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Degradation of the antibiotic chloramphenicol using photolysis and advanced oxidation process with UVC and solar radiation

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ABSTRACT

In this work, an aqueous solution of the antibiotic chloramphenicol was treated by photolysis and an advanced oxidation process using hydrogen peroxide combined with UVC and solar radiation. In this system, a reactor containing three UVC lamps (30 W) was used. A factorial plan 2^2 was designed with the following variables: time and a concentration of hydrogen peroxide and evaluated using the percentage of chloramphenicol degradation as the response. Twelve hours of exhibition to UVC and solar radiation obtained 83 and 21% of chloramphenicol degradation, respectively. When H_2O_2/UV was used, 98 and 5% of degradation were obtained after one and a half hours of exhibition to UVC and solar radiation with $3\,\text{mmol}\,\text{L}^{-1}$ of hydrogen peroxide. The time-based kinetic constant was calculated as $6.3 \times 10^{-2}\,\text{min}^{-1}$ with r^2 equal to 0.9878.

Keywords: Advanced oxidation; Antibiotic; Chloramphenicol; Photolysis

1. Introduction

Researchers are concerned about the presence of organic micropollutants in aquatic medium, because some of those, known as emerging pollutants, can be persistent and difficult to detect, causing damage to the environment and to human health [1]. Pharmaceutical, personal hygiene products, and hormones derived from cholesterol and various industrial by-products are considered to be emergent pollutants. These compounds appear in natural environments, mainly, from the discard of industrial and domestic effluents, which even in low concentrations can provoke noxious effects on living organisms [2,3].

Pharmaceuticals and personal care products (PPCP) have been increasingly detected in sewers, natural waters, superficial waters, and underground waters, emerging as potential threats to the ecosystem and to public health [4–7]. In addition, most sewage treatment facilities are not efficient in treating certain drugs [8]. As the presence of pharmaceuticals in the environment increases, abnormal physiological processes in reproduction can be seen, as well as an increase in cancer incidence, bacterial resistance to antibiotics, and an increase in chemical toxicity. For

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many drugs, the potential effects on people and the aquatic ecosystems are still not clearly understood [9].

Among pharmaceuticals, antibiotics deserve special attention, since their undisciplined use causes environmental problems such as the contamination of water bodies and the consequent resistance of microorganisms to drugs [10]. The monitoring of residual pharmaceuticals in the environment has been an object of great interest due to the fact that many of these substances are frequently found in wastewater treatment plants and natural waters, in concentrations in the vicinity of $\mu g\,L^{-1}$ and $ng\,L^{-1}$ [11].

Chloramphenicol (CAP) is an antibiotic applied to the inhibition of Gram-positive and Gram-negative bacteria which are present in metabolites from the excrement of humans and animals and remain in the surface water and ground water after sewage treatment [5]. Its structure is shown in Fig. 1.

CAP exercises its action on microorganisms through the inhibition of protein synthesis, being effective in the treatment of a number of infectious diseases, such as typhoid fever and other forms of salmonella, in infections related to *Haemophilus influenza*. This drug is also particularly used in the treatment of meningitis and in other serious infections of the central nervous system and in breathing treatment [12]. Because of its low cost and availability, since the 1950s it has become commonly used in the treatment of domestic animals all over the world. However, its use is also associated with serious toxic effects in susceptible human beings, such as bone marrow depression and fatal aplastic anemia. Since this result is independent of the dose, chloramphenicol has been prohibited for use in animals used for food in many countries, including the European Union [13]. Because of this, scientists are trying to discover ways to inactivate or eliminate residual CAP [14,15].

Conventional methods of treatment, such as biological, for the removal of chloramphenicol effluents have some disadvantages; for example in the problem of the elimination of mud and because of its poor efficiency [15]. Because of this, there is urgency to find new technologies that are cheap and easy to use and which prioritize the environmental component.

Advanced oxidative processes (AOP) have been extensively used in the treatment of water and residual waters to degrade organic and inorganic pollutants, as well as to improve the biodegradability of industrial residual waters [16–18]. AOP are oxidation processes that generate hydroxyl radicals, which are strong oxidizers, as a way to mineralize the organic matter in carbon dioxide, water, and inorganic ions [19]. The hydroxyl radicals can be generated through reactions involving strong oxidizers such as ozone and hydrogen peroxide, as well as by using semiconductors such as titanium dioxide, zinc oxide, or ultraviolet radiation [20]. Recently, different methods of AOP have been studied for the removal of pollutants in effluents of urban residual waters [21–23], waste industrial [24], and drinking water [25–27]. Unfortunately, the partial oxidation of organic pollutants may result in the formation of intermediate toxic compounds.

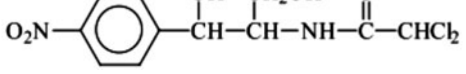

Fig. 1. Structure of Chloramphenicol.

A direct method for generation of •OH is to use photo cleavage of the hydrogen peroxide through UV irradiation. The H_2O_2/UV process results in complete degradation and the conversion CO_2 and H_2O of the inorganic salts of most of the organic pollutants. Photolysis of H_2O_2 with radiation UV generates two hydroxyl radicals, degrading the organic matter and forming simpler compounds.

The aim of this work was to study the removal of the antibiotic chloramphenicol in aqueous solutions using different types of oxidative processes. The efficiency of the treatment was verified through the quantification of the levels of compound elimination and mineralization. With the purpose of verifying the formation of less toxic products after treatment, acute toxicity tests were also carried out during the treatment.

2. Materials and methods

The experiments were carried out using glass recipients with capacity of 300 mL (with dimensions of 7.0 cm in diameter and 5.5 cm in height). The chloramphenicol used in this work was a commercial formulation donated by the LAFEPE laboratory (Recife, Brazil). In all the cases, 150 mL of the chloramphenicol solution with a concentration of $20\,mg\,L^{-1}$ was used to perform the experiments. The objective was to examine the degree of chloramphenicol degradation using two radiation sources: UVC (germicidal lamps) and solar radiation, with or without the presence of H_2O_2. In the experiments using UVC radiation, the recipients were placed in a reactor containing three germicide lamps (30 W each) with a capacity to irradiate 10 recipients. The reactor with germicide lamps emitted 2,500 lux and radiation of $53\,\mu W\,cm^{-2}$ for the wavelength between 290 and

390 nm and 18.6 $\mu W\,cm^{-2}$ for 254 nm. In the experiments carried out using solar radiation, the recipients were exposed to the sun. Experiments were conducted in Recife, Brazil (8°04´03´´ S; 34°55´00´´ W) at the same time of day, in order to minimize incident radiation variance. The average solar radiation was approximately 17 $mJ\,m^{-2}\,s^{-1}$ in the wavelength range of 380–780 nm.

The samples were analyzed before and after treatment using a fluorescence spectrometer for both ultraviolet and visible (UV–Vis), measuring concentrations in the wavelength of 278 nm, peak of greater absorbance for the chloramphenicol, and 254 nm, peak of absorbance for aromatic compounds [28].

2.1. Kinetics of degradation of the chloramphenicol using photolysis

The samples of chloramphenicol solution, with concentration of 20 $mg\,L^{-1}$, were exposed to UVC and to solar radiation for periods of: 1, 2, 4, 6, 8, and 10 h. Before starting the photochemical process, the lamps of the UVC reactor were heated for 10 min to stabilize their emissions.

2.2. Factorial planning using the H_2O_2/UV process

A factorial planning of 2^2 was elaborated with these variables: hydrogen peroxide (1.0, 2.0, and 3.0 $mmol\,L^{-1}$) and radiation time (30, 60, and 90 min), after which they were appraised using the percentage of chloramphenicol degradation as response. An aliquot of 150 mL of the pharmaceutical solution was used to carry out the experiments. All the runs were performed in duplicate and the central point in triplicate. The comparison between the percentage of chloramphenicol removals before and after photodegradation determined the efficiency of the process in each individual experiment.

2.3. Kinetics of degradation of the chloramphenicol using the H_2O_2/UV process

The kinetics of degradation of the chloramphenicol were carried out over a period of 5 h (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 30, 45 min and 1, 2, 3, 4, and 5 h) under the optimized condition obtained from the factorial plan.

The experiment that obtained the best degradation of chloramphenicol result was also analyzed in terms of total organic carbon (TOC), chemical oxygen demand (COD), biochemical oxygen demand (BOD), conductivity, total nitrogen, nitrite, dissolved oxygen (DO), and chlorides, following the standard methodology [29].

2.4. Toxicity

The acute toxicity of the samples before and after the 5 h of treatment with H_2O_2/UV was determined by a toxicity test using lettuce seeds *Lactuca Sativa*, according to the method used by Dutka [30]. The samples were placed in contact with the seeds in the first days of growth, corresponding to the germination period. In the accomplishment of the test, a Petri plate was covered with a humid paper disk (9 cm of diameter) with 5 mL of the samples in concentrations of 1, 3, 10, 30, and 100%, in distilled water. The seeds were distributed evenly on the paper.

After 120 h of incubation (at 15–20°C), we counted how many seeds had germinated as a way to evaluate the toxicant effects of the compounds present in the water containing this pharmaceutical, before and after the treatment by AOP.

The toxicity was estimated by the calculation of the inhibition concentration (IC50). IC50 is calculated as the concentration that provokes an inhibitory response in 50% of the exposed organisms. After the exhibition, the length of each seed root was measured and the percentage of inhibition was calculated.

3. Results and discussions

3.1. Photolysis

The degradation of the 20 $mg\,L^{-1}$ chloramphenicol solution using direct photolysis was analyzed for two wavelength removals: a peak of 278 nm for the greater absorbance peak for the chloramphenicol and the absorbance of 254 nm for the aromatic content. The results of the photolysis of chloramphenicol using UVC radiation and solar radiation are presented, respectively, in Figs. 2 and 3.

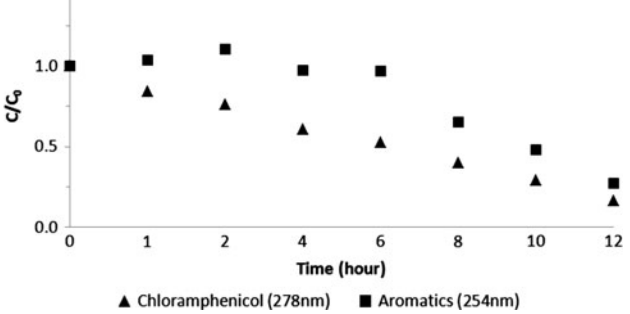

Fig. 2. Photolysis—UVC radiation.

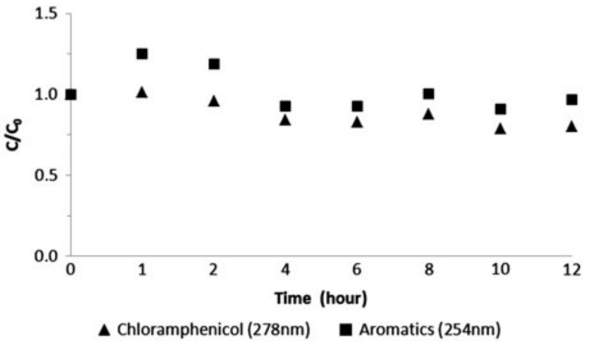

Fig. 3. Photolysis—solar radiation.

Fig. 2 indicates that the chloramphenicol concentration constantly decreases reaching a final concentration of 5 mg L^{-1} after 12 h of treatment using UVC radiation; however, the same cannot be observed in Fig. 3 (using solar radiation), where the concentration of the chloramphenicol decreased in a moderate way, stabilizing after 4 h of treatment, and reaching a final concentration of 18.8 mg L^{-1} after 12 h of treatment.

The use of the germicidal light reactor (UVC radiation) obtained a significant difference in the chloramphenicol degradation when compared to solar light, obtaining a maximum degradation of 83.35%, while solar light achieved 21.80%. This is due to the fact that the germicidal lamp emitted more radiation at the 254 nm wavelength, and the peak of absorbance of the target compound is in the region of 278 nm, thus the intramolecular bonds of the compound break more easily when compared with the solar radiation process which emits greater radiation in the visible spectra. Another factor would be that solar radiation is not constant during the whole day, as is in the case of the lamp irradiation. Thus, the total amount of photons which emanate from the solar reactor would be smaller when compared with UVC radiation.

3.2. Experiments using the UV/H_2O_2 process

For the experiments using the UV/H_2O_2 process, the effect of two variables was studied: time and the concentration of hydrogen peroxide.

Table 1 presents the results obtained in the degradation of the chloramphenicol and of the aromatic compounds using the UV/H_2O_2 method with the radiation from sunlight and from the germicidal lamps reactor with (UVC).

It was observed that the degradation of the aromatic content is lower than the chloramphenicol in both processes, because the intermediate compounds formed during the chloramphenicol oxidation still present aromaticity until a new step of oxidation occurs. The best result obtained in the studied conditions was 98.30 and 5.34% average degradation of chloramphenicol, using UVC and solar radiation, obtained using 3 mmol of H_2O_2, with a radiation exposure time of 90 min.

Using the data from Table 1 and with the aid of Statistic Experimental Design 6.0 software, the effects of the variables and your interaction were calculated. Fig. 4 presents a Pareto Chart to allow a study of the effects of all the variables and their interactions. The Y axis has the independent variables or the interactions among variables. The X axis has the absolute value of the effect, calculated by the ration between the effects and their respective standard deviations. All the val-

Table 1
Results of the factorial planning for the UV/H_2O_2 process

Exp	H_2O_2 (mmol)	Time (min)	UVC radiation		Solar radiation	
			Chloramphenicol degradation (%)	Aromatics degradation (%)	Chloramphenicol degradation (%)	Aromatics degradation (%)
1	1.0	30	60.71	25.94	–	–
1´	1.0	30	59.86	28.88	–	–
2	3.0	30	88.32	63.56	–	–
2´	3.0	30	88.27	67.87	–	–
3	1.0	90	98.33	93.96	2.88	–
3´	1.0	90	97.93	93.52	2.93	–
4	3.0	90	98.45	91.98	4.88	–
4´	3.0	90	98.15	93.55	5.80	–
5a	2.0	60	96.11	81.64	–	–
5b	2.0	60	96.11	81.98	–	–
5c	2.0	60	96.60	84.84	–	–

ues that appear on the Pareto Chart located to the right of the value p 0.05 are statistically significant.

It can be observed that the effect of the variables: the interaction among the variables H_2O_2 and time was statistically significant; the effect of the variable H_2O_2, however, did not present statistical significance, which indicates that the increase in the time would provide a greater degradation of chloramphenicol when the concentration of hydrogen peroxide is $1\,\mathrm{mmol\,L^{-1}}$. The kinetics of the chloramphenicol degradation was accomplished using the process H_2O_2/UVC, as the best result obtained with hydrogen peroxide in the concentration of $3\,\mathrm{mmol\,L^{-1}}$. So with the objective or reducing degradation time, the kinetic was accomplished using this concentration.

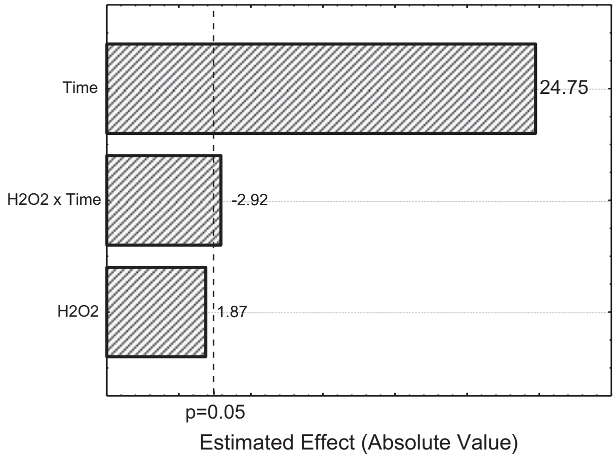

Fig. 4. Pareto Chart of the effects of the variables and their interactions.

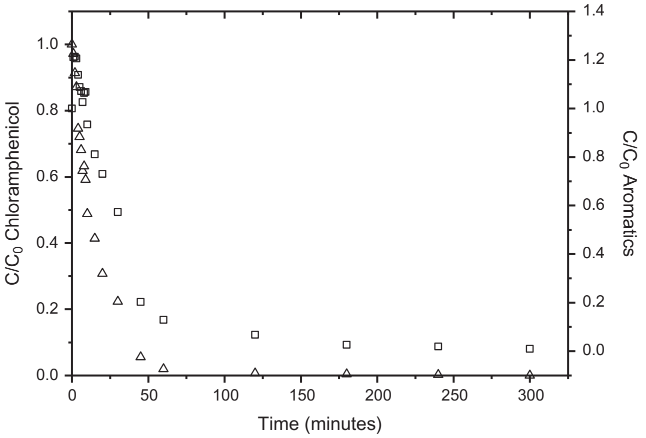

Fig. 5. Δ Chloramphenicol and □ Aromatics degradation curves using H_2O_2/UVC.

3.3. Kinetic degradation of chloramphenicol using H_2O_2/UVC

The kinetic evolution of the process of degradation of chloramphenicol was carried out with time of treatment varying from 1 min to 5 h in a germicide light reactor (Fig. 5).

The H_2O_2/UVC process was observed to be efficient in the degradation of chloramphenicol and in the elimination of aromaticity, reaching 100% of degradation in both cases, after 5 h of treatment. After just one hour of treatment, however, the chloramphenicol had already reached around 98% of degradation and the aromatics 87%. Chloramphenicol reached 100% of degradation after 2 h of treatment. The kinetic analysis took an additional three hours to verify the effective degradation for the aromatic compounds.

From the data of chloramphenicol degradation, the kinetic constant, k, was determined over a period of 60 min, because after that period the degradation curve was similar to a straight line.

The AOP usually obey the kinetics of pseudo-first order [31]. In order to carry out the kinetic constants calculation, a graphic ln ([pharmaceutical/pharmaceutical$_0$]) versus time was built. The graphic produced a straight line passing through the origin and with its slope determined by the kinetic constant based on time. The kinetic constant was equal to $6.3 \times 10^{-2}\,\mathrm{min^{-1}}$ with r^2 equal to 0.9878.

The results of the analyses of TOC, COD, BOD, DO, and chlorides before and after 5 h with H_2O_2/UVC in a reactor with germicide lamps are presented in Table 2.

Table 2 illustrates a reduction of 66% of TOC, 36% of COD, and 25% of BOD. The biodegradability increased about 21%. It was observed that before the

Table 2
Analyses accomplished before and after 5 h of treatment with H_2O_2/UV

Methods	TOC ($\mathrm{mg\,L^{-1}}$)	COD (mg of $O_2\,\mathrm{L^{-1}}$)	BOD (mg of $O_2\,\mathrm{L^{-1}}$)	Biodegradability (BOD/COD)	Conductivity ($\mathrm{\mu S\,cm^{-1}}$)	Chlorides ($\mathrm{mg\,L^{-1}}$)
Before the treatment	9.2	27.7	4.0	0.14	1.9	0.0
After the treatment	3.1	17.8	3.0	0.17	54.4	7.5

treatment there was no presence of chloride in the solution and after the treatment, the concentration of chloride was 7.5 mg L^{-1}, due to the breakdown of the of chloramphenicol molecules in the amine group with the subsequent liberation of the chloride ion in the solution.

The increase in conductivity after the treatment of 5 h was due to the mineralization of the pharmaceutical and the consequent formation of íons. The results found are in agreement with Rezende et al. [32], who observed the formation of inorganic chloride, nitrate, and nitrite ions starting with heteroatoms present in the chloramphenicol molecule.

3.4. Toxicity

The toxicity of the samples was evaluated before and after the 5 h treatment with H_2O_2/UV. The results demonstrated that the AOP applied induced a change in the toxicity of the sample. There was a reduction in the percentage of inhibition of the seeds cultivated in treated water in relation to those in the untreated water. From the data obtained, it was possible to calculate the IC50 for both treated and untreated samples.

It was shown that the H_2O_2/UV process with 5 h of UVC radiation, in the presence of 3 mmol L^{-1} of H_2O_2 was able to increase the IC50 from 3.98 to 16.47 mg L^{-1}. The increased IC50 implies toxicity reduction, thus it can be concluded that the by-products present in the treated sample have lower acute toxicity than the untreated sample. IC50 of the sample without treatment was low, indicating a high toxicity, and demonstrating the importance of the toxicity tests on the results of effluent treatment. These results are in agreement with Rizzo et al. [33], who affirm that the toxicity tests are effective for evaluating of the ecotoxicological risk of micropollutants.

4. Conclusion

In this work, the efficiency of an AOP was verified using UVC and solar radiation. A degradation of 83% of the pharmaceutical chloramphenicol after 12 h of exhibition to UVC radiation was obtained. The AOP results were obtained with the addition of a hydrogen peroxide concentration of 3 mmol L^{-1}, which resulted in a chloramphenicol degradation of 100% after 2 h of exposure to UV/H_2O_2. The use of solar radiation in both processes was not efficient, obtaining 21% of degradation using only direct photolysis and 5.34% of degradation when using UV/H_2O_2. From toxicity tests, it was observed that the IC50 increased significantly after treatment with an aqueous solution of chloramphenicol, resulting in toxicity reduction. It can be concluded that the by-products formed presented lower acute toxicity than the parent compound.

Acknowledgements

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