Degradation of polyethylene microplastics by O_3 and O_3/H_2O_2 in secondary effluent

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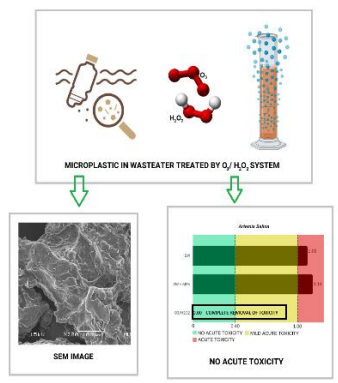
D.A.S Brito[1], T.F Silva[2], P.S. Cavalheri[2,3], A.K. Canatto[1], B.S. Machado[3], , L.C.S. Oliveira[2], G.A. Casagrande[2], F.J.C. Magalhães Filho[4], A. Machulek Junior[2]. (1) College of Engineering, Architecture and Urbanism and Geography, Federal University of Mato Grosso do Sul, Street, 527, Campo Grande, MS, Brazil, diegoasb@gmail.com. (2) Institute of Chemistry, Federal University of Mato Grosso do Sul, Av. Senador Filinto Muller, 1555, CP 549, Campo Grande, MS, Brazil (3) Agrosantech-Agrotechnology-Oriented Sustainable Sanitation Research Group, Department of Sanitary and Environmental Engineering, Dom Bosco Catholic University, Av. Tamandaré, 6000, Campo Grande, MS, Brazil. (4) Institute of Hydraulic Research, Federal University of Rio Grande do Sul, Av. Bento Gonçalves, 9500, Agronomia, Porto Alegre, RS, Brazil.



Microplastics found in aquatic environments can contaminate humans through different routes. However, conventional water and wastewater treatment plants (WWTPs) struggle to remove them effectively. This study explores the use of ozonation to combat microplastic contamination in wastewater. Polyethylene microplastics were subjected to O_3/H_2O_2 treatment, with conditions determined through a 2^3 factorial design. The optimal condition found involved a treatment duration of 110 minutes, H_2O_2 concentration of 100 mg L^{-1}, and O_3 concentration of 52 mg L^{-1}. Tests on *Artemia sp.* showed no acute toxicity post-treatment. Scanning electron microscopy (SEM) revealed surface alterations, indicating degradation, while Fourier-transform infrared spectroscopy (FTIR) confirmed degradation through the 1714 cm^{-1} carbonyl peak, demonstrating the process's effectiveness.

Introduction

Microplastics, microscopic plastic particles, are fragments of various types of plastic generated as waste from human activities. These microplastics are released into the environment and can re-enter the human body through different routes [1]. However, they are often not effectively removed in water and wastewater treatment plants (WWTPs). Therefore, this study aimed to investigate methods for removing this contaminant from wastewater.

Advanced oxidative processes (AOPs) have shown potential in degrading organic pollutants by utilizing reactive species such as hydroxyl radicals ($HO^{\bullet}$) [2,3]. Ozone-based AOPs, which can be enhanced by the addition of oxidizing agents like hydrogen peroxide (H_2O_2), have demonstrated effectiveness in reacting with both organic and inorganic substances [4]. Our research focused on examining the degradation of polyethylene microplastics in secondary effluent using a 2^3 factorial design to analyze the impacts of H_2O_2 and O_3 concentrations as well as treatment duration. Characterization of the degraded polyethylene and assessment of the resulting solution's toxicity to *Artemia Salina* contribute to enhancing our understanding and application of AOPs in microplastic treatment.

Material and Methods

Polyethylene microplastics were utilized for analysis in deionized water, and effluent samples were collected at the outlet of a UASB-type reactor at a local treatment plant. The interaction among variables was explored through a 2^3 factorial design, investigating peroxide concentration, ozone concentration, and reaction time. Analysis via total organic carbon (TOC) was performed by measuring the increase in chemical oxygen demand concentration [10]. Experiments with effluent were conducted at the optimal point of the experimental design. The samples were characterized by Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA). Toxicity tests were performed using *Artemia salina*.

Results and Discussion

Experiments assessing the pH impact revealed that both acidic and neutral levels yielded similar and superior results compared to basic levels. With the effluent's pH at 7.05, pH adjustments were deemed unnecessary to maintain the efficiencies observed in exploratory experiments, as large-scale pH alterations could significantly escalate the cost of ozonation treatment [6].

The experimental setup utilized minimum H_2O_2 and O_3 levels at 30 mg/L and 34 mg/L, respectively, and maximum levels at 100 mg/L and 52 mg/L. The trial employing the highest concentrations of ozone (O_3) and hydrogen peroxide (H_2O_2) concurrently demonstrated the highest degradation percentage, with a 125.4% increase in total organic carbon concentration after 110 minutes.

Figure 1 illustrates the principal influential variables in the process and, via a response surface graph, demonstrates the interaction among these significant factors. Elevated concentrations of H_2O_2 and O_3, along with their interaction, yielded superior outcomes in microplastic degradation.

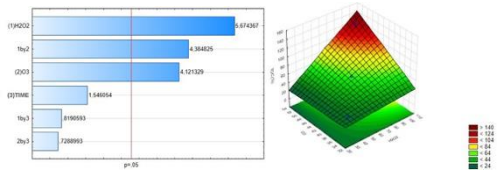


Figure 1. Pareto Chart and Response surface graph with H_2O_2 and O_3.

Figure 2 presents the FTIR and TGA analyses. Spectroscopy revealed characteristic peaks of the carbonyl group at 1714 cm^{-1}, indicating microplastic degradation. In the TGA analyses, besides the similar loss behavior among the samples, changes in the onset decomposition temperature (Tonset) were observed. In PE, Tonset was 436.18 ^{o}C, while for microplastic in the effluent, it was 449.35 ^{o}C. This shift may be related to the hydroxyl and carbonyl groups added to PE due to $HO^{\bullet}$ radical attacks.

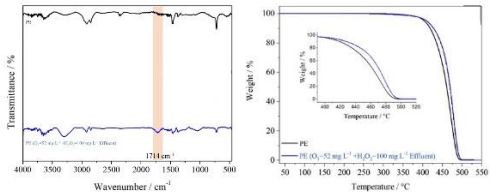


Figure 2. FTIR spectra of PE and PE degraded by 52 mg/L O_3 + 100 mg/L H_2O_2 in effluent after 110 min and Thermograms

Figure 3 illustrates a comparison of surface morphology analysis through SEM before and after treatment, indicating notable changes in microplastic surfaces with increased cracks and rough cavities observed. The addition of hydrogen peroxide promotes a higher concentration of radicals attacking the polymer, making the modifications more intense.

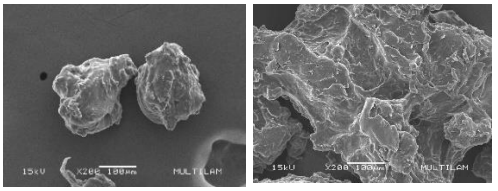


Figure 3. Pure PE before treatment and PE after treatment with O_3/H_2O_2.

For toxicity tests on *Artemia Salina*, there was a slight increase in the toxicity level of the raw effluent (TU 1.09) after the addition of microplastics (TU 1.14). Following ozonation treatment, both tests showed no toxicity with TU values of 0.00. Further research is warranted to elucidate the mechanisms underlying such toxicity.

Conclusions

In conclusion, the O_3/H_2O_2 system proved effective for degrading microplastics in effluent. The optimal degradation condition was achieved at the highest concentrations of O_3 and H_2O_2, 52mg/L and 100mg/L, respectively. This approach demonstrated a substantial increase in the overall concentration of organic carbon, attributable to intermediates formed during the degradation of microplastics.. Notably, post-treatment, no acute toxicity was found, emphasizing the importance of our findings in wastewater research and experimental design.

Acknowledgments

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