenton processes.

| Treatment type and conditions | INH% | 2,4 DCP removal (%) |
|--|------|---------------------|
| Original 2,4 DCP solution (0.46 mM) | 82 | – |
| UV-C only | | |
| pH ₀ = 7, 30 min | 78 | 46 |
| pH ₀ = 7, 40 min | 84 | 51 |
| pH ₀ = 7, 60 min | 74 | 61 |
| pH ₀ = 7, 90 min | 34 | 72 |
| H ₂ O ₂ /UV-C ^a | | |
| pH ₀ = 7, 3 min | 71 | 51 |
| pH ₀ = 7, 10 min | 27 | 85 |
| pH ₀ = 7, 20 min | 0 | 98 |
| pH ₀ = 7, 30 min | 6 | 100 |
| Fenton ^{a,b} | | |
| pH ₀ = 3, 10 min | 76 | 66 |
| pH ₀ = 3, 30 min | 65 | 69 |
| pH ₀ = 3, 60 min | 48 | 95 |
| pH ₀ = 3, 90 min | 48 | 100 |
| photo-Fenton ^{a,b} | | |
| pH ₀ = 3, 3 min | 47 | 49 |
| pH ₀ = 3, 10 min | 17 | 93 |
| pH ₀ = 3, 20 min | 0 | 100 |
| pH ₀ = 3, 30 min | 0 | 100 |

^a [H₂O₂]₀ = 10 mM.

^b [Fe²⁺]₀ = 0.2 mM.

accumulation of chlorinated oxidation intermediates being more toxic than the parent compound. These findings are also supported by the dechlorination data obtained for UV-C only. Krebel et al. [10] also concluded that the degradation of CPs via UV photolysis resulted in the generation of chlorinated aromatic and aliphatic degradation products being more toxic than the studied CPs. However, in the later stages of photolysis (>40 min) the acute toxicity of the reaction solution started to decrease gradually and in parallel to 2,4 DCP removal most possibly due to the formation of less toxic oxidation intermediates. It should also be emphasized here that poor TOC removals were obtained throughout 90 min UV-C photolysis, resulting in an overall TOC removal of 10% accompanied with 72% 2,4 DCP degradation and 34% relative inhibition of photoluminescent bacteria.

As can be followed from Table 2, during Fenton's treatment of 2,4 DCP, the original toxicity decreased to 48% after 60 min and remained stagnant thereafter. The corresponding 2,4 DCP and TOC removals were obtained as 95% and 28%, respectively. Taking into account the experimental data presented in Figs. 4 and 6 and Table 2, the Fenton's reaction was less efficient than the H₂O₂/UV-C and photo-Fenton treatment processes. In other words, the remaining acute toxicity of the reaction solution was relatively high although 2,4 DCP was completely degraded and dechlorination rates were ultimately as high as those observed for the other two studied AOPs (Fig. 3). This was most probably attributable to the formation and accumulation of non-chlorinated ring opening products including carboxylic acids as was evidenced in former related work [48,49].

The acute toxicity evolutions showed similar trends for the treatment of 2,4 DCP with H₂O₂/UV-C and photo-Fenton processes. A closer inspection of Fig. 3 and Table 2 revealed that the sharp release of chloride at the beginning of H₂O₂/UV-C and photo-Fenton processes was accompanied with an abrupt detoxification pattern, which is in line with the literature data postulating that the dechlorination of phenolic compounds is at least partially responsible for biodegradability enhancement and toxicity reduction. From the results presented in Table 2 it may be inferred that relatively less toxic oxidation products were formed during H₂O₂/UV-C and photo-Fenton treatment of 2,4 DCP under the investigated experimental conditions. The inhibition rates (71% for H₂O₂/UV-C; 47% for photo-Fenton process) obtained after 3 min 2,4 DCP treatment

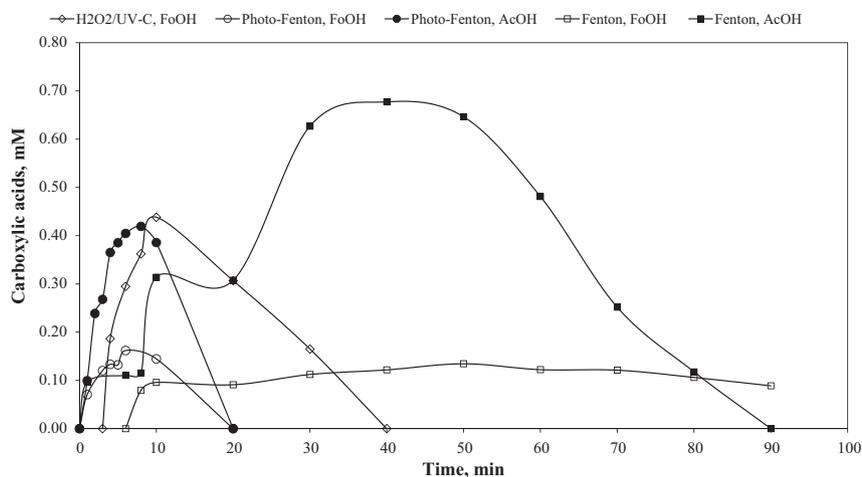


Fig. 6. Evolution of FoOH and AcOH during H₂O₂/UV-C, Fenton, and photo-Fenton treatment of 2,4 DCP. [2,4 DCP]₀ = 0.46 mM, [H₂O₂]₀ = 10 mM, [Fe²⁺]₀ = 0.2 mM, pH₀ = 7 for H₂O₂/UV-C and pH₀ = 3 for Fenton and photo-Fenton processes.

as well as the corresponding treatment efficiencies indicated that at the early stages of photochemical oxidation, the concentration and speciation of the formed oxidation intermediates (most probably being chlorinated aromatics) were different for H₂O₂/UV-C and photo-Fenton processes. In the same manner, TOC removals were found to be completely different for these processes at the same treatment time (0% for H₂O₂/UV-C; 24% for photo-Fenton process after 3 min oxidation). In the case of H₂O₂/UV-C treatment, the acute toxicity started to re-increase, suggesting that the inhibitory effects of the formed oxidation products became pronounced after 20 min treatment. Moreover, a comparison of data presented in Figs. 4–6 and Table 2 indicated that the increasing trend in toxicity could not be correlated to the formation of HQ, FoOH, AcOH or other oxidation products during the course of 2,4 DCP degradation, at least not at the concentrations being present in the reaction solution. Speculatively, some unidentified oxidation products formed towards the end of the H₂O₂/UV-C processes may account for the observed re-increase in toxicity. Similarly, Santiago et al. [50] reported a rapid decrease in toxicity parallel to fenofibric acid degradation by H₂O₂/UV-C. However, a degree of toxicity reappeared after extension of irradiation time, probably as a consequence of the formation of ring-opening products. Considering the photo-Fenton process, detoxification was more rapid and exhibited a parallel trend to 2,4 DCP degradation, dechlorination and mineralization rates. This observation supported by the general statement made in most related work for the superiority of photo-Fenton treatment [46].

4. Conclusions

The present experimental study aimed at investigating the possible relationships between oxidation products and acute toxicity towards *V. fischeri* during the oxidative degradation of 2,4 DCP by H₂O₂/UV-C, Fenton and photo-Fenton advanced oxidation processes. The following conclusions could be drawn from the present study:

- Rapid degradation of 2,4 DCP accompanied with high TOC removals was observed for H₂O₂/UV-C and photo-Fenton processes. Complete degradation of 2,4 DCP with Fenton process required longer treatment periods and resulted in incomplete mineralization. The photo-Fenton process exhibited the highest 2,4 DCP and TOC removal rates followed by H₂O₂/UV-C and Fenton processes.

- During the application of AOPs, an immediate release of chloride was evident as soon as the treatment processes were started, implying that the chlorine atoms on the aromatic ring were first removed. The rate of dechlorination was in the following decreasing order; photo-Fenton > H₂O₂/UV-C > Fenton processes.
- The degradation of 2,4 DCP was accompanied by the formation of chlorinated and hydroxylated aromatic intermediates as well as aliphatic oxidation products such as acetic, oxalic and formic acids. Hydroquinone and formic acid were found to be the common oxidation products of the studied treatment processes. As expected, the Fenton process was found to be least efficient in removing the carboxylic acids, while the H₂O₂/UV-C and photo-Fenton processes ensured the complete removal of these compounds.
- The results of toxicity assessments with *V. fischeri* on 2,4 DCP samples being subjected to H₂O₂/UV-C and photo-Fenton treatment revealed complete detoxification. The H₂O₂/UV-C and photo-Fenton treatment results implied that the removal of toxicity was highly correlated with the degradation of 2,4 DCP, and the rate of dechlorination, being an indicator of the rapid transformation of chlorinated oxidation intermediates. The Fenton process was also able to completely remove 2,4 DCP, however a relatively high toxicity was observed in the reaction solutions. The formation and accumulation of carboxylic acids was the most likely origin of the remaining toxicity of Fenton-treated samples.

Considering the results obtained in the present work, the toxicity parameter can be a valuable tool in order to ensure the environmentally safe discharge into receiving water bodies or promote a following biological treatment step. Overall speaking, both photo-Fenton and H₂O₂/UV-C processes have proven to be effective and fast in the removal of toxicity arising from waters containing significant concentrations of CPs including 2,4 DCP. However, these treatment processes should be carefully controlled to prevent possible accumulation of toxic oxidation products.

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