

Comparison of Different Advanced Oxidation Processes for Degrading 4-Chlorophenol

M.D. Murcia, M. Gomez, E. Gomez, J.L. Gomez, and N. Christofi

Abstract—The removal efficiency of 4-chlorophenol with different advanced oxidation processes have been studied. Oxidation experiments were carried out using two 4-chlorophenol concentrations: 100 mg L⁻¹ and 250 mg L⁻¹ and UV generated from a KrCl excilamp with (molar ratio H₂O₂: 4-chlorophenol = 25:1) and without H₂O₂, and, with Fenton process (molar ratio H₂O₂:4-chlorophenol of 25:1 and Fe²⁺ concentration of 5 mg L⁻¹).

The results show that there is no significant difference in the 4-chlorophenol conversion when using one of the three assayed methods. However, significant concentrations of the photoproducts still remained in the media when the chosen treatment involves UV without hydrogen peroxide. Fenton process removed all the intermediate photoproducts except for the hydroquinone and the 1,2,4-trihydroxybenzene. In the case of UV and hydrogen peroxide all the intermediate photoproducts are removed.

Microbial bioassays were carried out utilising the naturally luminescent bacterium *Vibrio fischeri* and a genetically modified *Pseudomonas putida* isolated from a waste treatment plant receiving phenolic waste. The results using *V. fischeri* show that with samples after degradation, only the UV treatment showed toxicity (IC₅₀ = 38) whereas with H₂O₂ and Fenton reactions the samples exhibited no toxicity after treatment in the range of concentrations studied. Using the *Pseudomonas putida* biosensor no toxicity could be detected for all the samples following treatment due to the higher tolerance of the organism to phenol concentrations encountered.

Keywords—4-chlorophenol, Fenton, photodegradation, UV, excilamp.

I. INTRODUCTION

CHLOROPHENOLS are classified as hazardous chemicals [1]-[3]. Most of these compounds are toxic, carcinogens and their toxicity increases with the degree of chlorination.

In general, chlorophenols are used as agricultural chemicals, pharmaceuticals, biocides and dyes, while the main uses of 4-chlorophenol are the following: for the extraction of

sulphur and nitrogen from coal, as an intermediate in the synthesis of dyes and drugs, as a denaturant in alcohol or a solvent in the refining of oils.

Current methods for the removal of those compounds include solvent extraction, microbial and enzymatic degradation, adsorption on activated carbon, and chemical oxidation. Although these methods are effective, there are problems to using them including high cost, concentration, formation of hazardous by-products, and applicability to only a limited concentration range [4]-[9].

Among the methods considered, photochemical degradation of the contaminants in water is of particular interest and potential. The use of UV radiation and strong chemical oxidizing agents constitutes one type of combined advanced oxidation processes (AOPs) [10], that can be particularly effective in the removal of toxic chlorophenols from water and wastewater [11]-[14].

In general, the high-, medium- and low-pressure UV mercury lamps, at a wavelength of primarily 254 nm, are typically used in photolysis of chlorophenols [10], [15], [16] and, frequently, catalysts have been used to improve the process efficiency, titanium dioxide being the most commonly used [17], [19].

Among other UV radiation sources, attention is focusing on the development of excimer lamps (excilamps) and their use in the destruction of toxic organic pollutants from wastewater [20], [21]. Excilamps are a class of spontaneous radiation sources based on transitions of exciplex (rare gas halides) or excimer molecules (rare gas or halogen dimers). They emit a narrow-band ultraviolet radiation. Excilamps are attractive alternatives to commonly used mercury lamps and lasers for applications in pollution control technology because of the absence of elemental mercury, long lifetime (from 1000 to 10000 h), geometric freedom, high photon flux and other lamp advantages [22].

The combination of hydrogen peroxide with ferrous ions in the so-called Fenton reagent is also used [23]. The Fenton process has been used in the removal of phenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol [24], [22].

In the present work three different advanced oxidation processes have been tested for the removal of 4-chlorophenol: UV photodegradation using a KrCl excilamp; combined UV oxidation with KrCl excilamp and H₂O₂, and, the use of Fenton reagent.

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II. MATERIALS AND METHODS

A. Reagents

4-chlorophenol (99%), 4-chlorocatechol (97%), resorcinol (99%), 4-chlororesorcinol (98%), chlorohydroquinone (85%) and p-benzoquinone (98%) were obtained from Aldrich. Hydroquinone (99%), catechol (99%) and hydrogen peroxide (30%) were purchased from Sigma. Phenol (99.5%) and FeSO_4 were purchased from BDH. 1,2,4-trihydroxybenzene (99%) was purchased from Alfa Aesar.

B. Materials

A KrCl excilamp, emitting maximum UV radiation at 222 nm, has been used. The excilamp was of cylindrical geometry covered by a metal case having an UV exit window with an area of 75 cm^2 . The exit window was oriented vertically in close proximity to a quartz tube with an operating length of 22 cm and external diameter of 2.6 cm. The output power of the excilamp was measured with a H8025-222 photodetector (Hamamatsu Photonics KK) and was tested using an electrochemical actinometer. The average radiation intensity delivered to the solution was 2.47 mW cm^{-2} .

C. 4-Chlorophenol Treatment Method

For the experiments with the UV lamp, 4-chlorophenol at two different concentrations, 100 and 250 mg L^{-1} (0.78 to 1.95 mM) was dissolved in 10 ml of distilled water, placed into the quartz tube covered with a reflector and irradiated at room temperature (23 – $25 \text{ }^\circ\text{C}$) under static conditions and for exposure times ranging from 20 to 90 minutes.

For the experiments with the UV lamp and hydrogen peroxide, 4-chlorophenol at two different concentrations, 100 and 250 mg L^{-1} was mixed with hydrogen peroxide at the appropriate concentration (molar ratio H_2O_2 : 4-chlorophenol = 25:1 was), and placed into the quartz tube covered with a reflector and irradiated at room temperature (23 – $25 \text{ }^\circ\text{C}$) under static conditions and for exposure times ranging from 20 to 60 minutes.

For the Fenton experiments, 4-chlorophenol at two different concentrations, 100 and 250 mg L^{-1} was treated with Fenton reagent (Hydrogen peroxide + FeSO_4). A constant molar ratio H_2O_2 : 4-chlorophenol = 25:1 was used, and different FeSO_4 concentrations (1 , 2.5 , 5 , 10 and 20 mg L^{-1}) were tested. All experiments were carried out at room temperature (23 – $25 \text{ }^\circ\text{C}$) under static conditions and for exposure times of 120 minutes.

D. Determination of 4-Chlorophenol and Photoproducts

Any 4-chlorophenol remaining after the treatment, as well as the main and minor photoproducts of the photodegradation process, were determined by HPLC analysis, at 283 nm, using a Varian Prostar 210 chromatograph with UV-vis detector and a C18 reverse phase column. The mobile phase was a mixture of methanol, acetic acid and water ($60:2.5:37.5 \text{ v/v}$) with a flow rate of 1 ml min^{-1} . Retention times for the different photoproducts were as follows: 1,2,4-trihydroxybenzene, 1.9 min; hydroquinone, 2.1 min; resorcinol, 2.26 min; benzoquinone, 2.39 min; 4-chlorohydroquinone, 2.46 min;

catechol, 2.59 min; 4-chlororesorcinol, 3.06 min; phenol, 3.49 min; 4-chlorocatechol, 4.2 min; chlorophenol, 6.2 min.

E. Hydrogen Peroxide Determination

A colorimetric method [25] has been used for hydrogen peroxide determination. To $20 \mu\text{l}$ of the sample containing hydrogen peroxide, 4.0 ml of HCl (50 mmol L^{-1}), 0.4 ml of KI (1.0 mol L^{-1}), 0.4 ml of ammonium molybdate (1.0 mmol L^{-1} prepared in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$) and 0.4 ml of starch solution (consisting of 5.0 g of soluble starch solved in 100 ml of water) were added. After 20 minutes the absorbance versus a water control was measured at 570 nm .

F. Toxicity Bioassays

Toxicity of untreated and treated samples was carried out using bioluminescence decay in the light emitting bacteria *V. fischeri* (natural isolate) and *Pseudomonas putida* (engineered to carry a stable chromosomal copy of the lux operon (luxCDABE) derived from *Photobacterium luminescens*). Assays were carried out using bacteria challenged with different concentration of sample and IC_{50} calculated. Luminescence decay measurements were undertaken using white microtitre plates in a 96-well plate luminometer (Fluorstar optima, BMG Labtech) with an integration time of 300 seconds at a temperature of $26 \text{ }^\circ\text{C}$. Luminescence values were expressed as a percentage of the luminescence of a control well [26], [27].

III. RESULTS AND DISCUSSION

A. 4-Chlorophenol Removal

Fig. 1 shows 4-chlorophenol degradation at two different concentrations, 100 and 250 mg L^{-1} using KrCl excilamp in the absence of hydrogen peroxide, in the presence of hydrogen peroxide with a molar ratio H_2O_2 :4-chlorophenol of 25:1 and with Fenton with a Fe^{2+} concentration of 5 mg L^{-1}

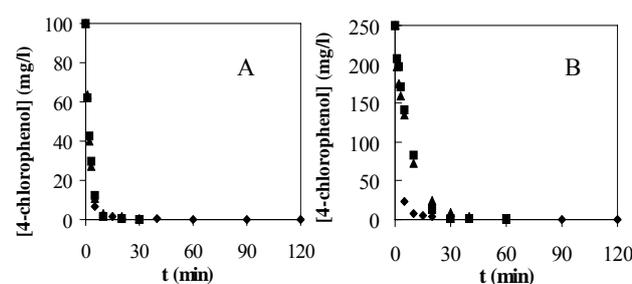


Fig. 1 Treatment of 4-chlorophenol solution of 100 mg L^{-1} (A) and 250 mg L^{-1} (B) with different methods: \blacktriangle KrCl excilamp without H_2O_2 , \blacksquare KrCl excilamp with H_2O_2 , \blacklozenge Fenton

In a previous work [28] three different excilamps were tested: XeBr, KrCl and Cl_2 . The results showed that the XeBr and KrCl excilamps attained total 4-chlorophenol degradation and much lower conversion were achieved with the Cl_2 excilamp. However, the KrCl excilamp is the one that attains higher conversions with lower UV dose. As a conclusion, the

KrCl seems to be the most appropriate for efficient 4CP degradation with low energy requirements.

The molar ratio $\text{H}_2\text{O}_2/4\text{-chlorophenol}$ 25:1 [29] was chosen for results comparison as using this ratio, total removal is achieved for the 4-chlorophenol and photoproducts, in about 20 and 40 minutes for initial 4-chlorophenol concentrations of 100 and 250 mg L^{-1} , respectively. Lower molar ratios do not achieve efficient photoproduct degradation and higher ratios would lead to an excess of hydrogen peroxide that remains at the end of the reaction process.

An Fe^{2+} concentration of 5 mg L^{-1} was chosen because this has been determined as the lowest concentration that completely removes the 4-chlorophenol.

Fig. 1 shows that there is no significant difference in 4-chlorophenol degradation when using the KrCl excilamp with or without H_2O_2 or Fenton with the initial 4-chlorophenol concentration of 100 mg L^{-1} , whereas for the 250 mg L^{-1} concentration the 4-chlorophenol is rapidly removed with the Fenton treatment. The efficacy of removal for the 4-chlorophenol removal with KrCl excilamp with and without H_2O_2 are practically the same.

In order to establish the most efficient treatment, intermediate reaction products have to be delineated and production and disappearance compared.

B. Photoproducts Removal

In 4-chlorophenol degradation different photoproducts have been identified: hydroquinone, benzoquinone, 4-chlorocatechol, resorcinol, 4-chlorohydroquinone, catechol, 4-chlororesorcinol, phenol and 1,2,4-trihydroxibenzene

In Fig. 2-10 the photoproducts concentration removal are represented for the two initial 4-chlorophenol concentrations 100 mg L^{-1} and 250 mg L^{-1} .

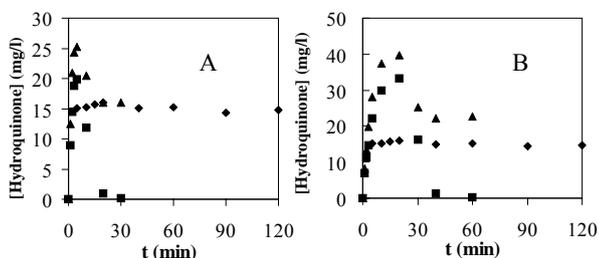


Fig. 2 Hydroquinone concentration variation over time for 4-chlorophenol initial concentration of 100 mg L^{-1} (A) and 250 mg L^{-1} (B) with different methods: ▲ KrCl excilamp without H_2O_2 , ■ KrCl excilamp with H_2O_2 , ◆ Fenton

In Fig. 2 we observed that with the KrCl excilamp, after 30 minutes of treatment, the concentration of hydroquinone remaining in the reaction is very high at $\sim 15 \text{ mg L}^{-1}$ and 22 mg L^{-1} for the two 4-chlorophenol concentrations, the same behaviour is observed over 120 minutes of treatment with Fenton whereas with the combination of the KrCl excilamp with hydrogen peroxide, total removal of hydroquinone is obtained with the two initial 4-chlorophenol concentration assayed.

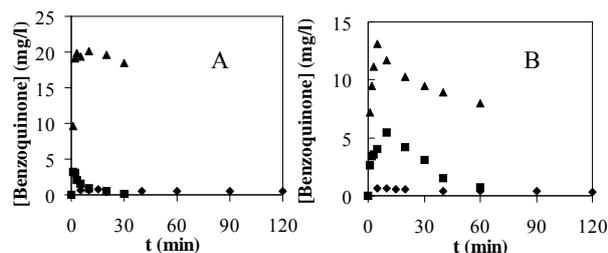


Fig. 3 Benzoquinone concentration variation over time for 4-chlorophenol initial concentration of 100 mg L^{-1} (A) and 250 mg L^{-1} (B) with different methods: ▲ KrCl excilamp without H_2O_2 , ■ KrCl excilamp with H_2O_2 , ◆ Fenton

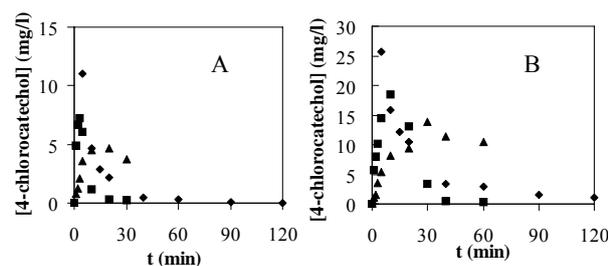


Fig. 4 4-chlorocatechol concentration variation over time for 4-chlorophenol initial concentration of 100 mg L^{-1} (A) and 250 mg L^{-1} (B) with different methods: ▲ KrCl excilamp without H_2O_2 , ■ KrCl excilamp with H_2O_2 , ◆ Fenton

In Fig. 3, we see that high benzoquinone concentrations remain after treatment with the excilamp. However, with hydrogen peroxide or treatment with Fenton, there is considerable improvement in the removal of this photoproduct.

In Figs. 4-9, the same behaviour previously described is seen with high photoproduct concentrations remaining following treatment with the KrCl excilamp.

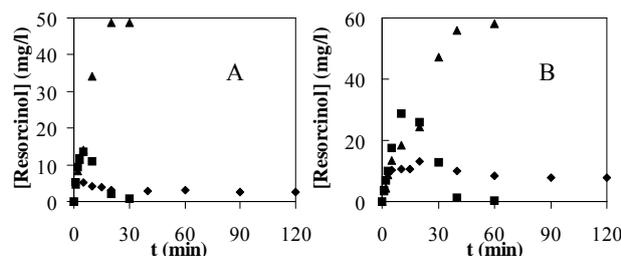


Fig. 5 Resorcinol concentration variation over time for 4-chlorophenol initial concentration of 100 mg L^{-1} (A) and 250 mg L^{-1} (B) with different methods: ▲ KrCl excilamp without H_2O_2 , ■ KrCl excilamp with H_2O_2 , ◆ Fenton

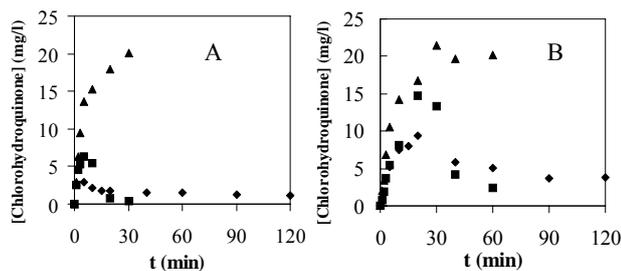


Fig. 6 Chlorohydroquinone concentration variation over time for 4-chlorophenol initial concentration of 100 mg L⁻¹ (A) and 250 mg L⁻¹ (B) with different methods: ▲ KrCl excilamp without H₂O₂, ■ KrCl excilamp with H₂O₂, ◆ Fenton

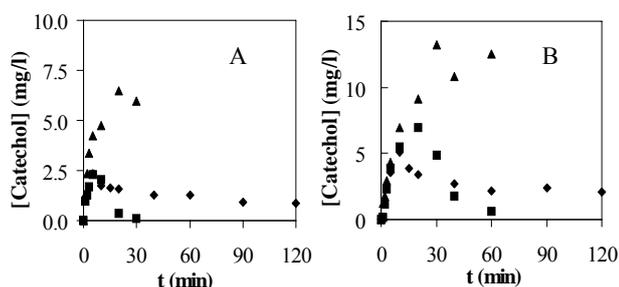


Fig. 7 Catechol concentration variation over time for 4-chlorophenol initial concentration of 100 mg L⁻¹ (A) and 250 mg L⁻¹ (B) with different methods: ▲ KrCl excilamp without H₂O₂, ■ KrCl excilamp with H₂O₂, ◆ Fenton

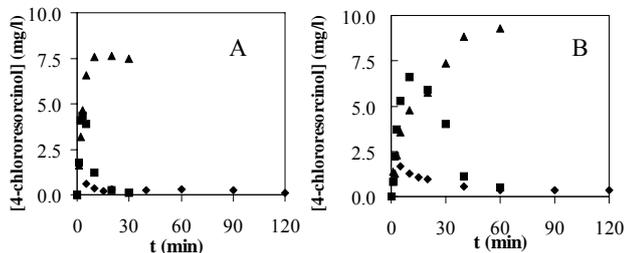


Fig. 8 4-chlororesorcinol concentration variation over time for 4-chlorophenol initial concentration of 100 mg L⁻¹ (A) and 250 mg L⁻¹ (B) with different methods: ▲ KrCl excilamp without H₂O₂, ■ KrCl excilamp with H₂O₂, ◆ Fenton

In Fig. 10 the photoproduct, 1,2,4-trihydroxybenzene, only appears with the Fenton reagents, being the only photoproduct that is not detected after treatment with the excilamp alone.

C. Toxicity Test

In order to study the efficacy of the three methods we have calculated the IC₅₀ at 5 minutes (Inhibitory concentration – reduction of luminescence in the bacteria by 50%) for each system before and after the treatment. Two biosensor bacteria have been used in these experiments: *V. fischeri* and *P. putida* (*P.p*) isolated from an aerobic waste treatment plant treating phenolic waste from a coking plant. The results are shown in

Table I. Non-toxic refers to assays carried out up to 250 mg L⁻¹ concentrations of 4-chlorophenol.

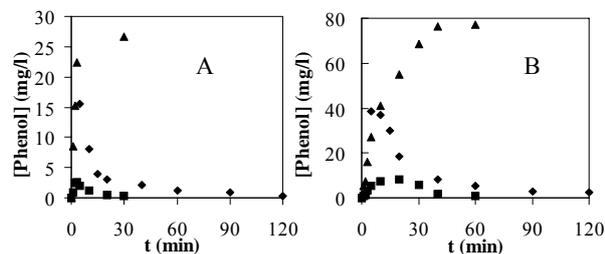


Fig. 9 Phenol concentration variation over time for 4-chlorophenol initial concentration of 100 mg L⁻¹ (A) and 250 mg L⁻¹ (B) with different methods: ▲ KrCl excilamp without H₂O₂, ■ KrCl excilamp with H₂O₂, ◆ Fenton

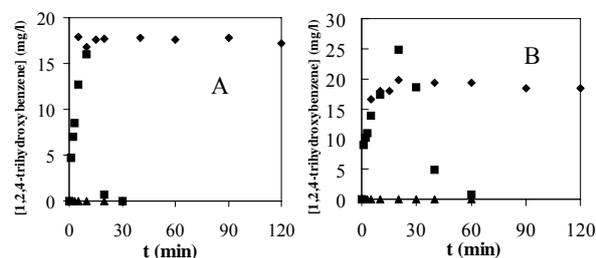


Fig. 10 1,2,4-trihydroxybenzene concentration variation over time for 4-chlorophenol initial concentration of 100 mg L⁻¹ (A) and 250 mg L⁻¹ (B) with different methods: ▲ KrCl excilamp without H₂O₂, ■ KrCl excilamp with H₂O₂, ◆ Fenton

	KrCl excilamp		KrCl excilamp + H ₂ O ₂		Fenton	
	<i>P.p</i>	<i>Vibrio</i>	<i>P.p</i>	<i>Vibrio</i>	<i>P.p</i>	<i>Vibrio</i>
Before treatment (mg L ⁻¹)	165	38	165	38	165	38
After treatment (mg L ⁻¹)	Non toxic	50	Non toxic	Non toxic	Non toxic	Non toxic

In Table I *V. fischeri* assays using samples from the three treatment methods, the toxicity is lower after the treatment. However, the reduction in toxicity is more pronounced with the combination of the KrCl with hydrogen peroxide and with the Fenton. For these two treatments the IC₅₀ values after the treatment are higher than 250 mg L⁻¹. The IC₅₀ after treatment with the KrCl is 50 mg L⁻¹ which are likely attributed to the presence of the photoproducts of the reaction.

The *P. putida* luminescent biosensor bacteria was isolated from an activated sludge plant where there are high concentrations of phenolic compounds. The organism is thus more tolerant to these compounds and hence not affected by concentrations to which they are challenged.

IV. CONCLUSION

4-chlorophenol concentration was totally removed with the three oxidation advanced processes assayed: KrCl excilamp, KrCl excilamp with hydrogen peroxide and Fenton reagent. However, the intermediates photoproducts of the reaction were only totally removed with the KrCl excilamp combined with hydrogen peroxide.

The KrCl excilamp without H₂O₂ does not completely remove the photoproducts and with the Fenton processes, hydroquinone and 1,2,4-trihydroxybenzene remained in the treatment systems. Low toxicity was seen using the sensitive *V. fischeri* after treatment, where the IC₅₀ values were higher than 250 mg L⁻¹ for the combined KrCl excilamp/hydrogen peroxide process and the Fenton one. This implies that at concentration normally found in most waste streams treatment systems used would reduce the toxicity of 4-chlorophenol and would not produce by-products that are toxic.

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