# INTEGRATION OF ADVANCED OXIDATION PROCESSES (OZONE/MAGNETITE) AND BIOLOGICAL TREATMENTS (UP-FLOW ANAEROBIC SLUDGE BLANKET REACTOR - UASB AND MICROALGAE) FOR THE TREATMENT OF LANDFILL LEACHATES

Dorance Becerra Moreno
Sanitary Engineer
Specialist in Pedagogical Practice
Master's degree in Sanitary and Environmental Engineering


FACULTY OF ENGINEERING
DOCTORATE IN ENGINEERING
EMPHASIS IN SANITARY AND ENVIRONMENTAL ENGINEERING
SANTIAGO DE CALI, COLOMBIA
2025

# INTEGRATION OF ADVANCED OXIDATION PROCESSES (OZONE/MAGNETITE) AND BIOLOGICAL TREATMENTS (UPFLOW ANAEROBIC SLUDGE BLANKET REACTOR - UASB AND MICROALGAE) FOR THE TREATMENT OF LANDFILL LEACHATES

Dorance Becerra Moreno (1703809-9706)
Sanitary Engineer
Specialist in Pedagogical Practice
Master's degree in Sanitary and Environmental Engineering

Thesis submitted as a partial requirement for the degree of Doctor in Engineering, with an emphasis in Sanitary and Environmental Engineering

Advisors:
Fiderman Machuca Martinez, PhD. Universidad del Valle
Andrés Fernando Barajas Solano, PhD. Universidad Francisco de Paula Santander


FACULTY OF ENGINEERING
DOCTORATE IN ENGINEERING
EMPHASIS IN SANITARY AND ENVIRONMENTAL ENGINEERING
SANTIAGO DE CALI, COLOMBIA
2025

## Dedication

To God, the source of wisdom and strength, for guiding me every step of the way and granting me the opportunity to achieve this milestone.

To my parents, Consuelo and Dorance, whose effort, sacrifice, and unconditional love made it possible for me to fulfill this dream. Becoming a doctor is the fruit of their dedication and teachings.

To Ginna, thank you for her constant support and for constantly reminding me of the importance of family.

To Luisa, for her patience, understanding, and unwavering support during the most challenging moments.

To Linda María, for inspiring me to improve daily.

To Professor Luz Edith Barba Ho, for her guidance and teachings and for believing in me.

To all of them, my deepest gratitude.

## Acknowledgments

Throughout this journey, I have been fortunate to have the support and guidance of extraordinary individuals to whom I wish to express my deepest gratitude.

First and foremost, I thank my thesis advisor, Fiderman Machuca Martínez, for his teachings, unwavering support, and patience. He is my role model as a professor, professional, and person. His commitment and passion for research have been a constant source of inspiration. I will always admire and appreciate him.

To my co-advisor, Andrés Fernando Barajas Solano, for his support and guidance throughout the research and publication process. His direction was essential in achieving each proposed objective.

To Professor Patricia Torres Lozada for her guidance, support, and generosity. Her kindness and dedication make her one of the most admirable educators I have known.

To Professor Irma Janeth Sanabria Gómez for her teachings and for planting the seed that made this dream possible. Their words and support have been instrumental in my academic and professional growth.

To Universidad del Valle, my alma mater, which not only shaped me as a professional but also transformed my life and that of my family. I owe everything to this institution: the knowledge, the opportunities, and the values that have guided my path. Its impact extends beyond the classroom, leaving a lasting mark on my journey and those around me. I will always carry the name of Universidad del Valle with pride and infinite gratitude for every lesson and for providing me with the tools to achieve my dreams.

I extend my sincerest gratitude to the Colombian Network of Advanced Oxidation Processes (COLPAOX) for providing a valuable learning and professional growth space. COLPAOX has been instrumental in deepening my understanding of advanced oxidation processes and connecting me with researchers dedicated to related topics.

To all my friends, who have stood by my side through every stage of this journey, offering their unwavering support and always motivating me to pursue my goals. Their companionship has been invaluable along the way.

Thank you for sharing this journey and contributing to the achievement of this milestone.

## Table of Contents

## 1. Abstract

This research addresses the treatment of landfill leachates by integrating advanced oxidation processes (AOPs) and biological treatments to enhance contaminant removal efficiency and reduce effluent toxicity. For this purpose, catalytic ozonation with magnetite, its coupling with an up-flow anaerobic sludge blanket (UASB) reactor, and the integration of microalgae as a post-treatment stage were evaluated. Experimental studies were conducted using leachates from two landfills with contrasting characteristics: one located in a municipality with predominantly agricultural activities (La Madera, Ocaña) and another in a city with industrial activity (El Guayabal, Cúcuta), allowing for a broader application of the results.

The study determined that catalytic ozonation with magnetite optimizes organic matter degradation and improves leachate biodegradability, achieving chemical oxygen demand (COD) reductions of 85.3% in El Guayabal and 75.8% in La Madera. Process optimization established optimal operating conditions with an ozone dose of 6 g/h, a magnetite concentration of 2.5 g/L, and a pH of 9, maximizing process efficiency while minimizing ozone consumption. However, a progressive decrease in catalyst efficiency was observed after successive reuse cycles, highlighting the need for regeneration strategies to maintain performance.

The coupling of catalytic ozonation with the UASB reactor improved the stability of the biological system, increasing the $BOD_5$/COD ratio from 0.26 to 0.38 in El Guayabal and from 0.23 to 0.32 in La Madera, facilitating the anaerobic biodegradation of organic matter. The UASB reactor, operating at a hydraulic retention time of 24 hours, achieved COD removals between 60% and 75%, with more excellent stability in leachates with higher concentrations of biodegradable compounds. However, ammoniacal nitrogen removal was limited, with residual concentrations reaching up to 546.1 mg/L, indicating the need for additional treatment to comply with discharge standards.

Microalgae as a post-treatment allowed for the removal of up to 65% of total nitrogen and 70% of phosphorus, demonstrating its potential as a final stage in landfill leachate treatment. However, its efficiency in organic matter removal was lower than that of the UASB reactor, suggesting that its application should focus primarily on nutrient reduction and improving final effluent quality.

This study's conclusions confirm that combining catalytic ozonation with magnetite, anaerobic treatment, and microalgae is a viable and efficient alternative for treating landfill leachates with different characteristics. The treatment configuration plays a crucial role in overall process efficiency, with catalytic ozonation being more effective as a pretreatment to facilitate subsequent biological degradation. The need to integrate additional nitrogen removal and catalyst regeneration strategies is emphasized, and the economic and energy feasibility of the process for large-scale implementation is assessed.

From a scientific perspective, this thesis contributes to advancing knowledge in landfill leachate treatment by developing optimization models for catalytic ozonation, evaluating catalyst stability during reuse cycles, studying the impact of ozonation on leachate biodegradability, and demonstrating the synergy between advanced oxidation processes and biological systems.

## Resumen

La presente investigación aborda el tratamiento de lixiviados de rellenos sanitarios mediante la integración de procesos avanzados de oxidación (PAOs) y tratamientos biológicos, con el fin de mejorar la eficiencia en la remoción de contaminantes y reducir la toxicidad del efluente. Para ello, se evaluó la ozonización catalítica con magnetita, su acople con un reactor anaerobio de flujo ascendente (UASB) y la integración de microalgas como etapa de postratamiento. Se llevaron a cabo estudios experimentales con lixiviados de dos rellenos sanitarios con características contrastantes: uno ubicado en un municipio con predominio de actividades agrícolas (La Madera, Ocaña) y otro en un municipio con actividad industrial (El Guayabal, Cúcuta), lo que permitió ampliar el ámbito de aplicación de los resultados.

El estudio determinó que la ozonización catalítica con magnetita optimiza la degradación de materia orgánica y mejora la biodegradabilidad del lixiviado, alcanzando reducciones de demanda química de oxígeno (DQO) del 85.3 % en El Guayabal y 75.8 % en La Madera. La optimización del proceso estableció condiciones operativas óptimas con una dosis de ozono de 6 g/h, una concentración de magnetita de 2.5 g/L y un pH de 9, lo que permitió maximizar la eficiencia del proceso con un consumo mínimo de ozono. Sin embargo, se observó una disminución progresiva en la eficiencia del catalizador tras sucesivos ciclos de reutilización, lo que plantea la necesidad de estrategias de regeneración para mantener su desempeño.

El acoplamiento de la ozonización catalítica con el reactor UASB permitió mejorar la estabilidad del sistema biológico, aumentando la relación $DBO_5$/DQO de 0.26 a 0.38 en El Guayabal y de 0.23 a 0.32 en La Madera, lo que facilitó la biodegradación anaerobia de la materia orgánica. El reactor UASB, operando con un tiempo de retención hidráulica de 24 horas, logró remociones de DQO entre el 60 % y el 75 %, con una mayor estabilidad en los lixiviados con mayor concentración de compuestos biodegradables. Sin embargo, la remoción de nitrógeno amoniacal fue limitada, con concentraciones residuales de hasta 546.1 mg/L, lo que evidencia la necesidad de un tratamiento adicional para el cumplimiento de los estándares de descarga.

El uso de microalgas como postratamiento permitió la remoción de hasta el 65 % del nitrógeno total y el 70 % del fósforo, evidenciando su potencial como una etapa final en el tratamiento de lixiviados. No obstante, su eficiencia en la eliminación de materia orgánica fue inferior a la del reactor UASB, por lo que su aplicación debe orientarse principalmente a la reducción de nutrientes y la mejora de la calidad del efluente final.

Las conclusiones de este estudio confirman que la combinación de ozonización catalítica con magnetita, tratamiento anaerobio y microalgas es una alternativa viable y eficiente para el tratamiento de lixiviados de rellenos sanitarios con diferentes características. La configuración de tratamiento influye en la eficiencia

global del proceso, siendo más efectiva la aplicación de ozonización catalítica como pretratamiento para facilitar la posterior degradación biológica. Se destaca la necesidad de integrar estrategias adicionales para la remoción de nitrógeno y la regeneración del catalizador, así como la evaluación de la viabilidad económica y energética del proceso para su implementación a gran escala.

Desde el punto de vista científico, esta tesis contribuye al avance del conocimiento en el campo del tratamiento de lixiviados mediante el desarrollo de modelos de optimización para la ozonización catalítica, la evaluación de la estabilidad del catalizador en ciclos de reutilización, el estudio del impacto de la ozonización sobre la biodegradabilidad del lixiviado y la demostración de la sinergia entre los procesos avanzados de oxidación y los sistemas biológicos.

## 2. Introduction

Landfill leachates are one of the primary sources of environmental pollution due to their high load of refractory organic matter, nutrients, heavy metals, and toxic compounds (Lestari et al., 2025). Its composition is not only complex but also highly variable, which makes its treatment through conventional technologies challenging. The coexistence of biodegradable and recalcitrant contaminants, along with suspended solids and persistent substances, can hinder process efficiency and pose a significant environmental risk if not properly managed (Das & Raj, 2025). The limited biodegradability of landfill leachates, combined with the presence of recalcitrant compounds, hinders their treatment through conventional biological processes. Therefore, it is essential to implement strategies that improve their physicochemical characteristics, reduce toxicity, and increase the biodegradable fraction, thereby enabling more efficient management of the effluent in subsequent treatment stages (Yu et al., 2025).

Biological processes, such as anaerobic digestion, have been widely applied in leachate treatment due to their low operational cost and ability to stabilize organic matter. However, the effectiveness of these systems can be limited by the presence of toxic and non-biodegradable compounds, which impair microbial activity and reduce treatment efficiency, making it necessary to implement complementary stages to ensure adequate effluent purification (Clemente et al., 2024). In this context, the integration of advanced oxidation processes with biological treatments has been widely explored as an effective strategy to improve leachate treatment. These processes enable the transformation of recalcitrant contaminants into more biodegradable compounds, thereby enhancing the overall efficiency of the system and reducing the toxicity of the treated effluent (Igwegbe et al., 2024). In particular, catalytic ozonation with magnetite has proven to be an efficient process for the degradation of organic contaminants, combining the strong oxidizing capacity of ozone with the catalytic activity of magnetite, which promotes the partial mineralization of compounds present in the leachate and reduces its toxicity (Yuan et al., 2022).

The coupling of advanced oxidation processes with biological treatments represents an innovative strategy to enhance contaminant removal efficiency in landfill leachates (H. Wang et al., 2023). Combining catalytic ozonation with biological processes, such as upflow anaerobic sludge blanket (UASB) reactors and microalgae treatment, can lead to a more significant reduction in pollutant load and better adaptation of biological systems to effluents with adverse characteristics (Yang et al., 2024). The UASB reactor is widely recognized for its ability to treat wastewater with high concentrations of organic matter (Tian et al., 2022). At the same time, using microalgae in leachate treatment has demonstrated its potential for nutrient removal and improving the quality of the final effluent (Lian et al., 2024). Integrating these processes into a combined treatment scheme can optimize overall system efficiency and reduce the environmental impact of landfill leachates.

In this context, the present study aims to evaluate the removal of organic matter, solids, nutrients, and heavy metals in landfill leachates through the coupling of advanced oxidation processes (ozone/magnetite) and biological processes (upflow anaerobic sludge blanket - UASB reactor and microalgae). The research is based on the premise that combining these processes will enhance leachate biodegradability, reduce its toxicity, and increase contaminant removal efficiency, thereby contributing to sustainable strategies for landfill leachate management. The interaction between these processes will be assessed through an experimental and analytical approach, optimizing operational conditions and establishing technical criteria for their implementation in real treatment systems.

## 2.1. Objectives

### 2.1.1. General Objective

Evaluate the removal of organic matter, solids, nutrients, and heavy metals in landfill leachates by coupling advanced oxidation processes (ozone/magnetite) and biological processes (up-flow anaerobic sludge blanket reactor - UASB and microalgae).

### 2.1.2. Specific Objectives

Determine the reduction of organic matter, solids, nutrients, and heavy metals in landfill leachates through a UASB reactor, an advanced oxidation process (ozone/magnetite), and a photoreactor with microalgae.

Study the reduction of organic matter, solids, nutrients, and heavy metals in coupled treatment systems: UASB - ozone/magnetite, UASB - microalgae, ozone/magnetite - microalgae, and UASB - ozone/magnetite - microalgae.

Estimate the toxicity on aerobic microorganisms, anaerobic microorganisms, and algae in landfill leachates treated using the evaluated systems.

## 2.2. Thesis Overview

This document is structured into chapters that reflect the achievement of the research objectives, comprising five research articles that present results and two literature review articles. The document is organized as follows:

- Theoretical Framework: A review of the state-of-the-art landfill leachate treatment through the combination of Advanced Oxidation Processes (AOPs) and biological processes is presented, providing the context of the problem and the justification for the chosen methodology (A Review of the Treatment of Landfill Leachate by Coupling Advanced Oxidation and Biological Processes) (Becerra

Moreno et al., 2023). Additionally, the use of ozone as an oxidizing agent for removing recalcitrant contaminants and its application to landfill leachates is analyzed (Advanced Oxidation Processes Based on Ozone as a Treatment Alternative for Landfill Leachates) (Becerra-Moreno et al., 2021).

The following chapters present the experimental results obtained:

- Chapter 1 (Synergistic Degradation of Organic Contaminants in Landfill Leachates Using Catalytic Ozonation with Magnetite): Analysis of the performance of magnetite as a catalyst in the degradation of organic contaminants through catalytic ozonation and optimization of process conditions (Becerra-Moreno et al., 2025).
- Chapter 2 (Response Surface and Ridge Regularization in Catalytic Ozonation of Leachate): Application of statistical models to evaluate the robustness of the catalytic ozonation process with magnetite, validating its efficiency and stability (Becerra-Moreno, MachucaMartínez, et al., Manuscript submitted for publication).
- Chapter 3 (Treatment of Landfill Leachates Using Magnetite-Catalyzed Ozone Coupled with an Up-flow Anaerobic Sludge Blanket Reactor): Evaluation of the coupling of catalytic ozonation with an up-flow anaerobic sludge blanket (UASB) reactor, analyzing its impact on biodegradability and treatment efficiency (Becerra-Moreno, Machuca-Martínez, et al., Manuscript submitted for publication).
- Chapter 4 (Heterogeneous Photocatalysis and an Anaerobic Biological Process for Leachate Treatment): Assessment of the anaerobic biodegradability and toxicity of leachates, applying heterogeneous photocatalysis with $TiO_2$/UV and an anaerobic biological process (Becerra Moreno et al., 2022).
- Chapter 5 (Alternative for the Treatment of Leachates Generated in a Landfill of Norte de Santander–Colombia, using the Coupling of a Photocatalytic and Biological Aerobic Process): Evaluation of the aerobic biodegradability and toxicity of landfill leachates through the coupling of heterogeneous photocatalysis and an aerobic biological process (Becerra et al., 2020).

Finally, the document concludes with:

- Chapter 6: Synthesis: Integration and comprehensive analysis of the results obtained, highlighting the study's main contributions and providing recommendations for applying these treatments in landfill leachate remediation.

Figure 1 presents a graphical summary illustrating the relationship between each product and the fulfillment of the project’s specific objectives.

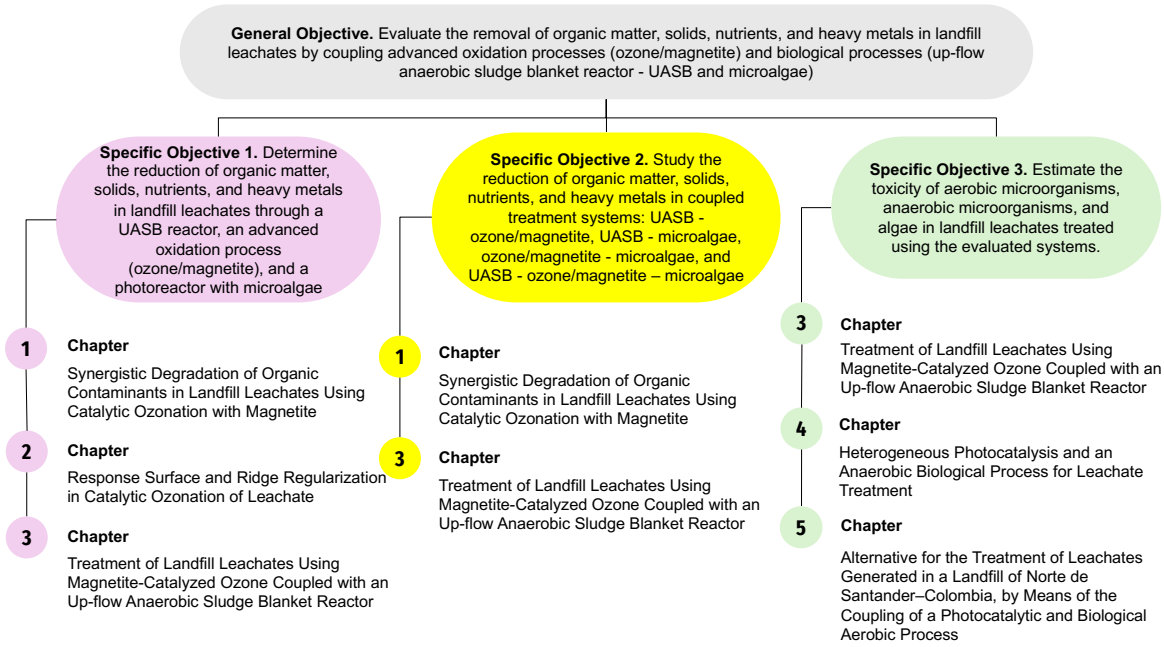



Figure 1 Graphical Summary of Each Product's Contribution to the Achievement of the Research's Specific Objectives

# 3. Theoretical Framework

## 3.1. A review on the treatment of landfill leachate by coupling advanced oxidation and biological processes

Ingeniería y
Competitividad
Vol 25 suplemento 2023; doi: 10.25100/iyc.v25isuplemento.11626

Artículo de Revisión

Número Suplemento

ISSN
0123-3033
e- 2027-8284

# Edición especial 25 años del doctorado en ingeniería

## Una revisión sobre el tratamiento para lixiviados de rellenos sanitarios mediante el acople de procesos avanzados de oxidación y biológicos

## A review on the treatment of landfill leachate by coupling advanced oxidation and biological processes

Cómo citar: Becerra-Moreno, D., Rubio-Gómez, Y.M., Barajas-Solano, A.F., Ramírez Ríos, L:F., Machuca-Martínez, F. Ingeniería y Competitividad. 25(suplemento) ,e- 30211626. doi: 10.25100/iyc.v25isuplemento.11626

Dorance Becerra-Moreno[1,2], Yrany M. Rubio-Gomez[1], Andrés F. Bara-jas-Solano[1], Luisa F. Ramírez Ríos[1], Fiderman Machuca-Martínez[2]

[1] Universidad Francisco de Paula Santander, Facultad de Ciencias Agrarias y del Ambiente, Norte de Santander, Colombia

[2] Universidad del Valle, Facultad de Ingenierías, Cali, Colombia

# Resumen

El tratamiento de lixiviados de rellenos sanitarios requiere de procesos que permitan la remoción eficaz de los diferentes contaminantes presentes en este tipo de residuos líquidos. Para el tratamiento de este tipo de residuos se han empleado una gran diversidad de procesos biológicos, los cuales aprovechan la capacidad de transformar los diferentes componentes del medio liquido en biomasa, sin embargo, estos procesos poseen limitaciones debido a las características intrínsecas del lixiviado. En los últimos años se ha impulsado la integración de los procesos biológicos con los Procesos Avanzados de Oxidación, lo cual permitiría reducir significativamente las características toxicas de estos residuos para así cumplir con las condiciones legales para ser vertidos al ambiente sin que se produzcan daños. En la presente revisión se investigan los trabajos recientes (2015 a 2021) referentes al tratamiento biológico y con procesos Avanzados de Oxidación (basados en ozono, procesos electroquímicos y fotocatálisis). Estos procesos se analizan en combinación, para describir las condiciones óptimas en las que se reducen las cargas contaminantes de los lixiviados de rellenos sanitarios. Finalmente es posible identificar que los procesos de tratamiento en estudio son tecnologías que pueden ser acopladas, registrando mayor eficacia y menor generación de subproductos de desecho o lodos.



Keywords: Electroquímico, Fotocatálisis, Lixiviado de rellenos sanitarios, Ozono, PAOs, Tratamiento biológico.



# Abstract

The treatment of landfill leachate requires processes that efficiently remove the different contaminants present in this type of liquid waste. To treat this type of waste, a great diversity of biological processes has been used, which take advantage of the capacity to transform the different components of the liquid medium into biomass; however, these processes have limitations due to the intrinsic characteristics of the leachate. In recent years, the integration of biological processes with Advanced Oxidation Processes has been promoted, which would significantly reduce the toxic characteristics of these wastes to comply with the legal conditions to be discharged into the environment without causing damage. In this work, the authors present a review (2015 to 2021) concerning the biological treatment, and Advanced Oxidation Processes (based on ozone, electrochemical processes, and photocatalysis). These processes are analyzed in combination to describe the optimal conditions under which pollutant loads of landfill leachate are reduced. Finally, it is possible to identify that the treatment processes under study are technologies that can be coupled, registering higher efficiencies and lower generation of waste by-products or sludge.



Keywords: Electrochemical, Photocatalysis, landfill Leachate, Ozone, AOPs, Biological treatment.

## Introducción

Los lixiviados son productos asociados a uno de los métodos de disposición de Residuos Sólidos Urbanos (RSU) utilizados ampliamente, como lo son los rellenos sanitarios o vertederos (1). En especial, los países en vía de desarrollo y subdesarrollados han implementado este método por su fácil operación y bajos costos relativos (2-3). Los lixiviados se generan en forma líquida de color obscuro y mal oliente (4-5-6), con alto contenido de componentes orgánicos, minerales y tóxicos. Estos líquidos complejos poseen características refractarias, altamente contaminantes para el ambiente (7-8).

La composición de los lixiviados está determinada de acuerdo con factores como la naturaleza de los residuos desechados, el clima, la frecuencia de lluvias y la edad del relleno sanitario (9). La generación de lixiviados ocurre cuando se infiltra la precipitación a través de las capas de residuos sólidos, permitiendo el transporte de los contaminantes solubles a la fase líquida, y donde a su vez, una serie de procesos químicos, físicos y biológicos, complejos ocurren simultáneamente (10). En la Figura 1 se presenta un esquema del proceso general de la generación de lixiviados en un relleno sanitario.

Los rellenos sanitarios deben estar equipados de un revestimiento que evite el paso de los lixiviados al suelo, de manera que sean conducidos y recolectados para someterse a un tratamiento adecuado. Las normas generalmente expedidas por entidades ambientales buscan proteger los recursos naturales, estableciendo límites permisibles para realizar descargas de los lixiviados tratados (4). La cantidad y características complejas de los lixiviados (contenidos de metales pesados, compuestos xeobióticos, compuestos biorefractarios, ácidos húmicos y fúlvicos) (11), representan un desafío, frente al cual se deben buscar alternativas de tratamiento que permitan el cumplimiento de las normativas y, por consiguiente, se proteja al ambiente y la población (12-13).

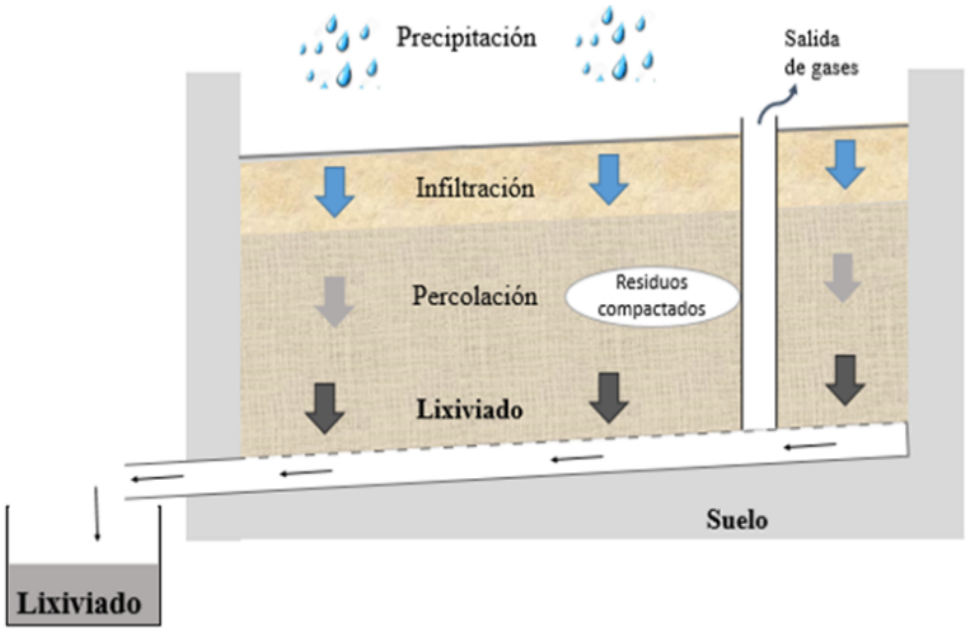



**Figura 1.** Generación de lixiviados en un relleno sanitario. Fuente: Autor.

Los rellenos sanitarios deben estar equipados de un revestimiento que evite el paso de los lixiviados al suelo, de manera que sean conducidos y recolectados para someterse a un tratamiento adecuado. Las normas generalmente expedidas por entidades ambientales buscan proteger los recursos naturales, estableciendo límites permisibles para realizar descargas de los lixiviados tratados (4). La cantidad y

características complejas de los lixiviados (contenidos de metales pesados, compuestos xeobióticos, compuestos biorefractarios, ácidos húmicos y fúlvicos) (11), representan un desafío, frente al cual se deben buscar alternativas de tratamiento que permitan el cumplimiento de las normativas y, por consiguiente, se proteja al ambiente y la población (12-13).

Entre los tratamientos principales para lixiviados generados en los rellenos sanitarios se encuentran, la recirculación y evaporación; coagulación-floculación; tratamientos biológicos aerobios, anaerobios y facultativos; tecnologías de membrana como microfiltración, ultrafiltración y osmosis inversa; y los Procesos Avanzados de Oxidación (14). Los rellenos sanitarios han implementado estos tratamientos de manera individual, o acoplados para conseguir la remoción de los contaminantes y aumentar la biodegradabilidad (7-15-16).

El tratamiento de lixiviados requiere ser un sistema eficiente, capaz de resistir la toxicidad del líquido y disminuirla (17). Entre los tratamientos más usados se encuentran los tratamientos biológicos (4), los cuales emplean reacciones asociadas a organismos vivos. Estos organismos crecen aprovechando los contaminantes del medio líquido como fuente de carbono o de energía (15). A pesar de que los tratamientos biológicos de lixiviados han presentado buenos resultados en cuanto a remoción de parámetros como la Demanda Química de Oxigeno (DQO) y Demanda Bioquímica de Oxigeno (DBO), la mayoría de las veces no es suficiente para alcanzar los estándares permisibles que dictan las autoridades ambientales (14-17). Los procesos biológicos son susceptibles de fallar debido a que los organismos vivos empleados, pueden verse superados por la alta cantidad de componentes orgánicos refractarios y de otras sustancias nocivas (18).

Otro de los métodos de tratamiento de lixiviados que se han venido estudiando sistemáticamente en los últimos años, son los Procesos Avanzados de Oxidación (PAOs). Los PAOs logran degradar compuestos recalcitrantes que no son degradados fácilmente por otros tratamientos (19). También, estos tratamientos aumentan la biodegradabilidad de los lixiviados, permitiendo disminuir el potencial tóxico (20). Se ha considerado en numerosos estudios que los PAOs resultan más ventajosos cuando se usan en acople con otro tratamiento, comparado con el tratamiento único (1-7-13). Es así como los métodos de tratamiento PAOs se han estudiado en combinación con los tratamientos biológicos, obteniendo resultados prometedores en términos de remoción de parámetros fisicoquímicos (21).

Se han clasificado los PAOs en procesos electroquímicos, basados en ozono, fotoasistidos, y varios (oxidación por aire húmedo, ultrasonido, oxidación con persulfato y otros) (22). Los procesos electroquímicos se caracterizan por que eliminan el color y la DQO del lixiviado, así como por convertir los compuestos orgánicos en otros compuestos como $CO_2$ y $H_2O$ (22-23). Los procesos basados en ozono han sido implementados por su capacidad para reducir la DQO, DBO, metales pesados, compuestos húmicos y fúlvicos (24). La mayor parte de los compuestos biodegradables pueden ser eliminados por los procesos fotoasistidos con tratamientos fotocatalíticos homogéneos y heterogéneos (25), los cuales son de especial interés por la posibilidad del aprovechamiento de la radiación solar en el tratamiento (22).

En este sentido, este trabajo presenta una revisión de los tratamientos de lixiviados producidos en rellenos sanitarios, particularmente del acople entre los tratamientos biológicos y los PAOs (procesos basados en ozono, proceso electroquímico, y tratamientos fotocatalíticos homogéneos y heterogéneos). Esto con el fin de evidenciar las ventajas, desventajas y condiciones de operación que se han obtenido mediante los trabajos de investigación sobre el tratamiento de lixiviados sometidos a los dos sistemas (PAOs y biológicos) como alternativas prometedoras para aumentar la eficacia en la remoción de la concentración de los contaminantes. Esta revisión es motivada por la necesidad de compilar información científica actualizada, que permita tener un panorama más detallado de la viabilidad de los tratamientos acoplados entre procesos biológicos y PAOs, con respecto a si se implementan de manera individual. También, se presentan algunas referencias para profundizar en el conocimiento del tema de estudio.

Se revisaron publicaciones entre los años 2015 y 2021 de revistas científicas de alto impacto. Una búsqueda en Scopus utilizando las palabras claves del tema de estudio (Biological treatment,

Electrochemical, Photocatalysis, landfill Leachate, Ozone, POAs, Treatment), arrojó que las revistas científicas que mayor cantidad de publicaciones registran, pertenecen al campo de las ciencias ambientales. Según esta revisión, las revistas con mayor número de publicaciones son Waste Management, Process Safety and Environmental Protection, Desalination and Water Treatment, Water Research, y Chemosphere.

## Tratamiento biológico

El tratamiento biológico es ampliamente usado en la remoción de contaminantes líquidos como las aguas residuales y los lixiviados (13-17-26). Este tratamiento se caracteriza por remover altas cantidades de sustancias orgánicas. También, es un método conveniente de aplicar por su simplicidad y rentabilidad (14-27). Son dos los principales procesos que condicionan el tratamiento biológico de lixiviados, en términos de la disponibilidad de oxígeno. Uno es el tratamiento aerobio, en el cual los microrganismos utilizan los contaminantes orgánicos como alimento, es decir, degradan la materia orgánica y la convierten en dióxido de carbono ($CO_2$) y una importante cantidad de lodos (13). El tratamiento anaerobio es otro de los procesos dentro de los tratamientos biológicos. Los tratamientos en condiciones anaerobias degradan compuestos orgánicos para convertirlos en su mayoría, en sustancias gaseosas como el dióxido de carbono y el metano ($CH_4$) (14-28).

Los procesos aerobios eliminan contaminantes orgánicos biodegradables y producen la nitrificación del nitrógeno amoniacal ($NH_4$+-N) (29). Por otra parte, en los procesos anaerobios suele presentarse una desventaja respecto a la baja reducción o incluso el aumento del $NH_4$+-N. Sin embargo, los tratamientos en condiciones anaerobias tienen otras características que los hacen ventajosos frente a otros tratamientos, por mencionar algunas, la posibilidad de la captación y aprovechamiento del biogás $CH_4$, la reducción de producción de lodos en comparación con los procesos aerobios, entre otros (30).

Los procesos de los tratamientos aerobios y anaerobios son esquematizados en la Figura 2, elaborada a partir del trabajo de Luo et al., 2020 (siglas de los nombres de los procesos en inglés).

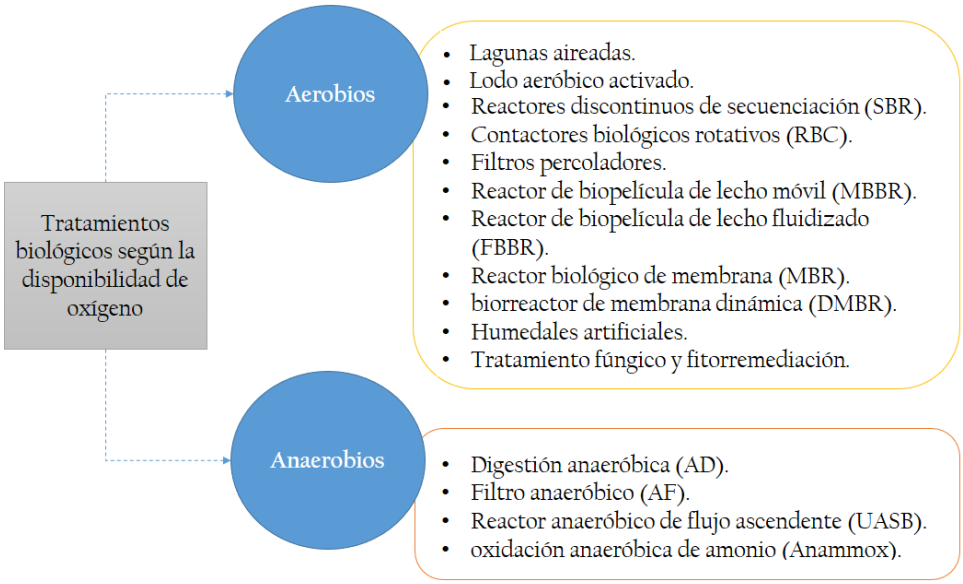



**Figura 2**. Procesos aerobios y anaerobios de los tratamientos biológicos. Fuente: Autor.

Se ha registrado en múltiples estudios científicos que los tratamientos biológicos son alternativas donde se obtienen buenos resultados de remoción de contaminantes en lixiviados jóvenes (<5 años) (3-21-31). Los lixiviados jóvenes contienen altas cantidades de contaminantes orgánicos biodegradables, con

baja masa molar y presentan un pH ácido (26-32). Mientras, los lixiviados de edad intermedia y maduros resultan menos favorables de tratar con procesos biológicos. Los lixiviados de rellenos sanitarios de edad intermedia (5-10 años) y los maduros (>10 años), se caracterizan por presentar alto contenido de compuestos húmicos y fúlvicos, así como, menor biodegradabilidad en comparación con los rellenos sanitarios jóvenes (26-33). La descripción de las características de los lixiviados de rellenos sanitarios de acuerdo a la edad, se pueden consultar en el manuscrito de Peng (2017) (6).

Un tratamiento biológico realizado al lixiviado de un relleno sanitario joven mediante el proceso SBR, alcanzó una remoción de Nitrógeno Total (NT) del 99 %, DQO del 87 % y fosforo del 49 % (34). Otro estudio registró un tratamiento de lixiviados utilizando el proceso DMBR, donde se obtuvieron remociones de $NH_4^+$-N y NT de 98 y 90 % respectivamente (35). No obstante, en el tratamiento biológico de lixiviados maduros, se ha determinado que a concentraciones de DQO > 2000 mg/L, $NH_4^+$-N > 1000 mg/L y alcalinidad alta, representan líquidos de alta complejidad para someter a este tratamiento (4). También, los compuestos refractarios pueden inhibir el desarrollo de los microrganismos que descomponen los contaminantes (4-18).

En una investigación realizada para tratar un lixiviado maduro en un biorreactor continúo utilizando Penicillium spp. se presentaron remociones para los parámetros fisicoquímicos como DQO (52 %), Carbono Orgánico Disuelto (COD) (54 %), Carbono Total (CT) (60 %) y Carbono Orgánico Total (COT) (68 %) (36). Un tratamiento que se ha considerado recomendable para disminuir las concentraciones de NT y DQO es el Anammox (37-38). Se han alcanzado reducciones del 94 % de NT y del 62 % de DQO mediante el tratamiento de lixiviados con Anammox (39). Una mayor información acerca de los tratamientos biológicos y su eficacia según la edad del lixiviado, puede ser consultada en el trabajo de Kamaruddin et al. (2015). Además, las remociones de los parámetros fisicoquímicos obtenidos en diferentes investigaciones sobre la aplicación de tratamientos biológicos, fueron recopiladas en el trabajo de Torretta et al. (2017).

## Procesos Avanzados de Oxidación

Los PAOs son tratamientos que se han venido estudiando sistemáticamente en los últimos años. Éstos han sido catalogados como tratamientos prometedores debido a sus ventajas en la eliminación de contaminantes refractarios y por aumentar la biodegradabilidad (14-40-41). La formación de radicales libres u oxidantes como radicales hidroxilos (·OH), es la base del proceso de tratamiento de los PAOs. Otro proceso dentro del tratamiento es la reacción química de radicales producidos con compuestos orgánicos (19). Los oxidantes que se involucran en el tratamiento con los PAOs permiten aumentar el rendimiento para la remoción de contaminantes (42). Estos oxidantes tienen asociado un potencial de oxidación $E^o$ (V), los cuales se encuentran listados en trabajo de Kow et al. 2016, donde se observa que, el radical hidroxilo (·OH) tiene el mayor poder oxidativo (2.8 V).

Los PAOs para el tratamiento de lixiviados se dividen en cinco procesos (42), presentados en la Figura 3.


**Figura 3.** Procesos Avanzados de Oxidación para el tratamiento de lixiviados de rellenos sanitarios.Fuente: Autor.


doi: 10.25100/iyc.v25isuplemento.11626

La clasificación de los PAOs se subdivide de acuerdo al tipo de tratamiento. A los procesos basados en ozono pertenecen la ozonización, ozonización fotocatalítica, ozono/peróxido de hidrógeno, ozono/ persulfato, fentozono y ozonización catalítica. Dentro de los procesos químicos se encuentran, el fenton, oxidación con persulfato y persulfato con calor. Los procesos electroquímicos pueden dividirse en oxidación electroquímica, electrocoagulación y electrofenton. En cuanto a los procesos fotoasistidos incluyen la fotocatálisis, fenton fotoasistido, persulfato/UV, Peoxono/UV, fotoelectroquímico y ozono/UV. Algunos métodos que aún se encuentran en desarrollo se clasifican como procesos varios, entre los más conocidos de este grupo, la oxidación con aire húmedo, cavitación hidrodinámica, ultrasonido y procesos asistidos con catálisis (42). En la Tabla 1 se presentan las ventajas y desventajas de acuerdo a cada PAOs.

Tabla 1. Ventajas y desventajas de los PAOs para el tratamiento de lixiviados.

| PAOs | Ventajas | Desventajas |
|---|---|---|
| **Procesos basados en ozono** | Reducen ampliamente la DQO y la DBO.<br>Elimina color y olor.<br>No aumenta la producción de contaminantes tóxicos.<br>Baja producción de lodos. | Es favorable solo como tratamiento previo o posterior.<br>Implican una transferencia de masa de ozono de gas a líquido que es muy baja.<br>Se deben tomar medidas especiales con el manejo de ozono. |
| **Procesos Fotoasistidos** | Los procesos fotoasistidos mejoran los demás procesos PAOs en términos de reducción de contaminantes, aprovechando su función catalítica. | Alto consumo de energía, lo cual se ha estudiado para bajar estos costos con tecnologías más limpias. |
| **Procesos Electroquímicos** | Eficiente para la eliminación de contaminantes (concretamente orgánicos).<br>El proceso se lleva a cabo a temperatura y presión ambiente y tiene una alta eficiencia de tratamiento.<br>Cuando las reacciones tienen lugar en fase homogénea, entonces no hay limitaciones de transferencia de masa. | Uso intensivo de energía.<br>Posible formación de compuestos orgánicos clorados.<br>Si el lixiviado tiene un alto contenido de ácidos húmicos y fúlvicos, existe la posibilidad de que se formen trihalometanos que generen mal olor. |

Fuente: Adaptado de (42).

Los tratamientos PAOs han demostrado que son muy eficaces para remover aquellos contaminantes complejos de tratar con la mayoría de otros tratamientos en forma única (40). También son tratamientos avanzados, en tanto no generan cantidades excesivas de lodos (19). No obstante, los PAOs se atribuyen un alto valor en costos de tipo energético, insumos químicos, etc., e inconvenientes del control operativo en su implementación a gran escala (14). Una estimación de los costos del tratamiento de lixiviados de rellenos sanitarios con ozonización fue de 7.06 €/$m^3$, el cual es mayor, comparado con el costo estimado para tratamiento biológico oxidativo de 4.0 €/$m^3$ (43). Además, el control operativo de la dosificación para el manejo de los altos volúmenes de lixiviados generados en rellenos sanitarios, debe permitir ajustarse a las posibles fluctuaciones de caudales asegurando la mayor eficiencia (14-44).

Por consiguiente, los investigadores han estado encaminando sus estudios en el aprovechamiento de los POAs como pretratamiento o postratamiento de lixiviados de rellenos sanitarios (7-16-45). Los tratamientos combinados han obtenido mayores eficiencias en términos de costos y disminución de las características contaminantes (46). Los tratamientos biológicos son los más comunes para ser acoplados con los PAOs (15). Los PAOs como pretratamiento mejoran las características de biodegradabilidad del líquido, lo cual favorece el posterior tratamiento con microorganismos, que acaban por eliminar la mayor parte de estos compuestos orgánicos (47), esto es favorable especialmente para tratar lixiviados maduros. Como postratamiento, los PAOs se encargan de pulir el tratamiento con la eliminación de la fracción recalcitrante y tóxica restante en el líquido, que no pudo ser removida por el tratamiento biológico anterior (7).

## Tratamiento de acople con procesos basados en ozono y biológico

Los procesos basados en ozono generan radicales hidroxilos que le otorgan un alto poder oxidativo (40). En estos procesos se pueden obtener resultados mejorados de la generación de radicales ·OH por medio de la adición de UV (47-48), Peróxido de hidrogeno ($H_2O_2$) (21-48), catalizadores (8-49), entre otros. El acoplamiento entre los procesos basados en ozono y los biológicos ha sido estudiado en su mayoría empleando un proceso basado en ozono como postratamiento, aprovechando las instalaciones comunes de tratamientos biológicos para lixiviados en los rellenos sanitarios (41-50).

Las vías de reacción del ozono (la formación / consumo de ·HO) están directamente influenciadas por el pH. El ozono tiene la capacidad de oxidar de manera eficiente la materia orgánica a un pH ligeramente alcalino, que es el pH típico de la mayoría de los lixiviados de vertederos (tratados biológicamente) (18). Operar la ozonización a pH alcalino favorece la producción de HO para acelerar la remoción de materia orgánica recalcitrante, según el proceso basado en ozono. En un tratamiento de lixiviados con procesos biológicos con lodos activados y ozonización, se obtuvieron remociones de 58 % de DQO y 35 % de COD en medio ácido, y un 30 % de DQO y 8 % de COD en medio alcalino (43). Algunos estudios han demostrado que en un tratamiento con oxígeno y peróxido de hidrogeno ($O_3/H_2O_2$) puede degradar compuestos aromáticos a pH bajos (51). Se ha afirmado que la oxidación biológica funciona eficazmente como postratamiento para eliminar la fracción orgánica biodegradable resultante del $O_3$/ $H_2O_2$ (52). También, el tratamiento con Fentozono ($O_3/H_2O_2/Fe^{+2}$) en conjunto con un pretratamiento con MBR, ha resultado en remociones de 48.82 y 63.59 % de DQO y absorbentes UV254, respectivamente (53) en condiciones de operación de pH ácido (3 unidades).

Otros tratamientos como la ozonización fotocatalítica ($O_3$/UV) y el Ozono/Persulfato ($O_3/S_2O_8^{2}$) en acople con sistemas biológicos han demostrado que el pH básico tiene una relación óptima con los resultados de remoción. Por ejemplo, para el tratamiento con $O_3$/UV de lixiviados tratados previamente con varios procesos biológicos (lagunas aireadas, lodos activados y un proceso anaerobio), en condiciones de pH básico (9) se permitió aumentar la biodegradabilidad en hasta un 91 % (54). En otra investigación se optimizó el tratamiento de $O_3/S_2O_8^{2}$, cuyo afluente provenía de dos tratamientos biológicos previos, a pH de 9. Es así, los autores registraron reducción de la DQO, color y toxicidad, en hasta 85, 87 y 80 %, respectivamente, además de un aumento de 47 % de $BOD_5$/COD (55).

Las sustancias húmicas, incluidos el ácido húmico (HA) y el ácido fúlvico (FA), se eliminaron eficazmente junto con la descomposición de los hidrocarburos aromáticos y la disminución del grado de humificación durante el proceso de ozonización (56-57). La materia orgánica de alto peso molecular (PM) se transformó en un peso molecular bajo. La mayoría de los compuestos orgánicos de alto PM pasan como moléculas de bajo PM de 10 kDa a 1 kDa (56). En la Tabla 2 se presentan los registros de tratamientos combinados entre biológicos y los procesos basados en ozono.

Tabla 2. Tratamiento de lixiviados mediante procesos biológicos y basados en ozono.

| Tipo de combinación de tratamiento | Condiciones óptimas de operación | Eficacia | Valor final del parámetro | Referencia |
|---|---|---|---|---|
| **Biológico (eliminación de nitrógeno autótrofo) y Ozono** | 90 ± 5 g/m³ de concentración de $O_3$, 5.4 g/h de suministro de $O_3$, 60 min de reacción, 6.0-7.0 de pH | 26.8 % de DQO y 80.4 de NT | Aprox. un 300 mg/L de DQO, 0.01-0.06 de $DBO_5$/DQO | (20) |
| **Proceso biológico, desinfección y Ozono/ Persulfato** | 0.79 g/h. de flujo másico de $O_3$, 4500 mg/L. de $S_2O_8^{2-}$, 9.0 de pH., 210 min de reacción | Remoción con Ozono/ Persulfato:<br>85 % de DQO, 87 % de color, aumento del 0.47 % de $BOD_5$/COD, disminución de la toxicidad en 80 % | 120 mg/L de DQO, 0.61 de $DBO_5$/DQO | (55) |
| **Efluente estabilizado anaeróbicamente y Ozono catalizado con $ZnSO_4$** | 27 g/m³ dosis de $O_3$, 1 g/6 g dosis de Zn, 4.0 de pH, 180 min de reacción | Remoción con ozono catalizado:<br>90 % de DQO, 99 % de color, 5 % de $NH_3$-N. | | (58) |
| **Humedal artificial y Ozonización catalítica con Zeolita** | 9 días de tratamiento biológico, planta Typha angustifolia,<br>1.5 g/L de Zeolita, 152 mg/L de Fe, pH de 8 | 97.76 % de DQO, cerca del 88 % de DBO | 186 mg/L de DQO, 115.7 mg/L DBO, 8.1 de pH, 8.5 NTU de turbidez, 244 mg/L de sólidos totales disueltos, 0.618 de $DBO_5$/ DQO | (59) |

Fuente: Autor.

## Tratamiento de acople con fotocatálisis y biológico

Durante las últimas décadas, la fotocatálisis de semiconductores ha atraído mucha atención debido a su excelente eficiencia para la purificación ambiental (1). Hasta ahora, se han ensayado más de 190 semiconductores como fotocatalizadores y uno de los más utilizados ha sido el TiO. Este semiconductor se destaca, pero a menudo no se considera una alternativa viable por sí sola (1-25). Los autores han puesto su interés en estos procesos, por el uso alternativo de energía solar como fuente de fotones junto con catalizadores de bajo costo (1-60). En la fotocatálisis es importante el tiempo de irradiación. El pH ácido y alcalino es favorable para la eliminación de contaminantes orgánicos y amoniaco respectivamente. La presencia de ciertos iones (tanto aniones como cationes) en el lixiviado del vertedero puede limitar la tasa de fotomineralización de contaminantes orgánicos (19).

Como se muestra en la Tabla 3, el pH 5 ha demostrado ser una condición óptima de tratamiento, en su mayoría posterior al tratamiento biológico, y se han obtenido valores que llegan a cumplir con la normatividad correspondiente (1). Adicionalmente, en la Tabla 3 se muestran las condiciones óptimas de tiempo radiación y energía, para cada caso, así como las eficiencias de remoción de los parámetros que caracterizan los lixiviados de rellenos sanitarios.

Tabla 3. Tratamiento de lixiviados mediante procesos biológicos y fotoasistidos.

| Tipo de combinación de tratamiento | Condiciones óptimas de operación | Eficacia | Valor final del parámetro | Referencia |
|---|---|---|---|---|
| **ARB y UV/$TiO_2$** | 1 g/ L de $TiO_2$ ; pH 5, 120 minutos de reacción con UV, y energía de irradiación de 900 Kj/ kg | Remoción con ARB: 72.3 % de DQO, 82.1 % de $NH_4$–N, 92.4 de NT<br><br>Remoción con UV/ $TiO_2$: 82 % de DQO | 92.16 mg/L de DQO | (7) |
| **ARB y UV/$S_2O_8^{2-}$** | 1.5 g/L de persulfato a pH 5, y energía de irradiación: 225 Kj/kg | Remoción con ARB: 72.3 % de DQO, 82.1 % de $NH_4$–N, 92.4 de NT<br><br>Remoción con UV/ $S_2O_8^{2-}$: 81 % de DQO | 97.28 mg/L de DQO | |
| **UV/$TiO_2$ y proceso aerobio** | 100 mg/L $TiO_2$, a un pH ácido de 3 | 68 % de DQO, 76 % de COD, 54.69 % de SSV | 160 mg/L de DQO, pH de 7.0 y 7.3, 928 de SSV | (15) |
| **Vertedero biológicamente estabilizado y UV/ $H_2O_2$** | 30 min de reacción, 8 de pH, 2.0 g $H_2O_2$/g DQO , | Remoción con UV/ $H_2O_2$:<br><br>6.9 % de DQO, 0.08 relación DBO/DQO | 756 mg/L de DQO | (61) |
| **SBBGR – (Sequencing Batch Biofilter Granular Reactor) y UV/$H_2O_2$** | 7 horas de degradación Biológica, 650 mg la dosis específica de $H_2O_2$ y 7 horas por L de lixiviado tratado, el tiempo de trabajo de la lámpara UV | 88.7 % de DQO, 82 % de COD, 92 % de SST, 98.6 % de NT, 99.9 % de $NH_3$, Y 93.3 % de color | 261 mg/L de DQO, 156 mg/L de COD, 20 mg/L de SST, 36.2 mg/L de NT, 0.5 mg N/L de $NH_3$, y 0.025 (abs) de color | (62) |

Fuente: Autor.

## Tratamiento de acople con procesos electroquímicos y biológico

Se conoce el lixiviado con alta concentración de sustancias orgánicas y nitrógeno, que son extremadamente tóxicos para el medio ambiente. Recientemente, la oxidación electroquímica ha recibido mucha atención debido a su bajo costo, viabilidad, respeto al medio ambiente y excelente eliminación de contaminantes en las aguas residuales (31). Según algunos autores, un pH bajo favorece las eficiencias de eliminación de sustancias orgánicas elevadas, pero restringe las eficiencias de eliminación de amonio bajas y viceversa (34).

La oxidación electroquímica, aunque tiene eficacia en el tratamiento de lixiviados de rellenos sanitarios, tiene la principal desventaja de ser un proceso que consume mucha energía y la formación de compuestos orgánicos clorados. Además, se logra una alta eficiencia en la eliminación de contaminantes con electrodos metálicos de alto costo, como el diamante dopado con boro y el Ti / $IrO_2$-$RuO_2$, lo que genera altos costos operativos. Esta es la razón por la que se favorece más como paso final o como unidad auxiliar en emergencias (42).

El tratamiento con electrocoagulación ha demostrado tener la capacidad de aumentar el valor del índice de biodegradabilidad de lixiviados de 0.27 a 0.45 (63). Este proceso se caracteriza por tener un alto costo relativo de inversión inicial, con la desventaja de generar lodos y corrosión en el ánodo que sirve para

producir los iones metálicos que forman los coágulos (63). No obstante, la electrocoagulación tiene una alta eficacia en la remoción de materia orgánica, de forma rápida y de fácil manejo (64). En una investigación se sometieron lixiviados biológicamente estabilizados a electrocoagulación, obteniendo remociones de 45% para el TOC, 57.4% para DQO y 77.1% para el color, concluyendo así que, éste es un método de los procesos electroquímicos, que puede ser una buena alternativa como postratamiento (65).

Aunque la tecnología electroquímica demuestra un excelente desempeño en el tratamiento de los lixiviados de los rellenos sanitarios, el efluente aún puede presentar una elevada carga contaminante, en referencia con la permitida por la normatividad legal (42). El acople con tratamientos biológicos ha permitido que las características del lixiviado alcancen una alta disminución de la toxicidad de los lixiviados, convirtiéndolo en un líquido apto para ser vertido (31). Esto se muestra en la Tabla 4, allí se describen las condiciones óptimas de los tratamientos combinados entre biológicos y electroquímicos y se evidencian los valores finales de las características de los lixiviados tratados.

Además, la tecnología electroquímica puede reducir la toxicidad del lixiviado de vertedero, por lo que es necesario estudiar más a fondo el punto extremo de reducción de la toxicidad durante la electrólisis en investigaciones futuras, lo que puede ahorrar el costo del tratamiento desde la perspectiva de las propiedades contaminantes (66).

Tabla 4. Tratamiento de lixiviados mediante procesos biológicos y electroquímicos

| Tipo de combinación de tratamiento | Condiciones óptimas de operación | Eficacia | Valor final del parámetro | |
|---|---|---|---|---|
| Reactor granular de biofiltro por lotes de secuenciación y un reactor electrolítico con celda de tipo discontinuo | Densidad de corriente de 200 mA/cm$^2$; tiempo de reacción de 8 horas el biológico y 240 min el electroquímico | 82% de N- Amoniacal; 93 % de DQO | Aprox. 278 mg/L de DQO | (17) |
| Sistema de aireación extendida de ciclo intermitente (ICEAS) y oxidación electroquímica utilizando Ti/BDD y Ti/ $RuO_2$ ánodos. | 83 mA/cm, pH bajo y 8 h | Ànodo Ti/BDD: 5.17 % de DQO, 91.89 % de COT, 81.18 % de $NH_4^+$-N y 63.54 % de NT<br>Ànodo Ti/$RuO_2$:<br>92.57 % de DQO, 78.76 % de COT, 97.85 % de $NH_4^+$-N y 72.12 % de NT | 32.26 mg/L de DQO con Ti/BDD y 49.68 mg/L de DQO con Ti/ $RuO_2$ | (31) |
| Proceso anaerobio y un biorreactor de Membrana electroquímica reactiva (MER) | 45 minutos de tiempo de reacción | Remoción con MER: 70 - 76 % de COT; 100 % N-Amoniacal | | (67) |
| Manto de lodos (UASB), proceso anóxico en un reactor anaerobio y electroquímico con un ánodo de $SnO_2$ - $Sb_2O_5$ a base de Ti. | Tiempo de retención hidráulica (TRH) de 2.75 días; Temperatura de 20-22 °C; tiempo de reacción de 40 a 80 minutos, energía de entrada al proceso electroquímico 10 kWh/m$^3$. | 95.4 % de DQO, 97.2 % de $NH_4$-N y 90.3 % de NT | 70 mg/L de DQO, 11.3 mg/L de $NH_4$-N y 39 mg/L de NT | (68) |
| Tratamiento biológico y reactor electroquímico de lecho fijo | Tiempo de reacción 12 minutos; 2.0 Voltios | 82.0 % de DQO; 86.5 % de $NH_4$-N; y 76.3 % de NT; 93.4 % de cromo . | 70 mg/L de DQO, 9.4 mg/L de $NH_4$ –N, 25.9 mg/L de NT | (69) |
| Pretratamiento biológico y proceso electroquímico con compuesto por un reactor de ánodo de hierro (IAR) y Ti / $RuO_2$ | Densidad de corriente de 50 mA / cm$^2$; tiempo de reacción 240 minutos | 90.9 ± 0.3 % de DQO; y 90.2 ± 1,0 % de NT. | | (70) |

Fuente: Autor.

### Tratamientos con procesos PAOs y biológicos en Colombia

En Colombia los rellenos sanitarios son el sistema de disposición final de residuos sólidos más utilizado, sin embargo, aún no se ha establecido completamente la implementación de tecnologías para el tratamiento de los lixiviados que aseguren una gestión ambientalmente viable (71). Dentro de los procesos comunes a nivel nacional para el manejo de los lixiviados en un relleno sanitarios se incluye la recirculación, evaporación y los sistemas con membrana. Así mismo, se han implementado algunos sistemas biológicos en plantas de tratamiento de lixiviados y escaso desarrollo utilizando los PAOs en la gestión de estos líquidos (71-72).

En el relleno sanitario Presidente, Valle del Cauca, se estableció un humedal para tratar lixiviados pretratados de un estanque anaeróbico de alta tasa (BLAAT®) (71). Se utilizaron en el humedal policultivos de especies tropicales: Gynerium sagittatum, Colocasia esculenta y Heliconia psittacorum. Estas especies nativas demostraron su capacidad fitorremediadora para los lixiviados pretratados en 60-90 % de remoción de contaminantes como DQO y metales pesados (73).

Los lixiviados provenientes del Relleno Sanitario Parque Tecnológico Ambiental el Guayabal ubicado en la ciudad de Cúcuta, se sometieron a tratamiento de fotocatálisis heterogénea TiO2/UV acoplada a un reactor de lodos activados. Este sistema obtuvo una eficiencia global del proceso en más de un 50 % (15). Otro sistema de PAOs con procesos electroquímicos se utilizó para tratar lixiviados de un relleno sanitario ubicado en la ciudad de Pasto, con el cual se demostró la eficiencia de desactivación de microorganismos en los lixiviados (74).

## Conclusiones

La composición compleja de los lixiviados de rellenos sanitarios requiere de una alternativa de tratamiento que alcance las remociones esperadas, de manera que no represente un riesgo para la salud y el ambiente. Recientemente, se ha avanzado en estudios sobre los PAOs y su acople con los procesos biológicos, para lograr mayores rendimientos de remoción en cuanto a las características de los lixiviados. Así, mismo, existe la necesidad de desarrollar sistemas de tratamiento que puedan cumplir con los límites permisibles de descarga según la normatividad. Adicionalmente deben tenerse en cuenta los costos económicos, controles de operación y facilidades de manejo. Con el avance en la investigación, algunas alternativas de tratamiento han resultado eficaces para gestionar los lixiviados, disminuyendo sus características nocivas. El acople de los procesos basados en ozono, los procesos asistidos por UV y los electroquímicos, junto con los procesos biológicos, para el tratamiento de lixiviados de rellenos sanitarios, se perciben como tecnologías complementarias de mayor eficacia y más limpias.

## Referencias


1. Hassan M, Zhao Y, Xie B. Employing TiO2 photocatalysis to deal with landfill leachate: Current status and development. Chem Eng J. 2016;285:264–75. Disponible en: http://dx.doi.org/10.1016/j.cej.2015.09.093

2. Bolyard SC, Reinhart DR. Application of landfill treatment approaches for stabilization of municipal solid waste. Waste Manag. 2016;55:22–30. Disponible en: http://dx.doi.org/10.1016/j.wasman.2016.01.024

3. Moradian F, Ramavandi B, Jaafarzadeh N, Kouhgardi E. Effective treatment of high-salinity landfill leachate using ultraviolet / ultrasonication / peroxymonosulfate system. Waste Manag. 2020;118:591–9. Disponible en: https://doi.org/10.1016/j.wasman.2020.09.018

4. Müller GT, Giacobbo A, dos Santos Chiaramonte EA, Rodrigues MAS, Meneguzzi A, Bernardes AM. The effect of sanitary landfill leachate aging on the biological treatment and assessment of photoelectrooxidation as a pre-treatment process. Waste Manag. 2015;36:177–83. Disponible en: https://doi.org/10.1016/j.wasman.2014.10.024

5. Cheng W, Quan X, Huang X, Cheng C, Yang L, Cheng Z. Enhancement of micro-filtration performance for biologically-treated leachate from municipal solid waste by ozonation in a

micro bubble reactor. Sep Purif Technol. 2018;207(June):535–42. Disponible en: https://doi.org/10.1016/j.seppur.2018.07.005

6. Peng Y. Perspectives on technology for landfill leachate treatment. Arab J Chem. 2017;10:S2567–74. Disponible en: http://dx.doi.org/10.1016/j.arabjc.2013.09.031

7. Hassan M, Wang X, Wang F, Wu D, Hussain A, Xie B. Coupling ARB-based biological and photochemical (UV/$TiO_2$ and UV/$S_2O_8^{2-}$) techniques to deal with sanitary landfill leachate. Waste Manag. 2017;63:292. Disponible en: http://dx.doi.org/10.1016/j.wasman.2016.09.003

8. Ma C, Yuan P, Jia S, Liu Y, Zhang X, Hou S, et al. Catalytic micro-ozonation by Fe3O4 nanoparticles @ cow-dung ash for advanced treatment of biologically pre-treated leachate. Waste Manag. 2019;83:23–32. Disponible en: https://doi.org/10.1016/j.wasman.2018.10.045

9. Mandal P, Dubey BK, Gupta AK. Review on landfill leachate treatment by electrochemical oxidation: Drawbacks, challenges and future scope. Waste Manag. 2017;69:250–73. Disponible en: https://doi.org/10.1016/j.wasman.2017.08.034

10. Youcai Z. Leachate Generation and Characteristics. In: Inc. E, editor. Pollution Control Technology for Leachate from Municipal Solid Waste. 2018. p. 1–30.

11. Yu M, Xi B, Zhu Z, Zhang L, Yang C, Geng C. Fate and removal of aromatic organic matter upon a combined leachate treatment process. Chem Eng J. 2020;401(June):126157. Disponible en: https://doi.org/10.1016/j.cej.2020.126157

12. Ogata Y, Ishigaki T, Ebie Y, Sutthasil N, Witthayaphirom C, Chiemchaisri C, et al. Design considerations of constructed wetlands to reduce landfill leachate contamination in tropical regions. J Mater Cycles Waste Manag. 2018;20(4):1961–8. Disponible en: http://dx.doi.org/10.1007/s10163-018-0755-0

13. Luo H, Zeng Y, Cheng Y, He D, Pan X. Recent advances in municipal landfill leachate: A review focusing on its characteristics, treatment, and toxicity assessment. Sci Total Environ. 2020;703:135468. Disponible en: https://doi.org/10.1016/j.scitotenv.2019.135468

14. Gao J, Oloibiri V, Chys M, Audenaert W, Decostere B, He Y, et al. The present status of landfill leachate treatment and its development trend from a technological point of view. Rev Environ Sci Biotechnol. 2015;14(1):93–122. Disponible en: https://doi.org/10.1007/s11157-014-9349-z

15. Becerra D, Soto J, Villamizar S, Machuca-Martínez F, Ramírez L. Alternative for the Treatment of Leachates Generated in a Landfill of Norte de Santander–Colombia, by Means of the Coupling of a Photocatalytic and Biological Aerobic Process. Top Catal. 2020;63(11–14):1336–49. Disponible en: https://doi.org/10.1007/s11244-020-01284-1

16. Baiju A, Gandhimathi R, Ramesh ST, Nidheesh P V. Combined heterogeneous Electro-Fenton and biological process for the treatment of stabilized landfill leachate. J Environ Manage. 2018;210:328–37. Disponible en: https://doi.org/10.1016/j.jenvman.2018.01.019

17. Del Moro G, Prieto-Rodríguez L, De Sanctis M, Di Iaconi C, Malato S, Mascolo G. Landfill leachate treatment: Comparison of standalone electrochemical degradation and combined with a novel biofilter. Chem Eng J. 2016;288:87–98. Disponible en: http://dx.doi.org/10.1016/j.cej.2015.11.069

18. Chys M, Oloibiri VA, Audenaert WTM, Demeestere K, Van Hulle SWH. Ozonation of biologically treated landfill leachate: Efficiency and insights in organic conversions. Chem Eng J. 2015;277:104–11. Disponible en: http://dx.doi.org/10.1016/j.cej.2015.04.099

19. Kow S, Fahmi MR, Abidin CZA, Soon□An O. Advanced Oxidation Processes: Process Mechanisms, Affecting Parameters and Landfill Leachate Treatment. Water Environ Res. 2016;88(11):2047–58. Disponible en: https://doi.org/10.2175/106143016X14733681695285

20. Gao JL, Oloibiri V, Chys M, De Wandel S, Decostere B, Audenaert W, et al. Integration of autotrophic nitrogen removal, ozonation and activated carbon filtration for treatment of landfill leachate. Chem Eng J. 2015;275:281–7. Disponible en: https://doi.org/10.1016/j.cej.2015.04.012

21. Xu Q, Siracusa G, Di Gregorio S, Yuan Q. COD removal from biologically stabilized landfill leachate using Advanced Oxidation Processes (AOPs). Process Saf Environ Prot. 2018;120:278–85. Disponible en: https://doi.org/10.1016/j.psep.2018.09.014

22. Han M, Duan X, Cao G, Zhu S, Ho SH. Graphitic nitride-catalyzed advanced oxidation processes (AOPs) for landfill leachate treatment: A mini review. Process Saf Environ Prot. 2020;139:230–40. Disponible en: https://doi.org/10.1016/j.psep.2020.04.046

23. Labiadh L, Fernandes A, Ciríaco L, Pacheco MJ, Gadri A, Ammar S, et al. Electrochemical treatment of concentrate from reverse osmosis of sanitary landfill leachate. J Environ Manage. 2016;181:515–21. Disponible en: https://doi.org/10.1016/j.jenvman.2016.06.069

24. Wang H, Wang Y nan, Li X, Sun Y, Wu H, Chen D. Removal of humic substances from reverse osmosis (RO) and nanofiltration (NF) concentrated leachate using continuously ozone generation-reaction treatment equipment. Waste Manag. 2016;56:271–9. Disponible en: http://dx.doi.org/10.1016/j.wasman.2016.07.040

25. Tasnim G, Sheikh Y, Mahtab M. Photocatalytic (UV-TiO2) Degradation Process For Landfill Leachate Treatment. In: International Conference on Recent Advances in Engineering and Science. 2020. p. 7.

26. Chen W, Zhang A, Jiang G, Li Q. Transformation and degradation mechanism of landfill leachates in a combined process of SAARB and ozonation. Waste Manag. 2019;85:283–94. Disponible en: https://doi.org/10.1016/j.wasman.2018.12.038

27. Ren Y, Ferraz F, Lashkarizadeh M, Yuan Q. Comparing young landfill leachate treatment e ffi ciency and process stability using aerobic granular sludge and suspended growth activated sludge. J Water Process Eng. 2017;17:161–7. Disponible en: http://dx.doi.org/10.1016/j.jwpe.2017.04.006

28. Azad Pashaki SG, Khojastehpour M, Ebrahimi-Nik M, Rohani A. Treatment of municipal landfill leachate: Optimization of organic loading rate in a two-stage CSTR followed by aerobic degradation. Renew Energy. 2021;163:1210–21. Disponible en: https://doi.org/10.1016/j.renene.2020.09.010

29. Bashir MJK, Aziz HA, Amr SSA, Sethupathi S, Ng CA, Lim JW. The competency of various applied strategies in treating tropical municipal landfill leachate. Desalin Water Treat. 2015;54(9):2382–95. Disponible en: https://doi.org/10.1080/19443994.2014.901189

30. Luo H, Zeng Y, Cheng Y, He D, Pan X. Recent advances in municipal landfill leachate: A review focusing on its characteristics, treatment, and toxicity assessment. Sci Total Environ. 2020;703:135468. Disponible en: https://doi.org/10.1016/j.scitotenv.2019.135468

31. Luu T Le. Post treatment of ICEAS-biologically landfill leachate using electrochemical oxidation with Ti/BDD and Ti/RuO2 anodes. Environ Technol Innov. 2020;20:101099. Disponible en: https://doi.org/10.1016/j.eti.2020.101099

32. Gautam P, Kumar S. Characterisation of Hazardous Waste Landfill Leachate and its Reliance on Landfill Age and Seasonal Variation : A Statistical Approach. J Environ Chem Eng. 2021;9(4):105496. Disponible en: https://doi.org/10.1016/j.jece.2021.105496

33. Chen W, Li Q. Chemosphere Elimination of UV-quenching substances from MBR- and SAARB-treated mature land fill leachates in an ozonation process : A comparative study. Chemosphere. 2020;242:125256. Disponible en: https://doi.org/10.1016/j.chemosphere.2019.125256

34. Ren Y, Ferraz F, Lashkarizadeh M, Yuan Q. Comparing young landfill leachate treatment efficiency and process stability using aerobic granular sludge and suspended growth activated sludge. J Water Process Eng. 2017;17(February):161–7. Disponible en: http://dx.doi.org/10.1016/j.jwpe.2017.04.006

35. Saleem M, Lavagnolo MC, Campanaro S, Squartini A. Dynamic membrane bioreactor (DMBR) for the treatment of landfill leachate; bioreactor's performance and metagenomic insights into microbial community evolution. Environ Pollut. 2018;243:326–35. Disponible en: https://doi.org/10.1016/j.envpol.2018.08.090

36. Islam M, Xu Q, Yuan Q. Advanced biological sequential treatment of mature landfill leachate using aerobic activated sludge SBR and fungal bioreactor. J Environ Heal Sci Eng. 2020;18(1):285–95. Disponible en: https://doi.org/10.1007/s40201-020-00466-z

37. Wu L, Li Z, Zhao C, Liang D, Peng Y. A novel partial-denitrification strategy for post-anammox to effectively remove nitrogen from landfill leachate. Sci Total Environ. 2018;633:745–51. Disponible en: https://doi.org/10.1016/j.scitotenv.2018.03.213

38. Miao L, Yang G, Tao T, Peng Y. Recent advances in nitrogen removal from landfill leachate using biological treatments – A review. J Environ Manage. 2019;235(January):178–85. Disponible en: https://doi.org/10.1016/j.jenvman.2019.01.057

39. Wang Z, Peng Y, Miao L, Cao T, Zhang F, Wang S, et al. Continuous-flow combined process of nitritation and ANAMMOX for treatment of landfill leachate. Bioresour Technol. 2016;214:514–9. Disponible en: http://dx.doi.org/10.1016/j.biortech.2016.04.118

40. Ikehata K, Li Y. Ozone-Based Processes. In: Elsevier Inc., editor. Advanced Oxidation Processes for Wastewater Treatment: Emerging Green Chemical Technology. 2018. p.115-34.

41. Chen W, Li Q. Elimination of UV-quenching substances from MBR- and SAARB-treated mature landfill leachates in an ozonation process: A comparative study. Chemosphere. 2020;242:125256. Disponible en: https://doi.org/10.1016/j.chemosphere.2019.125256

42. Gautam P, Kumar S, Lokhandwala S. Advanced oxidation processes for treatment of leachate from hazardous waste landfill: A critical review. J Clean Prod. 2019;237:117639. Disponible en: https://doi.org/10.1016/j.jclepro.2019.117639

43. Kattel E, Kivi A, Klein K, Tenno T, Dulova N, Trapido M. Hazardous waste landfill leachate treatment by combined chemical and biological techniques. Desalin Water Treat. 2016;57(28):13236–45. Disponible en: https://doi.org/10.1080/19443994.2015.1057539

44. Caroline E, Kozak C, Garcia H, Mansur M. Applicability of conventional and non-conventional parameters for municipal landfill leachate characterization. Chemosphere. 2020;251:126414. Disponible en: https://doi.org/10.1016/j.chemosphere.2020.126414

45. Selvabharathi G, Adishkumar S, Jenefa S, Ginni G, Rajesh Banu J, Yeom IT. Combined homogeneous and heterogeneous advanced oxidation process for the treatment of tannery wastewaters. J Water Reuse Desalin. 2016;6(1):59–71.

46. Lovato M, Buffelli JR, Abrile M, Martín C. Kinetics and efficiency of ozone for treatment of landfill leachate including the effect of previous microbiological treatment. Environ Sci Pollut Res. 2019;26(5):4474–87.

47. Sharma HB, Panigrahi S, Sarmah AK, Dubey BK. How does the pre-treatment of landfill leachate impact the performance of O3 and O3/ UVC processes? Chemosphere. 2019;135907. Disponible en: https://doi.org/10.1016/j.chemosphere.2021.130389

48. Wang H, Li X, Hao Z, Sun Y, Wang Y, Li W, et al. Transformation of dissolved organic matter in concentrated leachate from nanofiltration during ozone-based oxidation processes (O3,

O3/H2O2 and O3/UV). J Environ Manage. 2017;191:244–51. Disponible en: http://dx.doi.org/10.1016/j.jenvman.2017.01.021

49. Ranjbar-Vakilabadi D, Hassani AH, Omrani G, Ramavandi B. Catalytic potential of Cu/Mg/Al-chitosan for ozonation of real landfill leachate. Process Saf Environ Prot. 2017;107:227–37. Disponible en: http://dx.doi.org/10.1016/j.psep.2017.02.013

50. Ghahrchi M, Rezaee A. Electrocatalytic ozonation process supplemented by EDTA-Fe complex for improving the mature landfill leachate treatment. Chemosphere. 2021;263:127858. Disponible en: https://doi.org/10.1016/j.chemosphere.2020.127858

51. Umamaheswari J, Bharathkumar T, Shanthakumar S, Gothandam KM. A feasibility study on optimization of combined advanced oxidation processes for municipal solid waste leachate treatment. Process Saf Environ Prot. 2020;143:212–21. Disponible en: https://doi.org/10.1016/j.psep.2020.06.040

52. Barbosa ID, Gomes AI, Souza-chaves BM, Park M, Silva FC V, Boaventura RAR, et al. Incorporation of ozone-driven processes in a treatment line for a leachate from a hazardous industrial waste landfill : Impact on the bio-refractory character and dissolved organic matter distribution. J Environ Chem Eng J. 2021;9(April):105554. Disponible en: https://doi.org/10.1016/j.jece.2021.105554

53. Huang Z, Gu Z, Wang Y, Zhang A. Improved oxidation of refractory organics in concentrated leachate by a $Fe^{2+}$enhanced $O_3/H_2O_2$ process. Environ Sci Pollut Res. 2019;26(35):35797-806. Disponible en: https://doi.org/10.1007/s11356-019-06592-y

54. Gomes AI, Soares TF, Silva TFCV, Boaventura RAR, Vilar VJP. Ozone-driven processes for mature urban landfill leachate treatment: Organic matter degradation, biodegradability enhancement and treatment costs for different reactors configuration. Sci Total Environ. 2020;724. Disponible en: https://doi.org/10.1016/j.scitotenv.2020.138083

55. Soubh A, Mokhtarani N. The post treatment of composting leachate with a combination of ozone and persulfate oxidation processes. RSC Adv. 2016;6(80):76113–22. Disponible en: https://doi.org/10.1039/C6RA09539A

56. Wang Y, Wang H, Wu Y, Sun Y, Gong Z, Liu K, et al. Effective removal of contaminants from biotreated leachate by a combined Fe(III)/$O_3$ process: Efficiency and mechanisms. J Clean Prod. 2020;276(Iii):123379. Disponible en: https://doi.org/10.1016/j.jclepro.2020.123379

57. Wu C, Chen W, Gu Z, Li Q. A review of the characteristics of Fenton and ozonation systems in landfill leachate treatment. Sci Total Environ. 2021;762:143131. Disponible en: https://doi.org/10.1016/j.scitotenv.2020.143131

58. Abu Amr SS, Aziz HA, Hossain MS, Bashir MJK. Simultaneous removal of COD and color from municipal landfill leachate using Ozone/Zinc sulphate oxidation process. Glob Nest J. 2017;19(3):498–504.

59. Ikhlaq A, Javed F, Akram A, Qazi UY, Masood Z, Ahmed T, et al. Treatment of leachate through constructed wetlands using Typha angustifolia in combination with catalytic ozonation on Fe-zeolite A. Int J Phytoremediation. 2020;0(0):1–9. Disponible en: https://doi.org/10.1080/15226514.2020.1858753

60. Silva TFC V, Soares PA, Manenti DR, Fonseca A, Saraiva I, Boaventura RAR, et al. An innovative multistage treatment system for sanitary land fi ll leachate depuration : Studies at pilot-scale. Sci Total Environ. 2017;576:99–117. Disponible con: https://doi.org/10.1016/j.scitotenv.2016.10.058

61. Chys M, Declerck W, Audenaert WTM, Van Hulle SWH. UV/H2O2, O3 and (photo-) Fenton as treatment prior to granular activated carbon filtration of biologically stabilized landfill leachate. J Chem Technol Biotechnol. 2015;90(3):525–33. Disponible en: https://doi.org/10.1002/jctb.4344

62. Moro G Del, Mancini A, Mascolo G, Iaconi C Di. Comparison of UV / H 2 O 2 based AOP as an end treatment or integrated with biological degradation for treating landfill leachates. Chem Eng J. 2013;218:133–7. Disponible en: http://dx.doi.org/10.1016/j.cej.2012.12.086

63. Ghahrchi M, Rezaee A. Electro-catalytic ozonation for improving the biodegradability of mature landfill leachate. J Environ Manage. 2020;254(October 2019):109811. Disponible en: https://doi.org/10.1016/j.jenvman.2019.109811

64. Fu S, Jia H, Meng X, Guo Z, Wang J. Fe-C micro-electrolysis-electrocoagulation based on BFDA in the pre-treatment of land fi ll leachate : Enhanced mechanism and electrode decay monitoring. Sci Total Environ. 2021;781:146797. Disponible en: https://doi.org/10.1016/j.scitotenv.2021.146797

65. Guvenc SY, Dincer K, Varank G. Performance of electrocoagulation and electro-Fenton processes for treatment of nano fi ltration concentrate of biologically stabilized land fi ll leachate. J Water Process Eng. 2019;31:100863. Disponible en: https://doi.org/10.1016/j.jwpe.2019.100863

66. Deng Y, Zhu X, Chen N, Feng C, Wang H, Kuang P, et al. Review on electrochemical system for landfill leachate treatment: Performance, mechanism, application, shortcoming, and improvement scheme. Sci Total Environ. 2020;745:140768. Disponible en: https://doi.org/10.1016/j.scitotenv.2020.140768

67. Lin H, Peng H, Feng X, Li X, Zhao J, Yang K, et al. Energy-efficient for advanced oxidation of bio-treated landfill leachate effluent by reactive electrochemical membranes (REMs): Laboratory and pilot scale studies. Water Res. 2021;190. Disponible en: https://doi.org/10.1016/j.watres.2020.116790

68. Wu L na, Liang D wei, Xu Y ying, Liu T, Peng Y zhen, Zhang J. A robust and cost-effective integrated process for nitrogen and bio-refractory organics removal from landfill leachate via short-cut nitrification, anaerobic ammonium oxidation in tandem with electrochemical oxidation. Bioresour Technol. 2016;212:296–301. Disponible en: https://doi.org/10.1016/j.cej.2019.02.113

69. Hui H, Wang H, Mo Y, Li L, Yin Z, He B, et al. A three-stage fixed-bed electrochemical reactor for biologically treated landfill leachate treatment. Chem Eng J. 2019;376(February). Disponible en: https://doi.org/10.1016/j.cej.2019.02.113

70. Deng Y, Feng C, Chen N, Hu W, Kuang P, Liu H, et al. Research on the treatment of biologically treated landfill leachate by joint electrochemical system. Waste Manag. 2018;82:177–87. Disponible en: https://doi.org/10.1016/j.wasman.2018.10.028

71. Madera-Parra, C. Landfill leachate treatment by technological coupling of High Rate Anaerobic Pond-BLAAT® and Subsurface horizontal flow constructed wetlands. Ingeniería y competitividad. 2020: 22(2). Disponible en: https://doi.org/10.25100/iyc.v22i2.9740

72. García, P. Manejo y Tratamiento de Lixiviados en Rellenos Sanitarios: Revisión bibliográfica y Experiencia en Planta de Tratamiento de Lixiviados de Navarro (Doctoral dissertation, Universidad Santiago de Cali).

73. Madera-Parra, C. Tratamiento de lixiviados de relleno sanitario por medio de humedales construidos sembrados con policultivos de plantas nativas. Ingeniería y Competitividad. 2016: 18(2), 183-192. Disponible en: https://doi.org/10.25100/iyc.v18i2.2166

74. Revelo, D, Guerrero-Flórez, M, Ordóñez, A, Sánchez-Ortiz, I, Pusapaz-Villota, N, Yela, O, Galeano, L. Bacterial diversity of leachates retained in adsorbents regenerated by wet catalytic peroxide oxidation: potential driving bioelectrochemical systems. International Journal of Environmental Science and Technology.2021: 18(10), 2913-2924. Disponible en: https://doi-org.ezproxy.unal.edu.co/10.1007/s13762-020-03058-4

## 3.2. Advanced Oxidation Processes Based on Ozone as a Treatment Alternative for Landfill Leaches

Vol. 12 (núm. 2) pp. 95-108
Julio-Diciembre 2021

Ciencia en Desarrollo
Revista de la Facultad de Ciencias
Vicerrectoría en Investigación y Extensión - VIE
Centro de Investigaciones y Extensión de la Facultad de Ciencias - CIEC

https://doi.org/10.19053/01217488.v12.n2.2021.12503

# Procesos avanzados de oxidación basados en ozono como alternativa de tratamiento para lixiviados de rellenos sanitarios

## Advanced Oxidation Processes Based on Ozone as a Treatment Alternative for Landfill Leaches

Dorance Becerra-Moreno[1,2], Yrany Rubio-Gomez[1], Luisa Fernanda Ramírez-Ríos[1], Andrés Fernando Barajas-Solano[1] y Fiderman Machuca-Martínez[2,3]

**Resumen**

Los procesos basados en ozono hacen parte de los Procesos Avanzados de Oxidación que se han aplicado sobre los lixiviados de rellenos sanitarios. Las características altamente tóxicas de los lixiviados de rellenos sanitarios, pueden reducirse por medio de los procesos basados en ozono, los cuales han demostrado alcanzar altas remociones de contaminantes, en especial, de compuestos orgánicos recalcitrantes. En esta revisión se compila información reciente (2015 a 2021) referente a los procesos basados en ozono, donde se ha estudiado la eficacia como tratamiento, se analiza las condiciones óptimas de acuerdo al tipo de lixiviado y al método de tratamiento a emplear. Se identifica la tendencia de implementación como pretratamiento y postratamiento acoplado a procesos convencionales.

***Palabras clave*:** lixiviado de rellenos sanitarios, ozono, PAOs, tratamiento

**Abstract**

Ozone-based processes are part of the Advanced Oxidation Processes that have been applied on leachates from landfills. The highly toxic characteristics of landfill leachates can be reduced by ozone-based processes, which have been shown to achieve high removals of pollutants, especially recalcitrant organic compounds. In this review, recent information is compiled (2015 to 2021) regarding ozone-based processes, where the efficacy as a treatment has been studied, the optimal conditions are analyzed according to the type of leachate and the treatment method to be used. The implementation trend is identified as pre-treatment and post-treatment coupled with conventional processes.

***Keywords*:** landfill leachate, ozone, AOPs, treatment

**Recepción:** 20-feb-2021
**Aceptación:** 27-May-2021

[1]Departamento de Ciencias del Medio Ambiente, Facultad de Ciencias Agrarias y del Ambiente, Universidad Francisco de Paula Santander, Cúcuta, Colombia.
[2]Escuela de Ingeniería Química, Facultad de Ingeniería, Universidad del Valle, Cali Colombia.
[3]CENM, Facultad de Ingeniería, Universidad del Valle. Cali, Colombia.
Autor de correspondencia: fiderman.machuca@correounivalle.edu.co

## 1 Introducción

La generación de Residuos Sólidos Urbanos (RSU) va en aumento y los rellenos sanitarios son el método generalmente implementado para disponerlos de manera controlada [1]. Los rellenos sanitarios han sido considerados como una alternativa de destino final para los residuos sólidos, por ser de fácil operación, viables económicamente, y ambientalmente aceptables si son gestionados de forma adecuada [2, 3, 4].

Un aspecto negativo de la operación de los rellenos sanitarios son los lixiviados, los cuales son líquidos de color obscuro altamente contaminantes [5]. Éstos se producen principalmente a partir de la degradación de los residuos, tanto orgánicos como inorgánicos, y la percolación de agua de lluvia [6, 7, 8]. Youcai (2018) describe la formación de lixiviados en un relleno sanitario típico, lo cual consiste generalmente en el ingreso de agua lluvia a la zona de residuos en fase sólida, transportando los contaminantes solubles a la fase líquida. Al mismo tiempo, los residuos orgánicos se descomponen en materias orgánicas solubles (como los ácidos grasos volátiles). La humedad de los residuos, la acción de los microorganismos, entre otras condiciones, propician la degradación mediante una serie de procesos físicos, químicos y biológicos complejos [8]. En la Figura 1 se presenta un esquema sobre la producción de lixiviados a partir de residuos sólidos de rellenos sanitarios.


***Figura 1.*** Producción de lixiviados en un relleno sanitario.

Las características contaminantes de los lixiviados se ven influenciadas particularmente por la edad del relleno sanitario [9], es decir, los lixiviados de rellenos sanitarios jóvenes ($<$ 5 años) contienen altas cantidades de contaminantes orgánicos y presentan un pH ácido [10]. Mientras los lixiviados de rellenos sanitarios de edad intermedia (5-10 años) y los maduros ($>$ 10 años), se caracterizan por presentar alto contenido de compuestos húmicos y fulvicos, así como, menor biodegradabilidad en comparación con los rellenos sanitarios jóvenes [11]. Además, estos lixiviados presentan contaminantes como metales pesados, compuestos xenobióticos, altas concentraciones de amonio, entre otras sustancias tóxicas, perjudiciales tanto para el ambiente como la salud pública [12].

Debido a las características de los lixiviados de rellenos sanitarios, presentan altas concentraciones en, Demanda Química de Oxígeno (DQO), Demanda Biológica de Oxígeno (DBO), Carbono Orgánico Disuelto (COD), Carbono Orgánico Total (COT), compuestos absorbentes de $UV_{254}$ ($UV_{254}$) y nitrógeno amoniacal ($NH_3$-N), así también, una baja proporción de DBO/DQO (relación de biodegradabilidad) [13, 14]. En consecuencia, el tratamiento de los lixiviados es relevante dentro de los rellenos sanitarios, donde se deben incluir métodos que reduzcan las concentraciones de los contaminantes y disminuyan sus cualidades nocivas. Existen varios métodos de tratamiento como lo son: físicos (recirculación y evaporación) [14], biológicos (lodos activados, reactores con biopelículas sumergidas y fijas, reactores de manto de lodos de flujo ascendente) [15], tecnologías de membrana (microfiltración, ultrafiltración y osmosis inversa) y Procesos Avanzados de Oxidación (Procesos foto-asistido, procesos electroquímicos, procesos varios y procesos basados en ozono) [16].

Los Procesos Avanzados de Oxidación (PAOs) han sido utilizados como métodos de tratamiento de lixiviados por su ventaja para degradar compuestos recalcitrantes, superando a algunos de los demás tratamientos [17]. Principalmente, los PAOs presentan una alta eficacia de eliminación de compuestos orgánicos y aumentan la biodegradabilidad [18, 19]. Uno de los tratamientos PAOs más comunes son los procesos basados en ozono, los cuales presentan su alto valor oxidante para producir radicales hidroxilos (OH) que degradan los contaminantes orgánicos recalcitrantes [18, 2]. Asimismo, los procesos basados en ozono son tratamientos ventajosos en cuanto a la

remoción de color, olor y algunos metales pesados [20].

El presente trabajo es una revisión centrada en el desarrollo de los procesos basados en ozono para el tratamiento de lixiviados producidos en rellenos sanitarios, como un método de los PAOs que ha presentado una buena eficacia en la remoción de la concentración de los contaminantes. Se realiza un análisis descriptivo y comparativo de las investigaciones científicas recientes, entre los años 2015 y 2021, en el tema de los procesos basados en ozono para tratar lixiviados. Así mismo se citan referencias para profundizar y ampliar la información actualizada.

Las investigaciones consideradas para la presente revisión, se extrajeron de buscadores como Science Direct, Springer Link, Taylor & Francis, entre otros. De estas investigaciones, el 68% pertenecen a categoría Q1, el 29% a categoría Q2 y solo el 3% a categoría Q3. Las revistas científicas que mayor cantidad de publicaciones registran sobre el tema de estudio, según esta revisión son: Journal of Cleaner Production, Waste Management, Process Safety and Environmental Protection, Desalination and Water Treatment, Water Research, Chemosphere, Chemical Engineering Journal, y Environmental Science and Pollution Research. En cuanto a la distribución de las investigaciones según el año de publicación, al 2015 pertenece el 12% del total de las referencias bibliográficas, 2016 el 14%, 2017 el 12%, 2018 el 10%, 2019 el 20%, 2020 el 29%; y al año 2021 corresponde el 3% de las publicaciones científicas revisadas hasta el mes de febrero.

## 2 PAOs como tratamiento

Los PAOs han sido estudiados en múltiples investigaciones para demostrar la eficiencia de su aplicación como tratamiento en líquidos con características de alta toxicidad (aguas residuales y los lixiviados). La velocidad del tratamiento, la mejora de la biodegradabilidad y el alto porcentaje de remoción de contaminantes orgánicos recalcitrantes, posicionan a los PAOs como un método de tratamiento ventajoso frente a otros (físicos y biológicos entre los más comunes). Según Kow et al. (2016), son dos los procesos que se desarrollan dentro del tratamiento mediante los PAOs. Uno es la formación de radicales libres u oxidantes como radicales hidroxilos (OH) y otras especies [21]. Otro proceso es la reacción química de radicales producidos con compuestos orgánicos, lo cual se representa como reacción básica en la ecuación (1) [3].

$$\begin{aligned}&\text{Oxidante} + \text{Compuesto Orgánico} \rightarrow \\ &\text{Subproductos de Oxidación} \rightarrow CO_2 + H_2O \end{aligned} \quad (1)$$

Los PAOs como tratamiento, se les han atribuido un alto valor en términos de costo, por lo tanto, se considera que su implementación es más favorable como pretratamiento o postratamiento, que como tratamiento único [15, 22]. Por consiguiente, generalmente para el tratamiento de lixiviados de rellenos se opta por crear un sistema usando a los PAOs como complemento de uno o más métodos acoplados estratégicamente hasta alcanzar las remociones de contaminantes esperadas. Una de las combinaciones de métodos de tratamiento de lixiviados más usadas junto con los PAOs, son los tratamientos biológicos, por sus buenos resultados de eficacia de remoción en cuanto DQO, entre otros parámetros [7].

Se ha afirmado que el aumento del rendimiento de los PAOs se logra con la manipulación de las variables asociadas al tipo de oxidante (Radical hidroxilo, OH; radical sulfato, $SO_4^-$; ozono, $O_3$; anión persulfato, $S_2O_8{}^{2-}$; peróxido de hidrógeno, $H_2O_2$; radical hidroperóxido, $HO_2$; y radical superóxido, $O_2{}^-$) y sus concentraciones, de lo cual, la información del potencial de oxidación $E^0$ (V) y su funcionamiento dentro del tratamiento es compilada y presentada por Kow et al. (2016). Además, las pruebas realizadas a diferentes PAOs y otros métodos como el biológico, coagulación-floculación y demás, para determinar los rendimientos como tratamiento de lixiviados de un relleno sanitario, se encuentran en la investigación de Bashir et al. (2015).

## 3 Procesos basados en ozono como tratamiento de lixiviados

Los procesos basados en ozono se han catalogado como una de las categorías de los PAOs más

prometedoras para eliminar y/o reducir contaminantes de los lixiviados a estándares permisibles expedidos las autoridades ambientales [3]. Los procesos basados en ozono se muestran en la Figura 2, elaborada con base en los estudios de Ikehata & Li (2018) y Kow et al. (2016). Recientemente, se han documentado excelentes resultados de estos procesos, especialmente como pretratamiento y postratamiento.

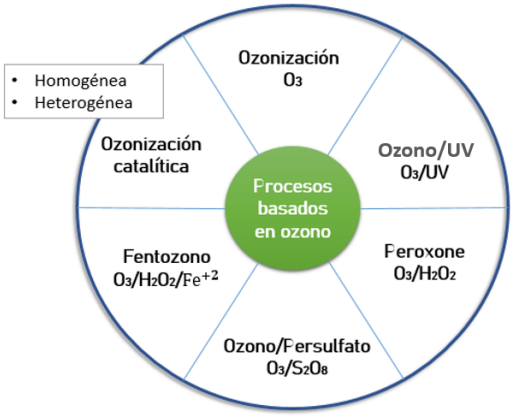



***Figura 2.*** Tratamientos de procesos basados en ozono.

El rendimiento como pretratamiento se le confiere al favorable aumento de la biodegradabilidad y reducción de la toxicidad de compuestos orgánicos [4, 24]. Por ejemplo, un pretratamiento con $O_3$ para tratar lixiviados en membranas de alta presión (osmosis inversa y nanofiltración), obtuvo una reducción de 55.5% de compuestos absorbentes de DQO y 54.4% de COD [4]. El proceso de $O_3$ puede exitosamente eliminar y convertir compuestos de ácido húmico y ácido Fulvico en fracciones hidrófilas que son biodegradables [4].

Como postratamiento, los procesos basados en ozono cumplen con la función de oxidar los compuestos orgánicos residuales del tratamiento anterior a este. Por ejemplo, el proceso con ozono/persulfato ($O_3/S_2O_8$) como postratamiento, se aplicó a un lixiviado tratado mediante un proceso biológico, obtuvo remociones de 87% de DQO y 85% de color, así como un aumento de la relación de biodegradabilidad de 0.13 a 0.61 [1]. A su vez, los procesos basados en ozono son ventajosos como método de tratamiento limpio, puesto que regularmente la generación de lodos es baja o poco significativa [26, 27], a excepción de los procesos asociados a iones metálicos [14].

Las reacciones químicas involucradas en cada proceso basado en ozono (ozonización, ozonización con radiación UV, peroxono, ozono/persulfato, fentozono, ozonización catalítica) están disponibles en el trabajo de Kow et al. (2016) y el libro de Ikehata & Li (2018).

### 3.1 Ozonización ($O_3$)

La oxidación es el proceso principal de la ozonización para degradar y mineralizar contaminantes orgánicos de gran tamaño, de líquidos como los lixiviados [14], en especial los aromáticos [10]. Los compuestos aromáticos se relacionan con los compuestos absorbentes ($UV_{254}$), a lo que las pruebas de tratamiento con $O_3$ han demostrado ser altamente eficaces [10, 25].

La ozonización degrada los compuestos orgánicos recalcitrantes en el lixiviado de vertederos mediante reacciones directas o indirectas. La reacción directa es el mecanismo en el cual se produce una reacción redox, entre las moléculas de ozono y la materia orgánica del lixiviado del vertedero. En cuanto al mecanismo mediante la reacción indirecta, se producen radicales OH altamente activos durante la oxidación, que luego inducen una reacción en cadena, que implican reacciones de iniciación, propagación y terminación [23]. El radical OH de alto potencial redox, interactúa con los contaminantes orgánicos del lixiviado, lo que propicia la apertura del anillo en compuestos orgánicos tóxicos, mejorando así la biodegradabilidad. La reacción indirecta es considera más eficiente en comparación con la reacción directa [3].

El $O_3$ como tratamiento de lixiviados remueve los contaminantes de formas distintas, de acuerdo a las condiciones de pH [3]. Las reacciones de iniciación principales se presentan en la ecuación(2) para un pH acido a neutro y las Ecuaciones (3) y (4) para un pH alcalino [23].

$$O_3 + OH^- \rightarrow HO_2 + O_2^- \quad (2)$$

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \quad (3)$$

$$O_3 + HO_2^- \rightarrow HO_2 + O_3^- \quad (4)$$

A pH ácidos, la remoción de contaminantes ocurre de forma directa por medio del proceso de reacción química con los compuestos orgánicos, por ejemplo, Kattel et al. (2016) obtuvieron remociones aproximadas del 45% de $DBO_7$ y 18% de toxicidad en medio ácido. En contraste, en este tratamiento se registraron remociones aproximadas del 65% de $DBO_7$ y 23% de toxicidad en medio alcalino, debido a la oxidación indirecta de los OH.

Huawei et al. (2016) por su parte, al tratar lixiviados efluentes de los tratamientos con osmosis inversa y nanofiltración, en medio alcalino, encontraron que se producían mayores valores de $NH_3$-N y $NO_3$-N después de la ozonización. Según explican los autores, esto es debido a la degradación de los grupos amino en las sustancias húmicas o la degradación de otros compuestos orgánicos que contienen nitrógeno. Por el contrario, un medio alcalino inicial es favorable en la remoción de contaminantes como el color y los compuestos absorbentes $UV_{254}$, por medio de procesos de generación de radicales OH u otras especies. Esto es representado en los estudios de, AlGburi et al. (2020) quienes alcanzaron una remoción de color de hasta 90% y, Soubh & Mokhtarani (2016) que obtuvieron en sus resultados una remoción de 90% de compuestos absorbentes $UV_{254}$. La Tabla 1 describe los parámetros iniciales, las condiciones óptimas de operación y la eficacia de los tratamientos realizados con $O_3$ a lixiviados de rellenos sanitarios.

### 3.2 Ozono/UV ($O_3$/UV)

La ozonización en presencia de irradiación ultravioleta, con una longitud de onda ($\lambda$) inferior a 300 nm, es el principio para degradar los contaminantes [24]. En este sistema, el $O_3$ se activa al absorber luz ultravioleta a 254 nm y se somete a fotólisis, aumentando la producción de $H_2O_2$, y éste también se someterán a fotólisis para producir OH [29]. Básicamente, el mecanismo del proceso de tratamiento $O_3$/UV es similar al de ozonización más la integración de fotones [3], como se representan en las ecuaciones (5) y 6, reacciones de iniciación principales [23].

$$O_3 + H_2O + hv \rightarrow H_2O_2 \quad (5)$$

$$H_2O_2 + hv \rightarrow 2OH \quad (6)$$

Los rayos UV actúan como catalizadores, oxidando los contaminantes, rompiendo los enlaces saturados complejos para degradarlos, aprovechando el alto potencial de absorción de luz del ozono [30]. El rendimiento de eliminación de los contaminantes con el tratamiento $O_3$/UV, ha demostrado ser mayor a pH de 9 [29, 30, 31]. El $O_3$/UV aumenta la biodegradabilidad en hasta un 91% [29], es eficaz en contaminantes refractarios, así como en sustancias húmicas y fulvicas, convirtiéndolas en intermedios alifáticos de bajo peso molecular [31]. Gomes et al. (2020) afirmaron que el rendimiento de este tratamiento para lixiviados puede estar relacionado con el diseño del fotorreactor, el cual debe asegurar que se permita un tiempo de contacto prolongado entre las moléculas de $O_3$ y los fotones UV para obtener mayores remociones. Los estudios asociados a la aplicación de procesos de $O_3$/UV, para tratar lixiviados de rellenos sanitarios, se presentan en la Tabla 2.

## 4 Peroxono ($O_3$/$H_2O_2$)

El Peroxono es una combinación de ozonización con la adición de oxidante fuerte, $H_2O_2$, lo cual mejora la transformación de $O_3$ en OH [33, 34]. Se han realizado varios ensayos con $O_3$/$H_2O_2$, como postratamiento de lixiviados tratados por procesos biológicos y con membrana [24, 35, 36]. Los resultados demuestran que este tratamiento puede degradar compuestos aromáticos a pH bajos [30, 35].

El mecanismo del proceso de tratamiento con $O_3$/$H_2O_2$ para líquidos como los lixiviados, se compone de reacciones de iniciación y de terminación. En este, el ozono se descompone muy rápidamente en presencia de $H_2O_2$ y la mayoría de contaminantes se degradan por reacción indirecta con los radicales OH. A continuación, se presentan las ecuaciones (7) y (8) de las reacciones de iniciación y la ecuación (9) de la reacción de terminación [3].

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \quad (7)$$

$$H_2O_2 + H_2O \rightarrow HO_2^- + H_3O^+ \quad (8)$$

$$OH + HO_2 \rightarrow H_2O + O_2 \quad (9)$$

***Tabla 1.*** Tratamiento de lixiviados con $O_3$

| Fase de tratamiento | Parámetros iniciales | Condiciones óptimas de operación | Eficacia | Referencia |
|---|---|---|---|---|
| | 824.6 ± 60 mg/L de DQO, 125.62 ± 2 mg/L de $NH_3$-N, 8.538 ± 0.002 de pH, 350-400 de color, 0.08 de $BOD_5$/COD | 8.5 de pH, 120 min de reacción | 55.06 de DQO, 90%. de absorbentes $UV_{254}$ | [25] |
| Postratamiento | Efluente de osmosis inversa: 2356 mg/L de DQO, 818 mg/L de COT, 64.5 mg/L de $NH_3$-N, 179.6 mg/L de $NO_3$-N, 7.84 de pH | 8.5 mg. $O_3$/g DQO, 110 min de reacción, 7.5 de pH | 55.5% de DQO, 55,4% de COT, aumento de NH3-N y NO3-N | [4] |
| | Efluente de nanofiltración: efluente de osmosis inversa: 5846 mg/L de DQO, 2082 mg/L de COT, 42.8 mg/L de NH3-N, 150.8 mg/L de NO3-N, 7.27 de pH | 3.4 mg $O_3$/g DQO, 110 min de reacción, 7.5 de pH | 43.2% de DQO, 5,6% de COT, aumento de NH3-N y $NO_3$-N | |
| | 2500 mg/L de DQO, 40 mg/L de $BOD_5$, 16200 PtCo de color, 8.2 de pH, 1100 mg/L de NO3-N, 0.016 de $BOD_5$/COD | 27 g/$Nm^3$ de dosis de $O_3$, 11 de pH, 120 minutos | 47% de DQO, 29% de Amoniaco, 90% de color | [32] |

En la Tabla 2 se presentan los resultados de optimización del tratamiento con peroxono para remover contaminantes de lixiviados de rellenos sanitarios. Este tratamiento depende de la dosis de ozono aplicado para la reacción [7, 18], puesto que, en los estudios citados, las condiciones óptimas de operación se obtuvieron con la mayor dosis de $O_3$.

### 4.1 Ozono/Persulfato ($O_3$/$S_2O_8{}^{2-}$)

El ozono/persulfato es una combinación de ozonización con oxidante fuerte, $S_2O_8{}^{2-}$, el cual, en el proceso de descomposición puede actuar como iniciador para producir $SO_{4-}$ [37]. También, se pueden producir iones $HSO_{4-}$ y $H_2O_2$ debido a la reacción conjunta con moléculas de agua. Las reacciones en el tratamiento con radical sulfato, se basa mayormente en la transferencia de electrones, lo cual produce radicales OH que aceleran la depuración de la materia orgánica [22]. El mecanismo del proceso $O_3$/$S_2O_8{}^2$ se componen de reacciones principales de iniciación y propagación como se representa en las ecuaciones (10), (11) y (12) [37].

$$S_2O_8^{-2} + 2H_2O \rightarrow 2HSO_4^- + H_2O_2 \qquad (10)$$

$$S_2O_8^{-2} + OH^- \rightarrow SO_4^{-2} + SO_4^- + 1/2O_2 + H^+ \qquad (11)$$

$$SO_4^{-2} + OH^- \rightarrow SO_4^- + OH^- \qquad (12)$$

El tratamiento con $O_3$/$S_2O_8{}^{2-}$ aplicado a los lixiviados, permite disminuir la toxicidad, al mismo tiempo que aumenta la biodegradabilidad, asimismo, ha sido considerado como una alternativa eficaz para la remoción simultanea de DQO y color [25]. Se asocia la condición de un pH Inicial básico para favorecer la reacción de los radicales sulfatos [22]. Soubh & Mokhtarani (2016) optimizaron el tratamiento, a pH de 9, para obtener disminuciones en los valores de parámetros como DQO, color y toxicidad, en hasta 85, 87 y 80%, respectivamente, además de un aumento de 47% de $BOD_5$/COD (Tabla 2).

Adicionalmente, se ha estudiado la implementación del tratamiento con $O_3$/$S_2O_8{}^{2-}$ en conjunto con un medio de activación del persulfato, con el fin de aumentar la oxidación que produce el $SO_4{}^-$ [3]. Entre los medios de activación del persulfato se destacan, la activación térmica, activación por microondas, activación UV, entre otros [38]. Poblete et al. (2019) realizaron experimentos con esta alternativa para tratar lixiviados por medio de $UV_{solar}$/$O_3$/$S_2O_8{}^{2-}$, aprovechando la energía del sol y el proceso de ozonización con persulfato lograron remover un 26.7% de DQO y 69.3% de color (Tabla 2).

El tratamiento de líquidos con $S_2O_8^{2-}$, puede atribuirse a una la elevada demanda del consumo de este oxidante [38]. Introducir una alta concentración de sulfato en el tratamiento, puede producir una serie de subproductos intermedios tóxicos. Por ejemplo, los iones sulfato y los cloruros puede dar lugar a la formación de compuestos orgánicos halogenados. En consecuencia, se inhibe la bioactividad, lo que conduce además a una baja biodegradabilidad en comparación con otros tratamientos como la ozonización única [38].

## 5 Fentozono ($O_3$/$H_2O_2$/$Fe^{+2}$)

Fentozono es la combinación de los procesos de ozonización y Fenton; donde, el OH producido en el proceso de Fenton reacciona con el $O_3$, acelerando su descomposición. Esto conduce a una producción de mayor cantidad de radicales y por lo tanto mejora el proceso de oxidación [36], mecanismo en forma básica representado en la reacción de la ecuación (13) [3]. El mecanismo de reacción del proceso de Fenton se explica en forma detallada en el trabajo de Wu et al. (2020) [3].

$$OH + O_3 \rightarrow HO_2 + O_2 \rightarrow HO_4 \qquad (13)$$

En el proceso $O_3$/$H_2O_2$/$Fe^{+2}$ pueden generarse lodos a causa de los iones metálicos producidos a partir del $Fe^{+2}$ [14]. Las investigaciones han coincidido en que el tratamiento de lixiviados con $O_3$/$H_2O_2$/$Fe^{+2}$ es altamente eficaz en la degradación de compuestos orgánicos recalcitrantes, como las sustancias húmicas y fúlvicas. También, los grupos funcionales se degradan y destruyen considerablemente en el medio líquido tratado [14, 36]. Las condiciones óptimas de operación que se registran en este tratamiento, se encuentran asociadas a un pH de 2 a 7 [35]. Asaithambi et al. (2017) obtuvieron remociones de 70.5% de DQO y 88% de color, en condiciones de pH 7.0, 3.5 g/h de dosis de $O_3$ y 180 min de reacción. Por otra parte, en condiciones de pH ácido (3.0), Huang et al. (2019) obtuvieron los porcentajes de 48.82 y 63.59% en remoción de DQO y absorbentes $UV_{254}$, respectivamente. Así mismo, Wang et al. (2021) obtuvieron remociones en condiciones óptimas de 36.45 y 54.73% de TOC y absorbentes $UV_{254}$, respectivamente (Tabla 2).

### 5.1 Ozonización catalítica

Para obtener un rendimiento satisfactorio del tratamiento de ozonización de lixiviados en un menor tiempo, se han desarrollado los catalizadores. El funcionamiento de los catalizadores consiste en mejorar el poder oxidante del ozono Según el tipo de catalizador se distinguen dos grupos: homogéneos y heterogéneos [23]. Por un lado, la ozonización catalítica homogénea utiliza iones de metales de transición que descomponen el ozono mediante uno de los procesos de generación de radicales libres o la oxidación directa [39]. Entre los iones de metales en transición comunes se encuentran los nitratos, sulfatos, entre otros solubles en agua [37, 40]. La activación del ozono se da por iones como Fe(II), Mn(II), Ni(II), Co(II), Cd(II) o Cu(II) [12, 14].

Se ha demostrado que un pH ácido es favorable para el tratamiento de lixiviados por ozonización catalítica homogénea [39]. Además, el tiempo de reacción es una condición importante del tratamiento, como en el estudio de Wang et al. (2020), quienes obtuvieron altas remociones de contaminantes orgánicos y metales pesados, en un tiempo de reacción de 25 minutos, a una dosis de 100 mg/min de $O_3$ y 6 g/L de Fe (III) como catalizador.

En cuanto a, la ozonización catalítica heterogénea se utilizan varios óxidos metálicos de Mn, Ti, Al, Fe, Si y Ce [21], así como el carbón activado [15], la zeolita natural [32] y otros materiales absorbentes de los contaminantes. Éste tratamiento hace uso de sistemas gas-liquido-solido donde el catalizador es un sólido soportado comúnmente [15, 42].

El pH básico en su mayoría, se ha caracterizado por ser la condición óptima en la ozonización catalítica heterogénea [43, 44]. Así mismo, la dosis de catalizador es una condición relevante para este tratamiento, ejemplo que lo demuestra, son los estudios realizados por He et al. (2018) y Xiang et al. (2020). Ambas investigaciones trataron lixiviados aplicando la ozonización catalizada con $Al_2O_3$, con similar condición inicial de DQO (1100-1317.5 mg/L) y similares condiciones de operación de pH (7.3-7.8), dosis de ozono (18.92-20 mg/min), en un tiempo de reacción de 30 minutos. No obstante, He et al. (2018) aplicaron una dosis de 50 g/L de $Al_2O_3$, con lo cual obtuvieron una remoción de 70%

***Tabla 2.*** Tratamiento de lixiviados con $O_3$/UV, $O_3/H_2O_2$, $O_3$/ $S_2O_8{}^{2-}$, $O_3/H_2O_2/Fe^{+2}$

| Fase de tratamiento | Parámetros iniciales | Condiciones óptimas de operación | Eficacia | Referencia |
|---|---|---|---|---|
| | | **$O_3$/UV** | | |
| Postratamiento | Efluente de nanofiltración | 90 min de reacción | 23.5% de COT, 43.8% de absorbentes $UV_{254}$ | [24] |
| | Lixiviado maduro | 18 mg/min dosis de $O_3$; 9.0 de pH; 3 horas de reacción; exposición del lixiviados a rayo UVC | 66.2% de DQO; 58.4% de COD; 91% de $BOD_5$/COD | [29] |
| | 4512-9600 mg/L de DQO; 2100-4230 mg/L de sólidos totales; 3100-3950 Pt Co. De Color; 8,3-8,94 de pH; altos contenidos de cloruro y metales pesados | 5 g/h. dosis de $O_3$; 9.0 de pH; 60 min tiempo de reacción; exposición bajo 15 W-UVC; $\lambda$: 254 nm | 72% de DQO; 80% de y $NH_3$-N | [30] |
| Postratamiento | Lixiviado de incineración tratado biológicamente | 11.2 mg/min. dosis de $O_3$; 9.0 de pH; 60 min de reacción; exposición a vacío ultravioleta (VUV) | 78% de aumento de $BOD_5$/COD | [31] |
| | | **$O_3/H_2O_2$** | | |
| Postratamiento | Efluente de tanque de regulación + MBR mesófilo-anaeróbico + ósmosis inversa: 1501 mg/L de DQO, 0.016 mg/L de $DBO_5$, 0.845 de CN, 13.25 de absorbentes $UV_{254}$, 8.52 de pH | 52.65 mg/min dosis de $O_3$, 6500 Mm dosis de $Fe^{+2}$, 18.8 mM dosis de $H_2O_2$, 3.0 de pH, 20 min de reacción | 30.84% de DQO y 24.59% de absorbentes $UV_{254}$ | [14] |
| Postratamiento | 1880 mg/L de DQO, 90 mg/L de DBO5, 7.1 de pH, 0.05 de $BOD_5$/COD. | 10 mg/min. de $O_3$, 4.0 g/L de $H_2O_2$, 9.0 de pH | 44% de DQO, 87% de color, 32% de $BOD_5$/COD | [18] |
| Postratamiento | Efluente de nanofiltración | 90 min de reacción | 14.9% de COT, 46.1% absorbentes $UV_{254}$ | [24] |
| | 4850-5150 de DOQ, 2650-2950 de DBO, 8.6-8.8 de pH | 3.5 g/h dosis de $O_3$, 7.0 de pH, 180 min de reacción | 35% de DQO y 47% de color | [35] |
| | | **$O_3/S_2O_8{}^{2-}$** | | |
| | | 0.2 g/L de $S2O_8{}^{2-}$; UV solar a 40°C | 26.7% de DQO y 69.3% de color | [22] |
| Postratamiento | 750 mg/L de DQO, 95 mg/L de $DBO_5$, 8.9 de pH, 0.13 de $BOD_5$/COD | 0.79 g/h. de flujo másico de $O_3$, 4500 mg/L de $S2O_8{}^{2-}$, 9.0 de pH., 210 min de reacción | 85% de DQO, 87% de color, aumento del 47% de $BOD_5$/COD, disminución de la toxicidad en 80% | [25] |
| | | 210 min de reacción | 72% de DQO, 96% de color, 76% de amoniaco y aumento hasta 0.29 de $BOD_5$/COD | [26] |
| | | **$O_3/H_2O_2/Fe^{+2}$** | | |
| Postratamiento | Efluente de tanque de regulación + MBR mesófilo-anaeróbico + ósmosis inversa: 1501 mg/L de DQO, 0.016 mg/L de $DBO_5$, 0.845 de CN, 13.25 de absorbentes $UV_{254}$, 8.52 de pH | 52.65 mg/min dosis de $O_3$, 6500 Mm dosis de $Fe^{+2}$, 18.8 mM dosis de $H_2O_2$, 3.0 de pH, 20 min de reacción | 48.82% de DQO y 63.59% de absorbentes $UV_{254}$ | [14] |
| | 4850-5150 de DOQ., 2650-2950 de DBO., 8.6-8.8 de pH | 3.5 g/h dosis de $O_3$, 7.0 de pH, 180 min de reacción | 70.5% de DQO y 88% de color | [35] |
| postratamiento | Efluennte de SAARS: $800 \pm 50$ mg/L de DQO; $0.05 \pm 0.02$ de DBO/DQO; 7.36 de pH; 2.526 $cm^{-1}$ de absorbancia $UV_{254}$; 0.218 $cm^{-1}$ de número de color (CN); 332 mg/L de TOC | 18.92 mg/min dosis de O3; 4.4 mg/L dosis de $H_2O_2$; 1.0 g/L dosis de $Fe^0$; 3.0 de pH | 54.74% de absorbentes $UV_{254}$ y 36.45% de TOC | [36] |

en términos de DQO, mientras Xiang et al. (2020), aplicaron una dosis de 10 g/L de $Al_2O_3$ y obtuvieron una reducción menor de DQO en un 54.3%.

En la Tabla 3 se presenta la descripción algunos de los estudios que han puesto a prueba los procesos de ozonización catalítica sobre lixiviados de rellenos sanitarios, donde se indica los resultados de remoción de contaminantes de acuerdo a las condiciones óptimas en cada caso.

## 6 Desafíos en la implementación de los procesos basados en ozono a escala industrial en países en desarrollo

Los países en desarrollo en su mayoría disponen los RSU en rellenos sanitarios o en vertederos [47]. Dentro de la gestión integrada de los rellenos sanitarios es de gran relevancia la gestión de los lixiviados, sin embargo, la mayoría no cuentan con la adecuada implementación de los procesos de tratamiento, que tengan la capacidad de manejar la cantidad y características del lixiviado generado [20]. Esto representa inminentes consecuencias para el medio ambiente y por consiguiente para la salud de la población de los países en desarrollo, lo cuales, se han visto afectados en varias ocasiones por el mal manejo de estos líquidos, que contaminan el suelo y las aguas subterráneas [48]. La gestión de lixiviados es un desafío [47, 49]; es necesario en los países en desarrollo, que los procesos de tratamiento sean altamente rentables, con un bajo requerimiento de área, simple de implementar, y mantener e identificar los factores significativos que los afectan [20, 47].

Los lixiviados están compuestos por múltiples contaminantes (altas cargas orgánicas, amonio y sales inorgánicas, así como, contenidos de hidrocarburos, pesticidas, entre otros), que lo caracterizan un líquido complejo [1, 32, 44, 50, 51]. El tratamiento de los lixiviados debe alcanzar unos estándares mínimos, generalmente expedidos por la autoridad ambiental para evitar los daños ecológicos y de la salud poblacional [52]. En los países en desarrollo se han implementado los procesos convencionales físicos, biológicos y/o filtración con membrana, sin embargo, muchas veces no es suficiente [53]. Por lo tanto, es requerido aumentar la reducción de la carga contaminate por medio de métodos avanzados, como lo PAOs [20], entre los cuales, procesos basados en ozono ha sido considerados unos de los más prometedores [3].

Como ya se ha mencionado anteriormente, los procesos basados en ozono como tratamiento, son muy valorados por sus ventajas de convertir los compuestos orgánicos recalcitrantes en compuestos de menor peso molecular, aumentar la biodegradabilidad, entre otras [23]. Sin embargo, la eficiencia del tratamiento con estos procesos depende de varios factores como, los costos de tratamiento relativamente altos y la aplicación de sistemas de control [20]. Por ejemplo, el costo para el tratamiento de lixiviados por medio de ozonizacion catalizada en un reactor con microburbujas, se ha estimado que es de 5.36 $/t para remover hasta un 96.25% de DQO [51]. Otra estimacion del costo realizada para el tratamiento de ozonizacion fue de 7.06 €/$m^3$, el cual es mayor, frente al costo estimado de 4.0 €/$m^3$ del tratamiento biologico oxidativo [28].

Así mismo, la aplicación exitosa de los procesos basados en ozono y en general los PAOs, está restringida por el limitado avance de los sistemas de control a escala industrial, lo cual es necesario para realizar la dosificación eficiente de acuerdo a los cambios de volumen del lixiviado a tratar, principalmente ocasionados por los periodos de lluvias [20]. Ademas, el sistema de control de ajuste del pH es relevante para obtener las eficiencias de remocion esperadas [12]. Cabe mencionar, los lixiviados generados en los paises en desarrollo suelen ser de pH neuro, en comparacion con los paises desarrollados, que generalmente, su pH se sitúan en el rango de los ácidos; ésta y otras caracteristicas comunes de los lixiviados generados en los paises en desarrollo se encuentran en Rajoo et al. (2020).

Las limitaciones de los procesos basados en ozono han provocado que se consideren no favorables como tratamiento único [16]. De hecho, varios estudios han demostrado que un tratamiento combinado es capaz de mejorar la calidad del lixiviado y minimizar el residuo generado a un costo de tratamiento menor que un tratamiento individual [20]. Adicionalmente, existe una complejidad de las características del lixiviado, puesto que, en ocasiones se disponen

***Tabla 3.*** Tratamiento de lixiviados mediante ozonización catalítica homogénea y heterogénea

| Fase del tratamiento | Catalizador | Parámetros iniciales | Condiciones de operación optimas | Eficacia | Referencia |
|---|---|---|---|---|---|
| | | **Homogénea** | | | |
| Postratamiento | $ZnSO_4$ | Efluente estabilizado anaeróbicamente: 4250 mg/L de DQO, 348 mg/L de $DBO_5$, 1897 mg/L de $NH_3$-N, 20300 Pt Co de color, 8.64 de pH | 27 g/m$^3$ dosis de $O_3$, 1 g/6 g dosis de Zn, 4.0 de pH, 180 min de reacción | 90% de DQO, 99% de color, 5% de $NH_3$-N | [9] |
| Postratamiento | Fe (III) | Efluente biotratado: 273 de DQO., 107.6 de TOC, 8.58 de, 0.05 de BOD5/COD, 3.71 $cm^{-1}$ de absorbentes $UV_{254}$ | 100 mg/min de $O_3$, 6 g/L de Fe (III), 6.5 de pH, 25 min de reacción | 80.23% de DQO y el 74.85% de COT, 85.01% de absorbentes $UV_{254.}$, reducción alta de metales tóxicos (Cu, Ni, As, Sr, Cr, Pb y Zn) | [41] |
| | | **Heterogénea** | | | |
| Postratamiento | $Al_2O_3$ | Efluente de osmosis inversa: 1317.5 mg/L de DQO, 20 mg/L de $DBO_5$, 57 mg/L de solidos suspendidos, 7.3 de pH, 0.01 de $BOD_5$/COD | 22 mg/min. de dosis de $O_3$, 50 g/L de $Al_2O_3$, 7.3 de pH, 30 $^o$ C, 30 min de reacción | 70% de DQO, 100% color, 0.2 de $DBO_5$/DQO | [6] |
| | SSCWM/$O_3$, Ti-SSCWM/$O_3$, Ti-Mn /SSCWM/$O_3$ (Stainless steel corrugated wire mesh-SSCWM) | 824.6 $\pm$ 60 mg/L de DQO, 125.62 $\pm$ 2 mg/L de $NH_3$-N, 8.538 $\pm$ 0.002 de pH, 350-400 de color, 0.08 de $BOD_5$/COD | 8.5 de pH, 120 min de reacción. | 64.44%, 68.97% y 78.43% de DQO para SSCWM/O3, Ti-SSCWM/O3, Ti-Mn /SSCWM/O3 respectivamente; hasta un 90% de absorbentes $UV_{254}$ | [25] |
| | Zeolita neutral (faujasita) | 2500 mg/L de DQO, 40 mg/L de $BOD_5$, 16200 PtCo de color, 8.2 de pH, 1100 mg/L de NO3-N, 0.016 de $BOD_5$/COD | 27 g/Nm$^3$ de dosis de $O_3$, 11 y 5 de pH óptimos para reducción de color y amoniaco respectivamente, 120 minutos | 66% de DQO, 63% de Amoniaco, 93% de color, 0.1 de $BOD_5$/COD | [32] |
| Postratamiento | $Al_2O_3$ | Efluente de un semi-aerobic aged refuse biofilter: 1100 mg/L de DQO, 3.0 de absorbentes $UV_{254}$, 0.4 $cm^{-1}$ de numero de color (CN), 0.04 de $BOD_5$/COD | 18.92 mg/min de dosis de $O_3$, 10 g/L de $Al_2O_3$, 7.8 $\pm$2 de pH, 30 min de reacción | 54.3% de DQO, 82.9% de absorbentes $UV_{254}$, 95.9% de CN | [45] |
| | Cu/Mg/Al-chitosan: Cu (0.89 mmol/L), Mg (4 mmol/L) y Al (2 mmol/L) | 40.70 mg/L de DQO, 2100 mg/L de $BOD_5$, 9.1 de pH, 0.052 de $BOD_5$/COD, 34.04 de COT | 20 mg/L de catalizador, 3.5 mg/min de $O_3$, 50 min de reacción | 69% de DQO, 48% de COT, 54% de absorbentes $UV_{254}$, 0.39 de $BOD_5$/COD | [46] |

en conjunto, los residuos urbanos y los residuos industriales [54]. Por lo cual, se afirma que no existe un proceso de tratamiento único que funcione para todos los lixiviados [54].

Realizar un tratamiento eficiente de los lixiviados generados en los rellenos sanitarios de los países en desarrollo, se convierte en un proceso relevante de responsabilidad ambiental y social. Incluir los procesos basados en ozono junto con los tratamientos convencionales implementados en los rellenos sanitarios, debe depender de un proceso investigativo, donde se aporten recursos financieros,

para lograr adaptar un acople de tratamiento adecuado, que optimice la gestión de los lixiviados cumpliendo con los estándares permisibles [54].

## 7 Conclusiones

La composición compleja de los lixiviados de rellenos sanitario requiere de una alternativa de tratamiento que alcance las remociones esperadas, de manera que no represente un riesgo para la salud y el ambiente. Recientemente, se han avanzado en estudios sobre los procesos basados en ozono para aprovechar sus ventajas oxidativas que degradan los compuestos recalcitrantes y mejoran la biodegradabilidad. Las técnicas de ozonización catalítica y peroxono son las más documentadas y desarrolladas como tratamiento. Se destaca la ozonización catalítica para remover altísimos porcentajes de DQO, COT, Color y compuestos absorbentes de $UV_{254}$, y para disminuir el tiempo de reacción del tratamiento (25 a 180 minutos). Cada técnica presenta condiciones de operación distintas, de acuerdo a los tipos de reacciones que permiten la degradación de contaminantes. A pesar de los resultados prometedores de los procesos basados en ozono, para los países en desarrollo, continúa siendo un desafío para su implementación a escala real en un relleno sanitario, entre las causas principales, la limitación en cuanto a costos y de los sistemas de control.

## Referencias


[1] M. Lovato, J. R. Buffelli, M. Abrile, and C. Martín, "Kinetics and efficiency of ozone for treatment of landfill leachate including the effect of previous microbiological treatment," Environ. Sci. Pollut. Res., vol. 26, no. 5, pp. 4474-4487, 2019.

[2] W. Cheng, X. Quan, X. Huang, C. Cheng, L. Yang, and Z. Cheng, "Enhancement of micro-filtration performance for biologically-treated leachate from municipal solid waste by ozonation in a micro bubble reactor," Sep. Purif. Technol., vol. 207, pp. 535-542, 2018.

[3] S. Kow, M. R. Fahmi, C. Z. A. Abidin, and O. Soon-An, "Advanced Oxidation Processes: Process Mechanisms, Affecting Parameters and Landfill Leachate Treatment," Water Environ. Res., vol. 88, no. 11, pp. 2047-2058, 2016.

[4] H. Wang, Y. nan Wang, X. Li, Y. Sun, H. Wu, and D. Chen, "Removal of humic substances from reverse osmosis (RO) and nanofiltration (NF) concentrated leachate using continuously ozone generation-reaction treatment equipment," Waste Manag., vol. 56, pp. 271-279, 2016.

[5] A. Mojiri et al., "Concentrated landfill leachate treatment with a combined system including electro-ozonation and composite adsorbent augmented sequencing batch reactor process," Process Saf. Environ. Prot., vol. 111, pp. 253-262, 2017.

[6] Y. He, H. Zhang, J. J. Li, Y. Zhang, B. Lai, and Z. Pan, "Treatment of Landfill Leachate Reverse Osmosis Concentrate from by Catalytic Ozonation with $\gamma$-Al2O3," Environ. Eng. Sci., vol. 35, no. 5, pp. 501-511, 2018.

[7] Q. Xu, G. Siracusa, S. Di Gregorio, and Q. Yuan, "COD removal from biologically stabilized landfill leachate using Advanced Oxidation Processes (AOPs)," Process Saf. Environ. Prot., vol. 120, pp. 278-285, 2018.

[8] Z. Youcai, "Leachate Generation and Characteristics," in Pollution Control Technology for Leachate from Municipal Solid Waste, E. Inc., Ed. 2018, pp. 1-30.

[9] S. S. Abu Amr, H. A. Aziz, M. S. Hossain, and M. J. K. Bashir, "Simultaneous removal of COD and color from municipal landfill leachate using Ozone/Zinc sulphate oxidation process," Glob. Nest J., vol. 19, no. 3, pp. 498-504, 2017.

[10] W. Chen, A. Zhang, G. Jiang, and Q. Li, "Transformation and degradation mechanism of landfill leachates in a combined process of SAARB and ozonation," Waste Manag., vol. 85, pp. 283-294, 2019.

[11] M. J. K. Bashir, H. A. Aziz, S. S. A. Amr, S. Sethupathi, C. A. Ng, and J. W. Lim, "The competency of various applied strategies in treating tropical municipal landfill leachate," Desalin. Water Treat., vol. 54, no. 9, pp. 2382-2395, 2015.

[12] H. Luo, Y. Zeng, Y. Cheng, D. He, and X. Pan, "Recent advances in municipal landfill leachate: A review focusing on its characteristics, treatment, and toxicity assessment," Sci. Total Environ., vol. 703, p. 135468, 2020.

[13] W. Chen and Q. Li, "Elimination of UV-quenching substances from MBR- and SAARB-treated mature landfill leachates in an ozonation process: A comparative study," Chemosphere, vol. 242, p. 125256, 2020.

[14] Z. Huang, Z. Gu, Y. Wang, and A. Zhang, "Improved oxidation of refractory organics in concentrated leachate by a Fe2+-enhanced O3/H2O2 process," Environ. Sci. Pollut. Res., vol. 26, no. 35, pp. 35797-35806, 2019.

[15] H. Qin and H. Chen, "Pretreatment of concentrated leachate by the combination of coagulation and catalytic ozonation with Ce/AC catalyst," Water Sci. Technol., vol. 73, no. 3, pp. 511-519, 2016.

[16] M. Han, X. Duan, G. Cao, S. Zhu, and S. H. Ho, "Graphitic nitride-catalyzed advanced oxidation processes (AOPs) for landfill leachate treatment: A mini review," Process Saf. Environ. Prot., vol. 139, pp. 230-240, 2020.

[17] M. Chys, V. A. Oloibiri, W. T. M. Audenaert, K. Demeestere, and S. W. H. Van Hulle, "Ozonation of biologically treated landfill leachate: Efficiency and insights in organic conversions," Chem. Eng. J., vol. 277, pp. 104-111, 2015.

[18] N. Amaral-Silva, R. C. Martins, S. Castro-Silva, and R. M. Quinta-Ferreira, "Ozonation and perozonation on the biodegradability improvement of a landfill leachate," J. Environ. Chem. Eng., vol. 4, no. 1, pp. 527-533, 2016.

[19] J. L. Gao et al., "Integration of autotrophic nitrogen removal, ozonation and activated carbon filtration for treatment of landfill leachate," Chem. Eng. J., vol. 275, pp. 281-287, 2015.

[20] J. Gao et al., "The present status of landfill leachate treatment and its development trend from a technological point of view," Rev. Environ. Sci. Biotechnol., vol. 14, no. 1, pp. 93-122, 2015.

[21] H.-J. Fan, Y.-Y. Chen, M.-Y. Chen, and D.-T. Chang, Landfill leachate treatment with Mn and Ce oxides impregnated GAC-ozone treatment process, vol. 482. Elsevier B.V., 2015.

[22] R. Poblete, I. Oller, M. I. Maldonado, and E. Cortes, "Improved landfill leachate quality using ozone, UV solar radiation, hydrogen peroxide, persulfate and adsorption processes," J. Environ. Manage., vol. 232, no. August 2018, pp. 45-51, 2019.

[23] K. Ikehata and Y. Li, "Ozone-Based Processes," in Advanced Oxidation Processes for Wastewater Treatment: Emerging Green Chemical Technology, Elsevier Inc., Ed. 2018, pp. 115-134.

[24] H. Wang et al., "Transformation of dissolved organic matter in concentrated leachate from nanofiltration during ozone-based oxidation processes (O3, O3/H2O2 and O3/UV)," J. Environ. Manage., vol. 191, pp. 244-251, 2017.

[25] A. Soubh and N. Mokhtarani, "The post treatment of composting leachate with a combination of ozone and persulfate oxidation processes," RSC Adv., vol. 6, no. 80, pp. 76113-76122, 2016.

[26] S. S. Abu-Amr, S. N. F. Zakaria, and H. A. Aziz, "Performance of combined ozone and zirconium tetrachloride in stabilized landfill

leachate treatment," J. Mater. Cycles Waste Manag., vol. 19, no. 4, pp. 1384-1390, 2016.

[27] A. P. J. Scandelai, L. Cardozo Filho, D. C. C. Martins, T. K. F. de S. Freitas, J. C. Garcia, and C. R. G. Tavares, "Combined processes of ozonation and supercritical water oxidation for landfill leachate degradation," Waste Manag., vol. 77, no. November, pp. 466-476, 2018.

[28] E. Kattel, A. Kivi, K. Klein, T. Tenno, N. Dulova, and M. Trapido, "Hazardous waste landfill leachate treatment by combined chemical and biological techniques," Desalin. Water Treat., vol. 57, no. 28, pp. 13236-13245, 2016.

[29] A. I. Gomes, T. F. Soares, T. F. C. V. Silva, R. A. R. Boaventura, and V. J. P. Vilar, "Ozone-driven processes for mature urban landfill leachate treatment: Organic matter degradation, biodegradability enhancement and treatment costs for different reactors configuration," Sci. Total Environ., vol. 724, 2020.

[30] J. Umamaheswari, T. Bharathkumar, S. Shanthakumar, and K. M. Gothandam, "A feasibility study on optimization of combined advanced oxidation processes for municipal solid waste leachate treatment," Process Saf. Environ. Prot., vol. 143, pp. 212-221, 2020.

[31] F. Jiang, B. Qiu, and D. Sun, "Degradation of refractory organics from biologically treated incineration leachate by VUV/O3," Chem. Eng. J., vol. 370, no. December 2018, pp. 346-353, 2019.

[32] H. R. AlGburi, H. A. Aziz, H. M. Zwain, and A. F. M. Noor, "Treatment of Landfill Leachate by Heterogeneous Catalytic Ozonation with Granular Faujasite Zeolite," Environ. Eng. Sci., vol. 00, no. 00, 2020.

[33] M. Bourgin et al., "Effect of operational and water quality parameters on conventional ozonation and the advanced oxidation process O3/H2O2: Kinetics of micropollutant abatement, transformation product and bromate formation in a surface water," Water Res., vol. 122, pp. 234-245, 2017.

[34] T. H. Van and T. V. Trinh, "Application of Regression Analysis for Ozone and Catalytic Ozonation of Organic Compounds from Landfill Leachate with Ceramic Raschig Rings and Natural Manganese Ore," Ozone Sci. Eng., vol. 38, no. 2, pp. 133-142, 2016.

[35] P. Asaithambi, B. Sajjadi, A. R. Abdul Aziz, and W. M. A. B. W. Daud, "Ozone (O3) and sono (US) based advanced oxidation processes for the removal of color, COD and determination of electrical energy from landfill leachate," Sep. Purif. Technol., vol. 172, pp. 442-449, 2017.

[36] F. Wang, Y. Huang, P. Wen, and Q. Li, "Transformation mechanisms of refractory organic matter in mature landfill leachate treated using an Fe0-participated O3/H2O2 process," Chemosphere, vol. 263, p. 128198, 2021.

[37] P. Gautam, S. Kumar, and S. Lokhandwala, "Advanced oxidation processes for treatment of leachate from hazardous waste landfill: A critical review," J. Clean. Prod., vol. 237, 2019.

[38] C. Wu, W. Chen, Z. Gu, and Q. Li, "A review of the characteristics of Fenton and ozonation systems in landfill leachate treatment," Sci. Total Environ., p. 143131, 2020.

[39] M. Ghahrchi and A. Rezaee, "Electro-catalytic ozonation for improving the biodegradability of mature landfill leachate," J. Environ. Manage., vol. 254, no. October 2019, p. 109811, 2020.

[40] A. P. J. Scandelai, E. Sloboda Rigobello, B. L. C. de Oliveira, and C. R. G. Tavares, "Identification of organic compounds in landfill leachate treated by advanced oxidation processes," Environ. Technol.

(United Kingdom), vol. 40, no. 6, pp. 730-741, 2019.

[41] Y. Wang et al., "Effective removal of contaminants from biotreated leachate by a combined Fe(III)/O3 process: Efficiency and mechanisms," J. Clean. Prod., vol. 276, no. Iii, p. 123379, 2020.

[42] Z. Liu, L. Pan, F. Hu, and Y. Hu, "Advanced landfill leachate biochemical effluent treatment using Fe-Mn/AC activates O3/Na2S2O8 process: process optimization, wastewater quality analysis, and activator characterization," Environ. Sci. Pollut. Res., vol. 27, no. 13, pp. 15337-15349, 2020.

[43] H. R. AlGburi, H. A. Aziz, H. M. Zwain, and A. F. M. Noor, "Treatment of Landfill Leachate by Heterogeneous Catalytic Ozonation with Granular Faujasite Zeolite," Environ. Eng. Sci., no. December, 2020.

[44] A. Ikhlaq et al., " Treatment of leachate through constructed wetlands using Typha angustifolia in combination with catalytic ozonation on Fe-zeolite A ," Int. J. Phytoremediation, vol. 0, no. 0, pp. 1-9, 2020.

[45] Y. Xiang, Y. Chen, S. Luo, J. Zou, and A. Zhang, "Degradation of recalcitrant organic matter in SAARB leachate by a combined process of coagulation and catalytic ozonation," Environ. Sci. Pollut. Res., vol. 27, no. 32, pp. 40219-40228, 2020.

[46] D. Ranjbar-Vakilabadi, A. H. Hassani, G. Omrani, and B. Ramavandi, "Catalytic potential of Cu/Mg/Al-chitosan for ozonation of real landfill leachate," Process Saf. Environ. Prot., vol. 107, pp. 227-237, 2017.

[47] M. A. Kamaruddin, M. S. Yusoff, L. M. Rui, A. M. Isa, M. H. Zawawi, and R. Alrozi, "An overview of municipal solid waste management and landfill leachate treatment: Malaysia and Asian perspectives," Environ. Sci. Pollut. Res., vol. 24, no. 35, pp. 26988-27020, 2017.

[48] R. A. Agarwal, A. K. Agarwal, T. Gupta, and N. Sharma, Introduction to Pollutants from Energy Sources: Characterization and Control. 2019.

[49] Y. Ogata et al., "Design considerations of constructed wetlands to reduce landfill leachate contamination in tropical regions," J. Mater. Cycles Waste Manag., vol. 20, no. 4, pp. 1961-1968, 2018.

[50] C. Ma et al., "Catalytic micro-ozonation by Fe3O4 nanoparticles @ cow-dung ash for advanced treatment of biologically pre-treated leachate," Waste Manag., vol. 83, pp. 23-32, 2019.

[51] X. Tang, S. Zhu, X. Quan, X. Huang, F. Qiu, and C. Feng, "Degradation Treatment of Concentrated Landfill Leachate by Catalytic Ozonation in a Microbubble Reactor," Ozone Sci. Eng., vol. 00, no. 00, pp. 1-14, 2020.

[52] K. S. Rajoo, D. S. Karam, A. Ismail, and A. Arifin, "Evaluating the leachate contamination impact of landfills and open dumpsites from developing countries using the proposed Leachate Pollution Index for Developing Countries (LPIDC)," Environ. Nanotechnology, Monit. Manag., vol. 14, no. September, p. 100372, 2020.

[53] W. L. M. Braga et al., "Optimization of the treatment of sanitary landfill by the ozonization catalysed by modified nanovermiculite in a rotating packed bed," J. Clean. Prod., vol. 249, p. 119395, 2020.

[54] S. M. Iskander et al., "A review of landfill leachate induced ultraviolet quenching substances: Sources, characteristics, and treatment," Water Res., vol. 145, pp. 297-311, 2018.

# Chapter 1: Synergistic Degradation of Organic Contaminants in Landfill Leachates Using Catalytic Ozonation with Magnetite

Sci

MDPI

Article

# Synergistic Degradation of Organic Contaminants in Landfill Leachates Using Catalytic Ozonation with Magnetite

**Dorance Becerra-Moreno [1,2,*], Fiderman Machuca-Martínez [3], Luisa F. Ramírez-Rios [4], Janet B. García-Martínez [1] and Andrés F. Barajas-Solano [1,*]**

[1] Department of Environmental Sciences, Universidad Francisco de Paula Santander, Av. Gran Colombia No. 12E-96, Cúcuta 540003, Colombia; janetbibianagm@ufps.edu.co
[2] School of Natural Resources and Environment, Universidad del Valle, Ciudad Universitaria Meléndez, Calle 13 # 100-00, Cali 760015, Colombia
[3] Center of Excellence in New Materials—CENM, School of Chemical Engineering, Universidad del Valle, Ciudad Universitaria Meléndez, Calle 13 # 100-00, Cali 760015, Colombia; fiderman.machuca@correounivalle.edu.co
[4] School of Engineering, Universidad De Los Llanos, km 12, Vda. Barcelona, Villavicencio 500003, Colombia; lfernandaramirez@unillanos.edu.co
* Correspondence: dorancebm@ufps.edu.co (D.B.-M.); andresfernandobs@ufps.edu.co (A.F.B.-S.)

**Abstract:** This study evaluated the efficiency of catalytic ozonation with magnetite ($Fe_3O_4$) in degrading recalcitrant organic compounds in leachates from two sanitary landfills in Colombia. The optimum treatment conditions were also analyzed by means of a response surface design, resulting in 6 g $O_3$/h, 2.5 g/L $Fe_3O_4$, and pH 9, which resulted in COD removal rates of 85.3% in El Guayabal and 75.8% in La Madera. Moreover, the $BOD_5$/COD ratio increased from 0.26 to 0.38 and from 0.23 to 0.32, respectively, suggesting increased effluent biodegradability. The most efficient ozone consumption (2.7 g $O_3$ per gram of COD removed) was obtained under alkaline conditions with a high catalyst concentration. Magnetite demonstrated structural stability, although its catalytic efficiency progressively decreased after three cycles of use, with COD removal decreasing from 85.3% to 73.6%. These findings validate catalytic ozonation with magnetite as an efficient alternative for advanced leachate treatment, with the potential to optimize contaminant removal in industrial effluents and strengthen environmental remediation strategies.

**Keywords:** catalytic ozonation; magnetite ($Fe_3O_4$); leachates; contaminant degradation



Academic Editor: José A. Peres

Received: 4 February 2025
Revised: 28 February 2025
Accepted: 3 March 2025
Published: 6 March 2025

**Citation:** Becerra-Moreno, D.; Machuca-Martínez, F.; Ramírez-Rios, L.F.; García-Martínez, J.B.; Barajas-Solano, A.F. Synergistic Degradation of Organic Contaminants in Landfill Leachates Using Catalytic Ozonation with Magnetite. *Sci* **2025**, *7*, 31. https://doi.org/10.3390/sci7010031



## 1. Introduction

A challenging problem in the management of urban solid waste is represented by leachates generated in sanitary landfills, which have heterogeneous compositions and high recalcitrant contaminant loads. Their chemical complexity—compounded by heavy metals, difficultly degrading organic matter, and emerging pollutants—has underscored the shortcomings of conventional treatment methods. Although such processes are based on biological or physicochemical strategies, they are limited to certain efficiencies, and they often do not comply with more stringent environmental regulations [1]. This has, in turn, put more pressure on the development of feasible solutions that promote the development of new technologies for optimizing contaminant removal and for making any process sustainable.

In this context, significant knowledge concerning the degradation of recalcitrant compounds has been obtained via advanced oxidation processes (AOPs). Among them, catalytic ozonation has proven to be a promising option, as it synergistically improves the

oxidizing ability of ozone through contact with selective catalytic materials [2]. This method aids in the conversion of difficult organic materials to biodegradable intermediates, greatly increasing the overall treatment efficiency [3]. Moreover, its use has been confirmed in multiple contexts, enabling deployment within different operating states and guaranteeing performance in practical systems [4].

One of the most studied and efficient catalysts in this process is magnetite ($Fe_3O_4$), which promotes the decomposition of ozone into hydroxyl radicals—highly reactive species that play a key role in the oxidation of hard-to-degrade organic contaminants [5]. In addition to its structural stability, its physicochemical properties make it a valuable tool for the effective removal of contaminants from leachates. Furthermore, its active surface serves as an efficient adsorption site, improving reaction kinetics and maximizing process efficiency [3]. Recent research has shown that magnetite can enhance organic matter removal efficiency when combined with other catalysts, such as iron nanoparticles and cerium compounds, expanding the possibilities for process optimization [6]. Moreover, doping magnetite with transition metals has been found to improve its catalytic activity and material stability [7]. The combination of these catalysts enhances process efficiency by increasing reaction rates and reducing the formation of undesirable byproducts.

Catalytic ozonation for leachate treatment is a new advancing topic. Multiple studies have confirmed that this approach not only facilitates the degradation of stubborn contaminants but also increases the biodegradability of the leachate after treatment. The process proved to be highly efficient for the removal of persistent organic compounds when it was coupled with electrocoagulation and adsorption, as demonstrated by recent research. [8]. In a related study, hybrid processes such as synergizing catalytic ozonation with membrane bioreactors (MBRs) have exhibited great potential for the removal of toxic constituents and also effectively lead to great reductions of chemical oxygen demand (COD) for optimal remediation levels [9]. Another promising approach has been the use of advanced catalysts, such as magnetite doped with transition metals, which has improved the efficiency of converting ozone into hydroxyl radicals while minimizing the formation of undesirable secondary byproducts. Research has reported that incorporating materials such as manganese ferrite ($MnFe_2O_4$) and Fe-$N_4$ nano-catalysts within carbon structures yields enhanced long-term stability and catalytic activity, facilitating their application under more demanding operational conditions [2]. Likewise, the inclusion of EDTA-Fe-based complexes has enhanced ozonation efficiency under neutral pH conditions, a key factor for implementation in industrial scenarios without requiring additional chemical adjustments [10].

Regarding process optimization, recent studies have explored the implementation of catalysts supported on activated carbon and porous structures, which has significantly reduced metal leaching and improved catalyst reusability over multiple treatment cycles [11]. Such innovations are fundamental to ensuring the economic and environmental viability of the process on an industrial scale. Moreover, integrating catalytic ozonation with photo assisted processes ($O_3$/UVC and $O_3/H_2O_2$/UVC) has been evaluated as a complementary strategy for degrading high-molecular-weight organic compounds, enhancing the conversion of contaminants into biodegradable products, and reducing the generation of toxic byproducts [12].

Various studies have demonstrated that the application of catalytic ozonation with magnetite not only facilitates organic matter removal but also significantly reduces leachate toxicity and improves its biodegradability [13]. This technology has proven particularly effective in eliminating aromatic compounds, humic substances, and other refractory contaminants that conventional methods fail to degrade efficiently [14]. Additionally, recent studies have shown that integrating catalytic ozonation with other processes, such as electrochemical treatment and biofiltration, can further improve treatment efficiency and

reduce chemical reagent demand [15]. Moreover, optimizing the ozone concentration and incorporating hybrid catalysts, such as $Fe_3O_4$ combined with fly ash, have led to enhanced degradation of persistent compounds and increased leachate biodegradability [2]. Another critical aspect is the reusability of the catalyst. Magnetite has shown high stability after multiple reaction cycles, maintaining its catalytic capacity and reducing the operational costs associated with the process [5]. However, the efficiency of catalytic ozonation depends on multiple factors, including the medium pH, ozone concentration, and presence of other substances in the leachate matrix. Therefore, optimizing operating conditions is essential to maximize process effectiveness and ensure feasibility at an industrial scale [1]. Exploring different reactor configurations and adjusting ozone and catalyst concentrations could provide practical solutions to these challenges.

In this context, the present study evaluated the performance of catalytic ozonation with magnetite for the treatment of leachates from two sanitary landfills in Colombia, aiming to determine the optimal operating conditions and their impact on the removal of recalcitrant contaminants. Key variables such as ozone dosage, catalyst concentration, and pH were analyzed to maximize process efficiency. Additionally, catalyst stability after multiple usage cycles was assessed, identifying potential modifications in catalyst structure and composition. Through this analysis, the study seeks to establish technical criteria for large-scale implementation, contributing to the development of sustainable strategies for landfill leachate remediation and the optimization of advanced effluent treatment technologies.

## 2. Materials and Methods

### *2.1. Leachate Sampling and Characterization*

Two sanitary landfills located in Norte de Santander, Colombia, were sampled for leachate. The first is Regional La Madera, which has been in function since 2001 in Ocaña (8°14′ N, 73°21′ W). Waste collected at the site comes mainly from municipalities, with the largest share of agricultural activity and no major industrial impact. On the other hand, the Environmental Technology Park El Guayabal has been operating since 2007; it is in the city of Cúcuta (8°05′ N, 72°30′ W) and receives waste from municipalities with industrial activities, which modifies the chemical characteristics of their leachates (CORPONOR, 2000; 2015).

Sampling was conducted following the methodology described by [16], employing a stratified scheme at three depth levels: surface (0–50 cm), intermediate (50–150 cm), and deep (>150 cm). This strategy allowed for the evaluation of contaminant distributions at different depths in the storage ponds, ensuring a representative characterization. To prevent sample alteration, sterile borosilicate bottles were used, preserved with 0.2% sodium azide, and stored at 4 °C immediately after collection [17]. Additionally, transportation was carried out in insulated containers with cold packs, maintaining a temperature between 2 and 4 °C to preserve the physicochemical and microbiological properties of the samples [18].

Table 1 summarizes the physicochemical parameters and heavy metals analyzed and the analytical methods used for the samples collected for this study. The standards used for all procedures were based on Standard Methods for the Examination of Water and Wastewater, 23rd Edition [19].

### *2.2. Catalyst Characteristics*

The selection of the catalyst used in this study followed the criteria described by [20]. Synthetic magnetite ($Fe_3O_4$) was chosen because of its high purity and chemical stability, making it suitable for advanced oxidation processes. Its interaction with ozone facilitates the generation of hydroxyl radicals, which are essential for the degradation of organic

contaminants in leachates, thereby optimizing treatment efficiency. Additionally, its homogeneous morphology enhances dispersion in aqueous media, ensuring greater surface contact and improving catalytic activity. The characterization of the commercial magnetite used, presented in Table 2, details the distribution of its main elements, highlighting its low impurity content and the presence of oxides such as magnesium oxide (MgO), titanium dioxide ($TiO_2$), and aluminum oxide ($Al_2O_3$), which may influence its stability and catalytic performance.

**Table 1.** Analytical methods for physicochemical characterization of leachates.

| Parameter | Method |
|---|---|
| pH | SM 4500 $H^+$ B |
| Temperature (°C) | SM 2550 B |
| Conductivity (µS/cm) | SM 2510 B |
| Chemical Oxygen Demand (COD) (mg/L) | SM 5220 D |
| Biochemical Oxygen Demand ($BOD_5$) (mg/L) | SM 5210 B |
| Total Suspended Solids (mg/L) | SM 2540 D |
| Cadmium (mg/L) | SM 3030 E, SM 3111 B |
| Chromium (mg/L) | SM 3030 E, SM 3111 B |
| Lead (mg/L) | SM 3030 E, SM 3113 B |
| Mercury (mg/L) | SM 3112 B |

**Table 2.** Chemical composition of synthetic magnetite.

| Component | Concentration | Units |
|---|---|---|
| $Fe_3O_4$ | >98 | % |
| MgO | 0.9 | |
| Mn | 0.3 | |
| $TiO_2$ | 0.25 | |
| Zn | 0.1 | |
| $Al_2O_3$ | 0.1 | |
| $SiO_2$ | 0.05 | |
| Pb | 5 | ppm |
| Cd | 5 | |
| As | 10 | |
| Hg | 0.5 | |

Source: (Alpha Chemicals, Karachi, Pakistan, N.D.).

### *2.3. Ozonation Process*

The ozonation process was conducted in a 500 mL glass reactor designed to maximize ozone mass transfer in the liquid phase. As shown in Figure 1, the reactor features an internal concentric tube for gas injection, facilitating the uniform dispersion of ozone through microbubbles generated by an aeration system with 0.45 µm holes. This configuration was employed to increase the efficiency of contact between ozone and leachate.

During operation, the system temperature was maintained at 20 ± 2 °C under controlled conditions. The ozone used in the experiment was generated from pure oxygen via a model O1 generator (Pacific Ozone, Lenntech, Delfgauw, The Netherlands) with a production capacity of 6 g/h and an adjustable flow rate between 3.3 and 4.7 L/min. The ozone concentration was regulated through a voltage controller, ensuring precise dosing throughout the experiment. Finally, residual gases were directed into a 30% potassium iodide (KI) solution to neutralize unreacted ozone and prevent its release into the atmosphere.

To avoid errors associated with the operation of the ozone generator and to ensure stable dosing, the gaseous ozone was continuously monitored by a BMT 964 BT ozone analyzer. This equipment employs a double-beam UV photometer (254 nm) and pressure

and temperature compensations, ensuring high-precision measurements with an error margin of less than 0.5%. Thanks to this monitoring, it was possible to detect and correct deviations in the ozone concentration supplied to the reactor, improving the reliability of the process. Also, to evaluate the efficiency of ozone transfer to the liquid phase, dissolved ozone was measured using a multi-parameter photometer HI 83300 (Hanna Instruments, Smithfield, RI, USA), based on the DPD (N,N-diethyl-p-phenylenediamine) reagent method. This technique makes it possible to quantify ozone in solution by the formation of colored complexes whose absorbance is measured spectrophotometrically. In this way, it was possible to determine precisely the amount of ozone dissolved in the medium and to evaluate its availability for the catalytic reaction with magnetite.

**Figure 1.** Schematic of glass reactor used in ozonation process.

### *2.4. Optimization of Catalytic Ozonation with Magnetite*

Evaluation of Factors via Box–Behnken Design

Ozonation process optimization was performed according to the Box–Behnken design with three factors (15 experiments) through Design Expert software (v22. 02, StatEase, Minneapolis, MN, USA). The study used untreated samples from two landfills (La Madera and El Guayabal). For case (a) and case (b), the ozone dosage (g/h—flow rate of 3.3 L/min) was provided as a variable in accordance with the ranges that were investigated by [21–25]; the magnetite concentration (g/L) was obtained from [5,25–27]; and the pH values were obtained on the basis of the results of [21,23,28–30] (Table 3). The response variable was the percentage removal of chemical oxygen demand (COD) compared with the initial value. COD removal was measured at time intervals of 0, 20, 40, 60, and 120 min for each experiment. In addition, three control runs were incorporated into the experimental design: (i) ozone (6 g/h), magnetite (0 g/L), and pH (9), (ii) ozone (0 g/h), magnetite (2.5 g/L), and pH (9), and (iii) ozone (0 g/h), magnetite (0 g/L), and pH (9). The data collected after 120 min were analyzed via variance analysis (ANOVA) based on the software settings to determine which of the independent variables and their interactions had a significant effect on COD elimination.

Once the variables with the most significant impact on COD removal were identified, a central composite design (CCD) was applied via Design Expert software (v22.02, StatEase, Minneapolis, MN, USA). This approach allowed for the determination of an optimal region for maximizing the selected response variables.

### *2.5. Assessment of Recoverability of the Catalyst*

After ozonation treatment, the magnetite was recovered via magnetic separation with a neodymium N35 magnet (10 mm × 2 mm). After that, it was rinsed with distilled water to wash away leachate residues and put in an oven to dry at 105 °C for 24 h, in accordance

with [5,31]. The structural and morphological properties of the catalyst were evaluated after each cycle via Fourier transform infrared spectroscopy (FTIR, FTIR-Jasco 4100 spectrometer, KBr pellet, Thermo Fisher Scientific, Waltham, MA, USA) to detect probable changes in the functional groups. Furthermore, to characterize the morphology and structure of the retrieved particles, scanning electron microscopy (SEM) was carried out with a Phenom Pro X microscope (Thermo Fisher Scientific, Waltham, MA, USA). In the United States with a backscattered electron detector. Finally, the catalytic capacity of the recovered magnetite was analyzed for COD removal in three consecutive ozonation cycles, as was the mass recovery of the material after each cycle.

**Table 3.** Resolved Box–Behnken experimental design.

| Run | Factor A $O_2$ g/h | Factor B $Fe_3O_4$ g/L | Factor C pH pH |
|---|---|---|---|
| 1 | 4 | 0.5 | 9 |
| 2 | 6 | 1.5 | 9 |
| 3 | 6 | 0.5 | 6 |
| 4 | 2 | 2.5 | 6 |
| 5 | 2 | 1.5 | 3 |
| 6 | 2 | 1.5 | 9 |
| 7 | 4 | 2.5 | 9 |
| 8 | 4 | 2.5 | 3 |
| 9 | 4 | 1.5 | 6 |
| 10 | 6 | 2.5 | 6 |
| 11 | 6 | 1.5 | 3 |
| 12 | 4 | 0.5 | 3 |
| 13 | 4 | 1.5 | 6 |
| 14 | 2 | 0.5 | 6 |
| 15 | 4 | 1.5 | 6 |

### *2.6. Evaluation of the Efficiency of Ozone Dosing and Transfer in Organic Matter Removal*

The ozone utilization efficiency ($EO_3$, expressed in mg COD/mg $O_3$) was evaluated based on the amount of chemical oxygen demand ($COD$) removed relative to the transferred ozone dose ($TOD$, in mg). This calculation determines the effectiveness of ozone in degrading the organic matter present in leachates, according to the methodology established by [32,33]. The relationship is expressed by the following Equation (1):

$$EO_3 = \frac{COD_{removal}}{TOD} \quad (1)$$

To determine the transferred ozone dose, a mass balance of ozone in the gas and liquid phases was employed. This method quantifies the amount of ozone dissolved in the system and distinguishes it from losses due to volatilization. The balance is described by the following Equation (2) [33]:

$$TOD = \int_0^t [O_3]_{gas\ in} Q_{gas} dt - \int_0^t [O_3]_{gas\ out} Q_{gas} dt \quad (2)$$

where $[O_3]_{gas\ in}$ is the ozone concentration in the gas phase (mg/L), $[O_3]_{gas\ out}$ is the ozone concentration in the aqueous phase at a specific moment during the reaction (mg/L), and $Q_{gas}$ corresponds to the gas flow rate (L/min). The ozone concentration in the aqueous phase was measured via a multiparameter photometer (model HI 83300, Hanna Instruments, Smithfield, RI, USA) via the DPD (N,N-diethyl-p-phenylenediamine) method, which uses the HI 93757-0 reagent, where DPD reacts with ozone to produce colored complexes,

the measurement of which was conducted photometrically. To avoid errors associated with the operation, the gas phase ozone concentration was continuously monitored by a BMT 964 BT ozone analyzer. This equipment employs a double-beam UV photometer (254 nm) and pressure and temperature compensations, ensuring high-precision measurements with an error margin of less than 0.5%.

## 3. Results

### *3.1. Chemical Caracterization of Landfill Leachates*

The physicochemical characteristics of the analyzed leachates are shown in Table 4, as reflected by the variability of the measured parameters. In El Guayabal, the highest values for conductivity, pH, and temperature were recorded, along with an elevated concentration of chromium. In contrast, La Madera presented the highest organic load, as evidenced by its elevated chemical oxygen demand (COD) and biochemical oxygen demand ($BOD_5$) values, coupled with lower conductivity and mercury detection. Chromium was detected in El Guayabal, whereas mercury was detected in La Madera, indicating differences in waste sources and leaching dynamics at each site. Moreover, the $BOD_5$/COD ratio was low in both cases, suggesting limited biodegradability.

**Table 4.** Characteristics of evaluated leachates.

| Parameter | El Guayabal | La Madera | Units |
|---|---|---|---|
| pH | 8.5 | 7.57 | pH units |
| Temperature (°C) | 30.1 | 29.4 | °C |
| Conductivity (µS/cm) | 18.740 | 1.128 | µS/cm |
| Chemical Oxygen Demand (COD) (mg/L) | 6.295 | 8.421 | mg $O_2$/L |
| Biochemical Oxygen Demand ($BOD_5$) (mg/L) | 1.664 | 1.933 | mg $O_2$/L |
| Total Suspended Solids (mg/L) | 8.309 | 5.151 | mg/L |
| Cadmium (mg/L) | <0.050 | <0.014 | mg/L |
| Chromium (mg/L) | 0.294 | n/a | mg/L |
| Lead (mg/L) | <0.10 | <0.10 | mg/L |
| Mercury (mg/L) | <0.001 | 0.28 | mg/L |

### *3.2. Ozonation Process*

The results revealed variations in chemical oxygen demand (COD) removal efficiency between the leachates from the two sanitary landfills (Figure 2). In El Guayabal, a maximum removal of 85.3% was achieved, whereas in La Madera, the highest recorded removal was 75.8%. However, the removal rates within the first 20 min were similar for both leachates, with removal values ranging between 30% and 40%, indicating that the initial stage of the process is critical to the degradation kinetics. After 60 min, the removal curve begins to stabilize, showing a trend toward a decrease in process efficiency over time.

Analysis of the extreme values indicated that, in both leachates, the highest removal rate occurred within the first 40 min, with a significant increase in the COD removal level. In contrast, in the control experiments conducted without the catalyst, COD removal remained below 42%, underscoring the contribution of magnetite to the generation of active oxidizing species. Additionally, variations in efficiency among the catalytic tests can be attributed to the influence of the initial composition and physicochemical conditions of the leachates.

### *3.3. Results of Design of Experiments Proposed*

The effects of light $O_2$ (A), $Fe_3O_4$ (B), and pH (C) on COD removal were statistically assessed via an ANOVA model (Table 5) for samples from El Guayabal and La Madera. Metrics such as the coefficient of determination ($R^2$), adjusted $R^2$, forecast $R^2$, and Adeq

Precision, which gauges the signal-to-noise ratio in the data, were used to evaluate the model's validity. In the case of the samples from El Guayabal, the findings show that the Model F value of 21.93 implies that the model is significant, with only a 0.01% chance that an F value that this large could occur due to noise. In this case, A, B, C, AC, and $C^2$ are significant model terms with *p*-values lower than 0.05. Finally, the lack of fit F value of 3.03 implies that the lack of fit is not significant relative to the pure error. There is a 27.07% chance that a lack of fit F value for this large value could occur due to noise. The predicted $R^2$ of 0.7344 is in reasonable agreement with the adjusted $R^2$ of 0.8820. Additionally, an Adeq Precision of 14.633 indicates an adequate signal.

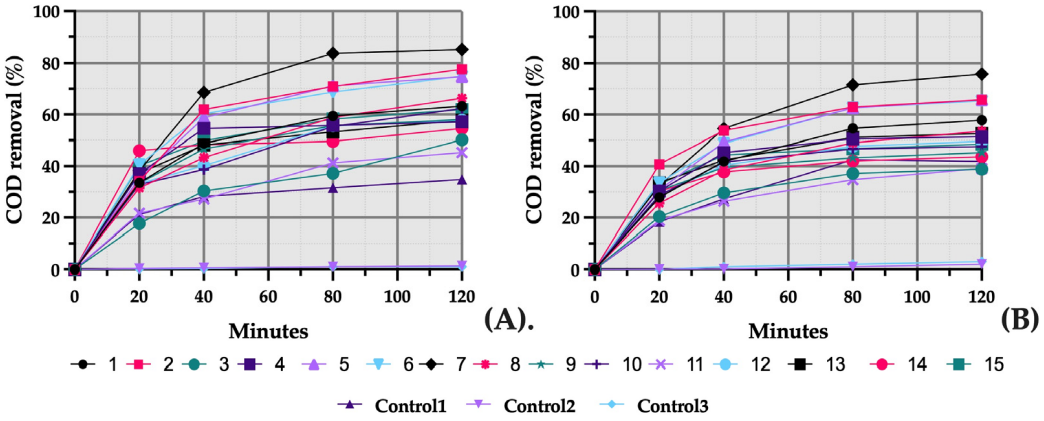



**Figure 2.** COD removal by catalytic ozonation ($Fe_3O_4$): (**A**) El Guayabal sanitary landfill, (**B**) La Madera sanitary landfill.

In the case of the samples from La Madera, the Model F value of 54.01 implies that the model is significant. There is only a 0.02% chance that an F value that is this large could occur due to noise. In this case, A, B, C, AC, BC, and $C^2$ are significant model terms. The lack of fit F value of 1.88 implies that the lack of fit is not significant relative to the pure error. There is a 36.56% chance that a lack of fit F value for this large value could occur due to noise. Finally, the predicted $R^2$ of 0.8737 is in reasonable agreement with the adjusted $R^2$ of 0.9715. An adequate precision of 28.047 indicates an adequate signal.

The response surface analysis highlights the influence of operational variables on the removal of chemical oxygen demand (COD) from the leachates of the El Guayabal and La Madera sanitary landfills. In El Guayabal (Figure 3A), pH and magnetite concentration were the factors with the greatest impact on process efficiency. The highest removal was achieved under alkaline conditions (pH 9), where the interaction between ozone and magnetite promoted the generation of hydroxyl radicals. The response surface exhibited significant curvature, suggesting that the combination of magnetite and pH had a synergistic effect on advanced oxidation. As the pH decreases, the removal efficiency decreases markedly, confirming the reduced production of oxidizing species under acidic conditions.

In La Madera (Figure 3B), the response patterns differ, with a greater dependence on the ozone dose. The linear trend of the surface suggests that increasing the ozone concentration progressively enhances COD removal, with no evident saturation within the evaluated ranges. Although magnetite contributes to this process, its impact is less pronounced than that of El Guayabal. This behavior indicates that the recalcitrant compounds present in this leachate respond more favorably to direct ozone oxidation than to the catalytic action of magnetite. The optimal combination of ozone and magnetite achieved a removal efficiency of approximately 76%, although at very high ozone concentrations, the trend began to stabilize, possibly because of excessive oxidant self-decomposition. For both leachates, the process demonstrates optimal performance under alkaline conditions; however, the

specific composition of the leachate determines the relevance of each variable. While in El Guayabal, magnetite plays a key role in degradation, in La Madera, the predominant effect is that of direct ozone oxidation. This underscores the need to adjust the treatment conditions according to the nature of the leachate to optimize process efficiency.

**Table 5.** ANOVA of experimental data from El Guayabal and La Madera.

| Sample | Source | Sum of Squares | Df | Mean Square | F Value | *p*-Value |
|---|---|---|---|---|---|---|
| El Guayabal | Model | 1509.16 | 5 | 301.83 | 21.93 | <0.0001 * |
| | A-$O_2$ | 143.65 | 1 | 143.65 | 10.43 | 0.0103 * |
| | B-$Fe_3O_4$ | 356.44 | 1 | 356.44 | 25.89 | 0.0007 * |
| | C-pH | 404.70 | 1 | 404.70 | 29.40 | 0.0004 * |
| | AC | 257.60 | 1 | 257.60 | 18.71 | 0.0019 * |
| | $C^2$ | 346.76 | 1 | 346.76 | 25.19 | 0.0007 * |
| | Residual | 123.90 | 9 | 13.77 | | |
| | Lack of Fit | 113.21 | 7 | 16.17 | 3.03 | 0.2707 ** |
| | Pure Error | 10.69 | 2 | 5.34 | | |
| | Total Cor | 1633.06 | 14 | | | |
| | | **$R^2$** | **Adj $R^2$** | **Pred $R^2$** | **Acq Pr** | **Std. Dev.** | **Mean** | **CV%** |
| | | 0.9241 | 0.8820 | 0.7344 | 14.6328 | 3.71 | 63.64 | 5.83 |
| La Madera | Model | 1924.28 | 9 | 213.81 | 54.01 | 0.0002 * |
| | A-$O_2$ | 228.98 | 1 | 228.98 | 57.85 | 0.0006 * |
| | B-$Fe_3O_4$ | 267.96 | 1 | 267.96 | 67.69 | 0.0004 * |
| | C-pH | 401.86 | 1 | 401.86 | 101.52 | 0.0002 * |
| | AB | 20.25 | 1 | 20.25 | 5.12 | 0.0732 ** |
| | AC | 182.25 | 1 | 182.25 | 46.04 | 0.0011 * |
| | BC | 49.70 | 1 | 49.70 | 12.56 | 0.0165 * |
| | $A^2$ | 12.13 | 1 | 12.13 | 3.06 | 0.1404 ** |
| | $B^2$ | 9.31 | 1 | 9.31 | 2.35 | 0.1858 ** |
| | $C^2$ | 719.82 | 1 | 719.82 | 181.84 | <0.0001 * |
| | Residual | 19.79 | 5 | 3.96 | | |
| | Lack of Fit | 14.61 | 3 | 4.87 | 1.88 | 0.3656 ** |
| | Pure Error | 5.18 | 2 | 2.59 | | |
| | Total Cor | 1944.07 | 14 | | | |
| | | **$R^2$** | **Adj $R^2$** | **Pred $R^2$** | **Acq Pr** | **Std. Dev.** | **Mean** | **CV%** |
| | | 0.9898 | 0.9715 | 0.8737 | 28.0471 | 1.99 | 52.43 | 3.79 |

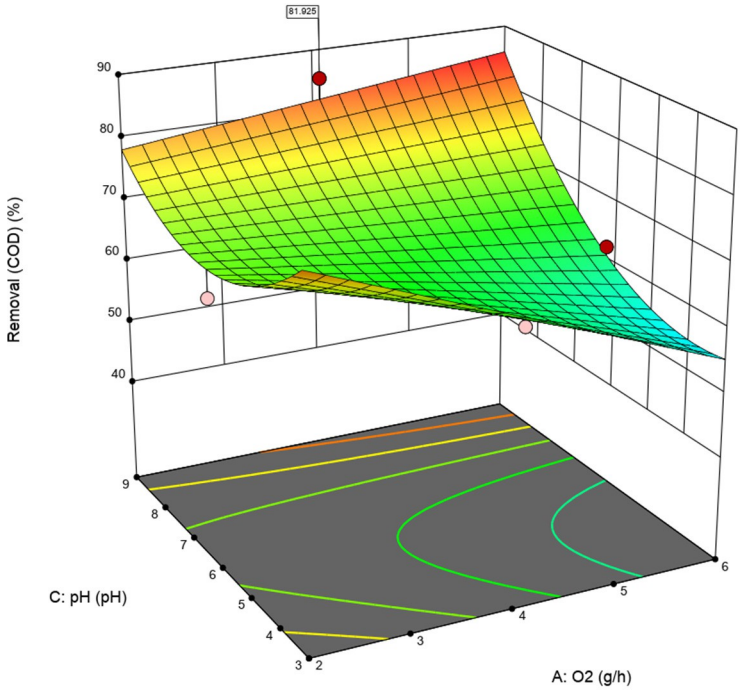
* Significant. ** Not significant.

### 3.3.1. Evaluation of Organic Matter Removal

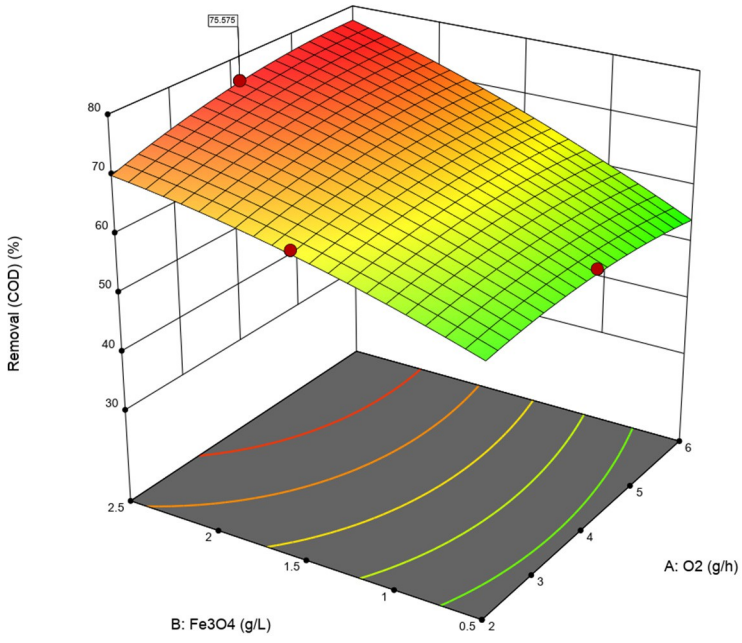
The ozone consumption per unit of chemical oxygen demand (COD) removed exhibited significant variability depending on the evaluated operational conditions, reflecting the impact of ozone dosage, magnetite concentration, and pH on process efficiency (Figure 4). In this context, optimizing the system is essential to minimize reagent usage and maximize organic matter degradation. Among all the tested conditions, treatment with 4 g $O_3$/h, 2.5 g/L $Fe_3O_4$, and pH 9 was the most efficient, with a minimum consumption of 2.7 g $O_3$ per gram of COD removed. This behavior can be attributed to the formation of highly reactive hydroxyl radicals in an alkaline medium, where the catalyst facilitates the conversion of ozone into more effective oxidizing species. Moreover, the high concentration of $Fe_3O_4$ enhances the generation of these radicals, thereby promoting the degradation of recalcitrant organic compounds.

Conversely, the least favorable conditions were observed under acidic pH and low magnetite concentrations, where higher ozone consumption values were recorded. A clear example is the treatment with 6 g $O_3$/h, 0.5 g/L $Fe_3O_4$, and pH 6, in which ozone con-

sumption increased to 4.8 g $O_3$ per gram of COD removed. In this case, the reduced availability of catalyst limits hydroxyl radical production, implying that oxidation occurs primarily through direct ozone attack, a mechanism that is less efficient in terms of energy consumption and contaminant degradation.




(**A**)




(**B**)

**Figure 3.** Surface response for COD removal using landfill leachate from El Guayabal (**A**) and La Madera (**B**).

Furthermore, experiments conducted without magnetite demonstrated markedly lower process efficiency, with an extreme ozone consumption of 7.7 g $O_3$ per gram of COD removed under conditions of 6 g $O_3$/h and pH 9. These values underscore the

importance of the catalyst in optimizing the ozonation process, as its absence prevents the effective conversion of ozone into hydroxyl radicals, thereby significantly reducing treatment efficiency.

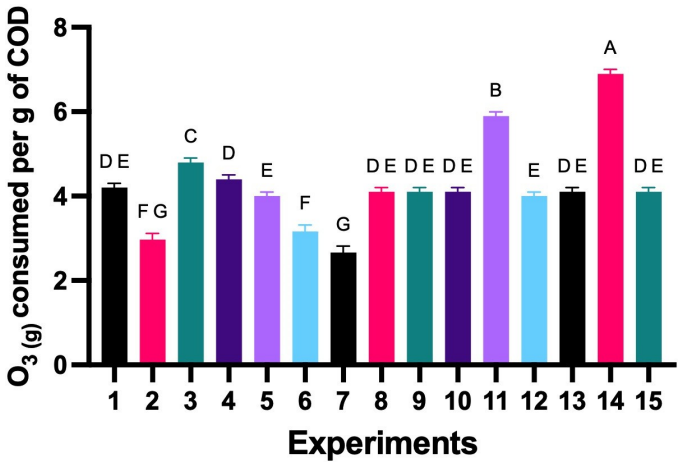



**Figure 4.** Ozone consumption efficiency in organic matter degradation. Different letters mean statistical significance.

### 3.3.2. CCD Optimization

Based on the results of the Box–Behnken experimental design, the variables with the greatest influence on COD removal were identified. Consequently, a central composite design (CCD) was implemented to optimize the process and determine the parameter combination that maximizes treatment efficiency for the leachates from La Madera and El Guayabal. The CCD considers the ozone dosage ($O_2$) and magnetite concentration ($Fe_3O_4$) as the main variables while maintaining the pH at 9 because of its role in hydroxyl radical generation. A total of 13 experimental runs were conducted with expanded variable combinations to assess the system response and develop a predictive optimization model. The resolved experimental design is presented in Table 6.

**Table 6.** Central composite design (CCD) experimental runs.

| Run | Factor A $O_2$ g/h | Factor B $Fe_3O_4$ g/L |
|---|---|---|
| 1 | 6 | 5.33 |
| 2 | 2 | 0.5 |
| 3 | 11.66 | 2.5 |
| 4 | 6 | −0.33 |
| 5 | 6 | 2.5 |
| 6 | 10 | 0.5 |
| 7 | 2 | 4.5 |
| 8 | 10 | 4.5 |
| 9 | 0.34 | 2.5 |
| 10 | 6 | 2.5 |
| 11 | 6 | 2.5 |
| 12 | 6 | 2.5 |
| 13 | 6 | 2.5 |

The data obtained after 120 min of treatment were analyzed via ANOVA in Design Expert v22.02 (StatEase, Minneapolis, MN, USA) to evaluate the significance of each

variable and interaction, enabling the determination of optimal conditions for future applications in leachate treatment.

The effects of light $O_2$ (A) and $Fe_3O_4$ (B) on COD removal were assessed statistically via an ANOVA model (Table 7). Metrics such as the coefficient of determination ($R_2$), adjusted $R_2$, predicted $R_2$, and Adeq Precision (which gauges the signal-to-noise ratio in the data) were used to evaluate the model's validity. The findings show that the Model F value of 1690.10 implies that the model is significant. There is only a 0.01% chance that an F value that is this large could occur due to noise. In this case, A, B, AB, $A^2$, and $B^2$ are significant model terms. The lack of fit F value of 2.40 implies that the lack of fit is not significant relative to the pure error. There is a 20.81% chance that a lack of fit F value for this large value could occur due to noise. Finally, the predicted $R^2$ of 0.9958 is in reasonable agreement with the adjusted $R^2$ of 0.9986. An Adeq Precision of 100.462 indicates an adequate signal.

**Table 7.** ANOVA anlysis for optimization data from El Guayabal and La Madera.

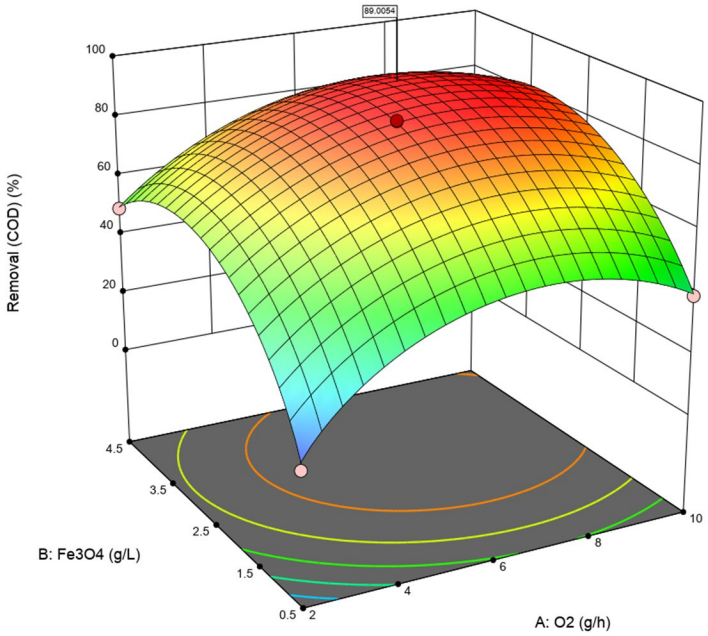
| Sample | Source | Sum of Squares | Df | Mean Square | F Value | *p*-Value |
|---|---|---|---|---|---|---|
| El Guayabal | Model | $8.826 \times 10^5$ | 5 | $1.765 \times 10^5$ | 1690.10 | <0.0001 * |
| | A-$O_2$ | $1.052 \times 10^5$ | 1 | $1.052 \times 10^5$ | 1007.71 | <0.0001 * |
| | B-$Fe_3O_4$ | $2.062 \times 10^5$ | 1 | $2.062 \times 10^5$ | 1974.04 | <0.0001 * |
| | AB | 1616.25 | 1 | 1616.25 | 15.47 | 0.0056 * |
| | $A^2$ | $2.570 \times 10^5$ | 1 | $2.570 \times 10^5$ | 2460.37 | <0.0001 * |
| | $B^2$ | $3.849 \times 10^5$ | 1 | $3.849 \times 10^5$ | 3685.68 | <0.0001 * |
| | Residual | 731.10 | 7 | 104.44 | | |
| | Lack of Fit | 470.23 | 3 | 156.74 | 2.40 | 0.2081 ** |
| | Pure Error | 260.87 | 4 | 65.22 | | |
| | Total Cor | $8.833 \times 10^5$ | 12 | | | |
| | | **$R^2$** | **Adj $R^2$** | **Pred $R^2$** | **Acq Pr** | **Std. Dev.** | **Mean** | **CV%** |
| | | 0.9992 | 0.9986 | 0.9958 | 100.4622 | 10.22 | 462.77 | 2.21 |
| La Madera | Model | 5774.09 | 5 | 1154.82 | 937.58 | <0.0001 * |
| | A-$O_2$ | 462.32 | 1 | 462.32 | 375.35 | <0.0001 * |
| | B-$Fe_3O_4$ | 669.77 | 1 | 669.77 | 543.78 | <0.0001 * |
| | AB | 9.00 | 1 | 9.00 | 7.31 | 0.0305 * |
| | $A^2$ | 3326.14 | 1 | 3326.14 | 2700.46 | <0.0001 * |
| | $B^2$ | 1880.45 | 1 | 1880.45 | 1526.72 | <0.0001 * |
| | Residual | 8.62 | 7 | 1.23 | | |
| | Lack of Fit | 4.51 | 3 | 1.50 | 1.47 | 0.3505 ** |
| | Pure Error | 4.11 | 4 | 1.03 | | |
| | Total Cor | 5782.71 | 12 | | | |
| | | **$R^2$** | **Adj $R^2$** | **Pred $R^2$** | **Acq Pr** | **Std. Dev.** | **Mean** | **CV%** |
| | | 0.9985 | 0.9974 | 0.9933 | 72.2616 | 1.11 | 53.55 | 2.07 |

* Significant. ** Not significant.

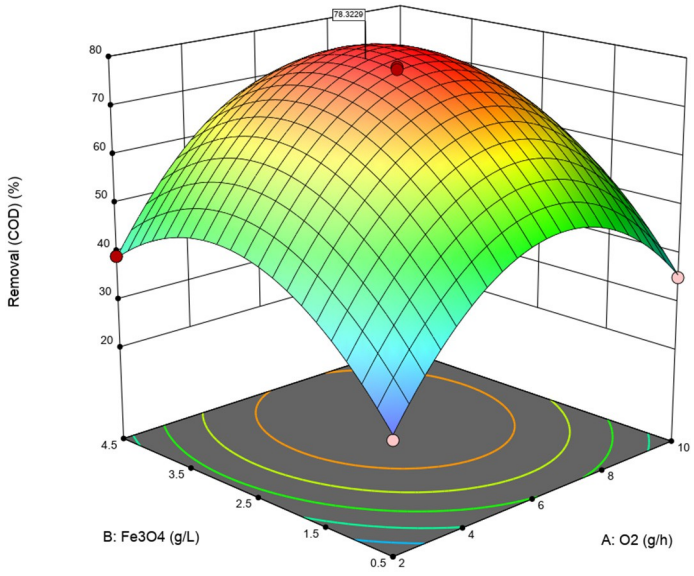
In the case of the La Madera samples, the Model F value of 937.58 implies that the model is significant. There is only a 0.01% chance that an F value that is this large could occur due to noise. In this case, A, B, AB, $A^2$, and $B^2$ are significant model terms. The lack of fit F value of 1.47 implies that the lack of fit is not significant relative to the pure error. There is a 35.05% chance that a lack of fit F value for this large value could occur due to noise. The nonsignificant lack of fit is good; we want the model to fit. The predicted $R^2$ of 0.9933 is in reasonable agreement with the adjusted $R^2$ of 0.9974. Finally, the Adeq Precision of 72.262 indicates an adequate signal.

Response surface analysis provides a visual representation of the interaction between the operational variables and their impact on chemical oxygen demand (COD) removal.

Figure 5 shows that the process efficiency is maximized at medium to high concentrations of magnetite ($Fe_3O_4$), ranging from 2.5 to 3.5 g/L, combined with a high ozone dosage (6 to 7 g/h). This pattern is consistent in the leachates from both sanitary landfills, El Guayabal (Figure 5A) and La Madera (Figure 5B), suggesting that the interaction between these two factors plays a key role in process optimization. In the response surface for El Guayabal (Figure 2A), a pronounced curvature is evident, indicating a parabolic relationship between the $Fe_3O_4$ concentration and COD removal. At low magnetite concentrations, removal is limited, whereas at optimal levels, the efficiency reaches values close to 90%. However, at excessively high concentrations, the trend begins to stabilize, suggesting possible catalyst saturation and a reduction in process efficiency due to particle agglomeration.




(**A**)




(**B**)

**Figure 5.** Surface response for COD removal using landfill leachate from El Guayabal (**A**) and La Madera (**B**).

In contrast, the response surface for La Madera (Figure 5B) shows a similar trend, albeit with a less pronounced slope, indicating greater process stability with respect to variations in magnetite concentration. The optimal response was also observed within the 2.5–3.5 g/L range of $Fe_3O_4$, with an ozone dosage of at least 6 g/h. However, in this case, the maximum efficiency does not reach the values observed in El Guayabal, suggesting differences in leachate composition and reactivity to advanced oxidation mechanisms.

The optimization of the experimental parameters via the Design Expert module enabled the identification of operating conditions that maximize chemical oxygen demand (COD) removal in the evaluated leachates. As reported in Table 8, the optimal conditions for El Guayabal included an ozone dosage of 7 g/h, a magnetite ($Fe_3O_4$) concentration of 3.47 g/L, and a pH of 9, achieving an estimated removal efficiency of 89%. For La Madera, the optimal conditions consisted of an ozone dosage of 6 g/h, a magnetite concentration of 2.94 g/L, and a pH of 9, with an expected removal efficiency of 78% (GraphPad Prism version 10.4.1 for Mac, GraphPad Software, Boston, MA, USA).

**Table 8.** Optimized conditions for maximum COD removal.

| Sample | Code | Variable | Unit | Value |
|---|---|---|---|---|
| Guayabal | A | $O_2$ | g/h | 7 |
| | B | $Fe_3O_4$ | g/L | 3.47 |
| | C | pH | - | 9 |
| | $Z_1$ | COD Removal | % | 89 |
| La Madera | A | $O_2$ | g/h | 6 |
| | B | $Fe_3O_4$ | g/L | 2.94 |
| | C | pH | - | 9 |
| | $Z_2$ | COD Removal | % | 78 |

To validate the model's predictions, additional tests were conducted with five replicates, and the experimental results were compared with the estimated values via a paired *t*-test in GraphPad Prism (version 10.2.3). As shown in Figure 6, no statistically significant differences were observed between the expected and actual values, confirming the robustness of the predictive model and the suitability of the established conditions for optimizing treatment efficiency.

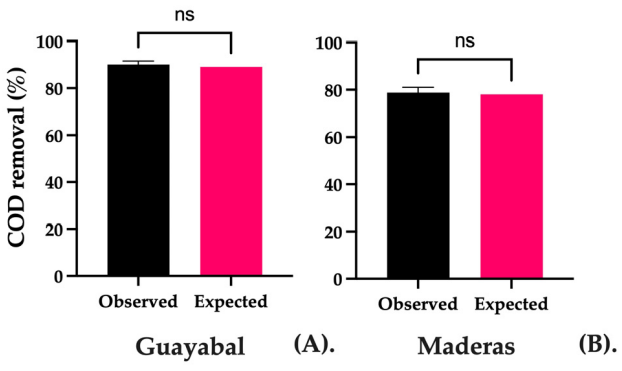



**Figure 6.** Results of one-sample t-test between expected and observed COD removal for leachates from El Guayabal (**A**) and La Madera (**B**).

The leachates were characterized after treatment to evaluate the effects of this process on their physicochemical properties. The final concentrations of COD in El Guayabal and La Madera were 925.8 mg/L and 2038 mg/L, respectively; the corresponding removal efficiencies were 85.3% and 75.8%, respectively (Table 9). The observed decrease in biodegradable organic load indicates successful elimination of recalcitrant compounds through treatment.

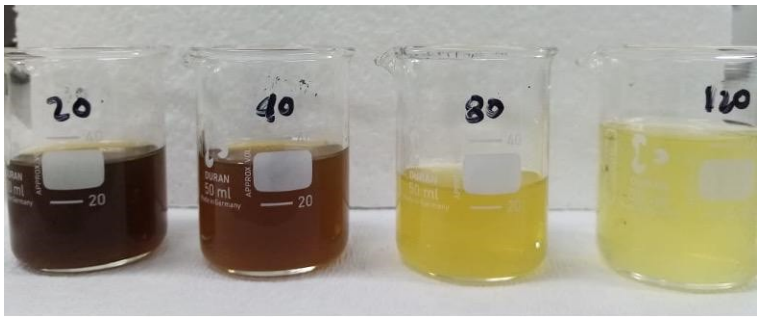
**Table 9.** Characteristics of treated leachates.

| Parameter | El Guayabal | La Madera | Units |
|---|---|---|---|
| pH | 9.4 | 9.1 | pH units |
| Temperature (°C) | 20.2 | 21.3 | °C |
| Conductivity (µS/cm) | 21.636 | 1663.28 | µS/cm |
| Chemical Oxygen Demand (COD) (mg/L) | 925.8 | 2038 | mg $O_2$/L |
| Biochemical Oxygen Demand ($BOD_5$) (mg/L) | 351.8 | 652.2 | mg $O_2$/L |
| Total Suspended Solids (mg/L) | <4.0 | <4.0 | mg/L |

The conductivity increased in both leachates, reaching 21,636.55 µS/cm in El Guayabal and 1663.28 µS/cm in La Madera. This behavior has been linked to the initial formation of ionic species such as sulfates, carbonates, and nitrates (known byproducts of advanced oxidation processes). This increase was more pronounced in El Guayabal, which indicates greater mineralization of preexisting inorganic compounds in this leachate.

The final pH slightly increased, stabilizing at 9.4 in El Guayabal and 9.1 in La Madera. This shift suggests the formation of bicarbonates and carbonates, contributing to the chemical stability of the medium. Finally, total suspended solids (TSS) were reduced to nearly undetectable levels (<4 mg/L), demonstrating the effective removal of suspended particles and an improvement in the clarity of the treated effluent.

Figure 7 illustrates the evolution of the leachate color during different phases of the treatment process. A significant reduction in color intensity was observed as catalytic ozonation progressed, confirming the degradation of organic compounds responsible for coloration. In comparison, treatment with ozone alone resulted in a lower color reduction under the same operating conditions.




(**A**)


(**B**)

**Figure 7.** Evolution of leachate color during treatment: (**A**) ozone alone and (**B**) ozone + magnetite.

### *3.4. Catalyst Recoverability*

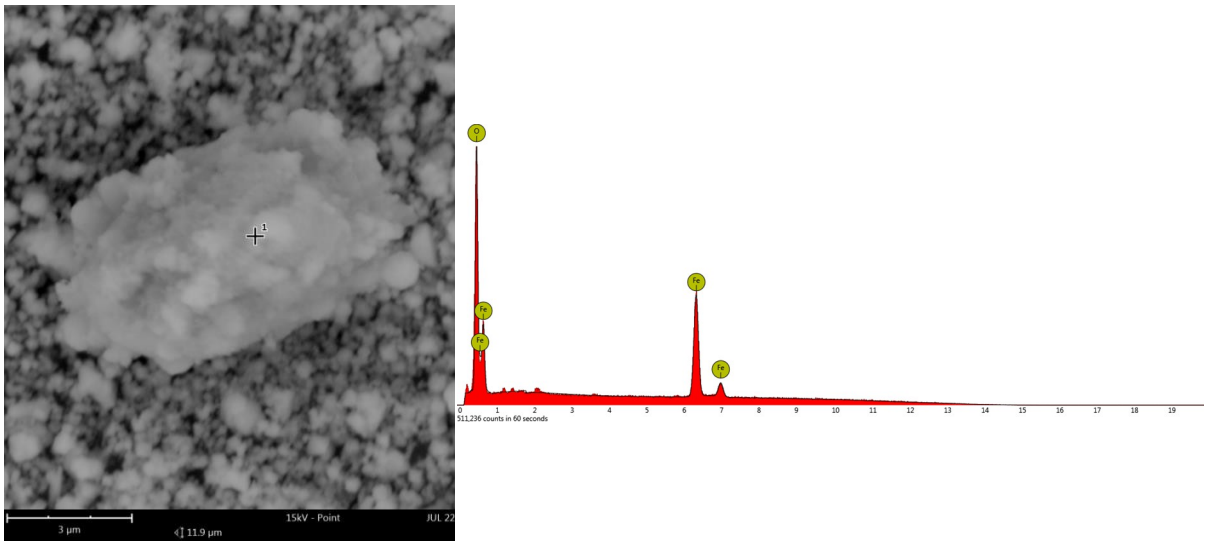
Figure 8 presents scanning electron microscopy (SEM) images used to assess the structure and composition of magnetite at different stages of use. Image (A) depicts unused synthetic magnetite, which is characterized by a homogeneous surface and a composition consisting entirely of $Fe_3O_4$ (100%). Image (B) corresponds to magnetite after one treatment cycle of leachate under optimal conditions (6 g $O_3$/h, 2.5 g/L $Fe_3O_4$, and pH 9), showing a reduction in the $Fe_3O_4$ concentration to 74.80%, along with the appearance of elements such as silicon (Si, 21.53%), suggesting possible adsorption of contaminants. Finally, image (C) of magnetite after two cycles of use shows an additional decrease in the concentration of $Fe_3O_4$ (65.12%) and new compounds, including $TiO_2$ (11.04%) and Ca (1.45%), indicating the progressive degradation of the material, as well as a possible interaction with the species present in the leachate. Images were taken at 22,500×, 22,000×, and 25,000× with a 15 kV acceleration voltage, and backscattered electron detectors for surface alterations corresponded to the catalytic use in ozonation.

### *3.5. Fourier Transform Infrared Spectroscopy (FTIR) Analysis*

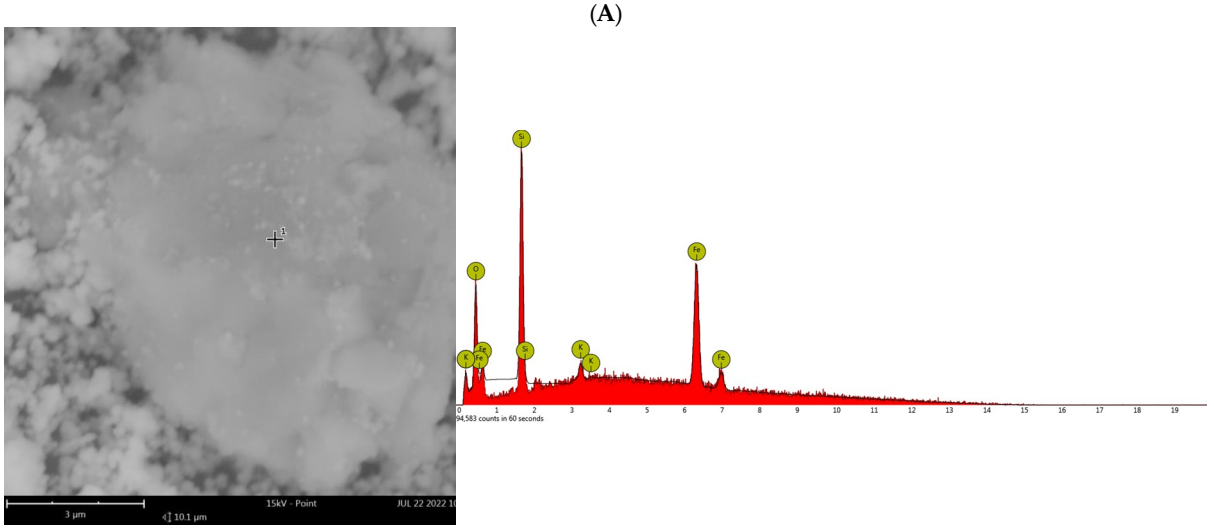
The structure and chemical properties of magnetite before and after catalytic ozonation were studied via Fourier transform infrared (FTIR) spectroscopy. The absorption spectra of the magnetite samples in three states are shown in Figure 9: (A) unused, (B) after the first treatment cycle, and (C) after the second treatment cycle. In the FTIR spectrum of unused magnetite (Figure 9A), characteristic absorption bands of $Fe_3O_4$ are observed, with a prominent peak at approximately 570 $cm^{-1}$, corresponding to Fe–O stretching vibrations. This finding confirms the high initial purity of the material and its unaltered crystalline structure. Furthermore, the absence of bands associated with foreign functional groups suggests that the material was free of surface contaminants prior to treatment.

After one cycle of use (Figure 9B), a reduction in the intensity of the primary $Fe_3O_4$ peak is observed, indicating structural modifications in the magnetite. Additionally, secondary bands emerge in the 1200–1600 $cm^{-1}$ region, suggesting the presence of adsorbed compounds, possibly carbonates or organic residues from the leachate. This observation aligns with previous scanning electron microscopy (SEM) images, which revealed changes in the surface texture of magnetite after its first cycle of use. Following two treatment cycles (Figure 9C), a further decrease in the $Fe_3O_4$ peak intensity is evident, along with an increase in the number of bands associated with secondary compounds. These changes indicate the accumulation of adsorbed residues on the catalyst surface, potentially limiting the availability of active sites for future interactions. Additionally, the progressive alteration in the intensity and position of the bands confirms that magnetite undergoes structural modifications with continued use, impacting its catalytic efficiency in subsequent treatments.

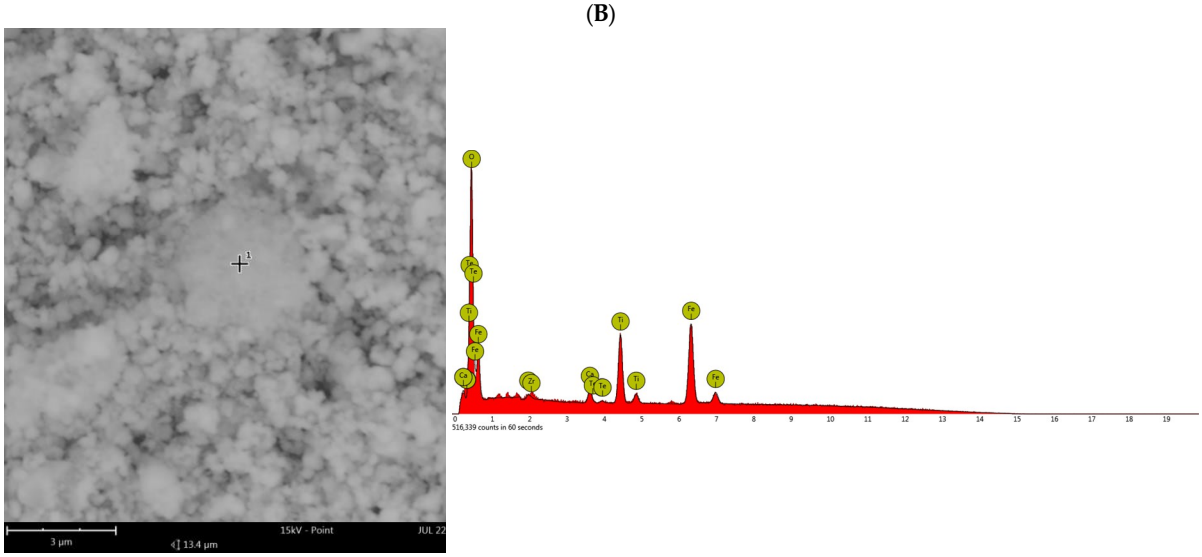
To evaluate the catalyst's stability after use, additional tests were performed to measure the amount of material recovered after each cycle and its performance in chemical oxygen demand (COD) removal. In the first test, when 2.5 g of initial magnetite was used, a COD removal efficiency of 85.3% was achieved. In the second cycle, with 2.275 g of recovered magnetite, the removal efficiency decreased to 79.4%. Finally, in the third cycle, with 2.0175 g of remaining material, the efficiency decreased to 73.6%. This trend suggests that, in addition to material loss, the decrease in catalytic activity may be associated with contaminant adsorption and saturation of the active sites.




(**A**)




(**B**)




(**C**)

**Figure 8.** Scanning electron microscopy (SEM) images. (**A**) Unused synthetic magnetite, (**B**) synthetic magnetite after one cycle of use, and (**C**) magnetite after two cycles of use.

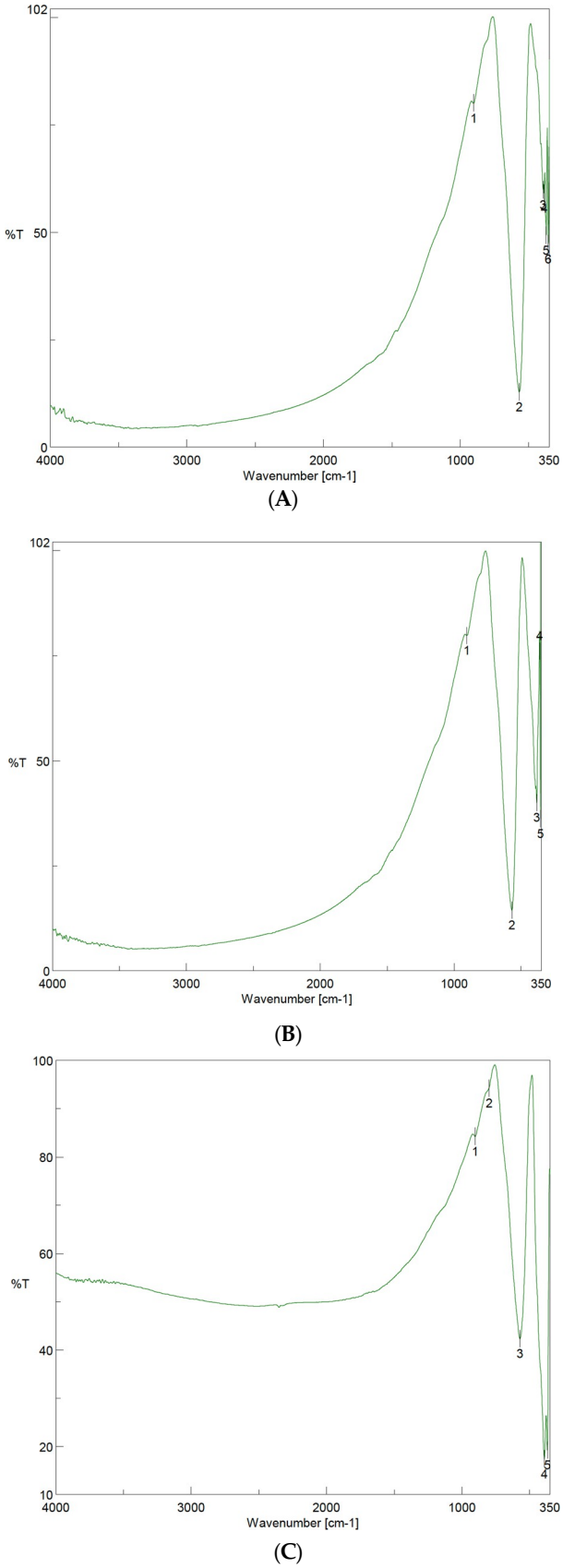



**Figure 9.** FTIR spectra of magnetite: (**A**) unused synthetic magnetite, (**B**) magnetite after one cycle of use, and (**C**) magnetite after two cycles of use.

## 4. Discussion

The observed variations in the evaluated leachates are directly related to the composition of the waste disposed of in each sanitary landfill (Table 5). First, the high conductivity in El Guayabal (18,740 µS/cm) indicates a greater concentration of dissolved salts, a characteristic of leachates generated at sites with a high presence of industrial and urban waste [34–36]. In contrast, La Madera exhibited considerably lower conductivity (1128.56 µS/cm), suggesting a lower load of ionic compounds and a predominance of biodegradable waste.

In addition, the organic load also differed between the landfills. La Madera had the greatest increase in chemical oxygen demand (COD) of 8421.4 mg/L, indicating the concentration of recalcitrant organic matter, whereas El Guayabal presented 6295.6 mg/L COD, indicating a lower concentration of undecomposed compounds. Many studies have shown that when the COD concentration is very high (generally above 5000 mg/L), the leachate contains a high quantity of refractory substances, thus limiting the feasibility of biologically based treatment [4,22,37]. Hence, the utilization of technologies such as advanced oxidation processes, adsorption, and electrocoagulation has been suggested as a potential solution to eliminate these compounds [38]. Additionally, the pH behavior of both leachates reflects the influence of microbial activity on the chemical stabilization of the leachate. El Guayabal recorded a relatively high pH (8.5), whereas La Madera presented a pH of 7.57. This phenomenon has been documented in previous studies, where methanogenic activity produces carbonates and bicarbonates that stabilize the pH in sanitary landfills during prolonged operational periods [39–41]. For leachates with these characteristics, techniques such as membrane filtration and adsorption using advanced materials have improved the contaminant removal efficiency.

The presence of heavy metals in the leachates highlights differences in the composition of the waste disposed of in each landfill. The detection of chromium in El Guayabal (0.294 mg/L) can be attributed to the disposal of industrial waste containing heavy metals, whereas the presence of mercury in La Madera (0.28 mg/L) suggests the disposal of electronic waste or batteries. Research has demonstrated that strategies such as adsorption on activated carbon and chemical precipitation can be highly effective for removing these metals [42]. In this regard, the development of emerging techniques such as bioadsorption and photocatalysis may represent promising alternatives to optimize the removal of heavy metals and other persistent contaminants in leachates from similar sanitary landfills.

Recent studies were found to determine the combination of advanced processes, besides traditional adsorption and chemical precipitation, for the effective removal of heavy metals from landfill leachates. Catalytic ozonation in the presence of functionalized adsorbents, e.g., metallic-nanoparticles-modified activated carbon, has been reported to offer improved retention of metallic cations, which reduces their mobility within the aqueous phase [11]. Similarly, investigations on the use of magnetite supported on a porous structure have shown its ability for the adsorption and oxidation of metals, including lead, chromium, and mercury, largely diminishing their toxicity in aqueous media [10]. Emerging technologies will provide new alternatives for removing heavy metals from leachates and improving the quality of the treated effluent.

The results obtained for the removal of chemical oxygen demand (COD) from the leachates of El Guayabal and La Madera reveal differences in treatment efficiency when ozone catalyzed by magnetite is used (Figure 2). The greater removal observed in El Guayabal (85%) than in La Madera (76%) underscores the influence of the leachate composition on the oxidation kinetics. The nature of the compounds present, as well as their degree of recalcitrance, can affect both the rate and extent of organic matter degradation. Previous

studies have reported that the presence of humic substances and fulvic acids in mature leachates limits ozone effectiveness and reduces overall process efficiency [3,4,43].

The process behavior suggests that catalytic ozonation is governed by a combination of direct and indirect oxidation. While molecular ozone preferentially attacks compounds containing double bonds and specific functional groups, the hydroxyl radicals generated on the surface of magnetite exhibit broader and nonselective reactivity [5]. This difference in reaction mechanism is crucial for explaining the variability in process efficiency between the two leachates. Recent studies have demonstrated that the capacity to generate hydroxyl radicals depends on the structural stability of the catalyst and its interaction with the leachate matrix [8]. Moreover, the temporal evolution of COD removal indicates that the most significant degradation occurs within the first 60 min, followed by gradual deceleration. This behavior is partly due to the decreasing concentration of available ozone and the possible adsorption of intermediates onto the catalyst surface. Competition among compounds in the medium may reduce the availability of active sites on magnetite, thereby affecting the generation of hydroxyl radicals during the later stages of treatment [15].

Another key aspect influencing process efficiency is the effect of pH. The conversion of ozone into hydroxyl radicals is relatively efficient in alkaline media because of the increased stability of these species in high-pH solutions [44]. However, extremely high pH values can promote the premature decomposition of ozone before it interacts with target compounds, thereby reducing treatment efficiency. In the present study, the leachates presented slightly alkaline pH values, which may have contributed to the improved degradation of recalcitrant compounds without adversely affecting oxidant stability [33]. Control tests confirmed that the synergy between ozone and magnetite is fundamental for achieving high contaminant removal efficiency. COD removal in tests using ozone alone was considerably lower, indicating that $Fe_3O_4$ not only facilitates the decomposition of ozone into reactive species but also stabilizes the process by maintaining the constant generation of hydroxyl radicals. In summary, these results reinforce the applicability of catalytic ozonation in the treatment of leachates with high organic loads and refractory compounds. Nevertheless, the optimization of key variables—such as ozone dosage and catalyst concentration—remains an area of interest.

In this context, various studies have demonstrated that the efficiency of catalytic ozonation can be enhanced through the incorporation of advanced catalysts and process optimization strategies. The use of magnetite modified with transition metal ions has shown an increase in the conversion of ozone into reactive oxygen species, thereby facilitating the degradation of recalcitrant compounds with reduced formation of secondary byproducts [12]. Additionally, the implementation of Fe-$N_4$-based catalysts supported on carbon structures has improved the selectivity of oxidation reactions without requiring drastic modifications to the pH of the medium [2]. These enhancements have been validated through advanced spectroscopic techniques, confirming the structural stability of the catalysts and their efficacy over multiple operational cycles.

For the first phase of optimization, statistical analysis via analysis of variance (ANOVA) (Table 6) confirmed the robustness of the predictive model, demonstrating that the evaluated variables have a significant effect on the removal of chemical oxygen demand (COD). The results indicate that the model has a coefficient of determination ($R^2$) of 0.9241 for El Guayabal and 0.9898 for La Madera, indicating that the model adequately explains the observed variability. Furthermore, the F values obtained for each factor were high, with $p$-values less than 0.05, reinforcing the statistical significance of the independent variables on the system response. This is supported by the significance values obtained in the analysis, where the model presented an F value of 21.93 for El Guayabal and 54.01 for La Madera, indicating that the evaluated variables account for a large portion of the variability in the

results. Additionally, the $R^2$ values of 0.9241 and 0.9898, respectively, demonstrate a high explanatory capacity of the model, whereas Adeq Precision values greater than 14 ensure a strong signal in the data, allowing for proper interpretation [21]. These findings are consistent with previous studies where the optimization of ozonation processes has shown similar levels of fit and precision in advanced leachate treatments [4].

pH was established as the most influential factor in COD removal, exerting a significant effect on both leachate matrices (Figure 3). The relationship between pH and hydroxyl radical generation has been extensively documented in the literature [4], and these results underscore the importance of operating under alkaline conditions to maximize oxidation efficiency. However, in El Guayabal, magnetite had a more pronounced influence, suggesting that the catalytic interaction with ozone was decisive in generating reactive oxygen species. In contrast, in La Madera, ozone plays a predominant role, implying that the organic fraction of the leachate is more susceptible to direct oxidation [15]. These results agree with the findings of [28], who reported that an alkaline pH favors the formation of highly reactive radicals, thereby increasing the degradation of recalcitrant organic contaminants. Response surface analysis demonstrated that the interactions among pH, ozone dose, and magnetite concentration play a key role in process efficiency. In El Guayabal, the impact of magnetite is more significant, likely because of the presence of a higher fraction of organic compounds resistant to direct oxidation, necessitating a catalytic process for effective degradation. In La Madera, the response surface indicates a greater influence of ozone, suggesting that the compounds present are more amenable to oxidation by ozone alone, without the need for additional catalytic assistance [25].

From a mechanistic perspective, COD removal in both leachates results from a mixed process involving direct and indirect oxidation. In El Guayabal, the presence of magnetite promoted the generation of hydroxyl radicals, which non-selectively attack recalcitrant compounds, whereas in La Madera, ozone primarily acted through direct oxidation mechanisms targeting specific chemical bonds [5]. The nature of these mechanisms has been widely explored in recent studies, which have demonstrated that combining ozone with iron-based catalysts significantly enhances process efficiency [8].

The continuous development of new catalysts facilitated the process efficiency by improving the interaction between ozone molecules and the organic materials which are included in leachates. Doping of magnetite has been shown to enhance the generation of reactive oxygen species and facilitate the degradation of recalcitrant compounds through radical and non-radical oxidation mechanisms [8]. Likewise, recent work had been focused on the combination of ozonation and electrochemical processes, leading to an effective removal of aromatic compounds and phenolic derivatives which minimizes the effect of humic substances in treatment performance [7]. The results suggest that differences in the chemical composition of the leachates directly influence treatment effectiveness, reinforcing the need to optimize operating conditions based on the type of leachate treated. Recent research has shown that leachates with higher metal contents may exhibit distinct removal kinetics due to the possible interference of cations in the generation of reactive oxygen species [28]. These differences could also explain why magnetite played a more relevant role in El Guayabal, whereas ozone demonstrated greater efficiency in La Madera.

Statistical analysis via analysis of variance (ANOVA) was conducted to evaluate the influence of independent variables on chemical oxygen demand (COD) removal in leachates from El Guayabal and La Madera (Table 7). The high statistical significance of the model in both cases (F = 1690.10 for El Guayabal and F = 937.58 for La Madera) confirms that oxygen ($O_2$) and magnetite ($Fe_3O_4$), along with their interactions and quadratic terms, have a significant effect on process efficiency. These findings align with previous studies demonstrating the relevance of operational parameters in optimizing advanced oxidation

processes through statistical design [5]. Additionally, the adjusted coefficients of determination (adjusted $R^2$ = 0.9986 for El Guayabal and 0.9974 for La Madera) and adequate precision values (Adeq Precisions of 100.462 and 72.262, respectively) indicate that the model accurately describes data variability and is suitable for predicting system behavior, which is consistent with recent studies on wastewater treatment optimization [45].

In terms of interactions, both the ozone dosage and the magnetite concentration have a substantial effect on the removal efficiency, but their effects vary depending on the leachate composition (Figure 4). In El Guayabal, magnetite has a more pronounced influence, suggesting a greater dependence on hydroxyl radical (•OH) generation for organic matter degradation. This observation is consistent with previous studies indicating that leachates with a higher content of recalcitrant compounds respond more effectively to catalytic processes [5]. Conversely, in La Madera, COD removal is more strongly controlled by ozone dosage, implying that direct oxidation is the dominant mechanism in this leachate [4]. Response surface analysis reinforced these observations. In El Guayabal, the removal efficiency is maximized at medium to high magnetite concentrations (2.5–3.5 g/L), whereas in La Madera, there is a greater dependence on ozone dosage. The pronounced curvature of the response surface in El Guayabal indicates the existence of an optimal magnetite concentration, beyond which no significant improvements in efficiency are observed. This phenomenon has been reported in studies where catalyst saturation reduces the availability of free ozone for reactions [46] and has been validated in heterogeneous advanced oxidation systems [47].

From a mechanistic perspective, the interaction between ozone and magnetite under alkaline pH conditions promotes high production of hydroxyl radicals (•OH), which are primarily responsible for the advanced degradation of persistent organic compounds [4]. Ozone adsorption on the active sites of magnetite, followed by its catalytic decomposition, facilitates the generation of highly reactive oxidizing species. The combination of these mechanisms explains the high efficiency observed in this study and has been documented in other advanced oxidation systems [8]. Additionally, recent studies have highlighted the influence of catalyst surface structure on ozone adsorption and decomposition. Active sites, such as oxygen vacancies and hydrated hydroxyl groups, increase process efficiency by facilitating the formation of atomic oxygen and hydroxyl radicals. This effect is amplified under alkaline conditions, where the increased availability of hydroxide ions ($OH^-$) enhances the generation of oxidizing species, improving the removal of recalcitrant contaminants [46]. This combination of mechanisms not only enables the mineralization of complex organic compounds but also broadens the applicability of the system to heterogeneous aqueous matrices, further establishing catalytic ozonation with magnetite as a viable and highly efficient alternative for leachate treatment [5].

The validation of the optimal parameters via the *t*-test confirmed the reliability of the predictive model, demonstrating that the selected conditions can be accurately replicated to maximize chemical oxygen demand (COD) removal (Table 8). This result aligns with previous studies in which statistical modeling of advanced oxidation processes has proven essential for predicting and optimizing wastewater treatment efficiency [8]. Moreover, the co-application of magnetite with ozone effectively removed TSS to levels very close to the detection limits, demonstrating that ozone actively causes chemical oxidation as well as coagulation and flocculation and aids in effluent clarification (Figure 5). This phenomenon has been reported in recent studies on advanced leachate treatments and the presence of metal catalysts to increase the removal efficiency for particulate matter [27].

Moreover, the increase in conductivity indicates enhanced mineralization of organic matter, which is consistent with the formation of inorganic ions such as sulfates, carbonates, and nitrates, common byproducts of oxidative degradation [4]. Likewise, the stabilization

of pH at alkaline levels after treatment agrees with findings from studies in which ozonation facilitates the formation of carbonates and bicarbonates, buffering pH fluctuations and enhancing the chemical stability of the treated medium [48].

The optimization of operational parameters has been supported by studies that have identified specific conditions to maximize the efficiency of the catalytic ozonation process. Applications of the Box–Behnken design have demonstrated high coefficients of determination ($R^2 > 0.98$) for predictive models of organic contaminant removal, confirming the direct relationship between operational variables and treatment efficiency [13]. Similarly, response surface analysis has allowed for the evaluation of the interaction among pH, ozone concentration, and catalyst dosage, establishing optimal conditions for the generation of hydroxyl radicals in the aqueous phase [12]. The characterization of intermediate products through chromatographic techniques has evidenced the transformation of refractory compounds into biodegradable species, thereby reinforcing the effectiveness of the process in removing persistent contaminants. The observed color change in the leachates (Figure 6) further confirms the degradation of chromophoric compounds, with a more pronounced reduction in trials involving ozone and magnetite, underscoring the catalytic effect in breaking down conjugated structures responsible for coloration. This effect has been widely documented in studies demonstrating that hydroxyl radical formation enhances the removal of aromatic and polyphenolic compounds [5].

Additionally, the reduction of total suspended solids (TSS) to nearly undetectable levels suggests that the combination of ozone and magnetite not only promotes chemical oxidation but also induces coagulation and flocculation, facilitating effluent clarification. This phenomenon has been described in recent research on advanced leachate treatments, where the presence of metal catalysts improved the particulate matter removal efficiency [27]. Overall, these findings reinforce the potential of catalytic ozonation with magnetite as an effective strategy for reducing the organic load and improving the quality of treated leachate, supporting its viability for integration into wastewater treatment systems with high chemical complexity.

The changes in magnetite composition following its use in the catalytic ozonation process reflect both physical and chemical modifications in the catalyst structure (Figure 7). The reduction in the $Fe_3O_4$ concentration after multiple treatment cycles suggests possible partial dissolution of the material or surface transformation induced by prolonged exposure to ozone and reactive oxygen species. Previous studies have reported that continuous exposure to oxidative conditions can lead to iron ion (Fe) leaching and the formation of secondary compounds on the catalyst surface [8]. The presence of elements such as silicon (Si) and titanium dioxide ($TiO_2$) in the samples used suggests an adsorption process involving components from the leachates, which may alter the catalyst's reactivity in subsequent applications (Figure 8). This phenomenon has been documented in prior studies, where the accumulation of contaminants on catalytic surfaces affects the distribution of active sites and the capacity to generate reactive oxygen species [48]. However, the catalyst's crystalline structure remains stable after multiple cycles, allowing for its reuse with relatively high performance in the degradation of organic compounds. This structural stability is crucial for ensuring the feasibility of the process for long-term industrial applications [45].

Given the progressive deterioration observed in magnetite composition, regeneration strategies to extend its lifespan and maintain catalytic efficiency are essential. Some studies suggest that washing with mildly acidic solutions or thermal treatments can partially restore the material's activity by removing surface impurities and regenerating active sites [49]. In this context, the recoverability of magnetite over multiple cycles will depend on the implementation of appropriate maintenance strategies to minimize catalytic activity loss and optimize performance in the treatment of complex leachates.

According to Nisticò et al. [46], magnetite ($Fe_3O_4$) may require treatment to maintain its catalytic activity over multiple use cycles. It explores strategies such as calcination in an oxidizing atmosphere and washing with mild acid solutions, as well as methods that restore the material's crystalline structure and magnetic properties. It points out that the conversion of magnetite to hematite ($\alpha$-$Fe_2O_3$), which occurs at temperatures above 600 °C, can be reversed by reduction treatments, enabling the recovery of the catalyst. This was corroborated by Bona et al. [47], who describe a method based on a two-step process that allows the complete recovery of the catalyst while maintaining its efficiency. Initially, the spent magnetite is subjected to calcination in an oxidizing atmosphere at 800 °C for 4 h, which allows the removal of residual organic compounds and the conversion of partially reduced magnetite ($Fe_3O_4$) into hematite ($\alpha$-$Fe_2O_3$). Subsequently, this calcined material is digested with 6 M HCl at 60 °C for 4 h, dissolving the Fe (III) in aqueous solution, which is neutralized with 6 M NaOH for subsequent re-synthesis of the catalyst by co-precipitation. The regenerated magnetite nanoparticles showed structural, physicochemical, and magnetic properties comparable to those of the fresh catalyst, which was reflected in their performance in the photo-Fenton degradation of paracetamol in water, reaching a removal of 96–98% after 120 min of UV irradiation, results superimposable to those obtained with magnetite without previous use. Similarly, Gautam and Tiwari [50] evaluated the regeneration and reuse of magnetite nanoparticles functionalized with humic acid ($Fe_3O_4$/HA) used as nanosorbents in the remediation of water contaminated with malachite green dye. For the regeneration of the material, different solvents were explored for the desorption of the adsorbed pollutant, finding that the treatment with 0.1 M HCl was the most effective, achieving a recovery of 95.8% of the adsorption capacity. The regeneration process consisted of immersion of the saturated material in the acid solution, followed by washing with distilled water to remove dye and acid residues before reuse. Recycling tests confirmed that the $Fe_3O_4$/HA nano sorbents could be reused for up to five cycles, maintaining a decolorization efficiency of over 85% for the first four uses. These results indicate that chemical regeneration with HCl can extend the catalyst's lifetime, reducing operational costs and contributing to the sustainability of the adsorption process for the treatment of contaminated water.

The results obtained demonstrate the key role of magnetite in optimizing ozone consumption and maximizing organic matter degradation (Table 9). The highest efficiency observed under alkaline conditions with elevated $Fe_3O_4$ concentrations aligns with previous studies that have shown that a high pH promotes the production of hydroxyl radicals, thereby increasing the rate of contaminant degradation without requiring an increased ozone dosage [32]. This effect has been widely reported in advanced wastewater treatments, where the alkalinity of the medium enhances the conversion of ozone into reactive species and improves the efficiency of oxidation processes [32].

Conversely, treatments conducted under acidic conditions and with low catalyst concentrations exhibit lower efficiency and higher ozone consumption, as also reported in previous leachate treatment studies. Under these conditions, the generation of hydroxyl radicals is more limited, resulting in a greater reliance on direct ozone oxidation, a less selective and less efficient mechanism for degrading recalcitrant compounds [45]. Comparisons with prior research indicate that optimal ozone consumption for organic matter removal falls within the range of 2.8–4.5 g $O_3$ per gram of COD removed, values that are consistent with those obtained in this study under optimal conditions [32].

The increased ozone consumption and lower removal efficiency due to the absence of a catalyst indicate the crucial role of the synergistic effect of ozonation with magnetite in enhancing the performance of the treatment process. Ozone utilization leads to a significant increase in hydroxyl radicals through the combination of ozone and iron-based catalysts,

thus increasing the degradation rate of contaminants and shortening the effective treatment time [8]. The coupling between the catalyst and ozone is essential for making the process technologically feasible at an industrial scale, as it leads to a decrease in costs linked with the consumption of reagents and increased efficiency in the elimination of organic matter.

The increase in conductivity observed during the ozonization process is an expected and technically justifiable result. This increase is due to the oxidation of organic and inorganic compounds in the leachate, leading to more oxidized species, such as soluble ions and salts. During ozonation, complex molecules can be degraded into smaller, highly ionized fragments, which increases the concentration of conductive species in the solution. Oxidizing nitrogenous and sulfurous compounds can generate nitrates, sulfates, and other anions, increasing electrical conductivity. This behavior is, therefore, consistent with the process's chemistry and confirms the contaminants' transformation during treatment. This behavior was observed by Maharaja et al. [51] in ozone treatment applied to reverse osmosis reject stream derived from tannery effluents, where an increase in the conductivity of the treated water occurred. This effect is due to the fragmentation of organic compounds and the generation of ionized byproducts, such as sulfates, chlorides, and nitrates, which increase the concentration of conductive species in solution. Electrochemical impedance spectroscopy (EIS) analysis confirmed that the decrease in charge transfer resistance after the ozonation process is correlated with an increased electrical conductivity of the system. In the Nyquist plots, a reduction in the semicircle diameter and an increase in the linearity of the curve were observed after ozone application, indicating an increased availability of ionic species in solution.

Furthermore, the combined treatment of ozonation with hydrogen peroxide ($H_2O_2$) showed an even more pronounced effect on the increase in conductivity due to increased mineralization of the compounds present. This is corroborated by Wang et al. [52], who evaluated the treatment of saline wastewater from a reverse osmosis (RO) concentrate of a coal-fired chemical plant in Hebei, China. Two technologies were compared: electron beam (EB) radiation and ozonation for organic pollutant degradation and organic load reduction. The results indicated that ozone treatment impacted the conductivity of the treated water, increasing its value compared to the original wastewater. This increase is attributed to the oxidation of organic compounds into more oxidized products, such as ions and inorganic salts, which contribute to the conductivity. A comparable result was obtained by Santos et al. [53] for ozone treatment applied to dairy effluent, which showed variations in electrical conductivity depending on the presence of an activated carbon filter. During the experiments without the filter, a decrease in electrical conductivity was observed at 60 min of ozonation, remaining stable until 120 min. However, in the tests with the charcoal filter, the electrical conductivity remained constant for the first 60 min, increasing at the 90 min interval and decreasing again at 120 min. This suggests that depending on its configuration and the filter material used, ozonation can induce changes in electrical conductivity, probably associated with the release or retention of salts and ions in the treated medium.

## 5. Conclusions

The catalytic ozonation process with magnetite ($Fe_3O_4$) demonstrated high efficiency in degrading organic matter, achieving chemical oxygen demand (COD) removal rates of 85.3% in El Guayabal and 75.8% in La Madera. These differences in efficiency reflect the influence of the leachates' chemical composition, where the presence of recalcitrant compounds affects the oxidation kinetics. In both cases, the highest removal rate was observed during the first 60 min of treatment, which was attributable to the generation of hydroxyl radicals promoted by the interaction between ozone and magnetite. However,

in later stages, degradation slowed, suggesting a reduced availability of easily oxidizable compounds and possible saturation of the catalyst's active sites.

Optimal condition analysis revealed that the combination of 6 g $O_3$/h, 2.5 g/L $Fe_3O_4$, and pH 9 maximized the process efficiency, with pH being the most influential variable. The alkalinity of the medium favored the production of hydroxyl radicals, thereby enhancing the removal of recalcitrant organic compounds. In contrast, tests conducted without magnetite revealed an increase in ozone consumption without a significant improvement in COD removal, confirming the catalyst's critical role in optimizing the treatment. Furthermore, the process response varied according to the specific composition of the leachate, indicating that while the catalytic effect of magnetite was decisive in El Guayabal, the predominant mechanism in La Madera was direct oxidation by ozone.

Regarding catalyst recoverability, structural and morphological analyses revealed progressive modifications on the magnetite surface after each cycle of use. A decrease in the $Fe_3O_4$ concentration and the adsorption of contaminants were observed, suggesting a partial loss of active sites and a potential deterioration in catalytic performance. Nevertheless, the material's structural stability allowed for its reuse over multiple cycles, albeit with a gradual decline in COD removal efficiency. The loss of material and surface changes could affect long-term performance, underscoring the need to implement regeneration strategies to prolong its service life.

Finally, the evaluation of ozone consumption confirmed that the optimal conditions minimized oxidant use, reaching a consumption of 2.7 g $O_3$ per gram of COD removed. In contrast, less favorable conditions, such as low magnetite concentrations or the absence of a catalyst, resulted in higher ozone demand and lower removal efficiency. These results highlight the synergy between ozone and magnetite as a key factor in optimizing the process and reducing operating costs. Based on these findings, it is recommended to explore catalyst regeneration strategies and assess their performance in continuous systems at pilot and industrial scales to ensure their viability and sustainability in managing leachates from sanitary landfills.

**Author Contributions:** Conceptualization, F.M.-M., A.F.B.-S. and D.B.-M.; methodology, L.F.R.-R. and J.B.G.-M.; software, A.F.B.-S. and D.B.-M.; validation, D.B.-M., L.F.R.-R. and J.B.G.-M.; formal analysis, F.M.-M. and A.F.B.-S.; investigation, D.B.-M. and L.F.R.-R.; resources, F.M.-M., A.F.B.-S. and J.B.G.-M.; data curation, F.M.-M., A.F.B.-S. and D.B.-M.; writing—original draft preparation, D.B.-M.; writing—review and editing, A.F.B.-S. and J.B.G.-M.; visualization, A.F.B.-S.; supervision, F.M.-M.; project administration, D.B.-M.; funding acquisition, F.M.-M. and A.F.B.-S. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by Universidad Francisco de Paula Santander (Colombia) (FINU 011-2023), the Ministry of Science and Technology of Colombia, and the Colombian Institute of Educational Credit and Technical Studies Abroad (MINCIENCIAS-ICETEX) under the project titled "FOTOLIX" with ID 2023-0686.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data are contained within the article.

**Acknowledgments:** We would like to express our sincere gratitude to Universidad del Valle, Universidad del Llano, and Universidad Francisco de Paula Santander (Colombia) for providing the equipment for this research. We also thank the Colombian Ministry of Science, Technology, and Innovation MINCIENCIAS for supporting national Ph.D. Doctorates through the Francisco José de Caldas scholarship program.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References


1. Ren, T.; Zhang, X.; Chen, S.; Huang, X.; Zhang, X. Hydrogen Peroxide and Peroxymonosulfate Intensifying Fe−doped C−$Al_2O_3$−framework−based Catalytic Ozonation for Advanced Treatment of Landfill Leachate: Performance and Mechanisms. *Sci. Total Environ.* **2022**, *843*, 156904. [CrossRef]
2. Ren, T.; Yin, M.; Chen, S.; Ouyang, C.; Huang, X.; Zhang, X. Single-Atom Fe-$N_4$ Sites for Catalytic Ozonation to Selectively Induce a Nonradical Pathway toward Wastewater Purification. *Environ. Sci. Technol.* **2023**, *57*, 3623–3633. [CrossRef] [PubMed]
3. Wang, H.; Zhang, S.; He, X.; Yang, Y.; Yang, X.; Van Hulle, S.W.H. Comparison of Macro and Micro-Pollutants Abatement from Biotreated Landfill Leachate by Single Ozonation, $O_3$/$H_2O_2$, and Catalytic Ozonation Processes. *Chem. Eng. J.* **2023**, *452*, 139503. [CrossRef]
4. Zhang, R.; Liu, J.; Gao, B.; Sillanpää, M. The Effect of Autochthonous Metal Ions and Humic Substances on Landfill Leachate Ozonation: Reactive Oxygen Species and 3D Fluorescence Analysis. *Sep. Purif. Technol.* **2025**, *354*, 129433. [CrossRef]
5. Moussavi, G.; Khosravi, R.; Omran, N.R. Development of an Efficient Catalyst from Magnetite Ore: Characterization and Catalytic Potential in the Ozonation of Water Toxic Contaminants. *Appl. Catal. A Gen.* **2012**, *445*, 42–49. [CrossRef]
6. Dong, S.; Ding, Y.; Feng, H.; Xu, J.; Han, J.; Jiang, W.; Xia, Y.; Wang, A. Source Preventing Mechanism of Florfenicol Resistance Risk in Water by VUV/UV/Sulfite Advanced Reduction Pretreatment. *Water Res.* **2023**, *235*, 119876. [CrossRef]
7. Li, S.; Lü, F.; Zhang, H.; Shao, L.; He, P. Electron Exchange Capacities of Colloidal Biochar: Affected by Spatial Structure Distribution Instead of Particle Size. *Chem. Eng. J.* **2023**, *455*, 140567. [CrossRef]
8. Ghahrchi, M.; Rezaee, A. Electrocatalytic Ozonation Process Supplemented by EDTA-Fe Complex for Improving the Mature Landfill Leachate Treatment. *Chemosphere* **2021**, *263*, 127858. [CrossRef]
9. Ma, C.; Ma, P.; He, Z.; Mi, X. A Combined Catalytic Ozonation-MBR Approach to Remove Contaminants from the Mature Landfill Leachate in the Yellow River Basin. *Toxics* **2022**, *10*, 505. [CrossRef]
10. Segundo, I.D.B.; Gomes, A.I.; Souza-Chaves, B.M.; Park, M.; dos Santos, A.B.; Boaventura, R.A.R.; Moreira, F.C.; Silva, T.F.C.V.; Vilar, V.J.P. Incorporation of Ozone-Driven Processes in a Treatment Line for a Leachate from a Hazardous Industrial Waste Landfill: Impact on the Bio-Refractory Character and Dissolved Organic Matter Distribution. *J. Environ. Chem. Eng.* **2021**, *9*, 105554. [CrossRef]
11. Braga, W.L.M.; de Melo, D.H.A.; de Morais, D.; Samanamud, G.R.L.; França, A.B.; Finzi Quintão, C.M.; Loures, C.C.A.; de Urzedo, A.P.F.M.; Naves, L.L.R.; de Freitas Gomes, J.H.; et al. Optimization of the Treatment of Sanitary Landfill by the Ozonization Catalysed by Modified Nanovermiculite in a Rotating Packed Bed. *J. Clean. Prod.* **2020**, *249*, 119395. [CrossRef]
12. Jin, X.; Wu, C.; Tian, X.; Wang, P.; Zhou, Y.; Zuo, J. A Magnetic-Void-Porous $MnFe_2O_4$/Carbon Microspheres Nano-Catalyst for Catalytic Ozonation: Preparation, Performance and Mechanism. *Environ. Sci. Ecotechnology* **2021**, *7*, 100110. [CrossRef] [PubMed]
13. Ghahrchi, M.; Rezaee, A. Electro-Catalytic Ozonation for Improving the Biodegradability of Mature Landfill Leachate. *J. Environ. Manag.* **2020**, *254*, 109811. [CrossRef] [PubMed]
14. de Brito, R.A.; Filho, H.J.I.; Aguiar, L.G.; de Alcântara, M.A.K.; Siqueira, A.F.; da Rós, P.C.M. Degradation Kinetics of Landfill Leachate by Continuous-Flow Catalytic Ozonation. *Ind. Eng. Chem. Res.* **2019**, *58*, 9855–9863. [CrossRef]
15. Tang, X.; Zhu, S.; Quan, X.; Huang, X.; Qiu, F.; Feng, C. Degradation Treatment of Concentrated Landfill Leachate by Catalytic Ozonation in a Microbubble Reactor. *Ozone Sci. Eng.* **2021**, *43*, 476–489. [CrossRef]
16. Yang, X.; Meng, L.; Meng, F. Combination of Self-Organizing Map and Parallel Factor Analysis to Characterize the Evolution of Fluorescent Dissolved Organic Matter in a Full-Scale Landfill Leachate Treatment Plant. *Sci. Total Environ.* **2019**, *654*, 1187–1195. [CrossRef]
17. Teng, C.; Zhou, K.; Peng, C.; Chen, W. Characterization and Treatment of Landfill Leachate: A Review. *Water Res.* **2021**, *203*, 117525. [CrossRef]
18. Caroline Baettker, E.; Kozak, C.; Knapik, H.G.; Aisse, M.M. Applicability of Conventional and Non-Conventional Parameters for Municipal Landfill Leachate Characterization. *Chemosphere* **2020**, *251*, 126414. [CrossRef]
19. American Public Health Association; American Water Works Association. *Water Environment Federation Standard Methods for the Examination of Water and Wastewater*, 24th ed.; Lipps, W.C., Braun-Howland, E.B., Baxter, T.E., Eds.; APHA Press: Washington, DC, USA, 2023.
20. Liu, M.; Ye, Y.; Ye, J.; Gao, T.; Wang, D.; Chen, G.; Song, Z. Recent Advances of Magnetite ($Fe_3O_4$)-Based Magnetic Materials in Catalytic Applications. *Magnetochemistry* **2023**, *9*, 110. [CrossRef]
21. Feng, H.; Mao, W.; Li, Y.; Wang, X.; Chen, S. Characterization of Dissolved Organic Matter during the $O_3$-Based Advanced Oxidation of Mature Landfill Leachate with and without Biological Pre-Treatment and Operating Cost Analysis. *Chemosphere* **2021**, *271*, 129810. [CrossRef]
22. Gu, Z.; Yang, Z.; Song, B.; Li, Q. Treatment of Landfill Leachate MBR Effluent by Ozone Combined with a Semi-Aerobic Aged Refuse Bioreactor. *J. Water Process Eng.* **2025**, *69*, 106625. [CrossRef]
23. Ricky, R.; Shanthakumar, S.; Gothandam, K.M. A Pilot-Scale Study of the Integrated Phycoremediation-Photolytic Ozonation Based Municipal Solid Waste Leachate Treatment Process. *J. Environ. Manag.* **2022**, *323*, 116237. [CrossRef] [PubMed]

24. Duan, Y.; Gao, B.; Liu, J.; Wang, X.; Sillanpää, M. Treatment of Landfill Leachate in the MBR and Catalytic Ozonation Coupled System Based on Mn Ni Catalyst: Efficiency and Bio/Chemical Mechanism. *J. Water Process Eng.* **2024**, *66*, 106033. [CrossRef]
25. Yang, Y.-Z.; Zhang, Y.; Zhan, Y.; Liu, J.-Q.; Yan, C.-C.; Zhang, Y.; Zhang, H.-L. Synergistic Enhancement of UASB Reactor for Leachate Treatment Using Fe2O3 Nanomodified Pumice and Ozone Oxidation. *Chem. Eng. J.* **2024**, *497*, 154891. [CrossRef]
26. Ma, C.; Yuan, P.; Jia, S.; Liu, Y.; Zhang, X.; Hou, S.; Zhang, H.; He, Z. Catalytic Micro-Ozonation by $Fe_3O_4$ Nanoparticles @ Cow-Dung Ash for Advanced Treatment of Biologically Pre-Treated Leachate. *Waste Manag.* **2019**, *83*, 23–32. [CrossRef]
27. Ma, C.; Jia, S.; Yuan, P.; He, Z. Catalytic Ozonation of 2, 2′-Methylenebis (4-Methyl-6-Tert-Butylphenol) over Nano-$Fe_3O_4$@cow Dung Ash Composites: Optimization, Toxicity, and Degradation Mechanisms. *Environ. Pollut.* **2020**, *265*, 114597. [CrossRef]
28. Bai, F.; Liu, S.; Zhang, Y.; Ma, J. Effective and Mechanistic Insights into Reverse Osmosis Concentrate of Landfill Leachate Treatment Using Coagulation-Catalytic Ozonation-Bioaugmentation-Based AnMBR. *Chem. Eng. J.* **2023**, *463*, 142430. [CrossRef]
29. Mu, S.; Chen, X.; Song, B.; Wu, C.; Li, Q. Enhanced Performance and Mechanism of the Combined Process of Ozonation and a Semiaerobic Aged Refuse Biofilter for Mature Landfill Leachate Treatment. *Chemosphere* **2022**, *308*, 136432. [CrossRef]
30. Yuan, Y.; Liu, J.; Gao, B.; Sillanpää, M. Landfill Leachate Treatment In-Depth by Bio-Chemical Strategy: Microbial Activation and Catalytic Ozonation Mechanism. *Chem. Eng. J.* **2022**, *444*, 136464. [CrossRef]
31. Zhu, Y.; Luo, H.; Wang, T.; Zhou, J.; Zhu, Y.; Hou, J. Advanced Treatment of Landfill Leachate by Catalytic Ozonation with MnCeOx/γ-$Al_2O_3$ Catalyst. *Surf. Interfaces* **2024**, *46*, 104113. [CrossRef]
32. Pophali, G.R.; Hedau, S.; Gedam, N.; Rao, N.N.; Nandy, T. Treatment of Refractory Organics from Membrane Rejects Using Ozonation. *J. Hazard Mater.* **2011**, *189*, 273–277. [CrossRef] [PubMed]
33. Yang, Y.; Demeestere, K.; Van Hulle, S. Ozone-Based Advanced Oxidation of Biologically Treated Landfill Leachate: Oxidation Efficiency, Mechanisms, and Surrogate-Based Monitoring for Bulk Organics. *J. Environ. Chem. Eng.* **2021**, *9*, 106459. [CrossRef]
34. Scott, M.; Millar, G.J.; Altaee, A. Process Design of a Treatment System to Reduce Conductivity and Ammoniacal Nitrogen Content of Landfill Leachate. *J. Water Process Eng.* **2019**, *31*, 100806. [CrossRef]
35. Sabba, F.; Kassar, C.; Zeng, T.; Mallick, S.P.; Downing, L.; McNamara, P. PFAS in Landfill Leachate: Practical Considerations for Treatment and Characterization. *J. Hazard Mater.* **2025**, *481*, 136685. [CrossRef]
36. Jolaosho, T.L. Characterization of Potentially Toxic Elements in Leachates from Active and Closed Landfills in Nigeria and Their Effects on Groundwater Systems Using Spatial, Indexical, Chemometric and Health Risk Techniques. *Chemosphere* **2024**, *369*, 143678. [CrossRef] [PubMed]
37. Clemente, E.; Domingues, E.; Quinta-Ferreira, R.M.; Leitão, A.; Martins, R.C. European and African Landfilling Practices: An Overview on MSW Management, Leachate Characterization and Treatment Technologies. *J. Water Process Eng.* **2024**, *66*, 105931. [CrossRef]
38. Parida, B.; Dash, A.K.; Verma, A.K. Technologies for Treatment of Landfill Leachate: A Brief Review. *Recent Innov. Chem. Eng. (Former. Recent Pat. Chem. Eng.)* **2023**, *16*, 260–284. [CrossRef]
39. Torres-Herrera, S.; Palomares-Cortés, J.; González-Cortés, J.J.; Cubides-Páez, D.F.; Gamisans, X.; Cantero, D.; Ramírez, M. Start-up and Long-Term Operation of the Nitrification Process Using Landfill Leachates in a Pilot Sequencing Batch Bioreactor. *J. Water Process Eng.* **2025**, *70*, 106895. [CrossRef]
40. Liu, C.; Li, D.; Li, J.; Zhao, C.; Liu, X.; Huang, X.; Yin, F.; Shi, W.; Yu, J.; Wu, J.; et al. Treatment of Landfill Leachate by Two-Stage Electrochemical Combination Technology. *J. Environ. Chem. Eng.* **2025**, *13*, 115355. [CrossRef]
41. Das, R.; Raj, D. Sources, Distribution, and Impacts of Emerging Contaminants—A Critical Review on Contamination of Landfill Leachate. *J. Hazard. Mater. Adv.* **2025**, *17*, 100602. [CrossRef]
42. Bilardi, S.; Calabrò, P.S.; Greco, R.; Moraci, N. Selective Removal of Heavy Metals from Landfill Leachate by Reactive Granular Filters. *Sci. Total Environ.* **2018**, *644*, 335–341. [CrossRef] [PubMed]
43. Song, B.; Wang, Q.; Ali, J.; Wang, Z.; Wang, L.; Wang, J.; Li, J.; Glebov, E.M.; Zhuang, X. Biochar-Supported $Fe_3C$ Nanoparticles with Enhanced Interfacial Contact as High-Performance Binder-Free Anode Material for Microbial Fuel Cells. *Chem. Eng. J.* **2023**, *474*, 145678. [CrossRef]
44. Zhe, J.; He, H.; Yi, Z.; Guo, Z.; Xu, H.; Huang, B.; Pan, X. Mechanism and Molecular Level Insight of Refractory Dissolved Organic Matter in Landfill Leachate Treated by Electroflocculation Coupled with Ozone. *Sep. Purif. Technol.* **2025**, *356*, 129812. [CrossRef]
45. Wang, F.; Liu, Y.; Yin, J.; Xiang, Y.; Yuan, Y.; Zhang, J.; He, C.; Zhang, H.; Xiong, Z.; Lai, B. Critical Role of Oxygen Vacancies in Catalytic Ozonation: Non-Radical Pathways and Enhanced Hydroxyl Groups. *Chem. Eng. J.* **2024**, *500*, 156952. [CrossRef]
46. Nisticò, R. A Synthetic Guide toward the Tailored Production of Magnetic Iron Oxide Nanoparticles. *Boletín Soc. Española Cerámica Y Vidr.* **2021**, *60*, 29–40. [CrossRef]
47. Bona, G.; Viganò, L.; Cantoni, M.; Mantovan, R.; Di Credico, B.; Mostoni, S.; Scotti, R.; Nisticò, R. An Experimental Demonstration on the Recyclability of Hybrid Magnetite-Humic Acid Nanoparticles. *Sustain. Mater. Technol.* **2025**, *43*, e01275. [CrossRef]
48. Zhou, L.; Liu, Y.; Shi, H.; Qing, Y.; Chen, C.; Shen, L.; Zhou, M.; Li, B.; Lin, H. Molecular Oxygen Activation: Innovative Techniques for Environmental Remediation. *Water Res.* **2024**, *250*, 121075. [CrossRef]

49. Bi, Z.; Wang, W.; Zhao, L.; Wang, X.; Xing, D.; Zhou, Y.; Lee, D.-J.; Ren, N.; Chen, C. The Generation and Transformation Mechanisms of Reactive Oxygen Species in the Environment and Their Implications for Pollution Control Processes: A Review. *Environ. Res.* **2024**, *260*, 119592. [CrossRef]
50. Gautam, R.K.; Tiwari, I. Humic Acid Functionalized Magnetic Nanomaterials for Remediation of Dye Wastewater under Ultrasonication: Application in Real Water Samples, Recycling and Reuse of Nanosorbents. *Chemosphere* **2020**, *245*, 125553. [CrossRef]
51. Maharaja, P.; Athithyan, I.; Karthiyayini, C.; Kameswari, K.S.B. Evaluation of Ozonation and Electro Oxidation Treatment for the Removal of Organics and Salt Recovery from RO Reject from Leather Industries: Sustainable Approach for the Management of Contaminated Salt in CETPs. *Appl. Catal. O Open* **2025**, *200*, 207028. [CrossRef]
52. Wang, S.; Hu, J.; Wang, J. Comparative Study of Saline Industrial Wastewater Treatment by Electron Beam Radiation and Ozonation Oxidation. *Chem. Eng. J.* **2025**, *505*, 159438. [CrossRef]
53. dos Santos, M.S.; de Mello Mattos, C.; de Mendonça, H.V. Dairy Effluent Treatment with Ozone Reactor, Zeolite and Porous Membrane in Sequential Filtration. *J. Water Process Eng.* **2025**, *71*, 107184. [CrossRef]

# Chapter 2: Response surface and ridge regularization in catalytic ozonation of leachate

Universidad Francisco de Paula Santander
Vigilada Mineducación

DORANCE BECERRA MORENO <dorancebm@ufps.edu.co>

# [RUI] Acuse de recibo de envío 16122

1 mensaje

**Alberto David Pertuz Comas** <uis.revistas1@gmail.com> 15 de febrero de 2025, 9:00
Para: Dorance Becerra Moreno <dorancebm@ufps.edu.co>

Dorance Becerra Moreno:

Gracias por enviar el manuscrito "Superficie de respuesta y regularización ridge en Ozonización Catalítica de lixiviados" a Revista UIS Ingenierías. Con nuestro sistema de gestión de revistas en línea, podrá iniciar sesión en el sitio web de la revista y hacer un seguimiento de su progreso a través del proceso editorial.

URL del manuscrito: https://revistas.uis.edu.co/index.php/revistauisingenierias/authorDashboard/submission/16122
Nombre de usuario/a: dbecerramoreno

En caso de dudas, contacte conmigo. Gracias por elegir esta revista para publicar su trabajo.

Alberto David Pertuz Comas

**Revista UIS Ingenierías**
**Email**:revistaingenierias@saber.uis.edu.co

**Superficie de respuesta y regularización ridge en Ozonización Catalítica de lixiviados**

**Response surface and ridge regularization in catalytic ozonation of leachate**

**Dorance Becerra-Moreno**[a,b*], Fiderman Machuca-Martínez[b], Joseph Soto-Verjel[c], Ángelo Soto-Vergel[d], Luisa Ramírez-Ríos[e]

[a] Escuela de Ingeniería Sanitaria y Ambiental, GAOX, CENM, Universidad del Valle, Cali, Colombia; email: dorancebm@ufps.edu.co; ORCID: https://orcid.org/0000-0001-8556-9914

[b] Departamento de Ciencias Ambientales, Universidad Francisco de Paula Santander, Cúcuta, Colombia; email: dorancebm@ufps.edu.co; ORCID: https://orcid.org/0000-0001-8556-9914

[c] Escuela de Ingeniería Sanitaria y Ambiental, GAOX, CENM, Universidad del Valle, Cali, Colombia; email: fiderman.machuca@correounivalle.edu.co; ORCID: https://orcid.org/0000-0002-4553-3957

[d] Departamento de Ciencias Ambientales, Grupo de Investigación en Procesos Ambientales GIPROAM, Universidad Francisco de Paula Santander, Cúcuta, Colombia; email: josephwbeimarsv@ufps.edu.co; ORCID: https://orcid.org/0000-0003-3162-9330

[e] Industrial and Systems Engineering Department, University at Buffalo, New York, USA; email: angeloso@buffalo.edu; ORCID: https://orcid.org/0000-0001-5093-0183

[f] Universidad de los Llanos, Facultad de Ciencias Básicas e Ingenierías. Villavicencio - Meta, Colombia; email: lfernandaramirez@unillanos.edu.co; ORCID: https://orcid.org/0000-0002-0973-3847

**Resumen**

El tratamiento de lixiviados de rellenos sanitarios es un desafío ambiental debido a su alta carga orgánica y compuestos recalcitrantes. Este estudio evaluó la eficiencia de la ozonización catalítica (OC) con magnetita ($Fe_3O_4$) para la remoción de Demanda Química de Oxígeno (DQO), utilizando un modelo de Superficie de Respuesta (RSM) con regularización Ridge. Se realizaron experimentos factoriales para analizar la influencia de la dosis de ozono, la concentración de catalizador, el pH y el tiempo de tratamiento en dos tipos de lixiviado.

Los resultados indicaron que la máxima remoción de DQO se logró con pH 9, alta dosis de catalizador (2.5 $g.L^{-1}$) y tiempo prolongado (120 min), en la dosis máxima de ozono (6 $g.h^{-1}$). Se identificó una relación no lineal entre la dosis de ozono y la eficiencia del proceso, con un punto de saturación donde incrementos adicionales no mejoraban la remoción. El análisis de Permutación de Importancia de Variables confirmó que el efecto cuadrático del ozono y el tiempo de contacto fueron los factores más influyentes. Además, el modelo predictivo mostró estabilidad ante variaciones experimentales del ±5%, validando su aplicabilidad en escenarios reales

**Palabras clave**: demanda química de oxígeno, lixiviados de relleno sanitario, modelado y optimización, ozonización catalítica, validación cruzada Leave-One-Out (LOO-CV).

**Abstract**

The treatment of landfill leachates is an environmental challenge due to their high organic load and recalcitrant compounds. This study evaluated the efficiency of catalytic ozonation (OC) with magnetite ($Fe_3O_4$) for Chemical Oxygen Demand (COD) removal using a Response Surface Methodology (RSM) model with Ridge regularization. Factorial experiments were conducted to analyze the influence of ozone dosage, catalyst concentration, pH, and treatment time on two types of leachate.

The results indicated that the highest COD removal was achieved at pH 9, high catalyst dosage (2.5 $g.L^{-1}$), and prolonged contact time (120 min), without requiring the maximum ozone dose (6 $g.h^{-1}$), optimizing energy consumption. A nonlinear relationship was identified between ozone dosage and process efficiency, with a saturation point where further increases did not improve removal. The Permutation Importance Variable analysis confirmed that the quadratic effect of ozone and contact time were the most influential factors. Additionally, the predictive model demonstrated stability against ±5% experimental variations, validating its applicability in real-world scenarios.

**Keywords**: catalytic ozonation, chemical oxygen demand, Leave-One-Out cross-validation (LOO-CV), landfill leachate, modeling and optimization.

## 1. Introducción

Los lixiviados de rellenos sanitarios son uno de los residuos líquidos más complejos que se generan por la actividad humana [1]. Estos efluentes contienen una amplia gama de compuestos orgánicos e inorgánicos, incluyendo sustancias recalcitrantes que dificultan su tratamiento [2]. Entre los parámetros más relevantes para evaluar la calidad de un lixiviado se encuentra la Demanda Química de

Oxígeno (***DQO***) [3], un indicador de la carga orgánica presente y donde su reducción eficiente es esencial para minimizar el impacto ambiental y cumplir con las normativas vigentes.

En los últimos años, el uso de Procesos de Oxidación Avanzada (***POA***), como la Ozonización Catalítica (***OC***), han surgido como tecnologías emergentes muy eficientes para degradar compuestos orgánicos persistentes [4]. En particular, la OC con magnetita ($Fe_3O_4$) ha demostrado ser una alternativa prometedora, ya que combina la oxidación directa del ozono con la generación de radicales hidroxilos altamente reactivos [5]. Sin embargo, la eficiencia de este proceso depende de diversas variables, como la dosis de ozono, la concentración del catalizador, el pH del medio y el tiempo de tratamiento [6], de allí la importancia de optimizar estas variables con el propósito de maximizar la remoción de DQO y que la aplicación del tratamiento sea viable en la descontaminación de lixiviados de relleno sanitario.

Los modelos de Superficie de Respuesta (***RSM***) han sido ampliamente utilizados para estudiar y optimizar procesos químicos y ambientales [7]. Estos modelos permiten analizar las interacciones entre variables independientes y predecir el comportamiento de sistemas complejos. Sin embargo, los enfoques convencionales de la RSM suelen basarse en suposiciones lineales o cuadráticas simples, que pueden limitar su capacidad para establecer relaciones no lineales y comportamientos más complejos en los datos [8]. Además de la presencia de sesgos en la distribución de los datos o la multicolinealidad entre variables, lo que puede afectar la exactitud y confianza de los modelos [9].
De acuerdo con lo anterior, el presente estudio propone un enfoque innovador que combina transformaciones estadísticas avanzadas, expansión del espacio de características y técnicas de regularización; esto con el fin de mejorar la capacidad predictiva de un modelo de RSM, como se ha propuesto en diversas investigaciones por otros métodos y técnicas [10], [11], [12]. En primer lugar, se aplican transformaciones logarítmicas y Box-Cox para normalizar la distribución de los datos y reducir sesgos [13]. Posteriormente, se expande el espacio de características mediante la generación de términos cuadráticos e interacciones, lo que permite capturar relaciones no lineales entre las variables independientes y la eficiencia de remoción de DQO . Finalmente, se incorpora la regularización Ridge con validación cruzada Leave-One-Out (***LOO-CV***) para evitar el sobreajuste y mejorar la generalización del modelo [14].
La integración de técnicas estadísticas avanzadas y métodos de regularización en el marco de un modelo de RSM, es la novedad de este enfoque, permitiendo obtener predicciones más precisas y robustas. Este estudio proporciona información valiosa sobre el efecto de variables clave en la eficiencia de remoción de DQO, así como condiciones óptimas para el proceso de ozonización catalizada con magnetita. Los resultados obtenidos contribuyen al avance del conocimiento en el tratamiento de lixiviados, y ofrecen una metodología para el modelado y optimización de procesos ambientales.

## 2. Metodología

### 2.1. Caracterización fisicoquímica de los lixiviados.

Los lixiviados analizados en este estudio provienen de dos rellenos sanitarios en Colombia con condiciones operativas y características de generación diferenciadas, ya que la composición de los residuos gestionados influye su variabilidad fisicoquímica, lo que afecta su tratabilidad y la eficiencia del proceso de tratamiento con la OC. Las determinaciones analíticas incluyeron Demanda Química de Oxígeno, Demanda Bioquímica de Oxígeno ($DBO_5$), Sólidos Suspendidos Totales (SST), pH, conductividad y temperatura; todas teniendo en cuenta los Métodos Estándar para el Análisis de Agua y Aguas Residuales (APHA, AWWA, WEF) 24th edición (2024) [15].

### 2.2. Proceso experimental Ozonización Catalítica (OC).

El ozono fue generado *in situ* a partir de una fuente de oxígeno utilizando un generador de ozono Pacific Ozone de Lenntech, con una capacidad máxima de producción de 6 g/h. La concentración de ozono gaseoso se reguló mediante un sistema de control de voltaje integrado en el equipo, permitiendo un ajuste preciso de la dosificación. El ozono residual que no reaccionó durante el proceso fue dirigido a una solución de yoduro de potasio, donde cuantitativamente es absorbido mediante su reducción a yodo molecular [16].

La OC se llevó a cabo en un reactor de vidrio de 500 mL, equipado con una entrada de gas en la parte inferior, conectado a un tubo concéntrico de difusión, y una salida lateral para la evacuación del gas residual. La disolución del ozono en la fase líquida se optimizó mediante un sistema de aireación con microburbujas de 0.45 μm, asegurando una transferencia de masa eficiente. Como catalizador se empleó óxido de hierro negro sintético, CAS No. 1317-61-9, de Alpha Chemicals, con una pureza de $Fe_3O_4$ superior al 98%.

El diseño experimental evaluó las variables de dosis de ozono (2 – 6 $gh^{-1}$), dosis de catalizador (0.5 – 2.5 $gL^{-1}$) y nivel de pH (3 – 9 unidades), teniendo como variable de respuesta el porcentaje de remoción de

DQO. Las muestras se tomaron en los tiempos de 20, 40, 80 y 120 minutos, con el fin de estudiar la evolución del porcentaje de remoción. El desarrollo de las combinaciones de las variables independientes, y la aleatorización de las corridas experimentales, se formuló teniendo en cuenta un diseño factorial completamente aleatorizado de 3 niveles $3^3$.

### 2.3. Análisis estadístico y validación

Se desarrolló un modelo basado en Superficie de Respuesta (RSM) con regularización Ridge para predecir la eficiencia de remoción de DQO (% Remoción DQO) en función de variables operativas clave en un sistema de tratamiento de aguas residuales. La novedad de nuestro enfoque radica en:

- Aplicación de transformaciones estadísticas avanzadas (logaritmo y Box-Cox) para mejorar la distribución de los datos y reducir sesgos.
- Expansión del espacio de características mediante la generación de términos cuadráticos e interacciones para capturar relaciones no lineales.
- Uso de regularization Ridge con validation Leave-One-Out Cross-Validation (LOO-CV) para mejorar la robustez del modelo y evitar sobreajuste.
- El modelo se desarrolló en lenguaje de programación de Python, utilizando la librería scikit-learn (sklearn). Sklearn es un proyecto de licencia libre con herramientas para ciencia de datos incluyendo machine learning y modelacion estadística.

#### 2.3.1. Definición del problema

Sea $\mathbf{X} \in R^{nxp}$ la matriz de variables predictoras con $n$ observaciones y $p$ características, y sea $\boldsymbol{y} \in R^n$ el vector de respuestas (% remoción DQO). El modelo de regresión lineal estándar se expresa como la Ec. (1).

$$\mathbf{y} = \mathbf{X}\beta + \epsilon \qquad (1)$$

donde $\beta$ es el vector de coeficientes del modelo y $\epsilon$ es el error aleatorio.

#### 2.3.2. Transformaciones de Datos

Dado que algunas variables presentan distribuciones sesgadas, se aplicó:

- Transformación Logarítmica para estabilizar la varianza en las variables de entrada: $\mathbf{X}' = \log(1 + \mathbf{X})$ [17].
- Transformación Box-Cox en la variable objetivo para mejorar su normalidad: $y' = \frac{y^{\lambda}-1}{\lambda}$, con $\lambda$ óptimo determinado por máxima verosimilitud [18].

#### 2.3.3. Expansión del espacio de características

Para capturar relaciones no lineales, se generaron términos cuadráticos e interacciones entre variables, formando un modelo de Superficie de Respuesta (RSM), como se muestra en la Ec. (2).

$$\hat{y} = \beta_0 + \sum_{i=1}^{p} \beta_i X_i + \sum_{i=1}^{p}\sum_{j=1}^{p} \beta_{ij} X_i X_j + \epsilon \qquad (2)$$

donde $\beta_{ij}$ representa los coeficientes de los efectos cuadráticos y de interacción.

#### 2.3.4. Regularización con Ridge Regression

Para evitar problemas de sobreajuste, se aplicó regresión Ridge, que introduce un término de penalización $\alpha \parallel \beta \parallel^2$, controlando la magnitud de los coeficientes, de acuerdo con la Ec. (3) [19].

$$\min_{\beta} (\parallel y - X\beta \parallel^2 + \alpha \parallel \beta \parallel^2) \qquad (3)$$

donde $\alpha$ se selecciona mediante validación cruzada en un rango logarítmico $[10^{-6}, 10^{6}]$.

#### 2.3.5. Validación Leave-One-Out Cross-Validation (LOO-CV)

Se evaluó la precisión del modelo utilizando LOO-CV, donde para cada observación $i$, se entrena el modelo con los datos restantes y se predice la observación excluida (Ec. (4)) [20].

$$LOO - MSE = \frac{1}{n}\sum_{i=1}^{n}\left(y_i - \hat{y}_{(i)}\right)^2 \qquad (4)$$

Donde $\hat{y}_{(i)}$ es la predicción de $y_i$ cuando el modelo se entrena sin la observación $i$.

#### 2.3.6. Optimización de Parámetros Experimentales

Para encontrar la mejor combinación de variables operativas que maximicen la remoción de DQO, se implementó una búsqueda sistemática dentro de los valores experimentales observados. Se definió la función objetivo que se muestra en la Ec. (5).

$$\max_{X} \hat{y}(\boldsymbol{X}) \qquad (5)$$

Donde $\hat{y}(\boldsymbol{X})$ es la predicción de la remoción de DQO dada una combinación de dosis de ozono, catalizador, pH y tiempo. La optimización se llevó a cabo utilizando el método L-BFGS-B, restringiendo las soluciones dentro del rango experimental [21].

### 2.3.7. Evaluación con Métodos de Interpretabilidad

Para mejorar la interpretabilidad del modelo, se aplicó el método de Permutación de Importancia de Variables que mide la reducción en el desempeño del modelo cuando se reordena aleatoriamente una variable, indicando su impacto en la predicción. Este método permite identificar que variables tienen un mayor impacto en la remoción del DQO y validar la consistencia del modelo con el conocimiento físico del proceso [22].

### 2.3.8. Robustez ante variabilidad experimental

Para evaluar la estabilidad del modelo, se realizaron 100 simulaciones en las que se introdujeron perturbaciones aleatorias de ±5% en las variables de entrada. Se analizó la variación en las predicciones para determinar la sensibilidad del modelo a fluctuaciones en los parámetros operativos [23].

## 3. Resultados y discusión

### 3.1. Caracterización fisicoquímica de los lixiviados.

La Tabla 1, muestra la caracterización fisicoquímica de las muestras de lixiviado, en el cual se evidencian diferencias significativas en su composición. El lixiviado No. 2 presenta una mayor carga orgánica. La relación $DBO_5$/DQO superior a 0.2 en ambas muestras indica que los lixiviados aún contienen una fracción biodegradable importante, lo que podría corresponder a lixiviados jóvenes o intermedios [24]. Sin embargo, la elevada conductividad del lixiviado No. 1, sugiere una mayor acumulación de sales disueltas, característica más común en lixiviados intermedios a viejos [25]. Referente al pH, es un parámetro importante porque los ambientes alcalinos indican que los lixiviados están en una etapa de estabilización, como el caso del lixiviado No. 1, mientras que el lixiviado No. 2, se encuentra más cercano a la neutralidad [26].

***Tabla 1.*** Caracterización lixiviados.

| Parámetro | Lixiviado No. 1 | Lixiviado No. 2 |
|---|---|---|
| DQO ($mg.L^{-1}$) | 6,295 | 8,421 |
| $DBO_5$ ($mg.L^{-1}$) | 1,664 | 1,933 |
| $DBO_5$/DQO | 0.26 | 0.23 |
| SST ($mg.L^{-1}$) | 157 | 96 |
| pH | 8.5 | 7.57 |
| Conductividad ($mS.cm^{-1}$) | 18 | 1.1 |
| Temperatura (°C) | 30.1 | 29.4 |

De acuerdo con el análisis anterior, se puede clasificar el lixiviado No. 2 como joven a intermedio, debido a su alta carga orgánica, mientras que el lixiviado No. 1 muestra características de un lixiviado intermedio a viejo, con una menor biodegradabilidad y un mayor contenido de sales disueltas [27].

### 3.2. Proceso experimental Ozonización Catalítica (OC)

La Tabla 2 presenta las corridas experimentales diseñadas para evaluar el proceso OC, considerando tres niveles para cada una de las variables independientes estudiadas. Estas condiciones se establecieron siguiendo el diseño de experimentos descrito en la sección 2.2 de la metodología. Cada experimento se diseñó como un ensayo independiente, asociado a un tiempo de muestreo específico y a los dos tipos de lixiviado analizados, con el porcentaje de remoción en términos de la DQO.

Adicionalmente, se incluyeron experimentos de control para establecer comparaciones y validar los resultados obtenidos. Estos consistieron en: (1) un ensayo utilizando únicamente ozono en la dosis máxima (6 $g.h^{-1}$), (2) un ensayo empleando solo magnetita en una dosis intermedia (2.5 $g.L^{-1}$), y (3) un ensayo sin la adición de ozono ni magnetita. Todos los experimentos de control se llevaron a cabo a un pH de 9, manteniendo las mismas condiciones operativas que los ensayos principales, con el fin de evaluar las contribuciones individuales del ozono y del catalizador, permitiendo la comparación entre ozonización simple y los procesos catalizados para identificar la sinergia entre el catalizador y los radicales hidroxilos generados [28], [29] en la remoción de DQO.

***Tabla 2.*** Combinaciones experimentales y resultados.

| Exp. | Dosis Ozono ($g.h^{-1}$) | Dosis Catalizador ($g.L^{-1}$) | pH | Tiempo (min) | % Remoción DQO (Lixiviado No. 1) | % Remoción DQO (Lixiviado No. 2) |
|---|---|---|---|---|---|---|
| 1 | 4 | 2.5 | 9 | 20 | 38.17 | 32.50 |
| 2 | 4 | 2.5 | 9 | 40 | 68.52 | 54.50 |
| 3 | 4 | 2.5 | 9 | 80 | 83.75 | 71.50 |
| 4 | 4 | 2.5 | 9 | 120 | 85.29 | 75.80 |
| 5 | 2 | 1.5 | 9 | 20 | 40.58 | 33.60 |
| 6 | 2 | 1.5 | 9 | 40 | 60.17 | 48.80 |
| 7 | 2 | 1.5 | 9 | 80 | 68.68 | 62.60 |
| 8 | 2 | 1.5 | 9 | 120 | 74.92 | 65.30 |
| 9 | 4 | 2.5 | 3 | 20 | 31.54 | 25.60 |
| 10 | 4 | 2.5 | 3 | 40 | 43.40 | 38.55 |
| 11 | 4 | 2.5 | 3 | 80 | 58.80 | 49.00 |
| 12 | 4 | 2.5 | 3 | 120 | 66.31 | 53.50 |
| 13 | 2 | 1.5 | 3 | 20 | 35.40 | 30.80 |
| 14 | 2 | 1.5 | 3 | 40 | 58.73 | 49.30 |
| 15 | 2 | 1.5 | 3 | 80 | 71.09 | 62.50 |
| 16 | 2 | 1.5 | 3 | 120 | 74.71 | 65.70 |
| 17 | 4 | 1.5 | 6 | 20 | 33.38 | 30.49 |
| 18 | 4 | 1.5 | 6 | 40 | 46.72 | 39.51 |
| 19 | 4 | 1.5 | 6 | 80 | 55.64 | 43.25 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 20 | 4 | 1.5 | 6 | 120 | 58.01 | 45.30 |
| 21 | 4 | 0.5 | 9 | 20 | 33.46 | 27.90 |
| 22 | 4 | 0.5 | 9 | 40 | 48.80 | 41.90 |
| 23 | 4 | 0.5 | 9 | 80 | 59.37 | 54.64 |
| 24 | 4 | 0.5 | 9 | 120 | 63.20 | 57.80 |
| 25 | 6 | 1.5 | 3 | 20 | 21.74 | 18.90 |
| 26 | 6 | 1.5 | 3 | 40 | 27.18 | 26.45 |
| 27 | 6 | 1.5 | 3 | 80 | 41.29 | 34.80 |
| 28 | 6 | 1.5 | 3 | 120 | 45.33 | 39.10 |
| 29 | 2 | 2.5 | 6 | 20 | 37.12 | 30.40 |
| 30 | 2 | 2.5 | 6 | 40 | 54.51 | 45.30 |
| 31 | 2 | 2.5 | 6 | 80 | 55.70 | 50.50 |
| 32 | 2 | 2.5 | 6 | 120 | 57.11 | 51.40 |
| 33 | 4 | 1.5 | 6 | 20 | 37.32 | 33.60 |
| 34 | 4 | 1.5 | 6 | 40 | 48.23 | 42.40 |
| 35 | 4 | 1.5 | 6 | 80 | 53.20 | 51.11 |
| 36 | 4 | 1.5 | 6 | 120 | 57.76 | 52.60 |
| 37 | 2 | 0.5 | 6 | 20 | 46.02 | 30.28 |
| 38 | 2 | 0.5 | 6 | 40 | 48.33 | 37.84 |
| 39 | 2 | 0.5 | 6 | 80 | 49.48 | 41.96 |
| 40 | 2 | 0.5 | 6 | 120 | 54.50 | 43.70 |
| 41 | 4 | 0.5 | 3 | 20 | 33.35 | 28.90 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 42 | 4 | 0.5 | 3 | 40 | 40.24 | 40.41 |
| 43 | 4 | 0.5 | 3 | 80 | 55.51 | 47.72 |
| 44 | 4 | 0.5 | 3 | 120 | 57.76 | 49.60 |
| 45 | 6 | 0.5 | 6 | 20 | 17.67 | 20.44 |
| 46 | 6 | 0.5 | 6 | 40 | 30.37 | 29.64 |
| 47 | 6 | 0.5 | 6 | 80 | 37.23 | 37.22 |
| 48 | 6 | 0.5 | 6 | 120 | 50.16 | 38.90 |
| 49 | 4 | 1.5 | 6 | 20 | 40.19 | 33.04 |
| 50 | 4 | 1.5 | 6 | 40 | 49.80 | 44.38 |
| 51 | 4 | 1.5 | 6 | 80 | 58.25 | 46.80 |
| 52 | 4 | 1.5 | 6 | 120 | 61.88 | 48.50 |
| 53 | 6 | 1.5 | 9 | 20 | 34.16 | 40.77 |
| 54 | 6 | 1.5 | 9 | 40 | 61.90 | 53.84 |
| 55 | 6 | 1.5 | 9 | 80 | 70.94 | 62.90 |
| 56 | 6 | 1.5 | 9 | 120 | 77.56 | 65.70 |
| 57 | 6 | 2.5 | 6 | 20 | 32.90 | 28.60 |
| 58 | 6 | 2.5 | 6 | 40 | 38.66 | 41.60 |
| 59 | 6 | 2.5 | 6 | 80 | 55.28 | 46.73 |
| 60 | 6 | 2.5 | 6 | 120 | 62.26 | 47.60 |
| 61 | 6 | 0 | 9 | 20 | 21.23 | 18.37 |
| 62 | 6 | 0 | 9 | 40 | 28.20 | 27.31 |
| 63 | 6 | 0 | 9 | 80 | 31.60 | 42.53 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 64 | 6 | 0 | 9 | 120 | 34.88 | 41.90 |
| 65 | 0 | 2.5 | 9 | 20 | 0.41 | 0.00 |
| 66 | 0 | 2.5 | 9 | 40 | 1.35 | 0.00 |
| 67 | 0 | 2.5 | 9 | 80 | 0.59 | 0.00 |
| 68 | 0 | 2.5 | 9 | 120 | 1.00 | 2.00 |
| 69 | 0 | 0 | 9 | 20 | 0.41 | 0.00 |
| 70 | 0 | 0 | 9 | 40 | 0.00 | 1.00 |
| 71 | 0 | 0 | 9 | 80 | 0.00 | 0.00 |
| 72 | 0 | 0 | 9 | 120 | 0.00 | 0.00 |

### 3.3. Análisis estadístico y validación

#### 3.3.1. Desempeño del modelo

La Tabla 3, muestra las métricas de los modelos optimizados que se ejecutaron para los dos tipos de lixiviado. Así mismo, se muestran las ecuaciones que modelan el proceso de OC, teniendo en cuenta la influencia de las variables evaluadas en función del porcentaje de remoción.

***Tabla 3***. Métricas de los modelos optimizados.

| Muestra | Métrica | |
|---|---|---|
| | **MSE** | **$R^2$** |
| Lixiviado No. 1 | 38.3335 | 0.9257 |
| Lixiviado No. 2 | 40.4431 | 0.9153 |

Estos resultados confirman que la combinación de expansión de características, regularización y validación Leave-One-Out Cross-Validation mejora la precisión del modelo.

Las ecuaciones para cada uno de los modelos RidgeCV, se muestran a continuación. La Ec. (6) modela el proceso de OC para el lixiviado No. 1; la Ec. (7) modela el proceso de OC para el lixiviado No. 2. En ambos casos, se deben tener en cuenta las siguientes convenciones:

- $Y$ : % Remoción en términos de DQO.
- $X_1$ : Dosis de ozono en g.h$^{-1}$.
- $X_2$ : Dosis de catalizador en g.L$^{-1}$.
- $X_3$ : Unidades de pH.
- $X_4$ : Tiempo (min).

$$\begin{aligned} \boldsymbol{Y} = 57.2811 &- 3.9739 * X_1 + 4.7102 * X_2 \\ &+ 5.6563 * X_3 + 9.5535 * X_4 \\ &- 9.0518 * X_1^2 \\ &+ 3.6838 * X_1X_2 \\ &+ 7.0935 * X_1X_3 \\ &+ 3.4129 * X_1X_4 - 2.1349 \\ &* X_2^2 + 3.0796 * X_2X_3 \\ &+ 2.1630 * X_2X_4 + 4.6534 \\ &* X_3^2 + 0.0252 * X_3X_4 \\ &- 1.7544 * X_4^2 \end{aligned} \quad (\mathbf{6})$$

$$\begin{aligned} \boldsymbol{Y} = 52.0825 &- 2.0335 * X_1 + 4.0156 * X_2 \\ &+ 6.3304 * X_3 + 9.4967 * X_4 \\ &- 7.5582 * X_1^2 \\ &+ 3.1217 * X_1X_2 \\ &+ 8.1764 * X_1X_3 \\ &+ 2.6591 * X_1X_4 - 1.5170 \\ &* X_2^2 + 2.8618 * X_2X_3 \\ &+ 1.1577 * X_2X_4 + 5.5163 \\ &* X_3^2 + 0.3943 * X_3X_4 \\ &- 2.3396 * X_4^2 \end{aligned} \quad (\mathbf{7})$$

#### 3.3.2. Optimización de Parámetros Experimentales

La optimización identificó la combinación óptima de variables para maximizar la remoción de DQO, para cada tipo de lixiviado (Tabla 4).

***Tabla 4***. Parámetros experimentales óptimos

| Variable | Valor óptimo | |
|---|---|---|
| | **Lixiviado No. 1** | **Lixiviado No. 2** |
| Dosis Ozono ($g.h^{-1}$) | 5.42 | 5.56 |
| Dosis Catalizador ($g.L^{-1}$) | 2.50 | 2.50 |
| pH | 9.0 | 9.0 |
| Tiempo (min) | 120 | 117.15 |
| % Remoción DQO predicho | 86.47 | 73.60 |

De acuerdo con los resultados obtenidos, se observó que la máxima eficiencia de remoción de DQO para ambos tipos de lixiviados se alcanzó en condiciones de alta dosificación de catalizador (magnetita) y pH alcalino, ya que la ozonización en condiciones alcalinas favorece la generación de radicales hidroxilos, aumentando la eficiencia en la degradación de los compuestos de interés [30].
Sin embargo, en el caso del Lixiviado No. 2, caracterizado por una mayor carga orgánica y un menor índice de biodegradabilidad, se requirió una dosis de ozono ligeramente superior en comparación con el Lixiviado No. 1. Este comportamiento puede atribuirse a la presencia de compuestos orgánicos recalcitrantes en el Lixiviado No. 2, los cuales demandan una mayor cantidad de oxidante para su degradación efectiva, los cuales demandan una mayor cantidad de oxidante para su degradación efectiva [31].

Cabe destacar que no fue necesario emplear la dosis máxima de ozono (6 $g.h^{-1}$) para alcanzar la máxima eficiencia de remoción de DQO en ninguno de los dos lixiviados. Este hallazgo es de particular relevancia, ya que una reducción en la dosificación de ozono, aunque sea marginal, podría traducirse en una disminución significativa de los costos operativos y del consumo energético asociado al proceso. Esta consideración es especialmente importante en procesos de ozonización, dado el elevado costo energético inherente a la generación de ozono y el consumo de oxígeno puro como materia prima, lo que determina que una dosificación óptima de ozono permite lograr altas eficiencias de remoción sin necesidad de sobredosificar el sistema, optimizando la relación costo-beneficio [32].

Respecto al tiempo de contacto, los resultados confirman que un mayor tiempo de exposición entre el lixiviado y el ozono favorece significativamente la degradación de los compuestos de interés, ya que la extensión del tiempo de ozonización mejora la eficiencia de remoción de DQO y aumenta la biodegradabilidad del lixiviado [33]. Por ello, el modelo predictivo establece que el tiempo óptimo de tratamiento para ambos lixiviados se aproxima al valor máximo evaluado (120 minutos), lo que sugiere que la extensión del tiempo de contacto es un factor importante para maximizar la eficiencia del proceso.

### 3.3.3. Análisis de importancia de variables

El análisis de Permutación de Importancia de Variables permitió identificar y cuantificar la influencia relativa de cada factor en la predicción de la eficiencia de remoción de DQO. De acuerdo con la Figura 1, y teniendo en cuenta ambas matrices del lixiviado, los resultados mostraron que los factores más significativos fueron:

- **Efecto cuadrático del ozono**. Este factor demostró ser el de mayor influencia en el modelo, lo que indica que la relación entre la dosis de ozono y la eficiencia de remoción de DQO no es lineal. En particular, se observó que un incremento en la dosis de ozono tiene un impacto positivo en la eficiencia del tratamiento, pero con una tasa de mejora decreciente a medida que se alcanzan dosis más altas. Este comportamiento sugiere la existencia de un punto de saturación, donde aumentos adicionales en la dosis de ozono no generan mejoras proporcionales en la remoción de DQO, posiblemente debido a limitaciones en la transferencia de masa o a la formación de subproductos que compiten por el ozono disponible [34].

- **Tiempo de contacto**. El tiempo de tratamiento se identificó como el segundo factor más influyente, aunque su impacto fue menor en comparación con el ozono. Un mayor tiempo de contacto entre el lixiviado y el ozono favorece la degradación de los compuestos orgánicos, ya que permite una mayor transferencia de masa y una oxidación más completa. Sin embargo, su influencia relativa menor sugiere que, después de un cierto tiempo, los beneficios marginales de extender el tratamiento disminuyen, lo que podría estar relacionado con la cinética de reacción y la disponibilidad de compuestos fácilmente oxidables [35].

- **Interacciones entre variables**. Las interacciones entre el ozono, el pH y la dosis de catalizador también mostraron una influencia significativa en el modelo. Estas interacciones validan la necesidad de utilizar un enfoque de RSM para capturar las relaciones no lineales y

sinérgicas entre las variables. En particular, se observó que el pH y la dosis de catalizador modulan la eficiencia del ozono, ya que un pH alcalino favorece la generación de radicales hidroxilos, mientras que la magnetita actúa como un catalizador heterogéneo que promueve la descomposición del ozono en especies oxidantes más reactivas [36].

Estos hallazgos resaltan la importancia de considerar no solo los efectos individuales de cada variable, sino también sus interacciones, para optimizar el proceso de ozonización catalítica. Además, confirman que el modelo evaluado fue una herramienta adecuada para predecir y optimizar la eficiencia de remoción de DQO en el tratamiento de lixiviados.

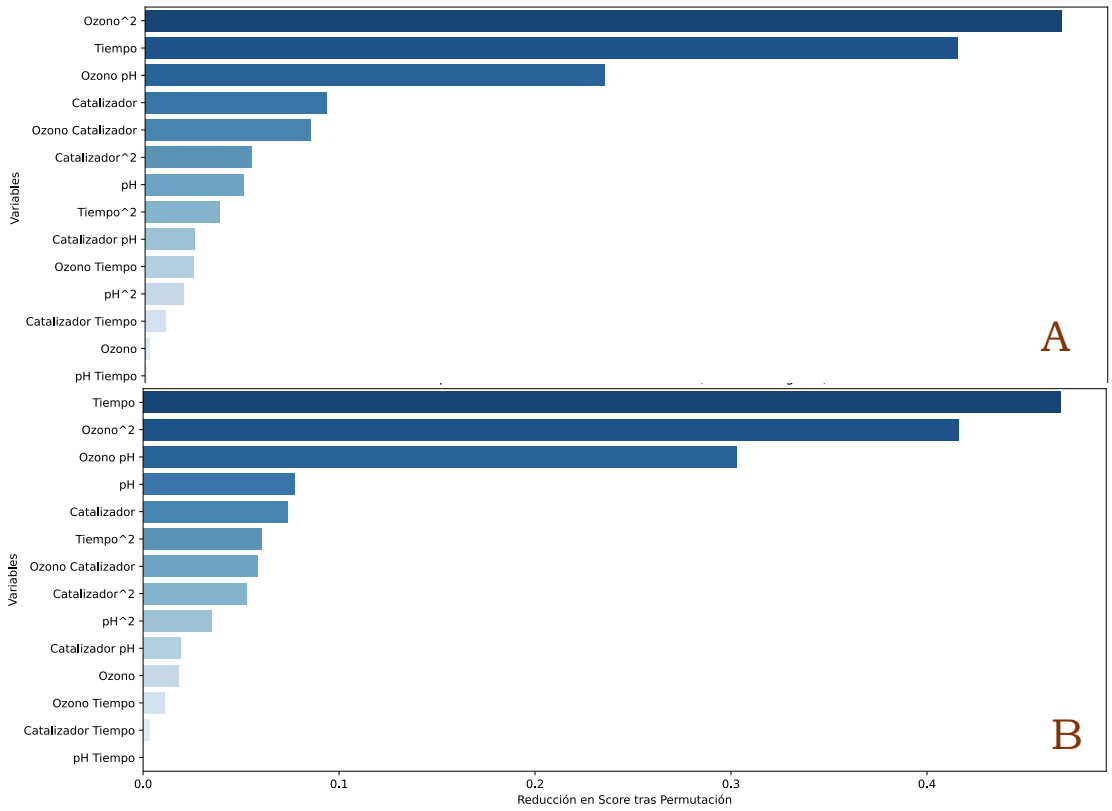



***Figura. 1***. Importancia de las variables evaluadas. **A.** Lixiviado No. 1; **B.** Lixiviado No. 2.

### 3.3.4. Robustez ante Variabilidad Experimental

Con el objetivo de evaluar la estabilidad y robustez del modelo predictivo frente a variaciones experimentales, se realizaron 100 simulaciones en las cuales las variables de entrada fueron modificadas aleatoriamente en un rango de ±5%. Este análisis permitió cuantificar la sensibilidad del modelo a pequeñas fluctuaciones en las condiciones operativas, lo cual es fundamental para garantizar su aplicabilidad en escenarios reales. Destacando estos análisis de sensibilidad como una herramienta clave en la optimización de procesos de ozonización, permitiendo evaluar el impacto de los parámetros operativos en la eficiencia de remoción de los contaminantes de interés [37].

Como caso ilustrativo, para el experimento No. 4 (Tabla 2), se obtuvo un valor experimental de remoción de DQO del 85.2%. Bajo las condiciones simuladas, el modelo predijo una remoción media del 81%, con una desviación estándar de 1.63. Estos resultados indican un buen ajuste entre los valores experimentales y las predicciones del modelo, respaldando su precisión y confiabilidad. Además, la baja desviación estándar sugiere que el modelo es estable ante pequeñas variaciones en las variables de entrada, lo cual es consistente con los resultados mostrados en la Figura 2, donde se observa que las predicciones del modelo se mantienen consistentes a lo largo de las simulaciones, sin presentar fluctuaciones significativas, lo cual es cogerente con otros modelos predictivos recientes que han logrado errores mínimos en la estimación de la remoción de DQO, utilizando técnicas avanzadas de simulación y aprendizaje automático, demostrando la capacidad de estos enfoques para garantizar estabilidad en escenarios experimentales variables [36].

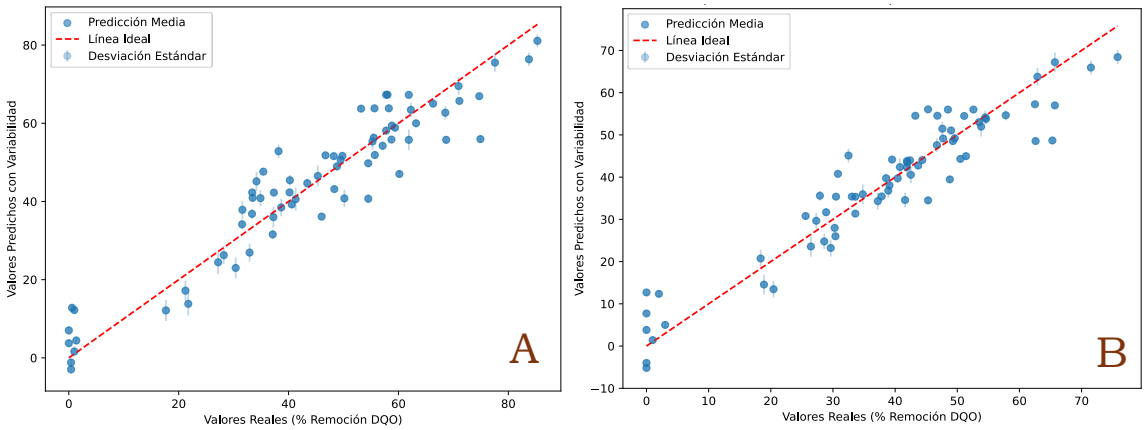



***Figura 2***. Importancia de las variables evaluadas. **A.** Lixiviado No. 1; **B.** Lixiviado No. 2.

Este comportamiento confirma que el modelo es robusto frente a perturbaciones experimentales y que pequeñas variaciones en las condiciones de operación como: la dosis de ozono, el pH, la concentración de catalizador o el tiempo de tratamiento, no generan cambios drásticos en las predicciones de remoción de la DQO. Esta característica es particularmente relevante para la aplicación del modelo en el tratamiento de lixiviados de rellenos sanitarios mediante OC, ya que garantiza su confiabilidad en entornos donde las condiciones operativas pueden presentar ligeras variaciones, destacando la importancia de la validación de los modelos en condiciones reales, enfatizando que una predicción precisa permite optimizar la eficiencia del tratamiento sin necesidad de sobredosificar reactivos, oxidantes y tiempo de experimentación [38].

## Conclusiones

- El modelo de Superficie de Respuesta (RSM) con regularización Ridge demostró ser una herramienta precisa y robusta para predecir la eficiencia de remoción de DQO en lixiviados de rellenos sanitarios mediante ozonización catalítica con magnetita. Las transformaciones estadísticas avanzadas y la expansión del espacio de características permitieron capturar relaciones no lineales y mejorar la generalización del modelo.

- Las condiciones óptimas para maximizar la remoción de DQO incluyen altas dosis de catalizador (2.5 $g.L^{-1}$), pH alcalino (9.0) y tiempos de tratamiento cercanos a 120 minutos.

- El análisis de Permutación de Importancia de Variables identificó que el efecto cuadrático del ozono es el factor más influyente, seguido del tiempo de contacto y las interacciones entre ozono, pH y catalizador. Esto resalta la importancia de considerar no solo los efectos individuales de las variables, sino también sus interacciones para optimizar el proceso.

- Las simulaciones con perturbaciones aleatorias de ±5% confirmaron que el modelo es estable frente a variaciones experimentales, lo que garantiza su aplicabilidad en escenarios reales donde las condiciones operativas pueden fluctuar.

- Este enfoque permite optimizar el tratamiento de lixiviados mediante ozonización catalítica, reduciendo costos operativos y mejorando la eficiencia del proceso, lo que es crucial para la gestión sostenible de residuos líquidos en rellenos sanitarios.

## Contribuciones de los autores

Todos los autores: conceptualización, metodología, software, validación, análisis formal, investigación, redacción (borrador original, redacción, revisión y edición), conservación de datos.

## Agradecimientos

Este trabajo contó con el apoyo de la Universidad Francisco de Paula Santander y la Universidad del Valle, a las cuales queremos expresar nuestro agradecimiento.

## Referencias

[1] F. Mohebbi, R. Dehghani, F. Tarazouj, M. Akbari, M. Rovan, and G. Mostafaii, "An overview of comparing chemical oxygen demand removal methods from landfill leachate," *International Archives of Health Sciences*, vol. 8, no. 3, pp. 1–6, 2021, doi: 10.4103/iahs.iahs_43_21.

[2] E. Caroline Baettker, C. Kozak, H. G. Knapik, and M. M. Aisse, "Applicability of conventional and non-conventional parameters for municipal landfill leachate characterization," *Chemosphere*, vol. 251, pp. 1–11, Jul. 2020, doi: 10.1016/j.chemosphere.2020.126414.

[3] A. Detho, Z. Daud, M. A. Rosli, M. B. Bin Ridzuan, and H. Awang, "Reduction of COD and ammoniacal nitrogen from landfill

leachate using granular activated carbon and green mussel adsorbent," *Desalination Water Treat*, vol. 223, pp. 218–226, May 2021, doi: 10.5004/dwt.2021.27140.

[4] S. Zarei, N. Fallah, and M. Mohseni, "Catalytic ozonation of a petrochemical wastewater containing high concentration of dinitrotoluene," *Journal of Water Process Engineering*, vol. 56, pp. 1–17, Dec. 2023, doi: 10.1016/j.jwpe.2023.104355.

[5] S. N. Malik, P. C. Ghosh, A. N. Vaidya, and S. N. Mudliar, "Hybrid ozonation process for industrial wastewater treatment: Principles and applications: A review," *Journal of Water Process Engineering*, vol. 35, pp. 1–21, Jun. 2020, doi: 10.1016/j.jwpe.2020.101193.

[6] M. Kermani, B. Kakavandi, M. Farzadkia, A. Esrafili, S. F. Jokandan, and A. Shahsavani, "Catalytic ozonation of high concentrations of catechol over TiO2@Fe3O4 magnetic core-shell nanocatalyst: Optimization, toxicity and degradation pathway studies," *J Clean Prod*, vol. 192, pp. 597–607, Aug. 2018, doi: 10.1016/j.jclepro.2018.04.274.

[7] S. S. Djimtoingar, N. S. A. Derkyi, F. A. Kuranchie, and J. K. Yankyera, "A review of response surface methodology for biogas process optimization," *Cogent Eng*, vol. 9, no. 1, pp. 1–35, Dec. 2022, doi: 10.1080/23311916.2022.2115283.

[8] H. Zaid, Z. Al-sharify, M. H. Hamzah, and S. Rushdi, "Optimization Of Different Chemical Processes Using Response Surface Methodology- A Review," *Journal of Engineering and Sustainable Development*, vol. 26, no. 6, pp. 1–12, Nov. 2022, doi: 10.31272/jeasd.26.6.1.

[9] M. A. Hadiyat, B. M. Sopha, and B. S. Wibowo, "Response Surface Methodology Using Observational Data: A Systematic Literature Review," *Applied Sciences*, vol. 12, no. 20, pp. 1–23, Oct. 2022, doi: 10.3390/app122010663.

[10] A. Al-Saffar and H. T. Mohammed Ali, "Using Power Transformations in Response Surface Methodology," in *2022 International Conference on Computer Science and Software Engineering (CSASE)*, IEEE, Mar. 2022, pp. 374–379. doi: 10.1109/CSASE51777.2022.9759781.

[11] M. P. Arancibia-Bravo, F. A. Lucay, F. D. Sepúlveda, L. Cortés, and L. A. Cisternas, "Response Surface Methodology for Copper Flotation Optimization in Saline Systems," *Minerals*, vol. 12, no. 9, pp. 1–20, Sep. 2022, doi: 10.3390/min12091131.

[12] V. Reungoat, M. Chadni, and I. Ioannou, "Response Surface Methodology Applied to the Optimization of Phenolic Compound Extraction from *Brassica*," in *Response Surface Methodology in Engineering Science*, IntechOpen, 2021, pp. 1–15. doi: 10.5772/intechopen.97655.

[13] G. E. P. Box and D. R. Cox, "An Analysis of Transformations," *J R Stat Soc Series B Stat Methodol*, vol. 26, no. 2, pp. 211–243, Jul. 1964, doi: 10.1111/j.2517-6161.1964.tb00553.x.

[14] G. James, D. Witten, T. Hastie, and R. Tibshirani, *An Introduction to Statistical Learning*. New York, NY: Springer US, 2021. doi: 10.1007/978-1-0716-1418-1.

[15] American Public Health Association (APHA), American Water Works Association (AWWA), and merican Water Works Association (AWWA), "Standard Methods for the Examination of Water and Wastewater - 24th Edition," Washington DC, 2023.

[16] P. H. Presumido *et al.*, "Ozone membrane contactor to intensify gas/liquid mass transfer and contaminants of emerging concern oxidation," *J Environ Chem Eng*, vol. 10, no. 6, pp. 1–13, Dec. 2022, doi: 10.1016/j.jece.2022.108671.

[17] W. L. Stevens, "The Logarithmic Transformation," *Nature*, vol. 158, no. 4018, pp. 622–622, Nov. 1946, doi: 10.1038/158622b0.

[18] J. I. Vélez, J. C. Correa, and F. Marmolejo-Ramos, "A new approach to the Box–Cox transformation," *Front Appl Math Stat*, vol. 1, pp. 1–10, Oct. 2015, doi: 10.3389/fams.2015.00012.

[19] V. W. Wessel N., "Lecture notes on ridge regression," *Cornell University*, 2015, doi: 10.48550/arXiv.1509.09169.

[20] V. Lumumba, D. Kiprotich, M. Mpaine, N. Makena, and M. Kavita, "Comparative Analysis of Cross-Validation Techniques: LOOCV, K-folds Cross-Validation, and Repeated K-folds Cross-Validation in Machine Learning Models," *American Journal of Theoretical and Applied Statistics*, vol. 13, no. 5, pp. 127–137, Oct. 2024, doi: 10.11648/j.ajtas.20241305.13.

[21] M. Rostampour, A. Unveren, and A. Acan, "A Novel Particle Filter Optimization Algorithm for the solution of Single-objective Numerical Optimization Problems," in *Proceedings of the Cognitive Models and Artificial Intelligence Conference*, New York, NY, USA: ACM, May 2024, pp. 202–207. doi: 10.1145/3660853.3660914.

[22] C. Ahmad, E. Denis A., and T. Bertrand, "Statistically Valid Variable Importance Assessment through Conditional

Permutations," *Cornell University*, 2023, doi: 10.48550/arXiv.2309.07593.

[23] J. Blanchet, P. Cui, J. Li, and J. Liu, "Stability Evaluation via Distributional Perturbation Analysis," *Cornell University*, 2024, doi: 10.48550/arXiv.2405.03198.

[24] E. Noerfitriyani, D. M. Hartono, S. S. Moersidik, and I. Gusniani, "Impact of Leachate Discharge from Cipayung Landfill on Water Quality of Pesanggrahan River, IndonesiaImpact of Leachate Discharge from Cipayung Landfill on Water Quality of Pesanggrahan River, Indonesia ," *IOP Conf Ser Earth Environ Sci*, vol. 120, pp. 1–9, Mar. 2018, doi: 10.1088/1755-1315/120/1/012002.

[25] A. Detho, A. Abdul Kadir, and M. A. Azhar, "Comparative Analysis of Contaminant Levels in Leachate and Soil from Young and Old Landfills," *Pertanika J Sci Technol*, vol. 32, no. 5, pp. 2299–2312, Aug. 2024, doi: 10.47836/pjst.32.5.20.

[26] R. B. Brennan, E. Clifford, C. Devroedt, L. Morrison, and M. G. Healy, "Treatment of landfill leachate in municipal wastewater treatment plants and impacts on effluent ammonium concentrations," *J Environ Manage*, vol. 188, pp. 64–72, Mar. 2017, doi: 10.1016/j.jenvman.2016.11.055.

[27] M. Gómez, F. Corona, and M. D. Hidalgo, "Variations in the properties of leachate according to landfill age," *Desalination Water Treat*, vol. 159, pp. 24–31, Aug. 2019, doi: 10.5004/dwt.2019.24106.

[28] C. He, J. Wang, C. Wang, C. Zhang, P. Hou, and X. Xu, "Catalytic ozonation of bio-treated coking wastewater in continuous pilot- and full-scale system: Efficiency, catalyst deactivation and in-situ regeneration," *Water Res*, vol. 183, p. 116090, Sep. 2020, doi: 10.1016/j.watres.2020.116090.

[29] Y. Li *et al.*, "Accurate prediction and intelligent control of COD and other parameters removal from pharmaceutical wastewater using electrocoagulation coupled with catalytic ozonation process," *Water Environment Research*, vol. 96, no. 8, Aug. 2024, doi: 10.1002/wer.11099.

[30] H. B. Bastos, L. L. S. Silva, É. C. A. N. Chrisman, F. V. Fonseca, and J. C. Campos, "Optimization of ozonation process for organic matter and ecotoxicity removal from landfill leachate by applying rotatable central composite design (RCCD)," *Journal of Environmental Science and Health, Part A*, vol. 56, no. 14, pp. 1457–1470, Dec. 2021, doi: 10.1080/10934529.2021.2006543.

[31] I. Y. Septiariva, I. W. K. Suryawan, N. K. Sari, and A. Sarwono, "Impact of Salinity on Stabilized Leachate Treatment from Ozonation Process," *Advances in Science, Technology and Engineering Systems Journal*, vol. 5, no. 6, pp. 1511–1516, Dec. 2020, doi: 10.25046/aj0506181.

[32] L. T. Hoffmann, M. C. B. Jorge, A. G. do Amaral, M. C. Bongiovani, and R. M. Schneider, "Ozonation as a pre-treatment of landfill leachate," *Ambiente e Agua - An Interdisciplinary Journal of Applied Science*, vol. 15, no. 6, pp. 1–12, Nov. 2020, doi: 10.4136/ambi-agua.2592.

[33] R. Kidak, M. N. Qadir, and F. H. Aziz, "Optimization of H2O2 and ozone-based advanced oxidation processes as pretreatment of sanitary landfill leachate," *Desalination Water Treat*, vol. 203, pp. 119–128, Nov. 2020, doi: 10.5004/dwt.2020.26238.

[34] S. Khurshid, A. R. Quaff, and R. Jha, "Treatment of Atrazine through Ozonation: Effect of Contact Time on COD and Atrazine Removal," *Res J Chem Environ*, vol. 28, no. 1, pp. 85–90, Dec. 2023, doi: 10.25303/281rjce85090.

[35] E. R. Toroz *et al.*, "Effects of Ozone Dose and Contact Time on Ozonation Process Performance for Treatment of High Rate Activated Sludge Process Effluent," *Ozone Sci Eng*, vol. 45, no. 5, pp. 431–445, Sep. 2023, doi: 10.1080/01919512.2022.2157243.

[36] Y. Li *et al.*, "Accurate prediction and intelligent control of COD and other parameters removal from pharmaceutical wastewater using electrocoagulation coupled with catalytic ozonation process," *Water Environment Research*, vol. 96, no. 8, Aug. 2024, doi: 10.1002/wer.11099.

[37] J. A. Lara-Ramos, M. A. Figueroa Angulo, F. Machuca-Martínez, and M. A. Mueses, "Sensitivity Analysis of the Catalytic Ozonation under Different Kinetic Modeling Approaches in the Diclofenac Degradation," *Water (Basel)*, vol. 13, no. 21, pp. 1–23, Oct. 2021, doi: 10.3390/w13213003.

[38] R. Singh, P. Bhunia, and R. R. Dash, "COD removal index — A mechanistic tool for predicting organics removal performance of vermifilters," *Science of The Total Environment*, vol. 643, pp. 1652–1659, Dec. 2018, doi: 10.1016/j.scitotenv.2018.07.272.

# Chapter 3: Treatment of Landfill Leachates Using Magnetite-Catalyzed Ozone Coupled with an Upflow Anaerobic Sludge Blanket Reactor

Green Chemical Engineering

# TREATMENT OF LANDFILL LEACHATES USING MAGNETITE-CATALYZED OZONE COUPLED WITH AN ANAEROBIC SLUDGE BLANKET REACTOR

--Manuscript Draft--

| | |
|---|---|
| **Manuscript Number:** | |
| **Full Title:** | TREATMENT OF LANDFILL LEACHATES USING MAGNETITE-CATALYZED OZONE COUPLED WITH AN ANAEROBIC SLUDGE BLANKET REACTOR |
| **Article Type:** | Research |
| **Keywords:** | Leachates; catalytic ozonation; magnetite; UASB; anaerobic treatment |
| **Corresponding Author:** | Andres Fernando Barajas-solano, Ph.D<br>Universidad Francisco de Paula Santander<br>Cucuta, Norte de Santander COLOMBIA |
| **Corresponding Author Secondary Information:** | |
| **Corresponding Author's Institution:** | Universidad Francisco de Paula Santander |
| **Corresponding Author's Secondary Institution:** | |
| **First Author:** | Dorance Becerra-Moreno, engineer, MSc |
| **First Author Secondary Information:** | |
| **Order of Authors:** | Dorance Becerra-Moreno, engineer, MSc |
| | Fiderman Machuca-Martínez, Engineer, MSc, PhD |
| | Luisa F. Ramírez-Rios, Engineer, MSc |
| | Janet B. García-Martínez, Engineer, MSc, PhD |
| | Andres Fernando Barajas-solano, Ph.D |
| **Order of Authors Secondary Information:** | |
| **Abstract:** | Sanitary landfill leachate treatment was evaluated using magnetite-catalyzed ozone, an upflow anaerobic sludge blanket (UASB) reactor, and microalgae, both individually and in combination, to improve biodegradability and remove organic matter, solids, metals, and nutrients. Leachates were characterized before and after each treatment, and their impacts on methanogenic activity, aerobic toxicity, and the BOD5/COD ratio were assessed. Magnetite-catalyzed ozone pretreatment enhanced biodegradability, enabling an optimal coupling point with the UASB at 40 minutes when the specific methanogenic activity reached 0.22 g CH4-COD/(gVSS·d). The UASB achieved COD removal rates of up to 75%, but high concentrations were maintained in the effluent with low ammoniacal nitrogen and phosphorus removal rates. Microalgae promoted nutrient removal, reducing total nitrogen and phosphorus by up to 65% and 70%, respectively, although with lower efficiency in terms of organic matter removal. Process coupling demonstrated that ozonation followed by UASB application improved anaerobic degradation, whereas the use of microalgae after biological treatment optimized the final effluent quality. Despite the improvements achieved, the final values for some parameters still exceed the discharge limits, indicating the need for operational adjustments or additional treatments to ensure effective purification. |
| **Opposed Reviewers:** | |
| **Additional Information:** | |
| **Question** | **Response** |
| **Free Preprint Service** | NO, I don't want to share my research early and openly as a preprint. |

| | |
|---|---|
| Do you want to share your research early as a preprint? Preprints allow for open access to and citations of your research prior to publication.<br><br>Green Chemical Engineering offers a free service to post your paper in a journal-branded First Look space on SSRN, an open access research repository, when your paper enters peer review. Once on SSRN, your paper will benefit from early registration with a DOI and early dissemination that facilitates collaboration and early citations. It will be available free to read regardless of the publication decision made by the journal. This will have no effect on the editorial process or outcome with the journal. Please consult the SSRN Terms of Use and FAQs. | |

March 2025.

Editorial Office
Green Chemical Engineering

Dear Editors,

We would like to submit our manuscript entitled “Treatment of Landfill Leachates Using Magnetite-Catalyzed Ozone Coupled with an Anaerobic Sludge Blanket Reactor” for consideration by Green Chemical Engineering. The present work introduces a novel method for enhancing the biodegradability and removal efficiency of organic matter, solids, metals, and nutrients from landfill leachates through a fusion of magnetite-catalyzed ozonation, an up-flow anaerobic sludge blanket (UASB) reactor, and microalgae.

The recalcitrant nature of leachate results in a series of pressing environmental issues, making its treatment a hot-button topic that warrants further investigation. Our study shows that magnetite-catalyzed ozonation improves the biodegradability of leachates, providing an ideal linking site for downstream anaerobic treatment. We also demonstrate how microalgae integration improves nutrient removal, resulting in a more environmentally sustainable treatment scheme. Our results indicate that this treatment approach reduces effluent contaminant loads by several orders of magnitude, further promoting the concepts of sustainable and green chemical engineering.

This manuscript has neither been published nor been submitted elsewhere. All authors have made significant contributions to the study and revised and approved the final version of the manuscript. The authors have no conflicts of interest to disclose. We have followed the journal’s ethical policy and the invigilators for article preparation.

Thank you for your time and consideration. We are excited to give the scientific community the potential benefit of sharing our work via Green Chemical Engineering. We shall be pleased to provide you with more details if required, so please do not hesitate to contact us.

Sincerely,

Corresponding author
Fiderman Machuca Martinez
Universidad del Valle
Colombia

# TREATMENT OF LANDFILL LEACHATES USING MAGNETITE-CATALYZED OZONE COUPLED WITH AN ANAEROBIC SLUDGE BLANKET REACTOR

Dorance Becerra-Moreno [1,2], Fiderman Machuca-Martínez [3,*], Luisa F. Ramírez-Rios [4], Janet B. García-Martínez [1], and Andrés F. Barajas-Solano [1]

1. Department of Environmental Sciences, Universidad Francisco de Paula Santander, Av. Gran Colombia No. 12E-96, Cúcuta 540003, Colombia.
2. School of Natural Resources and Environment, Universidad del Valle, Ciudad Universitaria Meléndez Calle 13 # 100-00, Cali 760015, Colombia
3. Center of Excellence in New Materials—CENM, School of Chemical Engineering, Universidad del Valle, Ciudad Universitaria Meléndez, Calle 13 # 100-00, Cali 760015, Colombia.
4. School of Engineering, Universidad De Los Llanos, km 12, Vda. Barcelona, Villavicencio, 500003, Meta; lfernandaramirez@unillanos.edu.co (L.R.)

*Correspondence: fiderman.machuca@correounivalle.edu.co

**Abstract:**

Sanitary landfill leachate treatment was evaluated using magnetite-catalyzed ozone, an upflow anaerobic sludge blanket (UASB) reactor, and microalgae, both individually and in combination, to improve biodegradability and remove organic matter, solids, metals, and nutrients. Leachates were characterized before and after each treatment, and their impacts on methanogenic activity, aerobic toxicity, and the $BOD_5$/COD ratio were assessed. Magnetite-catalyzed ozone pretreatment enhanced biodegradability, enabling an optimal coupling point with the UASB at 40 minutes when the specific methanogenic activity reached 0.22 g $CH_4$-COD/(gVSS·d). The UASB achieved COD removal rates of up to 75%, but high concentrations were maintained in the effluent with low ammoniacal nitrogen and phosphorus removal rates. Microalgae promoted nutrient removal, reducing total nitrogen and phosphorus by up to 65% and 70%, respectively, although with lower efficiency in terms of organic matter removal. Process coupling demonstrated that ozonation followed by UASB application improved anaerobic degradation, whereas the use of microalgae after biological treatment optimized the final effluent quality. Despite the improvements achieved, the final values for some parameters still exceed the discharge limits, indicating the need for operational adjustments or additional treatments to ensure effective purification.

**Keywords:** Leachates, catalytic ozonation, magnetite, UASB, anaerobic treatment.

## 1. Introduction

Waste leachates produced from sanitary landfills are an important environmental issue because of their high organic load, complex composition, and possible toxicity, which requires treatment. Landfill leachate can contain organic compounds, inorganic salts, toxic gases, halogenated hydrocarbons, and heavy metals, which can be hazardous to public health and the environment (Babaei et al., 2021). Several standard methods for treating these effluents, such as anaerobic processes, have been employed because of their efficient removal of organic matter; however, these methods have limitations in the degradation of recalcitrant compounds and nutrients, which poses a challenge for discharge compliance (H. Li et al., 2009).

Researchers have investigated advanced oxidation processes (AOPs) to decompose recalcitrant organic matter and enhance the biodegradability of leachates (Gautam et al., 2019) in response to these challenges. Coagulation, sedimentation, and adsorption are some of the methods traditionally used to treat leachate, but they have limited effectiveness in achieving complete treatment with low costs (Mohamad et al., 2023), and recently, the combined use of AOPs with biologics has been a promising alternative process (Ahn et al., 2002). Moreover, the use of MBRs to treat leachate was found to increase leachate treatment efficiency beyond biodegradable contaminants, as MBR alone had an excellent capability to remove biodegradable organic matter, and when combined with RO, it achieved the removal of nonbiodegradable organic matter as well (Fang et al., 2005).

While several technologies have been developed for leachate treatment, none of them alone have limitations. Biological methods, including upflow anaerobic sludge blanket (UASB) reactors, are very effective for the removal of organic matter and biogas generation but struggle with the reduction of recalcitrant pollutants and nutrients (Ismail et al., 2020). Alternatively, catalytic ozonation has been proposed to degrade refractory organics and increase leachate biodegradability, leading to better biological treatment (Braga et al., 2020). However, these processes alone cannot achieve efficient nutrient removal, making microalgae integration an appealing alternative for nitrogen and phosphorus accumulation while improving the quality of the overall effluent (Khen et al., 2022).

Since mixing treatment processes can produce synergies that enhance the performance of the entire system (Liu et al., 2020), recent studies have corroborated this. For example, the combination of anaerobic treatment and ozonation has been shown to increase organic contaminant removal and leachate biodegradability (Yenis Septiariva et al., 2019). Another way of doing this is to add them to biological processes; thus, greater nitrogen and phosphorus removal results in a more sustainable treatment scheme (Khen et al., 2022). Conversely, the integration of catalyzed ozonation with magnetite along with UASB reactors and microalgae treatment in this study represents a novel strategy to increase the removal of organic matter, heavy metals, and nutrients, thus ensuring increased efficiency of sanitary landfill leachate treatment to comply with stricter environmental requirements. This need for the integration of such processes is further prominent with recent evidence that the integration of advanced technologies, such as membranes and oxidation processes, can help reach removal efficiencies close to 99% for specific compounds (Jamrah et al., 2024). Therefore, the use of multistage treatment configurations with a combination of physicochemical and biological methods becomes crucial for both optimal performance and environmental compliance.

The Fenton oxidation process has been extensively investigated owing to its potential to mineralize organic contaminants in landfill leachate. The Fenton process results in 70% chemical oxygen demand (COD) removal from raw leachate and more than 50% removal from biologically treated leachate (Kanmani & Dileepan, 2023). Waste activated sludge has a relatively high COD, which leads to a reduction in treatment cost. In addition, the coupling of Fenton oxidation with biological aeration filters (BAFs) has been confirmed to improve the decomposition efficiency of COD, ammonium and total phosphorus (Wang et al., 2009). Research has shown that the highest removal efficiency for COD (99%) was achieved with combined treatment processes, such as the coupling of physicochemical and biological methods, e.g., membrane bioreactors (MBRs) with nanofiltration (NF), as well as oxidation with Fenton processes and adsorption (Jamrah et al., 2024). These results emphasize the necessity of integrated approaches involving advanced oxidation, biological treatment, and adsorption methods for effective leachate management.

Finally, recent research has also highlighted the role of ozone-based AOPs in improving the breakdown of organic contaminants. Ozone followed by combinations of denitrification,

coagulation and biological activated carbon effectively removes total nitrogen, COD and heavy metals from treated effluents that have passed stringent environmental discharge standards (Feng et al., 2021). Moreover, COD, BOD, and ammonia nitrogen can be significantly reduced after combined physicochemical treatment with ultrafiltration and nanofiltration methods. (Aziz et al., 2012).

In light of these findings, the aim of the present work was to assess the performance of magnetite-catalyzed ozonation, UASB reactors, and microalgae treatment individually and together for the removal of organic, solid, metal, and nitrogenous compounds. The results will help optimize process parameters and assist in the combined/combined treatment of pollutants to achieve better-quality final effluent.

## 2. Methods

Leachate samples were collected via polyethylene containers, pretreated with nitric acid, and rinsed with distilled water at the discharge points of the respective sanitary landfills via previously established methodological approaches (Chen et al., 2024). To avoid any changes in the composition of the studied compounds, the samples were transported in insulated containers at 4°C and, at most, 24 hours after they were taken, analyzed as specified in the 23rd edition of the Standard Methods for the Examination of Water and Wastewater and recognized sampling methods in recent studies (Becerra Moreno et al., 2022) (see Table 1).

Table 1. Analytical methods implemented for leachate characterization

| Parameter | Analytical Method |
|---|---|
| Heavy Metals | |
| - Cadmium | SM 3030 E, SM 3111 B |
| - Chromium | SM 3030 E, SM 3111 B |
| - Mercury | SM 3112 B |
| - Lead | SM 3030 E, SM 3113 B |
| Physicochemical Properties | |
| - pH | SM 4500 $H^+$ B |
| - Electrical Conductivity | SM 2510 B |

| | |
|---|---|
| - Temperature | SM 2550 B |
| - Total Suspended Solids (TSS) | SM 2540 D |
| - Volatile Suspended Solids (VSS) | SM 2540 E |
| Organic Matter | |
| - Biochemical Oxygen Demand ($BOD_5$) | SM 5210 B Modified, ASTM D 888-18 |
| - Chemical Oxygen Demand (COD) | SM 5220 D |
| Nutrients | |
| - Nitrates | SM 4500 $NO_3^-$ B |
| - Nitrites | SM 4500 $NO_2^-$ B |
| - Total Nitrogen | SM 4500-Norg C |
| - Phosphates | SM 4500-P E |

Aerobic biodegradability was also determined using the Zahn-Wellens/EMPA test (EMPA OECD 302B) (Becerra et al., 2020); aerobic toxicity trends were determined via the respiration inhibition test (EMPA OECD 209) (Becerra et al., 2020); and anaerobic biodegradability and toxicity were determined via the specific methanogenic activity test (AME) test (Becerra Moreno et al., 2022).

### 2.1.Characterization of the Inoculum Sludge

The test inoculum sludge in the UASB reactor was sourced from the second anaerobic lagoon of a palm oil extraction plant (corozo) in Tibú, Colombia. Before use, physicochemical characterization was carried out to assess its adequacy for anaerobic processes. This characterization was performed under the same conditions described in section 2.1 for the leachates concerning pH, temperature, total suspended solids (TSS), volatile suspended solids (VSS), chemical oxygen demand (COD), and the sludge volume index (SVI). In anaerobic reactor studies (Becerra Moreno et al., 2022) (K. Li et al., 2019), minimizing microbial degradation in transported sludge samples by collecting and storing them in polyethylene containers sealed in an airtight manner at 15°C before analysis is

recommended. They were then moved in a container to the laboratory, where analyses were performed within 24 hours of collection, ensuring the representativeness of the sample and the stability of its components.

### 2.2. Design and operation of the UASB reactor

The UASB (upflow anaerobic sludge blanket) reactor used in this study was a continuous flow design made with acrylic and had an 11.7 L working volume, 15 cm inner diameter, and 66 cm height. For operational stability, an electronic heater was installed in the intermediate section of the reactor; this heater operated to maintain a constant temperature between 35 and 40 °C throughout the experiment. Moreover, the influent pH was buffered in the range of 6.5--7.5 to prevent conditions that could be detrimental to microbial activity and promote the stability of the methanogenesis process. A peristaltic pump was used to feed the reactor to ensure continuous and controlled flow. During the startup phase, low organic loading rates were applied and gradually increased as the system stabilized. This stability was evaluated by monitoring the efficiency of organic matter removal. In contrast, the organic load was adjusted by regulating the feed flow rate and the influence of the COD concentration, which was modulated by diluting the leachate with distilled water. This controlled transition allows the microbial consortium to adapt without causing significant disturbances to the system.
Once the reactor could process the undiluted leachate and reach a hydraulic retention time (HRT) of 24 hours—a condition recommended for leachate treatment—the operational phase commenced (Y.-Z. Yang et al., 2024). During this stage, the system's performance was evaluated in terms of organic matter removal efficiency and microbiological stability (table 2). The controlled regulation of the organic load allowed for a progressive adaptation of the anaerobic system, minimizing the risk of inhibition and ensuring efficient organic matter conversion into biogas, favoring long-term process stability. In addition, the generated gases were collected through a port at the top of the reactor, allowing their monitoring and quantification to assess system performance.

Table 2. Operating conditions for the UASB reactor at the El Guayabal and La Madera landfills

| Stage | Time (days) | Hydraulic Retention Time (h) | Flow Rate (L/h) | L. Guayabal | | L. Madera | |
|---|---|---|---|---|---|---|---|
| | | | | Influent COD (mg/L) | Volumetric Organic Load (kg COD/m³·d) | Influent COD (mg/L) | Volumetric Organic Load (kg COD/m³·d) |
| Startup | 48 | 48 | 0.244 | 500 | 0.3 | 500 | 0.3 |
| | 27 | 42 | 0.279 | 1,950 | 1.1 | 2,480 | 1.4 |
| | 30 | 36 | 0.325 | 3,400 | 2.3 | 4,460 | 3 |
| | 30 | 30 | 0.39 | 4,850 | 3.9 | 6,440 | 5.2 |
| Operation | 27 | 24 | 0.487 | 6,296 | 6.3 | 8,421 | 8.4 |

### 2.3. Catalytic Ozonation with Magnetite

The ozonation process was carried out in a 500 mL glass reactor with a bottom gas inlet and a lateral outlet for residual gases, ensuring efficient and controlled ozone flow. Ozone was generated from pure oxygen via an O1 model unit (Pacific Ozone, Lenntech), with a maximum production of 6 g $O_3$/h and a flow rate of 3.3 L/min. Ozone was introduced into the reactor to ensure proper dispersion via microbubbles generated by a diffuser with 0.45 µm orifices, resulting in a homogeneous distribution of the gas in the solution. The reaction was conducted at ambient temperature (20 ± 2 °C), optimizing system stability. Synthetic magnetite ($Fe_3O_4$) was used as the catalyst with a purity > 98%, an average particle size of 0.30 µm , and a surface area of 7.0 $m^2$/g (VENATOR, 2017). Moreover, magnetite is characterized by traces of MgO (0.9%), Mn (0.3%), $TiO_2$ (0.25%), Zn (0.1%), $Al_2O_3$ (0.1%), and $SiO_2$ (0.05%), in addition to many heavy metals such as Pb, Cd, As, and Hg (Alpha Chemicals, N.D.), indicating that relatively minor quantities are released into the environment and allowing its use for advanced oxidation processes. The optimal process conditions, established in previous studies, were set at a flow rate of 6 g $O_3$/h, a flow rate of 3.3 L/h, an $Fe_3O_4$ concentration of 2.5 g/L, and a pH of 9—parameters that ensure maximum

efficiency in oxidizing the contaminants present in the leachates. Finally, the residual gases generated were directed to a 30% potassium iodide (KI) solution to neutralize unreacted ozone, thereby preventing its release into the environment and ensuring the safe operation of the system (Duan et al., 2024).

### 2.4. Process Integration

The efficiency of two treatment configurations was assessed via experimental tests: catalytic ozonation with magnetite in series with an upflow anaerobic sludge blanket (UASB) reactor and a UASB reactor in series with catalytic ozonation with magnetite. All systems were run under controlled conditions previously optimized in the study concerning the main parameters: hydraulic and organic retention times, hydraulic load, catalyst concentration, ozone dose, pH, reaction time, and temperature. The removal percentages of turbidity, chemical oxygen demand (COD), biochemical oxygen demand ($BOD_5$), total organic carbon (TOC), total suspended solids (TSS), nitrogen, and phosphorus were measured to assess the efficacy of each setup. The aerobic and anaerobic biodegradability, toxicity, and influence of the treated effluent on microalgae were also evaluated. Accordingly, these analyses were conducted following the leachate characterization methods detailed in the preceding sections to ensure the robustness and comparability of the results across methodologies.

### 2.5. Microalgal Strain

*Halochlorella* sp., was obtained from the INNOValgae collection (INNOValgae, Universidad Francisco de Paula Santander, Cúcuta, Colombia). Cultures were grown in 500 mL airlift reactors, with a working volume of 60%, maintaining Bold Basal as a nutrient source. The cultivation conditions included a photoperiod of 12 hours light/12 hours dark, a light intensity of 110 $\mu mol/m^{-2}\ s^{-1}$, and a supply of filtered air enriched with 1% (v/v) $CO_2$ (0.6 vvm used for the flow rate, which is defined as the volume of air for each volume of culture per minute) at 25 ± 2°C for temperature control. This process was continued every 15 days to maintain the strain under active conditions before the leachate coupling experiments.

### 2.6.Experimental Coupling of Microalgal Biomass

*Halochlorella* sp. was exposed to various leachate treatment units to assess the coupling of microalgal biomass to leachate treatment processes. To treat and untreated leachates through photobioreactor systems with a 2 L working volume operating under the following conditions: a 12/12-hour photoperiod (light/dark), airflow rate of 6 vvm, pH of 7 ± 0.2, temperature of 28 ± 2°C and light intensity of 110 $\mu molm^{-2}s^{-1}$. One hundred percent treated leachates and untreated leachates at a concentration of 5% were the evaluated treatments to verify the differential influence of the compounds found under each treatment on biomass production. The biomass was quantified according to the protocol described by (Moheimani et al., 2013). After 15 days of cultivation, 10 to 20 mL aliquots of the microalgal culture were collected. The samples were filtered with precombusted Whatman GF/C glass microfiber filters, dried at 60 °C in an oven for 24 h, and stored in a desiccator at 60 °C until a stable weight was reached for two h. After the filtration and drying processes were finished, the biomass concentration was calculated on the basis of the equation, which uses the weight of the filter with the biomass.

## 3. Results

### 3.1.Characteristics of the Inoculum Sludge

Characterization of the UASB (upflow anaerobic sludge blanket) inoculum sludge used in the reactor was performed to assess its intrinsic feature as a biological medium for leachate treatment. The investigation of selected parameters (COD, SVI, pH, TSS, and VSS) met essential needs by reflecting the sludge stability, biological activity, and degradation potential (the main characteristics are shown in Table 3). The inoculum had a high organic loading with a COD of 20,920 mg $O_2$/L. This parameter is essential, as sludge rich in fermentative organic matter can stimulate volatile fatty acid production and methanogenesis in the system (Cardeña et al., 2025). The SVI was also estimated to be 61.4 mL/g, which indicates good settling ability and, therefore, high biomass retention in the reactor (Lima et al., 2023). This type of SVI indicates a stable floc structure that promotes process efficiency

by reducing active biomass loss and enhancing cell retention time (Jiraprasertwong et al., 2020).

The sludge pH was 7.41, an appropriate range for anaerobic microorganism growth. This value is paramount, as anaerobic processes must balance volatile fatty acid production and consumption to avoid inhibiting methanogenic activity (López-Gutiérrez et al., 2021). The total solid composition was 21,990 mg/L of TSS and 14,733 mg/L of VSS, with VSS/TSS = 0.67. This ratio can indicate the organic part of the sludge, which has a high share of active biomass compared with inert solids. The minimum value of 0.60 is suitable for anaerobic reactors because most solids are active microorganisms critical for the biodegradation of organic matter and biogas generation (Y. Li et al., 2021).

Table 3. Characteristics of the Inoculum Sludge in the UASB Reactor

| Parameter | Result |
|---|---|
| Chemical Oxygen Demand (COD) (mg $O_2$/L) | 20,920 |
| Sludge Volume Index (SVI) (mL/g) | 61.4 |
| pH (pH Units) | 7.41 |
| Total Suspended Solids (TSS) (mg/L) | 21,990 |
| Volatile Suspended Solids (VSS) (mg/L) | 14,733 |
| VSS/TSS | 0.67 |

### 3.2.Performance of the UASB Reactor

The performance of the UASB reactor was evaluated in terms of organic matter removal efficiency, as measured by COD reduction. The system exhibited progressive performance improvement during operation, reflecting microbial adaptation and process stabilization (see Figure 1). In the early days of operation, the removal efficiency was limited, reaching only 20–30%. However, as the biomass acclimated to the applied organic load, COD removal steadily increased, reaching 65% in El Guayabal and 72% in La Madera by day 21. This behavior suggests proper acclimation of the microbial consortium to the reactor conditions, thereby optimizing the degradation of organic compounds in the leachates (Y.-Z. Yang et al., 2024). As the process continued, the system efficiency improved, achieving maximum removal values of 79% in El Guayabal and 81% in La Madera around day 39. Nevertheless,

after this point, fluctuations in COD removal were observed, possibly due to variations in leachate composition and the accumulation of metabolic byproducts that temporarily affected microbial activity (Fulazzaky et al., 2024). Ultimately, at the end of the experimental period, the removal efficiency stabilized at approximately 70% for both leachates. These findings indicate that the reactor achieved a dynamic equilibrium in terms of organic matter degradation, even under various operating conditions.

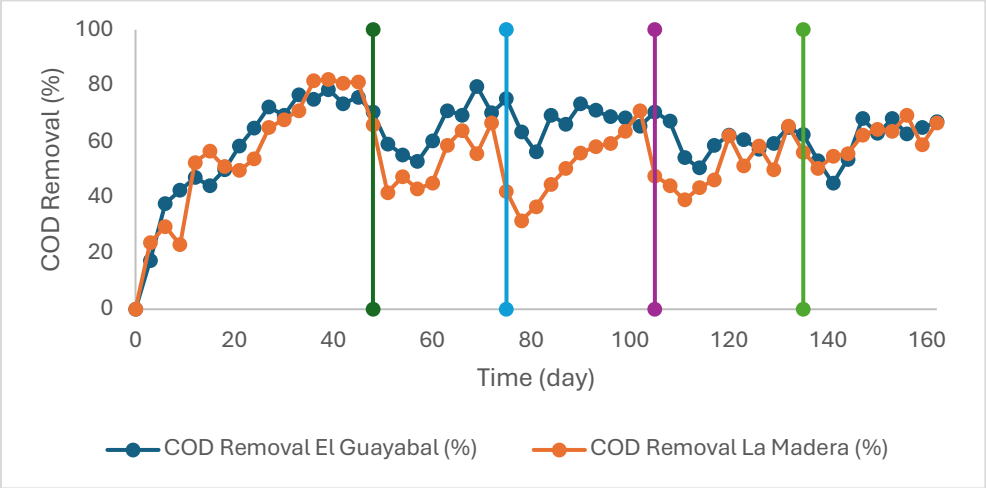



Figure 1. Evolution of COD and $BOD_5$ Removal in the UASB Reactor

### 3.3. Performance evaluation of individual treatment processes

Given the observed variation in the chemical characteristics of leachates from the La Madera and El Guayabal sanitary landfills, these differences are likely influenced by several factors, such as the age of the landfill, composition of the waste, and environmental conditions (Clemente et al., 2024). High concentrations of organic matter, nitrogenous compounds, and suspended solids, as illustrated in Table 4, validate specialized treatments for cost-effective purification. For the organic load, the initial COD obtained was 8,421.4 mg $O_2$/L in La Madera and 6,295.6 mg $O_2$/L in El Guayabal. Following ozone and magnetite treatment, these values were reduced to 3,832 mg $O_2$/L and 1,982 mg $O_2$/L, respectively, with removal efficiencies of 54.5% (La Madera) and 68.5% (El Guayabal). This observation suggests greater effectiveness in removing organic matter in El Guayabal, potentially due to the

particular composition of its leachate and the nature of the organic compounds present (Asaithambi et al., 2020). The total organic carbon (TOC) content also significantly decreased from 3,447 mg/L to 1,303 mg/L (62.2% removal) in La Madera and from 2,403 mg/L to 594 mg/L (75.3% removal) in El Guayabal. In contrast, ammonium nitrogen ($NH_4^+$) had high concentrations (751 mg/L in La Madera and 422 mg/L in El Guayabal) throughout all the raw leachates studied. Although the values decreased because of treatment with ozone and magnetite at 600.1 mg/L and 341.6 mg/L, respectively, ammoniacal nitrogen was the compound that presented the lowest removal percentage compared with the other compounds, with efficiencies of 20.1% in La Madera and 19.1% in El Guayabal. This is consistent with previous work that demonstrated that other processes, such as nitrification–denitrification, are needed to achieve better ammonium removal (Ricky et al., 2022) (Y. Yuan, Liu, Gao, & Sillanpää, 2022) (Gu et al., 2025).

The total TSS concentration also significantly decreased from 5,151 mg/L to 2,508 mg/L in La Madera (51.3% removal) and from 8,309 mg/L to 3,663 mg/L in El Guayabal (55.9% removal). TSS reduction enhances treated effluent quality and reduces water turbidity to ensure possible reuse or disposal. In addition to organic matter and solids, heavy metals were another critical parameter in the analyzed leachates. In El Guayabal, the initial chromium level of 0.294 mg/L was almost eliminated after treatment (<0.050 mg/L), highlighting the effectiveness of the process in removing this metal. Conversely, mercury, detected in La Madera at an initial concentration of 0.28 mg/L, was reduced to undetectable levels (<0.001 mg/L), suggesting that the applied treatments effectively captured and precipitated these contaminants. Another noteworthy aspect is the electrical conductivity, which reflects the concentration of dissolved salts in the leachates. In El Guayabal, the initial conductivity of 18,740 µS/cm decreased after treatment but did not reach optimal levels, indicating that the applied processes did not eliminate the salt load. In La Madera, the initial conductivity was much lower (1,128.6 µS/cm), suggesting a lower initial salt content.

Similarly, aerobic biodegradability is a key factor in evaluating treatment efficiency. The biodegradability of the raw leachates was 35% in La Madera and 38% in El Guayabal. After ozone and magnetite were applied, these values increased to 53% and 58%, respectively, representing improvements of 51.4% in La Madera and 52.6% in El Guayabal. This increase suggests that the applied processes transformed a considerable fraction of the recalcitrant

organic compounds into more biodegradable forms, facilitating their subsequent removal through biological treatments (Becerra et al., 2020). Furthermore, aerobic toxicity, measured via the inhibition of microbial respiration, was significantly reduced after the ozone treatment. In La Madera, the initial toxicity was 63%, which decreased to 45% following the application of ozone. In El Guayabal, toxicity decreased from 57% to 38% after ozonation. These results indicate that the toxic compounds present in the leachates, possibly derived from heavy metals and refractory organic substances, were either removed or transformed into less harmful forms due to the applied treatments (Becerra Moreno et al., 2022).

Table 4. Physicochemical composition of the analyzed leachates

| Parameter | Leachate | | UASB | | Ozone + Magnetite | |
|---|---|---|---|---|---|---|
| | El Guayabal | La Madera | El Guayabal | La Madera | El Guayabal | La Madera |
| Cadmium (mg/L) | <0.050 | <0.014 | <0.050 | <0.050 | <0.050 | <0.050 |
| Total Organic Carbon (TOC) (mg/L) | 2,403 | 3,447 | 978 | 1,251 | 594 | 1,303 |
| Conductivity (µS/cm) | 18,740.00 | 1,128.60 | 6,411.80 | 9,085.60 | 3,535.50 | 1,181.10 |
| Chromium (mg/L) | 0.294 | - | <0.050 | <0.050 | <0.050 | <0.050 |
| Biochemical Oxygen Demand – $BOD_5$ (mg $O_2$/L) | 1,664 | 1,933 | 666 | 751 | 714 | 1,098 |
| Chemical Oxygen Demand – COD (mg $O_2$/L) | 6,295.60 | 8,421.40 | 2,162 | 3,016 | 1,982 | 3,832 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Phosphates (mg/L) | 32.1 | 36.7 | 24.6 | 30.3 | 36.3 | 38.8 |
| Mercury (mg/L) | <0.001 | O,28 | <0.001 | <0.001 | <0.001 | <0.001 |
| Nitrates (mg/L) | 70.9 | 116.1 | 42.5 | 60.9 | 87.3 | 150.9 |
| Nitrites (mg/L) | 0.7 | 1.2 | 0.3 | 0.7 | 0.9 | 1.3 |
| Ammoniacal Nitrogen (mg/L) | 422 | 751 | 379.8 | 688.9 | 341.6 | 600.1 |
| Total Nitrogen (mg/L) | 528.5 | 890.6 | 459.2 | 751.6 | 433.5 | 753.9 |
| pH (pH Units) | 8.5 | 7.57 | 7.3 | 6.9 | 8.8 | 8.6 |
| Lead (mg/L) | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 | <0.10 |
| Total Suspended Solids – TSS (mg/L) | 8,309 | 5,151 | 3,305 | 1,906 | 3,663 | 2,508 |
| Volatile Suspended Solids – VSS (mg/L) | 5,717 | 3,096 | 2,812 | 1,158 | 1,023 | 914 |
| Temperature (°C) | 30.1 | 29.4 | 39.8 | 37.1 | 21.3 | 18.7 |
| Turbidity (NTU) | 298 | 196 | 185 | 96 | 102 | 87 |
| Aerobic Biodegradability (%) | 38 | 35 | 51 | 54 | 58 | 53 |
| Aerobic Toxicity – Microbial Respiration Inhibition (%) | 57 | 63 | 31 | 34 | 38 | 45 |
| Specific Methanogenic | 0.14 | 0.11 | - | - | 0.2 | 0.19 |

| Activity (g $CH_4$-COD/(g VSS·d)) | |
|---|---|

333

334 3.4.Performance of the Coupled Treatments

335 A comparative analysis of leachates treated by combining catalytic ozonation with magnetite
336 and a UASB (upflow anaerobic sludge blanket) reactor revealed significant differences in the
337 removal efficiency of organic matter, suspended solids, nutrients, and toxicity. This
338 underscores the influence of the treatment sequence on optimizing the final effluent. A
339 comparison of the initial values of the raw leachates with those obtained after individual and
340 combined treatments confirmed that integrating both processes enhances contaminant
341 elimination and improves effluent stability.
342 In terms of organic load, the "ozone (magnetite) + UASB" configuration resulted in a more
343 significant reduction in COD, with final values of 495.5 mg $O_2$/L in El Guayabal and 1034.6
344 mg $O_2$/L in La Madera, whereas the "UASB + ozone (magnetite)" scheme resulted in final
345 values of 561.4 mg $O_2$/L and 1366.0 mg $O_2$/L, respectively. This difference suggests that
346 preozonation before anaerobic treatment facilitates the degradation of refractory compounds,
347 increases the $BOD_5$/COD ratio, and enhances the biodegradability of the effluent (Y.-Z. Yang
348 et al., 2024) (Y. Yuan, Liu, Gao, & Sillanpää, 2022). The organic matter removal efficiency
349 in the coupled schemes exceeded that of the individual treatments, with COD reductions of
350 92% in the "ozone (magnetite) + UASB" scheme and 89% in the "UASB + ozone
351 (magnetite)" scheme, confirming the synergy between the two processes (table 5).
352 With respect to nitrogenous compound removal, different treatments yielded different
353 results depending upon the order of application. Partial removal of total and ammoniacal
354 nitrogen (361.5 mg/L and 331.4 mg/L in El Guayabal and 596.1 mg/L and 546.1 mg/L in La
355 Madera, respectively) was reported for pre-ozonation before the anaerobic reactor, whereas
356 the "UASB + ozone (magnetite)" configuration resulted in greater conversion of ammonium
357 into nitrate, attaining total nitrogen levels of 430.6 mg/L in El Guayabal and 751.3 mg/L in
358 La Madera. With respect to solids reduction, both the TSS and VSS were reduced
359 significantly after the combined treatment. The TSS and VSS values for the "ozone
360 (magnetite) + UASB" arrangement in La Madera were 602 mg/L and 283 mg/L, respectively,

whereas for the "UASB + ozone (magnetite)" configuration, the concentrations were 512 mg/L and 229 mg/L, respectively. These results indicate that applying ozonation as the final stage contributes to greater effluent clarification, reducing turbidity to 22 NTU in La Madera, as opposed to 52 NTU when ozonation was used before the UASB. The electrical conductivity also differed notably between the two treatment schemes, with lower values observed in the "ozone (magnetite) + UASB" configuration (3,158.3 µS/cm in El Guayabal and 1,055.1 µS/cm in La Madera) than in the "UASB + ozone (magnetite)" scheme (3,564.8 µS/cm and 1,211.4 µS/cm, respectively), suggesting that preozonation before the anaerobic process favors the removal of salts and soluble inorganic compounds.

The toxicity results indicate a reduction in the inhibition of aerobic respiration, reflecting a lower presence of toxic compounds in the treated leachates. Respiration inhibition was lower in the "ozone (magnetite) + UASB" configuration, with values of 28% in El Guayabal and 25% in La Madera. In contrast, the reverse configuration resulted in slightly more significant inhibition (32% and 30%, respectively). Finally, the specific methanogenic activity (SMA) was enhanced in the "UASB + ozone (magnetite)" configuration, reaching 0.17 g $CH_4$-COD/(g VSS·d) in El Guayabal and 0.19 g $CH_4$-COD/(g VSS·d) in La Madera, which suggests improved methane production efficiency from residual organic matter. These results demonstrate that combining both processes optimizes contaminant removal. However, the effectiveness varies depending on the treatment sequence, underscoring the need to adjust the operating conditions according to the specific treatment objectives.

Table 5. Physicochemical Composition of Leachates Treated with Ozone (Magnetite) + UASB or UASB + Ozone (Magnetite)

| **Parameter** | ***Ozone (Magnetite) + UASB*** | | ***UASB + Ozone (Magnetite)*** | |
|---|---|---|---|---|
| | **El Guayabal** | **La Madera** | **El Guayabal** | **La Madera** |
| Cadmium (mg/L) | <0.050 | <0.050 | <0.050 | <0.050 |
| Total Organic Carbon (TOC) (mg/L) | 141.70 | 317.30 | 133.10 | 335.80 |
| Conductivity (µS/cm) | 3,158.30 | 1,055.10 | 3,564.80 | 1,211.40 |

| | | | | |
|---|---|---|---|---|
| Chromium (mg/L) | <0.050 | <0.050 | <0.050 | <0.050 |
| Biochemical Oxygen Demand – $BOD_5$ (mg $O_2$/L) | 169.90 | 284.50 | 183 | 357 |
| Chemical Oxygen Demand – COD (mg $O_2$/L) | 495.5 | 1034.6 | 561.4 | 1366 |
| Phosphates (mg/L) | 25.4 | 23.6 | 31.4.4 | 33.4 |
| Mercury (mg/L) | <0.001 | <0.001 | <0.001 | <0.001 |
| Nitrates (mg/L) | 23.9 | 37.5 | 95.5 | 168.3 |
| Nitrites (mg/L) | 2.5 | 7.5 | 1 | 1.3 |
| Ammoniacal Nitrogen (mg/L) | 331.4 | 546.1 | 331.4 | 580.1 |
| Total Nitrogen (mg/L) | 361.5 | 596.1 | 430.6 | 751.3 |
| pH (pH Units) | 7.4 | 7.1 | 8.9 | 8.7 |
| Lead (mg/L) | <0.10 | <0.10 | <0.10 | <0.10 |
| Total Suspended Solids – TSS (mg/L) | 989 | 602 | 836 | 512 |
| Volatile Suspended Solids – VSS (mg/L) | 358 | 283 | 211 | 229 |
| Temperature (°C) | 39.2 | 38.3 | 20.2 | 19.8 |
| Turbidity (NTU) | 65 | 52 | 35 | 22 |
| Aerobic Biodegradability (%) | 61 | 66 | 66 | 68 |
| Aerobic Toxicity – Microbial Respiration Inhibition (%) | 28 | 25 | 32 | 30 |
| Specific Methanogenic Activity (g $CH_4$-COD/(g VSS·d)) | 0.14 | 0.16 | 0.17 | 0.19 |

### 3.5.Experimental Coupling of Microalgal Biomass

Statistical results of the treatments performed to compare the biomass concentrations produced in the leachates of the Guayabal and Madera landfills are presented, and the results are calculated in terms of average and standard deviation. The raw leachate had a low biomass concentration of 0.213 ± 0.012 g/L in Guayabal and 0.188 ± 0.001 g/L in Madera.

Afterward, the UASB treatment was applied, and the concentration ranged between 0.383 ± 0.051 g/L for Guayabal and 0.305 ± 0.009 g/L for Madera. The magnetite-assisted ozonation treatment resulted in biomass concentrations of 0.554 ± 0.018 g/L (Guayabal) and 0.431 ± 0.013 g/L (Madera). For the combined treatments, $O_3$ - UASB values of 0.724 ± 0.011 g/L were obtained in Guayabal, and 0.632 ± 0.026 g/L were obtained in Madera. Finally, the highest concentrations of biomass for the UASB-$O_3$ treatment were 0.895 ± 0.056 g/L and 0.809 ± 0.019 g/L, respectively, in Guayabal and Madera (Figure 2).

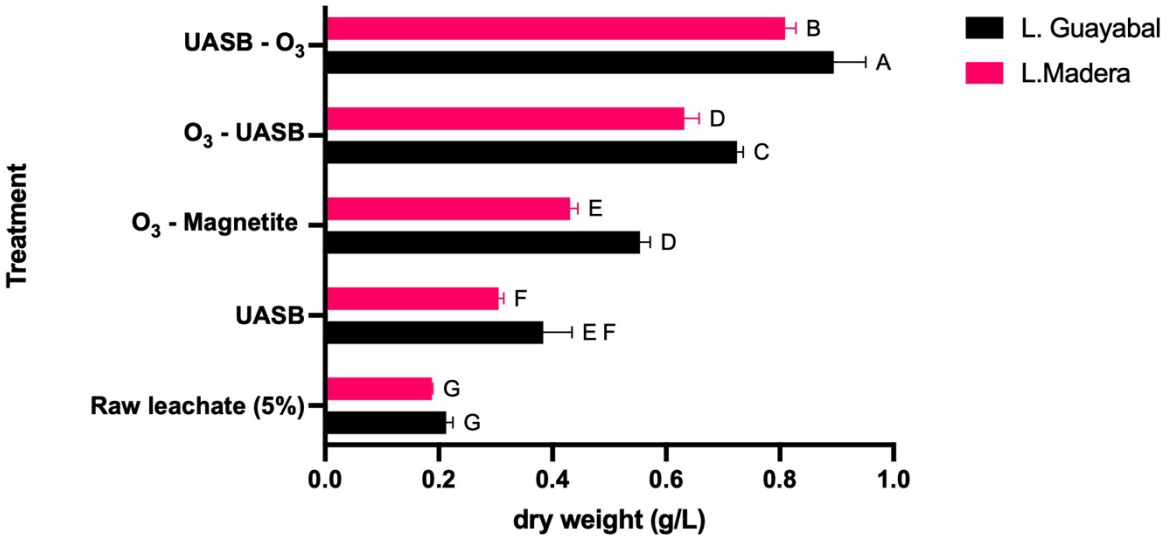



Figure 2. Microalgal biomass production (*Halochlorella* sp.) as a function of leachate treatment from Guayabal and Madera.

## 4. DISCUSSION

### 4.1. Characteristics of the Inoculum Sludge

The characteristics of the inoculum sludge provide a picture of its ability to be used as a leachate treatment in UASB reactors. The high chemical oxygen demand (COD) suggests that the active biomass can degrade complex organic compounds. Higher values of COD in sludge can be correlated with increased biogas production as long as the biodegradable fraction prevails (Xiao et al., 2024). However, when the recalcitrant organic fraction is

significant, methane conversion may be compromised, thereby reducing process efficiency (X. Wang et al., 2024). On the other hand, an SVI (sludge volume index) of 61.4 mL/g is an optimal value that promotes sludge settling and stability in the reactor. Reported SVI values between 50 and 80 mL/g support a high concentration of active microorganisms without significant washout. In contrast, excessively low values may indicate sedimentation issues and reduced reactor efficiency, and excessively high values may reflect a less compact sludge structure, negatively affecting anaerobic system performance (Kayan et al., 2021).

A pH of 7.41 suggests optimal conditions for methanogenic activity and overall anaerobic stability. pH values outside the range of 6.5–8.2 can impair microbial activity and reduce the efficiency of converting organic matter to methane (He et al., 2023). The stable pH of the sludge indicates an adequate buffering capacity, preventing fluctuations that might compromise reactor performance. Additionally, a VSS/TSS ratio (volatile suspended solids to total suspended solids) of 0.67 confirms that the inoculum sludge contains a high concentration of active biomass relative to inert solids. Research has established that ratios between 0.6 and 0.8 reflect an optimal balance between viable microorganisms and inert solids in anaerobic reactors (L. Li et al., 2020). A lower ratio could indicate excessive accumulation of inert material, reducing system efficiency, whereas higher values may indicate that the biomass is in a state of active growth (Yan et al., 2022).

### 4.2. Performance of the UASB Reactor

The performance of the UASB reactor throughout the experiment reflects the interplay between microbial adaptation, the applied organic load, and the operational conditions. The increasing trend in COD removal during the startup phase aligns with previous research that emphasized the need for a stabilization period for anaerobic biomass to adapt to the complex composition of leachates (Zou et al., 2022). This phenomenon occurs because the microbial community requires time to develop specific enzymes capable of efficiently degrading the organic compounds present (L. Yuan et al., 2020). A notable pattern in the results is the higher removal efficiency observed in La Madera than in El Guayabal, which may be attributed to the volumetric organic load—8.4 kg COD/$m^3$·d in La Madera versus 6.3 kg

COD/m³·d in El Guayabal. Higher organic loads favor the proliferation of methanogenic microorganisms specialized in degrading complex compounds (Pinpatthanapong et al., 2023). However, excessively high loads can cause inhibition due to the accumulation of volatile fatty acids or ammonium, possibly explaining the slight decline in efficiency observed after day 42 in both leachates (Fulazzaky et al., 2024).

Another important aspect is the stabilization of COD removal at approximately 70% by the end of the experiment. This result suggests that the reactor reached a dynamic equilibrium between producing and consuming metabolic intermediates, thereby avoiding severe inhibition. Studies have shown that the accumulation of intermediates such as propionate and butyrate can slow methanogenesis and reduce system efficiency (Xiao et al., 2024). Furthermore, regulating the hydraulic retention time (HRT) and organic load has been identified as a key strategy to avoid such imbalances and improve treatment efficiency (Y.-Z. Yang et al., 2024). While this study established an HRT of 24 hours during the operational phase, previous research has demonstrated that reducing the HRT to lower values can compromise the COD removal efficiency because of the reduced interaction between the biomass and the organic substrate (Trisakti et al., 2024) (Xiao et al., 2024). Additionally, implementing posttreatment systems, such as those combining aerobic reactors, has proven effective in enhancing treated effluent quality (Tian et al., 2022) (Y. Han et al., 2025).

### 4.3.Process Analysis of Uncoupled Treatments

The analysis of the treatments applied to the leachates from the La Madera and El Guayabal landfills demonstrated how the initial composition influences the efficiency of the processes employed. In addition to contaminant reduction, the results reveal key patterns that help elucidate the interactions among waste, environmental conditions, and treatment responses. The age and composition of leachate significantly affect treatment efficiency, explaining the variability observed in the results (Xiao et al., 2024). This variability underscores the need for combined strategies tailored to the specific nature of each leachate (Babu Ponnusami et al., 2023) (Tian et al., 2022).

The most important insights related to the differing gradients of organic matter degradability were analyzed regarding COD, BOD, and TOC. The reductions in these parameters were

most pronounced in El Guayabal, indicating that the organic matter in that leachate is more susceptible to oxidation and that complex recalcitrant fractions remain in La Madera. The BOD/COD ratios show that a large part of the organic matter is poorly biodegradable, which characterizes the need for an additional treatability step (Kayan et al., 2021) despite the results already reached with the treatments applied. (Zhe et al., 2025) recently demonstrated that advanced oxidation could render refractory organic compounds easier to degrade, as it increased the biodegradable fraction of the leachate. In addition, ozonation has shown reductions of 90% for COD and 85% for BOD in leachates with high organic loads (Bao et al., 2024).

The behavior of ammonium nitrogen highlights its resistance to the applied treatments. Although moderate reductions were observed, the persistence of high concentrations indicates that the processes are not entirely effective in its removal. Previous studies have noted that high ammonium concentrations can inhibit biological processes, affecting the efficiency of both anaerobic and aerobic reactors (Lin et al., 2024) (Wu et al., 2024) (S. Liu et al., 2024). The low elimination rate of ammoniacal nitrogen suggests that these treatments must be complemented with strategies such as nitrification-denitrification or adsorption using specific materials (Xiong et al., 2024) (Y. Li et al., 2023). In this context, research has demonstrated that ozone combined with a partial denitrification-anammox process can reduce the nitrogen concentration by up to 96%, significantly improving effluent quality (Zhao et al., 2023). Leachate treatment also reduced the phosphate concentration, indicating that the processes effectively precipitated and removed these compounds. Previous studies have shown that microbial activation and catalytic ozonation can increase the phosphate removal efficiency by up to 79% (Y. Yuan, Liu, Gao, & Sillanpää, 2022). This reduction is crucial, as the presence of phosphates in water bodies can contribute to eutrophication.

Another critical parameter is conductivity, which did not decrease significantly after treatment, indicating that the concentration of dissolved salts remains high. The high conductivity suggests the presence of inorganic ions that the applied processes did not efficiently remove. Research has demonstrated that membrane filtration and electrodialysis can effectively reduce conductivity and improve final effluent quality (H.-R. Yang et al., 2023). Similarly, reducing aerobic toxicity is a key indicator of treatment effectiveness, reflecting the elimination of compounds that inhibit microbial activity. In raw leachates, high

toxicity suggests the presence of heavy metals and refractory organic compounds that interfere with enzymatic activity (Jolaosho, 2024) (Z. Liu et al., 2024). Following treatment, the reduction in toxicity indicates that these compounds have been transformed into less toxic forms or removed, creating an environment more conducive to subsequent biological processes (De Sousa et al., 2023) (Amancio Frutuoso et al., 2025) (Kalčíková et al., 2016). This behavior suggests that advanced oxidation not only decomposes persistent organic contaminants but also improves the stability of the treated effluent. However, the persistence of moderate residual toxicity indicates that some compounds were not thoroughly degraded or that intermediate byproducts were formed, with effects on biological activity not yet fully characterized (De Sousa et al., 2023) (Kanmani & Dileepan, 2023) (Feng et al., 2021). In this context, combining physicochemical processes with specific biological treatments, such as the use of activated sludge, may be key to mitigating residual toxicity effects (Mishra et al., 2023) (Castillo-Suárez et al., 2019).

Concerning aerobic biodegradability, the increase observed after treatment suggests that the applied processes converted a significant fraction of the recalcitrant organic matter into forms more accessible for microbial degradation. Recent studies have indicated that advanced oxidation can increase the proportion of readily biodegradable organic matter by up to 50%, facilitating its removal in subsequent biological stages (Y. Yuan, Liu, Gao, & Sillanpää, 2022). However, the degree of improvement depends on the nature of the leachate compounds and the treatment operating conditions (Castillo-Suárez et al., 2019). The specific methanogenic activity (SMA) is another crucial parameter when determining the potential anaerobic biodegradability of treated leachate. (reduced methanogenic activity >40%), and hence, a negative impact on anaerobic reactor efficiency (Kalčíková et al., 2016) has also been reported under such high concentrations of ammonium and toxic compounds. The findings of this study indicate that although toxicity was considerably lower, certain inhibitory compounds were found to remain, which may hinder biogas production and the overall efficiency of anaerobic treatment. Therefore, the integration of specific pretreatments—such as ammonium adsorption via zeolite or pH adjustment—could optimize the conversion of organic matter into methane in anaerobic systems (Lima et al., 2023) (Mishra et al., 2023).

## 4.4.Performance of the Coupled Treatments

On the basis of the combined treatments of catalytic ozonation together with magnetite and a UASB (Upflow Anaerobic Sludge Blanket) reactor, their evaluation revealed that the coupling of physicochemical and biological processes could lead to increased removal of persistent contaminants as well as to process stability of the final effluent (Y.-Z. Yang et al., 2024). The degradation of organic matter is one of the most significant factors in treating leachate, and the results obtained with UASB reactors have been widely published in the literature (Tian et al., 2022) (Lakshmi & Raj, 2022). The chemical oxygen demand (COD) reflects the organic load of water and is an essential parameter for monitoring performance. Its reduction is of paramount importance for treatment efficiency. It has been reported that the application of catalytic ozonation as a pretreatment could promote the oxidization of some refractory compounds and thus enhance their subsequent biodegradation in UASB reactors (Duan et al., 2024) (Babu Ponnusami et al., 2023) (Bai et al., 2023). Similar observations have been made previously (S. Han et al., 2024), where chemical preoxidation broke complex molecules into smaller fragments, which increased the bioavailability of such biodegradable substrates for microorganisms.

On the other hand, biochemical oxygen demand ($BOD_5$) is a parameter that indicates the biodegradable fraction of organic matter, and the relationship between COD and $BOD_5$ can be used to elucidate the proportion of refractory compounds in the effluent. The higher $BOD_{27}$/COD ratios obtained with the combination treatments indicate that preozonation before the UASB reactor increased the bioavailability and organic matter removal efficiency of readily degradable substrates. This shift in metabolic direction has also been reported in comparable treatment systems, in which coupling physicochemical and biological processes improves final effluent stability and diminishes the occurrence of toxic metabolites. Moreover, total organic carbon (TOC) is another important parameter for estimating organic matter elimination. Research has shown that the TOC concentration is reduced after ozonation, and furthermore, the chemical structure of TOC is also transformed, leading to easier degradation in anaerobic reactors. This finding is in line with prior studies that showed that advanced oxidation (POD or Sm) can convert macromolecules into more minor, more biodegradable compounds (Zhu et al., 2024) (H. Wang et al., 2023) (Zhe et al., 2025).

With respect to nitrogenous compounds, reducing ammonium nitrogen is a challenge in leachate treatment because of its toxicity to anaerobic microorganisms and its persistence in the system. Preozonation has been shown to favor the conversion of ammonium to nitrates and nitrites, reducing its impact on methanogenic biomass (An et al., 2025) (Goli et al., 2023) (Y. Yuan, Liu, Gao, Sillanpää, et al., 2022). However, ozonation applied after anaerobic treatment may contribute to additional oxidation of these compounds, thereby improving the final effluent quality (Goli et al., 2023). Reducing the nitrogen load is critical to prevent eutrophication in receiving water bodies and to comply with environmental regulations (Guerrero-Brotons et al., 2024). Similarly, phosphorus is another crucial nutrient in leachate characterization, and its removal is essential for preventing the excessive growth of undesirable microorganisms in water bodies. Ozonation has proven effective in precipitating phosphates and facilitating their removal in combined treatment systems (H. Wang et al., 2023). In this study, the higher phosphorus removal efficiency observed in the UASB + ozone (magnetite) configuration suggests that prior biological degradation favors subsequent precipitation and removal, which is consistent with studies demonstrating that the combination of biological and oxidative processes achieves better nutrient elimination stability (Y.-Z. Yang et al., 2024).

Toxicity and biodegradability analyses confirmed the advantages of the combined schemes in reducing inhibitory compounds and enhancing microbial activity. Aerobic respiration inhibition decreased significantly, in agreement with studies showing that the elimination of refractory compounds through oxidative pretreatment supports the recovery of biological activity (H. Wang et al., 2023) (Babu Ponnusami et al., 2023). Moreover, aerobic biodegradability improved considerably in the combined schemes, indicating that the organic compounds were transformed into fractions more accessible to degradation by aerobic microorganisms. This increase suggests that ozonation is key in breaking complex chemical bonds, generating byproducts that are more easily assimilated by biological systems (Mu et al., 2022) (Tian et al., 2022). Furthermore, the enhanced biodegradability implies a lower content of toxic substances in the final effluent, reinforcing the viability of these combined treatments for improving water quality (Y. Yuan, Liu, Gao, Sillanpää, et al., 2022) (Gu et al., 2025).

Concerning specific methanogenic activity (SMA), the UASB + ozone (magnetite) configuration demonstrated higher biogas production efficiency, suggesting that prior biological stabilization favors the conversion of organic matter into methane. This is consistent with previous studies indicating that an initial anaerobic phase allows for greater adaptation of the microbial consortium to reactor conditions, thereby optimizing biogas production (Y.-Z. Yang et al., 2024). Additionally, the lower accumulation of inhibitory compounds in this configuration suggests that the subsequent oxidation step contributes to removing toxic metabolites that could impair the activity of methanogenic archaea, thus improving the overall system efficiency.

### 4.5.Experimental Coupling of Microalgal Biomass

The findings demonstrate the influence of biological and physicochemical treatments on leachate biomass outputs, providing a rationale for implementing hybrid technologies in industrial effluent remediation. The use of an anaerobic sludge blanket (UASB) reactor in conjunction with ozonation, an enhanced oxidation process, can improve the deftness of compounds in leachate and promote the conversion of recalcitrant compounds into intermediaries, which could be used in subsequent metabolic processes for microbes (Moussavi et al., 2012). This finding corroborates recent studies that integrated advanced oxidation systems with microbial biotechnologies to recover resources from industrial liquid wastes (Urbina-Suarez et al., 2025).

Although the raw leachate was diluted to 5%, the biomass values obtained under these conditions were the lowest in the present study, indicating the persistence of toxic or recalcitrant compounds that may inhibit microbial activity. It has been previously reported that leachates with lower $BOD_5$ values and ratios of $BOD_5$ to COD are less efficient in biological processes because they are predominantly composed of organic matter with lower biodegradability (Asaithambi et al., 2020). In contrast, the increase in biomass in the UASB reactor indicates that this system allowed anaerobic degradation of more accessible organic compounds, which promoted the growth of the microorganisms responsible for biogas generation. Research has demonstrated that UASB systems, in addition to reducing the organic load, can generate intermediate products, such as organic acids and alcohols, which

are utilized in subsequent oxidative processes (Y.-Z. Yang et al., 2024). When magnetite-assisted ozonation was incorporated into the treatment, an additional increase in biomass was observed compared with that with the UASB alone, suggesting that ozone decomposed complex compounds into smaller, more assimilable molecules. Ozonation has been widely employed in the treatment of industrial effluents because of its ability to reduce the toxicity of persistent organic contaminants, increase the biodegradability of wastewater, and generate intermediate products such as nitrates and phosphates, which are essential for microbial metabolism (Song et al., 2025).

The most significant increase in biomass was observed with the UASB–$O_3$ treatment, suggesting that the preceding anaerobic degradation may have generated metabolic precursors that, upon exposure to ozone, were transformed into compounds even more accessible to microorganisms (Song et al., 2025). A recent study on integrating oxidation with microbial bioprocesses in industrial effluents demonstrated that prior oxidative processes can create a more favorable environment for microbial activity, particularly when the ratio between organic carbon and essential nutrients is optimized (Sari et al., 2023). This pattern was also observed in the study by (Urbina-Suarez et al., 2025), in which an advanced oxidation system was integrated with microalgae cultivation to treat industrial wastewater. The authors reported that the application of hydrogen peroxide activated with bicarbonate not only improved the biodegradability of the effluent but also promoted increased biomass synthesis in cultures of *Chlorella* sp., reinforcing the notion that the intermediate products generated during oxidation can act as key substrates for microbial proliferation.

Furthermore, the difference in biomass generated between the leachates from Guayabal and Madera suggests that the initial composition of the leachate influences treatment efficiency. Research has reported that leachates with a higher content of readily biodegradable organic carbon favor greater microbial activity and, consequently, increased biomass production (Z. Wang et al., 2022) (Lian et al., 2024). This may explain why, in all the evaluated treatments, the biomass values from Guayabal were greater than those from Madera, suggesting that the leachates from the latter location may contain a more significant proportion of recalcitrant compounds that adversely affect the efficiency of biological processes.

## 5. Conclusions

Pretreatment with magnetite-catalyzed ozone improved leachate biodegradability by increasing the $BOD_5$/COD ratio and partially reducing aerobic toxicity. An optimal ozonation time of 40 min was determined, during which the specific methanogenic activity reached 0.22 g $CH_4$-COD/(gVSS·d), indicating improved conditions for anaerobic treatment. However, the process did not achieve efficient nutrient removal, maintaining high concentrations of total and ammonium nitrogen, which suggests the need for an additional treatment step to eliminate these compounds.

The UASB reactor achieved COD removals of 60–75%, with better stability observed in the leachate from El Guayabal. Nevertheless, the removal of suspended solids was limited, with reductions of up to 65%, and ammonium nitrogen remained high, with concentrations of 341.6 mg/L and 600.1 mg/L in the treated effluents. Although the UASB process partially reduced the organic load, the final values did not meet the discharge requirements, highlighting the need for further treatment.

Compared with UASB and magnetite-catalyzed ozone, microalgae treatment enhanced nutrient removal, significantly reducing total and ammonium nitrogen. Removal rates of up to 65% for total nitrogen and 70% for phosphorus were attained, confirming its potential to complement anaerobic processes. However, its efficiency in organic matter removal was lower than that of the UASB reactor, suggesting that its application should focus on the final polishing of the effluent.

The integration of treatment processes demonstrated that the combination of magnetite-catalyzed ozone and the UASB achieved the highest organic matter removal. In contrast, the reverse sequence (UASB followed by magnetite-catalyzed ozone) led to a more significant reduction in toxicity affecting anaerobic digestion. The use of microalgae after anaerobic treatment led to a more efficient reduction in nutrients, confirming the necessity of integrated strategies to optimize the final effluent quality.

**Acknowledgments**

This study received financial support from Universidad Francisco de Paula Santander (Colombia) (FINU 011-2023), the Ministry of Science and Technology of Colombia, and the Colombian Institute of Educational Credit and Technical Studies Abroad (MINCIENCIAS-ICETEX) under the project titled "FOTOLIX" grant No. ICETEX 2023-0686

**Author contributions**

All the authors contributed to the study's conception and design. D.B-M., F.M-M., L.F.R.R J.B.G-M., and A.F.B-S., performed material preparation, data collection, and analysis. D.B-M., and F.M-M wrote the first draft of the manuscript. All The authors commented on previous versions of the manuscript. All the authors read and approved the final manuscript.

## 6. References

Alpha Chemicals. (N.D.). *Black Iron Oxide – Synthetic, Typical Analysis*. Alpha Chemicals. https://0n.b5z.net/i/u/10066364/f/Black_Iron_Oxide_Synthetic_-_Spec.pdf

Amancio Frutuoso, F. K., P.S.G. Da Silva, V. E., C.V. Silva, T. F., P. Vilar, V. J., & Bezerra Dos Santos, A. (2025). Solids retention time (SRT) control in the cotreatment of leachate with domestic sewage in aerobic granular sludge systems: Impacts on system performance, operational stability, and bioresource production. *Bioresource Technology*, *415*, 131664. https://doi.org/10.1016/j.biortech.2024.131664

An, W., Xiao, S., Liu, H., & Ma, L. (2025). UV irradiation enhanced removal of ammonia nitrogen and mineralization of typical organic pollutants of high-chlorine wastewater in catalytic ozonation. *Journal of Environmental Chemical Engineering*, *13*(1), 115395. https://doi.org/10.1016/j.jece.2025.115395

Asaithambi, P., Govindarajan, R., Busier Yesuf, M., Selvakumar, P., & Alemayehu, E. (2020). Enhanced treatment of landfill leachate wastewater using sono(US)-ozone(O3)–electrocoagulation(EC) process: Role of process parameters on color, COD and electrical energy consumption. *Process Safety and Environmental Protection*, *142*, 212–218. https://doi.org/10.1016/j.psep.2020.06.024

723 Asociación Estadounidense de Salud Pública, Hidráulicas, A. E. de O., Federación
724 Ambiental del Agua. Lipps WC, EB, B.-H., & Baxter TE. (2017). *Métodos estándar*
725 *para el análisis de agua y aguas residuales* (23rd ed.). Asociación Estadounidense
726 de Salud Pública, Asociación Estadounidense de Obras Hidráulicas, Federación
727 Ambiental del Agua. Lipps WC, Braun-Howland EB, Baxter TE.
728 Babu Ponnusami, A., Sinha, S., Ashokan, H., V Paul, M., Hariharan, S. P., Arun, J.,
729 Gopinath, K. P., Hoang Le, Q., & Pugazhendhi, A. (2023). Advanced oxidation
730 process (AOP) combined biological process for wastewater treatment: A review on
731 advancements, feasibility and practicability of combined techniques. *Environmental*
732 *Research*, *237*, 116944. https://doi.org/10.1016/j.envres.2023.116944
733 Bai, F., Liu, S., Zhang, Y., & Ma, J. (2023). Effective and mechanistic insights into reverse
734 osmosis concentrate of landfill leachate treatment using coagulation-catalytic
735 ozonation-bioaugmentation-based AnMBR. *Chemical Engineering Journal*, *463*,
736 142430. https://doi.org/10.1016/j.cej.2023.142430
737 Bao, M., Fang, F., Luo, X., & Li, Q. (2024). Transformation characteristics of dissolved
738 organic matter in landfill leachate nanofiltrated concentrate during ozonation-based
739 advanced oxidation systems. *Journal of Environmental Chemical Engineering*, *12*(2),
740 112076. https://doi.org/10.1016/j.jece.2024.112076
741 Becerra, D., Soto, J., Villamizar, S., Machuca-Martínez, F., & Ramírez, L. (2020).
742 Alternative for the Treatment of Leachates Generated in a Landfill of Norte de
743 Santander–Colombia, by Means of the Coupling of a Photocatalytic and Biological
744 Aerobic Process. *Topics in Catalysis*, *63*(11–14), 1336–1349.
745 https://doi.org/10.1007/s11244-020-01284-1
746 Becerra Moreno, D., Caicedo Cáceres, N. Y., Velásquez Lázaro, C. M., Machuca Martínez,
747 F., & Soto Verjel, J. W. (2022). Heterogeneous photocatalysis and an anaerobic
748 biological process for leachate treatment. *Ciencia En Desarrollo*, *13*(2), 113–130.
749 https://doi.org/10.19053/01217488.v13.n2.2022.13851
750 Becerra Moreno, D., Rubio-Gomez, Y. M., Barajas-Solano, A. F., Ramírez Ríos, L. F., &
751 Machuca-Martínez, F. (2023). Una revisión sobre el tratamiento para lixiviados de
752 rellenos sanitarios mediante el acople de procesos avanzados de oxidación y

753 biológicos. *Ingeniería y Competitividad*, *25*(4).
754 https://doi.org/10.25100/iyc.v25i4.11626
755 Cardeña, R., Buitrón, G., Valdez-Vazquez, I., & Contreras, M. (2025). Biohydrogen
756 production from cheese whey in UASB and packed bed reactors: Impact of microbial
757 interactions on productivity. *International Journal of Hydrogen Energy*,
758 S0360319925001806. https://doi.org/10.1016/j.ijhydene.2025.01.159
759 Castillo-Suárez, L. A., Lugo-Lugo, V., Linares-Hernández, I., Martínez-Miranda, V.,
760 Esparza-Soto, M., & Mier-Quiroga, M. D. L. Á. (2019). Biodegradability index
761 enhancement of landfill leachates using a Solar Galvanic-Fenton and Galvanic-
762 Fenton system coupled to an anaerobic–aerobic bioreactor. *Solar Energy*, *188*, 989–
763 1001. https://doi.org/10.1016/j.solener.2019.07.010
764 Clemente, E., Domingues, E., Quinta-Ferreira, R. M., Leitão, A., & Martins, R. C. (2024).
765 European and African landfilling practices: An overview on MSW management,
766 leachate characterization and treatment technologies. *Journal of Water Process*
767 *Engineering*, *66*, 105931. https://doi.org/10.1016/j.jwpe.2024.105931
768 De Sousa, T. A. T., Dantas, E. R. B., Lopes, W. D. S., Leite, V. D., Sousa, J. T. D., & Lopes,
769 W. S. (2023). Toxicity assessment of sanitary landfill leachate before and after Fenton
770 treatment process. *Science of The Total Environment*, *893*, 164870.
771 https://doi.org/10.1016/j.scitotenv.2023.164870
772 Duan, Y., Gao, B., Liu, J., Wang, X., & Sillanpää, M. (2024). Treatment of landfill leachate
773 in the MBR and catalytic ozonation coupled system based on Mn Ni catalyst:
774 Efficiency and bio/chemical mechanism. *Journal of Water Process Engineering*, *66*,
775 106033. https://doi.org/10.1016/j.jwpe.2024.106033
776 Feng, H., Mao, W., Li, Y., Wang, X., & Chen, S. (2021). Characterization of dissolved
777 organic matter during the O3-based advanced oxidation of mature landfill leachate
778 with and without biological pretreatment and operating cost analysis. *Chemosphere*,
779 *271*, 129810. https://doi.org/10.1016/j.chemosphere.2021.129810
780 Fulazzaky, M. A., Yuzir, A., Messer, T., & Sofyan, A. (2024). Methanogenesis kinetics of
781 organic matter of the leachate in an upflow anaerobic sludge blanket reactor. *Waste*
782 *Management Bulletin*, *2*(4), 1–10. https://doi.org/10.1016/j.wmb.2024.08.003

Goli, T., Ahmadi, K., Pagilla, K. R., & Marchand, E. A. (2023). Dissolved organic nitrogen removal from reclaimed water by enhanced coagulation, ozonation, and biodegradation. *Journal of Water Process Engineering*, *55*, 104212. https://doi.org/10.1016/j.jwpe.2023.104212

Gu, Z., Yang, Z., Song, B., & Li, Q. (2025). Treatment of landfill leachate MBR effluent by ozone combined with a semiaerobic aged refuse bioreactor. *Journal of Water Process Engineering*, *69*, 106625. https://doi.org/10.1016/j.jwpe.2024.106625

Guerrero-Brotons, M., Gómez, R., Álvarez-Rogel, J., Sánchez-Monedero, M. Á., & Arce, M. I. (2024). The effect of leaf leachates addition on denitrification in subsurface flow constructed wetlands is shaped by the bed substrate type. *Journal of Water Process Engineering*, *68*, 106360. https://doi.org/10.1016/j.jwpe.2024.106360

Han, S., Wang, W., Xu, Z., & Qi, L. (2024). Research and perspective of heterogeneous catalytic oxidation by ozone in the removal of pollutants from industrial wastewater: A review. *Journal of Industrial and Engineering Chemistry*, S1226086X24008281. https://doi.org/10.1016/j.jiec.2024.12.015

Han, Y., Guo, J., Liu, T., Wang, N., Su, Z., Wang, S., Ma, X., Wang, J., & Zhao, F. (2025). Iron-carbon microelectrolysis and anaerobic-aerobic activated sludge integrated process for treating landfill leachate: Process optimization, stability, and mechanism. *Journal of Water Process Engineering*, *69*, 106704. https://doi.org/10.1016/j.jwpe.2024.106704

He, H., Liu, L., & Ma, H. (2023). The key regulative parameters in pilot-scale IC reactor for effective incineration landfill leachate treatment: Focus on the process performance and microbial community. *Journal of Water Process Engineering*, *51*, 103322. https://doi.org/10.1016/j.jwpe.2022.103322

Jiraprasertwong, A., Seneesrisakul, K., Pornmai, K., & Chavadej, S. (2020). High methanogenic activity of a three-stage UASB in relation to the granular sludge formation. *Science of The Total Environment*, *724*, 138145. https://doi.org/10.1016/j.scitotenv.2020.138145

Jolaosho, T. L. (2024). Characterization of potentially toxic elements in leachates from active and closed landfills in Nigeria and their effects on groundwater systems using spatial,

indexical, chemometric and health risk techniques. *Chemosphere*, *369*, 143678. https://doi.org/10.1016/j.chemosphere.2024.143678

Kalčíková, G., Tratar Pirc, E., & Žgajnar Gotvajn, A. (2016). Aerobic and anaerobic biodegradation potential of leachate from old active landfill. *Desalination and Water Treatment*, *57*(19), 8619–8625. https://doi.org/10.1080/19443994.2015.1024749

Kanmani, S., & Dileepan, A. G. B. (2023). Treatment of landfill leachate using photocatalytic based advanced oxidation process – a critical review. *Journal of Environmental Management*, *345*, 118794. https://doi.org/10.1016/j.jenvman.2023.118794

Kayan, I., Oz, N. A., & Kantar, C. (2021). Comparison of treatability of four different chlorophenol-containing wastewater by pyrite-Fenton process combined with aerobic biodegradation: Role of sludge acclimation. *Journal of Environmental Management*, *279*, 111781. https://doi.org/10.1016/j.jenvman.2020.111781

Lakshmi, A. A., & Raj, S. A. (2022). Natural gum based polymers as additives in enhancing the startup of UASB reactor treating municipal sewage—Comparative study. *Desalination and Water Treatment*, *252*, 89–97. https://doi.org/10.5004/dwt.2022.28268

Li, K., Yun, J., Zhang, H., & Yu, Z. (2019). Full-scale anaerobic reactor samples would be more suitable than lab-scale anaerobic reactor and natural samples to inoculate the wheat straw batch anaerobic digesters. *Bioresource Technology*, *293*, 122040. https://doi.org/10.1016/j.biortech.2019.122040

Li, L., Kong, Z., Xue, Y., Wang, T., Kato, H., & Li, Y.-Y. (2020). A comparative long-term operation using upflow anaerobic sludge blanket (UASB) and anaerobic membrane bioreactor (AnMBR) for the upgrading of anaerobic treatment of N,N-dimethylformamide-containing wastewater. *Science of The Total Environment*, *699*, 134370. https://doi.org/10.1016/j.scitotenv.2019.134370

Li, Y., Chen, Z., Zhou, S., Fan, J., Huang, L., Deng, Z., Zhang, C., & Wang, X. (2023). Improving stability and nitrogen removal performance of pilot-scale autotrophic process for mature landfill leachate treatment utilizing in situ organics. *Bioresource Technology*, *381*, 129118. https://doi.org/10.1016/j.biortech.2023.129118

Li, Y., Xu, H., Yi, X., Zhao, Y., Jin, F., Chen, L., & Hua, D. (2021). Study of two-phase anaerobic digestion of corn stover: Focusing on the conversion of volatile fatty acids

and microbial characteristics in UASB reactor. *Industrial Crops and Products*, *160*, 113097. https://doi.org/10.1016/j.indcrop.2020.113097

Lian, X., Wang, Z., Liu, Z., Xiong, Z., Dai, H., Yang, L., Liu, Y., Yang, J., Geng, Y., Hu, M., Shao, P., & Luo, X. (2024). A new microalgal negative carbon technology for landfill leachate treatment: Simultaneous removal of nitrogen and phosphorus. *Science of The Total Environment*, *948*, 174779. https://doi.org/10.1016/j.scitotenv.2024.174779

Lima, V. D. O., Barros, V. G. D., Duda, R. M., & Oliveira, R. A. D. (2023). Anaerobic digestion of vinasse and water treatment plant sludge increases methane production and stability of UASB reactors. *Journal of Environmental Management*, *327*, 116451. https://doi.org/10.1016/j.jenvman.2022.116451

Lin, X., Xu, L., Xiong, L., Wang, X., He, Y., Chen, H., Zhang, W., & Xue, G. (2024). Mechanistic insight into assimilation capture: Implication for high-efficiency nitrogen removal from mature landfill leachate. *Chemical Engineering Journal*, *498*, 155395. https://doi.org/10.1016/j.cej.2024.155395

Liu, S., Cai, C., Sun, F., Ma, M., An, T., & Chen, C. (2024). Advanced nitrogen removal of landfill leachate treatment with anammox process: A critical review. *Journal of Water Process Engineering*, *58*, 104756. https://doi.org/10.1016/j.jwpe.2023.104756

Liu, Z., Liu, J., Zhu, P., & Ma, Y. (2024). Interaction and coexistence characteristics of dissolved organic matter and toxic metals with per- and polyfluoroalkyl substances in landfill leachate. *Environmental Research*, *260*, 119680. https://doi.org/10.1016/j.envres.2024.119680

López-Gutiérrez, I., Montiel-Corona, V., Calderón-Soto, L. F., Palomo-Briones, R., Méndez-Acosta, H. O., Razo-Flores, E., Ontiveros-Valencia, A., & Alatriste-Mondragón, F. (2021). Evaluation of the continuous methane production from an enzymatic agave bagasse hydrolysate in suspended (CSTR) and granular biomass systems (UASB). *Fuel*, *304*, 121406. https://doi.org/10.1016/j.fuel.2021.121406

Mishra, S., Singh, V., Ormeci, B., Hussain, A., Cheng, L., & Venkiteshwaran, K. (2023). Anaerobic–aerobic treatment of wastewater and leachate: A review of process integration, system design, performance and associated energy revenue. *Journal of*

*Environmental Management*, *327*, 116898. https://doi.org/10.1016/j.jenvman.2022.116898

Moussavi, G., Khosravi, R., & Omran, N. R. (2012). Development of an efficient catalyst from magnetite ore: Characterization and catalytic potential in the ozonation of water toxic contaminants. *Applied Catalysis A: General*, *445–446*, 42–49. https://doi.org/10.1016/j.apcata.2012.08.002

Mu, S., Chen, X., Song, B., Wu, C., & Li, Q. (2022). Enhanced performance and mechanism of the combined process of ozonation and a semiaerobic aged refuse biofilter for mature landfill leachate treatment. *Chemosphere*, *308*, 136432. https://doi.org/10.1016/j.chemosphere.2022.136432

Pinpatthanapong, K., Puengpraput, T., Phattarapattamawong, S., Phalakornkule, C., Panichnumsin, P., Boonapatcharoen, N., Paensiri, P., Malila, K., Ponata, N., Ngamcharoen, T., Jutakanoke, R., Setsungnern, A., Tachapermpon, Y., Treesubsuntorn, C., & Boonnorat, J. (2023). Effect of propionate-cultured sludge augmentation on methane production from upflow anaerobic sludge blanket systems treating fresh landfill leachate. *Science of The Total Environment*, *881*, 163434. https://doi.org/10.1016/j.scitotenv.2023.163434

Ricky, R., Shanthakumar, S., & Gothandam, K. M. (2022). A pilot-scale study of the integrated phycoremediation-photolytic ozonation based municipal solid waste leachate treatment process. *Journal of Environmental Management*, *323*, 116237. https://doi.org/10.1016/j.jenvman.2022.116237

Sari, M. M., Septiariva, I. Y., Prayogo, W., Helmy, Q., & Suryawan, I. W. K. (2023). Effects of detention time and ozone dosage on organic content removal and biodegradability index in high salinity leachate. *Desalination and Water Treatment*, *284*, 81–86. https://doi.org/10.5004/dwt.2023.29271

Song, Q., Kong, F., Liu, B.-F., Song, X., Ren, N.-Q., & Ren, H.-Y. (2025). Ozone oxidation of actual waste leachate coupled with culture of microalgae for efficient lipid production under different temperatures. *Water Research*, 123305. https://doi.org/10.1016/j.watres.2025.123305

Tian, Z., Li, G., Bai, M., Hou, X., Li, X., Zhao, C., Zhu, Q., Du, C., Li, M., Liu, W., & Zhang, L. (2022). Microbial mechanisms of refractory organics degradation in old landfill

leachate by a combined process of UASB-A/O-USSB. *Science of The Total Environment*, *848*, 157737. https://doi.org/10.1016/j.scitotenv.2022.157737

Trisakti, B., Sidabutar, R., Irvan, Adriani, L., Manurung, J. F., Simbolon, D. K., Alexander, V., Takriff, Mohd. S., & Daimon, H. (2024). Effect of hydraulic retention time and effluent recycle ratio on biogas production from POME using UASB-HCPB fermentor assisted with ultrafiltration membrane at mesophilic condition. *South African Journal of Chemical Engineering*, *50*, 209–222. https://doi.org/10.1016/j.sajce.2024.08.012

Urbina-Suarez, N. A., Salcedo-Pabón, C. J., Contreras-Ropero, J. E., López-Barrera, G. L., García-Martínez, J. B., Barajas-Solano, A. F., & Machuca-Martínez, F. (2025). Biotechnological strategy for tannery wastewater treatment: Bicarbonate/H2O2 oxidation integrated with microalgae cultivation. *Case Studies in Chemical and Environmental Engineering*, *11*, 101060. https://doi.org/10.1016/j.cscee.2024.101060

VENATOR. (2017, April 26). *SAFETY DATA SHEET, SYNTHETIC BLACK IRON OXIDE BK5599*. VENATOR. https://n.b5z.net/i/u/10066364/f/Iron_Oxide_-_Synthetic_Black_SDS.PDF

Wang, H., Zhang, S., He, X., Yang, Y., Yang, X., & Van Hulle, S. W. H. (2023). Comparison of macro and micropollutants abatement from biotreated landfill leachate by single ozonation, O3/H2O2, and catalytic ozonation processes. *Chemical Engineering Journal*, *452*, 139503. https://doi.org/10.1016/j.cej.2022.139503

Wang, X., Han, M., Li, W., Liu, X., Lv, L., Gao, W., Liu, X., Sun, L., Liang, J., Zhang, G., Ren, Z., & Zhang, D. (2024). Enhanced anaerobic digestion of landfill leachate based on a novel redox mediator: Synergistic mechanism of enhancing extracellular electron transfer. *Chemical Engineering Journal*, *490*, 151649. https://doi.org/10.1016/j.cej.2024.151649

Wang, Z., Xiong, Z., Yang, L., Lai, L., Xiao, H., Ding, Y., & Luo, X. (2022). Enhancing nitrogen removal in mature landfill leachate by mixed microalgae through elimination of inhibiting factors. *Science of The Total Environment*, *828*, 154530. https://doi.org/10.1016/j.scitotenv.2022.154530

Wu, L., Yin, J., Zhang, Y., Luo, A., Tian, Y., Liu, Y., & Peng, Y. (2024). Nitrogen removal and carbon reduction of mature landfill leachate under extremely low dissolved oxygen conditions by simultaneous partial nitrification anammox and denitrification. *Bioresource Technology*, *401*, 130704. https://doi.org/10.1016/j.biortech.2024.130704

Xiao, J., Qaisar, M., Zhu, X., Li, W., Zhang, K., Liang, N., Feng, H., & Cai, J. (2024). Increasing methane production in an anaerobic membrane bioreactor for treating landfill leachate: Impact of organic concentration and HRT. *Journal of Environmental Management*, *367*, 122061. https://doi.org/10.1016/j.jenvman.2024.122061

Xiong, L., Li, X., Li, J., Zhang, Q., Zhang, L., Wu, Y., & Peng, Y. (2024). Efficient nitrogen removal from real municipal wastewater and mature landfill leachate using partial nitrification-simultaneous anammox and partial denitrification process. *Water Research*, *251*, 121088. https://doi.org/10.1016/j.watres.2023.121088

Yan, Z., Li, A., Shim, H., Wang, D., Cheng, S., Wang, Y., & Li, M. (2022). Effect of ozone pretreatment on biogranulation with partial nitritation—Anammox two stages for nitrogen removal from mature landfill leachate. *Journal of Environmental Management*, *317*, 115470. https://doi.org/10.1016/j.jenvman.2022.115470

Yang, H.-R., Li, B., Zhang, C.-Q., Yang, J.-C., Zheng, Y.-M., Younas, M., Jiang, Y.-H., & Yuan, Z.-H. (2023). Bipolar membrane electrodialysis for sustainable utilization of inorganic salts from the reverse osmosis concentration of real landfill leachate. *Separation and Purification Technology*, *308*, 122898. https://doi.org/10.1016/j.seppur.2022.122898

Yang, Y.-Z., Zhang, Y., Zhan, Y., Liu, J.-Q., Yan, C.-C., Zhang, Y., & Zhang, H.-L. (2024). Synergistic enhancement of UASB reactor for leachate treatment using Fe2O3 nanomodified pumice and ozone oxidation. *Chemical Engineering Journal*, *497*, 154891. https://doi.org/10.1016/j.cej.2024.154891

Yuan, L., Tang, R., Yao, H., Hu, Z.-H., Wang, Y., Yuan, S., & WeiWang. (2020). Start-up of partial nitrification-Anammox (PN/A) process treating piggery wastewater. *Desalination and Water Treatment*, *180*, 156–163. https://doi.org/10.5004/dwt.2020.25071

966 Yuan, Y., Liu, J., Gao, B., & Sillanpää, M. (2022). Landfill leachate treatment in-depth by
967 biochemical strategy: Microbial activation and catalytic ozonation mechanism.
968 *Chemical Engineering Journal*, *444*, 136464.
969 https://doi.org/10.1016/j.cej.2022.136464
970 Yuan, Y., Liu, J., Gao, B., Sillanpää, M., & Al-Farraj, S. (2022). The effect of activated
971 sludge treatment and catalytic ozonation on high concentration of ammonia nitrogen
972 removal from landfill leachate. *Bioresource Technology*, *361*, 127668.
973 https://doi.org/10.1016/j.biortech.2022.127668
974 Zhao, H., Zou, L., Jiang, M., Li, Y.-Y., & Liu, J. (2023). Ozone pretreatment combined with
975 partial denitrification-anammox process for efficient nitrogen removal from
976 nanofiltration concentrate of landfill leachate. *Chemical Engineering Journal*, *471*,
977 144641. https://doi.org/10.1016/j.cej.2023.144641
978 Zhe, J., He, H., Yi, Z., Guo, Z., Xu, H., Huang, B., & Pan, X. (2025). Mechanism and
979 molecular level insight of refractory dissolved organic matter in landfill leachate
980 treated by electroflocculation coupled with ozone. *Separation and Purification*
981 *Technology*, *356*, 129812. https://doi.org/10.1016/j.seppur.2024.129812
982 Zhu, Y., Luo, H., Wang, T., Zhou, J., Zhu, Y., & Hou, J. (2024). Advanced treatment of
983 landfill leachate by catalytic ozonation with MnCeOx/γ-Al2O3 catalyst. *Surfaces and*
984 *Interfaces*, *46*, 104113. https://doi.org/10.1016/j.surfin.2024.104113
985 Zou, X., Mohammed, A., Gao, M., & Liu, Y. (2022). Mature landfill leachate treatment using
986 granular sludge-based reactor (GSR) via nitritation/denitritation: Process startup and
987 optimization. *Science of The Total Environment*, *844*, 157078.
988 https://doi.org/10.1016/j.scitotenv.2022.157078
989

# Chapter 4: Heterogeneous Photocatalysis and an Anaerobic Biological Process for Leachate Treatment

Vol. 13 (núm. 2) pp. 113-130
Julio-Diciembre 2022

Ciencia en Desarrollo
Revista de la Facultad de Ciencias
Vicerrectoría en Investigación y Extensión - VIE
Centro de Investigaciones y Extensión de la Facultad de Ciencias - CIEC

https://doi.org/10.19053/01217488.v13.n2.2022.13851

# Heterogeneous Photocatalysis and an Anaerobic Biological Process for Leachate Treatment

## Fotocatálisis heterogénea y un proceso biológico anaerobio para el tratamiento de lixiviados

Dorance Becerra[1], Neldy Caicedo[2], Claudia Velásquez[3], Fiderman Machuca-Martínez[4] and Joseph Soto-Verjel[5]

**Abstract**

The research evaluates the treatment of landfill leachate by coupling $TiO_2$-$UV_{solar}$ photocatalysis and an anaerobic biological process (SMA test). The photocatalysis is developed in a Composite Parabolic Collector with an area of 0.83 $m^2$, 20L treatment tank and initial leachate concentration of 400 mg-$L^{-1}$ COD; $H_2O_2$ (fixed dose 300 mg.$L^{-1}$) as oxidation assistant and the combination of different $TiO_2$ levels (100, 350, 600 mg.$L^{-1}$) and pH (3, 6, 9). In the biological test, for a maximum load of 4,500 mg.$L^{-1}$ of COD of leachate, 2.0 g.$L^{-1}$ of VSS of inoculum and a HRT of 23 days, there were no significant percentages of COD removal, evidencing the recalcitrant character of these leachates. During the photocatalytic treatment there was a 57% DOC mineralization (100 mg.$L^{-1}$ $TiO^2$; pH = 3; Accumulated energy = 60kJ.$L^{-1}$), which evidences the capacity of the process to support the pollutant load of the leachate. The combined process (AOP-Biological) allows an additional mineralization in the biological process in terms of DOC of 21%, for a total contribution of the coupling of 78%, which demonstrates the capacity of the AOP to convert a toxic wastewater into one with characteristics more suitable for further degradation in anaerobic biological reactors.

***Keywords*:** Anaerobic biodegradability, Coupling of treatments, Heterogeneous photocatalysis, Leachate, Titanium dioxide $TiO_2$.

**Resumen**

La investigación evalúa el tratamiento de lixiviados de vertederos mediante el acoplamiento de fotocatálisis solar TiO2-UV y un proceso biológico anaeróbico (prueba SMA). La fotocatálisis se desarrolla en un Colector Parabólico Compuesto de 0.83 $m^2$ de área, tanque de tratamiento de 20 L y concentración inicial de lixiviados de 400 mg-$L^{-1}$ DQO; H2O2 (dosis fija 300 mg.$L^{-1}$) como auxiliar de oxidación y la combinación de diferentes niveles de TiO2 (100, 350, 600 mg.$L^{-1}$) y pH (3, 6, 9). En el ensayo biológico, para una carga máxima de 4500 mg.$L^{-1}$ de DQO de lixiviado, 2,0 g.L-1 de SVS de inóculo y un TRH de 23 días, no hubo porcentajes significativos de remoción de DQO, evidenciando el carácter recalcitrante de estos lixiviados. Durante el tratamiento fotocatalítico se presentó una mineralización de 57 % COD (100 mg.$L^{-1}$ TiO2; pH = 3; Energía acumulada = 60 kJ.$L^{-1}$), lo que evidencia la capacidad del proceso para soportar la carga contaminante del lixiviado. El proceso combinado (AOP-Biológico) permite una mineralización adicional en el proceso biológico en términos de DOC del 21 %, para un aporte total del acoplamiento del 78 %, lo que demuestra la capacidad del AOP para convertir un efluente tóxico en uno con características más adecuadas para su posterior degradación en reactores biológicos anaerobios.

***Palabras clave*:** Biodegradabilidad Anaeróbica, Acoplamiento de tratamientos, Fotocatálisis heterogénea, Lixiviados, Dióxido de Titanio $TiO_2$.

Recepción: 21-dic-2021
Aceptación: 15-mar-2022

[1,2,3]Facultad de Ciencias Agrarias y del Ambiente - Universidad Francisco de Paula Santander, Cúcuta, Colombia.
Email: 1dorancebm@ufps.edu.co
[1,4]Escuela de Ingeniería Sanitaria y Ambiental, GAOX, CENM, Universidad del Valle, Cali, Colombia.
[5]Departamento de Ingeniería Civil y Ambiental – Instituto de Estudios Hidráulicos y Ambientales IDEHA - Universidad del Norte, Barranquilla, Colombia.

## 1 Introduction

The current population growth and economic development are increasing, which is strongly related to the generation of urban solid waste, and this provides a challenge towards environmentally sustainable development [1, 2]. In this context, solid waste management in Latin America has been a challenge because of its continuous increase in quantity and diversity, and Colombia is a particular case since approximately 97% of the waste generated is disposed of in landfills [3], being this the most common approach but causing a problem because of the production of highly contaminated leachates [4]. Likewise, the landfill technique is one of the most used alternatives not only in the country but also in the department of Norte de Santander.

As a consequence of the compacting of solid waste in landfills, there are a series of physical and chemical changes that lead to the generation of leachates [5]. Similarly, the decomposition of these wastes and the percolation of rainwater over the cells where they are disposed to contribute to their production volume [6]. These leachates can be transported and contaminate surface and groundwater, which supports the need for adequate treatment before disposal [7-9]. The location of sanitary landfills in Norte de Santander supports the previous problem since they are built near streams or river crossings, which eventually flow into larger water sources that serve as the water supply for the population, which also highlights the impact on the communities surrounding these sites.

These leachates are characterized by a dark brown or black color with a very high concentration of chemical oxygen demand (COD), ammonia nitrogen, heavy metals, and other organic and inorganic contaminants [10], in addition, many types of contaminants of emerging concern (CECs) have been found in concentrations that may pose a risk to nearby water sources and surface water ecosystems [11], highlighting its high potential to contaminate soil and groundwater nearby, if not collected and treated. Therefore, leachate management is an important aspect [12], hence in the context where this research is developed, the technologies for the treatment and control of this residual liquid are direct recirculation to waste cells and evaporation by solar or artificial action [13, 14] but have represented little success because of technical and financial sustainability as treatment systems [15] and particularly under these alternatives is not providing a real solution to the problem, but the impact is being transported to other scenarios.

Knowing the high pollutant loads and recalcitrant characteristics of leachates, it is necessary to propose alternatives for their treatment capable of withstanding their toxic conditions, that is where the Advanced Oxidation Processes (AOP) based on the in situ generations of highly reactive oxygen species, are efficient in the decomposition and satisfactory mineralization of toxic and recalcitrant pollutants [16, 17], but the intensive use of reagents and energy that they require, makes the operating costs become a limitation of the system [18, 19], therefore, they can be implemented as a pretreatment to obtain wastewater with conditions suitable for subsequent biological treatment because the recalcitrant characteristics are reduced and the biodegradability is enhanced [20, 21]. This technique is known as AOP-Biological couplings and makes the proposed system an alternative of low energy cost, efficient removal of pollutants, and generation of non-toxic by-products [22], which provides promptly and more promising results.

Several investigations validate the AOP-Biological couplings as viable for the decontamination of leachates, as is the case of [23] who in the biological process obtained removals of 38% and 24% for COD and DOC, and after the process coupled to photocatalysis, the elimination of pollutants was favored up to 68% and 76% for COD and DOC. Similarly, [24] evaluated the efficiency of photocatalysis coupled to an anaerobic biological process mediated by SMA, for the removal of pesticides, resembling the low biodegradability and recalcitrant conditions shared with leachates, where they obtained an improvement in COD removal from 46.4% in the biological process to 72.2% after coupling. Research has also been reported, in which the coupling to the biological process achieves enhanced removal of contaminant load in leachates, as in the case of [25] who in photocatalysis obtained

a reduction of COD of 50% and after coupling to bioreactors the elimination of COD amounted to 87%.

Based on the described information, it is proposed to apply the described technique to the decontamination of leachates generated in a sanitary landfill in the department of Norte de Santander, with an ambient temperature of 33 °C and a warm climate, opting for adequate conditions to use the sun's energy as a source of UV radiation. First, the capacity of the SMA to treat the leachate is studied, then the study conditions in the AOP are optimized to determine the maximum mineralization in the operational aspects analyzed; finally, the coupling between the two processes comprises the biological process receiving the effluent coming from the AOP and thus learning how the chemical oxidation improves the conditions of the leachate for its subsequent biological degradation and enhance the degradation.

For this research, the process of heterogeneous photocatalysis catalyzed by Titanium Dioxide ($TiO_2$) Degussa P25 and photoassisted by UV solar radiation is proposed, knowing that the use of a semiconductor photocatalyst subjected to specific radiation, allows oxidation-reduction processes that make possible the removal of contaminants in leachates [26, 27] and also the use of Hydrogen Peroxide ($H_2O_2$) that works as a coadjuvant in the oxidation [28]. Such AOP is coupled to an anaerobic biological process, assisted by the SMA test following the volumetric method [29].

This study developed the heterogeneous photocatalysis process in a Response Surface method (RSM) with a factorial design in the variables of pH and catalyst concentration, as well as fixed cumulative energy ranges where the DOC response variable will be measured. Regarding the SMA biological process, the technique consists of the quantification of methane production through the use of a displacer substance. All this to apply a technological and economically viable option for the degradation of leachate, promoting the protection of natural resources and public health.

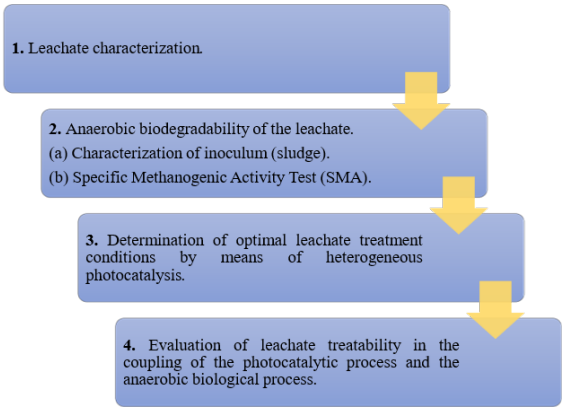



***Figure 1.*** Phases of the research process.

## 2 Materials and methods

Figure 1 illustrates the 4-phase methodological process that was carried out to meet the objectives of the research: in Phase 1, the leachate sample is taken from the landfill and characterized in the laboratory for the physicochemical parameters of interest that will be detailed further on; this summarizes the conditions of the wastewater to be treated and the starting point for the other processes. Subsequently, in phase 2, the biological part of the research is developed, which is related to the characterization of the sludge inoculum and the application of the Specific Methanogenic Activity Test, which results in the leachate's treatability under anaerobic conditions. Phase 3 comprises the development of the heterogeneous photocatalysis process, which will provide the optimum treatment conditions in terms of pH and catalyst dosage. Phase 4 comprises the coupling between the optimal processes developed in phases 2 and 3, and thus to know the contribution of the proposed system to the elimination of the pollutant load in the leachate.

All the analyses previously described were developed in the Environmental Quality Laboratories of Francisco de Paula Santander University, at Eliseos Campus, and under all the biosafety protocols required to apply the techniques, they were also based on all the guidelines proposed in the Standard Methods for the Analysis of Water and Wastewater (AWWA - APHA - WPCF) in the cases in which they were applied. The methodological phases are detailed below.

### 2.1 Leachate characterization

The characterization of the leachate was developed according to the Standard Methods for the Analysis of Water and Wastewater and the parameters analyzed: Dissolved Organic Carbon (DOC) following the protocol established in section 5310 B and using the Teledyne Tekmar TOC Torch equipment. Chemical Oxygen Demand (COD) by the closed reflux method established in section 5220 C.

The Total Suspended Solids (TSS) and the Volatile Suspended Solids (VSS) were analyzed by the Gravimetric method at 103-105 °C established in section 2540 B using an analytical balance, a desiccator for porcelain capsules and crucibles, a digital oven, and an electric muffle.

The pH and temperature parameters were taken with a multiparameter (Waterproof PCTestr 35) at the landfill on the day of leachate sample collection.

### 2.2 Leachate Anaerobic biodegradability

#### *2.2.1 Characterization of inoculum (sludge)*

The activated sludge inoculum used during the research was extracted from the second anaerobic lagoon of the wastewater treatment of the primary production process of wine palm (corozo) oil from the oil extraction plant of the Pal Norte Company, which is located in the farm La Natalia Kilometer 15 on the township of Campo Dos in the municipality of Tibú. This sludge was characterized in the physicochemical parameters of pH, temperature, TSS, VSS, and COD, to determine its effectiveness in the use of inoculation of anaerobic biological reactors. The sludge volume index (SVI) test was applied to this sludge inoculum to determine its sedimentation properties. The measurement of the physicochemical parameters listed above was developed following the standard methods for water and wastewater analysis, edition 20/AWWA-APHA-WEF.

Anaerobic sludge is favored by high values in TSS and SSV parameters because their presence indicates a higher organic loading rate and more biogas generation [30]. Temperature and pH are important and controlling factors in the use of anaerobic sludge because they significantly affect the process [31]. Finally, the characterization of these parameters allows determining that the collected sludge has optimal characteristics for the growth of microorganisms and that it is suitable for use as inoculum in biodegradability tests [24].

#### *2.2.2 Specific Methanogenic Activity (SMA) test*

This test allows quantifying the maximum methane production capacity by the group of microorganisms present in anaerobic sludge [32]. To evaluate the biodegradability of the substrate, NaOH (3%) was used as a displacing substance; it is important to maintain a pH higher than 12, to facilitate the reaction of the substrate with the $CO_2$ generated.

The theoretical methane production was calculated under the conditions of temperature and atmospheric pressure of SMA development and was corrected according to the expression described in equation 1 [33]:

$$K(t) = \frac{P * K}{R * (273 * T)} \tag{1}$$

Where:

- $K(t)$ is the correction factor (gCOD.L$^{-1}$).
- $P$ the atmosphere pressure ($atm$).
- $R$ the constant of gases (0.08206 atm.L. (mol. °C)$^{-1}$).
- $K$ is the digested organic load corresponding to one mole of $CH_4$ (64 gCOD.mol$^{-1}$).
- $T$ the operational temperature of the assembly (°C).

To conduct the test, a concentration of 2.0 gVSS.L$^{-1}$ of inoculum sludge was used because it was a test without agitation. The volume of sludge to be added was calculated considering that the mixture of inoculum and substrate should not exceed 90% of the useful volume of the biological reactor (900 ml); it was calculated as follows [29] according equation (2).

$$V_{sludge} = \frac{V_{mixture} * C_{fixed}}{C_{initialsludge}} \tag{2}$$

This type of test can be performed with DOC concentrations ranging from 3,500 - 4,500 mg.L$^{-1}$ for the substrate [29] since this test does not involve agitation. In addition, the addition of a certain amount of nutrients is required to make the degradation kinetics in the reactor approach a zero-order reaction, depending only on the concentration of microorganisms present in the inoculum.

The location of Reactor 1 ($R_1$) should be at a higher level than Reactor 2 ($R_2$), which prevents $R_1$ from being affected in case of sodium hydroxide (NaOH) suction due to negative pressures. In addition, the hose inside $R_2$ is placed in a "U" shape to act as a barrier and hinder the passage of NaOH to $R_1$. Figure 2 details the process earlier described.

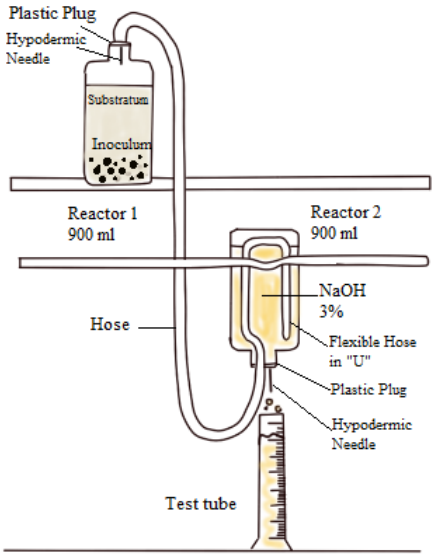



***Figure 2.*** SMA assembly. Adapted from [29].

Considering the methane production, the specific methanogenic activity (SMA) is calculated from the expression described in equation 3.

$$SMA\left(\frac{gCOD}{gVSS*d}\right)=\frac{m*24}{V_{CH4}*M} \tag{3}$$

Where:

- $m$ is the maximum slope of the methane production curve (Vol. accumulated $CH_4$ vs time).
- $M$ the sludge mass ($Volume of sludge added * Initial sludge concentration$) $(g)$.
- $V_{CH_4}$ the theoretical volume of methane produced $(L)$.

For the calculation of the slope $(m)$ a curve of "Accumulated $CH_4$ volume" vs "Test time" must be constructed, the latter may be suspended once the curve becomes asymptotic [29].

The theoretical volume of methane is calculated with the expression described in equation 4:

$$V_{CH4}=\frac{COD_{CH4}}{K(t)} \tag{4}$$

Where:

- $V_{CH_4}$ is the theoretical volume of methane produced $(L)$.
- $COD_{CH_4}$ is the COD load removed in $R_1$ and converted to methane $(gCOD)$.

### 2.3 Optimal conditions for leachate treatment using heterogeneous photocatalysis

The photocatalytic decomposition of the leachate was performed by heterogeneous photocatalysis, using a laboratory-scale solar Cylindrical Parabolic Collector (CPC), with an approximate reaction volume of 20 L, area of 0.83 m$^2$, composed of two aluminum parabolic structures which refract the light, equipped with borosilicate glass tubes through which the fluid circulates, secured in a concrete structure. This CPC configuration of the photocatalytic reactor is the most widely used in water treatment because it combines an efficient radiant field and suitable hydrodynamic conditions in the removal of various pollutants, as well as in other engineering applications [34-36].

$TiO_2$ (Degussa P-25) was used as catalyst [34, 37, 38]. $H_2O_2$ was used as the oxidizing agent, which is highly efficient when used in the development of wastewater decontamination treatments, mainly because of the generation of OH radicals, which enhance the removal of pollutants [39, 40], as showed by some investigations where the addition of $H_2O_2$ to the system led to an improvement in the average removal of pollutants than the $TiO_2$-UV system alone [41].

UV radiation favors the generation of hydroxyl radicals since they irradiate the TiO2 nanoparticles to produce photogenerating holes where oxidation reactions take place for the removal of the studied pollutants [42]. Similarly, various investigations on photocatalytic processes have determined that they achieved high pollutant mineralizations at cumulative energies greater than 100 kJ.L$^{-1}$ [43, 44] and considering that the aim of this phase is to eliminate only a percentage of the pollutant load to be subsequently subjected to the anaerobic biological process (coupling), a range of accumulated working energy from 220 kJ.L$^{-1}$ a 60 kJ.L$^{-1}$. is established.

The problem sample was prepared in the CPC tank, equipped with a 0.5 HP Humboldt pump and $Q_{\max}$ of 32 L.min$^{-1}$. The UV radiation measurement was conducted with an adaptation of a pyranometer functioning as a solar radiation sensor, connected to a multimeter. A general scheme of the photocatalytic reactor is shown in Figure 3.

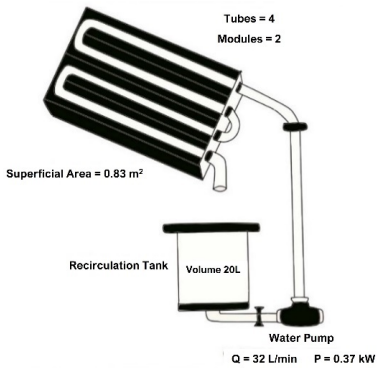



***Figure 3.*** Scheme of the photocatalytic process.

Response Surface Method (RSM) is a statistical tool based on fitting a polynomial equation to experimental data and has been applied to heterogeneous photocatalysis processes having $TiO_2$ dose and pH level as independent variables in response to pollutant removal [45, 46]. Therefore, in this research, the statistical program Statgraphics Centurion XV was used to combine randomly the various experiments associated with the catalyst dose of 100, 350 y 600 mg.L$^{-1}$ of $TiO_2$ and the pH levels 3, 6, and 9, under a factorial design $3^2$. The 9 randomized experiments with their $TiO_2$-pH combinations are represented in Table 1.

The selection of $TiO_2$ and pH levels allows establishing a wide working range to know the behavior of the elimination of the pollutant load present in the leachates under the described operating conditions and thus, through the optimization of the results, to choose the most adequate operating condition in terms of economic and treatment efficiency.

***Table 1.*** Photocatalysis optimization experiments.

| Experiment | $TiO_2$ Concentration (mg.L$^{-1}$) | pH |
|---|---|---|
| 1 | 100 | 9 |
| 2 | 350 | 6 |
| 3 | 600 | 3 |
| 4 | 600 | 9 |
| 5 | 600 | 6 |
| 6 | 100 | 3 |
| 7 | 100 | 6 |
| 8 | 350 | 9 |
| 9 | 350 | 3 |

The number of experiments described in Table 1 was carried out considering the established amounts of catalyst and pH units, constant concentrations of leachate (in terms of COD according to the characterization results), and $H_2O_2$. The duration or hydraulic retention time (HRT) of each test was a function of the solar radiation and therefore of the maximum accumulated energy reached, which depended on the climatic conditions of the area where the project was developed.

It is important to highlight that, during each test, the accumulated energy readings were taken in 10-minute intervals that define the time lapses. Subsequently, the mathematical conversion that 1 mV represents 5 W.m$^{-2}$ must be applied because the results obtained directly are from the Multimeter reading, which gives the values in units of mV. Finally, equation 5 is applied to calculate the energy in the units of interest.

$$Q_n = Q_{n-1} + \Delta t_n * I_n * A_f * V_T^{-1} \qquad (5)$$

Where:

$Q_n$: total accumulated energy kJ.L$^{-1}$.

$Q_{n-1}$: previous accumulated energy kJ.L$^{-1}$.

$\Delta t_n$: irradiation time (600 seg).

$I_n$: average irradation (W.m$^{-2}$ UV).

$A_f$: irradiated reactor surface (0,83 $m^2$).

$V_T$: volume discussed (20 L).

Similarly, samples of the treated solution were collected at the beginning 0 $kJ.L^{-1}$, at the intermediates of 20 $kJ.L^{-1}$ y 40 $kJ.L^{-1}$ and at the end of the process of 60 $kJ.L^{-1}$. The stored samples were monitored by COD and DOC to determine the degree of mineralization of contaminants present in the leachate.

### 2.4 Leachate treatability in the coupling of the photocatalytic process and the anaerobic biological process

This stage evaluates heterogeneous photocatalysis as a pretreatment before the anaerobic biological process to assess whether chemical oxidation can improve conditions in biological oxidation. This coupling allows the fact that the structures of the pollutants are modified to convert them into less toxic and more biodegradable by-products [20, 22], being able to be disposed of without causing drastic alterations in the environment.

The methodological design used in this part of the research consisted of running the two treatments in sequence: first, the leachate is treated by heterogeneous photocatalysis, and then the effluent from this process is the input for the specific methanogenic activity test (anaerobic biological process). In this case, the advanced oxidation process is evaluated with the optimal experiment found during the experimental development in section 2.3., in terms of catalyst dose, pH level, and accumulated energy; the effluent leaving the AOP is the input for the SMA test, where the whole process described in section 2.2.2 is developed again.

Finally, the treatment ends when the specific methanogenic activity test is completed, where the VSS, TSS, and DOC parameters were monitored during its development, finally reporting the contribution that the coupled process has towards the elimination of pollutants and concluding if the previous chemical oxidation process ($TiO_2$-$UV_{solar}$ heterogeneous photocatalysis) improves or not the conditions of the toxic effluent for its subsequent degradation in anaerobic biological reactors and if the use of the coupled processes is much better than developing each process separately, enhancing the efficiency of the treatment.

## 3 Results and analysis

### 3.1 Characterization of the leachate

Samples of the problem leachate were taken from the main leachate collection point, coming from the solid waste compaction cells. Each of the samples taken was characterized to get an approximate range of the contaminant load for subsequent treatment and were analyzed by COD, DOC, TSS, VSS, pH, and temperature parameters, the latter two being measured at the collection point with a multiparameter, extracting a sample of the leachate in a beaker. The results of this first phase of the research are detailed in Table 2.

***Table 2.*** Leachate characterization results.

| Parameter | Units | Value |
|---|---|---|
| COD | mg $O_2.L^{-1}$ | 7,920 – 8,334.36 |
| DOC | $mg.L^{-1}C$ | 2,756 – 2,777.59 |
| TSS | $mg.L^{-1}$ | 18,860 – 19,965.33 |
| VSS | $mg.L^{-1}$ | 8,192 – 8,821.33 |
| pH | - | 7.29 – 7.8 |
| Temperature | °C | 32.6 – 33.2 |

The results obtained in Table 2 allow inferring that the leachate presents high concentrations of DOC, which classifies it as young since mature leachates usually have a lower concentration of this physicochemical parameter [47] since the contaminants are more stabilized. This result is consistent because the target sample was taken from the key point of generation, i.e., the leachate comes directly from the disposal cells.

Similarly, [48] determined that those landfills in which only ordinary waste is treated stand out for high concentrations of organic matter in terms of TOC and BOD, which supports the DOC value reported in Table 2 and knowing that the leachate comes from ordinary solid waste disposal cells.

Leachates have recalcitrant characteristics that make them poorly biodegradable, this condition is calculated based on the $BOD_5$/COD ratio and is normally less than 0.3 for these cases [49], however

[50] validated the calculation of biodegradability as the DOC/COD ratio for leachates, having for our case a value of 0.34, which can corroborate the low biodegradability of this waste liquid [27].

The TSS and VSS contents reinforce the high content of organic matter present in the leachate. The pH condition classifies it in a value close to neutrality, while the temperature recorded is consistent with the landfill location area (min 24 °C – max 34 °C).

It is important to clarify that the physicochemical properties of the leachates are highly variable, attributing the reason to various factors such as the composition and depth of the waste, the availability of moisture and oxygen, the design and operation of the landfill, the age of the waste, the precipitation rate, among others [51].

## 3.2 Anaerobic biodegradability of leachate in biological reactors

### *3.2.1 Characterization of the inoculum (sludge)*

The parameters analyzed in the anaerobic sludge were Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), Chemical Oxygen Demand (COD), pH, and Temperature, and its sedimentability was determined using the Sludge Volumetric Index (SVI). The results of the inoculum characterization are presented in Table 3.

***Table 3.*** Results of sludge characterization (inoculum).

| Parameter | Unit | Value |
|---|---|---|
| pH | - | 6.6 -7.1 |
| Temperature (T) | °C | 39 – 40.6 |
| COD | $mgO_2.L^{-1}$ | 6,900 |
| TSS | $mg.L^{-1}$ | 24,124 |
| VSS | $mg.L^{-1}$ | 13,460 |
| VSS/TSS | - | 0.557 |
| SVI | $ml.g^{-1}$ | 13.265 |

The results in Table 3 allow inferring that the sludge inoculum presents a suitable state for the growth of anaerobic microorganisms and methane production, according to the ranges reported by [52], pH of 6.5 to 7.5 and temperatures higher than 35°C.

The concentration of de 24,124 $mg.L^{-1}$ of TSS and 13,460 $mg.L^{-1}$ of VSS and their ratio of 0.557, show a sludge with outstanding characteristics because of having a high content of microorganisms [52]. The SVI value of 13.256 $ml.g^{-1}$, places it within the range of sludge of excellent sedimentability, since a sludge with excellent sedimentation characteristics is considered having an SVI value below 80 $ml.g^{-1}$ [53]. These results categorize the analyzed sludge as suitable to be inoculum in anaerobic biological reactors, favoring the degradation of the leachate.

### *3.2.2 Evaluation of the biological treatment (SMA)*

The biodegradability test was conducted in 7 different reactors, each with a storage capacity of 900 ml. The first 3 corresponded to tests with leachate from the landfill ($R_1$, $R_2$, $R_3$). The next two contained Volatile Fatty Acids (VFA) ($R_4$ and $R_5$). And the last two contained samples of the previously inoculated sludge ($R_6$ and $R_7$). Figure 4 shows the scheme described above.


***Figure 4.*** Biological process assembly (SMA).

Reactors $R_6$ to $R_7$ contained as feed a mineral medium containing macronutrients ($N\text{-}NH^{4+}$, $P\text{-}PO_4^{3-}$, Mg, Ca) and micronutrients (Fe, Ni, Zn, Co), alkalinity ($NaHCO_3$ o $KH_2PO_4$ + $K_2HPO_4$), and a reducing agent ($Na_2S.7H_2O$). The reactors $R_4 and R_5$ contained as substrate a mixture of VFA (acetic-$C_2$, propionic-$C_3$, and butyric-$C_4$) [29]. Table 4 describes the culture media for each reactor with their corresponding addition volumes.

With reactors, $R_1$, $R_2$ and $R_3$ the degradation of the leachate was evaluated, while with $R_4$ and $R_5$ the effectiveness of the sludge against a substrate other than the leachate, in this case, AFVs, was determined.

***Table 4.*** Culture media for the SMA reactors.

| Culture medium | Unit | Reactors | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | $R_6$ | $R_7$ |
| Nutrients | ml | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| VFA | ml | - | - | - | 4 | 4 | - | - |
| Sludge | ml | 149 | 149 | 149 | 149 | 149 | 149 | 149 |
| Leachate | ml | 568 | 568 | 568 | - | - | - | - |
| Deionised water | ml | 281 | 281 | 281 | 845 | 845 | 849 | 849 |

Finally, reactors $R_6$ and $R_7$ were established as the targets to evaluate the sludge behavior.

The HRT was divided into two phases: the first phase corresponded to the initial set-up of the biological test in the SMA, which was carried out over 15 days, and where the acclimatization of the microorganisms was sought. The second phase corresponded to the reseeding of the reactors, which took place over 8 days and aimed to determine the percentage of leachate degradation after the previous acclimatization of the microorganisms.

Finally, an HRT was obtained for the biological process of 23 continuous days, in which samples were taken of the displaced volume of NaOH in each reactor, this was done twice a day at regular time intervals. It is important to ensure a temperature between 27°C and 34°C since this is the condition for the growth of methanogenic microorganisms [54].

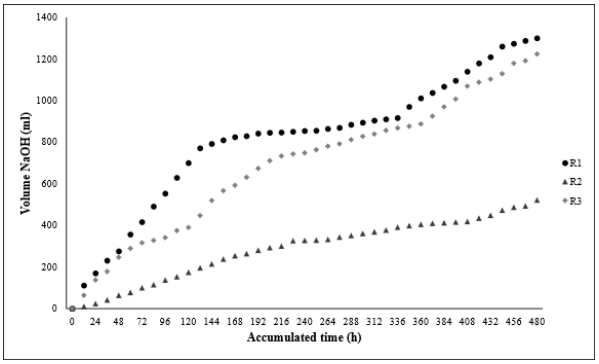



***Figure 5.*** NaOH production in the SMA.

In the first 8 days of treatment, an extensive amount of NaOH was produced, because of the development of the first phase of anaerobic digestion (hydrolysis), which comprises the breakdown of complex organic molecules [55]. While in the following 7 days, methane production was minimal compared to the initial days, since the bacteria were acclimatized, however, methane production rose again in the last 8 days, since for this period the reactors were reseeded, in this second phase the anaerobic microorganisms were adapted to the substrate. The accumulated volume during the biological test was 1300 ml for $R_1$ (leachate reactor), 521.2 ml for $R_2$ (VFA reactor) and 1223.5 ml for $R_3$ (white reactor). Figure 5 shows the results presented above.

The results of the parameters analyzed for the biological test in the 3 reactors during assembly and reseeding are presented in Tables 5 and 6 ($R_1$-Leachate, $R_2$-VFA, $R_3$-White).

***Table 5.*** Results of the SMA biological test in the first phase.

| | SMA gCOD.(gVSS.d)$^{-1}$ | COD ($mgO_2.L^{-1}$) | | TSS($g.L^{-1}$) | |
|---|---|---|---|---|---|
| | | I | F | I | F |
| $R_1$ | 1.697 | 44,800 | 54,400 | 13.8 | 16.42 |
| $R_2$ | 4.892 | 8,147.2 | 12,160 | 6.95 | 10.21 |
| $R_3$ | 2.133 | 4,499.2 | 8,998.4 | 6.72 | 7.86 |

| | VSS ($g.L^{-1}$) | | VSS/TSS | | DOC ($mg.L^{-1}$) | |
|---|---|---|---|---|---|---|
| | I | F | I | F | I | F |
| $R_1$ | 6.61 | 6.89 | 0.47 | 0.41 | 6,546.18 | 574.62 |
| $R_2$ | 4.26 | 6.81 | 0.61 | 0.60 | 1,056.61 | 161.15 |
| $R_3$ | 3.98 | 4.57 | 0.59 | 0.58 | 8,57.18 | 173.06 |

**Nota:** I: Initial phase. F: Final phase.

***Table 6.*** Results of the SMA biological test in the second phase.

| | SMA gCOD.(gVSS.d)$^{-1}$ | COD ($mgO_2.L^{-1}$) | | TSS ($g.L^{-1}$) | |
|---|---|---|---|---|---|
| | | I | F | I | F |
| $R_1$ | 2.236 | 48,000 | 96,000 | 16.02 | 16.28 |
| $R_2$ | 5.644 | 20,800 | 12,800 | 8.32 | 9.08 |
| $R_3$ | 2.361 | 14,400 | 9,600 | 8.09 | 10.65 |

| | VSS ($g.L^{-1}$) | | VSS/TSS | | DOC ($mg.L^{-1}$) | |
|---|---|---|---|---|---|---|
| | I | F | I | F | I | F |
| $R_1$ | 7.71 | 6.94 | 0.48 | 0.42 | 6,033.95 | 3,763.85 |
| $R_2$ | 5.23 | 6.06 | 0.62 | 0.66 | 780.52 | 614.07 |
| $R_3$ | 5.25 | 7.22 | 0.64 | 0.67 | 554.20 | 562.71 |

**Nota:** I: Initial phase. F: Last phase.

Methane production is increased, which is a mixture of methane and carbon dioxide, and the carbon dioxide is removed by a sodium hydroxide solution, so only methane is measured, which are presented in the second phase are because of the degradation of organic matter for the three reactors,

as shown by the COD data (Table 5 and 6). It should be noted that the COD for $R_1$ (leachate) did not present degradation (Table 5 and 6). However, this does not mean that no CH4 production occurred, but on the contrary, in $R_1$ two processes occurred simultaneously, the degradation of organic matter and cell lysis, which because of the toxicity of the substrate, comprises the rupture of the cell membrane of the bacteria presenting a release of intracellular material [55], which directly affects the amount of organic matter in the reactor.

The COD values during the first phase suffered an increase mainly because of the acclimatization of the microorganisms [55], similarly generating an organic matter removal of 0%; while in the second phase the COD increased again for $R_1$ (there was no degradation), while the COD for $R_2$ and $R_3$ decreased, presenting a removal efficiency of 38.46% and 53.13%.

In addition, it was observed that both TSS and VSS increased for the 3 reactors in the first phase, since the microorganisms were in a process of acclimatization, and cell lysis occurred [55]. While the VSS/TSS ratio decreased because of the increase in DOC, showing a reduction in the microorganisms present in the reactors. For the second phase, the TSS increased for $R_1$ because the substrate was very toxic, producing the death of some microorganisms, while the VSS decreased due to the increase in DOC, this means that in the reactors there was a greater presence of inorganic than organic matter. On the other hand, in reactors $R_2$ and $R_3$ there was an increase in the TSS, due to the decrease of feed in the reactors, but the VSS of these reactors increased due to the decrease of COD.

The results of the mineralization measured in DOC for the first phase were 91.22%, 84.74%, and 79.87%, for $R_1$, $R_2$ y $R_3$ respectively, while for the second phase there was less mineralization for the reactors evaluated, which is evidenced in the percentages of 37.63%, 21.32%, and 0%.

According to the results, it was possible to establish that anaerobic biological treatment alone is not efficient for leachate treatment, so integrated systems should be implemented because a single technology cannot achieve the expected treatment and a preliminary treatment is recommended to stabilize the concentration of contaminants [56,57]. However, several authors have got high degradations in terms of COD under anaerobic biological treatments such as the UASB reactor, but high costs were reported in the complete removal of contaminants [58,59], similarly [60] got COD degradations of less than 50% under the same technology and under long treatment times (310 days).

Even with the identified limitations, in wastewater treatment, anaerobic processes have gained importance and special attention mainly because of their economic merits over aerobic biological systems [61].

### 3.3 Optimal conditions for leachate treatment by photocatalysis

The leachate sample used for treatment was 1.02 L, which was mixed with water to complete 20 L of solution, to obtain a concentration of 400 $mgO_2.L^{-1}$ of COD of the pollutant load, because it seeks to treat the concentration range used and accepted in the anaerobic biological process, additionally it can have a better performance, since it would reduce the turbidity level that could prevent the solar rays from passing through the entire influent, preventing the absorption of light in the solution and the adsorption of pollutants on the surface of the catalyst [62].

The concentrations of $TiO_2$ comprised 100, 350 and 600 $mg.L^{-1}$ and pH values of 3, 6, and 9 units, as established for each assay. The oxidant ($H_2O_2$) was worked constantly with a concentration of 300 $mg.L^{-1}$, a value optimized by [63] in a photocatalytic leachate treatment using ($TiO_2$/UV). When the solution to be treated was ready, it was recirculated through the solar reactor, until the accumulated energy of 60 $kJ.L^{-1}$ was achieved.

The results from each test are presented in Table 7, which show that at basic (high) pH the system does not have a good performance, reaching removal percentages below 50%, these values could be explained considering that at pH values above the isoelectric point of $TiO_2$ (pH = 6.5) the adsorption of organic matter decreases [64]. With acid pH high efficiencies are achieved, hence the optimum dose to perform the coupling, according to the

mineralization percentages is 100 mg.L$^{-1}$ de $TiO_2$at a pH of 3 units.

***Table 7.*** Photocatalysis results.

| $TiO_2$ Concentration (mg.L$^{-1}$) | HRT (h) | DOC mg.L$^{-1}$ | | Mineralization (%) |
|---|---|---|---|---|
| pH 9 | | | | |
| 100 | 1.5 | I | 183.146 | 1.427 |
| | | F | 180.532 | |
| 350 | 1.5 | I | 190.766 | 8.900 |
| | | F | 173.786 | |
| 600 | 2 | I | 62.527 | 22.436 |
| | | F | 48.498 | |
| pH 6 | | | | |
| 100 | 1.66 | I | 182.554 | 23.894 |
| | | F | 138.934 | |
| 350 | 4.66 | I | 178.152 | 7.185 |
| | | F | 165.351 | |
| 600 | 2.83 | I | 169.432 | 5.016 |
| | | F | 160.932 | |
| pH 3 | | | | |
| 100 | 4.16 | I | 174.590 | 57.907 |
| | | F | 73.506 | |
| 350 | 4.66 | I | 103.312 | 29.846 |
| | | F | 72.487 | |
| 600 | 2.83 | I | 144.286 | 12.479 |
| | | F | 126.280 | |

**Nota:** I: Initial. F: Final.

It is important to highlight that acidic solutions help the adsorption of the pollutant on the surface of the $TiO_2$ catalyst, similarly favoring the percentage of degradation in the photocatalytic process [65]. This is justified by several investigations that have shown that at acidic pH the surface of the catalyst is positively charged, which leads to the attraction of negatively charged organic pollutant compounds, generating an important photocatalytic activity [66, 67]. Similarly, the best results for heterogeneous photocatalysis are obtained at acidic pH [68, 69].

The photocatalytic process achieved a mineralization of 57.90% in terms of DOC for the highest energy, corroborating this using the results of the Response Surface Analysis performed by Statgraphics software as shown in Figure 6.

Considering the interpretation of DOC as total mineralization of carbonaceous organic matter [70], and analyzing the behavior of the parameter, it is

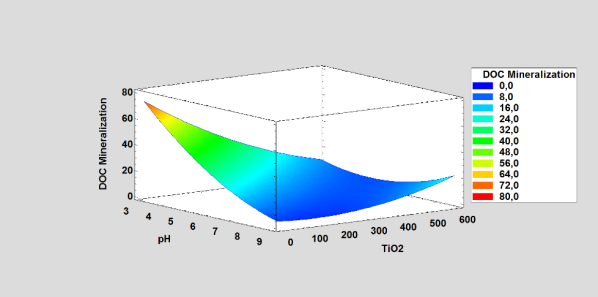



***Figure 6.*** Response Surface.

identified that the treated problem sample was mineralized in 57.907 % for the maximum accumulated energy evaluated (60 kJ.L$^{-1}$). This result is acceptable since the effluent is not required to present a total degradation since it will serve as pretreatment in front of the biological process.

According to the above, photocatalysis cannot be disqualified as an alternative to treat leachate, since the main interest is to make a coupling with biological processes, where this partially decontaminated effluent is polished by the action of the microorganisms of the biological reactor, which is justified because the AOPs emerge as an adequate pretreatment because chemical oxidation allows eliminating non-biodegradable and hazardous compounds, and in combination with a biological process significantly reduces costs [57, 71].

### 3.4 Treatability of the leachate in the coupling of the photocatalytic process and the anaerobic biological process

The first stage of the coupling comprised the evaluation of the photocatalytic process by performing the test again with the optimum dose (concentration of 100 mg.L$^{-1}$ of $TiO_2$ at a pH of 3 units), obtaining a mineralization percentage of 56.56%, with an HRT of 3.40 hours. The lower HRT reported than the previous one, which was 4.66 hours, is because of this optimum test the solar radiation conditions were stronger, i.e., the day was sunnier.

The second stage consisted of evaluating the treatability of the effluent produced in the photocatalytic test, which became the effluent of the biological test. Here, only the physicochemical parameter of DOC was analyzed, which was used as a

comparison input for the subsequent anaerobic biological degradation and to measure the efficiency of the AOP.

The assembly of the biological coupling test (SMA) lasted 23 continuous days similarly: one day 1, the initial assembly was carried out with the conditions described in the method, remaining similar for the first 15 days. After this, a reseeding was carried out, which comprised adding the same concentrations of the problem sample: VFA and nutrients as one day 1, to have acclimatized sludge and getting better yields, ending the test after the following 8 days.

Table 8 summarizes the results of the mineralization percentages in terms of DOC in each of the treatment phases applied for the decontamination of the landfill leachate.

***Table 8.*** Mineralization in each treatment phase.

| Parameter | Anaerobic biological test | Heterogeneous photocatalysis | Coupling |
|---|---|---|---|
| DOC | Mineralization (%) | | |
| | 0 | 57 | 78 |

According to the information described in Table 8, the development of the anaerobic biological process alone did not provide any pollutant degradation because of the recalcitrant characteristics of the leachate, as mentioned in the previous section regarding this phase of the research. The heterogeneous photocatalysis process with SMA contributed a 57% mineralization of the leachate in terms of DOC, which corroborated the capacity of these AOPs to treat non-biodegradable substances and with toxic compounds.

Finally, the combination of the two processes provided an increase in leachate mineralization of 21% in terms of DOC, for a total contribution of 78% of the coupling, which shows the capacity of the AOP as a strong pretreatment to convert toxic wastewater into another with more suitable characteristics for subsequent degradation in anaerobic biological reactors, which is showed by the capacity of the SMA to receive the treated effluent and provide an additional mineralization of 21%, about the first test conducted where there was no mineralization.

The treatment time of the coupling was less than 24 days: biological treatment of 23 days and photocatalytic treatment of 3.4 hours, which shows an efficient and low-cost alternative since the AOP-Biological configuration reduces the time of chemical oxidation and enhances biological oxidation, which contributes to the decrease in treatment costs and improves process efficiencies.

Current research validates the results obtained, such as the case of [72] who with a treatment between a bioreactor with anoxic conditions and a $TiO_2$/UV photocatalysis process achieved 82% COD removal from a leachate, under optimal conditions of acid pH and the second-lowest catalyst dose. [73] treated landfill leachate under a system combining an advanced process and an anaerobic biological process and found that the biological alone provided 11.9% COD removal, while the coupling of the two systems provided 68% COD removal for the same parameter, concluding that the coupling reduces reagent consumption and costs.

## 4 Conclusions

Heterogeneous photocatalysis as a primary treatment presented good degradation yields (57.90%), with 100 $mg.L^{-1}$ de $TiO_2$ being the concentration with the best performance, since the lower the turbidity, the greater the absorption of light in the solution, indicating that photocatalysis presents good yields in acid solutions since they help $TiO_2$ to better adsorb the contaminants on the surface of the catalyst.

In the first phase of the biological process (SMA), there was no biodegradation of the organic load in the three reactors, since during this period, the microorganisms acclimatized to the operating conditions. In the second phase, in R1, there was no COD removal, showing that the leachate had high toxicity and low biodegradability (despite the results obtained in its characterization), while in $R_2$ y $R_3$ percentages of 38.46% and 53.13% were generated, respectively, indicating that the inoculum was not a limiting factor in the biodegradation process. Consequently, it can be concluded that the toxicity and biodegradability of a substance are directly related, since the higher the level of inhibition of the microorganisms, the lower the percentage of biodegradability.

For accumulated energies of maximum 60 kJ.L$^{-1}$ photocatalysis acts on the leachate, transforming it into less toxic and more biodegradable substances without completely mineralizing it.

During the biological process of the coupling, the yield of $R_1$ (leachate sample) is attributed to the previous treatability of the leachate in the photocatalytic process, which generated an effluent assimilable by the microorganisms facilitating the degradation identifying better yields compared to the anaerobic biological process alone. This is because photocatalysis is efficient for non-biodegradable pollutants and biological treatments are always the most economical processes, therefore, only when the pollutants are difficult to degrade, photocatalytic processes are suitable.

The mineralization rate of photocatalysis for leachate treatment is higher compared to the mineralization rate presented in biological reactors. Through the photocatalytic processes, DOC removals of 57.90% are achieved in 4.16 hours (the time it took to reach cumulative energy of 60 kJ.L$^{-1}$), while in the biological coupling process the additional contribution was 21% in 23 days.

## Author's contributions

This work was planned, executed, and discussed by all authors in equal contribution.

## Acknowledgments

This work was supported by the Universidad Francisco de Paula Santander, Cucuta, Colombia. Machuca thanks the Universidad del Valle Colombia for supporting the work

## References

[1] A. V. Shah, V. K. Srivastava, S. S. Mohanty, S. Varjani, Municipal solid waste as a sustainable resource for energy production: State-of-the-art review, *J. Environ. Chem. Eng.* 9 (2021) 105717. https://doi.org/10.1016/j.jece.2021.105717

[2] P. R. Yaashikaa, P. S. Kumar, A. Saravanan, S. Varjani, R. Ramamurthy, Bioconversion of municipal solid waste into bio-based products: A review on valorisation and sustainable approach for circular bioeconomy, *Sci. Total Environ.* 748 (2020) 141312. https://doi.org/10.1016/j.scitotenv.2020.141312

[3] A. J. Calderón Márquez, E. W. Rutkowski, Waste management drivers towards a circular economy in the global south – The Colombian case, Waste Manag. 110 (2020) 53-65. https://doi.org/10.1016/j.wasman.2020.05.016

[4] H. Luo, Y. Zeng, Y. Cheng, D. He, X. Pan, Recent advances in municipal landfill leachate: A review focusing on its characteristics, treatment, and toxicity assessment, *Sci. Total Environ.* 703 (2020) 135468. https://doi.org/10.1016/j.scitotenv.2019.135468

[5] T. Setiadi, S. Fairus, Hazardous waste landfill leachate treatment using an activated sludge-membrane system, Water Sci. Technol. 48 (2003) 111-117. https://doi.org/10.2166/wst.2003.0459

[6] C. Pastore, E. Barca, G. Del Moro, C. Di Iaconi, M. Loos, H.P. Singer, G. Mascolo, Comparison of different types of landfill leachate treatments by employment of nontarget screening to identify residual refractory organics and principal component analysis, *Sci. Total Environ.* 635 (2018) 984-994. https://doi.org/10.1016/j.scitotenv.2018.04.135

[7] K. Parameswari, A. Majid Salim Al Aamri, K. Gopalakrishnan, S. Arunachalam, A. Ali Said Al Alawi, T. Sivasakthivel, Sustainable landfill design for effective municipal solid waste management for resource and energy recovery, *Mater. Today Proc.* (2021). https://doi.org/10.1016/j.matpr.2021.04.528

[8] D. Fatta, A. Papadopoulos, M. Loizidou, A study on the landfill leachate and its impact on the groundwater quality of the greater area, Environ. *Geochem. Health.* 21 (1999) 175-190. https://doi.org/10.1023/A:1006613530137

[9] W. Sornil, Solid Waste Management Planning Using Multi-Objective Genetic Algorithm, *J.*

*Solid Waste Technol. Manag.* 40 (2014) 33-43. https://doi.org/10.5276/JSWTM.2014.33

[10] P. Gautam, S. Kumar, Characterisation of Hazardous Waste Landfill Leachate and its Reliance on Landfill Age and Seasonal Variation: A Statistical Approach, *J. Environ. Chem. Eng.* 9 (2021) 105496. https://doi.org/10.1016/j.jece.2021.105496

[11] V. R. Propp, A. O. De Silva, C. Spencer, S. J. Brown, S. D. Catingan, J. E. Smith, J. W. Roy, Organic contaminants of emerging concern in leachate of historic municipal landfills, *Environ. Pollut.* 276 (2021) 116474. https://doi.org/10.1016/j.envpol.2021.116474

[12] H. Najafi Saleh, S. Valipoor, A. Zarei, M. Yousefi, F. Baghal Asghari, A. A. Mohammadi, F. Amiri, S. Ghalehaskar, A. Mousavi Khaneghah, Assessment of groundwater quality around municipal solid waste landfill by using Water Quality Index for groundwater resources and multivariate statistical technique: a case study of the landfill site, Qaem Shahr City, Iran, Environ. *Geochem. Health.* 42 (2020) 1305-1319. https://doi.org/10.1007/s10653-019-00417-0

[13] A. Martinez-Lopez, W. Padrón-Hernández, O.F. Rodríguez-Bernal, O. Chiquito-Coyotl, M. A. Escarola-Rosas, J. Hernández-Lara, E. A. Elvira-Hernández, G. A. Méndez, J. Tinoco-Magaña, J. Martínez-Castillo, Alternativas actuales del manejo de lixiviados, 9 (2014) 37-47

[14] A. Pellón Arrechea, M. López Torres, M. del C. Lloréns Espinosa, E. Díaz González, Propuesta para tratamiento de lixiviados en un vertedero de residuos sólidos urbanos, *Ing. Hidraúlica y Ambient.* 36 (2015) 14.

[15] E. Giraldo, Tratamiento de lixiviados de rellenos sanitarios: avances recientes, *Rev. Ing.* 0 (2001) 44-55. https://doi.org/10.16924/riua.v0i14.538

[16] X. Duan, H. Sun, Z. Shao, S. Wang, Non-radical reactions in environmental remediation processes: Uncertainty and challenges, *Appl. Catal. B Environ.* 224 (2018) 973-982. https://doi.org/10.1016/j.apcatb.2017.11.051

[17] Y. Li, H. Dong, L. Li, L. Tang, R. Tian, R. Li, J. Chen, Q. Xie, Z. Jin, J. Xiao, S. Xiao, G. Zeng, Recent advances in waste water treatment through transition metal sulfides-based advanced oxidation processes, *Water Res.* 192 (2021) 1-23. https://doi.org/10.1016/j.watres.2021.116850

[18] P.V. Nidheesh, C. Couras, A. V. Karim, H. Nadais, A review of integrated advanced oxidation processes and biological processes for organic pollutant removal, *Chem. Eng. Commun.* (2021) 1-43. https://doi.org/10.1080/00986445.2020.1864626

[19] N. Wardenier, Z. Liu, A. Nikiforov, S.W.H. Van Hulle, C. Leys, Micropollutant elimination by O3, UV and plasma-based AOPs: An evaluation of treatment and energy costs, *Chemosphere.* 234 (2019) 715-724. https://doi.org/10.1016/j.chemosphere.2019.06.033

[20] N. Vela, M. Calín, M.J. Yáñez-Gascón, A. el Aatik, I. Garrido, G. Pérez-Lucas, J. Fenoll, S. Navarro, Removal of Pesticides with Endocrine Disruptor Activity in Wastewater Effluent by Solar Heterogeneous Photocatalysis Using ZnO/Na2S2O8, Water. *Air. Soil Pollut.* 230 (2019) 1-11. https://doi.org/10.1007/s11270-019-4185-y

[21] L. Liberatore, M. Bressan, C. Belli, G. Lustrato, G. Ranalli, Chemical and biological combined treatments for the removal of pesticides from wastewaters, Water. *Air. Soil Pollut.* 223 (2012) 4751-4759. https://doi.org/10.1007/s11270-012-1230-5

[22] N. Taoufik, W. Boumya, M. Achak, M. Sillanpää, N. Barka, Comparative overview of advanced oxidation processes and biological approaches for the removal pharmaceuticals, *J. Environ. Manage.* 288 (2021) 112404. https://doi.org/10.1016/j.jenvman.2021.112404

[23] D. Becerra, J. Soto, S. Villamizar, F. Machuca-Martínez, L. Ramírez, Alternative for the

Treatment of Leachates Generated in a Landfill of Norte de Santander-Colombia, by Means of the Coupling of a Photocatalytic and Biological Aerobic Process, *Top. Catal.* 63 (2020) 1336-1349. https://doi.org/10.1007/s11244-020-01284-1

[24] D. Becerra, I. Barrientos, A. Rodriguez, F. Machuca-Martinez, L. Ramírez, Treatment of Agricultural Wastewater with Chlorpyrifos by Coupling of Heterogeneous Photocatalysis and Anaerobic Biological Process, *Top. Catal.* 63 (2020) 1261-1271. https://doi.org/10.1007/s11244-020-01281-4

[25] R. Chemlal, L. Azzouz, R. Kernani, N. Abdi, H. Lounici, H. Grib, N. Mameri, N. Drouiche, Combination of advanced oxidation and biological processes for the landfill leachate treatment, *Ecol. Eng.* 73 (2014) 281-289. https://doi.org/10.1016/j.ecoleng.2014.09.043

[26] J.J. Rueda-Marquez, I. Levchuk, P. Fernández Ibañez, M. Sillanpää, A critical review on application of photocatalysis for toxicity reduction of real wastewaters, *J. Clean. Prod.* 258 (2020) 120694. https://doi.org/10.1016/j.jclepro.2020.120694

[27] M. Hassan, Y. Zhao, B. Xie, Employing TiO2 photocatalysis to deal with landfill leachate: Current status and development, *Chem. Eng. J.* 285 (2016) 264-275. https://doi.org/10.1016/j.cej.2015.09.093

[28] E. Han, K. Vijayarangamuthu, J. Youn, Y.-K. Park, S.-C. Jung, K.-J. Jeon, Degussa P25 TiO2 modified with H2O2 under microwave treatment to enhance photocatalytic properties, *Catal. Today.* 303 (2018) 305-312. https://doi.org/10.1016/j.cattod.2017.08.057

[29] P. Lozada Torres, A. Pérez, Actividad Metanogénica Específica: una herramienta de control y optimización de sistemas de tratamiento anaerobio de aguas residuales, Univ. Del Val. 9 (2010) 5-14.

[30] A. Zhu, Y. Qin, J. Wu, M. Ye, Y.-Y. Li, Characterization of biogas production and microbial community in thermophilic anaerobic co-digestion of sewage sludge and paper waste, *Bioresour. Technol.* 337 (2021) 1-10. https://doi.org/10.1016/j.biortech.2021.125371

[31] I.G. Ezemagu, M.I. Ejimofor, M.C. Menkiti, C. Diyoke, Biofertilizer production via composting of digestate obtained from anaerobic digestion of post biocoagulation sludge blended with saw dust: Physiochemical characterization and kinetic study, Environ. Challenges. 5 (2021) 1-10. https://doi.org/10.1016/j.envc.2021.100288

[32] S.F. Aquino, C.A.L. Chernicharo, E. Foresti, M. de L.F. dos Santos, L.O. Monteggia, Metodologias para determinação da atividade metanogênica específica (AME) em lodos anaeróbios, *Eng. Sanit. e Ambient.* 12 (2007) 192-201. https://doi.org/10.1590/S1413-41522007000200010

[33] M.G. Noelia, Degradación de contaminantes emergentes mediante TiO2 inmovilizado e irradiación solar, Universidad de Almería, 2015.

[34] J. Diaz-Angulo, A. Arce-Sarria, M. Mueses, A. Hernandez-Ramirez, F. Machuca-Martinez, Analysis of two dye-sensitized methods for improving the sunlight absorption of TiO2 using CPC photoreactor at pilot scale, *Mater. Sci. Semicond. Process*. 103 (2019) 104640. https://doi.org/10.1016/j.mssp.2019.104640

[35] S. McMichael, M. Waso, B. Reyneke, W. Khan, J.A. Byrne, P. Fernandez-Ibanez, Electrochemically assisted photocatalysis for the disinfection of rainwater under solar irradiation, *Appl. Catal. B Environ.* 281 (2021) 119485. https://doi.org/10.1016/j.apcatb.2020.119485

[36] Q. Wei, Y. Yang, J. Hou, H. Liu, F. Cao, L. Zhao, Direct solar photocatalytic hydrogen generation with CPC photoreactors: System development, *Sol. Energy.* 153 (2017) 215-223. https://doi.org/10.1016/j.solener.2017.05.064

[37] N. Vela, M. Calín, M.J. Yáñez-Gascón, I. Garrido, G. Pérez-Lucas, J. Fenoll, S. Navarro, Photocatalytic oxidation of six pesticides listed

as endocrine disruptor chemicals from wastewater using two different $TiO_2$ samples at pilot plant scale under sunlight irradiation, J. Photochem. *Photobiol. A Chem.* 353 (2018) 271-278. https://doi.org/10.1016/j.jphotochem.2017.11.040

[38] M. Hassan, Y. Zhao, B. Xie, Employing TiO 2 photocatalysis to deal with landfill leachate: Current status and development, *Chem. Eng. J.* 285 (2016) 264-275. https://doi.org/10.1016/j.cej.2015.09.093

[39] D. Fu, Y. Huang, X. Zhang, T.A. Kurniawan, T. Ouyang, Uncovering potentials of integrated TiO2(B) nanosheets and H2O2 for removal of tetracycline from aqueous solution, *J. Mol. Liq.* 248 (2017) 112-120. https://doi.org/10.1016/j.molliq.2017.10.020

[40] H. Lachheb, C. Guillard, H. Lassoued, M. Haddaji, M. Rajah, A. Houas, Photochemical oxidation of styrene in acetonitrile solution in presence of H2O2, TiO2 /H2O2 and ZnO/H2O2, *J. Photochem. Photobiol. A Chem.* 346 (2017) 462-469. https://doi.org/10.1016/j.jphotochem.2017.06.026

[41] D. Camacho-Muñoz, A.-S. Fervers, C.J. Pestana, C. Edwards, L.A. Lawton, Degradation of microcystin-LR and cylindrospermopsin by continuous flow UV-A photocatalysis over immobilised TiO2, *J. Environ. Manage.*, 276 (2020) 111368. https://doi.org/10.1016/j.jenvman.2020.111368

[42] M.R. Al-Mamun, S. Kader, M.S. Islam, M.Z.H. Khan, Photocatalytic activity improvement and application of UV-TiO2 photocatalysis in textile wastewater treatment: A review, *J. Environ. Chem. Eng.* 7 (2019) 103248. https://doi.org/10.1016/j.jece.2019.103248

[43] E.M.R. Rocha, J.P. Vilar, A. Fonseca, I. Saraiva, R.A.R. Boaventura, Landfill leachate treatment by solar-driven AOPs/H2O2, *Sol. Energy*. 85 (2011) 46-56. https://doi.org/10.1016/j.solener.2010.11.001

[44] L.M. Losada, E.J.L. Castillo, E.A.O. Restrepo, E.A.S. Galvis, R.A.T. Palma, Tratamiento de aguas contaminadas con colorantes mediante fotocatalisis con TiO2 usando luz artificial y solar, Prod. + Limpia. 12 (2017).

[45] R.X. de S. Furtado, C.A. Sabatini, M. Zaiat, E.B. Azevedo, Perfluorooctane sulfonic acid (PFOS) degradation by optimized heterogeneous photocatalysis (TiO2/UV) using the response surface methodology (RSM), *J. Water Process Eng.* 41 (2021) 101986. https://doi.org/10.1016/j.jwpe.2021.101986

[46] S. Archin, S.H. Sharifi, G. Asadpour, Optimization and modeling of simultaneous ultrasound-assisted adsorption of binary dyes using activated carbon from tobacco residues: Response surface methodology, *J. Clean. Prod.* 239 (2019) 118136. https://doi.org/10.1016/j.jclepro.2019.118136

[47] Y. Zegzouti, A. Boutafda, L. El Fels, M. El Hadek, A. Lebrihi, F. Bekkaoui, M. Hafidi, Quality and quantity of leachate with different ages and operations in semi-arid climate, Desalin. *WATER Treat.* 152 (2019) 174-184. https://doi.org/10.5004/dwt.2019.24017

[48] C.M. Moody, T.G. Townsend, A comparison of landfill leachates based on waste composition, *Waste Manag.* 63 (2017) 267-274. https://doi.org/10.1016/j.wasman.2016.09.020

[49] M. Ghahrchi, A. Rezaee, Electro-catalytic ozonation for improving the biodegradability of mature landfill leachate, *J. Environ. Manage.* 254 (2020) 109811. https://doi.org/10.1016/j.jenvman.2019.109811

[50] Y.-C. Chou, S.-L. Lo, J. Kuo, C.-J. Yeh, Microwave-enhanced persulfate oxidation to treat mature landfill leachate, *J. Hazard. Mater.* 284 (2015) 83-91. https://doi.org/10.1016/j.jhazmat.2014.10.043

[51] B. K. Mavakala, S. Le Faucheur, C. K. Mulaji, A. Laffite, N. Devarajan, E. M. Biey, G. Giuliani, J.-P. Otamonga, P. Kabatusuila, P. T. Mpiana, J. Poté, Leachates draining

from controlled municipal solid waste landfill: Detailed geochemical characterization and toxicity tests, *Waste Manag.* 55 (2016) 238-248. https://doi.org/10.1016/j.wasman.2016.04.028

[52] M. Nakasima-López, P. Taboada-González, Q. Aguilar-Virgen, N. Velázquez-Limón, Adaptación de Inóculos Durante el Arranque de la Digestión Anaerobia con Residuos Sólidos Orgánicos, *Inf. Tecnológica.* 28 (2017) 199-208. https://doi.org/10.4067/S0718-07642017000100020

[53] G. Ferrara Giner, A. Ramírez, Análisis de la sedimentabilidad de los lodos biológicos producidos en un RCS durante la desnitrificación de un efluente de un biorreactor de crecimiento adherido, *Rev. La Fac. Ing. Univ. Cent. Venez.* 28 (2013) 37-44

[54] J.L. Ortiz Carrillo, J.A. Rodríguez Chona, ç.M. Cajiao Pedraza, J.I. Maldona Maldonado, Estudio cinético de bacterias metanogénicas a diferentes temperaturas, Bistua *Revista la Fac. Ciencias Básicas.* (2016) 39-48.

[55] L.B. Ho, D. Becerra Moreno, V. çngulo, L. Salazar, Biodegradabilidad de aguas residuales agroindustriales fototratadas mediante catalisis heterogénea, Afinidad. 68 (2011).

[56] K. Mojiri, Assessment of various tropical municipal landfill leachate characteristics and treatment opportunities, 2015.

[57] S.M.A. Abuabdou, W. Ahmad, N.C. Aun, M.J.K. Bashir, A review of anaerobic membrane bioreactors (AnMBR) for the treatment of highly contaminated landfill leachate and biogas production: Effectiveness, limitations and future perspectives, *J. Clean. Prod.* 255 (2020) 120215. https://doi.org/10.1016/j.jclepro.2020.120215

[58] L. Wu, Z. Yan, S. Huang, J. Li, B. Su, C. Wang, Y. Peng, Rapid start-up and stable maintenance of partial nitrification-anaerobic ammonium oxidation treatment of landfill leachate at low temperatures, *Environ. Res.* 191 (2020) 110131. https://doi.org/10.1016/j.envres.2020.110131

[59] O. N. Ağdağ, D. T. Sponza, Anaerobic/aerobic treatment of municipal landfill leachate in sequential two-stage up-flow anaerobic sludge blanket reactor (UASB)/completely stirred tank reactor (CSTR) systems, *Process Biochem.* 40 (2005) 895-902. https://doi.org/10.1016/j.procbio.2004.02.021

[60] S. Ismail, M. Nasr, E. Abdelrazek, H. M. Awad, S. Zhaof, F. Meng, A. Tawfik, Techno-economic feasibility of energy-saving self-aerated sponge tower combined with up-flow anaerobic sludge blanket reactor for treatment of hazardous landfill leachate, *J. Water Process Eng.* 37 (2020) 101415. https://doi.org/10.1016/j.jwpe.2020.101415

[61] S. Chelliapan, N. Arumugam, M. F. Md. Din, H. Kamyab, S. S. Ebrahimi, Anaerobic treatment of municipal solid waste landfill leachate, in: Bioreactors, Elsevier, 2020, pp. 175-193. https://doi.org/10.1016/B978-0-12-821264-6.00011-5

[62] L.F. Garcés Giraldo, E.A. Mejía Franco, J.J. Santamaría Arango, Fotocatalisis como alternativa para el tratamiento de aguas residuales, Rev. *Lasallista Investig.* 1 (2004) 83-92.

[63] D.R. Giraldo Valentín, Eficiencia del proceso de fotocatálisis heterogénea con tio2 y h2o2 en la reducción de dbo5 y dqo de los lixiviados del botadero la mejorada el tambo Huancayo, Repos. Inst. - UAP. (2016).

[64] S.H. Valencia, J.M. Marín, G.M. Efecto del pH en la Degradación Fotocatalítica de Materia Orgánica Natural, *Inf. Tecnológica*, 22 (2011) 57-66. https://doi.org/10.4067/S0718-07642011000500008

[65] G. Llanes, Y. Carolay, M. Benavides, A. Consuelo, Fotocatalisis heterogénea con TiO2 para el tratamiento de desechos líquidos con presencia del indicador verde de bromocresol, *Rev. Ing.* 10 (2011) 79-88.

[66] D. Lu, M. Yang, P. Fang, C. Li, L. Jiang, Enhanced photocatalytic degradation of aqueous phenol and Cr(VI) over visible-light-driven Tb x O y loaded $TiO_2$-oriented nanosheets, *Appl. Surf. Sci.* 399 (2017) 167-184. https://doi.org/10.1016/j.apsusc.2016.12.077

[67] D. Chen, Y. Cheng, N. Zhou, P. Chen, Y. Wang, K. Li, S. Huo, P. Cheng, P. Peng, R. Zhang, L. Wang, H. Liu, Y. Liu, R. Ruan, Photocatalytic degradation of organic pollutants using $TiO_2$-based photocatalysts: A review, *J. Clean. Prod.* (2020) 121725. https://doi.org/10.1016/j.jclepro.2020.121725

[68] R. Arshad, T.H. Bokhari, T. Javed, I.A. Bhatti, S. Rasheed, M. Iqbal, A. Nazir, S. Naz, M.I. Khan, M.K.K. Khosa, M. Iqbal, M. Zia-ur-Rehman, Degradation product distribution of Reactive Red-147 dye treated by UV/H2O2/TiO2 advanced oxidation process, *J. Mater. Res. Technol.* 9 (2020) 3168-3178. https://doi.org/10.1016/j.jmrt.2020.01.062

[69] O.N.E.H. Kaabeche, R. Zouaghi, S. Boukhedoua, S. Bendjabeur, T. Sehili, A Comparative Study on Photocatalytic Degradation of Pyridinium - Based Ionic Liquid by $TiO_2$ and ZnO in Aqueous Solution, *Int. J. Chem. React. Eng.* 17 (2019). https://doi.org/10.1515/ijcre-2018-0253

[70] P. Torres Lozada, L.E. Barba Ho, C. Ojeda, J. Martínez, Y. Castaño, Influencia de la edad de lixiviados sobre su composición físico-química y su potencial de toxicidad, *Rev. U.D.C.A Actual. Divulg. Científica*, 17 (2014) 245-255.

[71] M. N. Chong, A. K. Sharma, S. Burn, C. P. Saint, Feasibility study on the application of advanced oxidation technologies for decentralised wastewater treatment, *J. Clean. Prod.* 35 (2012) 230-238. https://doi.org/10.1016/j.jclepro.2012.06.003

[72] M. Hassan, X. Wang, F. Wang, D. Wu, A. Hussain, B. Xie, Coupling ARB-based biological and photochemical (UV/TiO2 and UV/S2O82-) techniques to deal with sanitary landfill leachate, *Waste Manag.* 63 (2017) 292-298. https://doi.org/10.1016/j.wasman.2016.09.003

[73] L. A. Castillo-Suárez, V. Lugo-Lugo, I. Linares-Hernández, V. Martínez-Miranda, M. Esparza-Soto, M. de los ç. Mier-Quiroga, Biodegradability index enhancement of landfill leachates using a Solar Galvanic-Fenton and Galvanic-Fenton system coupled to an anaerobic-aerobic bioreactor, *Sol. Energy.* 188 (2019) 989-1001. https://doi.org/10.1016/j.solener.2019.07.010

# Chapter 5: Alternative for the Treatment of Leachates Generated in a Landfill of Norte de Santander–Colombia, by Means of the Coupling of a Photocatalytic and Biological Aerobic Process

Topics in Catalysis
https://doi.org/10.1007/s11244-020-01284-1

ORIGINAL PAPER

# Alternative for the Treatment of Leachates Generated in a Landfill of Norte de Santander–Colombia, by Means of the Coupling of a Photocatalytic and Biological Aerobic Process

Dorance Becerra[1,2] · Joseph Soto[1,3] · Salvador Villamizar[1,3] · Fiderman Machuca-Martínez[2] · Luisa Ramírez[1]



**Abstract**
In the present study, the use of heterogeneous photocatalysis TiO2/UV coupled to an activated sludge reactor was evaluated as an alternative treatment for the leachate coming from a Landfill, located in Cucuta (Colombia). $TiO_2$ (Degussa P-25) between 100 and 600 mg.$L^{-1}$ was used as a catalyst, semi-continuous type reactors for the photocatalysis, a batch for the biological stage, UV light with accumulated energies from 20 to 60 kJ.$L^{-1}$ were also used, a constant concentration of $H_2O_2$ was used as an adjuvant in all tests. The research consisted of four main phases: leachate characterization, biological treatment, optimization of photocatalytic and AOP-biological coupling. For the optimization of the photocatalytic step, an experimental design was carried out through the statistical program Statgraphics Centurion XV of factorial type 3^2 (3 levels 2 variables), modeling the results by means of a response surface, the variables of the pH and the concentration of the catalyst were included, having this as input for the response of interest the percentage (%) of DOC removal. The biological process itself provided a removal of 38 and 24% for COD and DOC, respectively. The AOP-biological coupling provided a removal of 68 and 76% in terms of COD and DOC, respectively. Thus, the coupling significantly improves the overall efficiency of the process by more than 50%, which represents a promising improvement compared to the removal of organic matter for the treatment of the same type of water using only the biological process. The results show a viable alternative for the treatment of leachate because higher removal levels are achieved in residence times, which are considered shorter than the ones in conventional processes.

**Keywords** Leachates · $TiO_2$ · Heterogeneous photocatalysis · Activated sludge · Zahn Wellens Test

## 1 Introduction

Landfills are one of the most common and frequent alternatives used as deposits of solid waste worldwide. There, leachates are generated as a result of the contact of rainwater with the waste and the percolation of these [1], which contain high amounts of heavy metals, solids (suspended and sedimentable) and organic material, which if it is not properly treated becomes a problem that directly impacts the environment and the population surrounding these sites [2]. Therefore, it is essential to implement methodologies capable of removing the contaminants and avoid generating impacts on the environment or human health by ensuring the conservation of natural resources.

Within these leachate decontamination processes, there is heterogeneous photocatalysis, which is an advanced oxidation process that consists of the use of a semiconductor photocatalyst that, when subjected to specific radiation, allows

✉ Fiderman Machuca-Martínez
fiderman.machuca@correounivalle.edu.co

Dorance Becerra
dorancebm@ufps.edu.co

Joseph Soto
jwsoto@uninorte.edu.co

Salvador Villamizar
salvadorv@uninorte.edu.co

[1] Departamento de Ciencias del Medio Ambiente, Facultad de Ciencias Agrarias y del Ambiente, Universidad Francisco de Paula Santander, Norte de Santander, Cúcuta, Colombia

[2] Facultad de Ingeniería, Universidad del Valle, Cali, Colombia

[3] Universidad del Norte, Barranquilla, Atlántico, Colombia

Published online: 28 May 2020

the generation of oxide-reduction processes and makes it possible to remove the contaminants and it produces effluents with lower toxicity [3], which are suitable for continuing their treatment in less complex processes such as biological ones. Several research projects have been carried out based on these technological couplings, such as the case of the Oued Smar landfill, located in Algeria, North Africa, where the treatment of leachates was carried out by means of a heterogeneous photocatalysis coupling ($TiO_2$/UV) and a biological process of bioreactors sown with different types of inoculums (raw leachate, soil extract and activated sludge). These results were very important because a reduction between 50 and 84% of the initial COD maintained at pH 5 was obtained after the heterogeneous photocatalysis; because of this, the ratio BOD5/COD was favorable for the biological treatment, along with the coupling of advanced oxidation-bioreactor there was a reduction of 90% of the initial BOD5 and 87% of the initial COD of the leachate [4].

Similarly, it is possible to state that after the review of the research material, it was found that other recent research, specifically those combining heterogeneous TiO2/UV photocatalysis with batch activated sludge for leachate decontamination, are limited. However, there are studies which have been developed in the last years such as those made by [5–9], who couple the photocatalytic process using TiO2 as a catalyst in the presence of UV radiation with diverse alternatives of aerobic biological processes, achieving outstanding removals of organic matter and emerging contaminants. These results are achieved through the optimization of experimental variables such as catalyst concentration and pH range.

Now with this project, the aim is to evaluate the efficiency of the removal of contaminants present in the leachates of the El Guayabal Landfill in Cúcuta—Norte de Santander, by coupling a heterogeneous photocatalytic process, using a compound parabolic collector and TiO2 as a catalyst, in coupling with an aerobic biological process (through batch activated sludge reactors—Zahn Wellens Test / EMPA OECD 302B) according to Fig. 1, in order to evaluate the possibility of its use for the removal of organic matter and total suspended solids in the leachates, thus minimizing the negative effects on the environment and human health.

The development of this type of alternatives with solar radiation contributes to the search for economic and environmental sustainability alternatives to advanced oxidation processes [3, 10], promotes the implementation and operation of them by reducing energy costs compared to techniques that use other types of UV radiation. Also, with the results obtained, it is possible to make comparisons with other treatments implemented in the decontamination of leachates and provide information to the scientific world about the usefulness and efficiency of the implementation of couplings between heterogeneous photocatalysis with $TiO_2$ and activated sludge. Although it is true that these combinations have been implemented on several occasions over time to treat water with complex chemical structures such as pharmaceuticals [11] or pesticides [12], there is not enough recent bibliographic information on their use applied to contaminant removal in leachates, which contributes to reducing the existing knowledge gap and provides innovative solutions capable of giving effect to the sustainable development objectives.

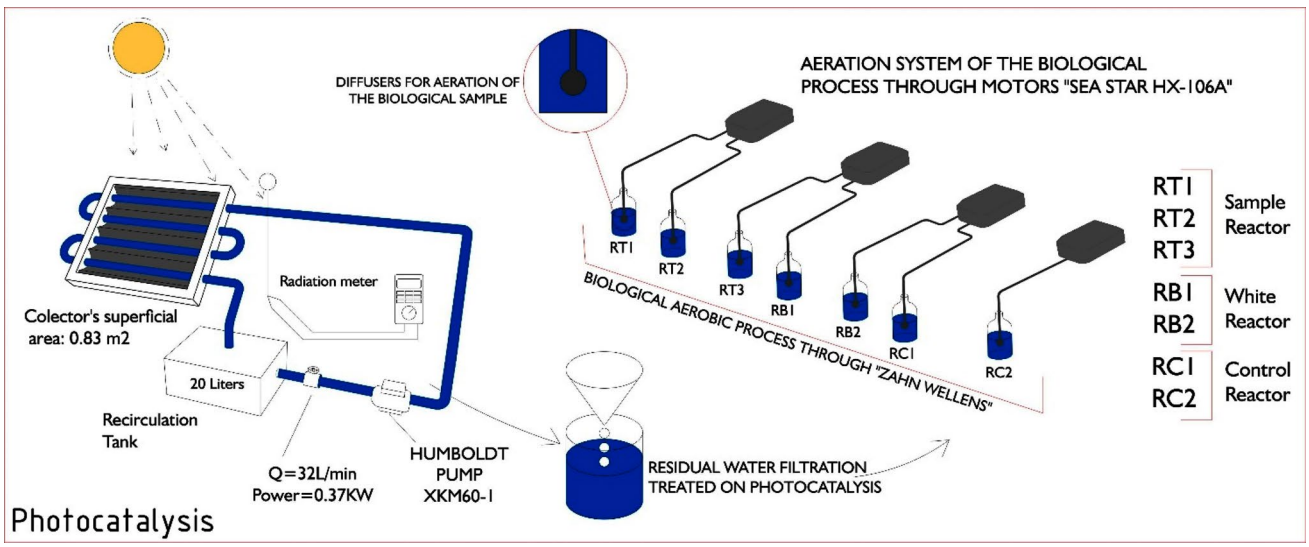



**Fig. 1** General scheme of the coupling processes

## 2 Materials and Methods

The experimental process of the project was based on the scientific approach, the feasibility of the procedures and the application of the results obtained. The analyses were carried out at the Environmental Quality Laboratory of Francisco de Paula Santander University in Campos Eliseos headquarters. The methodology was developed in the following phases:

### 2.1 Leachate Characterization

The leachate sample from El Guayabal Landfill was characterized by the physicochemical parameters of Chemical Oxygen Demand (COD), Dissolved Organic Carbon (DOC), Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS), the pH and temperature were also part of these characteristics, and they were measured in the field afterwards. The methodologies were carried out taking as reference the Standard Methods for Water and Wastewater Analysis (AWWA—APHA—WPCF).

The COD measurement was carried out using the closed reflow and volumetric method, following the protocol set out in Sect. 5220C. COD measurement was performed by the high temperature combustion method, following the protocol set out in Sect. 5310B. The Teledyne Tekmar TOC Torch equipment was used. Initially, the assembly should be done in the Curve and Calibration Method program, for this, the "Total Organic Carbon Equipment (Teledyne Tekmar TOC Torch) Operating Protocol" was followed. TOS and TOC Torch were performed following the protocol set in Sect. 2540D. The use of analytical balance, porcelain capsule and crucible dryer, Digital Binder Furnace model ED-53 and Electric Ground Muffle model D-8 were used. The temperature and pH parameters were taken in the field at the time of collecting the leachate sample at Guayabal Landfill with a Waterproof PCTestr 35 multiparameter.

### 2.2 Aerobic Biological Treatment Process

#### 2.2.1 Characterization of the Inoculum Sludge

The inoculum sludge used to carry out the research came from the wastewater treatment plant of Ciudadela "El Country" neighborhood, located in Jamundí, Valle del Cauca, as a result of an aerobic biological treatment process. This mud was fed every other day with wastewater from San Pablo farm which belongs to the Francisco de Paula Santander University in order to ensure its fast activation. This sludge was characterized in physicochemical parameters of Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS). In addition to this, the Sludge Volumetric Index (SVI) and the Oxygen Consumption Rate (OCR) were applied. The Sludge Volumetric Index (SVI) is a parameter that allowed evaluating the behavior of the aerobic sludge according to its good or bad sedimentability (a good sedimentability occurs when the sedimentation rate is higher than the ascension rate of the influent). The method was used to find a standard dilution for the sludge under study, so that after sedimentation it gets a volume of 300 ml in the 1000 ml test tube.

#### 2.2.2 Oxygen Consumption Rate

The Oxygen Consumption Rate (OCR) is a technique based on the measurement of oxygen consumption by microorganisms working on an organic substrate, which is degraded and oxidized to $CO_2$ [13]. The dissolved oxygen analysis allowed the acquisition of data on oxygen consumption in response to the metabolism of a substrate due to the respiration of the microorganisms. The test was carried out in a Winkler bottle (300 ml capacity) and a range of concentrations related to those allowed in the Zahn Wellens test was handled (100 to 1000 mg $COD.L^{-1}$), which were 0, 200, 400, 600 and 800 mg $COD.L^{-1}$, taking into account that the first test mentioned represents the control concentration and the OCR value for the aerobic sludge, because the mixture only contains nutrient solution and the one which was previously mentioned. The amount of aerobic sludge in the tests, depends on the concentration of VSS that is required within each concentration, for this case is 1500 mg $VSS.L^{-1}$. The content of each test is shown in Table 1.

The dissolved oxygen was measured with an Oxygen Meter model DO -5510 for each study concentration. These measurements were made for 30 min, and the data was recorded every 15 s. A graph of Dissolved Oxygen Vs. Time is made with these values, and the OCR is determined from the slope.

#### 2.2.3 Respiration Inhibition Test

This method determined the effect of the leachate on the microorganisms by measuring the respiration rate of the inoculated sludge under defined conditions in the presence of various concentrations of the test substance. It was carried

**Table 1** Volumes used in the OCR

| Compound | Concentration ($mg.L^{-1}$ COD) | | | | |
|---|---|---|---|---|---|
| | 0 | 200 | 400 | 600 | 800 |
| Aerobic Inoculum Sludge (ml) | 27,4 | 27,4 | 27,4 | 27,4 | 27,4 |
| Nutrients (ml) | 272,6 | 265 | 257,4 | 249,9 | 242,3 |
| Leachate (ml) | 0 | 7,6 | 15,2 | 22,7 | 30,3 |

out with the purpose of identifying non-leaching inhibitory concentrations that could be used in the Biodegradability Test (Zahn Wellens) [14].

The respiration rate is the oxygen consumption of the microorganisms in an aerobic sludge expressed as mg $O_2$. $mg^{-1}$ sludge.$h^{-1}$. The procedure described in the Oxygen Consumption Rate in Sect. 3.2.2 of this document is an input for determining the percentage inhibition, which is calculated by Eq. 1.

$$\%\textbf{Inhibition} = \left(1 - \frac{\mathbf{R_s}}{\mathbf{R_c}}\right) \times 100 \quad (1)$$

where:

Rs: OCR of each leachate's concentration employed

Rc: OCR of control

#### 2.2.4 Aerobic Biodegradability Test—Zahn Wellens

The objective of the Biodegradability Test, Zahn Wellens Test / EMPA OECD 302B, was to determine the potential for biodegradation of organic substances under aerobic conditions. This test is applicable on non-volatile and water-soluble compounds at least 100 mg/L; which show low adsorption in activated sludge, which have no foaming activity, and which do not inhibit microorganisms at the evaluated concentrations. The contents of each reactor are given in Table 2 [15].

The sample reactors were taken in triplicate, the target and reference compound reactors were taken in duplicates. The concentration (mg.$L^{-1}$ COD) within the sample reactors was determined from the results obtained in the Oxygen Consumption Rate and the Respiration Inhibition Test. Similarly, the ratio was maintained for the concentration of the sludge in mg.$L^{-1}$ VSS (3:1). In the case of the reference compound (Ethylene Glycol).

The test lasted 28 days. The monitoring parameters were the pH and the temperature, in order to guarantee optimal conditions for the development of the biological process. The samples were taken on days 0, 4, 8, 12, 16, 20, 24 and 28, each of them filtered and characterized in terms of COD and DOC, to determine the percentages of biodegradation based on Eq. 2.

$$\%\textbf{Biodegrability} = \left(1 - \frac{\mathbf{R_T} - \mathbf{R_B}}{\mathbf{R_{t0}} - \mathbf{R_{B0}}}\right) \times 100 \quad (2)$$

where:

$R_T$: is the quantity in mg/L of DOC or COD at time t in the test vessel

$R_B$: is the quantity in mg/L of DOC or COD at time t in the blank test

$R_{T0}$: is the quantity in mg/L of DOC or COD of the test vessel after 3.5 h

$R_{B0}$: is the quantity in mg/L of DOC or COD of balnk test after 3.5 h

**Table 2** Composition of the biological reactors

| Reactor | Composition | Amount (ml) |
|---|---|---|
| Sample | Inoculum Sludge | 73 |
| | Nutrient solution | 676,5 |
| | Leachate | 50,5 |
| Blank | Inoculum Sludge | 73 |
| | Nutrient solution | 727 |
| Reference Composite | Inoculum Sludge | 73 |
| | Nutrient solution | 726,45 |
| | Ethylene glycol | 0,55 |

### 2.3 Optimization of Photocatalysis

The leachate sample from El Guayabal Landfill was submitted to the heterogeneous photocatalysis process, using $TiO_2$ (Degussa P25) as catalyst, which [16] has shown high efficiency when it is used in leachate decontamination treatments due to the generation of hydroxyl radicals, especially when photolysis is submitted. Besides, it has been used in numerous studies oriented to the removal of recalcitrant contaminants or with structures difficult to treat, and it obtains efficiencies of more than 70% [17–21]. Furthermore, according to [22] who carried out a similar wastewater treatment employing $TiO_2$ (Degussa P25), this has a band gap energy from 2.90 to 3.15 eV, [23]. The BET of this catalyst has a value between 51 and 56 $m^2g^{-1}$[24]. $TiO_2$ (Degussa P25) is mainly composed of Anatase (80%) and Rutile Crystallites (20%) and its particle size is between 20 and 30 nm.[25–27].

Subsequently, $H_2O_2$ is used as an oxidation coadjutant, since having previous research as reference such as that carried out by [28–30] has shown that the use of this type of oxidant promotes the formation of OH radicals, helping the degradation of contaminating compounds. A Compound Parabolic Collector (CPC) was used at laboratory scale, with a system that allowed the measurement of accumulated energies in kJ × L-1. The use of this kind of Collector allows the concentration of solar energy, and it generates a higher intensity radiation [31], which results in a high degradation capacity of the system [32].

This CPC has a surface area of 0.83 $m^2$. It is composed of two aluminum structures (UV light-reflective film), each equipped with a set of borosilicate tubes (material sensitive to UV adsorption), and a 20 L capacity storage tank, where the treatment mixture is prepared. In addition, it is equipped with a Humboldt pump (Qmax: 32 L.$min^{-1}$) which is responsible for recirculating the treatment throughout the system. The connections and pipes

**Table 3** Independent variables and their coded levels for the experimental design

| Parameter | Level of the variable | | |
|---|---|---|---|
| | − 1 | 0 | 1 |
| pH | 3 | 6 | 9 |
| $TiO_2$ | 100 | 350 | 600 |

**Table 4** Design of experiments—photocatalysis process

| No. Assay | [mg.L$^{-1}$] $TiO_2$ | pH |
|---|---|---|
| 1 | 100 (− 1) | 9 (1) |
| 2 | 350 (0) | 6 (0) |
| 3 | 350 (0) | 9 (1) |
| 4 | 600 (1) | 9 (1) |
| 5 | 100 (− 1) | 6 (0) |
| 6 | 600 (1) | 6 (0) |
| 7 | 600 (1) | 3 (− 1) |
| 8 | 100 (− 1) | 3 (− 1) |
| 9 | 350 (0) | 3 (− 1) |
| 10 | 350 (0) | 6 (0) |

are made of half inch PVC tube, as well as accessories that allow the operation of the prototype.

To optimize the photocatalytic process, an experimental design was carried out through the statistical program Statgraphics Centurion XV of factorial type 3^2 (3 levels 2 variables), modeling the results by means of a response surface. The ranges of the independent variables and their coded levels are shown in Table 3 having + 1 as the maximum level and -1 as the minimum level.

$H_2O_2$, is a variable that remained constant throughout the process. The working concentration was of 300 mg. L$^{-1}$, this value was optimized by [33], under acidic pH conditions (4 units), applying a heterogeneous photocatalytic treatment process ($TiO_2$/UV) for leachates, where it obtained percentages of biodegradation higher than 94.7%.

The accumulated energy was used in a range from 0 to 60 kJ.L$^{-1}$, it was considered that in heterogeneous photocatalytic processes high accumulated energies are used: 111 kJ.L$^{-1}$ [34]; 1850 and 250 kJ.L$^{-1}$ [35] that allow high removal percentages of the evaluated pollutants, and as the intention of the project is not to totally degrade the leachate, but to make a partial transformation where subsequent biodegradability in biological reactors is promoted, the range of work is justified.

With the ranges of the independent variables already established, we proceed to model the program, for which we have the design of experiments set forth in Table 4.

#### 2.3.1 Calculation of the Accumulated Energy

For the calculation of the accumulated energy (UV radiation), a system was assembled that would allow the measurement of the total solar radiation, and to be able to determine at each moment of measurement the energy in the units of interest (kJ L$^{-1}$) an equation and basic conversions were used.

This system consisted of a multimeter (Uni-T UT71C) connected to a pyranometer (SP-110) which, when it comes into contact with the radiation, marks a value sequentially in millivolts (mV). The precise data acquisition is defined by timescales in which the information will be given, which in this case is every 10 min (600 s).

The following step is to make the mathematical conversion of mV to W × m-2 for which 1 mV represents 5 W.m$^{-2}$. Finally, what remains is to apply the Eq. 3 for the calculation of the energy:

$$Q_n = Q_{n-1} + \Delta t_n \times I_n \times A_f \times V_T^{-1} \quad (3)$$

where:

$Q_n$: total accumulated energy kJ.L$^{-1}$.
$Q_{n-1}$: previous accumulated energy kJ.L$^{-1}$.
$\Delta t_n$: irradiation time (600 s).
$I_n$: Average irradation (W.m$^{-2}$ UV).
$A_f$: irradiated reactor surface (0,83 m$^2$).
$V_T$: volume discussed (20 L).

### 2.4 CPC Effluent Coupling—Zahn Wellens Test

With the obtained results in the optimization of the photocatalysis process, the coupling took place which consisted of the sequential operation of the Compound Parabolic Collector and the aerobic biological process of treatment (biodegradability test). This coupling is based on the fact that different researchers have applied photocatalysis ($TiO_2$/UV) as a pre-treatment for landfill leachate, in order to improve the biodegradability of the organic compounds present in this waste liquid and thus consider the application of a subsequent treatment that allows a discharge of waste with less impact on the environment [16].

The degradation of the pollutants is monitored in terms of the percentage of COD and DOC removal at the end, compared to the start of the test.

In the biological coupling process, the sample coming from the optimal photocatalytic treatment was used, and with this, 3 reactors with mineral medium and activated aerobic sludge were adapted, as well as two white reactors (aerobic sludge and mineral medium) and 2 reference compound reactors (activated aerobic sludge + mineral medium + ethylene glycol). In addition to this, each of them

**Table 5** Leachate characterization

| Parameter | Units | Value |
|---|---|---|
| COD | mg $O_2$.$L^{-1}$ | 7920 |
| DOC | mg C.$L^{-1}$ | 2767 |
| TSS | mg TSS.$L^{-1}$ | 19,941 |
| VSS | mg VSS.$L^{-1}$ | 8587 |
| pH | – | 7,29 |
| Temperature | °C | 33,2 |

**Table 6** Results characterization of the inoculated sludge

| Parameter | Measurement | Units |
|---|---|---|
| TSS | 45,529,33 | mg TSS.$L^{-1}$ |
| VSS | 16,450,67 | mg VSS.$L^{-1}$ |
| SVI | 66,16 | mg.$L^{-1}$ |
| OCR | 14,64 | mg.$g^{-1}$ VSS.$h^{-1}$ |
| Ethylene glycol Degradation (8 days) | 100 | % |

was monitored in terms of COD and DOC on days 0, 4, 8, 12, 16, 20, 24, 28, and TSS and VSS on days 0, 16 and 28, in order to provide a percentage of biodegradation and to determine the efficiency of the coupled treatment.

## 3 Results and Analysis

### 3.1 Leachate Description

Following the methodologies proposed in the methodological design to characterize the leachate, the obtained results are represented in Table 5.

It is concluded that the leachates from "El Guayabal" Landfill have a COD of 7920 mg O2*L-1, which according to the consolidated classification by [31], It is listed as a leachate of average age, since it is in the range of 5000—10,000 mg $O_2$.$L^{-1}$.

It was determined that the leachate sample from "El Guayabal" Landfill has a concentration of 2767 mg C.$L^{-1}$, and taking into account its COD/DOC ratio (0.35), it is categorized as having low biodegradable properties [16].

The concentration of suspended solids in the leachate coming from "El Guayabal" Landfill is of 19,941 mg TSS.$L^{-1}$ and 8587 mg VSS.$L^{-1}$, which is interpreted as a high content of them, and the VSS contributes with a great amount of microorganisms due to the high contribution of organic matter in this residual liquid.

The leachate sample has a pH of 7.29, which indicates a value close to neutral, and it allows the development of a biological treatment process. The temperature recorded as 33.2 °C is consistent with the normal temperature of the location area (Max. 33 °C; Min. 24 °C).

### 3.2 Aerobic Biological Treatment Process

#### 3.2.1 Description of the Inoculum Sludge

Table 6 consolidates the results obtained from the analyses carried out on the inoculum sludge.

According to the results presented above, the sludge comes from the treatment plant of the "El Country" neighborhood, it has a volumetric index of sludge of 66.16 mg.$L^{-1}$, a value that places it within the range of sludge with good sedimentation characteristics, considering that a sludge with good sedimentation characteristics should present a value of VIS in the low range [36]. This parameter is very important to consider because in a biological treatment the organic matter is transformed into microorganisms that become part of the slurry, and if it is not removed in the spillage before being discharged, in fact, it transforms the organic materials into slurry and it is discharged as an effluent avoiding the polluting agents to be removed. Therefore, the idea of having a settled slurry is beneficial because after the biological process in real conditions, a settler can be available where this slurry is removed (as settled solids), providing the discharge of an effluent free of pollution.

The Oxygen Consumption Rate of 14.64 mg.$g^{-1}$.$h^{-1}$ indicates an adequate development of microbial metabolism and a high biological activity of the sludge, and places it in the range of 12 and 20 mg.$g^{-1}$.$h^{-1}$, for which they are considered under normal conditions and capable of degrading pollutants [37].

The result obtained in the degradation of a reference compound such as ethylene glycol, shows a high biological activity and microorganisms capable of degrading organic material, as well as having optimal conditions for the development of them, which are relevant when performing the biological treatment, The methodology proposed by the Zahn Wellens Test / EMPA OECD 302B establishes that this compound must be degraded in less than 14 days, which guarantees the viability of using this sludge as inoculum in the biodegradability tests.

#### 3.2.2 Oxygen Consumption Rate

In Table 7, the Oxygen Consumption Rate data is reported for each concentration. According to the studies, a OCR is considered low when it shows values lower than 12 mg $O_2$.$g^{-1}$.VSS.$h^{-1}$, indicating that there are too many solids or the presence of toxics elements, because a high toxicity of the leachates is corroborated, due to the large amount of contaminating constituents that form the waste that the landfill in study has.

**Table 7** Oxygen consumption rates

| Concentration (mg $O_2.L^{-1}$) | Slope of the graph (mg $O_2.L^{-1}.S^{-1}$) | OCR (mg $O_2.g^{-1}SSV.h^{-1}$) |
|---|---|---|
| 0 | 0,0061 | 14,64 |
| 200 | 0,0027 | 6,48 |
| 400 | 0,0026 | 6,24 |
| 600 | 0,0026 | 6,24 |
| 800 | 0,0026 | 6,24 |

### 3.2.3 Respiration Inhibition Test

According to Fig. 2, from the concentration of 400 mg $O_2.L^{-1}$, a trend associated with the percentage of inhibition of 57% begins to occur, indicating that 43% of microorganisms are available to give rise to biodegradability in the biological process.

That is the reason why it is decided to work with an intermediate concentration, in which the biological process is not affected by the toxicity of the residual liquid. Therefore, a concentration of 500 mg $COD.L^{-1}$ is selected for the biodegradability test (Zahn Wellens).

### 3.2.4 Biodegradability Test—Zahn Wellens

This biodegradability test by Zahn Wellens simulates an aerobic biological treatment process of activated sludge in a laboratory scale. It was carried out following the protocol established by EMPA OECD 302B. It should be clarified that the COD of the leachate from "El Guayabal" Landfill was 7920 $mg.L^{-1}$, but the concentration of 500 mg $O_2.L^{-1}$ in the sample reactors was chosen because the working range established by the test is 100 to 1000 mg $O_2.L^{-1}$, and taking as a reference the results obtained in the respiration inhibition test, where the use of such concentration is supported.

The test establishes that the method is validated when the reference compound, in this case ethylene glycol, is degraded by more than 70% within 14 days from the beginning of the test. After 4 days, this compound had already fulfilled this condition, in terms of COD and DOC, which supports optimal conditions of the inoculum used for the treatment, as well as the correct application of the test under the established minimum conditions and requirements, which validate the accuracy of the obtained results.

The degree of volatilization that could occur in the test was evaluated, because it was considered that the compounds present in the leachate may be of a volatile type, and that in an activated sludge process where there is constant airflow the compounds may go into the atmosphere. That is the reason why a reactor was prepared with the same leachate concentration, calibrated to 800 ml with a nutrient solution and in the absence of inoculum slurry, where there are no microbiological biodegradation processes. This reactor was evaluated in terms of COD and DOC at the beginning and end of the test (28 days), and a percentage of volatilization of the compound was determined through these values, which must be adjusted to the percentages of biodegradation determined during the test. These results are presented in Table 8.

A percentage of volatilization is determined in the test of 47 and 55%, for COD and DOC respectively. According to Fig. 3, with the percentages of biodegradation adjusted to volatilization, we determined a maximum biodegradation for COD of 38% and 24% for DOC. This Zahn Wellens test establishes a limit of biodegradation of more than 70% after 28 days of the test, in order to consider a substance as biodegradable. It is concluded that the treated leachate sample is not biodegradable under the requirements of this test, for this reason it is important to carry out previous treatment processes that allow the transformation of the compound into simpler substances, capable of breaking down and degrading the toxic constituents, and thus be able to apply subsequent

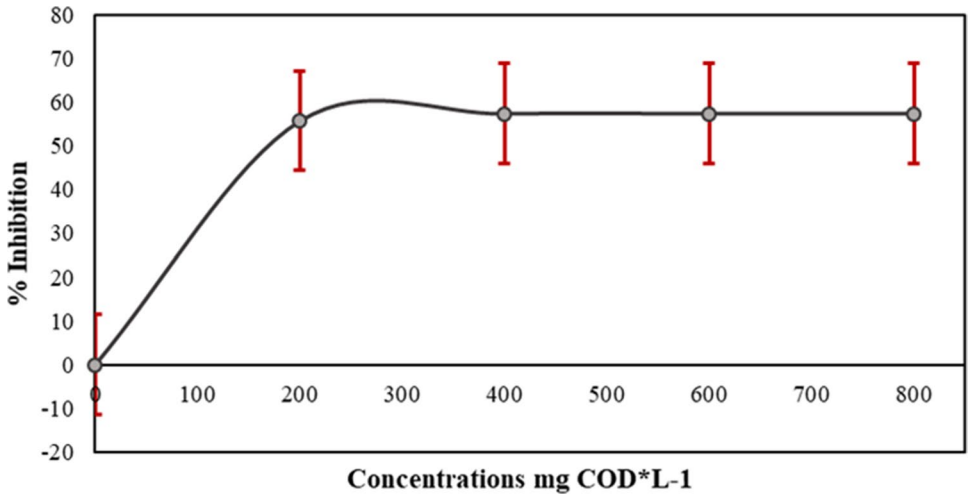



**Fig. 2** Breathing Inhibition Test

**Table 8** Volatilization results biodegradability test

| Time (Days) | COD (mg. $L^{-1}$) | Volatilization (% COD) | DOC (mg. $L^{-1}$) | Volatilization (% DOC) |
|---|---|---|---|---|
| 0 | 1152 | 47 | 358 | 55 |
| 28 | 608 | | 160 | |

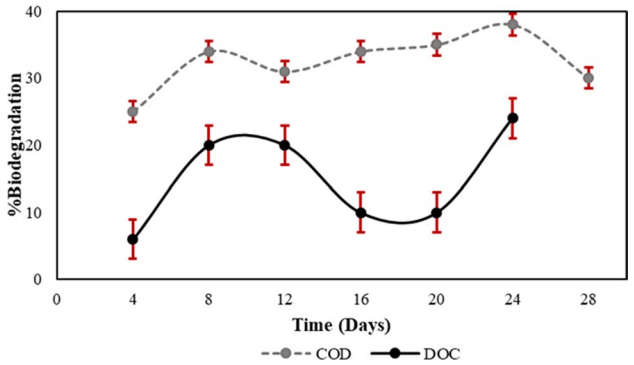



**Fig. 3** Percentage (%) Biodegradation COD and DOC on Zahn Wellens test

biological processes that have the ability to remove contaminants [13].

Similarly, the results mentioned above are comparable to those obtained in the study done by [38], where a similar process for the treatment of leachate from Mermuelo Landfill in Spain was carried out, in which a 57% biodegradation using the same biological process was obtained, and it also failed to exceed the percentage of degradation required by the methodology, which implies the need to couple this system with another treatment alternative. The mentioned study obtained a higher biodegradation due to the initial characteristics of the leachate, which presented a COD and a DOC notably lower than those coming from "El Guayabal" Landfill.

During the test, a pH between 7.03 and 7.13 (adjusted from buffer solutions) was handled in the reactors, as well as temperatures ranging from 24.5 to 25.7 °C, which allowed optimal conditions for the development of metabolic activities by the microorganisms during the biological treatment, and contributed to the biodegradation of the contaminating compounds provided by the leachate.

### 3.3 Optimization of Photocatalysis

Based on the percentages (%) of removal determined in each of the tests, and when the established accumulated energies were accomplished, it was determined that the maximum degradations were recorded when 60 $kJ.L^{-1}$ was reached. Table 9 consolidates the results of photocatalysis

**Table 9** Removal of DOC—Optimization of photocatalysis

| Assay | [$TiO_2$] (mg*$L^{-1}$) | pH | Percentage (%) of final removal COD |
|---|---|---|---|
| 1 | 100 (− 1) | 9 (1) | 1,4 |
| 2 | 350 (0) | 6 (0) | 7,2 |
| 3 | 350 (0) | 9 (1) | 5,5 |
| 4 | 600 (1) | 9 (1) | 22,4 |
| 5 | 100 (− 1) | 6 (0) | 23,9 |
| 6 | 600 (1) | 6 (0) | 5,0 |
| 7 | 600 (1) | 3 (− 1) | 12,5 |
| 8 | 100 (− 1) | 3 (− 1) | 57,9 |
| 9 | 350 (0) | 3 (− 1) | 29,8 |
| 10 | 350 (0) | 6 (0) | 11,9 |

optimization, highlighting for each test the percentages of final removal in terms of the parameter of DOC.

Considering the response surface of Fig. 4, the optimal region is between the orange and red zone, which represents a desirability of 0.9 and 1.0 respectively, therefore, this region is limited between the $TiO_2$ concentration of 100 and 200, and the pH of 3 to 4.

It is also concluded that the optimal test is No. 8, since it presents the highest DOC removal (57.9%) with the lowest catalyst concentration evaluated of 100 mg $TiO_2.L^{-1}$, at an acid pH of 3 units. Becerra et al.[39] found that photocatalytic treatment with $TiO_2$ provided a removal of more than 80% of the contaminants present in the leachate, under acidic pH conditions (4 units) and with the lowest dose of catalyst evaluated, which is in accordance with the results obtained in this investigation.

The hydraulic retention times for each one of the tests varied, due to the fact that they were carried out in sunny and cloudy days, where the accumulated energies were reached faster or slower, respectively. We conclude that for a hot climate like the city of Cúcuta, Norte de Santander, in sunny days the accumulated energies of 60 $kJ.L^{-1}$ are reached in HRT in less than 3 h, and for cloudy days in HRT greater in more than 3 h. According to [7], the amount of illumination falling on the catalyst leads to a high rate of photocatalytic degradation, because as irradiation times increase, so does the removal of contaminants. It should be noted that this optimal test obtained one of the highest irradiation times (4.3 h), which is consistent with the obtained results.

Considering the application of treatment on a real scale, the leachates can be mixed with domestic wastewater, in the necessary quantities to maintain the working concentrations carried out in the investigation. In addition to this, the physicochemical characteristics of these domestic wastewater (COD and DOC), allow their mixing to maintain the concentrations at the required dilution, and thus apply the techniques described above.

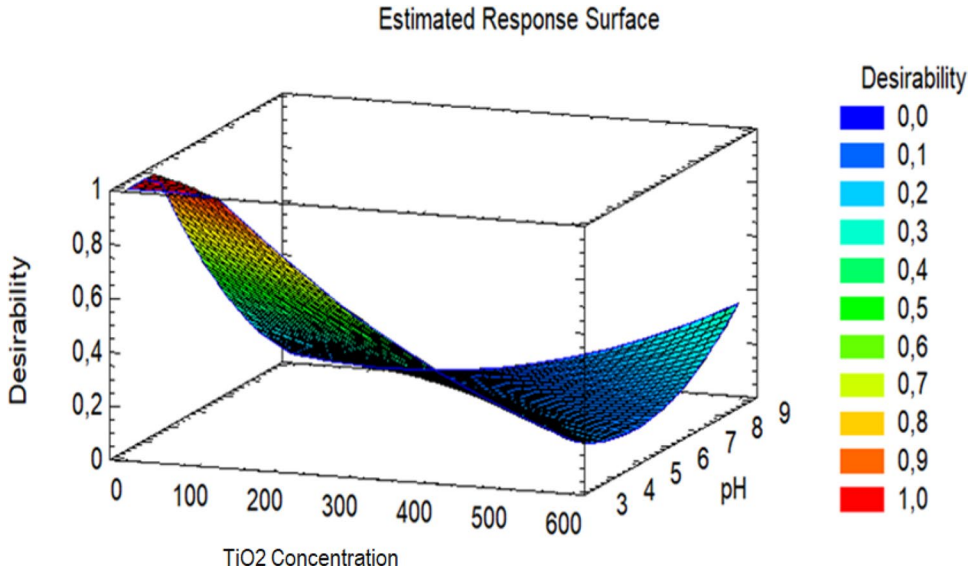



**Fig. 4** Response surface for photocatalysis optimization

It must be concluded that for the concentrations represented by 100 and 350 mg $TiO_2.L^{-1}$ the highest removal percentages (in terms of DOC) occur when in the treatment the pH is controlled in 3 units, which is consistent with the work done by [40] which showed that photodegradation of the leachate that was strongly favored at a higher acidic pH than the neutral and alkaline solutions.

Similarly, several studies [41–44], prove that this treatment alternative produces better results when it is developed at acidic pH, since at acidity levels, the surface of the catalyst is positively charged which leads to the attraction of negatively charged organic pollutants generating an important photocatalytic activity [45, 46]. That is why, the closer the pH is to the alkalinity, the removal behavior throughout the treatment is usually very dispersed, and it is not possible to determine a reliable reduction of the contaminants. It must also be argued that at pH near neutrality (pH = 6), removal maintains a consistent trend line, although it does not present degradation results that are relevant, since they are very low.

The behavior of the removal at each concentration shows that not necessarily the best treatment is not necessarily the one that uses the highest concentration of the catalyst. Generally, what can be concluded with (from) the behavior of the treatment under the different configurations is that, in high concentrations of catalyst (600 $mg.L^{-1}$ $TiO_2$), there are better removal levels at basic pH, and in the case of low catalyst concentrations (100 $mg.L^{-1}$ $TiO_2$) or with average values (350 $mg.L^{-1}$ $TiO_2$), the best removal levels are given at acidic pH levels.

Photocatalytic degradation using $TiO_2$ as a catalyst has revealed great potential for economical and environmentally consistent, non-toxic, chemically stable, high photoactivity treatment [16]. Its main advantage is the possibility of incorporating solar energy in the photoactivation of the catalyst, so the degradation process acquires a significant additional environmental value and it becomes a sustainable technique [47]. The use of sunlight in the photodegradation of wastewater pollutants makes it an economically viable process, particularly for large-scale applications [19].

Losada et al. [35], determined that the addition of $H_2O_2$ in a $TiO_2$/UV photocatalytic treatment, improves the process notably, since it contributes positively to the speed of degradation of the contaminants, which is related to the chemical action of this element as an oxidizing agent. Thus, for the same period of time, in the absence of $H_2O_2$, 50% of the contaminants present were degraded, while in the presence of peroxide, more than 90% were removed, which shows a high contribution to the efficiency of the treatment. For this reason, with each accumulated energy, a concentration of hydrogen peroxide was maintained, which was determined from an optimal dose as a reference for a research project.

### 3.4 Photocatalysis Coupling–Aerobic Biological Process.

Once the optimal conditions are set to develop the photocatalytic treatment, with a concentration of $TiO_2$ of 100 $mg.L^{-1}$ and a pH of 3, the treatment of the leachate in the compound parabolic collector (CPC) is carried out again until it gets to 60 $kJ.L^{-1}$ of accumulated energy.

Once it is completed, the resulting effluent is subjected to a filtration process, in order to eliminate the excess $TiO_2$ present to avoid any effects on the microorganisms, and it is ready to begin the coupling with the biological treatment.

To start the biological treatment, the methodology proposed by the Zahn Wellens Test / EMPA OCDE 302B was followed, showing 3 reactors containing inoculum sludge + mineral medium + phototreated effluent previously

filtered, 2 white reactors with mineral medium + inoculum sludge and 2 control reactors with mineral medium + inoculum sludge + reference compound. A reactor capacity of 800 ml and a concentration of VSS by the slurry of 1500 mg $VSS.L^{-1}$ (ratio 3:1) was handled. The degradation in COD and DOC parameters was monitored for 28 days, with measurements on days 0, 4, 8, 12, 16, 20, 24, 28 and TSS and VSS on days 0, 16, 28.

Considering Fig. 5, in terms of COD, the highest degradation is evident, with a value of 68% of the compound analyzed. As for DOC, it shows a maximum level of degradation equivalent to 87%. In both parameters, a remarkable improvement in degradation within the biological process is seen after treating the sample with photocatalysis, which shows that photocatalytic processes can either decompose or reorganize the molecular structures of non-biodegradable organic materials into more easily biodegradable products, and it improves the efficiency and it allows biological post-treatments [48]. In addition, the requirement set out by the EMPA OECD 302B methodology is accomplished, and at the end of the test, biodegradation results of more than or close to 70% have been obtained.

The suspended solids results are listed in Table 10. According to the results presented above, a final removal of 54% and 6% is obtained, in terms of VSS and TSS, respectively. This removal is provided by the biological process, for which the solids are settle in the reactors, this is a real-scale process which is evident in a subsequent settler.

A better behavior of the compound after coupling is detailed, since much higher degradation percentages are evidenced than those of the initial biodegradability test, which corroborates that this heterogeneous photocatalysis process ($TiO_2$/UV and $H_2O_2$) provides a much more stabilized effluent with adequate characteristics for degradation in biological reactors under controlled aerobic processes.

**Table 10** Solid results suspended in the coupling

| Time (days) | TSS (mg.L) | Removal (%) | VSS (mg.L) | Removal (%) |
|---|---|---|---|---|
| 0 | 3932 | – | 2048 | – |
| 16 | 3786 | 3,71 | 1344 | 34,38 |
| 28 | 3688 | 6,21 | 928 | 54,69 |

Finally, the results of removal for coupling, register percentages of 61 and 74%, for COD and DOC of the leachate respectively, in relation to the input in the photocatalysis process and the output in the biological process. It is estimated that the efficiency of the coupling is more than 50%, which supports the hypothesis that the leachates coming from the El Guayabal Landfill, by the coupling of a heterogeneous photocatalytic and biological activated slurry process, allow a considerable removal of the constituents present in this liquid residual, and that it is considered a viable alternative for the treatment on a real scale of them.

Dacosta et al. [49] found that two leachate samples from different landfills had low aerobic biodegradability (65% and 30%) after 28 days under the Zahn Wellens test, and that after applying advanced oxidation pretreatment, the effluent within the biological process showed higher biodegradability characteristics, increasing in final removals by 89% and 69% respectively. Silva et al. [50] determined a similar efficiency in the evaluation of leachate biodegradability improvement by applying the same method (Zahn-Wellens Test), which after an advanced oxidation process, increased its degradation to 70%, in relation to the initial values of between 4 and 20%. This supports and evidences the need to couple this type of treatment towards the reduction of contaminants and toxics present in leachates, because due to their harmful characteristics, they do not allow a removal of contaminants under conventional treatment processes,

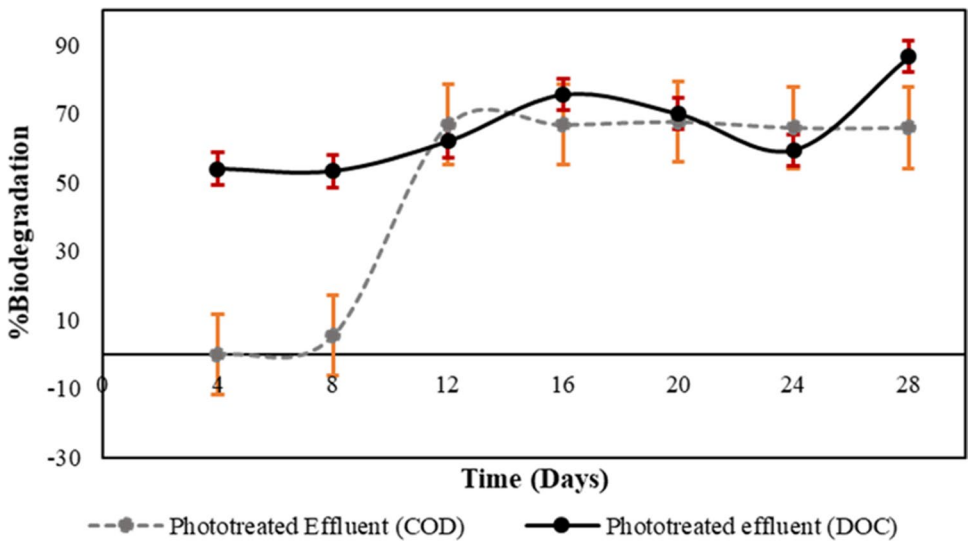



**Fig. 5** Percentage (%) of Biodegradation of COD and DOC—Coupled biodegradability test

requiring the application of these new techniques that have proven to be an efficient alternative, as well as applicable in real settings, besides their easy application, such as low operation costs.

The biological reactor most often combined with advanced laboratory-scale oxidation processes for leachate treatment is the Sequential Biological Reactor (SBR) that simulates an activated sludge process, and the anaerobic biodegradability analyses are less common [51]. However, [52] evaluated an aerobic (rotary biological contactor) and anaerobic (upflow anaerobic sludge reactor) biological process for leachate treatment, finding 54% and 62% removals of contaminants present in terms of COD respectively [53]. evaluated the performance of a pilot-scale anaerobic biofilm digester (ABD) for leachate treatment, determining that, despite the complex characteristics of this residual liquid, the system demonstrated high performance in maintaining removal levels in terms of COD of 96%, at hydraulic retention times of 10 days. With the above, it is possible that in later studies a coupling of heterogeneous photocatalysis with an anaerobic biological process can be evaluated, in which the process with the efficiencies found by the alternative developed in this research can be compared, this later studies can also determine which one can be more viable, starting from the high organic loads of the leachate.

### 3.5 Catalyst Comparison

One of the main challenges faced by researchers working with heterogeneous photocatalytic processes is the selection of the catalyst, because with this type of alternatives the research has not been as broadly developed as for other advanced oxidation processes [3]. There are several variables that influence the performance of catalysts, such as the pH of the treating wastewater, inorganic ions, dissolved oxygen, radiation and the hydraulic retention time of the treatment, which leads to the use of optimization processes that allow reproducible and accurate results [16]. This activity that was carried out in the current project allowed us to know the optimal dose of the catalyst used.

From bibliographical revision, it was determined that several catalysts based on metal oxides are frequently implemented in photocatalytic treatments, and they are focused on the removal of contaminants present in wastewater, such as Iron Oxide ($Fe_2O_3$) [54], Cerium Oxide ($CeO_2$) [55], Zinc Oxide (ZnO) [54], Titanium Dioxide ($TiO_2$) [56], this being the one that has shown the best results, When it is irradiated with UV light, electrons are propelled into the conduction band of the catalyst from the valence band which in turns, generates holes that leads to the production of OH radicals, while the electron located in the conduction band by its negative charge repels oxygen molecules generating a significant amount of OH radicals.[57, 58]. Among its advantages, it is mentioned that it is cheap, it has a good band position, it is non-toxic and it has an adequate biocompatibility [59].

Diez et al. [60], compared the removal efficiencies and kinetic behavior of $Fe_2O_3$ and $TiO_2$ when subjected to a photocatalysis process, found that although with iron oxide higher degradations are achieved in terms of TOC, iron leaching occurs, which would require a subsequent treatment. Besides, the $TiO_2$ achieves a better bond with the reactor surface favoring the reaction kinetics. Additionally, it is proven that the addition of oxidants such as $H_2O_2$ favors the efficiency of the treatment, which is also validated by [29, 61] and it was applied to the heterogeneous photocatalytic process developed in numbers 3.3 and 3.4 of the present document. Another catalyst frequently used in photocatalytic processes and that has evidenced high removals is Zinc Oxide (ZnO) [12, 62, 63], however it has been shown that the photocorrosion generated is considered to be the main disadvantage of this catalyst and according to [64, 65], it presents lower photocatalytic activity compared to $TiO_2$.

The statement made by the authors mentioned above is true, because by implementing a heterogeneous photocatalytic process using $TiO_2$, COD and TOC removals higher than 57% are obtained using small doses of it, a similar event to the results was obtained by [66–68] who also achieved removals higher than 60% of organic materials, metals and contaminants emerging from leachates when they used the same catalyst.

It should be noted that the product used was not chemically or laboratory scale modified, but it is for commercial use and easily accessible for anyone wishing to repeat the experiments. As for new alternatives when applying this type of treatment, there is the modification of the chemical structures of the catalyst, in this case, of the TiO2. An example of the this is the fact that [69], who combined cerium oxide with titanium dioxide found that the heterostructure generated can enhance the degradation of recalcitrant contaminants through photocatalysis processes. It is also possible to conclude that future research should focus on catalyst doping in order to favor oxide reduction processes as to increase the kinetics reaction for the removal of emerging and recalcitrant contaminants [70, 71], which are present in large quantities in landfill leachate.

## 4 Conclusions

Based on the characterization of the leachate from the Guayabal Landfill, in terms of COD, DOC, TSS and VSS, it can be classified as a middle-aged leachate, whose COD/DOC ratio illustrated low biodegradable characteristics, therefore, in a biological process very low levels of degradation can occur, making it necessary to implement a previous phase

that allows a more stable effluent and with more appropriate conditions to carry out this process.

The sludge coming from the treatment plant of El Country neighborhood, located in Jamundí, Valle del Cauca, provided the optimal and necessary characteristics to carry out the biodegradability test, since it showed a concentration of SVI (66.16 $mg.L^{-1}$), which categorizes it with good sedimentability, according to its use in a biological process.

Based on the biodegradability test (Zahn Wellens / EMPA OECD 302B), the leachates are not biodegradable, as less than 70% biodegradation rates were obtained, indicating that a process is needed prior to biological treatment, allowing for a more stable effluent with more consistent conditions so that significant removal levels exist and the test can be validated.

Taking into account the OCR (14.64 $mg.g^{-1}$ $VSS.h^{-1}$) indicating an adequate development of the microbial metabolism and a high biological activity of the sludge, it allowed the total degradation of ethylene glycol, used as a reference compound. Therefore, the fact that a considerable removal was not obtained in the biological process is due to the characteristics and toxic components that make up the leachate.

Heterogeneous photocatalysis ($TiO_2$/UV), provides higher removal percentages in acidic pH, and low $TiO_2$ concentrations, since taking into account the latter; the higher the catalyst concentrations, the incidence levels of UV rays decrease on the sample, which is reflected in the fact that the 600 mg $TiO_2.L^{-1}$ concentration for this project has provided the lowest removal percentages.

The results obtained in the coupling showed that after treating the leachate sample through the photocatalysis process, a much more stable effluent was available for the biological process, since within the biodegradability test, the efficiency in the removal of the contaminants increased by 50%, which improved the treatment conditions.

The need to couple this type of treatment for the reduction of contaminants and toxins present in the leachates is evident, since due to their harmful characteristics, they do not allow a removal of the contaminants present under conventional treatment processes, making it necessary to apply these new techniques that have proven to be an efficient alternative, as well as applicable in real scenarios.

In accordance with the country's current regulations, Resolution 0631 of 2015, issued by the Ministry of the Environment and Sustainable Development, taking into account the concentration of 500 mg $COD.L^{-1}$ of leachate used in this research, the final effluent from the coupled treatment process meets the characteristics for discharge in the COD (160 $mg.L^{-1}$) and pH (7.0 and 7.3) parameters. As for the suspended solids, high loads are still maintained, so in a real process, already having a sedimentation mechanism available, the values of these solids would begin to be significantly removed.

## References


1. Pastore C et al (2018) Comparison of different types of landfill leachate treatments by employment of nontarget screening to identify residual refractory organics and principal component analysis. Sci Total Environ 635:984–994. https://doi.org/10.1016/j.scitotenv.2018.04.135
2. Vahabian M, Hassanzadeh Y, Marofi S (2019) Assessment of landfill leachate in semi-arid climate and its impact on the groundwater quality case study: Hamedan, Iran. Environ Monit Assess 191(2):1–19. https://doi.org/10.1007/s10661-019-7215-8
3. Rueda-Marquez JJ, Levchuk I, Fernández Ibañez P, Sillanpää M (2020) A critical review on application of photocatalysis for toxicity reduction of real wastewaters. J. Clean. Prod. 258:120694. https://doi.org/10.1016/j.jclepro.2020.120694
4. Chemlal R et al (2014) Combination of advanced oxidation and biological processes for the landfill leachate treatment. Ecol Eng 73:281–289. https://doi.org/10.1016/j.ecoleng.2014.09.043
5. He H, Ma H, Liu L (2020) Combined photocatalytic pre-oxidation reactor and sequencing batch bioreactor for advanced treatment of industrial wastewater. J Water Process Eng 36:101259. https://doi.org/10.1016/j.jwpe.2020.101259
6. Elleuch L et al (2020) A new insight into highly contaminated landfill leachate treatment using Kefir grains pre-treatment combined with Ag-doped TiO2 photocatalytic process. J Hazard Mater 382:121119. https://doi.org/10.1016/j.jhazmat.2019.121119
7. Hassan M, Wang X, Wang F, Wu D, Hussain A, Xie B (2017) Coupling ARB-based biological and photochemical (UV/TiO 2 and UV/S 2 O 8 2− ) techniques to deal with sanitary landfill leachate. Waste Manag 63:292–298. https://doi.org/10.1016/j.wasman.2016.09.003
8. Padovan RN, Azevedo EB (2015) Combining A Sequencing Batch Reactor With Heterogeneous Photocatalysis (TiO2/UV) For Treating A Pencil Manufacturer's Wastewater. Brazilian J Chem Eng 32(1):99–106. https://doi.org/10.1590/0104-6632.20150321s00003103
9. Silva LS, Gonçalves MMM, Raddi de Araujo LR (2019) Combined photocatalytic and biological process for textile wastewater treatments. Water Environ Res 91(11):1490–1497. https://doi.org/10.1002/wer.1143
10. Borges ME, Sierra M, Méndez-Ramos J, Acosta-Mora P, Ruiz-Morales JC, Esparza P (2016) Solar degradation of contaminants in water: TiO2 solar photocatalysis assisted by up-conversion luminescent materials. Sol Energy Mater Sol Cells 155:194–201. https://doi.org/10.1016/j.solmat.2016.06.010
11. Talwar S, Sangal VK, Verma A (2018) Feasibility of using combined TiO2 photocatalysis and RBC process for the treatment of real pharmaceutical wastewater. J Photochem Photobiol A Chem 353:263–270. https://doi.org/10.1016/j.jphotochem.2017.11.013
12. Vela N et al (2018) Photocatalytic oxidation of six pesticides listed as endocrine disruptor chemicals from wastewater using two different TiO2 samples at pilot plant scale under sunlight irradiation. J Photochem Photobiol A Chem 353:271–278. https://doi.org/10.1016/j.jphotochem.2017.11.040
13. D. Becerra Moreno, "Acople De Procesos Fotocatalíticos Y Biológicos Para El Tratamiento De Aguas Residuales Con Residuos De Plaguicidas," Universidad Del Valle, 2010.
14. OCDE (Organización para la cooperación y el desarrollo económico), "Lodos Activados, Prueba de Inhibición de la Respiración (Oxidación de Carbono y Amonio)," 1998.
15. OCDE (Organización para la cooperación y el desarrollo económico), "Ensayo de Biodegradabilidad Inherente: OECD302 Zahn-Wellens / Método EMPA," 1992.
16. Hassan M, Zhao Y, Xie B (2016) Employing TiO 2 photocatalysis to deal with landfill leachate: Current status and

development. Chem Eng J 285:264–275. https://doi.org/10.1016/j.cej.2015.09.093
17. Malini TP, Selvi JA, Arthanareeswari M, Kamaraj P (2019) Photocatalytic Degradation of Organo Phosphorus Herbicide Anilofos in Aqueous Solution Using TiO2 (Degussa P25) Photocatalyst. Mater Today Proc 14:574–579. https://doi.org/10.1016/j.matpr.2019.04.181
18. Ammari Y, El Atmani K, Bay L, Bakas I, Qourzal S, Ait Ichou I (2020) Elimination of a mixture of two dyes by photocatalytic degradation based on TiO2 P-25 Degussa. Mater. Today Proc 22:126–129. https://doi.org/10.1016/j.matpr.2019.08.142
19. Cai F-F, Yang Z-H, Huang J, Zeng G-M, Wang L, Yang J (2014) Application of cetyltrimethylammonium bromide bentonite–titanium dioxide photocatalysis technology for pretreatment of aging leachate. J Hazard Mater 275:63–71. https://doi.org/10.1016/j.jhazmat.2014.04.050
20. Murgolo S et al (2017) A new supported TiO 2 film deposited on stainless steel for the photocatalytic degradation of contaminants of emerging concern. Chem Eng J 318:103–111. https://doi.org/10.1016/j.cej.2016.05.125
21. Abdel-Maksoud YK, Imam E, Ramadan AR (2018) Sand supported TiO2 photocatalyst in a tray photo-reactor for the removal of emerging contaminants in wastewater. Catal Today 313:55–62. https://doi.org/10.1016/j.cattod.2017.10.029
22. Saggioro EM et al (2014) Solar CPC pilot plant photocatalytic degradation of bisphenol A in waters and wastewaters using suspended and supported-TiO2. Influence of photogenerated species. Environ Sci Pollut Res 21(21):12112–12121. https://doi.org/10.1007/s11356-014-2723-0
23. Hossain MK et al (2018) A comparative study on the influence of pure anatase and Degussa-P25 TiO2 nanomaterials on the structural and optical properties of dye sensitized solar cell (DSSC) photoanode. Optik (Stuttg) 171:507–516. https://doi.org/10.1016/j.ijleo.2018.05.032
24. Prieto-Rodriguez L, Miralles-Cuevas S, Oller I, Agüera A, Puma GL, Malato S (2012) Treatment of emerging contaminants in wastewater treatment plants (WWTP) effluents by solar photocatalysis using low TiO2 concentrations. J Hazard Mater 211–212:131–137. https://doi.org/10.1016/j.jhazmat.2011.09.008
25. Miranda SM et al (2015) Solar photocatalytic gas-phase degradation of n-decane—a comparative study using cellulose acetate monoliths coated with P25 or sol-gel TiO2 films. Environ Sci Pollut Res 22(2):820–832. https://doi.org/10.1007/s11356-014-2952-2
26. Ohtani B, Prieto-Mahaney OO, Li D, Abe R (2010) What is Degussa (Evonik) P25? Crystalline composition analysis, reconstruction from isolated pure particles and photocatalytic activity test. J Photochem Photobiol A Chem 216(2–3):179–182. https://doi.org/10.1016/j.jphotochem.2010.07.024
27. Joseph K, Raj A, Viswanathan B (2009) Effect of surface area, pore volume and particle size of P25 titania on the phase transformation of anatase to rutile. Indian J Chem 48:1378–1382
28. Lachheb H, Guillard C, Lassoued H, Haddaji M, Rajah M, Houas A (2017) Photochemical oxidation of styrene in acetonitrile solution in presence of H 2 O 2, TiO 2 /H 2 O 2 and ZnO/H 2 O 2. J Photochem Photobiol A Chem 346:462–469. https://doi.org/10.1016/j.jphotochem.2017.06.026
29. Han E, Vijayarangamuthu K, Youn J, Park Y-K, Jung S-C, Jeon K-J (2018) Degussa P25 TiO 2 modified with H 2 O 2 under microwave treatment to enhance photocatalytic properties. Catal Today 303:305–312. https://doi.org/10.1016/j.cattod.2017.08.057
30. Fu D, Huang Y, Zhang X, Kurniawan TA, Ouyang T (2017) Uncovering potentials of integrated TiO2(B) nanosheets and H2O2 for removal of tetracycline from aqueous solution. J Mol Liq 248:112–120. https://doi.org/10.1016/j.molliq.2017.10.020
31. Spasiano D, Marotta R, Malato S, Fernandez-Ibañez P, Di Somma I (2015) Solar photocatalysis: Materials, reactors, some commercial, and pre-industrialized applications. A comprehensive approach. Appl Catal B 170–171:90–123. https://doi.org/10.1016/j.apcatb.2014.12.050
32. Borges ME, Sierra M, Cuevas E, García RD, Esparza P (2016) Photocatalysis with solar energy: Sunlight-responsive photocatalyst based on TiO2 loaded on a natural material for wastewater treatment. Sol Energy 135:527–535. https://doi.org/10.1016/j.solener.2016.06.022
33. D. R. Giraldo Valentín, "Eficiencia del proceso de fotocatálisis heterogénea con tio2 y h2o2 en la reducción de dbo5 y dqo de los lixiviados del botadero la mejorada el tambo Huancayo," *Repos. Inst. - UAP*, 2016.
34. Rocha EMR, Vilar JP, Fonseca A, Saraiva I, Boaventura RAR (2011) Landfill leachate treatment by solar-driven AOPs/H 2 O 2; Fe 2+ /H 2 O 2 /UV; TiO 2 /H 2 O 2 /UV; Pilot Plant with CPCs. Sol Energy 85:46–56. https://doi.org/10.1016/j.solener.2010.11.001
35. LM Losada, EJL Castillo, EAO Restrepo, EAS Galvis, RAT Palma, (2017) "Tratamiento de aguas contaminadas con colorantes mediante fotocatálisis con TiO2 usando luz artificial y solar. *Prod + Limpia*, 12(2)
36. R. Ramalho, "Introduction to Wastewater Treatment Processes - R Ramalho - Google Libros," 1977, 403.
37. Becerra D et al (2020) Coupling of heterogeneous photocatalysis and aerobic biological process of activated sludge to treat wastewater containing Chlorpyrifos. Ing Y Compet Rev CIENTÍFICA y TECNOLÓGICA 22:13. https://doi.org/10.25100/iyc.v22i1.8135
38. E. A. Solana, "Contribución al tratamiento de lixiviados de vertedero de residuos sólidos urbanos mediante procesos de oxidación avanzada," Universidad de Cantabria, departamento de Ingeniería Química y Orgánica, España, 2013.
39. Wiszniowski J, Robert D, Surmacz-Gorska J, Miksch K, Weber J (2006) Leachate detoxification by combination of biological and TiO2-photocatalytic processes. Water Sci Technol 53:181–190
40. S. P. Cho, S. C. Hong, and S.-I. Hong, "Photocatalytic degradation of the landfill leachate containing refractory matters and nitrogen compounds," 2002.
41. Arshad R et al (2020) Degradation product distribution of Reactive Red-147 dye treated by UV/H2O2/TiO2 advanced oxidation process. J Mater Res Technol. https://doi.org/10.1016/j.jmrt.2020.01.062
42. Boutiti A, Zouaghi R, Bendjabeur SE, Guittonneau S, Sehili T (2017) Photodegradation of 1-hexyl-3-methylimidazolium by UV/H2O2 and UV/TiO2: Influence of pH and chloride. J Photochem Photobiol A Chem 336:164–169. https://doi.org/10.1016/j.jphotochem.2016.12.030
43. Kaabeche ONEH, Zouaghi R, Boukhedoua S, Bendjabeur S, Sehili T (2019) A Comparative Study on Photocatalytic Degradation of Pyridinium Based Ionic Liquid by TiO2 and ZnO in Aqueous Solution. Int J Chem React Eng. https://doi.org/10.1515/ijcre-2018-0253
44. A. Mahmoodi, S. Mahmood Mehdinia, A. Rahmani, and H. Nassehinia, "IRANIAN JOURNAL OF CATALYSIS Investigation efficiency of nano photocatalytic compound of TiO 2 and rice husk silica in removal of reactive red 198 dye from synthetic aqueous solutions."
45. Lu D, Yang M, Fang P, Li C, Jiang L (2017) Enhanced photocatalytic degradation of aqueous phenol and Cr(VI) over visible-light-driven Tb x O y loaded TiO 2 -oriented nanosheets. Appl Surf Sci 399:167–184. https://doi.org/10.1016/j.apsusc.2016.12.077
46. Chen D et al (2020) Photocatalytic degradation of organic pollutants using TiO2-based photocatalysts: A review. J. Clean. Prod. https://doi.org/10.1016/j.jclepro.2020.121725

47. Moreira NFF et al (2018) Solar treatment (H2O2, TiO2-P25 and GO-TiO2 photocatalysis, photo-Fenton) of organic micropollutants, human pathogen indicators, antibiotic resistant bacteria and related genes in urban wastewater. Water Res 135:195–206. https://doi.org/10.1016/j.watres.2018.01.064
48. Luo H, Zeng Y, Cheng Y, He D, Pan X (2020) Recent advances in municipal landfill leachate: A review focusing on its characteristics, treatment, and toxicity assessment. Sci Total Environ. https://doi.org/10.1016/j.scitotenv.2019.135468
49. Moraes Da Costa F, Dario S, Daflon A, Bila DM, Valeria Da Fonseca F, Campos JC (2018) Evaluation of the biodegradability and toxicity of landfill leachates after pretreatment using advanced oxidative processes. Waste Manag 76:606–613. https://doi.org/10.1016/j.wasman.2018.02.030
50. Silva TFCV et al (2013) Multistage treatment system for raw leachate fromsanitary landfill combining biological nitrification-denitrification/solar photo-Fenton/biological processes, at a scale close to industrial - Biodegradability enhancement and evolution profile of trace pol. Water Res 47(16):6167–6186. https://doi.org/10.1016/j.watres.2013.07.036
51. Wang K, Li L, Tan F, Wu D (2018) Treatment of Landfill Leachate Using Activated Sludge Technology: A Review. Archaea. https://doi.org/10.1155/2018/1039453
52. Castillo E, Vergara M, Moreno Y (2006) "Landfill leachate treatment using a rotating biological contactor and an upward-flow anaerobic sludge bed reactor. Waste Manage. https://doi.org/10.1016/j.wasman.2006.08.003
53. Arij Y et al (2018) "Performance of pilot scale anaerobic biofilm digester (ABD) for the treatment of leachate from a municipal waste transfer station. Biores Technol. https://doi.org/10.1016/j.biortech.2018.03.131
54. Wu Q et al (2020) Peculiar synergetic effect of γ-Fe2O3 nanoparticles and graphene oxide on MIL-53 (Fe) for boosting photocatalysis. Chem Eng J 390:124615. https://doi.org/10.1016/j.cej.2020.124615
55. Zhu L et al (2020) Photo-catalytic pretreatment of biomass for anaerobic digestion using visible light and Nickle oxide (NiOx) nanoparticles prepared by sol gel method. Renew Energy 154:128–135. https://doi.org/10.1016/j.renene.2020.02.119
56. Védrine JC (2019) Importance, features and uses of metal oxide catalysts in heterogeneous catalysis. Chinese J Catal 40(11):1627–1636. https://doi.org/10.1016/S1872-2067(18)63162-6
57. Al-Dawery SK (2013) Photo-catalyst degradation of tartrazine compound in wastewater using Tio2 and UV light. J Eng Sci Technol 8(6):683–691
58. Chekir N et al (2017) A comparative study of tartrazine degradation using UV and solar fixed bed reactors. Int J Hydrogen Energy 42(13):8948–8954. https://doi.org/10.1016/j.ijhydene.2016.11.057
59. Qian R et al (2019) Charge carrier trapping, recombination and transfer during TiO2 photocatalysis: An overview. Catal Today 335:78–90. https://doi.org/10.1016/j.cattod.2018.10.053
60. Díez AM et al (2018) A step forward in heterogeneous photocatalysis: Process intensification by using a static mixer as catalyst support. Chem Eng J 343:597–606. https://doi.org/10.1016/j.cej.2018.03.041
61. Monteagudo JM, Durán A, Martín IS, Vellón B (2020) Photocatalytic degradation of aniline by solar/TiO2 system in the presence of the electron acceptors Na2S2O8 and H2O2. Sep Purif Technol 238:116456. https://doi.org/10.1016/j.seppur.2019.116456
62. Kosera VS, Cruz TM, Chaves ES, Tiburtius ERL (2017) Triclosan degradation by heterogeneous photocatalysis using ZnO immobilized in biopolymer as catalyst. J Photochem Photobiol A Chem 344:184–191. https://doi.org/10.1016/j.jphotochem.2017.05.014
63. Liu J, Wang Y, Ma J, Peng Y, Wang A (2019) A review on bidirectional analogies between the photocatalysis and antibacterial properties of ZnO. J Alloys Compd 783:898–918. https://doi.org/10.1016/j.jallcom.2018.12.330
64. Souza RP et al (2016) Photocatalytic activity of TiO2, ZnO and Nb2O5 applied to degradation of textile wastewater. J Photochem Photobiol A Chem 329:9–17. https://doi.org/10.1016/j.jphotochem.2016.06.013
65. Çifçi DI, Meriç S (2015) Optimization of suspended photocatalytic treatment of two biologically treated textile effluents using TiO2 and ZnO catalysts. Glob Nest J 17(4):653–663. https://doi.org/10.30955/gnj.001715
66. Nomura Y, Fukahori S, Fujiwara T (2020) Removal of 1,4-dioxane from landfill leachate by a rotating advanced oxidation contactor equipped with activated carbon/TiO2 composite sheets. J Hazard Mater 383:121005. https://doi.org/10.1016/j.jhazmat.2019.121005
67. Gossard A, Lepeytre C (2017) An innovative green process for the depollution of Cr(VI)-contaminated surfaces using TiO2-based photocatalytic gels. J Environ Chem Eng 5(6):5573–5580. https://doi.org/10.1016/j.jece.2017.10.026
68. Fang Z, Hu Y, Cheng J, Chen Y (2019) Continuous removal of trace bisphenol A from water by high efficacy TiO2 nanotube pillared graphene-based macrostructures in a photocatalytically fluidized bed. Chem Eng J 372:581–589. https://doi.org/10.1016/j.cej.2019.04.129
69. de Matos Rodrigues MH et al (2019) "Enhanced degradation of the antibiotic sulfamethoxazole by heterogeneous photocatalysis using Ce0,8Gd0,2O2-δ/TiO2 particles. J. Alloys Compd. https://doi.org/10.1016/j.jallcom.2019.151711
70. Castañeda-Juárez M, Martínez-Miranda V, Almazán-Sánchez PT, Linares-Hernández I, Santoyo-Tepole F, Vázquez-Mejía G (2019) Synthesis of TiO2 catalysts doped with Cu, Fe, and Fe/Cu supported on clinoptilolite zeolite by an electrochemical-thermal method for the degradation of diclofenac by heterogeneous photocatalysis. J Photochem Photobiol A Chem 380:111834. https://doi.org/10.1016/j.jphotochem.2019.04.045
71. Mohan Reddy K, Devaraju J (2019) Kinetics of Photo Fenton Process and Ag-TiO2 Photocatalyst under UV-light". Mater. Today Proc. 17:235–238. https://doi.org/10.1016/j.matpr.2019.06.424

# Chapter 6: Synthesis

## 6.1. General Overview of the Research

The present research addresses the treatment of landfill leachates through the integration of advanced oxidation processes (AOPs) and biological treatments—an approach widely recognized for its potential to manage complex and low-biodegradability effluents (Sangkham et al., 2025) (Gopal et al., 2025) (Abo et al., 2025). Throughout the study, various treatment combinations were evaluated with the aim of optimizing organic matter degradation, toxicity reduction, and the removal of nutrients and heavy metals. This aligns with the challenges frequently reported in the literature regarding comprehensive leachate treatment strategies (Varma & Singh, 2025) (Singh et al., 2025). Experimental studies were conducted using leachates from two sanitary landfills with contrasting characteristics: one located in a municipality with predominantly agricultural activity (La Madera Landfill, Ocaña) and the other in an urban area with significant industrial activity (El Guayabal Landfill, Cúcuta). This comparative approach enables a more representative assessment of treatment performance, considering the strong spatial and temporal variability in leachate composition (Jia et al., 2025) (Goukeh et al., 2025).

The experimental tests included the application of catalytic ozonation with magnetite, upflow anaerobic sludge blanket (UASB) reactors, and microalgae treatments, evaluating the efficiency of each process both individually and in combined treatment schemes. This type of integration has been highlighted in the literature as a promising alternative to address the diversity and complexity of contaminants present in landfill leachates (Yang et al., 2024) (F. Wang et al., 2024). The inclusion of leachates with different chemical compositions not only broadens the applicability of the results, but also allows for the validation of the proposed treatments under real operational conditions—an essential consideration given the variability reported in previous studies of leachates generated in regions with diverse urban and industrial dynamics (Sabba et al., 2025) (Goukeh et al., 2025).

The results obtained from the evaluation of catalytic ozonation with magnetite in leachates from the La Madera and El Guayabal landfills demonstrated high efficiency in organic matter removal, with chemical oxygen demand (COD) reductions of 85.3% and 75.8%, respectively. These values are consistent with those reported by other authors who have highlighted the effectiveness of metal oxides as catalysts in heterogeneous ozonation processes for the degradation of recalcitrant compounds (Xiang et al., 2025) (Javaid et al., 2025). The higher efficiency observed in El

Guayabal suggests that the chemical composition of the leachate significantly influences the oxidation kinetics, a factor previously identified as critical in the performance of AOPs (Shi et al., 2025) (Song et al., 2025). Furthermore, the increase in the $BOD_5$/COD ratio—from 0.26 to 0.38 in El Guayabal and from 0.23 to 0.32 in La Madera—reflects an improvement in the biodegradability of the treated effluent, in line with findings from previous studies showing that catalytic ozonation can transform non-biodegradable organic compounds into more readily degradable fractions (Yang et al., 2024).

Process optimization using response surface methodology determined that the optimal conditions corresponded to an ozone dose of 6 g/h, a magnetite concentration of 2.5 g/L, and a pH of 9. These parameters allowed for maximum process efficiency and reduced specific ozone consumption, reaching a ratio of 2.7 g $O_3$ per gram of COD removed. This finding aligns with previous studies emphasizing the critical role of pH and catalyst dosage in the generation of hydroxyl radicals during catalytic ozonation (Feng et al., 2021). The observed effectiveness under alkaline conditions is attributed to the enhanced stability and reactivity of the oxidizing species generated, particularly in the presence of metal oxides such as magnetite (Yang et al., 2024). In contrast, under suboptimal conditions, such as acidic pH or absence of a catalyst, ozone consumption increased to 4.8 g $O_3$ per gram of COD removed, demonstrating lower overall process efficiency. This behavior has been reported as a standard limitation in non-catalytic ozonation systems (Moussavi et al., 2012).

The analysis of catalyst stability indicated that magnetite retains its crystalline structure after several reuse cycles, although a progressive decline in catalytic efficiency was observed. By the third reuse cycle, COD removal efficiency decreased from 85.3% to 73.6%, suggesting the accumulation of organic compounds on the catalyst surface and potential saturation of active sites. This phenomenon has been widely reported as a primary limitation in the continuous use of heterogeneous catalysts in advanced water treatment processes (F. Wang et al., 2024). Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) analyses confirmed the presence of residues and oxidation products on the magnetite surface after successive cycles, reinforcing the need to implement physical or chemical regeneration strategies to extend the catalyst's service life and maintain consistent process performance (Moussavi et al., 2012).

The results of this study highlight the feasibility of catalytic ozonation with magnetite as an effective strategy for the degradation of recalcitrant contaminants in landfill

leachates. This finding aligns with previous studies that have demonstrated the ability of heterogeneous ozonation to oxidize hard-to-degrade compounds, thereby improving effluent quality and biodegradability (F. Wang et al., 2024) (Moussavi et al., 2012). However, differences in process efficiency were observed depending on the leachate composition, reinforcing earlier observations about the critical influence of the wastewater matrix on oxidation kinetics and by-product formation (Feng et al., 2021). In this study, it was found that in El Guayabal, the interaction between magnetite and ozone played a more significant role in COD removal, whereas in La Madera, the process was primarily driven by direct ozone action. This may be attributed to the differential presence of readily oxidizable organic compounds or those with greater affinity for the catalyst.

In terms of applicability, the high efficiency in contaminant removal and the improvement in leachate biodegradability suggest that catalytic ozonation with magnetite is a viable strategy as a pretreatment within sequential treatment schemes. This is consistent with several studies reporting substantial improvements in organic matter degradation and in the stability of biological processes when an advanced oxidation stage is introduced before anaerobic treatment (Liu et al., 2025) (Javaid et al., 2025). In the present study, catalytic ozonation used as a pretreatment significantly increased the $BOD_5$/COD ratio and reduced aerobic toxicity, with an optimal ozonation time of 40 minutes, during which the specific methanogenic activity reached 0.22 g $CH_4$-COD/(gVSS·d), indicating favorable conditions for anaerobic microbial activity. Similar results have been reported in studies where pre-oxidation helped overcome microbial inhibition typically associated with low-biodegradability leachates (F. Wang et al., 2024) (Moussavi et al., 2012). However, consistent with previous findings, ozonation alone was not effective for nutrient removal, and high concentrations of total nitrogen and ammoniacal nitrogen remained in the treated leachates (F. Wang et al., 2024).

The UASB reactor, operating at a hydraulic retention time of 24 hours, achieved COD removal efficiencies between 60% and 75%, with greater stability observed in leachates from the El Guayabal landfill. These results are consistent with previous studies, where UASB-type anaerobic reactors have demonstrated good performance in removing organic matter from partially stabilized leachates. However, their efficiency may be affected by toxic loads and low biodegradability (Dhamsaniya et al., 2023) (Abdel-Shafy et al., 2024). However, suspended solids removal was limited, with reductions of up to 65%, and high concentrations of ammoniacal nitrogen remained in the treated effluents (341.6 mg/L and 546.1 mg/L). This has been identified as one of the main limitations of anaerobic processes and

supports the need for subsequent treatment stages designed explicitly for nitrogen compound removal (Igwegbe et al., 2024) (Dhamsaniya et al., 2023).

Microalgae treatment was evaluated as a complementary strategy for nutrient removal, achieving reductions of up to 65% in total nitrogen and 70% in phosphorus. These results are consistent with previous studies that have documented the ability of particular microalgae species to assimilate nitrogenous and phosphorous compounds present in wastewater, particularly during tertiary treatment stages (Geng et al., 2025) (Paiva et al., 2021). However, the observed efficiency in organic matter removal was lower than that achieved by the UASB reactor, suggesting that the application of microalgae should be focused on effluent polishing, prioritizing nutrient reduction and the improvement of final water quality, as proposed in studies centered on hybrid treatment systems (Z. Wang et al., 2022) (Pinpatthanapong et al., 2022).

The coupling of treatment processes demonstrated that combining catalytic ozonation with magnetite and a UASB reactor achieved the highest organic matter removal. In contrast, the reverse configuration (UASB followed by catalytic ozonation) led to a more significant reduction in toxicity, including microalgae treatment after the biological stage, improved nutrient removal, confirming the need for integrated strategies to optimize final effluent quality. These results are consistent with studies highlighting the synergy between physicochemical and biological processes in sequential schemes, which enable targeting different contaminant fractions present in landfill leachates (Dhamsaniya et al., 2023) (Tian et al., 2022) (Yang et al., 2024) (Geng et al., 2025). The implementation of these coupled systems has also been promoted for their potential to reduce reagent consumption, improve energy efficiency, and enhance the stability of biological systems, reinforcing their feasibility for full-scale applications (Yang et al., 2024).

### 6.2. Comparison of Advanced Oxidation Processes

The treatment of landfill leachates using advanced oxidation processes has been evaluated through catalytic ozonation with magnetite and heterogeneous photocatalysis coupled with biological processes. These methods have been widely studied for their capacity to degrade recalcitrant compounds in complex wastewater matrices, improving biodegradability and reducing toxicity (Moussavi et al., 2012) (Sangkham et al., 2025) (Zhang et al., 2025) (Q. Wang et al., 2025). In this study, catalytic ozonation with magnetite showed higher efficiency in organic matter removal, achieving COD reductions of up to 85.3% in leachates from La Madera

landfill and 75.8% in El Guayabal, along with an increase in the $BOD_5$/COD ratio, indicating a significant improvement in the biodegradability of the treated leachate. On the other hand, heterogeneous photocatalysis with $TiO_2$ achieved up to 57% COD removal under optimized conditions. It yielded an additional 21% mineralization when coupled with an anaerobic biological process, reaching a total efficiency of 78%. Such hybrid configurations have been reported in the literature as effective strategies for enhancing the degradation of persistent organic compounds, especially in matrices with low biodegradability (Jari et al., 2025) (Silerio-Vázquez et al., 2024) (Zarzzeka et al., 2024).

While both processes improve leachate biodegradability and reduce toxicity, catalytic ozonation enables more effective contaminant removal in a shorter treatment time (40 minutes compared to the 5 hours of solar exposure required for photocatalysis). This difference in removal kinetics has been previously documented, highlighting the high reactivity of ozone under alkaline catalytic conditions compared to the weather-dependent performance of solar photocatalytic systems (F. Wang et al., 2024) (Xiang et al., 2025). However, photocatalysis has the advantage of operating with solar radiation, which reduces energy consumption and allows for lower use of chemical reagents, as emphasized in studies focused on sustainable water treatment systems (Bah et al., 2023) (Fauziyen et al., 2024) (Hazaraimi et al., 2024). Regarding nutrient removal, photocatalysis achieved up to 76% reduction in dissolved organic carbon (DOC) and enabled partial degradation of nitrogen compounds. In contrast, catalytic ozonation maintained elevated concentrations of ammoniacal nitrogen in the treated effluent, which is consistent with findings in the literature and supports the need for a subsequent treatment step specifically designed for the removal of such compounds (Moussavi et al., 2012).

The coupling of these processes with biological reactors improves overall treatment efficiency by leveraging synergies between physicochemical and biological stages. The combination of catalytic ozonation with a UASB reactor optimized anaerobic degradation, enhancing process stability and increasing biogas production. This approach has been reported in previous studies as an effective strategy to overcome the limitations of anaerobic digestion in leachates with high organic loads and low biodegradability (Moussavi et al., 2012) (Yang et al., 2024). In contrast, photocatalysis followed by an activated sludge reactor improved final effluent quality, promoting the removal of both organic matter and nutrients—findings consistent with research highlighting the usefulness of hybrid photocatalytic-biological systems in polishing stages (Hassan et al., 2017) (Kanmani & Dileepan, 2023). These differences in performance and application suggest that the selection of the optimal

treatment should be based on the specific composition of the leachate and the defined purification objectives, enabling the development of integrated schemes that maximize process efficiency and minimize environmental impact.

## 6.3. Conclusions

The results demonstrated that the integration of advanced oxidation processes (AOPs), specifically ozone catalyzed by magnetite, with biological treatments such as upflow anaerobic sludge blanket (UASB) reactors and microalgae, represents an efficient strategy for the treatment of landfill leachates.

The catalytic ozonation process with magnetite proved effective in degrading recalcitrant organic contaminants, achieving chemical oxygen demand (COD) reductions of 85.3% in El Guayabal and 75.8% in La Madera. This efficiency was significantly influenced by the chemical composition of the leachate, highlighting the need to adjust operational parameters based on the effluent characteristics. Process optimization determined that the ideal conditions included an ozone dose of 6 g/h, a magnetite concentration of 2.5 g/L, and a pH of 9, maximizing organic matter degradation while minimizing ozone consumption (2.7 g $O_3$ per gram of COD removed).

The catalyst stability analysis indicated that magnetite retains its structure after multiple reuse cycles, although its catalytic efficiency gradually decreases. By the third cycle, COD removal efficiency dropped from 85.3% to 73.6%, attributed to the adsorption of reaction by-products on the catalyst surface. This highlights the need for regeneration strategies to extend the catalyst's lifespan and maintain its efficiency.

The coupling of catalytic ozonation with the UASB reactor improved leachate biodegradability, increasing the $BOD_5$/COD ratio from 0.26 to 0.38 in El Guayabal and from 0.23 to 0.32 in La Madera, facilitating its biological degradation. The UASB reactor, operating at a hydraulic retention time of 24 hours, achieved COD removal efficiencies between 60% and 75%, with more excellent stability in the leachates from the El Guayabal landfill. However, ammoniacal nitrogen concentrations in the treated effluents remained high (341.6 mg/L and 546.1 mg/L, respectively), indicating the need for an additional stage for nitrogen removal.

Microalgae treatment proved to be an effective strategy for nutrient removal, achieving reductions of 65% in total nitrogen and 70% in phosphorus. However, its

efficiency in removing organic matter was lower than that of the UASB reactor, indicating that its application should focus on polishing the final effluent.

The sequence of processes played an important role in overall efficiency. The combination of catalytic ozonation followed by UASB achieved the highest organic matter removal, whereas the reverse configuration (UASB followed by catalytic ozonation) was more effective in reducing toxicity, including microalgae as a final step improved nutrient removal, reinforcing the need for integrated treatment strategies adapted to the specific composition of landfill leachates.

### 6.4. Recommendations

- **Process Optimization for Full-Scale Applications:**
  - It is recommended that pilot-scale studies be conducted and operational parameters optimized to enhance treatment efficiency and economic feasibility.
  - The development of continuous-flow systems is suggested to assess the stability and performance of the process under actual operating conditions.

- **Catalyst Regeneration and Lifespan Extension:**
  - The progressive reduction in magnetite efficiency indicates the need for periodic regeneration strategies, such as thermal or chemical treatments, to maintain its catalytic activity.
  - The evaluation of low-cost alternative catalysts with similar or improved activity is recommended to enhance the sustainability of the process.

- **Nitrogen and Phosphorus Management in the Treated Effluent:**
  - Due to the high residual concentrations of ammoniacal nitrogen, implementing biological nitrification-denitrification processes or adsorption technologies is suggested to meet discharge standards.
  - The obtained microalgal biomass could be valorized as a biofertilizer or biotechnological input, promoting circular economy approaches.

- **Toxicity Reduction and Environmental Impact Assessment:**
  - Additional ecotoxicological tests are recommended to evaluate the long-term effects of the treated effluent on aquatic and soil ecosystems.
  - Implementing toxicity monitoring protocols will help verify the reduction of environmental impacts associated with treated landfill leachates.

- **Energy Efficiency and Economic Feasibility Assessments:**
  - A detailed techno-economic analysis is necessary to evaluate the large-scale feasibility of the process, considering energy consumption and reagent costs.
  - To improve the energy efficiency of the process, it is recommended that renewable energy sources, such as solar-assisted ozonation, be explored.

### 6.5. Scientific Contributions of the Study

The present study has contributed to advancing knowledge in treating landfill leachates by coupling advanced oxidation processes (AOPs) and biological treatments. Through experimental development, mathematical modeling, and the evaluation of process synergies, significant results have been generated with theoretical and applied implications for the sustainable management of leachates. The main scientific contributions of this study are as follows:

- **Optimization of Catalytic Ozonation with Magnetite in Leachate Treatment:** The optimal conditions for the degradation of organic contaminants through catalytic ozonation with magnetite were established, determining the influence of variables such as pH, magnetite dosage, and ozone concentration. The results demonstrated improved organic matter degradation efficiency and reduced toxicity compared to conventional ozonation. This finding expands knowledge of heterogeneous oxidation mechanisms and their applicability in complex wastewater treatment systems.

- **Evaluation of the Impact of Catalytic Ozonation on Leachate Biodegradability:** Catalytic ozonation with magnetite was shown to enhance leachate biodegradability by promoting the conversion of refractory compounds into more accessible byproducts for subsequent biological treatment. This contribution is a foundation for designing sequential treatment schemes, where advanced oxidation functions as an effective pretreatment before biological degradation.

- **Coupling of Catalytic Ozonation with Up-flow Anaerobic Sludge Blanket (UASB) Reactor:** The combination of these processes was evaluated, demonstrating that pre-oxidation with ozone/magnetite enhances UASB reactor stability and allows for greater utilization of biodegradable organic matter. An increase in chemical oxygen demand (COD) removal efficiency and a reduction

in the inhibition of methanogenic activity were observed, contributing to the improved viability of anaerobic processes for landfill leachate treatment.

- **Integration of Microalgae in the Treatment of Leachates Post-Treated with AOPs and UASB:** The potential of microalgae for nutrient removal and improving the quality of the final effluent was explored. The results indicated that microalgal growth is enhanced in pretreated leachates, enabling efficient nitrogen and phosphorus removal. This finding suggests that integrating microalgae-based bioprocesses can be a complementary strategy for treating leachates with high nutrient loads.

- **Reduction of Toxicity in Treated Leachates:** A detailed toxicity assessment of treated leachates was conducted using bioassays with aerobic, anaerobic, and microalgae. The results confirmed that combining AOPs and biological processes improves effluent quality and significantly reduces toxicity, minimizing the environmental impacts associated with leachate disposal.

- **Contribution to Scientific Literature and Applicability in Leachate Treatment:** This research has published several scientific articles that contribute to the understanding and application of advanced oxidation processes in leachate treatment. These publications facilitate disseminating the knowledge generated and serve as a reference for developing new research in this field.

### 6.6. Participation in Academic and Scientific Events

As part of the dissemination of the progress and partial results of this research, presentations were delivered at various national and international academic events. The following is a list of the presentations, with corresponding certificates attached to this document:

- **Event:** III Summer School of the European PhD School on Advanced Oxidation Processes
  **Presentation:** Coupling of Heterogeneous Photocatalysis and Aerobic and Anaerobic Biological Processes for the Treatment of Wastewater
- **Event:** VI International Week of Science, Technology, and Innovation
  **Presentation 1:** Biodegradability and Toxicity of Landfill Leachates Treated by Heterogeneous Photocatalysis Using $TiO_2$ in a Compound Parabolic Collector
  **Presentation 2:** Protocol for the Maintenance of Strains and Scale-Up in the Production of Microalgae of Industrial Interest

- **Event:** I International Congress of Environmental Engineering
  **Presentation:** Aerobic Biodegradability of Leachates Generated in the El Guayabal Landfill, Cúcuta – Norte de Santander, Using the Zahn-Wellens EMPA OECD 302B Test
- **Event:** 1st International Symposium in Agrarian and Environmental Sciences
  **Presentation 1:** Optimization of Carotenoid Production in Scenedesmus sp. Based on Carbon Source Selection
  **Presentation 2:** Selection of Thermotolerant Cyanobacteria with C-Phycocyanin (C-PC) Production Capacity

As documentary support, the certificates corresponding to each of the presentations above are included, providing evidence of the academic dissemination of the progress and results achieved within the framework of this doctoral research.

UNIVERSITAT POLITÈCNICA DE VALÈNCIA

# CERTIFICATE OF ATTENDANCE
# CERTIFICADO DE ASISTENCIA



The Universitat Politècnica de València certifies that

**DORANCE BECERRA MORENO**

passport 14838047, attended the event **III SUMMER SCHOOL OF THE EUROPEAN PhD SCHOOL ON ADVANCED OXIDATION PROCESSES**, held from 6/3/19 to 6/7/19 (mm/dd/yy), and it witness whereof, it is issued this certificate.

The participant presented contributions. Titles on the back.

La Universitat Politècnica de València certifica que

**DORANCE BECERRA MORENO**

con pasaporte número 14838047, ha participado en el evento **III SUMMER SCHOOL OF THE EUROPEAN PhD SCHOOL ON ADVANCED OXIDATION PROCESSES**, realizado del 3/06/19 al 7/06/19, y para que conste a los efectos oportunos, se expide el presente certificado.

El participante ha presentado comunicaciones. Títulos al dorso.

Valencia, June 11, 2019 / Valencia, 11 de junio de 2019

Registration number / Nº de registro: 19/19812

Title/s of the paper/s presented by DORANCE BECERRA MORENO Título/s presentados por DORANCE BECERRA MORENO

**POSTER COMMUNICATION: COUPLING OF HETEROGENEOUS PHOTOCATALYSIS AND AEROBIC AND ANAEROBIC BIOLOGICAL PROCESSES FOR THE TREATMENT OF WASTEWATER CONTAINING CHLORPYRIFOS**

VI SEMANA INTERNACIONAL DE CIENCIA TECNOLOGÍA E INNOVACIÓN 2019.

Universidad Francisco de Paula Santander
Vigilada Mineducación

Universidad Francisco de Paula Santander
Vigilada Mineducación

# LA UNIVERSIDAD FRANCISCO DE PAULA SANTANDER CÚCUTA Y SECCIONAL OCAÑA

## CERTIFICA QUE:

**DORANCE BECERRA MORENO**
**C.C. 14838047**

Participó como **PONENTE** en modalidad **Póster** en el evento **VI SEMANA INTERNACIONAL DE CIENCIA, TECNOLOGÍA E INNOVACIÓN** que se desarrolló del 19 al 22 de noviembre del año 2019 en San José de Cúcuta, Norte de Santander Colombia, con el tema **"**BIODEGRADABILIDAD Y TOXICIDAD DE LIXIVIADOS DE RELLENOS SANITARIOS TRATADOS POR FOTOCATÁLISIS HETEROGÉNEA, USANDO TIO2 EN UN COLECTOR PARABÓLICO COMPUESTO**"**.

VICERRECTOR ASISTENTE DE INVESTIGACIÓN
UNIVERSIDAD FRANCISCO DE PAULA SANTANDER

DIRECTOR DE INVESTIGACIÓN Y EXTENSIÓN
UNIVERSIDAD FRANCISCO DE PAULA SANTANDER OCAÑA

VI SEMANA INTERNACIONAL DE CIENCIA TECNOLOGÍA E INNOVACIÓN
2019.

Universidad Francisco de Paula Santander
Vigilada Mineducación

Universidad Francisco de Paula Santander
Vigilada Mineducación

# LA UNIVERSIDAD FRANCISCO DE PAULA SANTANDER CÚCUTA Y SECCIONAL OCAÑA

## CERTIFICA QUE:

**DORANCE BECERRA MORENO**
**C.C. 14838047**

Participó como **PONENTE** en modalidad **Póster** en el evento **VI SEMANA INTERNACIONAL DE CIENCIA, TECNOLOGÍA E INNOVACIÓN** que se desarrolló del 19 al 22 de noviembre del año 2019 en San José de Cúcuta, Norte de Santander Colombia, con el tema "PROTOCOLO PARA EL MANTENIMIENTO DE CEPAS Y ESCALAMIENTO EN LA PRODUCCIÓN DE MICROALGAS DE INTERÉS INDUSTRIAL".

**VICERRECTOR ASISTENTE DE INVESTIGACIÓN**
**UNIVERSIDAD FRANCISCO DE PAULA SANTANDER**

**DIRECTOR DE INVESTIGACIÓN Y EXTENSIÓN**
**UNIVERSIDAD FRANCISCO DE PAULA SANTANDER OCAÑA**


**La Universidad Francisco de Paula Santander,**
**La Facultad de Ciencias Agrarias y del Ambiente y**
**El Plan de Estudios de Ingeniería Ambiental**

Certifican que:

***DORANCE BECERRA MORENO***

Con Cédula de Ciudadanía: ***CC 14.838.047*** de Cali

PARTICIPÓ COMO **CONFERENCISTA** EN EL:

# I CONGRESO INTERNACIONAL DE INGENIERÍA AMBIENTAL

***BIODEGRABILIDAD AEROBIA DE LOS LIXIVIADOS GENERADOS EN EL RELLENO SANITARIO EL GUAYABAL, CÚCUTA - NORTE DE SANTANDER, MEDIANTE LA PRUEBA ZAHN WELLENS EMPA OECD 302B***

CELEBRADO DEL 21 AL 23 DE NOVIEMBRE DEL AÑO 2018 EN EL CAMPUS SEDE CENTRAL DE LA UNIVERSIDAD FRANCISCO DE PAULA SANTANDER, EN LA CIUDAD DE CÚCUTA, NORTE DE SANTANDER - COLOMBIA.

**NESTOR ANDRÉS URBINA SUÁREZ**
**Decano Facultad de Ciencias Agrarias y del Ambiente UFPS**

**JUDITH YAMILE ORTEGA CONTRERAS**
**Directora Plan de Estudios de Ingeniería Ambiental UFPS**

Universidad Francisco de Paula Santander
Vigilada Mineducación

Ingeniería Ambiental

Fellows Colombia

ICETEX

FRADIEAR

ANDEAN REGIONAL FORUM FOR THE DIALOGUE AND INTEGRATION OF AGRICULTURAL AND RURAL EDUCATION

1st INTERNATIONAL SYMPOSIUM IN AGRARIAN AND ENVIRONMENTAL SCIENCES

October 23, 2018

# LA UNIVERSIDAD FRANCISCO DE PAULA SANTANDER

*Certifica que:*

**María Daniela Ortiz Álvarez, Esthefania Guarín Villegas, Michael Edgardo Pérez Roa, Andrés Fernando Barajas Solano, Néstor Andrés Urbina Suarez, Dorance Becerra, John Hermogenes Suarez Gelvez**

Participaron como **PONENTES** con la investigación: Optimización de la producción de carotenoides en *scenedesmus sp* a partir de la selección de la fuente de carbono en el 1st International Symposium in Agrarian and Environmental Sciences

Realizado en San José de Cúcuta, los días 23 y 24 de Octubre de 2018

PhD. Moraima Estéves González
Vicerrectora de Investigación y Posgrado de la Universidad Pedagógica Experimental Libertador

MSc. Jhan Piero Rojas Suárez
Vicerrector Asistente de Investigación y Extensión de la Universidad Francisco de Paula Santander

FRADIEAR
ANDEAN REGIONAL FORUM FOR THE DIALOGUE AND INTEGRATION OF AGRICULTURAL AND RURAL EDUCATION

1st INTERNATIONAL SYMPOSIUM IN AGRARIAN AND ENVIRONMENTAL SCIENCES
October 23, 2018

# LA UNIVERSIDAD FRANCISCO DE PAULA SANTANDER

*Certifica que:*

**Sandra Oriana Mogollón Londoño, Michael Edgardo Pérez Roa, María Daniela Ortiz Álvarez, Andrés Fernando Barajas Solano, Néstor Andrés Urbina Suarez, Dorance Becerra, John Hermogenes Suarez Gelvez**

Participaron como **PONENTES** con la investigación: Selección de cianobacterias Termotolerantes con capacidad de producción de C-PC en el 1st International Symposium in Agrarian and Environmental Sciences

Realizado en San José de Cúcuta, los días 23 y 24 de Octubre de 2018

PhD. Moraima Estéves González
Vicerrectora de Investigación y Posgrado de la Universidad Pedagógica Experimental Libertador

MSc. Jhan Piero Rojas Suárez
Vicerrector Asistente de Investigación y Extensión de la Universidad Francisco de Paula Santander

## 7. Bibliography

Abdel-Shafy, H. I., Ibrahim, A. M., Al-Sulaiman, A. M., & Okasha, R. A. (2024). Landfill leachate: Sources, nature, organic composition, and treatment: An environmental overview. *Ain Shams Engineering Journal*, *15*(1), 102293. https://doi.org/10.1016/j.asej.2023.102293

Abo, L. D., Jayakumar, M., Jeyapaul, A. S., Rangaraju, M., Areti, H. A., & Assefa Adugna, A. (2025). Comprehensive review on co-integration of conventional systems and advanced oxidation processes for industrial and agricultural wastewater treatment applications. *Environmental Advances*, *20*, 100638. https://doi.org/10.1016/j.envadv.2025.100638

Bah, A., Chen, Z., Bah, A., Qian, Q., Tuan, P. D., & Feng, D. (2023). Systematic literature review of solar-powered landfill leachate sanitation: Challenges and research directions over the past decade. *Journal of Environmental Management*, *326*, 116751. https://doi.org/10.1016/j.jenvman.2022.116751

Becerra, D., Soto, J., Villamizar, S., Machuca-Martínez, F., & Ramírez, L. (2020). Alternative for the Treatment of Leachates Generated in a Landfill of Norte de Santander–Colombia, by Means of the Coupling of a Photocatalytic and Biological Aerobic Process. *Topics in Catalysis*, *63*(11–14), 1336–1349. https://doi.org/10.1007/s11244-020-01284-1

Becerra Moreno, D., Caicedo Cáceres, N. Y., Velásquez Lázaro, C. M., Machuca Martínez, F., & Soto Verjel, J. W. (2022). Heterogeneous photocatalysis and an anaerobic biological process for leachate treatment. *Ciencia En Desarrollo*, *13*(2), 113–130. https://doi.org/10.19053/01217488.v13.n2.2022.13851

Becerra Moreno, D., Rubio-Gomez, Y. M., Barajas-Solano, A. F., Ramírez Ríos, L. F., & Machuca-Martínez, F. (2023). Una revisión sobre el tratamiento para lixiviados de rellenos sanitarios mediante el acople de procesos avanzados de oxidación y

biológicos. *Ingeniería y Competitividad*, *25*(4). https://doi.org/10.25100/iyc.v25i4.11626

Becerra-Moreno, D., Machuca-Martínez, F., Ramírez-Rios, L. F., García-Martínez, J. B., & Barajas-Solano, A. F. (2025). Synergistic Degradation of Organic Contaminants in Landfill Leachates Using Catalytic Ozonation with Magnetite. *Sci*, *7*(1), 31. https://doi.org/10.3390/sci7010031

Becerra-Moreno, D., Machuca-Martínez, F., Ramírez-Rios, L., García-Martínez, J. B., & Barajas-Solano, A. F. (Manuscript submitted for publication). Treatment of Landfill Leachates Using Magnetite-Catalyzed Ozone Coupled With an Anaerobic Sludge Blanket Reactor. *Green Chemical Engineering*.

Becerra-Moreno, D., MachucaMartínez, F., Soto-Verjel, J., Soto-Verjel, A., & Ramírez-Rios, L. (Manuscript submitted for publication). Superficie de respuesta y regularización ridge en Ozonización Catalítica de lixiviados. *Revista UIS Ingenierías*.

Becerra-Moreno, D., Rubio-Gomez, Y., Ramírez-Ríos, L. F., Barajas-Solano, A. F., & Machuca Martínez, F. (2021). Procesos Avanzados De Oxidación Basados En Ozono Como Alternativa De Tratamiento Para Lixiviados De Rellenos Sanitarios. *Ciencia en Desarrollo*, *12*(2). https://doi.org/10.19053/01217488.v12.n2.2021.12503

Clemente, E., Domingues, E., Quinta-Ferreira, R. M., Leitão, A., & Martins, R. C. (2024). European and African landfilling practices: An overview on MSW management, leachate characterization and treatment technologies. *Journal of Water Process Engineering*, *66*, 105931. https://doi.org/10.1016/j.jwpe.2024.105931

Das, R., & Raj, D. (2025). Sources, distribution, and impacts of emerging contaminants – a critical review on contamination of landfill leachate. *Journal of Hazardous Materials Advances*, *17*, 100602. https://doi.org/10.1016/j.hazadv.2025.100602

Dhamsaniya, M., Sojitra, D., Modi, H., Shabiimam, M. A., & Kandya, A. (2023). A review of the techniques for treating the landfill leachate. *Materials Today: Proceedings*, *77*, 358–364. https://doi.org/10.1016/j.matpr.2022.11.496

Fauziyen, S. P., Saputera, W. H., & Sasongko, D. (2024). Advancement and prospects in photocatalytic degradation of sulfamethoxazole (SMX) pharmaceutical waste. *South African Journal of Chemical Engineering*, *48*, 375–394. https://doi.org/10.1016/j.sajce.2024.03.008

Feng, H., Mao, W., Li, Y., Wang, X., & Chen, S. (2021). Characterization of dissolved organic matter during the O3-based advanced oxidation of mature landfill leachate with and without biological pre-treatment and operating cost analysis. *Chemosphere*, *271*, 129810. https://doi.org/10.1016/j.chemosphere.2021.129810

Geng, Y., Lian, C.-A., Yang, L., Pavlostathis, S. G., Qiu, Z., Qiao, X., Xiong, Z., Dong, N., Hu, J., Luo, X., & Yu, K. (2025). Self-adaptation of tolerant microalgae-bacterial consortia in landfill leachate: Simultaneous achievement of efficient nitrogen removal and value-added utilization. *Chemical Engineering Journal*, *504*, 158912. https://doi.org/10.1016/j.cej.2024.158912

Gopal, S., Jayabalan, J., Jayaraman, D., Perumal, M., & Santhi, V. M. (2025). Amalgamation of advanced oxidation process with biological techniques for treatment of tannery wastewater. *Physics and Chemistry of the Earth, Parts A/B/C*, *138*, 103883. https://doi.org/10.1016/j.pce.2025.103883

Goukeh, M. N., Ssekimpi, D., Asefaw, B. K., & Tang, Y. (2025). Comprehensive evaluation of chemicals in residual and condensate during landfill leachate evaporation. *Chemosphere*, *380*, 144458. https://doi.org/10.1016/j.chemosphere.2025.144458

Hassan, M., Wang, X., Wang, F., Wu, D., Hussain, A., & Xie, B. (2017). Coupling ARB-based biological and photochemical (UV/TiO 2 and UV/S 2 O 8 2− ) techniques to deal with sanitary landfill leachate. *Waste Management*, *63*, 292–298. https://doi.org/10.1016/j.wasman.2016.09.003

Hazaraimi, M. H., Goh, P. S., Lau, W. J., Ismail, A. F., Hashim, N., Kerisnan@Kerishnan, N. D., Yahaya, N. K. E. M., & Mamat, R. B. R. (2024). Advancing photocatalytic membrane for efficient endocrine disrupting compounds removal: Progresses and challenges. *Journal of Water Process Engineering*, *68*, 106338. https://doi.org/10.1016/j.jwpe.2024.106338

Igwegbe, C. A., López-Maldonado, E. A., Landázuri, A. C., Ovuoraye, P. E., Ogbu, A. I., Vela-García, N., & Białowiec, A. (2024). Sustainable municipal landfill leachate management: Current practices, challenges, and future directions. *Desalination and Water Treatment*, *320*, 100709. https://doi.org/10.1016/j.dwt.2024.100709

Jari, Y., Najid, N., Necibi, M. C., Gourich, B., Vial, C., Elhalil, A., Kaur, P., Mohdeb, I., Park, Y., Hwang, Y., Garcia, A. R., Roche, N., & El Midaoui, A. (2025). A comprehensive review on TiO2-based heterogeneous photocatalytic technologies for emerging pollutants removal from water and wastewater: From engineering aspects to modeling approaches. *Journal of Environmental Management*, *373*, 123703. https://doi.org/10.1016/j.jenvman.2024.123703

Javaid, R., Ikhlaq, A., Rizvi, O. S., Abid, M., Qi, F., & Qazi, U. Y. (2025). Enhancing biodegradability of landfill leachate by hybrid treatment process: Coagulation followed by catalytic ozonation with Z5Å-Fe-Zn for environmental sustainability. *Journal of Water Process Engineering*, *75*, 107938. https://doi.org/10.1016/j.jwpe.2025.107938

Jia, H., Zhang, S., Sun, Z., Wang, Y., & Bai, R. (2025). Migrating characteristics of pollutants from landfill leachate in cold regions and impact on hydrothermal conditions. *Journal of Cleaner Production*, *493*, 144882. https://doi.org/10.1016/j.jclepro.2025.144882

Kanmani, S., & Dileepan, A. G. B. (2023). Treatment of landfill leachate using photocatalytic based advanced oxidation process – a critical review. *Journal of Environmental Management*, *345*, 118794. https://doi.org/10.1016/j.jenvman.2023.118794

Lestari, P., Purwiandono, G., Amalia, A. N., Ma'Rufi, E. K. I., Firdaus, M. R., & Wacano, D. (2025). Coexistence of microplastic particles and heavy metals in landfill leachate: A case study of a landfill in Indonesia. *Case Studies in Chemical and Environmental Engineering*, *11*, 101082. https://doi.org/10.1016/j.cscee.2024.101082

Lian, X., Wang, Z., Liu, Z., Xiong, Z., Dai, H., Yang, L., Liu, Y., Yang, J., Geng, Y., Hu, M., Shao, P., & Luo, X. (2024). A new microalgal negative carbon technology for landfill leachate treatment: Simultaneous removal of nitrogen and phosphorus. *Science of The Total Environment*, *948*, 174779. https://doi.org/10.1016/j.scitotenv.2024.174779

Liu, J., Zhang, Y., Zhan, Y., Yang, L., Chen, X., Deng, G., Hu, D., & Jiang, F. (2025). Catalytic ozonation with ferric oxide loaded pumice: Enhancing catalytic ozonation and microbial community dynamics in anaerobic leachate treatment. *Journal of Environmental Chemical Engineering*, 117290. https://doi.org/10.1016/j.jece.2025.117290

Moussavi, G., Khosravi, R., & Omran, N. R. (2012). Development of an efficient catalyst from magnetite ore: Characterization and catalytic potential in the ozonation of water toxic contaminants. *Applied Catalysis A: General*, *445–446*, 42–49. https://doi.org/10.1016/j.apcata.2012.08.002

Paiva, A. L. P., Gonçalves Da Fonseca Silva, D., & Couto, E. (2021). Recycling of landfill leachate nutrients from microalgae and potential applications for biomass valorization. *Journal of Environmental Chemical Engineering*, *9*(5), 105952. https://doi.org/10.1016/j.jece.2021.105952

Pinpatthanapong, K., Khetkorn, W., Honda, R., Phattarapattamawong, S., Treesubsuntorn, C., Panasan, N., Boonmawat, P., Tianthong, Y., Lipiloet, S., Sorn, S., Jutakanoke, R., Prachanurak, P., & Boonnorat, J. (2022). Effects of high-strength landfill leachate effluent on stress-induced microalgae lipid production and post-

treatment micropollutant degradation. *Journal of Environmental Management*, *324*, 116367. https://doi.org/10.1016/j.jenvman.2022.116367

Rigotto, L., Aquino, S. F., Rigotto, J., Santos, G., Silva, L. M. L., & Santiago, A. F. (2023). Dynamics of dissolved organic matter (DOM) in waste stabilization ponds: Insights into co-treatment of sanitary sewage and landfill leachate. *Journal of Water Process Engineering*, *55*, 104236. https://doi.org/10.1016/j.jwpe.2023.104236

Sabba, F., Kassar, C., Zeng, T., Mallick, S. P., Downing, L., & McNamara, P. (2025). PFAS in landfill leachate: Practical considerations for treatment and characterization. *Journal of Hazardous Materials*, *481*, 136685. https://doi.org/10.1016/j.jhazmat.2024.136685

Sangkham, S., Pitakpong, A., & Kumar, R. (2025). Advanced approaches to microplastic removal in landfill leachate: Advanced oxidation processes (AOPs), biodegradation, and membrane filtration. *Case Studies in Chemical and Environmental Engineering*, *11*, 101056. https://doi.org/10.1016/j.cscee.2024.101056

Shi, Y., Sun, A., Zhang, G., & Zhang, G. (2025). Combined coagulation-adsorption-VUV (persulfate)-electrochemical oxidation processes for efficient treatment of aged landfill leachate. *Journal of Water Process Engineering*, *71*, 107281. https://doi.org/10.1016/j.jwpe.2025.107281

Silerio-Vázquez, F. D. J., González-Burciaga, L. A., Antileo, C., Núñez-Núñez, C. M., & Proal-Nájera, J. B. (2024). Photocatalytic degradation of antibiotics in water via TiO2-x: Research needs for technological advancements. *Journal of Hazardous Materials Advances*, *16*, 100506. https://doi.org/10.1016/j.hazadv.2024.100506

Singh, D., Dikshit, A. K., & Dangi, M. B. (2025). Technological advances in per- and polyfluoroalkyl substances (PFAS) removal from landfill leachate: Source identification and treatment options. *Emerging Contaminants*, *11*(2), 100458. https://doi.org/10.1016/j.emcon.2024.100458

Song, Z., Wu, X., Gao, T., Yao, F., Tang, X., Mahmood, Q., & Tang, C.-J. (2025). Performance enhancement strategies for electrooxidation degradation of landfill leachate: A review. *Chinese Chemical Letters*, 111008. https://doi.org/10.1016/j.cclet.2025.111008

Tian, Z., Li, G., Bai, M., Hou, X., Li, X., Zhao, C., Zhu, Q., Du, C., Li, M., Liu, W., & Zhang, L. (2022). Microbial mechanisms of refractory organics degradation in old landfill leachate by a combined process of UASB-A/O-USSB. *Science of The Total Environment*, *848*, 157737. https://doi.org/10.1016/j.scitotenv.2022.157737

Varma, S. K., & Singh, R. (2025). Bioelectrochemical treatment of emerging contaminants and molecular characterization of transformation products in landfill leachate. *Bioresource Technology Reports*, *30*, 102153. https://doi.org/10.1016/j.biteb.2025.102153

Wang, F., Liu, Y., Yin, J., Xiang, Y., Yuan, Y., Zhang, J., He, C., Zhang, H., Xiong, Z., & Lai, B. (2024). Critical role of oxygen vacancies in catalytic ozonation: Non-radical pathways and enhanced hydroxyl groups. *Chemical Engineering Journal*, *500*, 156952. https://doi.org/10.1016/j.cej.2024.156952

Wang, H., Zhang, S., He, X., Yang, Y., Yang, X., & Van Hulle, S. W. H. (2023). Comparison of macro and micro-pollutants abatement from biotreated landfill leachate by single ozonation, O3/H2O2, and catalytic ozonation processes. *Chemical Engineering Journal*, *452*, 139503. https://doi.org/10.1016/j.cej.2022.139503

Wang, Q., Wang, T., Li, H., & Xu, Q. (2025). Role of leachate characteristics on carbon dots/TiO2 photocatalytic and bactericidal inactivation mechanism. *Journal of Environmental Chemical Engineering*, *13*(2), 116022. https://doi.org/10.1016/j.jece.2025.116022

Wang, Z., Xiong, Z., Yang, L., Lai, L., Xiao, H., Ding, Y., & Luo, X. (2022). Enhancing nitrogen removal in mature landfill leachate by mixed microalgae through elimination

of inhibiting factors. *Science of The Total Environment*, *828*, 154530. https://doi.org/10.1016/j.scitotenv.2022.154530

Xiang, Z., Zhang, Y., Bo, L., Shen, Z., Wang, D., Shen, Z., & Tang, Y. (2025). Removal performance and mechanism of aniline from landfill leachate by ozone oxidation process using iron-based packed catalyst. *Journal of Environmental Management*, *375*, 124397. https://doi.org/10.1016/j.jenvman.2025.124397

Yang, Y.-Z., Zhang, Y., Zhan, Y., Liu, J.-Q., Yan, C.-C., Zhang, Y., & Zhang, H.-L. (2024). Synergistic enhancement of UASB reactor for leachate treatment using Fe2O3 nanomodified pumice and ozone oxidation. *Chemical Engineering Journal*, *497*, 154891. https://doi.org/10.1016/j.cej.2024.154891

Yu, X., Tang, L., Yan, R., Wang, J., Zhao, W., Lyu, S., & Sui, Q. (2025). Quantifying PFAS Contamination and Environmental Risk in Municipal Solid Waste Landfill Refuse: Implications for Landfill Reuse. *Water Research*, 123881. https://doi.org/10.1016/j.watres.2025.123881

Yuan, Y., Liu, J., Gao, B., Sillanpää, M., & Al-Farraj, S. (2022). The effect of activated sludge treatment and catalytic ozonation on high concentration of ammonia nitrogen removal from landfill leachate. *Bioresource Technology*, *361*, 127668. https://doi.org/10.1016/j.biortech.2022.127668

Zarzzeka, C., Goldoni, J., De Paula De Oliveira, J. D. R., Lenzi, G. G., Bagatini, M. D., & Colpini, L. M. S. (2024). Photocatalytic action of Ag/TiO2 nanoparticles to emerging pollutants degradation: A comprehensive review. *Sustainable Chemistry for the Environment*, *8*, 100177. https://doi.org/10.1016/j.scenv.2024.100177

Zhang, R., Liu, J., Gao, B., & Sillanpää, M. (2025). The effect of autochthonous metal ions and humic substances on landfill leachate ozonation: Reactive oxygen species and 3D fluorescence analysis. *Separation and Purification Technology*, *354*, 129433. https://doi.org/10.1016/j.seppur.2024.129433