

Removal of 4-Chlorophenol in the Presence of Methyl Green using KrCl Excilamp and H₂O₂: An Approach to the Treatment of Dye Effluents

María Gómez^{1,2*}, María Dolores Murcia^{1,2}, Elisa Gómez¹, José Luis Gómez¹,
Nick Christofi²

¹Department of Chemical Engineering, Murcia University, 30071 Murcia, Spain;

²Pollution Research Unit, School of Life Sciences, Edinburgh Napier University
maria.gomez@um.es

Chlorophenols constitute a group of priority pollutants widely found in industrial wastewaters and often originate from dye works. In the present work, a combined AOP treatment using a KrCl UV excilamp with hydrogen peroxide has been tested for the degradation of 4-chlorophenol in the presence of a common dye, methyl green. The presence of the dye constitutes a first step in order to simulate a real effluent and study how the different compounds present can affect the degradation of phenolics. The obtained results have shown that variation of the dye concentration, in the range 25 to 100 mg L⁻¹, does not affect chlorophenol degradation, while, on the contrary, lower 4-chlorophenol initial concentrations lead to faster removal of the dye. A molar ratio hydrogen peroxide: 4-chlorophenol of 25:1 was determined to be the optimum one.

1. Introduction

The massive industrialization of our society has to deal with the increase of polluted wastewaters. Chlorophenols are usually found in the wastewaters of numerous industries including the pulp and paper, dyes, wood, steel and other metals, petroleum refining, resins and plastic based industries, being commonly released from these industrial wastewaters to the environment (Bhunia et al., 2001; Wagner et al., 2001). Many of them originate from dye works and the effluents, once released into the receiving water bodies, can be extremely dangerous to aquatic life, as toxicants and as substances that reduce penetration of photosynthetic radiation curtailing biological activity (Sarnalka and Kanekar, 1995).

Although conventional physical, chemical and biological methods have been used for the removal of phenolic pollutants, none of them has provided a convenient, robust and cost effective treatment. One of the most promising alternatives to conventional treatments are the so-called Advanced Oxidation Processes (AOPs). The development of new UV sources from excimer lamps or excilamps has lead to increasing research over recent years (Tarasenko et al., 2003; Lomaev et al. 2006). They are attractive alternatives to commonly used mercury lamps because they have some important advantages such as the absence of elemental mercury, long lifetime (from 1000 to

10000 h), geometric freedom, high photon flux, etc. (Kogelschatz, 2003; Sosnin et al., 2006).

Excimer lamps have been successfully used for the removal of phenolic compounds, alone or in combination with oxidants like hydrogen peroxide to improve the removal process and facilitate complete mineralization (Gomez et al., 2009a; Gomez et al 2009b; Gomez et al. 2010a).

The removal of phenolic compounds in the presence of other organic compounds such as dyes, typically found in real wastewater is the next step of this research. However, as far as we are aware no works have been publishing including quantitative specific data of the removal of both phenolic compounds and dyes using these new processes.

The removal of dyes from effluents has been also studied by conventional methods, but recent research has revealed that dyes and simulated dye-effluents can also be treated by advanced oxidation processes (Arslan et al., 2000; Mohey et al., 2003; Behnajady et al., 2006; Shu, 2006; Huang et al., 2008), and they have been used to minimize the organic content in coloured effluents (Pérez et al., 2002; Kušić et al., 2007). Methyl green is included in the Triphenylmethane dyes, which are common dyes extensively used in the paper, leather, cosmetic, and food industries (Duxbury, 1993) and as a result they are normally present in wastewater discharged from such industries.

The present paper focuses on the removal of 4-chlorophenol in the presence of methyl green using a combined advanced oxidation treatment based on UV photodegradation employing excimer lamp (KrCl) and further oxidation with H₂O₂. The presence of the dye constitutes a first step in order to simulate a real effluent and study how the different compounds present can affect the degradation of phenolic compounds.

2. Materials and Methods

2.1 Reagents

4-chlorophenol and hydrogen peroxide were purchased from Sigma-Aldrich Fine Chemicals. Methyl green was purchased from Raymond A. Lamb (waxes and general laboratory supplies).

2.2 Materials

A barrier discharge excilamp (purchased from the Institute of High Current Electronics of the Siberian Branch, Russian Academy of Sciences) was used in the photodegradation of 4-chlorophenol. KrCl excilamp emitting maximum UV radiation at 222 nm was used. The excilamp was of cylindrical geometry covered by a metal case having an UV exit window with an area of 75 cm². The exit window was oriented vertically in close proximity to a quartz tube (2.2 cm) with an operating length of 22 cm and external diameter of 2.6 cm.

2.3 Operational procedure

Hydrogen peroxide was added to a mixture containing the phenolic compound and methyl green both at different concentrations ranging between 25 and 100 mg L⁻¹. The mixture was placed into the quartz reaction tubes covered with a reflector and UV irradiated at laboratory temperature (24±10C) under static conditions for periods up to 30 minutes.

2.4 Analytical determinations

4-chlorophenol and methyl green remaining following treatment were analysed spectrophotometrically. Methyl green removal was measured at 630 nm, the maximum absorption wavelength for this dye, combined pollutants tested at this wavelength showed that there were no interferences with the main chlorophenol absorption bands. Concentrations of 4-chlorophenol were measured by a colorimetric method using solutions of potassium ferricyanide (83.4mM in 0.25M sodium bicarbonate solution) and 4-aminoantipyrine (20.8mM in 0.25M sodium bicarbonate solution). Aliquots (2.4 ml) of the sample were placed in a spectrophotometer cuvette (3 ml) together with 0.3 ml of ferricyanide solution and 0.3 ml AAP solution. After a few minutes to allow the colour to develop fully, absorbance was measured at 505 nm against a blank (2.4 ml of water, 0.3 ml ferricyanide solution and 0.3 ml AAP solution). Absorbance values were transformed to concentrations by using the corresponding calibration curves ([4-chlorophenol] = $13.17 \times \text{Abs}_{505}$, $R^2 = 0.9994$; [methyl green] = $31.98 \times \text{Abs}_{630}$, $R^2 = 0.9896$).

3. Results

Three experimental series were carried out, to study the influence of methyl green and 4-chlorophenol concentration and the molar ratio hydrogen peroxide: 4-chlorophenol. The results corresponding to each series are shown below.

3.1 Influence of methyl green concentration on 4-chlorophenol degradation

In the first series, a molar ratio H_2O_2 : 4-chlorophenol of 25:1, previously established as optimum for degradation (Gomez et al., 2010b), was used and 4-chlorophenol concentration was kept constant at 100 mg L^{-1} , while methyl green was varied between 25 and 100 mg L^{-1} . Results are shown in Figure 1, where it can be seen that the variation of dye concentration does not have an influence on the 4-chlorophenol degradation. Both the chlorophenol and the dye are completely removed in all cases.

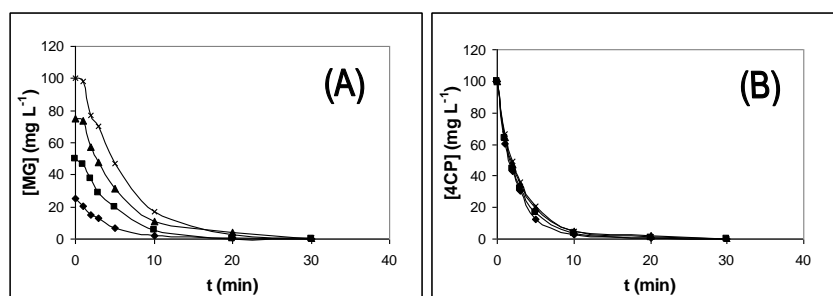


Figure 1. Variation of methyl green concentration: \blacklozenge 25, \blacksquare 50, \blacktriangle 75, \times 100 mg L^{-1} . (A) Methyl green removal. (B) 4-chlorophenol removal.

3.2 Influence of 4-chlorophenol concentration on methyl green degradation

In the second series, the same molar ratio H_2O_2 : 4-chlorophenol was kept, and 4-chlorophenol concentration was varied within the same range previously used for

methyl green. The dye concentration was 100 mg L^{-1} . It can be seen from Figure 2 that photodegradation of the dye was faster with lower 4-chlorophenol concentrations. Again, both compounds were totally degraded.

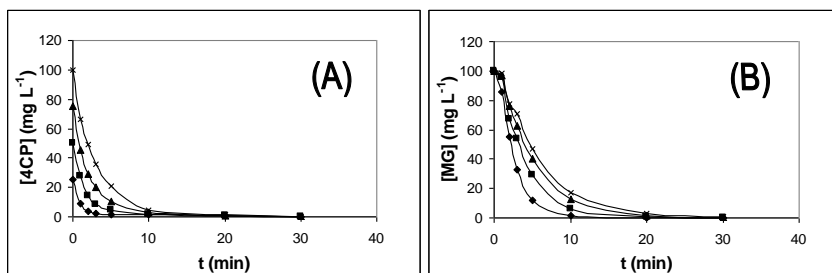


Figure 2. Variation of 4-chlorophenol concentration: \blacklozenge 25, \blacksquare 50, \blacktriangle 75, \times 100 mg L^{-1} . (A) 4-chlorophenol removal. (B) Methyl green removal.

3.3 Influence of molar ratio hydrogen peroxide: 4-chlorophenol on methyl green and 4-chlorophenol degradation

In the last series, four different molar ratios H_2O_2 : 4-chlorophenol were tested: 25:1, 35:1, 50:1 and 90:1, using chlorophenol and methyl green initial concentrations of 100 mg L^{-1} . The results in Figure 3 show that the molar ratio H_2O_2 : 4-chlorophenol has no influence on 4-chlorophenol photodegradation and slightly influence on methyl green photodegradation, so the previously chosen ratio, 25:1, remains as the optimum one.

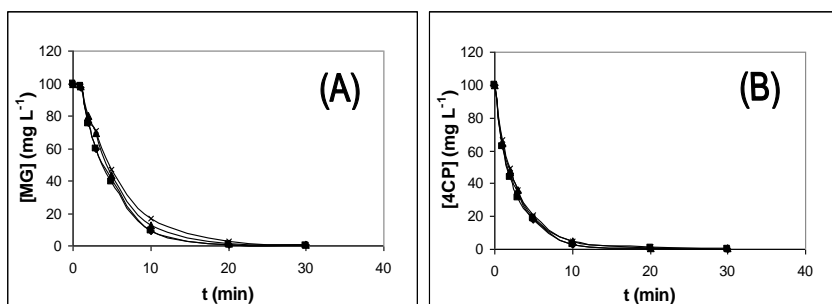


Figure 3. Variation of molar ratio H_2O_2 : 4-chlorophenol: \blacklozenge 90:1, \blacksquare 50:1, \blacktriangle 35:1, \times 25:1. (A) Methyl green removal. (B) 4-chlorophenol removal.

As it can be seen from the previous figure, faster chlorophenol removal is attained in all cases. This might be due to the fact that the wavelength of maximum emission of the KrCl excilamp (222 nm) matches with the maximum absorption band of 4-chlorophenol, while methyl green presents higher absorption bands close to 200 nm (see Figure 4).

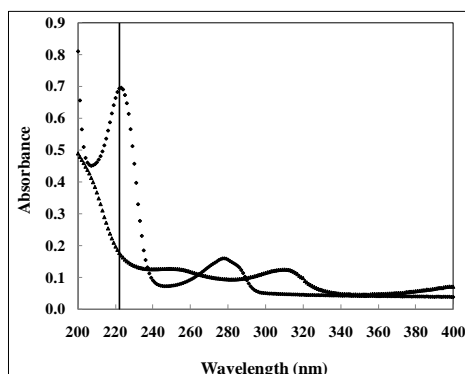


Figure 4: Absorption spectrum between 200 and 400 nm for: \blacklozenge 4-chlorophenol; \blacktriangle methyl green.

4. Conclusions

A combined AOP treatment using a KrCl UV excilamp with hydrogen peroxide has been tested for the degradation of 4-chlorophenol in the presence of a common dye, methyl green. Variation of the dye concentration, ranging between 25 and 100 mg L⁻¹, did not have any significant effect on the removal of 4-chlorophenol 100 mg L⁻¹. On the contrary, when 4-chlorophenol was varied in the same range at a fixed dye concentration, it was observed that lower chlorophenol concentrations lead to faster methyl green photodegradation. A molar ratio hydrogen peroxide: 4-chlorophenol of 25:1 was determined to be the optimum one and higher ratios showed no influence on 4-chlorophenol removal and only a slightly improvement in the dye degradation. These results must be considered a first step with a view to the simulation of real phenolic effluents, where the effect of all the present compounds, including dyes, must be considered.

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