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

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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

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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)	1.664	1.933	mg O_2/L
Biochemical Oxygen Demand (BOD_5) (mg/L)	6.295	8.421	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.

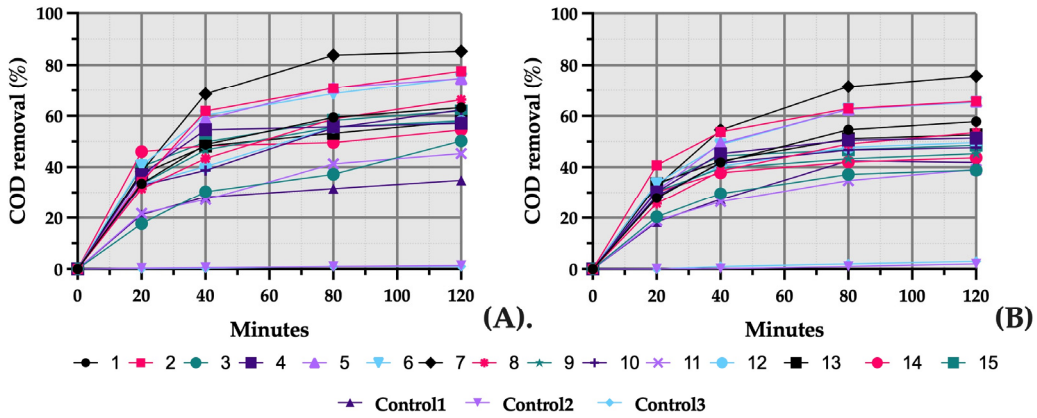


Figure 2. COD removal by catalytic ozonation (Fe_3O_4): (**A**) El Guayabal sanitary landfill, (**B**) La Madera sanitary landfill.

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

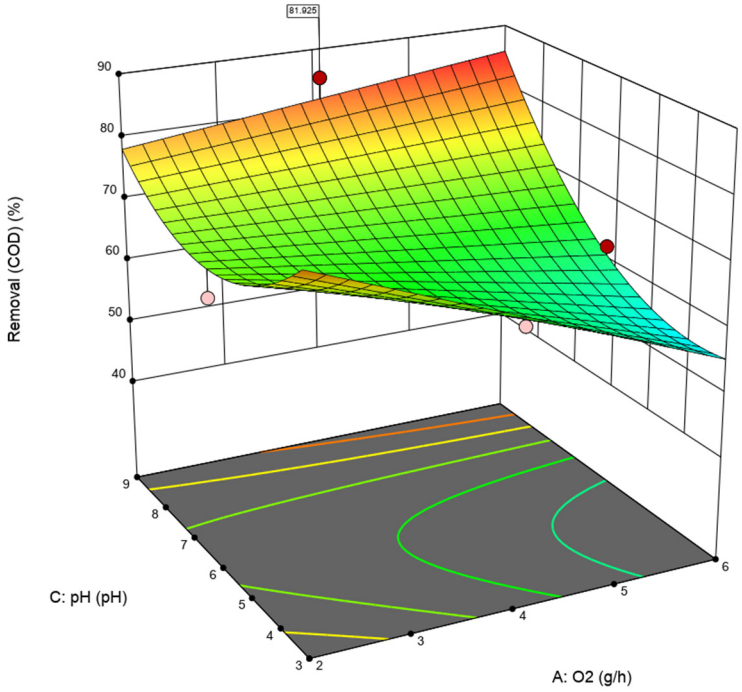
* Significant. ** Not significant.

3.3.1. Evaluation of Organic Matter Removal

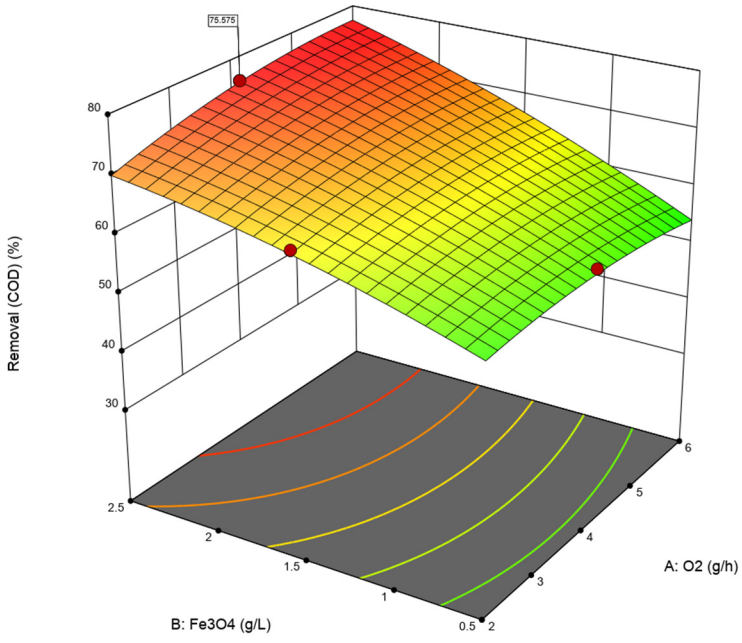
The ozone consumption per unit of chemical oxygen demand (COD) removed exhibited significant variability depending on the evaluated operational conditions, reflecting the impact of ozone dosage, magnetite concentration, and pH on process efficiency (Figure 4). In this context, optimizing the system is 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.

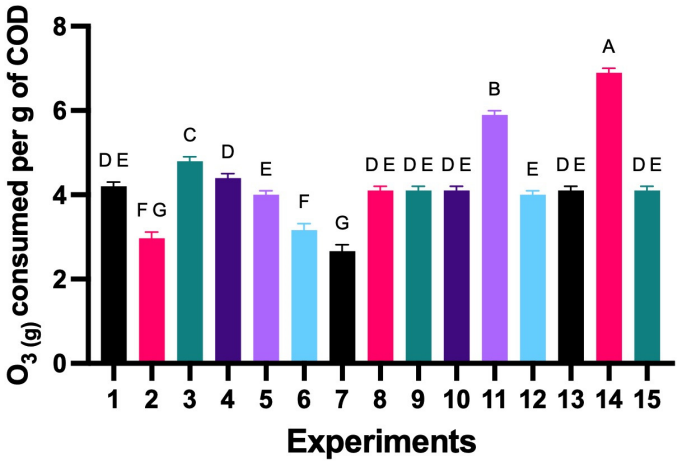


Figure 4. Ozone consumption efficiency in organic matter degradation. Different letters mean statistical significance.

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	8.826×10^5	5	1.765×10^5	1690.10	<0.0001 *
	A-O_2	1.052×10^5	1	1.052×10^5	1007.71	<0.0001 *
	B-Fe_3O_4	2.062×10^5	1	2.062×10^5	1974.04	<0.0001 *
	AB	1616.25	1	1616.25	15.47	0.0056 *
	A^2	2.570×10^5	1	2.570×10^5	2460.37	<0.0001 *
	B^2	3.849×10^5	1	3.849×10^5	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	8.833×10^5	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

Sample	Source	Sum of Squares	Df	Mean Square	F Value	*p*-Value
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			

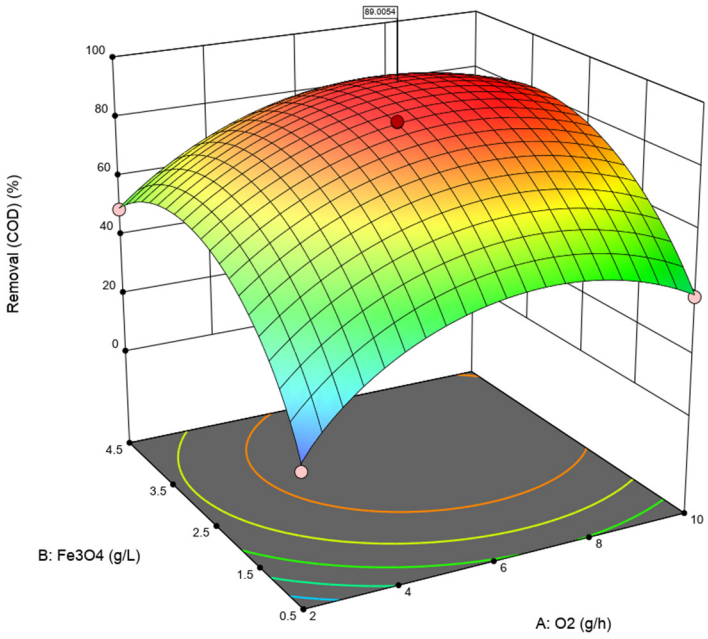
R^2	Adj R^2	Pred R^2	Acq Pr	Std. Dev.	Mean	CV%
0.9985	0.9974	0.9933	72.2616	1.11	53.55	2.07

* Significant. ** Not significant.

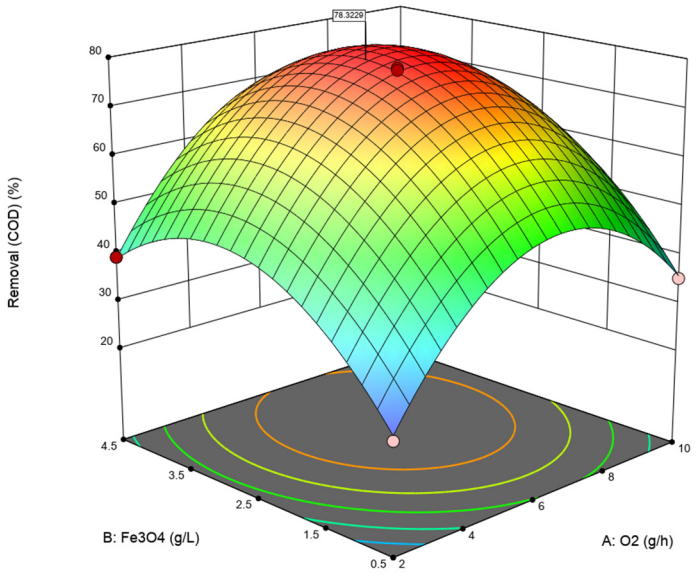
In the case of the La Madera samples, the Model F value of 937.58 implies that the model is significant. There is only a 0.01% chance that an F value that is this large could occur due to noise. In this case, A, B, AB, A^2, and B^2 are significant model terms. The lack of fit F value of 1.47 implies 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.

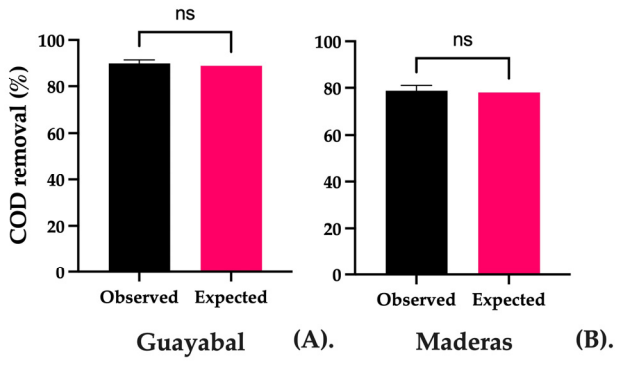


Figure 6. Results of one-sample t-test between expected and observed COD removal for leachates from El Guayabal (**A**) and La Madera (**B**).

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.

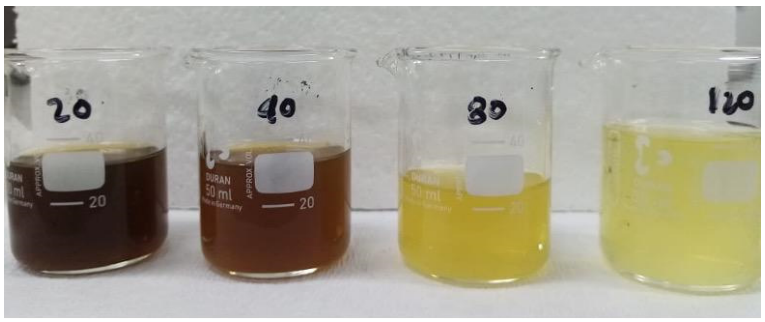
Table 9. Characteristics of treated leachates.

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

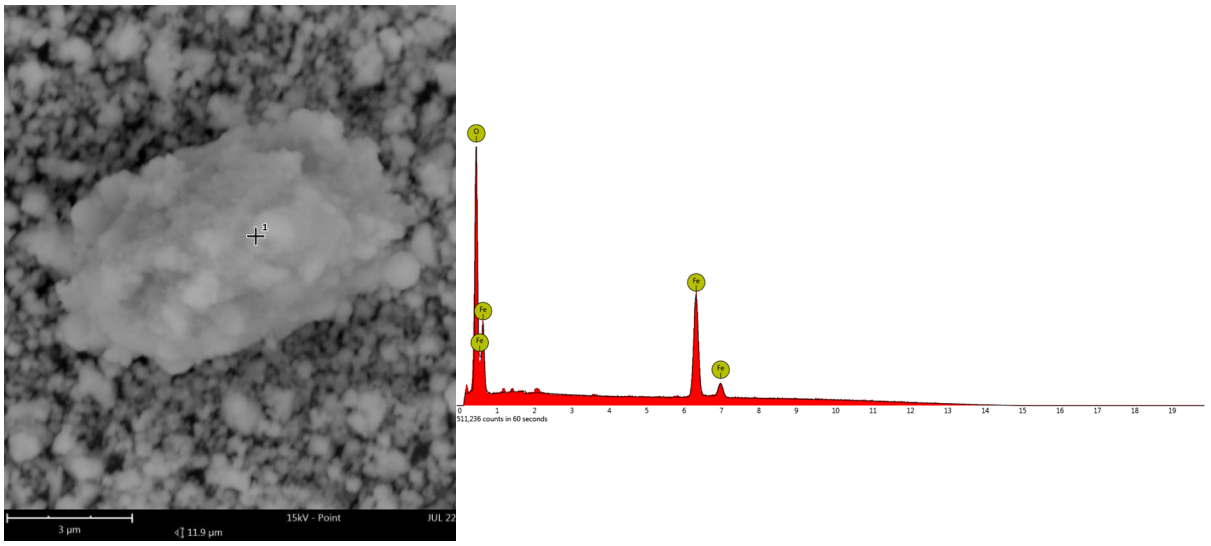
Figure 8 presents scanning electron microscopy (SEM) images used to assess the structure and composition of magnetite at different stages of use. Image (A) depicts unused synthetic magnetite, which is characterized by a homogeneous surface and a composition consisting entirely of Fe_3O_4 (100%). Image (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

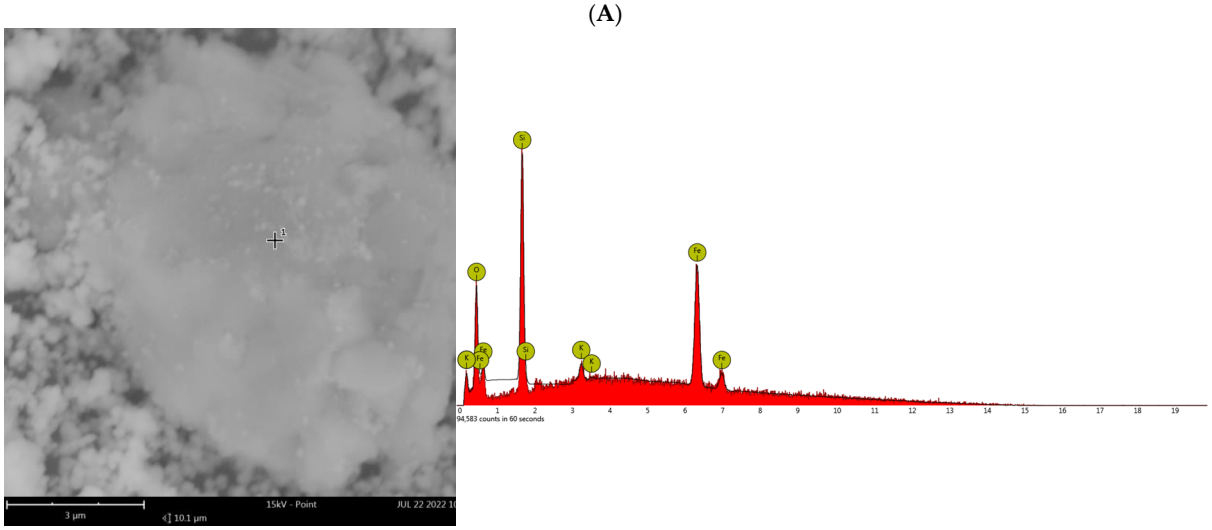
The structure and chemical properties of magnetite before and after catalytic ozonation were studied via Fourier transform infrared (FTIR) spectroscopy. The absorption spectra of the magnetite samples in three states are shown in Figure 9: (A) unused, (B) after the first treatment cycle, and (C) after 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.

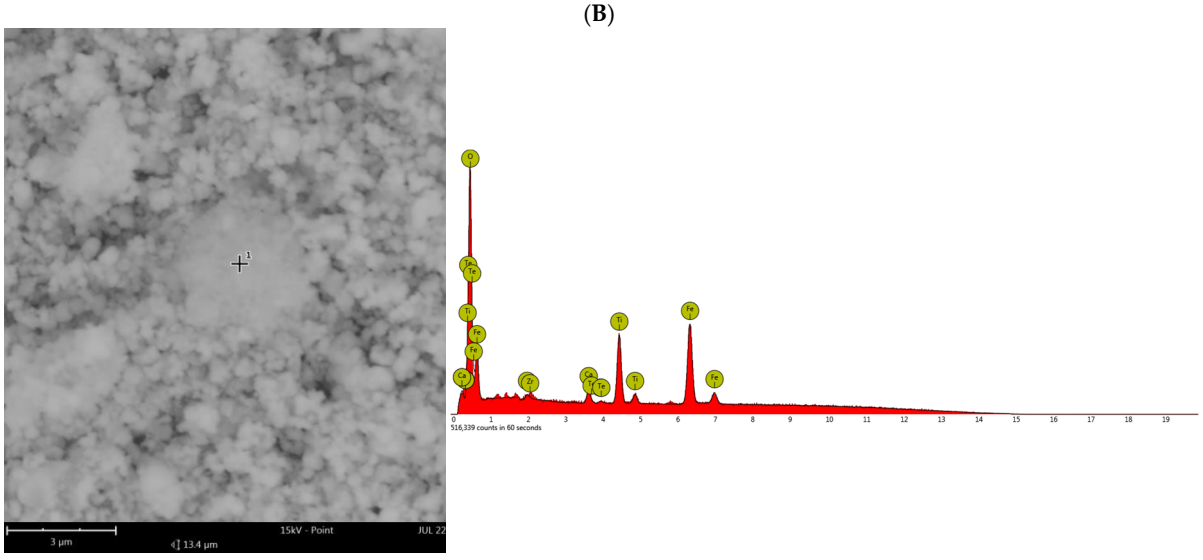
To evaluate the catalyst's stability after use, additional tests were performed to measure the amount of material recovered after each cycle and its performance in chemical oxygen demand (COD) removal. In the first test, when 2.5 g of initial magnetite was used, a COD removal efficiency of 85.3% was 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.

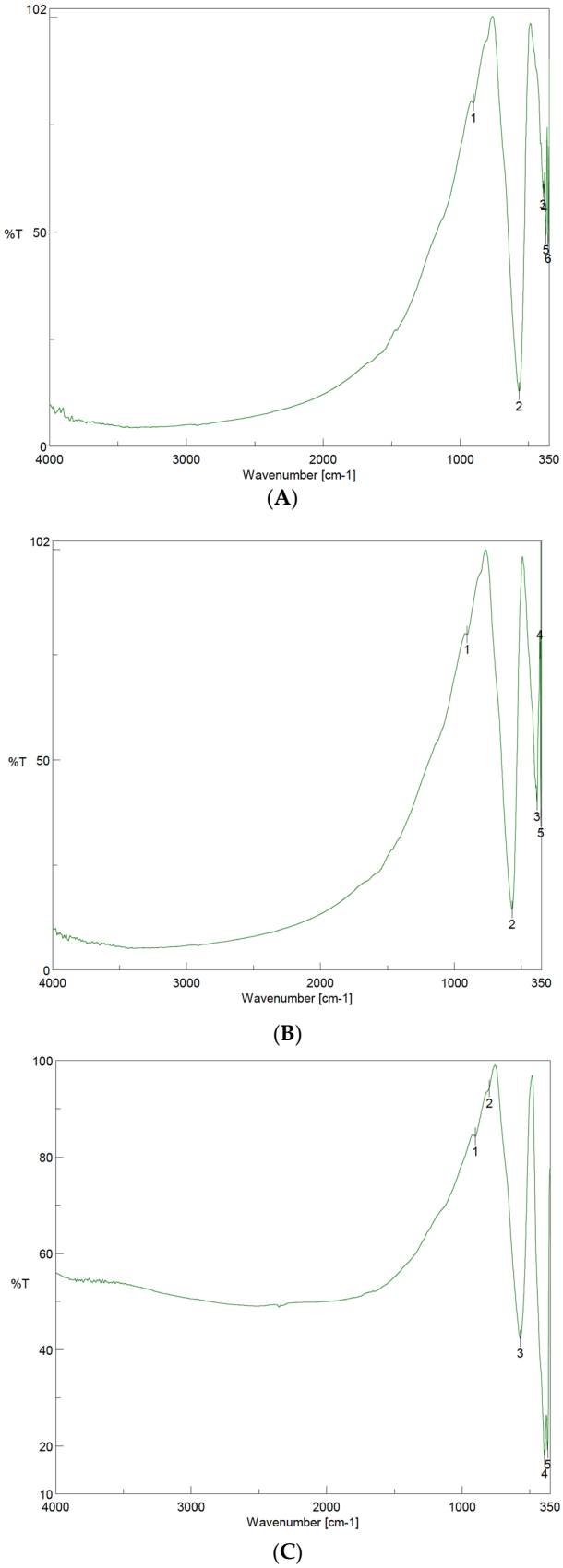


Figure 9. FTIR spectra of magnetite: (**A**) unused synthetic magnetite, (**B**) magnetite after one cycle of use, and (**C**) magnetite after two cycles of use.

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 (α-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 (α-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.

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