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Photochemical treatment of 2-chlorophenol aqueous solutions using ultraviolet radiation, hydrogen peroxide and photo-Fenton reaction

S.G. Poulopoulos, M. Nikolaki, D. Karampetsos, C.J. Philippopoulos *

Chemical Process Engineering Laboratory, School of Chemical Engineering, National Technical University of Athens, Heroon Politechniou 9, Zografou Campus, 157 80 Athens, Greece

Abstract

In the present work, the photochemical oxidation of 2-chlorophenol aqueous solutions in a batch recycle photochemical reactor using ultraviolet irradiation and hydrogen peroxide was studied. Specifically, the effect of hydrogen peroxide initial concentration (0–$10316\,\mathrm{mg\,L^{-1}}$) and 2-chlorophenol initial concentration (150–$3000\,\mathrm{mg\,L^{-1}}$) was examined. The process was attended via total organic carbon (TOC), 2-chlorophenol, chloride ion, acetic acid, formic acid and pH measurements. The conversion of 2-chlorophenol observed was always much higher than the corresponding total organic carbon removal, whereas the increase in hydrogen peroxide amount in the solution led to higher values of 2-chlorophenol conversion and total organic carbon removal. Finally, the photo-Fenton reaction was applied to the oxidation of 2-chlorophenol, leading to a higher degree of mineralization of the parent compound.
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Keywords: Photo-Fenton; Photo-oxidation; Chlorinated compounds

1. Introduction

Drinking water is vital for supporting life on earth and as such, we should do everything within our power to safeguard its quality. Despite the fact that the greatest part of earth is covered by water, only a small percentage of this water is appropriate for drinking. According to WHO estimations, one quarter of the world's population lacks hygienic drinking water. Unfortunately, our daily routine as well as the production of various goods results in the discharge of many organic compounds in the aquatic environment. Among them, chlorophenols constitute a group of contaminants that has been designated as priority pollutants by the U.S. EPA [1]. In Europe, their direct and indirect releases to water have been estimated as 1323 tonnes in total in 2003, according to the European Pollutant Emissions Register [2].

Due to the low biodegradability of chlorophenols, alternative treatment technologies have received increased interest. Among the various ways of wastewater treatment, *Advanced Oxidation Processes* (AOPs) can be proved very effective in the effort to eliminate hazardous compounds. The term "AOPs" is used to describe the oxidation mechanism that depends on the production of very active species like hydroxyl radicals ($^{\bullet}\mathrm{OH}$). Hydrogen peroxide ($\mathrm{H_2O_2}$) is commonly used as the source of these radicals since it decomposes to $^{\bullet}\mathrm{OH}$ under ultraviolet irradiation.

There are various studies in the related literature concerning the oxidation of phenol and chlorophenols using $\mathrm{UV/H_2O_2}$ [3–12], the photo-Fenton process [13–16] or photocatalysis [17,18].

The objective of this study was to investigate the feasibility of treating high concentrated 2-chlorophenol aqueous solutions by the $\mathrm{UV/H_2O_2}$ process. Experiments at various initial 2-chlorophenol and $\mathrm{H_2O_2}$ concentrations were conducted to investigate the effects of their initial concentration on the oxidation. Finally, the effect of photo-Fenton's system on the

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* Corresponding author. Tel.: +30 210 772 3224; fax: +30 210 772 3155.
  E-mail address: kphilip@chemeng.ntua.gr (C.J. Philippopoulos).

photo-oxidation of 2-chlorophenol was investigated. The specific work was conducted in the context of a joint research effort for the mineralization of chlorinated compounds combining chemical and biological methods. Since chloride removal from the carbon chain is an essential step for the successful operation of the biological stage, special attention was given on following the dechlorination of 2-CP and its intermediates via chloride concentration measurements.

2. Experimental details

2.1. Materials

2-Chlorophenol (>99.5% purity) was purchased from Merck. Sodium chloride, acetic acid and formic acid were used for calibration in ion chromatography analysis. Sodium hydrogen carbonate ($NaHCO_3$) and potassium hydrogen phthalate ($C_6H_4(COOK)(COOH)$) were used for calibration in TOC analysis. $FeCl_3 \cdot 6H_2O$ was used as the source of ferric ions, whereas a hydrogen peroxide solution 28% (w/w) was used as the source of hydroxyl radicals. Only deionized water was used.

2.2. Apparatus, procedure and analysis

The apparatus used consisted of a low-pressure mercury vapor lamp of 18 W, which was placed at the center of the reactor and produced monochromatic ultraviolet light of 253.7 nm (Fig. 1). The reactor was a cylindrical vessel of 20 mL effective volume operated in batch recycle mode. The total volume of the solution was 200 mL. The non-irradiated part of the solution was continuously agitated by a magnetic stirrer. A peristaltic pump was used to re-circulate the solution with a rate of 110 mL min^{-1}. A WTW-pH90 pH-meter was used for pH measurements. Samples were periodically withdrawn from the reactor and analyzed using total organic carbon analyzer (Shimadzu TOC-V) for quantifying total organic carbon (TOC), and ion chromatography (Dionex DX-600 IC) for chloride ion, formic and acetic acid quantitative determination. A gas chromatographer (HP 6890) equipped with a mass spectrometry detector (MSD 5973) was used to determine the 2-chlorophenol concentration. The concentration of hydrogen peroxide was measured using the standard titanate (IV) method. Each experiment lasted 150 min.
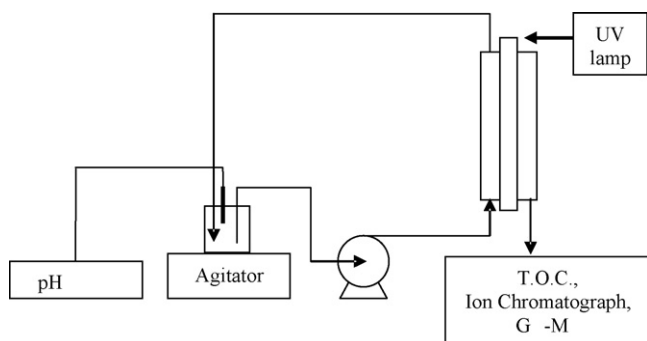
3. Results and discussion

3.1. Influence of H_2O_2 initial concentration

Primarily, the effect of hydrogen peroxide initial concentration on 2-CP photo-oxidation was investigated. All experiments were conducted under UV radiation, the initial concentration of 2-CP was held constant at 1500 mg L^{-1}, whereas the H_2O_2 initial concentration was 516, 2579, 5158 and 10316 mg L^{-1}. Defining λ as

$$\lambda = \frac{\text{initial } H_2O_2 \text{ concentration}}{\text{stoichiometric } H_2O_2 \text{ concentration}},$$

these concentrations correspond to λ = 1/10, 1/2, 1 and 2, respectively. The value λ = 0 means no hydrogen peroxide is present (photolysis of 2-CP), whereas the value λ = 1 denotes the concentration of H_2O_2 required for total mineralization of 2-CP according to the following equation:

$$2\text{-CP} + 13H_2O_2 \rightarrow 6CO_2 + HCl + 15H_2O.$$

As it can be seen in Fig. 2, 2-CP undergoes a significant direct photolysis (77% conversion) due to the fact that the compound is a strong absorber at the wavelength emitted by the source of UV radiation, while for values of λ higher than 1/2, 2-CP conversions above 90% were achieved after 150 min. The 2-CP conversion increased with increasing initial concentrations of hydrogen peroxide due to the fact that the solution was enriched with hydroxyl radicals. However, the corresponding values of TOC removal were significantly lower and on no occasion higher than 35% (Fig. 3). As it can be seen in Fig. 4, the values of Cl$^-$ yield were higher than the values of TOC removal but lower than those of 2-CP conversion. Also, the chloride ion yield was independent of the H_2O_2 initial concentration for values of the stoichiometric ratio λ below 1.

Taking into account the results arising from the experiments, it is established that 2-CP is partially mineralized (TOC conversion), whereas the rest of the 2-CP degradation should be attributed to dechlorination of the phenolic ring (chloride ion yield) and to the formation of organic intermediates during the process. The step of dechlorination, was rather easily developed, as it is indicated by the rate of chloride ion production, whereas the oxidation of the aromatic ring to carbon dioxide was a significantly slower step.
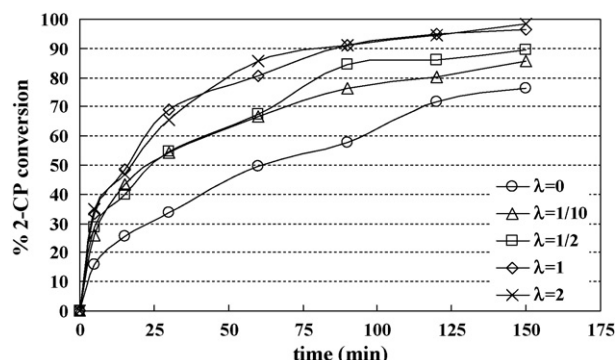

Fig. 1. The experimental setup.

Fig. 2. The effect of H_2O_2 initial concentration on 2-CP conversion.

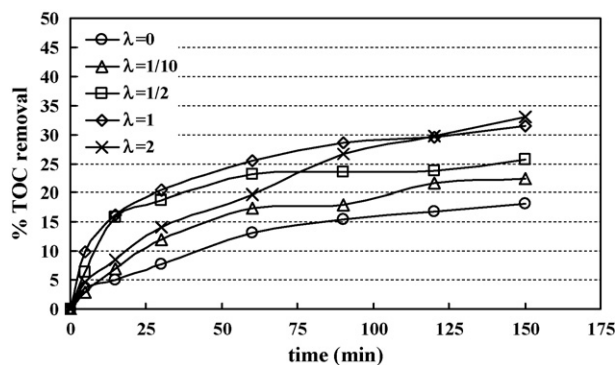Fig. 3. The effect of H$_2$O$_2$ initial concentration on TOC removal.

Fig. 5. The effect of H$_2$O$_2$ initial concentration on HCOOH formation.

Low molecular weight acids arise as intermediates during the photochemical oxidation of 2-CP, due to the destruction of the aromatic ring [19–21]. In the experiments conducted in the presence of hydrogen peroxide, acetic acid was detected in traces, whereas the production of formic acid in the course of the reaction is depicted in Fig. 5. For $\lambda < 2$, the formic acid concentration follows a complicated behavior, as it is gradually produced and decomposed as the reaction proceeds, exhibiting two local maximums, probably due to parallel reactions taking place in the reactor system. It must be noted that the highest formic acid production is accomplished for the stoichiometric ratio $\lambda = 2$, indicating that the 2-CP molecule has undergone dechlorination and ring cleavage to a large extent.

The pH values of the reactor solution were recorded during the reaction. It was established that the pH gradually decreases and tends to stabilize at the end of the reaction, due to the production of organic acids during the photo-oxidation of 2-CP. Moreover, the pH evolution was not affected by the initial H$_2$O$_2$ concentration.

Measuring the hydrogen peroxide left at each sample using the standard titanate (IV) method, it was found that for values of λ in the range of 1/10 to 1, hydrogen peroxide was decomposed at a percentage around 18%, whereas for $\lambda = 2$ that percentage decreased to 10%. The cost of hydrogen peroxide is a significant disadvantage of the photo-oxidation process. Aiming at maximizing the decomposition of hydrogen peroxide, another experiment was conducted where hydrogen peroxide was gradually added in the reaction mixture. Specifically, the amount of H$_2$O$_2$ corresponding to $\lambda = 1$ was added at a rate of one fifth of the
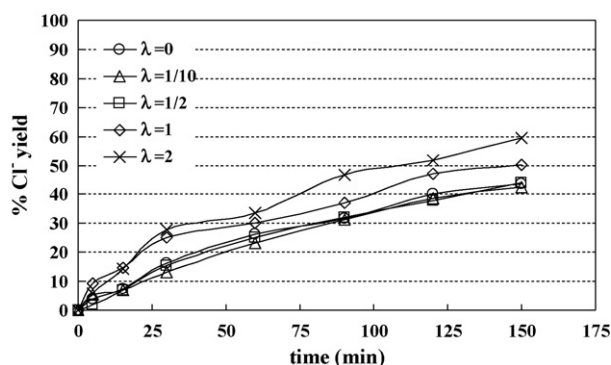
total amount every 30 min. However, no change was observed after 150 min compared to the base experiment of $\lambda = 1$.

3.2. Influence of 2-chlorophenol initial concentration

The effect of 2-chlorophenol initial concentration on the process was also examined. In order to find the concentration range of photo-oxidation efficient application using the specific apparatus, the initial concentration of 2-CP was varied in the range of 150–3000 mg L^{-1}, keeping the initial concentration of H$_2$O$_2$ always at the stoichiometric ratio.

2-CP conversion exhibits a similar behavior for 2-CP initial concentrations 500 and 1500 mg L^{-1}, reaching 95% final conversion (Fig. 6). For an initial concentration of 150 mg L^{-1}, 2-CP was totally decomposed within the first 15 min of the reaction and TOC removal reached 70% at the end of the reaction. On the other hand, for 2-CP initial concentration 3000 mg L^{-1}, the lowest 2-CP initial degradation rate is observed, as well as the lowest final 2-CP conversion (90%).

Finally, as it can be observed in Fig. 7, the chloride ion yield is rising for decreasing 2-CP initial concentrations, indicating that a larger degree of dechlorination takes place for lower initial organic loads.

3.3. Photo-Fenton treatment of 2-chlorophenol

The feasibility of treating 2-CP aqueous solutions under the synergistic effect of the photo-Fenton reaction and of hydrogen peroxide as an extra oxidative agent was investigated. The

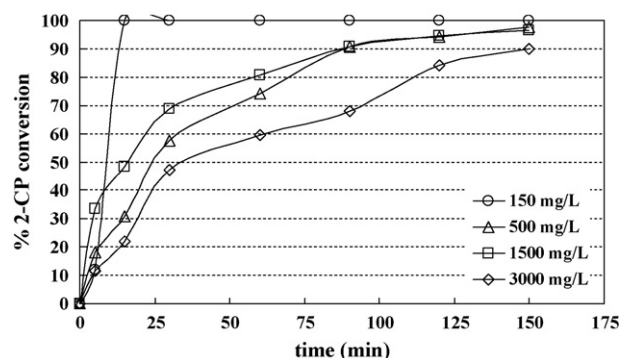Fig. 4. The effect of H$_2$O$_2$ initial concentration on Cl$^-$ yield.
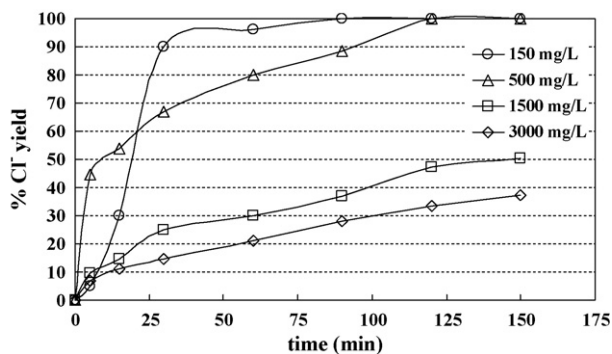

Fig. 6. The effect of 2-CP initial concentration on its conversion.

Fig. 7. The effect of 2-CP initial concentration on Cl$^-$ yield.

Fig. 9. The effect of Fe(III) addition on Cl$^-$ yield after 150 min.

initial concentration of 2-chlorophenol was $1500\,mg\,L^{-1}$, the amount of Fe(III) added was in the range of 6–112 ppm and the hydrogen peroxide initial amount was the one dictated by the stoichiometry.

The addition of ferric ions promoted significantly the photo-oxidation process. First of all, the decomposition of H_2O_2 took place at a remarkably higher extent, exceeding 80% in all cases of Fe(III) presence in contrast to 18% in the absence of Fe(III). Fe(III) increases the concentration of hydroxyl radicals in the solution by the following reactions:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe(II) + OH^-$$

$$Fe(II) + H_2O_2 \rightarrow {}^\bullet OH + OH^- + Fe(III)$$
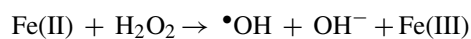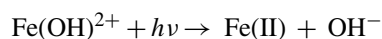
As a result, more hydroxyl radicals were produced and released in the reaction mixture to attack organic molecules. 2-CP conversion reached 100% within a few minutes in all cases of Fe(III) presence in the solution. However, only concentrations of Fe(III) above 28 ppm resulted in TOC removals around 95% after 150 min, as shown in Fig. 8. In any case, the difference in TOC removal after 150 min was pretty remarkable: from 31% in the absence of Fe(III) to 95% for 28 ppm Fe(III) added. Dechlorination of 2-CP was also greatly enhanced even at 6 ppm Fe(III), as it is obvious in Fig. 9. The production of formic acid and acetic acid, as well as the pH evolution showed that even the acids formed in the course of the process were gradually converted to carbon dioxide at the end of the experiments with Fe(III) above 28 ppm.
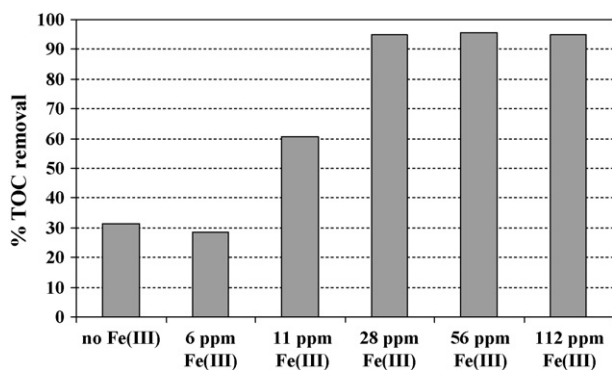
3.4. Chlorinated intermediates

The microorganisms that have the ability to biodegrade phenolic compounds include bacteria, such as *Alcaligenes eutrophus*, *Bacillus stearothermophilus*, *Pseudomonas* sp., *Rhodococcus* sp., *Phanerochaete chrysosporium*, *Cryptococcus elivonii*, yeasts such as *Candida tropicalis*, *Trichosporon cutaneum*, and fungi such as *Fusarium flocciferum* [22–24]. 2-chlorophenol is a very toxic and poorly biodegradable pollutant and wastewaters containing 2-chlorophenol over 200 ppm may not be treated efficiently by direct biological methods [16]. Generally, chlorinated compounds exhibit resistance to biodegradation, and chemical oxidation is usually employed to treat solutions of these compounds prior to biological process [15]. The knowledge of the concentration of chlorinated intermediates of 2-CP during its photo-oxidation is of great importance, if the process is to be combined with a biological unit. In the present study, quantitative determination of formic acid, acetic acid, 2-chlorophenol and chloride ion concentration allowed the indirect estimation of the chlorinated intermediate. According to previous studies, among the various possible intermediates (i.e. catechol, hydroxyhydroquinone, hydroxybenzaldehyde), chlorohydroquinone is the only chlorinated intermediate during 2-chlorophenol photochemical oxidation, or at least the only one detected in considerable amounts [17,18]. So, converting all concentrations measured to equivalent carbon, the concentration of the chlorinated intermediate can be calculated by means of chloride ion concentration. In Fig. 10, the concentration of the
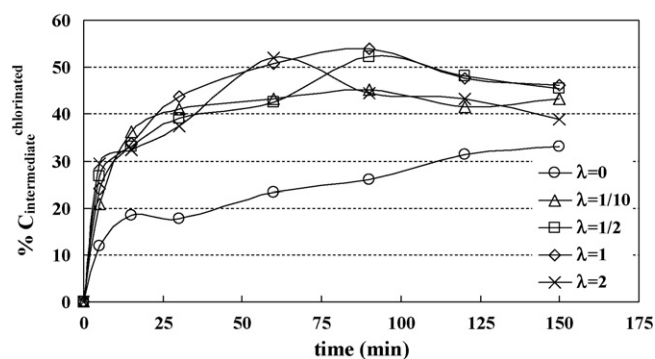

Fig. 8. The effect of Fe(III) addition on TOC removal after 150 min.

Fig. 10. The effect of H_2O_2 initial concentration on the formation of chlorinated intermediate.
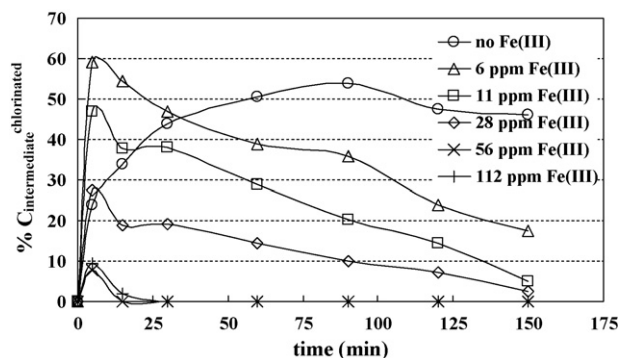
Fig. 11. The effect of Fe(III) presence on the formation of chlorinated intermediate.

chlorinated intermediate is presented, expressed as percentage (%) of the initial carbon inserted in the reactor, in the case of H_2O_2 initial concentration variation. The differences in the concentration of the chlorinated intermediate due to the change of H_2O_2 initial concentration were not so important. The photolysis of 2-CP ($\lambda = 0$) led to the formation of lower amounts of chlorinated intermediate, simply because lower conversions of 2-CP had been achieved. In the experiments of 2-CP initial concentration variation, the formation of the chlorinated intermediate was estimated to be above 7% only for 2-CP concentrations above $500 \, mg \, L^{-1}$.

The evolution of the chlorinated intermediate in the reactor solution in the photo-Fenton reaction is of particular interest. As it can be seen in Fig. 11, after the addition of Fe(III) the chlorinated intermediate was gradually eliminated. The increase in Fe(III) amount added led to lower amounts of chlorinated intermediate formed. Rao et al. [17] reported that the aryl-Cl bond undergoes cleavage very quickly, resulting in the release of inorganic Cl^- in the solution. This means that the toxicity of 2-CP is considerably reduced, since the hydroxylated intermediates may be easily biodegraded. In other words, an enhancement of biodegradability takes place. In total agreement with these observations, since the intermediate products were not largely chlorinated phenolic compounds, a great decrease in the toxicity can be considered to have been achieved by using Fe(III) in the process.

4. Conclusions

In the present study the photochemical oxidation of 2-CP was studied, as well as the photo-Fenton reaction of 2-CP. The main conclusions of this work are the following:

(a) The photo-oxidation process was much more effective for 2-chlorophenol initial concentrations below $500 \, mg \, L^{-1}$.
(b) The initial concentration of hydrogen peroxide had no significant impact on total organic carbon removal, whereas the gradual addition of H_2O_2 in the reaction mixture did not promote the process.
(c) The addition of ferric ions in the reaction mixture enhanced significantly the photo-oxidation of 2-CP, leading to complete dechlorination of organic load and total organic carbon

removals of 95% after 150 min for Fe(III) concentrations above 28 ppm.

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