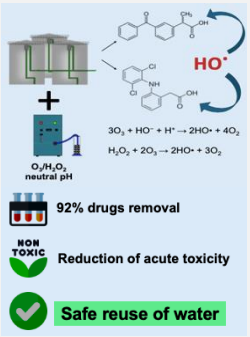
Optimizing Wastewater Treatment With UASB Reactor And O_3/H_2O_2: Ketoprofen And Diclofenac Removal And Toxicity Abatement

POSTER
Ph.D. Student: N
Journal: JECE

*P.S. Cavalheri[1,2], **T.F.Silva[3],** E.S.C. Miguel[2], F. J. C. Magalhães Filho[4], R.P. Cavalcante[5], A. Machulek Jr[6]. (1) Dom Bosco Catholic University, Av. Tamandaré, 6000 Campo Grande, MS, Brazil, (2) Institute of Physics, Federal University of Mato Grosso do Sul, Av. Costa e Silva, s/nº. Bairro Universitário. Campo Grande,MS, Brazil, (3) São Carlos Institute of Chemistry, University of São Paulo (USP), Av. Trab. São Carlense, 400, São Carlos, SP, Brazil (4) Institute of Hydraulic Research, Federal University of Rio Grande do Sul, Av. Bento Gonçalves, 9500 Porto Alegre, RS, Brazil, (5) School of Technology, University of Campinas – UNICAMP, Paschoal Marmo, 1888, Limeira, SP, Brazil, (6) Institute of Chemistry, Federal University of Rio Grande do Norte, Av. Senador Salgado Filho, s/n, Natal, RN, Brazil. thalita.quim@gmail.com*



Advanced oxidation processes (AOPs) offer alternative solutions for effluent treatment, but their integration with existing technologies at real scales remains limited. This study assessed the efficacy of the integration of O_3 and O_3/H_2O_2 and Upflow Anaerobic Sludge Blanket Reactor (UASB) in degrading ketoprofen (KET), diclofenac (DCF). 25 mg L^{-1} of KET and DCF was added to the effluent and, through a factorial experimental design, the O_3/H_2O_2 process was optimized. The integrated system showed good performance in degrading KET (92%), DCF (86%), enhancing effluent quality in terms of physicochemical parameters and toxicity removal. The treated effluent exhibited characteristics suitable for reuse.

Introduction

Several advanced treatment methods have been investigated for the removal of emerging contaminants (EC) from wastewater. Among these contaminants, non-steroidal anti-inflammatory drugs (NSAIDs), such as ketoprofen (KET) and diclofenac (DCF), have been frequently detected in water matrices across various countries. Ozonation in sewage treatment, as a tertiary treatment, can remove approximately 90% of ECs resistant to primary and secondary treatment stages, making it a promising technology [1]. However, ozone has a limited mineralization performance, potentially forming more toxic by-products [2]. The integration of ozonation with biological treatments is suggested for improved mineralization of wastewater [3]. This approach improves pollutant removal efficiency and reduces the potential for toxic by-product formation. The objective of this study was to evaluate the removal efficiency of KET and DCF by application of an integrated process between a UASB reactor and O_3/H_2O_2, using experimental design and effluent from a full-scale sewage treatment plant. Ecotoxicity and physicochemical were parameters used to evaluate the performance of the processes.

Material and Methods

The UASB post-reactor effluent (SW) was enriched with individual solutions of the drugs KET and DCF, in the final concentration of 25 mg L^{-1}. 300 mL of effluent (SW) enriched with drugs (SW-KET, SW-DCF, or SW-KET+DCF) were added to a 1L graduated cylinder and subjected to ozonation aeration using an ozone reactor with the aid of a bubble diffuser, during a 30 min experiment. Hydrogen peroxide was added at the beginning of the experiment. A 2^4 factorial experimental design, with the addition of a central point, was applied to investigate the variables that influenced the KET and DCF degradation in SW. The quantities of H_2O_2 varied between 10 mg L^{-1} and 60 mg L^{-1}, the pH ranged from 3.0 to 10.0, and the ozone concentrations varied between 16 and 48 mg L^{-1}. The toxicity of the degradation products was evaluated using the bioindicators *Artemia sp.* and *Lactuca sativa.*

Results and Discussion

The experimental design, high degradation values were obtained (92 ± 1.48%) in 30 min of experiment (10 mg L^{-1} of H_2O_2; 16 mg L^{-1} of O_3 ; pH 10) with a significance level of 95%.

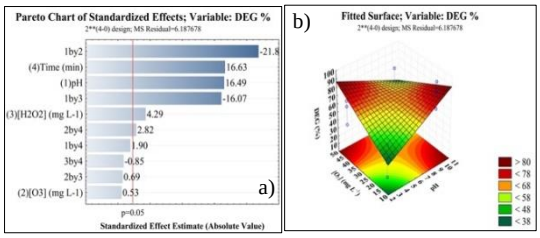


Figure 1. a) Pareto chart of KET degradation and (b) Response surface graph of KET degradation for UASB+O_3/H_2O_2 process

The Pareto chart (Figure 1a) was used to determine the significance level of each variable. The [O_3] x pH interaction was the most important factor in this model ($p < 0.05$). The [O_3] x [H_2O_2] interaction was also significant, indicating that ozone concentration was an important variable in the process when other variables are present. The variable [O_3] did not show significance for degradation. This suggests that the degradation reaction of ketoprofen preferably occurs through the indirect mechanism and that the hydroxyl radical ($HO^{\cdot}$) plays an important role in the elimination of KET. Figure 1b shows an antagonistic interaction between pH and ozone concentration. Increasing the pH and decreasing the ozone concentration leads to degradation rates above 80%. For optimal results, pH close to neutral and ozone concentration between 30 and 35 mg L^{-1} can achieve degradation percentages of KET above 70%.

The conditions of the central points (O_3 = 32.0 mg L^{-1}; H_2O_2 = 35.0 mg L^{-1}) were selected to conduct the reactions with KET and DCF at pH 6.5 and the natural pH of the effluent (7.5 ± 0.20). Ozonation without the addition of hydrogen peroxide and without pH adjustment was used as a blank.

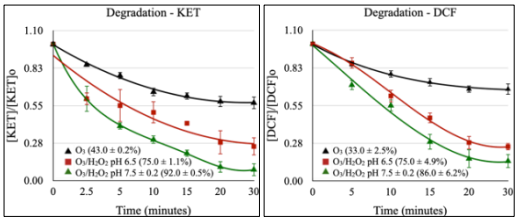


Figure 2. Degradation of KET (a) and DCF (b) by O_3 and O_3/H_2O_2 in pH 6.5 and pH 7.5 (natural pH).

Figure 2 showed the important contribution of the addition of hydrogen peroxide and pH in the O_3/H_2O_2 process in the degradation of KET and DCF drugs. The efficiency of the ozonation reaction is generally affected by the concentration of H_2O_2, pH, experimental time, and the dose of O_3 [4]. H_2O_2 increases the rate of ozone decay and accelerates its transformation into $HO^{\cdot}$ [5]. For the toxicity evaluation of the treated effluent the percentage of germination of the negative control seeds was above 90% and the coefficient of variation was less than 30% (CV=18%), indicating that the assays were statistically valid ($p < 0.05$). Table 1 shows the results obtained for *Artemia* sp. and *Lactuca sativa*, with toxicity levels expressed in toxicity units (TUs) e germination index (GI). Treatment with SW + O_3/H_2O_2 natural pH reduced acute toxicity, making the effluent non-toxic, confirming treatment efficiency. However, the SW + O_3 process increased effluent toxicity.

Table 1. Effluent toxicity after treatment through UASB combined with O_3/H_2O_2 process.

Process	*Artemia sp.*	*Lactuca sativa*	
	TU(1)	GI%(2)	TU(1)
SW	0.5	94±0.6	0.5
SW-KET	1.6	81± 1.6	1.4
SW-DCF	1.4	70 ±	16.4
SW-KET+O_3	1.7	74 ±	1.7
SW-DCF+O_3	2.7	67± 5.6	15.4
SW-KET+O_3/H_2O_2 natural pH	Non-toxic	97 ± 6.1	Non-toxic
SW-DCF+O_3/H_2O_2 natural pH	Non-toxic	95 ± 6.3	Non-toxic
Negative control	0	100	0

SW= UASB post-reactor effluent; (1)TU=Toxic Unit; (2)GI=Germination Index.

Conclusions

The integration of the O_3/H_2O_2 process with the UASB reactor optimized sewage treatment, removing organic matter, reducing effluent toxicity, and efficiently degrading emerging pollutants such as diclofenac and ketoprofen. Therefore, it is recommended to use the UASB reactor combined with O_3/H_2O_2, with 32 mg L of O_3, a flow rate of 2 L min of O_3, and 35 mg L^{-1} of H_2O_2, for a 30 min time period for sewage treatment plant effluent. Advanced technologies, when combined with conventional methods, enhance wastewater treatment processes in both large and small cities.

Acknowledgments

The authors thank the financial support of the São Paulo Research Foundation (FAPESP) [grant numbers #2022/00454-0; #2019/26210-8]; *Coordination* for the *Improvement* of *Higher Education Personnel* (*CAPES*); National Council for Scientific and Technological Development (CNPq); and *Foundation* for the *Support* to the *Development of Teaching*, *Science and Technology of the State of Mato Grosso do Sul* (Fundect).

References

[1] Hidayaturrahman, H., Lee, T.G., Mar Pollut Bull, 146 (2019) 696.

[2] da Silva, D., Cavalcante, R.P., Barbosa, E.B., et al, Sep Purif Technol, 263 (2021) 118415

[3] Granzoto, M.R., Seabra, I., Malvestiti, J.A.,et al, Sci Total Environ, 759 (2021) 143498.

[4] Malvestiti, J.A., Fagnani, E., Simão, et al,. Environ Technol (United Kingdom), 40 (2019) 1910.

[5] Katsoyiannis, I.A., Canonica, S., von Gunten, U., Water Res, 45 (2011) 3811.