Application of O_3, H_2O_2 and UV Light For Degradation of Recalcitrant Compounds in Distilled Landfill Leachate

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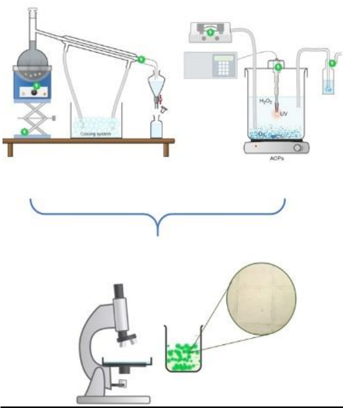

Landfill leachate (LL) is an effluent characterized by heterogeneity of its composition, potentially containing several types of organic and inorganic contaminants. Therefore, this effluent needs to be efficiently treated before being discharged into the environment. The objective of this study was to evaluate the efficiency of the simple distillation process followed by the application of AOPs (O_3, UV, and H_2O_2) and their combinations for the treatment of LL (LD). With the focus on evaluating the toxicity of LD after treatment with AOPs, bioassays with microalgae were performed as a tool to determine the effects of residual compounds present in LL on the aquatic environment. Through the application of this methodology, excellent removal rates were achieved for the main physicochemical parameters related to LL toxicity: COD, chlorides, alkalinity, and ammoniacal N. Furthermore, bioassays with *Scenedesmus sp.* demonstrated that LD treated with AOPs can be beneficial for its proliferation.

Introduction

Landfills are widely used worldwide for municipal solid waste (MSW) disposal due to their simplicity, adaptability, and significantly lower cost compared to other disposal options [1, 2]. Because of landfill operations, two by-products are generated: landfill leachate (LL) and biogas, the former being the subject of this work. LL is characterized by high chemical and biological oxygen demand (COD and BOD), ammonia, heavy metals, toxic substances and emerging pollutants [3, 4]. It is a persistent and toxic effluent that poses a significant risk of pollution, therefore, treating this effluent is crucial to avoid adverse impacts on soil, air and water [4, 5]. The simple distillation process is carried out through partial evaporation followed by condensation. This method has emerged as a viable alternative and an efficient solution for the separation and purification of substances and compounds found in LL [6]. However, the persistence of certain toxic compounds, even after the simple distillation requires additional treatment steps. Thus, advanced oxidation processes (AOPs) emerge as a treatment step, aiming to remove the remaining toxicity in the distilled leachate (DL). The effectiveness of AOPs can be substantially enhanced when combined with pre-treatment such as simple distillation. This pre-treatment can remove more volatile contaminants and concentrate persist pollutants, allowing for more efficient and target treatment [6]. This study is mainly focused on the qualitative assessment of the reduction of refractory compounds in the distilled leachate (DL) after the application of AOPs (O_3, H_2O_2 and UV), as well as the toxicity on unicellular green algae.

Material and Methods

Samples of raw leachate were collected from the Santa Maria Landfill, located in the state of Rio Grande do Sul, Brazil. These samples were subjected to the simple distillation process, resulting in DL. The following physicochemical parameters were measured for the raw and treated samples: COD, chloride, alkalinity and ammoniacal nitrogen. The selection of these parameters was based on the study by [7], as they are the four main parameters related to the ecotoxicity of LL. The DL was subjected to three AOPs: ozone (O_3), radiation (UV), and hydrogen peroxide (H_2O_2), as well as their combinations O_3/UV, O_3/H_2O_2, and UV/H_2O_2. The O_3 generator used in the experiment (Tholz model), coupled with an air compressor set to a fixed flow rate and pressure of approximately 5 L/min. A mercury vapor lamp 80W was inserted into the solution. Finally, the H_2O_2 (35% P.A.) was added. The LD after POA treatments was added to a solution containing *Scenedesmus sp.* algae. The microalgae were cultivated until the logarithmic phase in 30 mL test tubes placed in a photobioreactor, with a 12h photoperiod of illumination and oxygenation.

Results and Discussion

The physicochemical parameters obtained for the raw leachate (RL), distilled leachate (DL), and leachate after AOPs are presented in Table 1. It can be observed that in the first treatment step (DL column), excellent removal efficiencies were achieved for all the analyzed parameters, with 97,5% for COD, 90,2% for chlorides, 36,5% for alkalinity, and 61% for ammoniacal nitrogen. However, using liquid chromatography, the presence of persistent compounds was detected. These compounds are currently under study to better understand their behavior during the treatment processes and their relevance to the toxicity of the LL. Analyzing the results obtained after the AOPs and their combinations, a significant reduction in organic matter (COD) was observed, with concentrations around 25 mg/L. Chloride concentrations showed a slight increase after the DL+O_3, DL+UV, and DL+H_2O_2 treatments, which can be attributed to the increased conductivity in these samples. The results obtained from the ecotoxicity assays with *Scenedesmus sp.* are presented in Figure 1. It can be observed that from day 6 of the experiment, the proliferation of microalgae becomes more pronounced, as indicated by the increase in absorbance values. The AOP O_3/UV demonstrated the most favorable performance regarding microalgae proliferation, likely due to the presence of mineral compounds in its composition.

Conclusions

LL used has a high organic and inorganic load, making its treatment essential before disposal into water bodies. After the simple distillation treatment, up to 95% of some physicochemical parameters and inorganic compounds were removed. However, due to high concentrations of biodegradability parameters and the presence of recalcitrant compounds, a second treatment step is necessary. The application of AOPs resulted in increased biodegradability of the leachate through •OH, which further oxidized the remaining recalcitrant compounds in the DL, making it suitable for disposal and useful as a mineral source for some organisms. Bioassays with *Scenedesmus sp.* revealed that the application of the hybrid AOP (O_3/UV) resulted in greater microalgae proliferation, indicating a significant reduction in leachate toxicity.

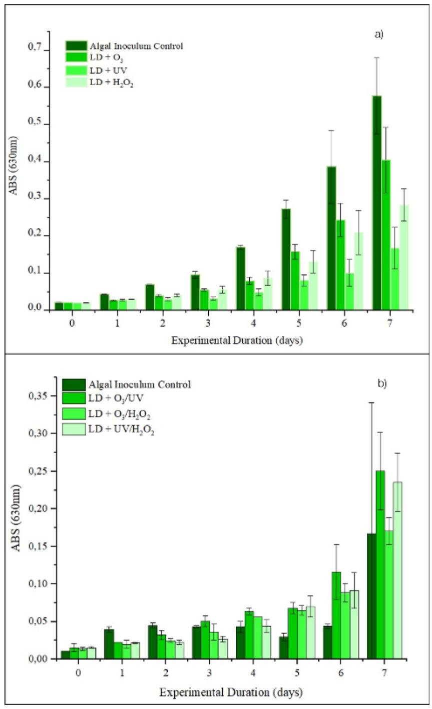

Figure 1. Bioassays with microalgae (a) with standalone AOPs and (b) hybrid AOPs.

Table 1. Physicochemical parameters for RL, DL, and leachate post treated with AOPs.

Parameter (mg/L)	RL	DL	DL+O_3	DL+UV	DL+H_2O_2	DL+O_3/UV	DL+O_3/H_2O_2	DL+UV /H_2O_2
COD	7350	185	< 25	< 25	< 25	28	< 25	< 25
Chloride	4817	470	1656	1671	1633	806	839	868
Alkalinity	15855	10063	4356	4172	4937	5791	6013	4440
N-ammoniacal	2871	1120	1329	1173	1080	1022	1134	1050

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