17th International Conference on Environmental Science and Technology

Athens, Greece, 1 to 4 September 2021

Catalytic Enhancement of Ozone-Based Processes for Removal of Selected Antibiotics from Wastewaters

ŽGAJNAR GOTVAJN A.[1], DERCO J.[2], ANTONČIČ T.[1,*] and VRABEL M.[2]

[1]University of Ljubljana, Faculty of Chemistry and Chemical Tehnology, Večna pot 113, Ljubljana, Slovenia Affiliation and address
[2] Slovak Technical University, Faculty of Chemical and Food Technology, Department of Environmental Engineering, Radlinského 9, 812 37 Bratislava, Slovak Republic

*corresponding author:
A. Žgajnar Gotvajn: andreja.zgajnar@fkkt.uni-lj.si

Abstract The aim of our work was to use advanced oxidation processes based on formation of reactive hydroxyl radicals (OH·) due to ozonation and its combination with H_2O_2, Fe^{2+} as catalyst and UV light for removal of Amoxicillin and Levofloxacin from model wastewaters at different pHs. Removal efficiencies were monitored by TOC (Total Organic Carbon) and COD (Chemical Oxygen Demand) measurements. Kinetics of oxidation was determined based on two-stage consecutive reaction presuming pseudo first order kinetics. Amoxicillin degraded during ozontion up to 33%. The most efficient was combination of $O_3/Fe^{2+}/H_2O_2$/UV (76%). In the case of Levofloxacin removal efficiencies for were up to 83% 8. Addition of H_2O_2 did not improve treatment efficiency, Kinetics of degradation confirmed rapid first degradation stages of both antibiotics, while the by-products degradation was slower. Investigated procedures exhibited potential for efficient removal of antibiotics from wastewaters.

Keywords: antibiotics, biotreatability, kinetics, ozonation

1. Introduction

Typical characteristics of antibiotics reduces their susceptibility to biological treatment in terms of persistency and toxicity. They still represent one of the most daunting groups of emerging contaminants, detected in various environmental compartments word-wide. Conventional wastewater treatment plants are one of the hot spots and their upgrade for removal of those pollutants should be priority (Anjali et al., 2019).

There are several methods that are producing promising results belonging to a group of AOPs (Advanced Oxidation Processes). AOPs are based on the formation of hydroxyl radicals (HO•) which can strongly non-selectively oxidize organic molecules (Dimitrakopoulou et al, 2012). Processes could involve energy enhancement in terms of light involvement (UV photochemical methods) in combination with ozone, H_2O_2, ozone/H_2O_2, Fe^{2+}/H_2O_2 (photo-Fenton process) and TiO_2 (Mojiri et al., 2019). There are also several non-photochemical methods available (Fe^{2+}/H_2O_2-Fenton process, ozonation, combination of ozone and H_2O_2, ozone with different catalysts, etc.) (Wang et al., 2020).

Ozone may react with organic compounds by direct reaction as molecular ozone or by indirect reaction through formation of secondary oxidants like free radical species (Nasuhoglu et al., 2012). At low pH the predominant reaction mechanisms is the direct electrophilic attack by molecular ozone, a rather selective oxidant. It can react directly with certain functional groups of organic compounds found in water and wastewaters, such as unsaturated and aromatic hydrocarbons with substitutes such as hydroxyl, methyl and amine groups giving rise to degradation products. On the other hand, ozone decomposes at alkaline pH conditions in water to form •OH, which are stronger oxidizing agents than ozone itself, thus inducing so-called indirect ozonation (Rekhate et al, 2019). Our work was focused on study of feasibility of ozone-based processes with addition of H_2O_2, Fe^{2+} as catalyst and UV light for removal of Amoxicillin and Levofloxacin from model wastewaters.

2. Materials and Methods

In the laboratory experimental set-up ozone generator was connected to a cylindrical glass reactor with volume of 300 mL. Experiments were conducted in a batch mode. The gas flow was 30 $L.h^{-1}$, the nominal concentration of ozone in the gas phase was 0.1 g L^{-1} and an overall system capacity of ozone production was 3 $g.h^{-1}$. As a result, ozone dose in experiments increased with time and it was 0, 3.75, 12.00, 30.00, 60.0, 120 and 240 $mg_{ozone}.mg^{-1}_{substance}$ at 0, 5, 10, 15, 30, 60 and 120 minutes, respectively. Samples were redrawn at 0, 5, 10, 15, 30, 60 and 120 minutes, where chemical oxygen demand (COD) and total organic carbon (TOC) was determined, according to ISO 8245 (1999) and ISO 6060 (1989), respectively. Kinetics of oxidation was determined based on two-stage consecutive reaction presuming pseudo first order kinetics.

3. Results and Discussion

Amoxicillin degraded during ozontion up to 33%. Ozonation at increased pH ($O_3/pH_{9.5}$) resulted in 51%

removal, which was not afected by addition of H_2O_2 (O_3/$pH_{9.5}$/H_2O_2; 50%). Addition of Fe^{2+} before ozonation removed 55% (O_3/Fe^{2+}), while additional of UV (O_3/Fe^{2+}/UV) led to 64% removal. The most efficient was combination of O_3/Fe^{2+}/H_2O_2/UV (76%). Based on the comparison of TOC and COD removal rates and TOC/COD ratios at the beginning and at the end of oxidation processess it was assumed, that Amoxicillin mineralised completely without significant by-products formed. In the case of Levofloxacin removal efficiencies for ozonation, O_3/$pH_{9.5}$, O_3/$pH_{9.5}$/H_2O_2, O_3/Fe^{2+}, O_3/Fe^{2+}/UV and O_3/Fe^{2+}/H_2O_2/UV were 36, 59, 56, 56, 75 and 83%, respectively. Addition of H_2O_2 did not improve treatment efficiency significantly, due to possible reaction of excess peroxide with formed OH· (Figure 1, Figure 2). Mineralisation of the Levofloxacin was not attained. Assessment of kinetics of degradation of both antibiotics fit first order reaction with rapid first degradation stages while the second stage contributed to degradation of formed transformation products was slower. Kinetics calculations were made using TOC as well as COD measurements.

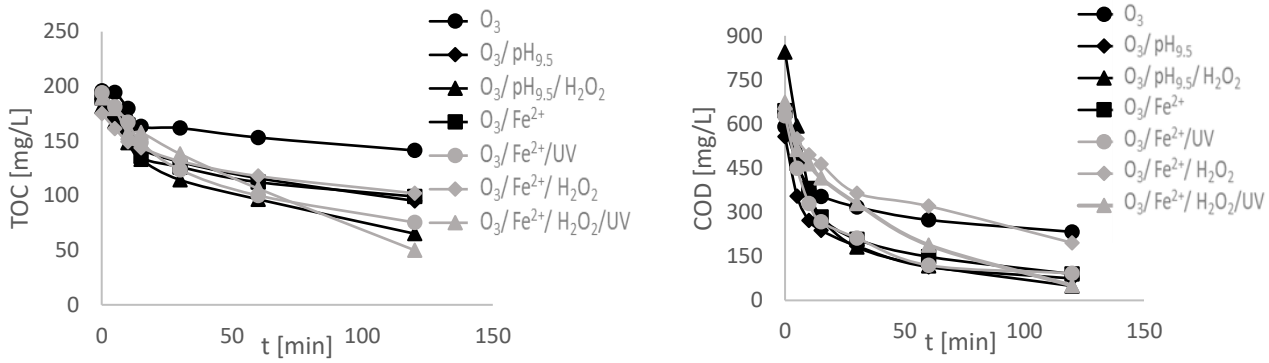

Figure 1. TOC and COD removal of Amoxicillin in all investigated ozone-based oxidation processes.

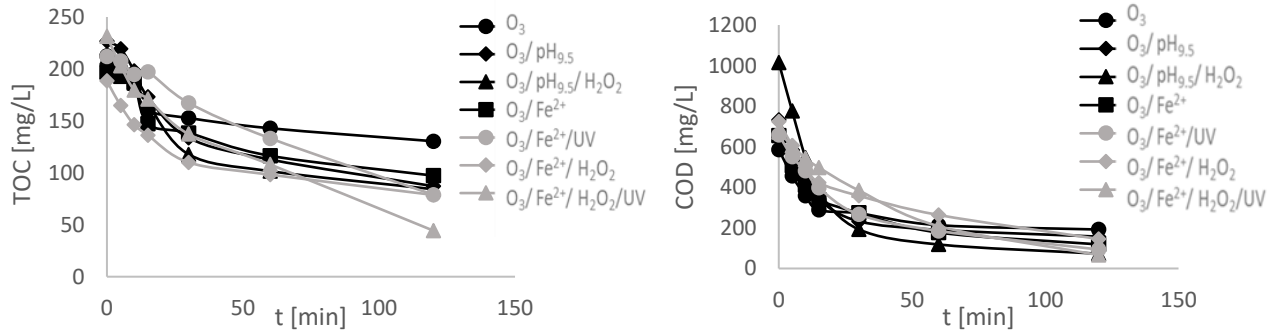

Figure 2. TOC and COD removal of Levofloxacin in all investigated ozone-based oxidation processes.

4. Conclusion

Chemical oxidation processes are viable options for effective removal of antibiotics, but they are relatively demanding to accomplish complete mineralization of pollutants. Upgrading direct ozonation with different catalysts and UV radiation could led to better efficiency of the processes in terms of time- and cost-efficiency. Decision about applying oxidative treatment as single-step procedure should be carefully considered to adapt them and make technically feasible.

References

Anjali, R., Shanthakumar, S. (2019), Insights on the Current Status of Occurrence and Removal of Antibiotics in Wastewater by Advanced Oxidation Processes. *J. Environ. Manage.*, **246**, 51–62.

Dimitrakopoulou, D., Rethemiotaki, I., Frontistis, Z., Xekoukoulotakis, N.P., Venieri, D., Mantzavinos, D. (2012). Degradation, Mineralization and Antibiotic Inactivation of Amoxicillin by UV-A/TiO 2 Photocatalysis. *J. Environ. Manage.*,***98,*** 168–174.

Mojiri, A., Vakili, M., Farraji, H., Aziz, S.Q. (2019). Combined Ozone Oxidation Process and Adsorption Methods for the Removal of Acetaminophen and Amoxicillin from Aqueous Solution; Kinetic and Optimisation. *Environ. Technol. Innov.*, ***15,*** 100404.

Nasuhoglu, D., Rodayan, A., Berk, D., Yargeau, V. (2012). Removal of the Antibiotic Levofloxacin (LEVO) in Water by Ozonation and TiO2 Photocatalysis. *Chem. Eng. J.*, ***189–190***, 41–48.

Rekhate, C. V., Srivastava, J.K. (2020). Recent Advances in Ozone-Based Advanced Oxidation Processes for Treatment of Wastewater-A Review. *Chem. Eng. J. Adv.* **3**.

Wang, J., Zhuan, R. (2020). Degradation of Antibiotics by Advanced Oxidation Processes: An Overview. *Sci. Total Environ.*, ***701***, 135023.

Žgajnar Gotvajn, A., Rozman, U., Antončič, T., Urbanc, T., Vrabel', M., Derco, J. (2021). Fe^{2+} and UV catalytically enhanced ozonation of selected environmentally persistent antibiotics. *Processes*, **9(3)**, 1-17.