A comparative study of the advanced oxidation of 2,4-dichlorophenol

Fares Al Momani, Carmen Sans, Santiago Esplugas*

Departament d'Enginyeria Química i Metal·lúrgia, Universitat de Barcelona, Martí i Franquès 1, 08028 Barcelona, Spain

Abstract

Advanced oxidation processes (AOPs) using UV, UV/H_2O_2, Fenton and photo-Fenton treatment were investigated at laboratory scale for aqueous solutions of 2,4-dichlorophenol (DCP). The effects on degradation of different reactant concentrations, irradiation time, temperature and pH were assessed. DCP removal, TOC mineralization, dechlorination and change in oxidation state were monitored. UV photolysis was less efficient for total DCP degradation than other AOPs. In contrast, photo-Fenton reaction in acidic conditions led to a higher DCP degradation in a short time. Sixty minutes of treatment were sufficient for 100% DCP removal with $75 \, \mathrm{mg \, l^{-1}}$ H_2O_2 and $10 \, \mathrm{mg \, l^{-1}}$ Fe(II) initial concentrations. In these conditions, a first-order degradation constant for DCP of $0.057 \, \mathrm{min^{-1}}$ was obtained.
© 2003 Elsevier B.V. All rights reserved.

Keywords: UV; Photo-Fenton; Modified Fenton; UV/H_2O_2; DCP

1. Introduction

Chlorophenols constitute an important category of organic water pollutants that are not readily biodegradable [1]. The adsorption on activated carbon is commonly used to remove chlorophenols from chemical effluents. However, the need of frequent carbon reactivation renders this process both inconvenient and costly [2].

Various advanced oxidation processes, such as O_3/UV, O_3/H_2O_2, UV/H_2O_2, Fenton and photo-Fenton, have been applied successfully in wastewater treatment to mineralize many synthetic organic chemicals [3–6]. However, the costs of chemical oxidation alone can often be prohibitive for wastewater treatment. This factor should be taken into account when the chemical treatment is proposed. The simplest oxidation process is hence recommended for each target contaminant.

To be effective, photolysis requires strong UV-light with a short wavelength and chemical oxidants such as hydrogen peroxide and ozone.

Fenton's reagent [7], a mixture of ferrous (Fe(II)) ion and hydrogen peroxide which produces OH• radicals (reaction 1), has been used extensively for oxidation of organic matter in water such as phenols, chlorinated phenol and herbicides,

and to reduce the chemical oxygen demand and total organic carbon (TOC) content [8]. The use of Fe(II)/H_2O_2 as an oxidant for wastewater is attractive since iron is highly abundant and non-toxic, and a 30% hydrogen peroxide aqueous solution is easy to handle and environmentally friendly.

$$\mathrm{Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^\bullet + OH^-} \quad (1)$$
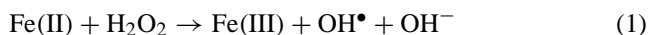
On the other hand, the modified Fenton process consists of a mixture of ferric ion (Fe(III)) and hydrogen peroxide. During this process, Fe(II) is produced in situ from the reaction between Fe(III) and H_2O_2, which in turn reacts with H_2O_2 to produce more OH• radicals (reactions 1 and 2). This may also be used to avoid high local concentrations of Fe(II) in the reaction vessel [9].

$$\mathrm{Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2^\bullet + H^+} \quad (2)$$

$$\mathrm{Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^\bullet + OH^-} \quad (1)$$

The rate of organic pollutant degradation could be increased by irradiation of Fenton/Fenton-like reagents with UV-light (photo-Fenton process). UV-light leads not only to the formation of additional hydroxyl radicals but also to recycling of ferrous catalyst by reduction of Fe(II). In this way, the concentration of Fe(II) increases and the overall reaction is accelerated [10]. The increased efficiency of the photo-Fenton process is attributed to: the photo reduction of ferric ion, the efficient use of light quanta and the photolysis of Fe(III)-organic intermediate chelates [8].

* Corresponding author. Tel.: +34-93-402-1290;
fax: +34-93-402-1291.
E-mail address: esplugas@angel.qui.ub.es (S. Esplugas).

Because of its many uses, 2,4-dichlorophenol (DCP) was chosen as a model compound of chlorophenols. It is a common pollutant in industrial wastewaters. It is used as a chemical intermediate in the production of pesticides and herbicides and as a feedstock for the manufacture of certain methyl compounds used in mouth proofing, antiseptics and seed disinfectants [11]. DCP is also reacted with benzene sulfonyl chloride to produce miticide or further chlorinated to pentachlorophenol in a wood preservative. These compounds are highly resistant to biological treatment [12]. So, wastewater contaminated with chlorophenols must be pre- or post-treated.

Hence, the objective of this study was the assessment of DCP photo-degradation by different AOPs (UV, UV/H_2O_2, Fenton and photo-Fenton). Several parameters, including DCP removal, TOC mineralization, H_2O_2 and iron consumption as well as the change in oxidation state were monitored. Moreover, the kinetic study of experimental results was carried out.

2. Materials and methods

2.1. Reagents

2,4-Dichlorophenol (DCP) (>98%, Merck), hydrogen peroxide (H_2O_2) (30%, Merck), iron sulphate 7-hydrate ($FeSO_4\cdot7H_2O$) (98%, Panreac), iron chloride 6-hydrate ($FeCl_3\cdot6H_2O$) (98%, Panreac), sodium hydrogen sulphite solution (40% W/V, Panreac), uranyl nitrate (98%, Panreac), oxalic acid (99.5%, Panreac), acetonitrile (99.8%, isocratic grade for HPLC, Merck), potassium dichromate (99%, Probus), mercury sulphate (98%, Probus), silver sulphate (98%, Probus), sulphuric acid (95–98%, Fluka) and Millipore water (Milli-Q Millipore system with a $18\,M\Omega\,cm^{-1}$ resistivity).

2.2. Installation

All experiments were carried out in a 1.5 l jacketed thermostatic photo reactor (diameter 12 cm and height 13.3 cm, see Fig. 1) equipped wi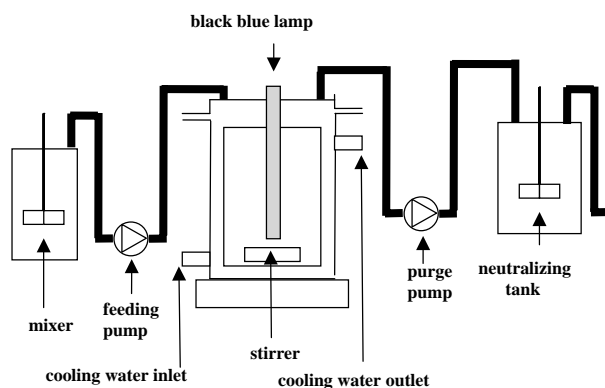th black–blue lamp placed in its center. This lamp, with nominal power of 4 W, emits radiation basically at 350 nm. The reactor is equipped with a magnetic stirrer that provides good mixing. All the reactions were performed at atmospheric pressure. The temperature was maintained at $25 \pm 0.5\,°C$ by circulating water from a thermostatic bath (Haake C-40).

The radiation flux entering the reactor was determined by actinometric experiments based on the photochemical decomposition of oxalic acid in the presence of uranyl ion [13]. For 350 nm wavelength, the quantum yield of this system is equal to $0.51\,mol\,Einstein^{-1}$. According to the actinometry, the flux of radiation entering the reactor was $2.5\,\mu Einstein\,s^{-1}$.

2.3. Photo-degradation procedure

All the experiments were carried out in batch mode. In each experiment a DCP solution of $100\,mg\,l^{-1}$ ($0.614\,mmol\,l^{-1}$) was prepared with Millipore water in a mixing tank (see Fig. 1). The solutions were perfectly mixed to guarantee that all DCP was dissolved, and the required concentrations of iron salt $FeSO_4\cdot7H_2O$ ($FeCl_3\cdot6H_2O$ in case Fe(III)) were added when necessary. The solution pH was 4.5–6 (not buffered). The photo-reactor was filled with the solution, and it was stirred for 5 min. A 30% aqueous hydrogen peroxide solution was injected into the reactor at different concentrations and the UV-light was switched on at the same time. During the experiments, samples were withdrawn from the reactor at several time intervals, tested for H_2O_2 consumption with Quantofix test sticks and quenched with sodium hydrogen sulphite to avoid further reactions. The samples were stored for TOC and COD analysis.

2.4. Analytical methods

The DCP concentration was measured by reverse-phase high-performance liquid chromatography (HPLC). A Waters' HPLC apparatus (photodiode array detector 996, auto sampler 717, controller 600) using Millennium software. The reverse-phase column used was a Spherisorb ODS2. The mobile phase was a mixture of water, acetonitrile and phosphoric acid (60%:40%:5%) isocratically delivered by a pump at a flow rate of $1\,ml\,min^{-1}$. The wavelength of the UV absorbance detector was 280 nm. Under these conditions, the DCP retention time was 15 min with an experimental error margin of $\pm0.5\,mg\,l^{-1}$.

The dissolved organic carbon was measured using a TOC analyzer (Rosemaunt Dohrmann D-C-190), provided with an auto-sampler and using potassium phthalate solution as the calibration standard. The precision of the TOC measurements were in the range of $\pm1\,mg\,C\,l^{-1}$.

The chemical oxygen demand (COD $\pm3\,mg\,O_2\,l^{-1}$) was carried out via a photometer (LF 2400, Windows) following the procedure stipulated in Standard Methods [14].

Fig. 1. Experimental layout.

The consumption of H_2O_2 during the reaction was monitored using Quantofix test sticks. Stock solutions and all reagents were prepared with Millipore water.

2.5. Quantum yield (φ)

One experiment using UV radiation alone and with $100 \, mg \, l^{-1}$ of DCP initial concentration ($0.614 \, mmol \, l^{-1}$) was performed to evaluate the quantum yield for DCP degradation [15,16]. The quantum yield is the number of molecules that react divided by the number of photons absorbed. It may be evaluated through the slope of the compound degradation rate at initial irradiation time and the absorption radiation rate. It is important to take into account that the photoproducts from DCP also absorb radiation and, the determination of the quantum yield must be hence done at low conversion of DCP. According to the actinometrical results, the quantum yield at initial time was $1.2 \pm 0.2 \, mmol \, Einstein^{-1}$.

3. Results and discussion

Results obtained by each AOP will be presented and discussed. In this work, each point presented in the figures corresponds to an average of three repeated experiments under the same conditions.

3.1. UV and UV/H_2O_2

Direct UV-light did not totally degrade the DCP: in 2 h of reaction just 9% of original DCP was degraded into other organic intermediates and only 4% of TOC was mineralized.

When UV irradiation was combined with hydrogen peroxide, the rate of DCP degradation increased significantly compared to that of direct photolysis. Fig. 2 presents DCP and TOC removal percentages using H_2O_2/UV as a function of the initial H_2O_2 concentration at an irradiation time of 2 h. The combination of UV with H_2O_2 improved the degradation. A H_2O_2 concentration of $250 \, mg \, l^{-1}$ ($7.53 \, mmol \, l^{-1}$) gave 37% DCP removal and 13% TOC
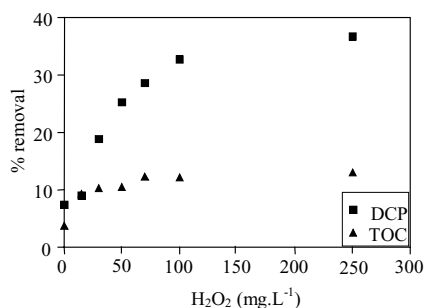
mineralization. However, not all the added H_2O_2 was consumed. When $250 \, mg \, l^{-1}$ ($7.53 \, mmol \, l^{-1}$) was used, at least $60 \, mg \, l^{-1}$ ($1.76 \, mmol \, l^{-1}$) H_2O_2 remained in the reactor at the end of the reaction. This could be attributed to the absorption spectrum of hydrogen peroxide. Photolysis of H_2O_2 requires $\lambda < 360 \, nm$. It has a favorable absorption spectrum around $250 \, nm$, which leads to efficient H_2O_2 photolysis generating more $OH^{\bullet}$ radicals [16,17]. The molar absorption coefficient was low at reactor working wavelength ($350 \, nm$). Thus, only a small fraction of H_2O_2 was photolyzed to produce more hydroxyl radicals.

3.2. Fe(III)/UV

Iron, in its ferrous and ferric form, acts as catalyst. In the photo-catalytic process, not only do the absorbed UV photons lead to organic matter degradation but also ferric ion undergoes a photo-redox reaction producing more hydroxyl radicals. In this part, experiments were carried out to determine the influence of UV/Fe(III) combination on DCP photo-degradation.

The combination of ferric ion (Fe(III)) with UV-light was more efficient than UV radiation alone. A ferric ion concentration of $30 \, mg \, l^{-1}$ ($0.545 \, mmol \, l^{-1}$) gave 30% DCP degradation in 90 min (see Fig. 3). Moreover, the degradation efficiency was improved by increasing the initial Fe(III) concentration up to $110 \, mg \, l^{-1}$. At this concentration and with 90 min irradiation time, more than 61% DCP was eliminated, combined with 12% TOC and 32% COD removal (see Fig. 3). This indicates the continuous formation of hydroxyl radicals as a result of ferric ion photo-redox reactions. But, it was also observed that higher iron concentrations led to a slight decrease in DCP elimination, and the degradation tendency leveled off. The DCP degradation tendency and evolution could be attributed to the formation of several Fe(III)–hydroperoxy complexes like $Fe(HO_2)^{2+}$ and $Fe(OH)(HO_2)^{2+}$ which decompose to produce the hydroperoxy radical $HO_2^{\bullet}$ and Fe(II). If $HO_2^{\bullet}$ is formed, it is relatively non-reactive with organic matter [18]. Furthermore, the presence of chloride in the water solution might act as a scavenger of hydroxyl radicals [19], thus, decreasing the DCP degradation.

Fig. 2. DCP and TOC removals as function of initial H_2O_2 concentration in the H_2O_2/UVA process.
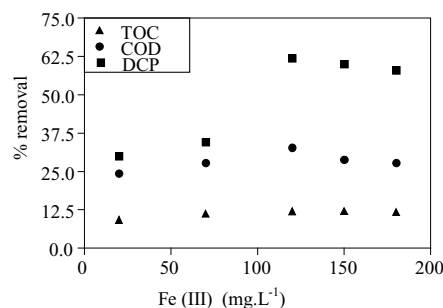

Fig. 3. DCP, COD and TOC removal as function of initial Fe(III) in the UV/Fe(III) process, for free pH evolution and 90 min irradiation time.
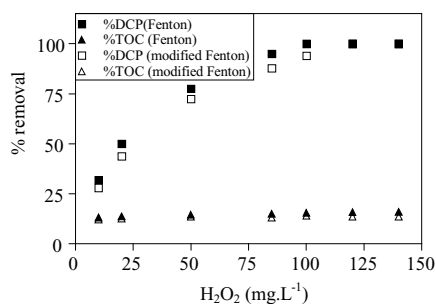
Fig. 4. DCP and TOC removals in Fenton and modified Fenton process as function of the initial H_2O_2 [Fe(II)]$_i$ or [Fe(III)]$_i$ = 10 mg l^{-1}, for free pH evolution and 60 min reaction time.

3.3. Fenton and modified Fenton

The DCP and TOC removal by Fenton and modified Fenton methods at different initial hydrogen peroxide concentrations is shown in Fig. 4. Fenton and modified Fenton were efficient processes for the elimination of DCP from aqueous solutions. The degradation rate in both processes depended on the initial H_2O_2 concentration; increasing the amount of H_2O_2 led to increased DCP removal percentages. At 60 min reaction time and low ferric ion concentration (10 mg l^{-1}), 100% DCP removal was obtained when 100 mg l^{-1} (2.84 mmol l^{-1}) and 115 mg l^{-1} (3.38 mmol l^{-1}) of H_2O_2 were used in Fenton and modified Fenton processes, respectively. There was no difference between starting with Fe(II) or Fe(III) since the degradation percentages were of the same order of magnitude (see Fig. 4). Moreover, both Fenton and modified Fenton processes gave almost the same mineralization (TOC decreased between 12 and 16%).

Experiments were carried out by changing the initial Fe(II) (or Fe(III) in the case of the modified Fenton) concentration. DCP and TOC removal as a function of initial Fe(II) concentration for Fenton reaction, at a fixed initial H_2O_2 concentration of 20 mg l^{-1} (0.588 mmol l^{-1}), are shown in Fig. 5. It was observed that the iron ion concentration has a positive effect on DCP removal at small concentrations (less than 15 mg l^{-1}). But, at higher concentrations the degradation decreases and a maximum DCP removal around 75% was reached. The TOC removal for all
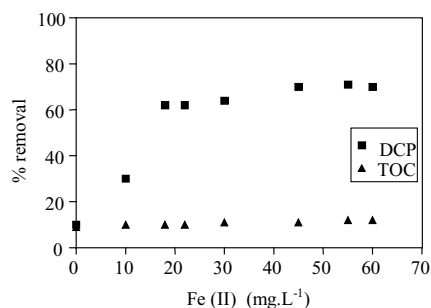

Fig. 5. DCP and TOC removals as function of initial Fe(II) in Fenton reaction. Conditions: [H_2O_2]$_i$ = 20 mg l^{-1} and 60 min reaction time.
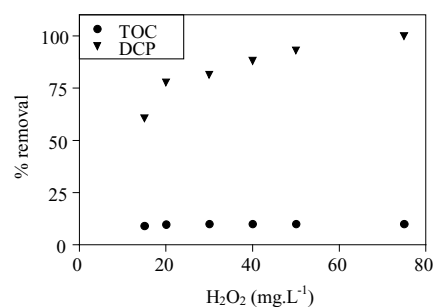

Fig. 6. DCP and TOC removals as function of the initial H_2O_2 concentration in photo-Fenton reaction [Fe(II)]$_i$ = 10 mg l^{-1}.

the studied concentrations was of the same order of magnitude (between 11 to 13%). The Fenton and modified Fenton behavior can be explained by the same effects as observed with the UV/Fe(III) process. Moreover, the catalytic effect of Fe(III) on the decomposition of H_2O_2 to H_2O and O_2 [20] may support this tendency.

3.4. Photo-Fenton

Photo-Fenton reactions were carried out at different initial H_2O_2 concentrations. The DCP and TOC removals are reported in Fig. 6. The H_2O_2 concentration declined significantly, which led to a significant DCP degradation. However, not all the H_2O_2 degraded to produce hydroxyl radicals: about 15% of the initial H_2O_2 concentration remained at the end of each experiment, again due to the incomplete photolysis at the working wavelength (350 nm). 100% elimination of DCP was obtained under the following conditions: 75 mg l^{-1} H_2O_2, 10 mg l^{-1} Fe(II) and 60 min reaction time.

Considering the mineralization, the TOC removal was not affected by increasing the initial H_2O_2 concentration. An average TOC removal of 10% was obtained for all H_2O_2 concentrations.

The effect of the initial Fe(II) concentration on the photo-Fenton process was tested by carrying out experiments with various amounts of the iron salt and a fixed H_2O_2 initial concentration of 15 mg l^{-1}. The DCP and TOC removal as function of initial Fe(II) concentration are shown in Fig. 7. As a result of iron photo-redox reaction
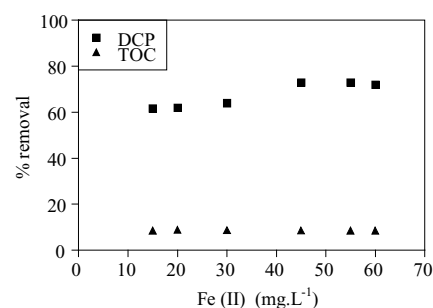

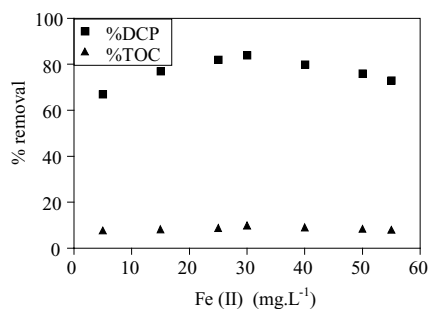Fig. 7. DCP and TOC removals as function of different initial Fe(II) concentrations: [H_2O_2]$_i$ = 15 mg l^{-1} and reaction time: 60 min.

Fig. 8. DCP and TOC removals as function of different initial Fe(II) concentrations: $[H_2O_2]_i = 30 \, mg \, l^{-1}$ and reaction time: 60 min.

and formation of hydroxyl radicals, the DCP elimination increased by increasing the initial Fe(II) concentration up to $45 \, mg \, l^{-1}$. At this concentration, approximately 75% DCP elimination and 8% TOC reduction was obtained. Again, as observed before, at concentrations of Fe(II) higher than $45 \, mg \, l^{-1}$, the DCP degradation efficiency decreased.

Moreover, it was decided to examine the DCP photo-Fenton degradation under higher initial H_2O_2 (30 and $50 \, mg \, l^{-1}$) and varying iron ion concentrations. Results for initial H_2O_2 concentration of $30 \, mg \, l^{-1}$ are shown in Fig. 8. For both concentrations, it was observed that the DCP degradation increased by increasing iron concentration, up to $30 \, mg \, l^{-1}$. But, starting photo-Fenton reaction at higher iron concentration led to the formation of a brown turbidity in the reaction vessel, and no more improvement in the degradation was noticed. Ghaly et al., [21] remarked that this turbidity decreased the absorption of UV-light and promoted the recombination of hydroxyl radicals.

In all photo-Fenton experiments, 100% DCP elimination was achieved at initial a H_2O_2 concentration of $75 \, mg \, l^{-1}$. The reaction conditions were: 60 min irradiation time, free pH evolution and $10 \, mg \, l^{-1}$ Fe(II). In these experimental conditions, only 9% TOC reduction was achieved. Within the context of our research, Contreras et. al. [22] studied the degradation of DCP by mean of ozone. Reported values indicate that DCP was completely removed after 30 min of ozonation (corresponding to ozone dose of $0.12 \, g \, l^{-1}$). At that point, only 14% of TOC and 70% dechlorination have been produced.

The influence of other photo-Fenton operating conditions such as initial pH, operating temperature and initial DCP concentrations on DCP removal were also studied. At the same initial reactant concentrations ($15 \, mg \, l^{-1} \, H_2O_2$, $10 \, mg \, l^{-1}$ Fe(II)) and 60 min of reaction time, a maximum DCP degradation (66.9%) was obtained at pH = 3. The elimination decreased (<48%) at pH = 9. This can be attributed to the partial decomposition of H_2O_2, and to the reduction in radiation transmission as result of iron hydroxide precipitation [23].

It was also observed that the DCP removal increased with operating temperature: when the temperature increased from 25 to 45 °C, the DCP degradation improved from 60.5 to 80%.

The rate of degradation also depended on the initial DCP concentration, even for the same initial reactant concentrations. For $[H_2O_2]_i = 30 \, mg \, l^{-1}$, $[Fe(II)]_i = 10 \, mg \, l^{-1}$ and 60 min of irradiation time, 83% of DCP was removed when an initial concentration of $100 \, mg \, l^{-1}$ was used, and 57% removal for $200 \, mg \, l^{-1}$ initial H_2O_2 concentration. However, the TOC removal at all the studied concentrations was of the same order of magnitude (8.7–9.7%). The oxidation affinity confirms the non-selectivity of the hydroxyl radical reaction in the degradation of DCP and the intermediates being formed.

4. Comparison between different AOPs studied

The present section compares the different AOPs processes studied (UV, H_2O_2/UV, Fe(III)/UV, Fenton and Photo-Fenton).

Fig. 9 presents the normalized DCP concentrations as a function of time for the different processes studied. Photo-Fenton shows the best capacity for DCP degradation, whereas, UV irradiation alone only shows a slow degradation. In 60 min of reaction, $100 \, mg \, l^{-1}$ of DCP were completely removed using $75 \, mg \, l^{-1}$ of H_2O_2 and $10 \, mg \, l^{-1}$ of Fe(II).

The experimental data were fitted by first-order kinetics. Table 1 presents the pseudo-first-order kinetic constant and the experimental half-life time ($t_{1/2}$). The results confirm the significant accelerating effect of photo-Fenton and Fenton reactions on DCP degradation in comparison with the other
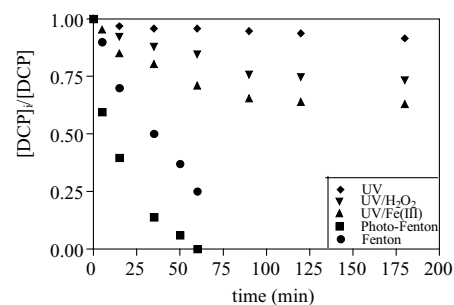

Fig. 9. Evolution of normalized DCP concentration as function of time for different AOPs: $[H_2O_2]_i = 50 \, mg \, l^{-1}$, $[Fe(II)]_i = 10 \, mg \, l^{-1}$, $[Fe(III)]_i = 70 \, mg \, l^{-1}$ and free pH evolution.

Table 1
First-order kinetic constants for DCP degradation by different oxidation processes

Oxidation process	$t_{1/2}$ (min)	$10^{-2} \times K_0$ (h^{-1})[a]
UV	>90	0.3 ± 0.2
UV/H_2O_2	>120	1.56 ± 0.5
UV/Fe(III)	>90	3.72 ± 0.2
Fenton	34	144 ± 8
Photo-Fenton	10	342 ± 5

[a] Data were calculated at a 95% confidence level.
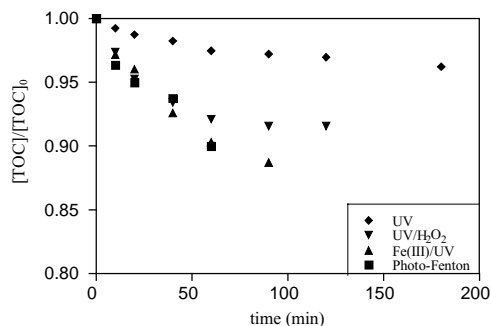
Fig. 10. Normalized TOC concentrations as function of time for the different AOPs processes: $[H_2O_2]_i = 50\,mg\,l^{-1}$, $[Fe(II)]_i = 10\,mg\,l^{-1}$, $[Fe(III)]_i = 70\,mg\,l^{-1}$ and free pH evolution.

Fig. 11. Dechlorination during different AOPs: $[H_2O_2]_i = 50\,mg\,l^{-1}$, $[Fe(II)]_i = 10\,mg\,l^{-1}$, $[Fe(III)]_i = 70\,mg\,l^{-1}$ and free pH evolution.

processes studied. The data also show that adding Fe(II) to the UV/H_2O_2 has a significant influence on the DCP oxidation rate. Trapido et al., [24] studied the degradation of chlorophenols by UV and UV/H_2O_2 and they reported apparent rate constants for DCP degradation of the same order of magnitude as those found in the present study.

Fig. 10 presents the normalized TOC mineralization for the different processes studied. Major TOC mineralization occurred for the Fenton reaction with initial H_2O_2 and Fe(II) concentrations of 50 and $10\,l^{-1}$, respectively. The Fenton reaction mineralized 16% of the original TOC in 90 min, while only 3% was mineralized in 180 min using UV-light. By the other hand, photo-Fenton showed the highest TOC mineralization rate of all the processes that use UV as an oxidation source. 10% TOC mineralization was achieved under the following conditions: $50\,mg\,l^{-1}$ H_2O_2, $10\,mg\,l^{-1}$ Fe(II) and 50 min of reaction time. In contrast, UV/H_2O_2 with initial H_2O_2 of $50\,mg\,l^{-1}$ and 120 min irradiation yielded only 8% TOC reduction.

Previous studies pointed out that chlorophenol mineralization follows a pseudo first-order kinetics [25]. The apparent first-order rate constants based on TOC mineralization was determined (see Table 2). Almost all the processes followed the first-order kinetics except UV/H_2O_2, which showed a slight deviation from linearity ($R^2 = 0.96$). Thus, it was not compared with the other processes. Further investigation to verify and explain this tendency should be done.

The dechlorination rate was also analyzed (Fig. 11). The photo-Fenton process showed a greater tendency to liberate
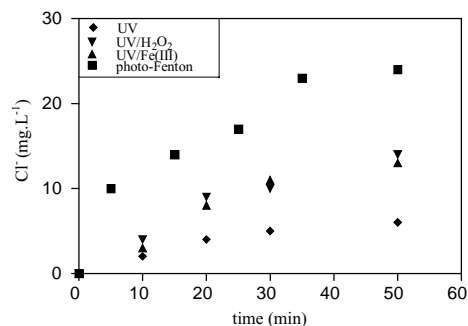
Table 2
Apparent first-order rate constants based on TOC mineralization for different AOPs

Process	$10^{-3} \times K_{TOC}$ (min^{-1})[a]
UV	0.37 ± 0.04
UV/H_2O_2	0.12 ± 0.08
UV/Fe(III)	0.15 ± 0.02
Fenton	1.7 ± 0.3
Photo-Fenton	0.18 ± 0.02

[a] Results were calculated at a 95% confidence level.

Cl^- ions than the other processes. For 94% DCP elimination about 60% of Cl^- was released. The Fenton process also liberated chlorine: 77% DCP elimination gave 39% Cl^- release. Other processes had lower capacity to liberate chlorine. The superiority of photo-Fenton in dechlorination may be attributed to the high attackable capacity of photo-Fenton by direct nucleophilic displacement of chloride by $OH^\bullet$. Trapido et al. [24] reported 62% dechlorination for 97% DCP elimination, which is in agreement with the value obtained in this study.

Although intermediates were not identified, the degradation of DCP into other by-products was monitored by the change in the degree of oxidation. Two parameters were studied: COD/TOC and the average oxidation state (AOS). The average oxidation state of the organic carbon was calculated from formula [25]:

$$AOS = \text{average oxidation state} = \frac{4(TOC - COD)}{TOC} \qquad (3)$$

where TOC is in $mol\,C\,l^{-1}$ and COD in $mol\,O_2\,l^{-1}$.

Both COD/TOC and AOS indicate how chemical substances in the effluent become more oxidized: lower COD/TOC ratios imply a higher degree of oxidation while higher ratios mean lower oxidation. This parameter ranges theoretically between 4 and 5.3 for alkanes and 0.6 for very oxidized substances like oxalic acids [25]. At the same time, AOS has a value of +4 for CO_2, the most oxidized state of C, and −4 for CH_4, the most reduced state of carbon. Average oxidation stages of organic carbon in several organic compounds were listed in Stumm and Morgan [26]. Benzene is −1, formaldehyde and acetic acids are 0, formic acid is +2 and oxalic acid is +3.

The oxidation state evolution during the reaction of the different studied processes is compared in Fig. 12. Among the oxidation processes studied, the photo-Fenton reaction has the highest oxidizing capacity: 50 min reaction was sufficient to decrease the COD/TOC ratio by 26%, while the maximum reduction was only 18 and 4% for UV/Fe(III) and UV/H_2O_2, respectively. The same affinity was observed in AOS values; in the photo-Fenton process the value increases from −0.58 to 0.58 and from −0.56 to 0.29 in UV/Fe(III).
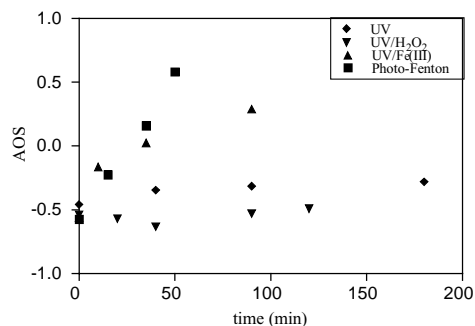
Fig. 12. Change in oxidation state for different AOPs: $[H_2O_2]_i = 50 \text{ mg l}^{-1}$, $[Fe(II)]_i = 10 \text{ mg l}^{-1}$, $[Fe(III)]_i = 70 \text{ mg l}^{-1}$ and free pH evolution.

5. Conclusions

UV radiation alone slightly degrades DCP in aqueous solution (less than 10%). The combinations of UV with H_2O_2 and with Fe(III) (i.e. UV/H_2O_2 and UV/Fe(III)) were much more efficient. The degradation rate of DCP was strongly accelerated by the Fenton and Photo-Fenton processes. The degradation rate was influenced by many factors, such as initial hydrogen peroxide concentration, initial iron concentration, pH, and temperature in addition to initial DCP concentrations. The Photo-Fenton and Fenton reactions can be used successfully for the total DCP degradation. Total DCP elimination was obtained by the photo-Fenton process in only 60 min irradiation time, and initial reactant concentrations of 75 mg l^{-1} H_2O_2 and 10 mg l^{-1} Fe(II). At the same time, 10% of TOC reduction was obtained and the corresponding first-order kinetic constant was 0.057 min^{-1}. On the other hand, the Fenton reaction required 60 min, 100 mg l^{-1} H_2O_2 and 10 mg l^{-1} Fe(II) to achieve total DCP removal. From all the processes studied, the photo-Fenton reaction showed the best efficiency in DCP elimination, chlorine ion release and in the change of oxidation state: for 94% DCP elimination 60% of the stoichiometric chlorine was liberated, and there was a 26% reduction in oxidation state.

Acknowledgements

References

[1] K. Abe, K. Tanaka, Fe^{3+} and UV-enhanced ozonation of chlorophenolic compounds in aqueous medium, Chemosphere 35 (12) (1997) 2837–2847.

[2] W.S. Kuo, Synergistic effect of combination of photolysis and ozonation on destruction of chlorophenols in water, Chemosphere 39 (11) (1999) 1853–1860.

[3] J. Prado, J. Arantegui, E. Chamarro, S. Esplugas, Degradation of 2,4-D by ozone and light, Ozone Sci. Eng. 16 (1994) 235–254.

[4] J. Prousek, Advanced oxidation processes for water treatment. Chemical processes, Chem. Lis. 90 (4) (1996) 229–237.

[5] Y.S. Shen, Y. Ku, K.C. Lee, The effect of light absorbance on the decomposition of chlorophenols by UV radiation and UV/H_2O_2 processes, Water Res. 29 (3) (1995) 907–914.

[6] O. Legrini, E. Oliveros, A.M. Braun, Photochemical processes for water treatment, Chem. Rev. 93 (1993) 671–698.

[7] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater. 98 (1–3) (2003) 33–50.

[8] A. Safarzadeh, R. James, R. Stephen, The use of iron in advanced oxidation processes, J. Adv. Oxid. Technol. 1 (1) (1996) 18–25.

[9] T.M. El-Morsi, M.M. Emara, M.H. El Bary, A.S. El-Aziz, K.J. Friesen, Homogeneous degradation of 1,2,9,10-tetrachlorodecane in aqueos solution using hydrogen peroxide, iron and UV light, Chemosphere 47 (2002) 343–348.

[10] E. Lipczynska-Kochany, Degradation of aqueous nitrophenols and nitrobenzene by means of the Fenton reaction, Chemosphere 22 (5–6) (1991) 529–536.

[11] H.F. Mark, D.F. Othmer, C.G. Overberger, G.T. Seaburg, Kirk-Othmer Encyclopedia of Chemical Technology, fourth ed., Wiley–Interscience Publication, New York, USA, 1992.

[12] Y.-H. Yu, S.-T. Hu, Preoxidation of chlorophenolic wastewaters for their subsequent biological treatment, Water Sci. Technol. 29 (1994) 313–320.

[13] L.J. Heidt, G.W. Tregay, F.A. Middleton, Influence of the pH upon the photolysis of the uranyl oxalate actinometer system, J. Phys. Chem. 74 (1979) 1876–1882.

[14] Standard Methods for the Examination of Water and Wastewater, 16th ed., American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1985.

[15] M.L. Rodriguez, V.I. Timokhin, S. Contreras, E. Chamarro, S. Esplugas, Rate equation for the degradation of nitrobenzene by 'Fenton-like' reagent, Adv. Environ. Res. 7 (2) (2003) 583–595.

[16] S. Esplugas, M. Vicente, A. Ibarz, C. Prat, J. Costa, Influence of lamp position on available radiation flux in an annular photoreactor, Chem. Eng. J. 34 (3) (1987) 111–115.

[17] J.J. Pignatello, Dark and photoassisted Fe(III) catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, Environ. Sci. Technol. 26 (1992) 944–951.

[18] J. De Laat, H. Gallard, Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: mechanism and kinetic modeling, Environ. Sci. Technol. 33 (1999) 2726–2732.

[19] P. Maltezky, R. Bauer, The photo-Fenton method-degradation of nitrogen containing organic compounds, Chemosphere 37 (1998) 899–909.

[20] A.P. Murphy, W.J. Boegli, M.K. Price, C.D. Moody, A Fenton-like reaction to neutralize formaldehyde waste solutions, Environ. Sci. Technol. 23 (1989) 166–169.

[21] M.Y. Ghaly, G. Hartel, R. Mayer, R. Haseneder, Photochemical oxidation of p-chlorophenol by Uv/H_2O_2 and photo-Fenton process. A comparative study, Water Manage. 21 (2001) 41–47.

[22] S. Contreras, M. Rodriguez, F. Al Momani, C. Sans, S. Esplugas, Contribution of the ozonation pre-treatment to the biodegration of aqueous solution of 2,4-dichlorophenol, Water Res. 37 (2003) 3164–3171.

[23] B.C. Faust, J. Hoigne, Photolysis Fe(III)-hydroxy complexes as sources of radicals in clouds, fog and rain, Atoms. Environ. 22 (5–6) (1990) 79–89.

[24] M. Trapido, A. Hirvonen, Y. Veressina, J. Hentunen, R. Munter, Ozonation, ozone/UV and UV/H_2O_2 degradation of chlorophenols, Ozone Sci. Eng. 19 (1) (1997) 75–96.

[25] S. Esplugas, P.L. Yue, M.I. Pervez, Degradation of 4-chlorophenol by photolytic oxidation, Water Res. 28 (1994) 1323–1328.

[26] W. Stumm, J.J. Morgan, Aquatic Chemistry, second ed., Wiley, New York, 1981.