Rev. Int. Contam. Ambie. 41, 761-774, 2025
https://doi.org/10.20937/RICA.55585

ADVANCED OXIDATION WITH OZONE AND HYDROGEN PEROXIDE FOR THE REMOVAL OF DYES IN AGROINDUSTRIAL WASTEWATERS

Oxidación avanzada con ozono y peróxido de hidrógeno para la eliminación de colorantes en aguas residuales agroindustriales

Carlos Augusto BENJUMEA-HOYOS[1]*, Jaime Andrés GUTIÉRREZ-MONSALVE[2]
and Santiago SALDARRIAGA GIRALDO[1]

[1] Facultad de Ingeniería, Universidad Católica de Oriente, Carrera 46 No. 40B-50, Rionegro, Antioquia, Colombia.
[2] Facultad de Ingeniería y Ciencias Agropecuarias, Institución Universitaria Digital de Antioquia, Cra. 55 #42-90, Medellín, Antioquia, Colombia.

*Autor para correspondencia: cbenjumea@uco.edu.co

(Received: April 2025; accepted: July 2025)

Key words: decolorization, recalcitrant pollutants, mineralization, advanced oxidation processes, wastewater treatment, hydroxyl radical, agroindustrial effluents.

ABSTRACT

This study assesses the effectiveness of peroxone, an advanced oxidation process (AOP) that combines ozone and hydrogen peroxide, for treating agro-industrial wastewater contaminated with dyes from the floral industry. Various ratios of O_3/H_2O_2 (0, 0.35, 0.7, and 0.8) and exposure times (ranging from 95 to 265 min) were tested to assess their impact on chemical oxygen demand (COD) and color removal. The results showed significant pollutant removal, achieving up to 91.44% reduction in color in Treatment 5 (O_3/H_2O_2 ratio = 0.7; treatment time = 240 min). COD reduction reached 77.78% in Treatment 8 (O_3/H_2O_2 ratio = 0.35; treatment time = 265 min). Statistical analyses, indicated that color removal was significantly influenced by the treatment time and the O_3/H_2O_2 ratio ($p < 0.05$), although these factors had a lesser impact on COD attenuation ($p > 0.05$). A desirability function was implemented to optimize COD and color removals simultaneously, obtaining the optimal conditions at an O_3/H_2O_2 ratio of 1.6 and a treatment time between 60 and 264 min. Finally, correspondence analysis revealed relationships between pH, conductivity, redox potential, and total dissolved solids. This analysis suggested that while redox potential and conductivity play important roles in color removal, COD mitigation remains relatively stable across varying treatment conditions. This study offers valuable data about the efficient treatment for removing color and COD in agro-industrial wastewater using the peroxone process, providing a sustainable solution for wastewater management in the floral industry.

Palabras clave: decoloración, contaminantes recalcitrantes, mineralización, procesos de oxidación avanzada, tratamiento de aguas residuales, radical hidroxilo, efluentes agroindustriales.

RESUMEN

Este estudio evalúa la efectividad del proceso peróxono, que combina ozono y peróxido de hidrógeno, para el tratamiento de aguas residuales agroindustriales contaminadas con tintes de la industria de las flores. Se probaron varias proporciones de O_3/H_2O_2 (0, 0.35, 0.7 y 0.8) y tiempos de exposición (entre 95 y 265 min) para evaluar su impacto en la demanda química de oxígeno (DQO) y la eliminación de color. Los resultados mostraron una eliminación significativa de contaminantes, alcanzando hasta un 91.44% de reducción del color en el tratamiento 5 (proporción O_3/H_2O_2= 0.7; tiempo de tratamiento = 240 min). La reducción de DQO fue del 77.78% en el tratamiento 8 (proporción O_3/H_2O_2= 0.35; tiempo de tratamiento = 265 minutos). Los análisis estadísticos, incluyendo Anova, indicaron que tanto el tiempo de tratamiento como la proporción de O_3/H_2O_2 influyeron significativamente en la remoción de color ($p < 0.05$), mientras que su efecto sobre la atenuación de la DQO fue menor ($p > 0.05$). Para optimizar simultáneamente la eliminación de DQO y color, se aplicó una función de deseabilidad, identificando condiciones óptimas con una proporción de O_3/H_2O_2 de 1.6 y un tiempo de tratamiento entre 60 y 264 min. Finalmente, el análisis de correspondencia reveló relaciones entre el pH, la conductividad, el potencial redox y los sólidos disueltos totales. Este análisis sugirió que, mientras el potencial redox y la conductividad desempeñan roles importantes en la remoción de color, la reducción de DQO se mantiene relativamente estable bajo diferentes condiciones de tratamiento. Este estudio aporta datos valiosos sobre el tratamiento eficiente de aguas residuales agroindustriales coloreadas mediante el proceso peróxono, proporcionando una solución sostenible para la gestión de aguas residuales en la industria florícola.

INTRODUCTION

The agroindustrial sector consumes over 25% of the world's freshwater resources, producing wastewater that presents significant environmental challenges when not managed properly (Castro and Durán 2014, IDEAM 2023). This effluent often contains chemicals that increase toxicity, threaten aquatic life, and alter water bodies' color, pH, and chemical oxygen demand (COD) (Jorge et al. 2023, García et al. 2025). In Colombia, the floriculture industry is a crucial economic sector, ranking as the second-largest exporter of fresh flowers, following the Netherlands (Benjumea-Hoyos et al. 2023, Benjumea-Hoyos et al. 2024). However, this sector generates substantial volumes of colored wastewater from dyeing processes, demanding effective treatment before disposal.

Agroindustrial wastewater, particularly from the floriculture industry, contains contaminants that resist degradation through natural processes such as photolysis, thermal decomposition, and microbial activity (Jorge et al. 2023). The synthetic dyes in this industry often exhibit complex molecular structures, with some compounds being carcinogenic or mutagenic. The untreated discharge of this wastewater can severely harm aquatic ecosystems by reducing photosynthetic efficiency and increasing toxicity levels, thereby disrupting ecological balance and biodiversity (Zhang et al. 2021).

Dyes are organic compounds containing chromophoric and auxochromic groups, widely used across many industries to color various materials. Azo dyes, such as acid orange 9 (AA9), are commonly employed in floriculture (Alzain et al. 2021, Restrepo et al. 2021). These synthetic dyes pose significant risks to human health, including dermatitis, asthma, allergies, and gastrointestinal issues (Manu and Chaudhari 2003, Yonni et al. 2008). The persistence of these dyes complicates their removal in conventional wastewater treatment systems, primarily due to their resistance to biological degradation and the presence of additional toxic compounds, such as heavy metals and surfactants (Ulson et al. 2010).

The release of colored industrial effluent is a primary environmental concern, and conventional treatment methods often fail to remove these substances adequately. As a result, further tertiary treatments, including advanced oxidation processes (AOPs), have been implemented to address these issues. AOPs are particularly effective in remediating water contaminated with chemicals resistant to biodegradation (Rodríguez 2011, Benjumea-Hoyos et al. 2024). These processes influence the high reactivity of hydroxyl radicals ($OH^{\bullet}$) to oxidize and degrade complex pollutants, ultimately transforming them into benign end products such as carbon dioxide and water (Khan and Yadav 2019). Standard AOP methodologies include ozone (O_3) and hydrogen peroxide (H_2O_2), with their reactions outlined as follows (Pourgholi et al. 2018, Luna and Benjumea-Hoyos 2019, Rekhate and Srivastava 2020):

$$\begin{array}{l} H_2\,O_2 \rightarrow HO_2 - + H^+ \\ HO_2 - + O_3 \rightarrow H_2^{\bullet} + O_3^{\bullet} - \\ O_3^{\bullet} - + H + \rightarrow HO_3^{\bullet} - \\ HO_3^{\bullet} - \rightarrow O_2 + OH^{\bullet} \end{array} \qquad (1)$$

O_3 is a highly reactive molecule that spontaneously decomposes into molecular oxygen, allowing it to be an oxidant in advanced oxidation processes. However, O_3 alone is often insufficient to achieve complete degradation; therefore, it is frequently combined with hydrogen peroxide (H_2O_2) to increase the production of hydroxyl radicals (Esplugas et al. 2007). This synergistic combination, known as the peroxone process, significantly enhances degradation efficiency by increasing hydroxyl radicals oxidative and non-selective properties (Rekhate and Srivastava 2020).

Optimization methods, particularly response surface methodology (RSM), are essential for improving the efficiency of water treatment operations, especially AOPs. RSM is a statistical technique that systematically examines the interactions among different operational factors and their effects on process response (Rezaee et al. 2021). By employing a central composite design (CCD), RSM enables the identification of optimal operational conditions for pollutant removal with minimal experimental effort. Additionally, the desirability function methodology is often integrated into RSM, providing a comprehensive approach to optimizing multiple responses, such as color removal, COD reduction, and hydroxyl radical generation. This approach effectively balances competing objectives, maximizing treatment efficiency while minimizing reagent usage and operational costs (Patel and Brahmbhatt 2018).

Improving treatment parameters through RSM enhances the efficient and economical use of AOPs, ensuring the removal of persistent contaminants, such as azo dyes, under optimal conditions. This methodology increases contaminant removal effectiveness while reducing treatment time, energy consumption, and chemical usage, making it essential for large scale wastewater treatment applications (Chaturvedi et al. 2021). Moreover, RSM ability to model and predict complex interactions among multiple variables makes it particularly suited for industrial scale applications, where precise control of treatment parameters is essential to ensure consistent and reliable performance (Kim et al. 2025).

Numerous studies have examined the application of AOPs for removing dyes from agro-industrial effluents, explicitly highlighting the synergy between ozone and hydrogen peroxide (O_3/H_2O_2). For instance, a study by Ulson et al. (2010) assessed the efficacy of the O_3/H_2O_2 method in treating textile effluent containing azo dyes. The results indicated that combining ozone with hydrogen peroxide significantly improved color removal and reduced the COD. This technology demonstrated efficient degradation of recalcitrant persistent organic pollutants, which have proven refractory to conventional remediation techniques. Ulson et al. (2010) attributed this performance to the interaction between ozone (O_3) and hydrogen peroxide (H_2O_2), which led to increased production of hydroxyl radicals, the principal agents for breaking down complex dye molecules.

A study by Sabri et al. (2018) evaluated the effectiveness of the O_3/H_2O_2 system for treating dye wastewater, which is characterized by a mix of colors and organic pollutants. The research found that the O_3/H_2O_2 process was highly efficient in removing color and reducing COD, with optimal efficiencies achieved at specific pH levels and reagent concentrations. The researchers observed that the method effectively mineralizes contaminants, converting them into less harmful byproducts. This characteristic causes the method to be particularly suitable for the treatment of agroindustrial wastewater. This research confirmed that O_3/H_2O_2 AOP provides a robust and environmentally sustainable alternative to conventional chemical treatment methods, particularly for wastewater containing persistent contaminants like dyes.

Conversely, Tosik and Wiktorowski (2001) used the O_3/H_2O_2 process to eliminate dyes in agroindustrial wastewater. The study emphasized the challenges of treating wastewater containing organic dyes and inorganic contaminants, such as salts and heavy metals. The researchers found that the peroxone process significantly enhances the decolorization of the wastewater, achieving over 90% color removal under optimized conditions. Additionally, a notable increase in the biochemical oxygen demand (BOD_5) to chemical oxygen demand (COD) ratio was observed, indicating improved biodegradability. The findings highlight the potential of O_3/H_2O_2 as an effective pretreatment step for facilitating subsequent biological treatments in dye industry effluent management (Tosik and Wiktorowski 2001).

The present study aims to evaluate the efficiency of the peroxone process (O_3/H_2O_2) for the degradation of synthetic dyes and the reduction of COD in aqueous systems, with a specific focus on agroindustrial wastewater generated by the Colombian floriculture sector. Given the complexity and recalcitrant nature of these effluents, the study examines the impact of key operational variables, including the oxidant ratio and reaction time, on treatment performance.

To optimize and statistically validate the process conditions, a rotating central composite design (RCCD) was employed as the experimental design framework. As demonstrated in recent environmental studies (Asaithambi et al. 2023), this design approach enhances the accuracy of predictive modeling and facilitates the identification of optimal operational parameters in advanced oxidation processes. Its application in the present research supports a rigorous and reproducible evaluation of peroxone-based treatment for recalcitrant wastewater matrices.

MATERIALS AND METHODS

The ozonation process was conducted using a BioGP-branded ozone generator operating at a production rate of 1 g/h, 110 V, 60 Hz. Ozone (O_3) was generated by passing atmospheric air through electrical discharges, dissociating oxygen molecules to form O_3. The ozone concentration was measured using the iodometric volumetric method, following established protocols for wastewater treatment (APHA 2017).

In this experiment, ozone was continuously introduced into a stirred reactor (operating at 200 rpm) with a capacity of 1000 mL, containing colored effluent collected from the floriculture industry in the region of eastern Antioquia, Colombia (6° 9’ 18.5” N 75° 22.4 23’ O). Concurrently, 30% hydrogen peroxide (analytical grade, MERCK brand) was added dropwise, with the quantity determined by the experimental design and the O_3/H_2O_2 ratio established in previous research (Acero and Von Gunten 2001, Chaparro and Rueda-Bayona. 2021).

Key physical and chemical parameters, including pH, electrical conductivity (EC), and redox potential (ORP), were continuously monitored using HACH HQ 40D multiparameter instrumentation. The equipment and various measurement probes were routinely calibrated before each test. Additionally, COD and color were quantified as response variables for the different treatments in the experimental procedure; **figure 1** provides a schematic of the experimental setup.

Micro COD was assessed using the method outlined in the Standard Methods for the Examination of Water and Wastewater (APHA 2017). Color determination measured like absorbance at wavelengths of $\lambda = 436$, 525, and 620 nm following Colombian legislation, Resolution 0631 of 2015 (MADS 2015) and prior research (Tizaoui et al. 2007). A Spectroquant® Prove 600 UV-VIS spectrophotometer was used for this analysis. The proportion of color elimination was calculated using the following equation:

$$\%\ \text{color removal} = \frac{(\text{Initial Abs} - \text{Final Abs.})}{\text{Initial Abs.}} \times 100 \qquad (2)$$

A rotating composite central design (RCCD) was implemented for the experimental design. This design offered an alternative to the conventional 3k design for fitting second order response surfaces. It comprises multiple combinations, including a) treatments from the 2k factorial design (F) or a subset of

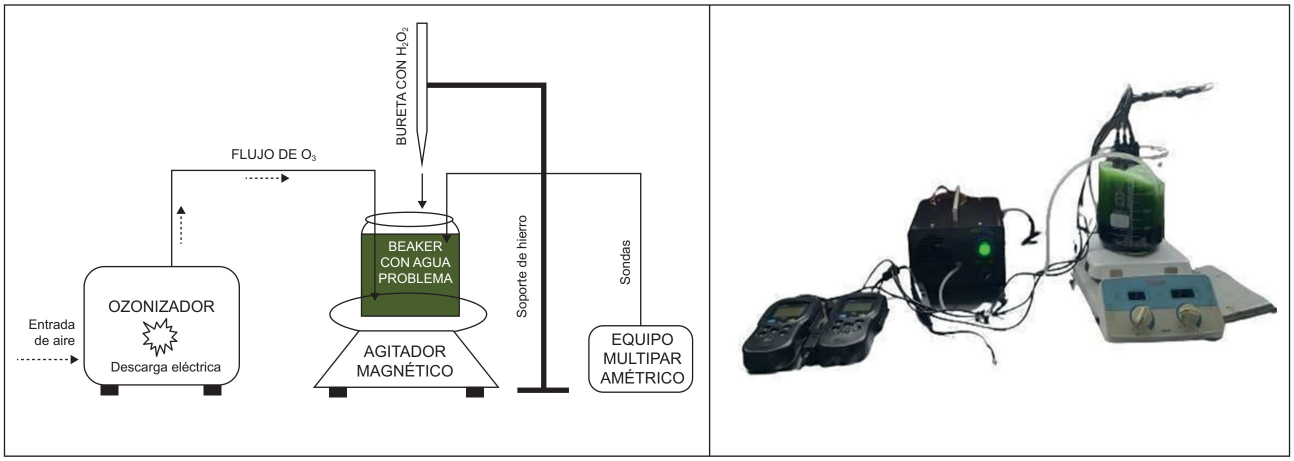


Fig. 1. Schematic and assembly of the peroxone method for coloured wastewater.

that, with factor levels encoded as -1 and +1; b) axial or star points; and c) repetitions of the center point (Montgomery 2017).

To evaluate the peroxone process, the exposure duration to ozone (O_3) and the dosage of hydrogen peroxide (H_2O_2) were varied, resulting in 11 experimental trials. The ozone concentration was directly correlated with the exposure duration, while the application of H_2O_2 was based on the relationship established by Acero and Von Gunten (2001). The O_3/H_2O_2 ratios examined in the study were 0, 0.35, 0.7, and 0.8, as detailed in **table I**.

TABLE I. EXPERIMENTAL DESIGN.

Trial	O_3 / H_2O_2 ratio	Time (min)	O_3 concentration (mg/L)
Control	0	0	0
1	0.35	180	223.2
2	0	240	297.6
3	0	120	148
4	0.35	180	223.2
5	0.7	240	297.6
6	0.7	120	148
7	0.35	180	223.2
8	0.35	265	328.6
9	0	180	223.2
10	0.8	180	223.2
11	0.35	95	117.8

Data obtained from the experimental trials were analyzed using Excel, R Commander, and R Wizard 4.8 software. Descriptive statistics for central tendency and dispersion were employed to characterize each treatment and its repetitions. An analysis of variance (Anova) was conducted to identify the factors and treatments that significantly influenced COD reduction and color removal. A second order polynomial function was used to determine the optimal conditions for maximum COD and color removal, delineated by the following equation:

$$Y_i = \beta_0 + \sum_{j=1}^{3} \beta_j X_i + \sum_{j=1}^{3} \beta_{ii} X_i^2 + + \sum_{j=1}^{3} \beta_{ij} X_i X_j + \epsilon_i \quad (3)$$

In this equation, Y_i denotes the response variable (either COD or color decrease), X_i and X_j signify the experimental factors, β_0 is the intercept coefficient, β_i is the linear coefficient for factor i, β_{ij} is the quadratic coefficient for factor i, and β_{ij} represents the interaction coefficient between factors i and j. The coefficients were calculated using statistical software based on the experimental outcomes. All hypothesis testing was conducted at a 95% confidence level (Montgomery 2017).

A desirability function was employed to optimize multiple responses and identify simultaneous optimal points for color and COD reduction (Derringer and Suich 1980). **Table I** provides details of the experimental design, including tests, doses, exposure times to ozone (O_3), and ozone concentrations in mg/L.

In addition to conducting regression analysis and Anova to evaluate the effects of O_3 and H_2O_2 on COD and color depletion, correspondence analysis (CA) was applied to examine the influence of various physical and chemical parameters, including pH, conductivity, redox potential, and total dissolved solids (TDS). CA is advantageous for exploring the relationships among multiple variables, providing a comprehensive understanding of how these factors interact and impact treatment efficiency for COD and color reduction.

The analysis was conducted on a dataset generated from 11 experimental trials, where the response variables of COD and color mitigation were assessed against the levels of time, the O_3/H_2O_2 ratio, and the measured physical and chemical properties. This method facilitated the identification of patterns and associations most closely related to the effectiveness of the treatments. The graphical representation of the CA provided a visual interpretation of the interactions between different treatments and their associated variables interacting with each other, as well as their relative impact on COD and color reduction.

RESULTS

The colored wastewater's initial appearance was a deep, dark green hue. During treatment with hydrogen peroxide, foam generation was observed in the initial minutes, indicating the presence of surfactants (**Fig. 2**). After 15 min, foam production stopped, and the water changed to a reddish tint with increased transparency.

Throughout the designated treatment periods of 95, 120, 180, 240, and 265 min, discoloration occurred after 240 min, with the water resembling the color of tea. By the end of the experiment, the maximum reduction percentages for COD and color were recorded at 77.78% and 91.44%, respectively, by treatment 8 (**Table II**).

The results indicated that the COD attenuation did not vary significantly across the tests. The maximum COD reduction was performed with an O_3/H_2O_2 ratio

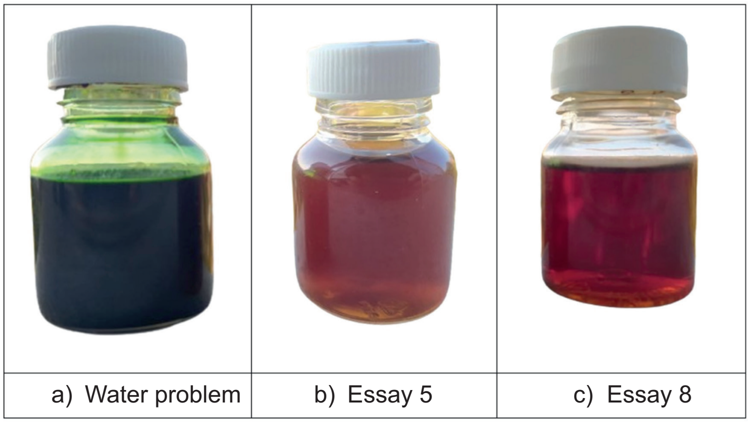

a) Water problem b) Essay 5 c) Essay 8

Fig. 2. Colored wastewater a) initial; b) test 5; c) test 8.

TABLE II. PERCENTAGE OF CHEMICAL OXYGEN DEMAND (COD) AND COLOR REMOVAL.

Treatment	O_3 / H_2O_2 ratio	Time (min)	COD removal (%)	color removal (%)
Control	0	0	0	0
1	0.35	180	74.9	82.56
2	0	240	75.21	84.76
3	0	120	74.2	73.74
4	0.35	180	74.85	85.26
5	0.7	240	75.86	91.44
6	0.7	120	75.71	79.54
7	0.35	180	76.92	81.62
8	0.35	265	77.78	89.46
9	0	180	76.97	73
10	0.8	180	77.33	88.68
11	0.35	95	77.08	74.92

of 0.35 over 265 min, with 328.6 mg/L O_3 and 1 mL H_2O_2 concentrations. In contrast, trial 5 recorded the maximum color removal rate of 91.44%, using an O_3/H_2O_2 ratio of 0.7, with a treatment duration of 240 min and 2 mL of H_2O_2. This process resulted in a noticeable color change, achieving a lighter reddish hue and increased transparency while modifying various color properties, including tone, brightness, and saturation.

Figures 2a and **2b** compare a transformation from a dark green color to a lighter reddish hue, along with increased transparency. **Figure 3** demonstrates the efficiency of different O_3/H_2O_2 ratios in removing both COD and color from agroindustrial wastewater. Trials shown in **figure 3** suggest that at a ratio of 0.0, the removal percentage was 77.17% for COD (Me. COD) and 75.46% for color (Me.color). Increasing the O_3/H_2O_2 ratio to 0.35 enhanced removal, with COD reaching 82.76% and color at 76.31%. At a

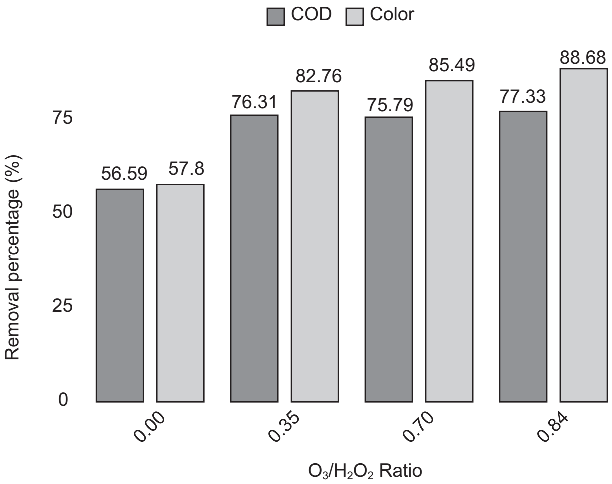


Fig. 3. Color removal and chemical oxygen demand (COD) reduction of different trials according to experimental design.

ratio of 0.70, the treatment efficiency further improved, achieving a COD reduction of 85.49% and a 75.79% decrease in color. The highest performance was observed at a ratio of 0.84, with COD reduction reaching 88.68% and color decrease at 77.33%. These results indicate that the O_3/H_2O_2 ratio plays a crucial role in enhancing both COD and color reduction in agroindustrial wastewater, with higher ratios leading to more favorable outcomes.

According to modeling data, **table III** presents the linear model results and the variance analysis (Anova) analysis for the response variables. The R^2 value of 0.936 for color removal indicates that this parameter was well modeled, with 93.6% of the variance explained. The linear model using the quadratic form revealed that time, with a P-value of 0.00311, showed significant differences, suggesting that it is the primary factor influencing color removal. Longer reaction times were associated with higher percentages of color removal. These results indicate that time is the most influential factor in achieving color decrease.

An R^2 value of 0.115 was obtained for the variable COD, indicating that this parameter was explained by only 11.5% of the variance. This result suggests that the model does not adequately fit the % of COD decrease. Additionally, no significant differences were observed between the variables in the quadratic model based on P-values.

In the Anova, the results for color removal demonstrated statistically significant effects for both time and the O_3/H_2O_2 ratio (**Fig. 3**). The O_3/H_2O_2 ratio showed the most substantial impact on the removal of color, suggesting that increasing the ratio may enhance the efficiency of the process. In contrast, the Anova results for COD reduction revealed no statistical differences for any examined factors, including time and the O_3/H_2O_2 ratio. These results indicate that none of the variables significantly influenced the COD decrease efficiency under the tested conditions.

The Pareto charts in **figure 4** picture these findings by displaying the F-statistics for each factor. The chart for color removal demonstrates the central role of the O_3/H_2O_2 ratio. In contrast, the chart for COD mitigation shows that none of the factors had a significant effect, as all F-statistics for COD are relatively low.

Figure 5A illustrates the relationship between the O_3/H_2O_2 ratio and time (O_3 concentration) concerning the percentage of COD reduction. The surface plot does not display any curvature, suggesting an optimal dose for this response parameter has not been achieved. The optimal dose is likely higher than those analyzed; however, the maximum removal recorded was 91.44%, a notably high result. Based on these findings, the response surface may begin to curve with a time slightly exceeding 265 min and an O_3/H_2O_2 ratio greater than 0.8. These results suggest

TABLE III. LINEAR MODEL AND ANALYSIS OF VARIANCE (ANOVA) TABLE RELATED TO PERCENTAGE OF COLOR REMOVAL AND PERCENTAGE OF CHEMICAL OXYGEN DEMAND (COD) REDUCTION.

Linear model				
	% color Removal		% COD removal	
	Estimator	Pr (>|t|)	Estimator	Pr (>|t|)
Intercept	62.3080	0.0000	74.2867	0.0000
Time	0.0868	0.0031	0.0081	0.5750
O_3 / H_2 O_2	10.4910	0.2567	2.7940	0.6520
Time: O_3 / H_2 O_2	0.0105	0.8261	–0.0102	0.7590
^{R2}adjustment	0.9369		0.1158	

Anova				
	% color removal		% COD removal	
Factors	Sum Sq	Pr (>|F)	Sum Sq	Pr (>|t|)
Time	236320.00	0.00	0.58	0.59
O_3 / H_2 O_2	150.12	0.00	0.89	0.51
Time: O_3 / H_2 O_2	0.19	0.83	0.18	0.76

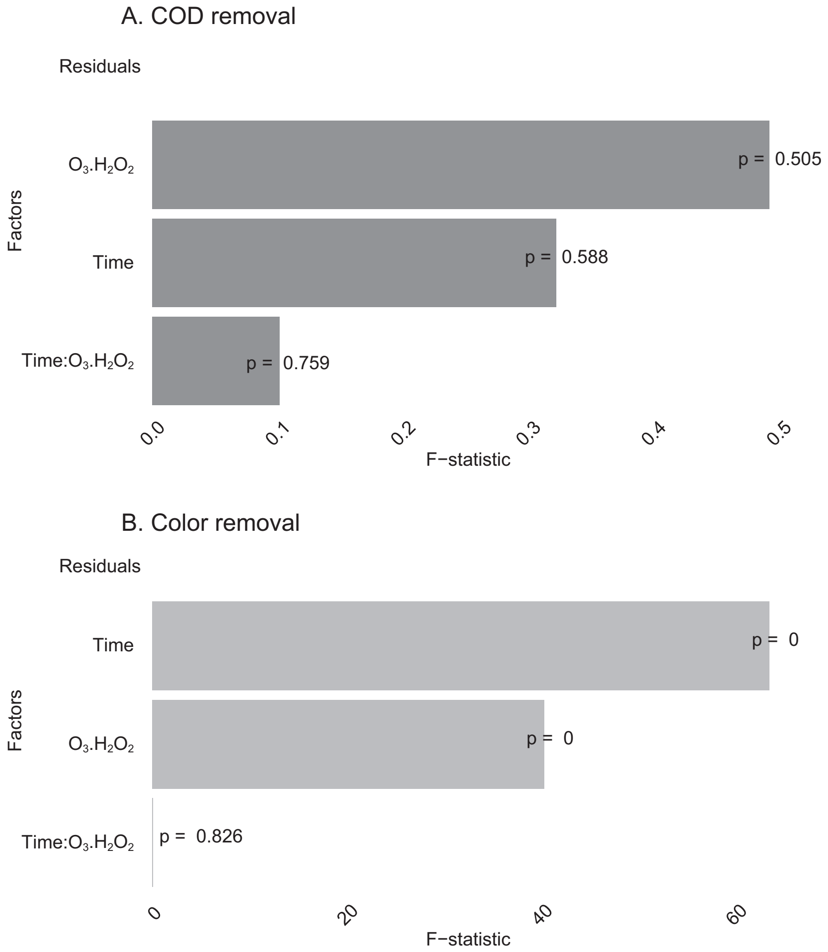


Fig. 4. Relative effect of factors on the percentage of chemical oxygen demand (COD) reduction (A) and color removal (B). F-statistics indicate the ratio of the variation explained by each factor to the unexplained variation, and low p-values indicate statistically significant effects of the factors on the response.

that an equal concentration of ozone and hydrogen peroxide (a 1:1 ratio) may be necessary for optimal results.

Figure 5B presents the relationship between the variables (O_3/H_2O_2) and time and the percentage of color removal. The data shows a significant curvature, indicating that the optimal ozone exposure time is 264 min, with the highest O_3/H_2O_2 dose being 0.8. Longer exposure times to ozone are associated with higher percentages of COD reduction.

The multi-optimization approach using the desirability function evaluated the global desirability for both COD decrease and color removal across the treatment conditions. The multiple optimization plot (**Fig. 6**) shows the influence of the O_3/H_2O_2 ratio and treatment time on the desirability of achieving optimal removal of both COD and color. The analysis revealed that the highest desirability for color removal was achieved at the maximum ozone exposure (O_3/H_2O_2 ratio of 1.6) over a treatment time of 60 to 264 min. These results suggest that a higher ozone concentration, with an extended reaction time, improves the overall effectiveness of the treatment process. If the analysis estimates the multiple optimizations, the red point marks the maximum desirability, demonstrating the optimal conditions for achieving the highest efficiency in color removal.

The peroxone method emerges as an effective alternative for treating this type of wastewater due to the abundant generation of hydroxyl radicals from the combination of ozone and hydrogen peroxide. This process significantly accelerates the transformation and mineralization of dyes, resulting in high removals of color and COD depletion.

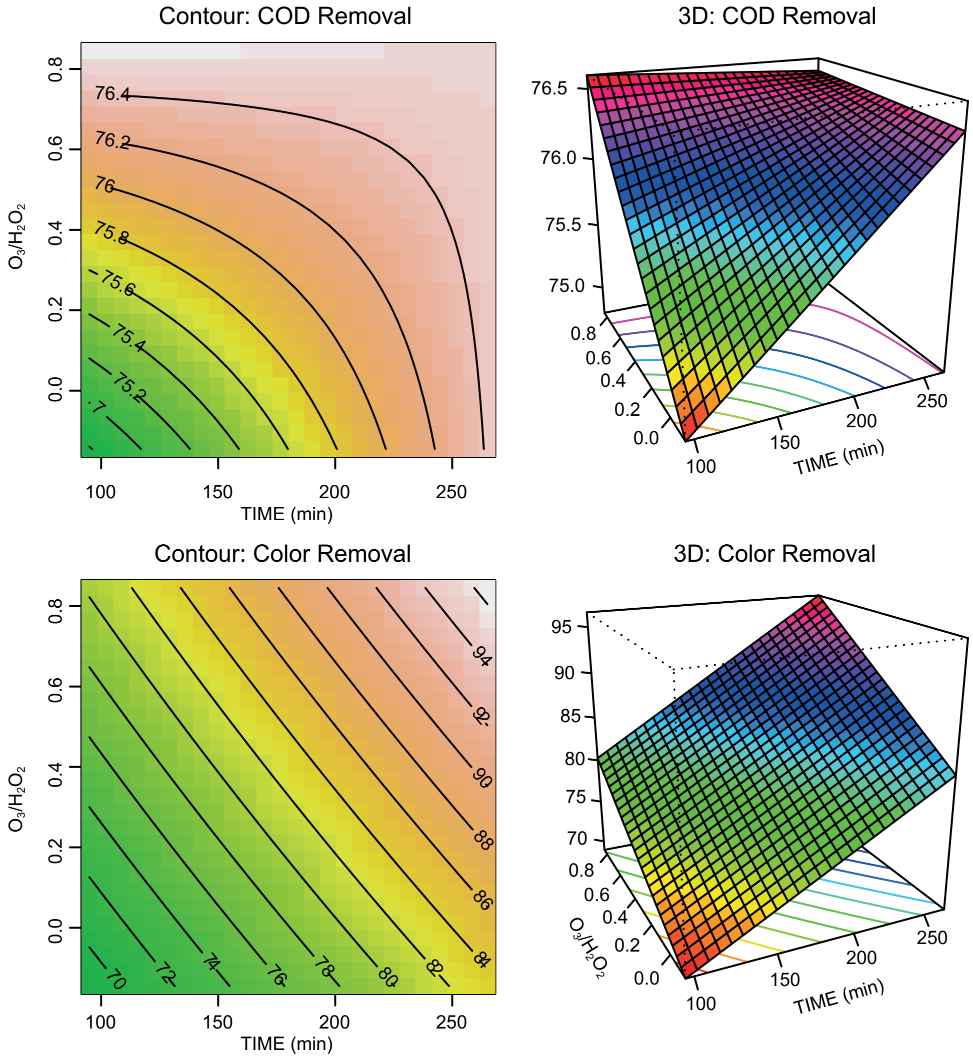
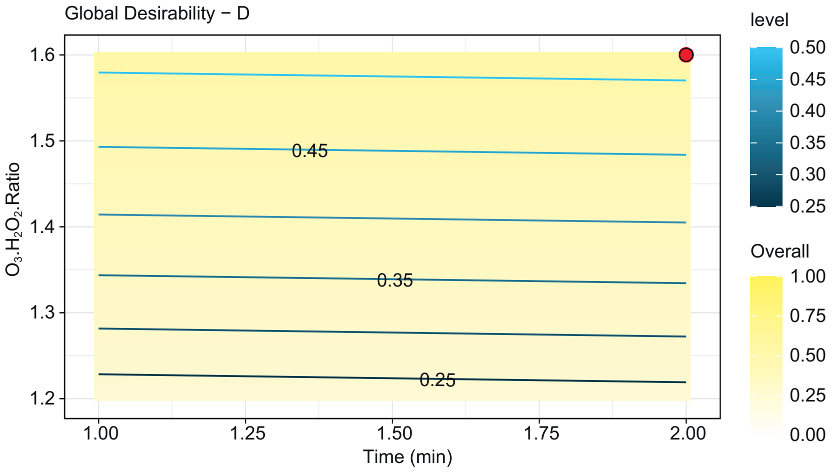


Fig. 5. Chemical oxygen demand (COD) reduction and color removal response surfaces in 3D and 2D.

Furthermore, the percentage of COD decrease across all tests remained relatively consistent, suggesting that the duration of ozone exposure has a more significant impact than the combination of the two oxidizing agents, with only a 3.58% variation observed. Tests that utilized 0 mL of H_2O_2 demonstrated low color removal, indicating that ozone alone is insufficient for complete decolorization.

The correspondence analysis (CE) presented in **figure 7** provides the interrelationships between pH, conductivity, redox potential (P.Redox.mv.), and total dissolved solids (TDS) and their influence on the COD reduction and color removal across the treatment shown in **table I** and **II**. **Figure 7** reveals that the variables associated with COD decrease and color removal are prominently located along dimension 1, which accounts for 94.2% of the variability. These results suggest that the treatment conditions significantly influence these removal parameters, with pH and redox potential showing opposing trends. In another way, pH is positioned in a quadrant distinct from COD reduction and color removal, indicating that increases in oxidation potential, probably facilitated by higher ozone concentrations, are associated with enhanced color removal. In contrast, the effects of COD depletion are comparatively less pronounced. This finding aligns with previous results indicating that prolonged ozone exposure leads to more significant color degradation.



TIME	$O_3.H_2O_2$	Pred.COD.Removal	Pred.color.Removal	D1	D2	Overall
60	1.6	78.74	79.30	0.80	0.33	0.52

Fig. 6. Multiple optimization trough a desirability function.

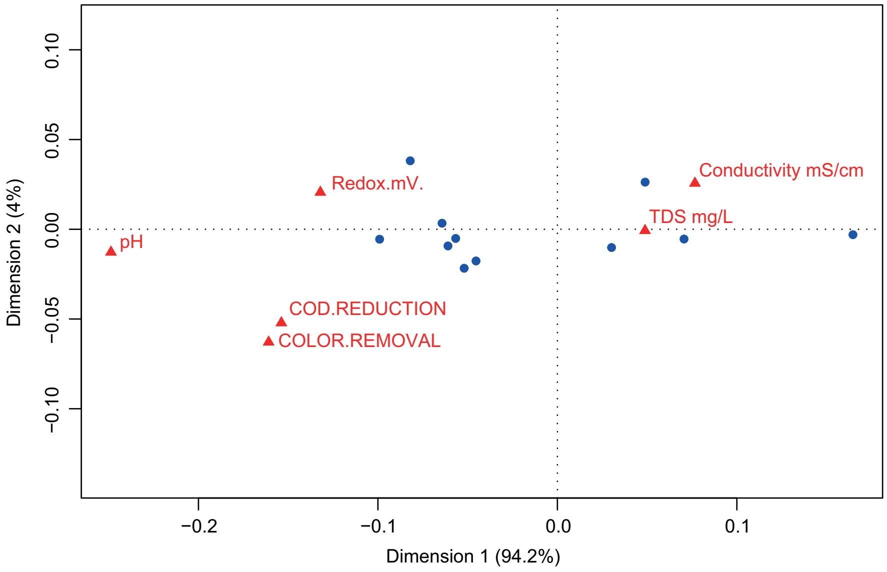


Fig. 7. Correspondence analysis shows the effect of multiple variables on different treatments. Redox. mV denotes Redox Potential (mV), TDS mg/L = Total Dissolved Solids (mg/L), and COD = Chemical Oxygen Demand.

Additionally, **figure 7** shows strong associations between conductivity and total dissolved solids (TDS), which are closely positioned within the plot, suggesting their mutual dependence. These variables are closely linked to the oxidation process and reflect the increased mineralization of pollutants. Notably, the redox potential and conductivity variables correlate with higher treatment effectiveness, particularly in treatments involving extended ozone exposure, as seen with the increased values for conductivity and TDS. This tendency also shows that color removal is more sensitive to changes in treatment parameters compared to COD reduction, which remained relatively stable across the treatments. These findings suggest that while oxidizing agents significantly impact color removal, COD decrease is less sensitive to variations in treatment time and O_3/H_2O_2 ratios under the tested experimental conditions.

DISCUSSION

While hydroxyl radicals ($^{\bullet}OH$) serve as the primary oxidizing agents in the peroxide process, the influence of secondary free radicals on process efficiency cannot be ignored. Side reactions, such as hydroperoxyl radicals ($HO_2^{\bullet}$) forming in the presence of excess hydrogen peroxide, can compete with $^{\bullet}OH$, affecting reaction kinetics and overall oxidative efficiency. This competition stems from the dual nature of $HO_2^{\bullet}$, which can act as an oxidizing and reducing agent, altering the dynamics of radical-mediated reactions. Hydroperoxyl radicals ($HO_2^{\bullet}$) are often generated from the fragmentation of peroxyl radicals ($ROO^{\bullet}$), particularly in systems containing antioxidants (Baschieri et al. 2023).

The presence of $HO_2^{\bullet}$ can lead to the formation of less reactive species, which inhibit chain propagation reactions and reduce the overall efficiency of oxidation processes (Silaev 2018). Although $^{\bullet}OH$ radicals are critical for oxidative degradation, their generation can be suppressed by $HO_2^{\bullet}$, which competes for available reagents and alters reaction pathways (Sonntag and Schuchmann 1993).

In electrochemical systems, excess hydrogen peroxide can exacerbate the formation of $HO_2^{\bullet}$, further inhibiting $^{\bullet}OH$ production and impacting reaction kinetics (Dinç et al. 2019). Despite these challenges, the formation of $HO_2^{\bullet}$ can also create opportunities for antioxidant synergy, potentially enhancing the efficiency of specific reactions under controlled conditions (Baschieri et al. 2023).

The nature of contaminants in wastewater also influences the effectiveness of peroxide-based treatments. Colored wastewater, particularly those containing complex aromatic structures or azo bonds, exhibits significant resistance to direct oxidation by ozone and H_2O_2.

Azo dyes, such as reactive green 19 and reactive orange 16, are notable for their chemical stability and resistance to degradation, often requiring prolonged exposure times for effective treatment. While ozonation can achieve color removal efficiencies exceeding 97% within short timeframes, the incomplete mineralization of these compounds is evidenced by low total organic carbon (TOC) removal rates (Castro et al. 2017, Sabri et al. 2018). The complex aromatic structures of these dyes hinder the ability of hydroxyl radicals to effectively attack and degrade them, necessitating extended treatment durations (Patel and Brahmbhatt 2018).

AOPs, including ozonation and H_2O_2-based systems, effectively break down recalcitrant compounds. However, their efficiency is often constrained by the need for optimal operational conditions, such as pH and initial dye concentration (El Nemr 2018, Sabri et al. 2018). While the high reactivity of hydroxyl radicals enables the degradation of persistent pollutants, the slow kinetics of these reactions often require prolonged exposure times (Xie et al. 2022). Despite their promise, the high energy and capital costs associated with AOPs, coupled with the potential formation of toxic byproducts, present significant challenges for widespread implementation. These byproducts may necessitate additional biological treatment to ensure compliance with environmental regulations (Castro and Durán 2014, Xie et al. 2022).

The environmental and energy sustainability of the peroxide process, particularly in its peroxone variant, is a critical consideration. The peroxone process combines ozone and hydrogen peroxide to generate hydroxyl radicals, highly effective in degrading recalcitrant compounds such as dyes and pharmaceuticals. For instance, the peroxone process has demonstrated exceptional efficiency, achieving nearly 100% decolorization of azo dyes like C.I. reactive black 5 within 60 min (Koulini et al. 2022).

Innovations such as micro-nanobubble (MNB) aeration systems have further enhanced ozone transfer rates, achieving 98.6% removal efficiency for trace pharmaceuticals in hospital wastewater (Zhang et al. 2024). However, the process generates chemical byproducts that require careful management to mitigate environmental impacts. Energy consumption is another critical factor, as maintaining optimal operating conditions is essential for maximizing efficiency without excessive energy use (Benjumea-Hoyos et al. 2024).

Innovations such as tandem continuous flow configurations in the e-peroxide process have improved oxygen self-sufficiency, reducing reliance on external oxygen supplies and enhancing energy efficiency (Zhang et al. 2024). Nevertheless, the energy demands of maintaining optimal conditions remain a challenge to the overall sustainability of the process.

CONCLUSIONS

This research has shown that the peroxone method is a viable alternative for treating wastewater contaminated with dyes from the flower industry. In this study, color removals of up to 91.44% were achieved, which is a significant result considering the presence of these substances in contaminated water.

In addition to color removal, relevant results were obtained regarding the reduction of COD, reaching a value of 77.78%. Although complete mineralization of the pollutants is not achieved, the possibility of increasing the oxidation rate by controlling the pH in a range of 6 to 8 is highlighted. For this purpose, a hydrogen peroxide mixture slightly higher than the maximum dose analyzed in this work was used, and exposure times greater than 256 min were applied. This strategy could be further optimized by improving ozone production and diffusion.

It is essential to note that, by adhering to these conditions, it is possible to achieve significantly high percentages of contaminant removal, thereby complying with current Colombian regulations for the discharge of wastewater into bodies of water or public sewers. This approach helps mitigate the negative impact on aquatic ecosystems. This work represents a gateway to research on the treatment of difficult-to-remove waters, aligning with the Sustainable Development Goals (SDGs) established by the United Nations in its 2030 Agenda (UN 2015).

For future research, it is recommended to scale the process to continuous-flow pilot-scale reactors to assess its effectiveness under real-time conditions and ensure operational stability over longer periods. Additionally, evaluating the biodegradability and potential ecotoxicity of the treated effluent is essential to confirm environmental safety prior to discharge. This includes the application of standardized assays to measure residual toxicity and biodegradation potential. Furthermore, advanced analytical techniques should be employed to identify and characterize intermediate by-products, ensuring that no harmful transformation products persist after treatment.

It is also suggested to explore other AOPs with proven efficiency in industrial wastewater treatment, such as photo-Fenton, electro-Fenton, and other emerging AOPs, which could offer complementary or superior performance in terms of decolorization and pollutant load reduction. Investigating these alternative or synergistic approaches may enhance the overall sustainability and adaptability of treatment strategies for complex effluent matrices.

ACKNOWLEDGMENTS

The authors would like to express their sincere gratitude to the Limnology and Water Resources Research Group, along with its affiliated research teams, for their invaluable support throughout the duration of this project. We also extend our thanks to the Universidad Católica de Oriente and the Institución Universitaria Digital de Antioquia for their institutional backing and collaboration, which were essential to the successful completion of this work.

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