

Kinetics of Chloramphenicol Degradation in Water by Hydrogen Peroxide and UV Radiation

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Highlights

- The kinetics of chloramphenicol degradation by UV/H₂O₂ was investigated.
- A kinetic model was developed to describe the effects of the main process variables.
- The degradation rate varied non-monotonically with H₂O₂ concentration.
- The extent of degradation was correlated with applied UV dose and H₂O₂ concentration.

1. Introduction

Recently, the presence of antibiotics in industrial effluents and natural water bodies has attracted increasing attention because of the negative effects they can have on ecosystems and human health [1]. In fact, in addition to being responsible for the emergence of multi-resistant strains of microorganisms, antibiotic residues are suspected to affect the endocrine system of aquatic organisms and exert other toxic effects.

Chloramphenicol (CHL) is a broad-spectrum antibiotic that is effective against a variety of Gram-positive and Gram-negative bacteria. In the 90's, its use in food-producing animals was banned because of its potential side-effects in humans, but it is still widely used in aquaculture and shrimp farming for pond disinfection and prophylactic purposes. The removal of CHL from water by conventional treatment processes is extremely low. This has stimulated the search for more powerful methods, such as the advanced oxidation processes (AOPs), which are based on the generation of highly reactive radical species, like the hydroxyl radicals ($\bullet\text{OH}$), by chemical, electrical or other energy sources [2].

In a previous study, we found that the combined use of hydrogen peroxide and UV radiation can completely eliminate the antibacterial activity from CHL solutions [3]. In order to better understand how H₂O₂ concentration and UV dose affect the degree of antibiotic removal, in this paper we investigate the kinetics of CHL degradation in aqueous solution by UV/H₂O₂.

2. Methods

CHL (C₁₁H₁₂Cl₂N₂O₅, purity >98%) and H₂O₂ (30% v/v aqueous solution) were purchased from Sigma-Aldrich (Milano, Italy). All other chemicals were of reagent grade and used without further purification.

Experiments were carried out at 20 °C on a CHL solution at pH 5.5 containing the appropriate amount of H₂O₂ and exposed to UV light. A low-pressure mercury lamp (6 W at 254 nm) was used as the UV source. The degradation kinetics was followed by monitoring the absorbance changes at 290 nm.

The study was performed by varying the initial CHL concentration ($c_{0,\text{CHL}} = 25\text{--}100$ ppm), the radiation intensity ($I_{\text{UV}} = 750\text{--}2500$ $\mu\text{W cm}^{-2}$) and the hydrogen peroxide concentration ($c_{\text{H}_2\text{O}_2} = 0\text{--}60$ mM). All experiments were repeated two or three times and the results were averaged.

3. Results and discussion

A first series of experiments showed that the simultaneous use of UV and H₂O₂ caused a significant reduction in CHL concentration, contrary to what was observed when they were applied singly (Figure 1).

The degradation process can be described by the following reaction scheme, accounting for direct photolysis of CHL by UV radiation and free-radical oxidation by the $\bullet\text{OH}$ species produced from H₂O₂:



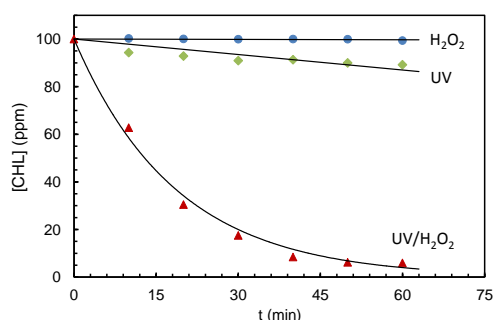


Figure 1. Effect of UV and H₂O₂ on CHL degradation ([H₂O₂] = 40 mM, I_{UV} = 1000 μW cm⁻²).

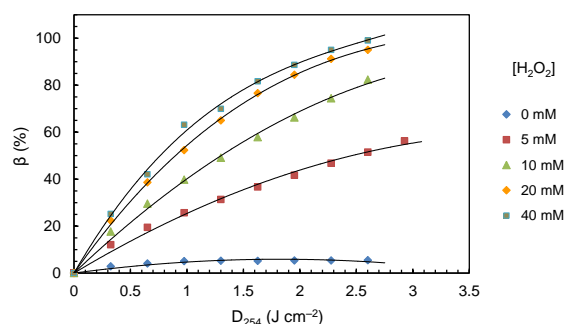


Figure 2. CHL concentration decay (β) as a function of radiation dose (D_{254}) and [H₂O₂] concentration (I_{UV} = 1000 μW cm⁻²).

Evaluation of the quantum yield at 254 nm for reaction (1) and the value of the kinetic constant of reaction (2) confirmed that these reactions give a negligible contribution to the overall degradation process. Accordingly, the rate of CHL degradation was expressed as:

$$-d[\text{CHL}]/dt = k [\text{CHL}]^m [\text{H}_2\text{O}_2]^n \quad (5)$$

where k is an apparent rate constant depending on the intensity of UV radiation and m , n are apparent reaction orders. Kinetic parameters were estimated by the method of excess coupled with differential analysis of data for a batch system. The degradation process was found to be first-order with respect to CHL concentration, while the apparent reaction order for H₂O₂ varied non-monotonically with the concentration of this reactant. This suggests that an optimal H₂O₂ concentration exists, close to 40 mM, at which the rate of CHL degradation is maximal. The presence of a maximum in the dependence of degradation rate on H₂O₂ concentration has been observed in other studies using UV/H₂O₂ [3,4]. It can be explained by considering that an increase in H₂O₂ concentration results in enhanced •OH production and hence higher degradation. However, at high H₂O₂ levels, hydroxyl radicals can be scavenged according to the following reaction:



HO₂• radicals are much less effective than •OH, thus decreasing the degradation rate. Moreover, H₂O₂ can absorb UV light to an appreciable degree [ϵ (254 nm) = 19.6 M⁻¹ cm⁻¹], further reducing CHL degradation. Finally, CHL concentration decay data were analysed in terms of applied radiation dose: $D_{254} = I_{UV} \cdot t$. Figure 2 shows some of the resulting curves, from which the extent of CHL degradation at given UV light intensity and H₂O₂ concentration can be easily evaluated.

4. Conclusions

The kinetic analysis of CHL degradation by UV/H₂O₂ indicates that UV light and H₂O₂ levels synergistically affect the effectiveness of the treatment and that an optimal H₂O₂ concentration exists. The model developed can help provide a deeper insight into the role of the most important process variables in CHL degradation.

References

- [1] N. Milić, M. Milanović, N.G. Letić, M.T. Sekulić, J. Radonić, J. Mihajlović, M.V. Miloradov, *Int. J. Environ. Health Res.* 23 (2013) 296–310.
- [2] G. Lofrano, G. Libralato, R. Adinolfi, A. Siciliano, P. Iannece, M. Guida, M. Giugni, A. Volpi Ghirardini, M. Carotenuto, *Ecotox. Environ. Safe.* 123 (2016) 65–71.
- [3] A. Zuurro, M. Fidaleo, M. Fidaleo, R. Lavecchia, *J. Environ. Manage.* 133 (2014) 302–308.
- [4] A. Zuurro, R. Lavecchia, *Desalin. Water Treat.* 52 (2014) 1571–1577.

Keywords

Chloramphenicol; Degradation; Kinetics; UV/H₂O₂.