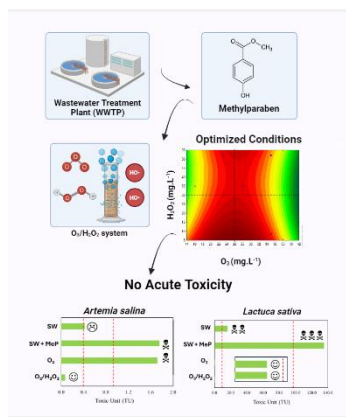


Degradation Of Methylparaben By Ozonation Process At Neutral pH Integrated with Anaerobic Treatment System

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The insufficient removal of endocrine disruptors, as parabens, from wastewater discharge remains a primary route of environmental contamination, necessitating the development of advanced technologies integrated into conventional known systems. This study explores the use of ozone combined with hydrogen peroxide (O₃/H₂O₂) for treating effluent post-UASB reactor enriched with 30.0 mg.L⁻¹ of methylparaben. Through Factorial and Doehlert optimization designs, optimal conditions of 25.0 mg.L⁻¹ of O₃ and 30.0 mg.L⁻¹ of H₂O₂ at neutral pH were identified, resulting in methylparaben removal efficiencies of 71.60% after 60 minutes and 85.49% after 120 minutes. Furthermore, a 95.0% removal of organic matter was achieved after 60 minutes, accompanied by no acute toxicity to *Artemia salina* and *Lactuca sativa*, demonstrating the efficiency of the integrated AOP with the anaerobic system.

Introduction

The conventional treatment applied in most of wastewater treatment plants (WWTPs) occurs through the action of anaerobic or aerobic microorganisms, but alone it cannot eliminate endocrine disruptors [1], ensuring the continuous entrance of parabens, especially of methylparaben (MeP), into natural ecosystems, being an obstacle to environmental management systems striving to safeguard water quality and promote Circular Economy principles [2]. Advanced Oxidative Processes (AOPs), such as ozonation, have emerged as promising solutions for treating toxic effluents, capable of rapidly degrading organic pollutants into less harmful byproducts [3] through direct ozone (O₃) and indirect hydroxyl radical oxidation (HO•) [4,5]. Despite the high degradation rates, mineralization in simple ozonation processes is low, while one strategy adopted is the addition of oxidizing agents, such as hydrogen peroxide (H₂O₂), accelerating the decomposition of ozone and increasing the formation of highly oxidative HO• radicals [6]. This study aimed at evaluating the efficiency of O₃/H₂O₂ process in the removal of MeP added to the effluent post-UASB reactor, optimizing the most significant variables through an experimental designs.

Material and Methods

To investigate the influence of variables, a 2⁴ Factorial experimental design, followed by a 2² Doehlert optimization design was implemented. The

performance of the process was evaluated by monitoring the degradation of MeP through high-performance liquid chromatography (HPLC) analysis, mineralization through total organic carbon (TOC) analysis, and assessing physicochemical parameters and acute toxicity for *Artemia salina* and *Lactuca sativa*.

Results and Discussion

In the statistical analysis of the results obtained in the Factorial design, according to the Pareto chart (Figure 1.a), time, ozone concentration and hydrogen peroxide concentration were statistically significant. These preliminary results also indicated that the optimal pH is neutral, consistent with the effluent's natural pH, and does not necessitate the addition of reagents for acidification or neutralization. This suggests a potential decrease in future treatment costs.

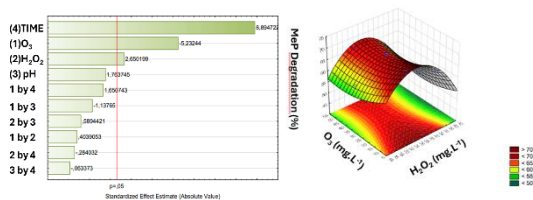


Figure 1. (a) Pareto chart for degradation of MeP by a Factorial design. (b) Response surface plot with an optimal concentrations to O₃ and H₂O₂ to MeP degradation.

The experimental values of the 2² Doehlert matrix indicated the optimal concentrations for ozone and hydrogen peroxide to be 25.0 mg L⁻¹ and 30.0 mg L⁻¹, respectively, while maintaining the pH neutral and the total reaction time at 60 minutes. This was demonstrated by the response surface plot (Figure 1.b). Subsequently, experiments were conducted in triplicate to evaluate the addition of H₂O₂ to the ozonation process under these conditions. The results demonstrate that the combined O₃/H₂O₂ process exhibited superior efficiency in degrading MeP compared to ozonation (O₃) (Figure 2). After 60 minutes, the removal rates were 71.60% and 56.73% for the combined process and O₃, respectively. After 120 minutes, these rates increased to 85.49% and 66.35%, respectively. However, the mineralization of total organic carbon (TOC) showed differing outcomes. Up to 60 minutes, both methods achieved similar TOC removal rates, with O₃ at 42.39% and the combined system at 40.49%.

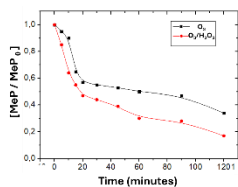


Figure 2. Degradation of the initial MeP concentration by the O₃ and O₃/H₂O₂ processes.

In the physicochemical analysis, the O₃/H₂O₂ process was superior, reducing 95.0% of the organic matter (including COD and BOD) and eliminating the initial turbidity of the effluent, demonstrating ozone's ability to remove color. This highlights the necessity of integrating conventional systems with advanced oxidation technologies, enabling compliance with

Conclusions

The successful application of the O₃/H₂O₂ process demonstrates its effectiveness and provides a strong argument for the integration between advanced and conventional treatments. Through experimental designs, optimal conditions of 25.0 mg.L⁻¹ of O₃ and 30.0 mg.L⁻¹ of H₂O₂ at neutral pH were identified, resulting in MeP removal efficiencies of 85.49% after 120 minutes. Besides this it was achieved the removal of 95.0% of organic matter in 60 minutes, and additionally the reduction of acute toxicity to non-toxic levels, highlights the potential for a water reuse for more sustainable production and consume actions.

Acknowledgments

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References

- [1] P.S. Cavalheri, et al. J Environ Chem Eng 11 (2023) 110699.
- [2] M. Duc Nguyen, et al. Environ Technol Innov 28 (2022) 102651.
- [3] D.B. Miklos, et al. Water Res 139 (2018).
- [4] Q.Y. Wu, et al. J Hazard Mater 418 (2021) 126327.
- [5] K. Ikehata, Y. Li, Emerging Green Chemical Technology, 2018.
- [6] C. von Sonntag, U. von Gunten, 2015.

regulatory frameworks, such as Brazilian Resolutions CONAMA No. 357/2005 and 430/2011.

Ecotoxicity tests were devised to evaluate acute toxicity following ozonation processes, acknowledging that incomplete mineralization in such processes can yield highly toxic intermediates. Table 1 demonstrates the results obtained for *Artemia salina* and *Lactuca sativa*, expressed in toxicity units (TUs) e germination index (GI). For the bioindicator *Artemia salina*, the addition of 30.0 mg.L⁻¹ increased the acute toxicity of the effluent (SW+MeP), shifting from low acute toxicity (0.4 < TU < 1.0) to acute toxicity (1.0 < TU < 10.0). In ozone-based processes, only the O₃/H₂O₂ system reduced the acute toxicity to a non toxic levels. (TU < 0.4). This demonstrates the significance of H₂O₂ not only for the degradation of MeP but also for the improvement of the physicochemical and ecotoxicological quality of the sewage. For *Lactuca sativa* seeds, MeP is even more toxic, increasing from high acute toxicity (10.0 < TU < 100) to very higher acute toxicity (TU > 100). In the evaluation of POAs, both systems were efficient, reducing the initial acute toxicity to non-toxic level, representing the generation of harmful by-products to the environment.

Table 1. Effluent toxicity after treatment through O₃/H₂O₂ and O₃ process.

Process	Artemia sp.	Lactuca sativa	
	TU ⁽¹⁾	GI (%) ⁽²⁾	TU ⁽¹⁾
SW	0.42 ± 0.1	69.9 ± 8.6	16.0 ± 0.1
SW + MeP	1.77 ± 0.1	58.3 ± 7.6	135.1 ± 0.1
O ₃	1.72 ± 0.02	81.1 ± 10.0	< 0.4
O ₃ /H ₂ O ₂	0.07 ± 0.01	81.2 ± 12.6	< 0.4

(1) TU=Toxic Unit; (2) GI=Germination Index.