Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Online publication date: 19 July 2010

To cite this Article Gomez, M. , Murcia, M. D. , Gomez, E. , Gomez, J. L. , Dams, R. and Christofi, N.(2010) 'Enhancement of 4-Chlorophenol Photodegradation with KrCl Excimer UV Lamp by Adding Hydrogen Peroxide', Separation Science and Technology, 45: 11, 1603 — 1609
To link to this Article: DOI: 10.1080/01496395.2010.487714
URL: http://dx.doi.org/10.1080/01496395.2010.487714

Separation Science and Technology, 45: 1603–1609, 2010

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.487714

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Enhancement of 4-Chlorophenol Photodegradation with KrCl Excimer UV Lamp by Adding Hydrogen Peroxide

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4-Chlorophenol removal combining KrCl excimer UV lamp and H_2O_2 has been studied, using 4-chlorophenol concentrations of 100 and 250 mg L^{-1} and molar ratios H_2O_2: 4-chlorophenol = 1:1, 10:1, 25:1, and 50:1. A ratio of 25:1 achieves the total removal for both 4-chlorophenol and the photoproducts. Comparing these results with those corresponding to the use of excilamp treatment in the absence of H_2O_2, there is no difference in 4-chlorophenol degradation. The excilamp alone, however, leads to the incomplete removal of photoproducts. Additionally, significant COD decrease is attained in the samples treated with UV/H_2O_2 and toxicity bioassays with *Pseudomonas putida* show important toxicity alleviation.

Keywords 4-chlorophenol; AOPs; excilamp; hydrogen peroxide; photodegradation

INTRODUCTION

Chlorophenols are one of the most important groups of pollutants in various wastewaters, such as pulp and paper industry (1,2). Most of these compounds are toxic, and carcinogens and their toxicity increases with the degree of chlorination. They are classified as hazard chemicals (3–5) and constitute a particular group of priority toxic pollutants listed by the US EPA in the Clean Water Act (6) and by the European Directive 2455/2001/EC (7). Among the monochlorophenols, 4-chlorophenol is much more toxic than either 2- or 3-chlorophenol. The value of the 50% Lethal Doses (LD_{50}) of 4-chlorophenol for rats is 261 mg kg^{-1} for oral doses and 1390 mg kg^{-1} for percutaneous injection.

Current methods for the removal of those compounds include solvent extraction (8), membrane technology (9), microbial degradation (10), adsorption on activated carbon (11), and chemical oxidation. Although these methods are effective, they suffer from such defects as high cost, formation of hazardous by-products, and applicability to only a limited concentration range.

The chemical oxidation of toxic and hazardous organic pollutants is often carried out using single oxidants such as air or oxygen in wet oxidation and supercritical wet oxidation (12), using chlorine, potassium permanganate, ozone, and hydrogen peroxide (13). However, decomposition by conventional treatments may be difficult if pollutants are present in low concentrations or if they are especially resistant to the oxidants used. In such situations, it has been necessary to develop more effective processes for the destruction of the contaminants. Among these, systems based on the generation of very reactive and oxidizing free radicals, especially hydroxyl radicals, have aroused increasing interest due to their high oxidant power. Such systems are commonly named Advanced Oxidation Processes (AOPs), and, the radicals are produced by combining ozone, hydrogen peroxide, and UV radiation. The combination of hydrogen peroxide with ferrous ions in the so-called Fenton reagent is also used (14).

AOPs embrace a number of degradation methods for removal (15). The use of UV radiation and strong chemical oxidizing agents constitutes one type of combined advanced oxidation process that can be particularly effective in the removal of toxic chlorophenols from water and wastewater (16–18).

In general, high-, medium-, and low-pressure UV mercury lamps, at a wavelength of primarily 254 nm, are typically used in photolysis of chlorophenols (15,19). Current research in UV oxidation using excimer lamps is showing promise as an alternative to traditional UV sources (20,21). Excimer lamps, or excilamps, are a class of spontaneous radiation sources based on transitions of exciplex (rare gas halides) or excimer molecules (rare gas or halogen dimers) that emit in a narrow-band ultraviolet radiation. Excilamps are considered effective alternatives to mercury lamps and lasers for applications in pollution

Received 9 November 2009; accepted 20 April 2010.
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control technology because of the absence of elemental mercury, long lifetime (from 1000 to 10000 h), geometric freedom, high photon flux, and other advantages. Excimer lamps have been proven to be of great interest in wastewater treatment, since the majority of components contained in water absorb radiation in the same range (200–320 nm) of the excilamp emissions.

However, although advanced oxidation processes have demonstrated high efficiency in removing chlorophenolic compounds, less attention has been given to the evaluation of the treatment results as a whole. Complete mineralization into carbon dioxide is hardly ever obtained and hydroxylated aromatics, such as catechol, hydroquinone, benzoquinone, and 1,2,4-trihydroxybenzene and carbonyl compounds are typically involved in contaminant degradation (22–24). The residual oxidation products can persist after treatment because of their low reactivity towards the oxidants (25). For this reason, prior to the discharge into the environment, it is necessary to evaluate the formation of toxic intermediates as a result of the partial oxidation of the original pollutant compound.

Toxicity bioassay techniques are suitable to evaluate the overall effectiveness of wastewater treatment (26). A common method utilizes the bioluminescent bacterium *Vibrio fischeri* because of its rapid response time, widespread use, and quality controlled reagents (27). Other rapid methods use stress-inducible bioluminescent bacteria containing a fusion of a stress promoter to the *lux*CDABE gene operon (28). Different genetically modified bacteria have been used to study the toxicity, GC2 (*lac::luxCDABE*) (29), TV1061 (*grpE::luxCDABE*) (30), DPD2540 (*fabA::luxCDABE*) (31), DPD2794 (*recA::luxCDABE*) (32), DPD2511 (*kat::luxCDABE*) (33).

In the present work, a combined AOP treatment, based on photodegradation with a KrCl excilamp and further oxidation with H_2O_2, has been tested for the removal of 4-chlorophenol. In order to establish the final toxicity after the treatment, toxicity bioassays with a bacterial strain *Pseudomonas putida BS566::luxCDABE* were carried out.

MATERIALS AND METHODS

Reagents

4-Chlorophenol (purity 99%), hydrogen peroxide (30%), 4-chlorocatechol (97%), resorcinol (99%), 4-chlororesorcinol (98%), chlorohydroquinone (85%), p-benzoquinone (98%), hydroquinone (99%), and catechol (99%) were purchased from Sigma-Aldrich Fine Chemicals. Phenol (99.5%) was purchased from BDH and 1,2,4-trihydroxybenzene (99%) was purchased from Alfa Aesar. Other chemicals were of analytical grade and were used without further purification.

Materials

A KrCl excilamp, purchased from the Institute of High Current Electronics of the Siberian Branch of the Russian Academy of Sciences and emitting maximum UV radiation at 222 nm, was used. The excilamp is of cylindrical geometry covered by a metal case having an UV exit window with an area of 75 cm^2. The exit window is 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 tested using an electrochemical actinometer. The average radiation intensity delivered to the solution was determined at 2.47 mW cm^{-2}.

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 and 1.95 mM) was dissolved in 10 ml of distilled water, and, placed into quartz reaction tubes covered with a reflector and UV irradiated at laboratory temperature ($24 \pm 1°C$) under static conditions for periods up to 60 minutes.

For the experiments with the UV lamp and hydrogen peroxide, 4-chlorophenol at 100 and 250 mg L^{-1} was combined with hydrogen peroxide at appropriate concentrations (molar ratios H_2O_2: 4-chlorophenol of 1:1, 10:1, 25:1, and 50:1 were used), placed into quartz reaction tubes covered with a reflector and UV irradiated following the above procedure.

Determination of 4-Chlorophenol and Photoproducts

4-chlorophenol and different photoproducts remaining following UV treatment were analysed by HPLC analysis. Detection of photoproducts was done 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 v/v) with a flow rate of 1 mL min^{-1}.

Hydrogen Peroxide Determination

A colorimetric method (34) was used for hydrogen peroxide determination. To 20 µl of the sample containing hydrogen peroxide, 4.0 ml of HCl (50 m mol L^{-1}), 0.4 ml of KI (1.0 mol L^{-1}), 0.4 ml of ammonium molybdate (1.0 m mol L^{-1} prepared in 0.5 mol L^{-1} H_2SO_4), and 0.4 ml of starch solution (consisting of 5.0 g of soluble starch dissolved in 100 ml of water) were added. After 20 minutes the absorbance versus a water control was measured at 570 nm.

COD Determination

Chemical Oxygen Demand (COD) was measured using commercial COD vials of mid range (0–1500 mg L^{-1}) and a CAMLAB direct reading spectrophotometer DR/2000.

Toxicity Bioassays

Toxicity of 4-chlorophenol and each photoproduct was determined using bioluminescence decay in the light emitting bacteria *Pseudomonas putida* (engineered to carry a stable chromosomal copy of the lux operon (luxCDABE) derived from *Photorhabdus luminescens*). The bacterium was originally isolated from an activated sludge plant treating phenolic waste from a coke plant. Assays were carried out using bacteria challenged with a different concentration of the sample. Luminescence decay measurements were undertaken using black microtitre plates in a 96-well plate luminometer (Fluorstar optima, BMG Labtech) with an integration time of 30, 90, 180, and 240 min at a temperature of 26°C. Luminiscence (IC-Inhibitory Concentration) values were expressed as a percentage of the luminescence of a control well (35).

The IC values are calculated using a statistical program that was developed in-house. The program fits a three parameter logistic model to the logarithm of the concentration by weighted least squares.

RESULTS AND DISCUSSION

Optimum Molar Ratio H_2O_2/4-Chlorophenol

In order to choose the optimum molar ratio H_2O_2:4-chlorophenol for the process, two 4-chlorophenol concentrations, 100 and 250 mg L^{-1}, were tested with four different molar ratios, 1:1, 10:1, 25:1, and 50:1. The results for the two 4-chlorophenol concentrations are shown in Figs. 1 and 2, respectively, expressed as variation of the concentration of the different species involved in the process with time.

It can be seen from Fig. 1 that complete removal of 4-chlorophenol is achieved with the four molar ratios assayed. However, complete removal of all the by-products is achieved in approximately 20 minutes of treatment only with molar ratios of H_2O_2:4-chlorophenol 25:1 and 50:1 (Figs. 1c and d, respectively). Using lower molar ratios (Figs. 1a and b) a mixture of photoproducts still remains in the reaction media. In order to check the toxicity of this final mixture, the non-effect concentrations (in this study this represented the concentration needed to inhibit 0.1% of the biosensor organisms) for all the compounds involved in the process were determined by using the pure compounds. For all the assayed treatments, the values were compared with the photoproduct concentrations remaining to estimate the final toxicity. The results are presented in Table 1, showing the values at 4 different exposure times (30, 90, 180, and 240 min) and the average values. From Table 1 it can be observed that the 4-chlorophenol has a moderate toxicity and also that toxicity generally decreases with incubation time. This can be explained by the fact that microorganisms may become acclimatized to the pollutant and hence more resistant. For this reason, the average

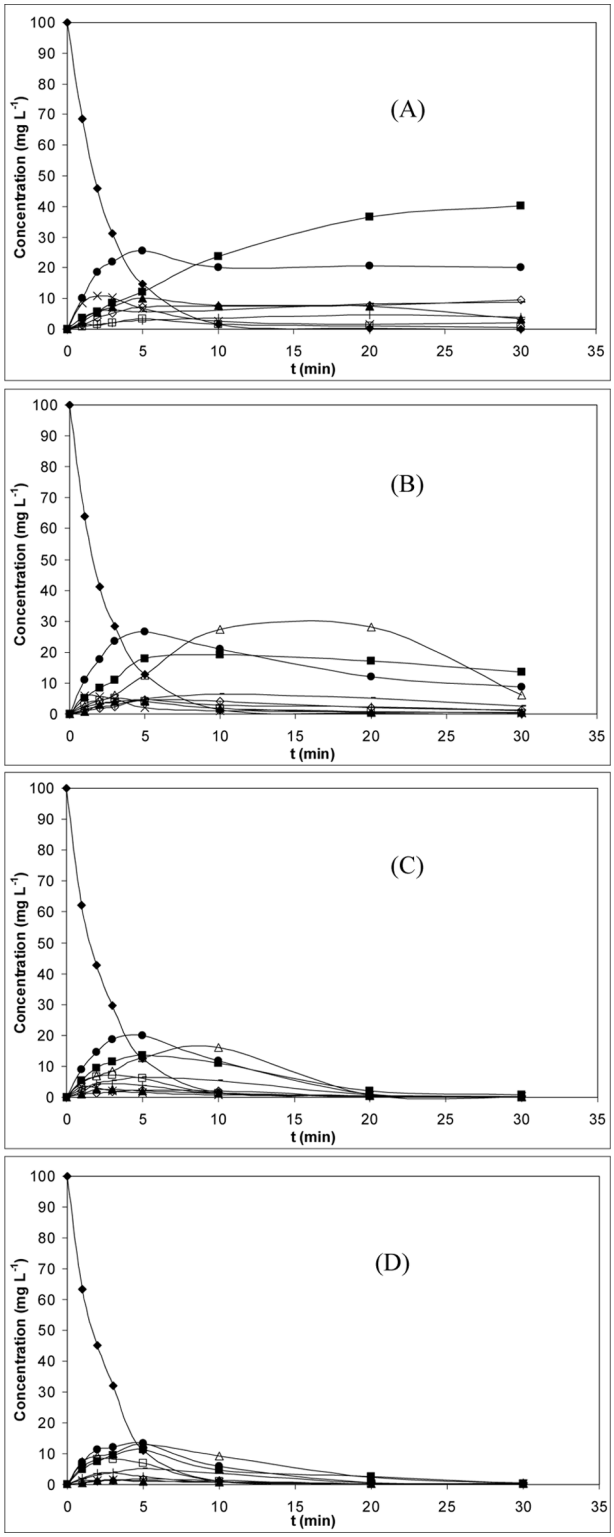

FIG. 1. Treatment of 4-chlorophenol 100 mg L^{-1} with UV/H_2O_2. Variation of substrates and photoproduct concentration versus time. ◆ 4-chlorophenol, ∗ H_2O_2, Δ 1,2,4-Trihydroxybenzene, ● Hydroquinone, ■ Resorcinol, – Chlorohydroquinone, x Benzoquinone, ◇ Catechol, + 4-chlororesorcinol, ▲ Phenol, □ 4-chlorocatechol. Molar ratios H_2O_2:4CP: (A) 1:1, (B) 10:1, (C) 25:1, and (D) 50:1.

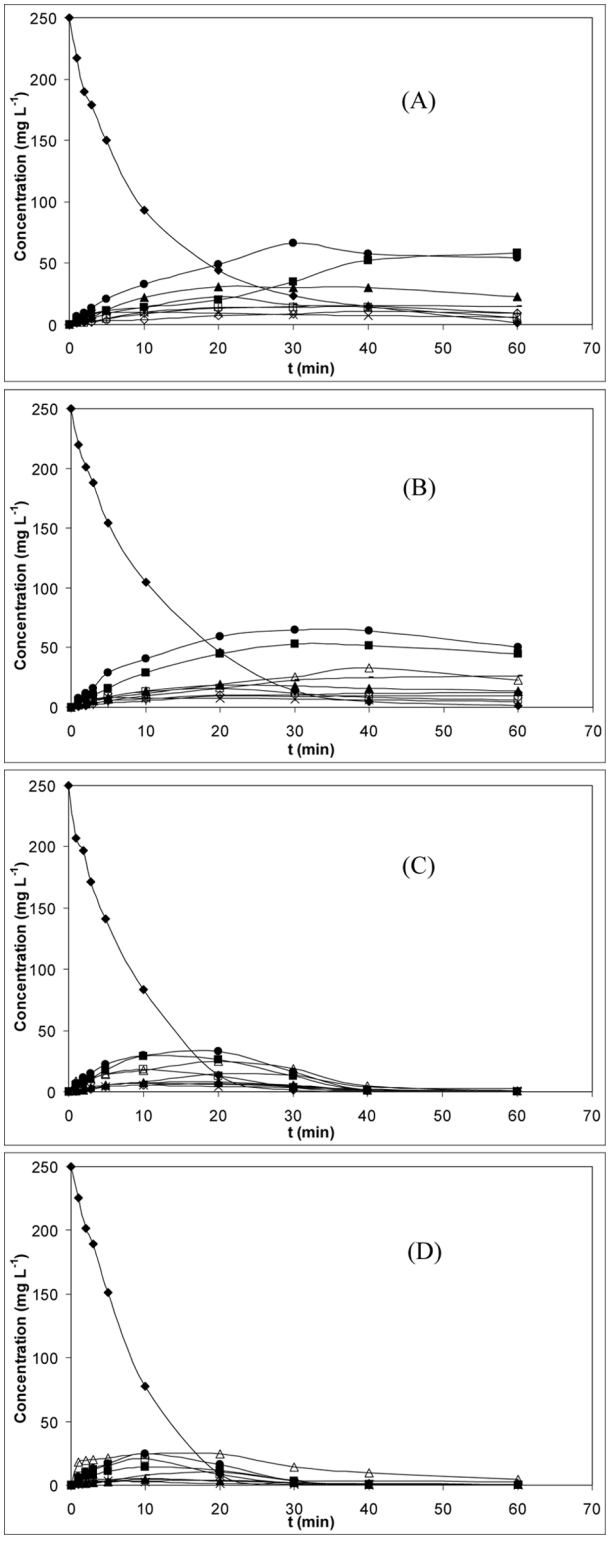

FIG. 2. Treatment of 4-chlorophenol 250 mg L^{-1} with UV/H_2O_2. Variation of substrates and photoproduct concentration versus time. ◆ 4-chlorophenol, ∗ H_2O_2, Δ 1,2,4-Trihydroxybenzene, ● Hydroquinone, ■ Resorcinol, – Chlorohydroquinone, x Benzoquinone, ◇ Catechol, + 4-chlororesorcinol, ▲ Phenol, □ 4-chlorocatechol. Molar ratios H_2O_2:4CP: (A) 1:1, (B) 10:1, (C) 25:1, and (D) 50:1.

TABLE 1
No-effect concentrations for 4-chlorophenol and photoproducts after 30, 90, 180, and 240 min. Values presented are an average of at least 3 independent experiments carried out with different batches, standard deviation between 1 and 20%

No-effect concentration ($IC_{0.1}$ mg L^{-1})					
Time (min)	30	90	180	240	Mean values
4-Chlorophenol	12.70	2.70	0.30	5.35	5.26
Phenol	0.25	0.67	20.0	49.70	17.70
Catechol	0.01	0.45	8.30	56.4	16.30
Chlorocatechol	6.70	9.80	9.90	3.10	7.38
Chlorohydroquinone	0.05	0.40	2.80	5.60	2.21
Hydroquinone	0.60	1.26	11.20	11.80	6.22
Resorcinol	0.004	0.29	4.95	21.60	6.71
Chlororesorcinol	0.03	0.13	0.97	1.36	0.62
Benzoquinone	0.01	0.02	0.025	0.03	0.02
1,2,4-Trihydroxybenzene	1.80	15.90	29.70	28.00	18.90

values have been used in the following discussion. Taking into account the results presented in Table 1, it is possible to establish that most of the photoproducts obtained with

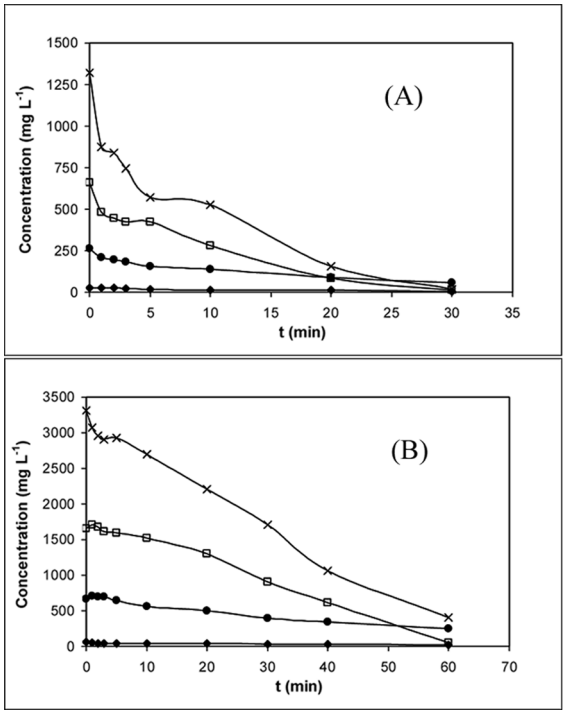

FIG. 3. Variation of hydrogen peroxide concentration over time. Molar ratios H_2O_2:4CP: ◆ 1:1, ● 10:1, □ 25:1, x 50:1. 4-Chlorophenol initial concentration: (A) 100 mg L^{-1}, (B) 250 mg L^{-1}.

the molar ratio H_2O_2:4-chlorophenol 1:1 (Fig. 1a) show some toxicity at the end of the treatment. For instance, after 30 minutes of treatment concentrations higher than the minimum no-effect value can be seen in the case of hydroquinone (20.18 mg L^{-1}), benzoquinone (2.03 mg L^{-1}), resorcinol (40.27 mg L^{-1}), chlorohydroquinone (8.72 mg L^{-1}), and 4-chlororesorcinol (3.80 mg L^{-1}) . The same behavior is obtained with the molar ratio H_2O_2:4-chlorophenol 10:1 (Fig. 1b), where toxic concentrations of hydroquine (8.72 mg L^{-1}), benzoquinone (0.35 mg L^{-1}), resorcinol (13.49 mg L^{-1}), chlorohydroquinone (2.43 mg L^{-1}), and 4-chlororesorcinol (0.96 mg L^{-1}) remain in the medium after the treatment.

Results for an initial 4-chlorophenol concentration of 250 mg L^{-1} are depicted in Fig. 2, showing that total 4-chlorophenol removal is attained with the four molar ratios H_2O_2:4-chlorophenol tested, similar to Fig. 1, but with slightly longer exposure times (40 minutes). The molar ratio H_2O_2:4-chlorophenol 25:1 has proved to be the optimum one since it is the lowest molar ratio that achieves total removal of both 4-chlorophenol and the by-products. In Figs. 2a and 2b it can be seen that toxic by-product concentrations are present after 60 minutes of treatment, as follows: hydroquinone (54.54 and 50.18 mg L^{-1}), benzoquinone (6.11 and 5.01 mg L^{-1}), resorcinol (58.15 and 44.84 mg L^{-1}), chlorohydroquinone (14.46 and 26.39 mg L^{-1}), 4-chlororesorcinol (9.47 and 9.54 mg L^{-1}), phenol (22.83 mg L^{-1} for a molar ratio 1:1) and 1,2,4-trihydroxybenzene (22.70 mg L^{-1} for a molar ratio 10:1).

In addition to the 4-chlorophenol and photoproduct degradation study, hydrogen peroxide consumption over time for each one of the H_2O_2:4-chlorophenol molar ratios tested was determined (Figs. 3a and b). Figure 3b shows that a molar ratio H_2O_2:4-chlorophenol of 50:1 leads to an excess of hydrogen peroxide at the end of the reaction process, increasing both the oxygen demand and cost of treatment.

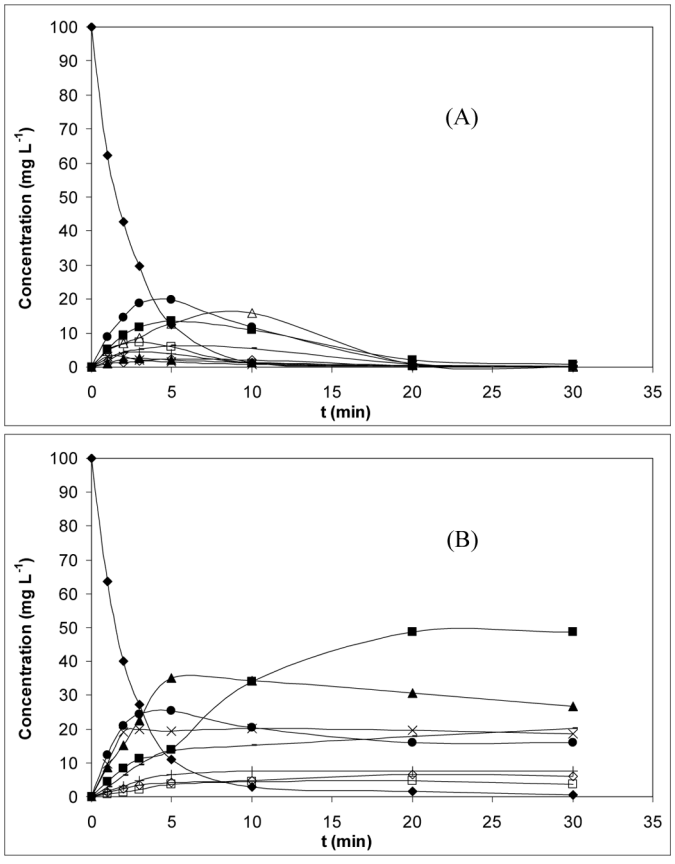

FIG. 4. Treatment of 4-chlorophenol 100 mg L^{-1} with UV in the presence and absence of H_2O_2. Variation of substrates and photoproduct concentration versus time. ◆ 4-chlorophenol, ∗ H_2O_2, Δ 1,2,4-Trihydroxybenzene, ● Hydroquinone, ■ Resorcinol, – Chlorohydroquinone, x Benzoquinone, ◇ Catechol, + 4-chlororesorcinol, ▲ Phenol, □ 4-chlorocatechol. (A) UV/H_2O_2, molar ratio H_2O_2:4-chlorophenol = 25:1, (B) UV.

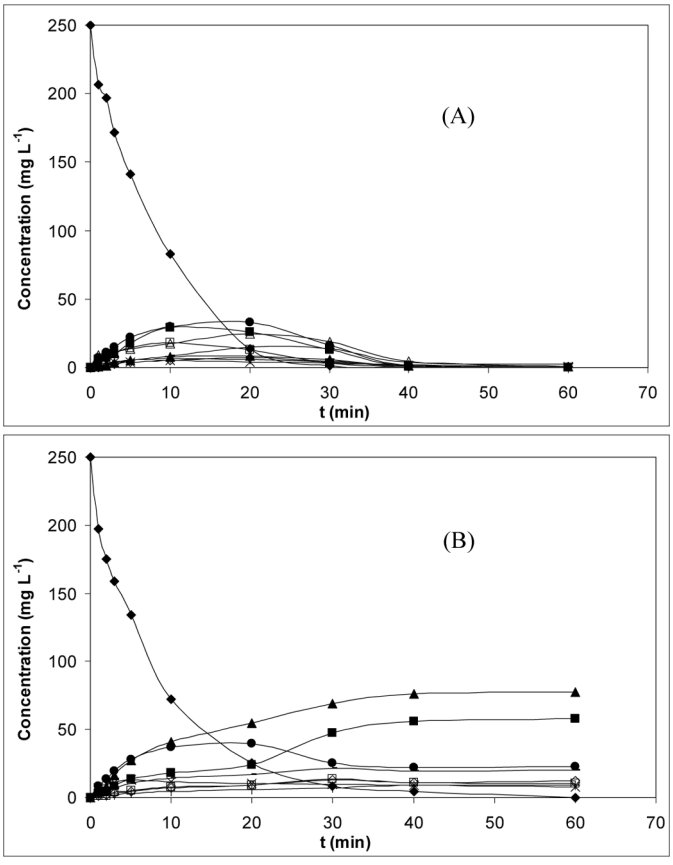

FIG. 5. Treatment of 4-chlorophenol 250 mg L^{-1} with UV in the presence and absence of H_2O_2. Variation of substrates and photoproduct concentration versus time. ◆ 4-chlorophenol, ∗ H_2O_2, Δ 1,2,4-Trihydroxybenzene, ● Hydroquinone, ■ Resorcinol, – Chlorohydroquinone, x Benzoquinone, ◇ Catechol, + 4-chlororesorcinol, ▲ Phenol, □ 4-chlorocatechol. (A) UV/H_2O_2, molar ratio H_2O_2:4-chlorophenol = 25:1, (B) UV.

Comparison of Treatments with Krcl Excilamp with and without Hydrogen Peroxide

Following optimum molar H_2O_2/4-chlorophenol ratio selection, the data were compared with those corresponding to the excilamp treatment in the absence of hydrogen peroxide and with the same starting 4-chlorophenol concentrations. Changes in concentration with time for all the compounds, with and without hydrogen peroxide, are shown in Figs. 4 and 5. The data show that there is no significant difference in 4-chlorophenol degradation. However, the presence of hydrogen peroxide considerably improves the removal of photoproducts, while some of them remain at high concentrations when treating with excimer lamp only. For instance Fig. 4b shows that 16.00 mg L^{-1} of hydroquinone, 18.46 mg L^{-1} of benzoquinone, 48.70 mg L^{-1} of resorcinol, 20.04 mg L^{-1} of chlorohydroquinone, 7.49 mg L^{-1} of 4-chlororesorcinol and 26.63 mg L^{-1} of phenol remain and all of them are higher than the no-effect concentration. It is possible to observe the same behavior from Fig. B.

Figure 6 shows that a significant COD decrease can be achieved with combined UV/ H_2O_2, while the sole use of the excilamp results in a constant value, due to the relatively high amount of photoproducts remaining following the treatment.

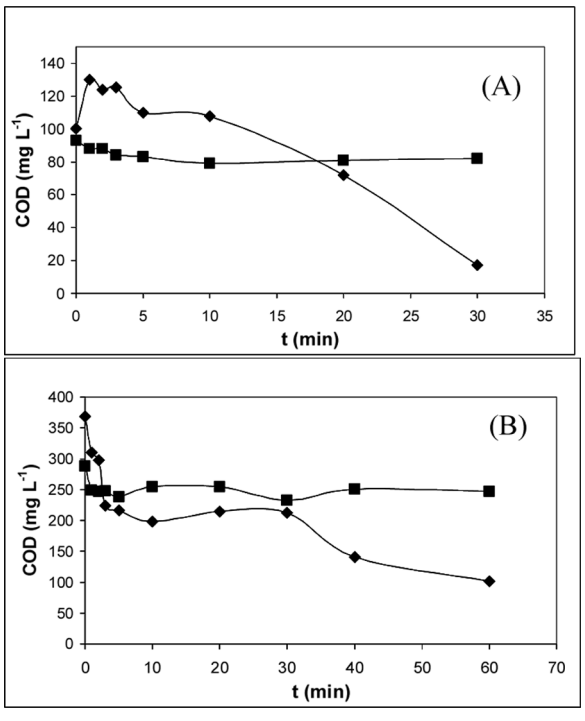

FIG. 6. COD changes versus time. ◆ UV/H_2O_2, molar ratio H_2O_2:4-chlorophenol = 25:1, ■ UV. (A) [4CP] = 100 mg L^{-1}, (B) [4CP] = 250 mg L^{-1}.

CONCLUSIONS

4-chlorophenol removal has been studied by means of two advanced oxidation processes, involving irradiation with KrCl excimer UV lamp and the combination of the excimer UV lamp with hydrogen peroxide. Different molar ratios H_2O_2:4-chlorophenol (1:1, 10:1, 25:1, and 50:1) were used and similar results were obtained with the two initial 4-chlorophenol concentrations assayed (100 and 250 mg L^{-1}) and the molar ratio H_2O_2:4-chlorophenol of 25:1. Such conditions were able to remove all the 4-chlorophenol and by-products in 20 and 40 minutes for the two 4-chlorophenol concentrations. Lower molar ratios could not achieve efficient photoproduct degradation, with toxic concentrations remaining in the final reaction medium according to the toxicity bioassays results. Higher ratios lead to excess hydrogen peroxide remaining at the end of the reaction process, increasing both the oxygen demand and cost of treatment.

The molar ratio H_2O_2:4-chlorophenol of 25:1 chosen as the optimum treatment regimen was used to compare degradation using the excilamp in the absence of hydrogen peroxide. Results confirm that toxic concentrations of hydroquinone, benzoquinone, resorcinol, chlorohydroquinone, chlorocathecol, 4-chlororesorcinol, and 1,2,4-trihydroxibenzene still remain in the media when treated without the hydrogen peroxide. Additionally, COD analyses confirm that with combined UV/H_2O_2 a significant decrease in the COD can be achieved whereas using excilamp alone, the COD practically remains constant.

ACKNOWLEDGEMENTS

During this study, M. Gómez and M. D. Murcia were beneficiaries of scholarships from Fundación Séneca (Comunidad Autónoma de la Región de Murcia, Spain). This work is part of Project 08683/PI/08 with funding from "Programa de Generación de Conocimiento Científico de Excelencia de la Fundación Séneca, Agencia de Ciencia y Tecnología de la Región de Murcia, en el marco del II PCTRM 2007–10". R Dams was funded by the Brazilian National Council for Scientific and Technological Development (CNPq).

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