17th International Conference on Environmental Science and Technology

Athens, Greece, 1 to 4 September 2021

Toxicity study of Norfloxacin degradation by advanced oxidative process.

COSTA B.[1], CORDEIRO S. G.[2], SCHWEİZER Y. A.[3], WEBER A.C.[4], HAAS P.[5] , DE OLIVEIRA, L. [6], ETHUR E.M.[7] and HOEHNE H.[8*]

[1] Universidade do Vale do Taquari – Univates, Rua Avelino Tallini, 171, Bairro Universítário, Lajeado, RS, Brazil, zip code: 95914-014.

[2] Universidade do Vale do Taquari – Univates, Rua Avelino Tallini, 171, Bairro Universítário, Lajeado, RS, Brazil, zip code: 95914-014.

[3]Universidade do Vale do Taquari – Univates, Rua Avelino Tallini, 171, Bairro Universítário, Lajeado, RS, Brazil, zip code: 95914-014.

[4] Universidade do Vale do Taquari – Univates, Rua Avelino Tallini, 171, Bairro Universítário, Lajeado, RS, Brazil, zip code: 95914-014.

[5] Universidade do Vale do Taquari – Univates, Rua Avelino Tallini, 171, Bairro Universítário, Lajeado, RS, Brazil, zip code: 95914-014.

[6] Universidade do Vale do Taquari – Univates, Rua Avelino Tallini, 171, Bairro Universítário, Lajeado, RS, Brazil, zip code: 95914-014.

[7] Universidade do Vale do Taquari -Univates, Programa de Pós-Graduação e Biotecnologia, Rua Avelino Tallini, 171, Bairro Universítário, Lajeado, RS, Brazil, zip code: 95914-014.

[8] Universidade do Vale do Taquari – Univates, Programa de Pós-Graduação e Biotecnologia, Rua Avelino Tallini, 171, Bairro Universítário, Lajeado, RS, Brazil, zip code: 95914-014.

*corresponding author:
e-mail: luceliah@univates.br

Abstract Advanced oxidative processes (AOPs) are promising techniques that have been developed to treat and remove these organic contaminants in surface waters and effluents. The objective of this work was to evaluate the toxicity of products generated from UV/H_2O_2 degradation of solutions containing 5 µg/mL of Norfloxacin (NOR) and 1.4 mmol/L of H_2O_2 at pH 4.0, 7.0 and 9.0 against the micro crustacean *Artemia salina*. For the toxicity test, *Artemia salina* eggs were hatched in a solution containing 2.7% sea salt, for 48 h, with temperature at 27 °C and forced aeration. The ecotoxicity test was performed on 24-well plates. For each well, 10 nauplii of *A. salina* containing a control of the dilution solution, a positive control of toxicity and test solutions in the proportions of 100% were transferred, 50% and 25%, after 48 h mortality was verified. The data show that there was 100% mortality of *A. salina* in the wells containing 100% of the solution obtained through the degradation in all tested pH ranges, whereas the solutions containing 50 and 25% of the degraded drug showed a low rate of mortality demonstrating that there is no toxicity of products formed from degradation in the last two conditions described.

Keywords: micropollutant; ecotoxicity, antibiotics UV/H_2O_2

1. Introduction

Norfloxacin (NOR) is an antibiotic in the fluoroquinolone class used on a large scale in both human and veterinary medicine. It is the second antibiotic in the fluoroquinolone class most found in wastewater and surface water, and although it is found in concentrations of nanograms (ng / L) or micrograms per liter (µg / L), it is considered a contaminant, since the bioaccumulation in aquatic organisms, plants and humans can develop pharmacodynamic effects, in addition to producing bacterial genes with antimicrobial resistance (JIN et al., 2019). Thus, it is considered an emerging micropollutant. In view of the resistance to biodegradation of these contaminants (YIN et al., 2019), and the difficulty of total degradation of the conventional applied processes, it is necessary for a more effective treatment capable of degrading them. Seeking the degradation of these micropollutants, advanced oxidative processes (AOP) have been widely used (IKE et al., 2019).

Although the AOPs is effective in degrading compounds, in most cases it does not promote complete mineralization and therefore the compounds are partially oxidized to other molecules that may or may not be more toxic than the starting molecule (WANG et al. 2018). Since the formation of more toxic products can be a problem, toxicity tests are evaluated to assess products generated from degradation by AOP (BABU et al. 2019). *Artemia salina* is a microcrustacean used in several studies as an ecotoxicity indicator due to the ease and low cost of the tests performed with this organism (MADHAV et al. 2017). It is also widely used in feeding larval fish, and for this reason, the microcrustacean can act as a mediator in the transfer of pollutants to other organisms. Then, the objective of this work was to evaluate the toxicity of products generated from UV/H_2O_2 degradation of solutions containing 5 µg/mL of NOR at pH 4.0, 7.0 and 9.0 against the micro crustacean *Artemia salina*.

2. Methodology

The irradiation test was adapted from Sarkar et al. (2014). A bench reactor with a capacity of 250 mL was used. About 5 cm from the bottom of the reactor, a quartz tube (14 cm long and 4 cm in diameter) was inserted containing a 125 W mercury vapor lamp (Osram) serving as a source of UV radiation. The solutions of 5 µg / mL of NOR were inserted into the reactor and 1.4 mmol/L of H_2O_2 was added at pH 4.0, 7.0 and 9.0. After 21 min the samples were collected and analyzed the degradation by High performance liquid chromatography with mass detector (HPLC-MS) and for the ecotoxicity tests. During the experiments, the reactor was kept in an ice bath in order to balance the analyte temperature, considering that the reaction has an exothermic character.

The ecotoxicity test was carried out based on Madhav et al. (2017). The outbreak of *Artemia salina* cysts was performed in a 5 L beaker containing a 2.7% saline solution prepared with ultrapure water and sea salt, with forced aeration in a thermostated bath at 26-28 ° C for 48 hours. For the analysis, negative control solutions (1.5% saline) and positive control solutions ($K_2Cr_2O_7$ 1mg/mL) were prepared. The irradiated samples were prepared at 100%, 50%, 25% and 12.5% dilutions in 1.5% saline. In 24 microwell plates, 10 nauplii of *Artemia salina* were transferred to each well and then 3 mL of each previously prepared solution was added, all tests were performed in triplicate. The counting of surviving organisms was carried out in 48 h.

3. Results

All results using HPLC showed in 21 min the NOR degradation was about 95%. And the ecotoxicity results are showed in Table 1**.**

Table 1. Mortality of *A. salina* after 48 hours of exposure (DS = dilution solution; NC = negative control; TS = test solution)

pH 4.0					
Replicate	DS	NC	TS 100%	TS 50%	TS 25%
1	0	10	10	0	0
2	0	10	10	0	0
3	0	10	10	0	0
pH 7.0					
Replicate	DS	NC	TS 100%	TS 50%	TS 25%
1	0	10	10	0	0
2	0	10	10	2	2
3	0	10	10	0	0
pH 9.0					
Replicate	DS	NC	TS 100%	TS 50%	TS 25%
1	0	10	10	0	0
2	0	10	10	0	3
3	0	10	10	0	0

The data described in Table 1 show that there was 100% mortality of *A. salina* in the wells containing 100% of the solution obtained through the degradation in all tested pH ranges, whereas the solutions containing 50 and 25% of the degraded drug showed a low rate of mortality (equal to or less than 20%) demonstrating that there is no toxicity of products formed from degradation in the last two conditions described.

4. Conclusion

It was important to evaluate the efficient the AOP treatment in micropollutant using ecotoxicity test with *Artemia saline*, to guarantee the quality of the effluent at the end of a treatment.

References

Babu, D.S., Srivastava, V., Nidheesh, P.V., Suresh K. M., (2019). Detoxification of Water and Wastewater by Advanced Oxidation Process. Science of The Total Environmental, **696**, 133961.

Ike, I. A., Karanfil, T., Cho, J., Hur, J. (2019) Oxidation byproducts from the degradation of dissolved organic matter by advanced oxidation processes – A critical review. *Water Research*, **164**, 16-24.

Jin, X., Zhou, X., Sun, P., Lin, S., Cao, W., Li, Z., Liu W. (2019), Photocatalytic degradation of norfloxacin using N-doped TiO2: Optimization, mechanism,identification of intermediates and toxicity evaluation. *Chemosphere*, **237**, 124433.

Madhav M. R., David, S.E.M., R.S. S. Kumar., Swathy J.S., Bhuvaneshwari M., Mukherjee A., Chandrasekaran, N. 2017. Toxicity and Accumulation of Copper Oxide (CuO) Nanoparticles in Different Life Stages of Artemia Salina. *Environmental Toxicology and Pharmacology* **52**, 227–38.

Sarkar, S., Ali S., Rehmann, R., Nakhla G., Ray, M.B. (2014). Degradation of Estrone in Water and Wastewater by Various Advanced Oxidation Processes. *Journal of Hazardous Materials*, **278**, 16–24.

Wang, W., Quian Y., Wu, Na H., Zi-Bi, X., Min-Young L.,Hong-Ying H.(2018). Potential Risks from UV/H_2O_2 Oxidation and UV Photocatalysis: A Review of Toxic, Assimilable, and Sensory-Unpleasant Transformation Products. *Water Research*, **141**, 109–25

Yin, F., Wang, C., Lin, K. A., Tong, S. (2019) Persulfate activation for efficient degradation of norfloxacin by a rGO-Fe_3O_4 composite. *Journal of the Taiwan Institute of Chemical Engineers*, **102**, 163–169.