



Research article



Optimization of the Photo-Fenton process for the effective removal of chemical oxygen demand and phenols in portable toilet wastewater: A treatment study under real world conditions

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ABSTRACT

Wastewater from portable toilets (WWPT) is characterized by a high content of organic matter and a variety of chemical compounds that retain bad odors, especially phenols, a type of pollutant that is difficult to degrade by conventional treatments; in addition, it is persistent, toxic, and accumulates in the aquatic environment. Although different successful experiences with the use of Photo-Fenton are reported in the scientific domain, its application in WWPT is scarce and warrants study due to the wide use of portable toilets. The objective of this study was to evaluate the Photo-Fenton oxidation process in the removal of organic matter expressed as COD in a WWPT, as well as the reduction of phenols and BOD₅. The experimental runs were carried out in a 0.50 L batch reactor to evaluate the effect of the factors (H₂O₂: 0.019, 25.56, 40.67, 87.24, 148.91, 174.45 g L⁻¹ and pH: 2.80, 3.00, 3.27, 4.40, 5.53, 6.00 UNT) on COD removal and sludge production. It was found that the optimum operating conditions of pH 4.72 and H₂O₂ dosage of 174.45 g L⁻¹ reduced the concentration of phenols by 97.83 % and 95.49 % of COD. In addition, 98.01 % of BOD₅ was reduced, resulting in a biodegradability ratio (BOD₅/COD) of 0.23 compared to the untreated wastewater of 0.53. From a cost perspective, the use of Photo-Fenton to treat wastewater under these conditions would be US\$ 1.15 per liter.

1. Introduction

It is estimated that 3.6 million portable sanitation units are used worldwide in scenarios where there are no fixed sanitation

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facilities [1]; in the specific case of Colombia, no information is available due to the lack of regulation of this activity. Each portable toilet has a different capacity according to its manufacturer, but they are designed to store significant amounts of wastewater, composed of drinking water, fecal matter and a variety of chemical compounds that inhibit the spread of bad odors, the latter being responsible for increasing the chemical oxygen demand (COD) of wastewater due to their low biodegradability [2,3]. The major chemical compounds present in portable toilet wastewater (WWPT) include phenols (C_6H_6O), anodic surfactant compounds such as sodium dodecyl benzene sulfonate ($C_{18}H_{29}NaO_3S$), sodium alkyl benzene sulfonate ($C_{11.6}H_{24.2}C_6H_4SO_3Na$) and dodecylbenzene sulfonic acid ($C_{18}H_{30}O_3S$), ationic compounds such as benzalkonium chloride ($C_9H_{13}ClNR$) and halogen isocyanurates such as sodium dichloroisocyanurate ($C_3N_3O_3Cl_2Na$) [2,4]. Despite the diversity of chemical compounds and organic matter (OM) present in WWPT, phenols are its main constituent [2].

Phenols are contaminants commonly found in industrial wastewater from the textile, pharmaceutical, agricultural, and plastics industries, among others [5,6]. These compounds are called refractory and belong to the contaminants of emerging concern (“CECs”), characterized by their toxicity, persistence and ability to accumulate in organisms and plants [7]. In addition, CECs are often combined with typical contaminants in municipal wastewater [8]. The negative impact of phenols and their derivatives lies in their resistance to degradation by conventional methods, such as the unit processes used in a municipal wastewater treatment plant (WWTP) [9,10]. The low efficiency of conventional systems to completely degrade contaminants such as phenols is since the processes are primarily designed to improve quality indicators such as dissolved organic carbon (DOC and BOD), suspended solids, and nutrients [11,12]. This results in the release of phenolic pollutants into the treated effluent, as is the case with WWPT.

Due to the limitations of conventional treatments, advanced oxidation processes (AOPs) have emerged as a potential solution to degrade recalcitrant and persistent contaminants of emerging concern in urban or industrial wastewater by highly reactive species [10,13]. AOPs can be chemical (H_2O_2/Fe^{2+} and O_3/H_2O_2), photochemical (H_2O_2/UV , O_3/UV , TiO_2/UV , $H_2O_2/Fe^{2+}/UV$), electrochemical and sonochemical, depending on their mechanism of action [14]. Photo-Fenton (PF) has the option of using the catalyst in the same medium as the substrate (homogeneous) or in a different medium from the substrate (heterogeneous) [15]. PF is a technology that involves the generation of short-living free radicals such as hydroperoxide ($HO_2^\bullet$ con $E^0 = 1.48$ V) and hydroxyl radical ($\bullet OH$ con $E^0 = 2.8$ V) for the rapid and non-selective oxidation of organic and inorganic pollutants present in wastewater, converting them to carbon dioxide and water or biodegradable products [16,17]. It reduces the toxicity of the effluent, improves the biodegradability and increases the efficiency of subsequent treatments [18].

On the other hand, PF combines the action of the Fenton process with ultraviolet (UV) light exposure to enhance iron regeneration and $\bullet OH$ production, increasing the efficiency of the process [19]. PF Consists of the decomposition of H_2O_2 in the presence of the reducing agent ferrous ion (Fe^{2+}). In an acidic medium to produce $\bullet OH$ (Equations (1) and (2)) and $HO_2^\bullet$ (Equations (3) and (4)) with lower oxidative power, a reaction known as Fenton-Like [20,21]. The oxidation of Fe^{2+} to ferric ion (Fe^{3+}) makes the reaction autocatalytic [22].



UV radiation causes charge transfer on Fe^{3+} complexes, leading to their dissociation into Fe^{2+} and $\bullet OH$, in this way, so that the reduced iron Fe^{2+} reacts again with H_2O_2 to produce more $\bullet OH$ (Equation (5)), which can increase process efficiency and reduce sludge production [23,24]. Therefore, the $Fe(OH)^{2+}$ is needed to regenerate iron and produce more $\bullet OH$ [10]. In turn, UV has a germicidal effect on pathogenic microorganisms, viruses and bacteria because it affects the structure of DNA, proteins and lipids [11], which inhibits cell replication [20,25].



The performance of the PF process depends on the concentration of the Fenton reagents (Fe^{2+} and H_2O_2), the pH, the reaction time and the intensity of the UV radiation [26,27]. It also depends on the nature of the contaminants being degraded [26–28]. However, it is the Fenton reagents and pH that are the parameters affecting the degradation, with pH being the critical factor influencing the generation of $\bullet OH$ and the nature of the iron species [29]. It has been shown that an optimal pH range between 2.50 and 4.0 units (UNT) favors the formation of $\bullet OH$ and reduces the precipitation of iron and its species, with a specific value of 2.80 UNT considered the most appropriate [22,27].

Previous experience has reported removal rates of 95 % in 20 mg L⁻¹ of phenols at pH 3.50 UNT, a dosage of 50 mmol L⁻¹ of H_2O_2 and 0.20 g L⁻¹ of cobalt ferrite by Ref. [30]. Likewise [31], indicate that they achieved 99 % of phenol removal in an olive mill wastewater with 2.00 mg L⁻¹ of Fe^{3+} and 144 mg L⁻¹ of H_2O_2 under circumneutral pH conditions. As well as other studies that achieved 88.20 % and 99 % reduction of phenol concentration under specific pH conditions and Fenton reagents [32,33]. On the other hand, 90 % of the COD in a real leachate wastewater was removed using an H_2O_2 /COD ratio of 1.06 and a pH of 5.00 UNT [34]. Similarly, 93.20 % of the COD was removed from a textile effluent at a pH of 3.00 UNT, a concentration of Fe^{2+} and 300 mg L⁻¹ of H_2O_2 [32], and 86 % of the COD was removed from the same type of effluent at a pH of 3.00 UNT, a dosage of 1 mM of Fe^{2+} and 11.70 mM of H_2O_2 [28].

Çiner and Gökkuş [35] conducted Fenton oxidation (FO) experiments to obtain maximum COD and color removal at pH, FeSO_4 and H_2O_2 doses and optimum oxidation time for Disperse Yellow 119 and Disperse Red 167 wastewater, showing COD removals above 97 %. However, the study was limited to a one variable at a time analysis (OVAT) which may not reflect the nonlinear relationships of the factors studied and affect the response variable. Also, Gökkuş et al. [36] determined the optimal operational conditions for initial pH, Fe^{2+} , and H_2O_2 concentrations for the removal of Reactive Blue 19. They found that the Fenton oxidation process achieves 98.90 % color removal and 100 % COD removal. Despite these results, a regional optimization approach has not been developed. Although various successful applications of the Fenton process have been reported in the scientific literature, its implementation in WWTP is limited and warrants further study, especially considering that 3.6 million portable sanitation units are used globally in areas without fixed sanitation facilities. Furthermore, optimization approaches using response surface methodology to reduce phenol or COD concentrations in WWTPs under real conditions are also limited.

Therefore, in the present study, homogeneous PF was evaluated as a treatment method to remove organic matter (OM) in terms of COD, BOD_5 and phenols in a WWPT generated in a developing country like Colombia, particularly in the city of Aguachica, Cesar. To achieve this objective, analyses of the physical and chemical parameters of the untreated and treated WWPT were carried out, and the interaction between H_2O_2 concentration and pH was analyzed to determine the optimal PF operating condition. For this purpose, the response surface optimization methodology is used to define regions where COD and phenol removal is promoted and the best operating conditions for the WWPT analyzed.

2. Materials and methods

2.1. Characterization of wastewater from portable toilets

The WWPT studied was supplied by a company in the municipality of Aguachica (Colombia), dedicated to the rental of mobile sanitation units and the collection of waste generated during events or constructions in the city. Once the water has been collected from the toilets, it is transported by truck to the municipal wastewater treatment plant for treatment and subsequent discharge into the stream known as “El Cristo”. It is known that each of the company’s portable toilets has a maximum capacity of 300 L and can produce between 240 and 480 L of wastewater per week. However, the amount of wastewater is subject to uncontrollable variables such as: i) the number of personnel using the toilet and ii) the frequency with which they go to the toilet. It is important to note that the number of toilets varies depending on the activity performed at the site where they are located.

The sampling site was located at coordinates $8^\circ 18' 18.56''\text{N}$ and $73^\circ 35' 54.19''\text{W}$ (Fig. 1). A grab sample of 24.5 L was collected from mobile toilets through a gate valve connected to the WWTP transport vehicle, using a polyethylene container (Fig. 1-

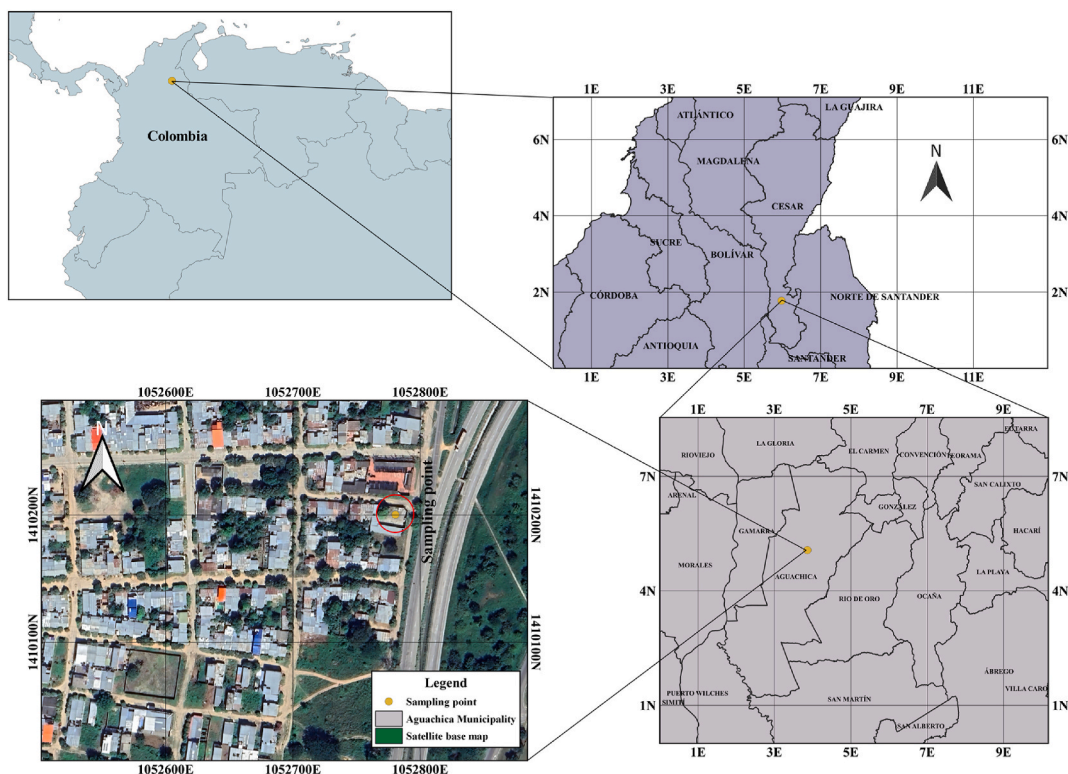


Fig. 1. Map of Colombia. Zoom: Map of the department of Cesar, municipality of Aguachica, sampling site.

Supplementary). The sampling was conducted before the portable toilet company delivered the WWTP to the municipal treatment plant, so no pretreatment was applied. *In-situ* measurements of pH, electric conductivity, color, and turbidity parameters were made at the site. A 4.0 L sample was analyzed for BOD₅, COD, and phenols, and in 1.5 L a sample of residual water was taken to measure the concentrations of sulfates, chlorides and total alkalinity. The same time the point sample was taken, it was transported to the laboratory of the Universidad Popular del Cesar-Aguachica section where it was filtered through a 15 cm diameter sieve to remove larger suspended solids. Finally, the sample was kept at a temperature below 10 °C. The selected parameters were used because they are required by the country's dumping regulations (Resolution 631 of 2015).

2.2. Setup and experimental design

Fig. 2 corresponds to the stages developed during the experiments carried out to identify the effect of Photo-Fenton on the removal of chemical oxygen demand and phenols present in portable toilet wastewater.

The experiments were carried out in a batch reactor (Fig. 3) with a treatment capacity of 0.50 L, equipped with a Puriplus lamp 22.50 cm long and 16 mm in diameter, with a UV-C radiation power of 6 Watts and a wavelength between 200 and 295 nm. In conjunction, a TECNAL model TE-0854 magnetic stirring plate was used to keep the wastewater in motion for 240 min. To adjust the pH of the raw WWPT to the established experimental conditions, 37 % hydrochloric acid (HCl) was used. In addition, to generate the •OH, isolated Fe²⁺ was used as a catalyst to decompose H₂O₂ 30 % as an oxidant.

The 2^K central composite design (CCD) was performed using Minitab® 21.4.2.0 software, considering H₂O₂ and pH as study factors. The factors and ranges evaluated were selected because they were the most reported for wastewater treatment. Each factor had six levels corresponding to 0.019, 25.56, 40.67, 87.24, 148.91, 174.45 g L⁻¹ for H₂O₂ concentration and 2.80, 3.00, 3.27, 4.40, 5.53, 6.00 for pH. In total, there were nine treatments consisting of one central point with five replicates (R) and eight triplicate axial points with H₂O₂ dosages ranging from 0.019 to 174.45 g L⁻¹ and pH values ranging from 2.80 to 6.00 UNT (Table 1). In addition, two other axial points were included, one without pH control or H₂O₂ dosage, where only Fe²⁺ was added, and the other where the wastewater was exposed to UV radiation only. As constant operating parameters of the process, a Fe²⁺ dosage of 1.79 g L⁻¹ and a reactor with a capacity of 0.50 L of wastewater exposed to a UV-C radiation power of 6 Watts during a reaction time of 240 min were set. The reduction in COD concentration and sludge production in each experiment were set as response variables.

2.3. Analytical methods

The parameters were analyzed following the Standard Methods for examination of water and wastewater. Total Alkalinity, Chlorides and Sulfates were determined using the Methods/References: Potentiometer/2320 B, Argentometric/4500-C- B and Turbidimetric/4500-SO₄²⁻ E, respectively. The pH was determined by Electrometric method/4500-H⁺ B (pHmeter: HI98191) in 38 samples of 0.50 L before and after PF. The Electrical Conductivity/2510 A of the same extracts was determined with an EC and TDS DiST® 4 HI98304 m. Turbidity was analyzed using the Nephelometric method/2130 B with an HI98703 Turbidity Meter and Color was measured by Spectrophotometric method/2120C with an HI83399 Multiparametric Spectrophotometer. COD was measured Spectrophotometrically/5220 B on 35 samples after PF treatment using an HI839800 Thermoreactor and an HI83399 Multiparametric Spectrophotometer. Sludge drying was performed after PF at a temperature of 105 °C in a WINCON W-20 oven. The parameters of the replicates of each treatment were averaged ($\bar{X}$) and the standard deviation (S) was calculated. Phenols were determined in the final effluent treated with optimum pH and H₂O₂ dosage, using the Distillation method/5530 B, D; likewise, BOD₅ and COD were calculated using the incubation method 5 days Optical Electrode/5210 B/4500-OH and Volumetric Closed Reflux/5220C. In addition, the maximum allowable limits according to Colombian regulations (Resolution 0631 of 2015) for parameters such as BOD₅, COD and phenols were considered to verify the compliance with the parameters analyzed in the WWPT before and after PF treatment. Equation

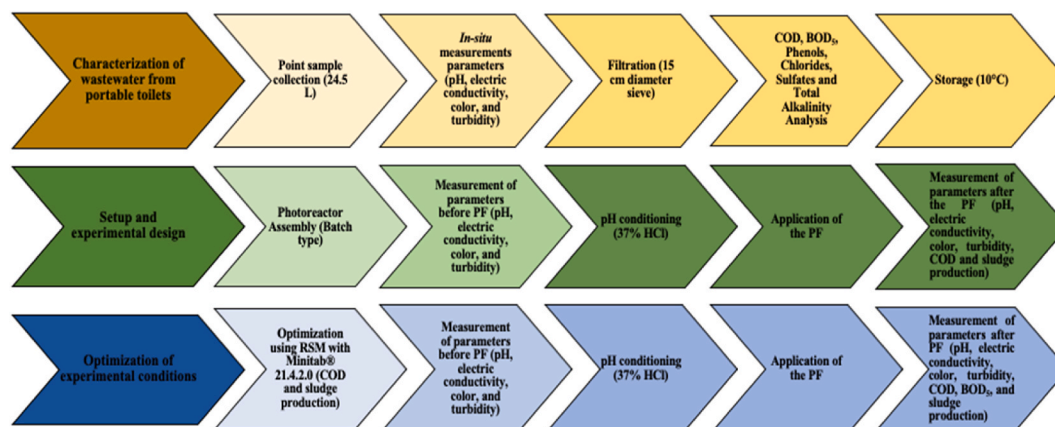


Fig. 2. Diagram of the experimental stages of the research.

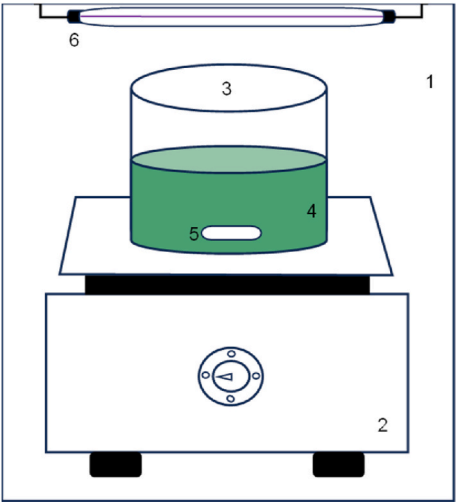


Fig. 3. Schematic diagram of the photoreactor: 1) photoreactor frame 2) magnetic stirring plate 3) beaker 4) wastewater 5) magnetic stirring bar 6) ultraviolet lamp.

Table 1
Experimental design.

Treatment	Natural variables		Coded variables	
	pH	H ₂ O ₂ dosage (g L ⁻¹)	X ₁	X ₂
T ₁	3.27	25.56	1	1
T ₂	4.40	0.019	-1	1
T ₃	4.40	174.45	-1	1
T ₄	3.27	148.91	1	1
T ₅	3.00	40.67	0	0
T ₆	5.53	148.91	1	1
T ₇	5.53	25.56	1	1
T ₈	6.00	87.24	-1	1
T ₉	2.80	87.24	-1	1
T ₁₀	No pH control	No dosage control	-	-
T ₁₁	No pH control	No dosage control	-	-

(6) was used to calculate the percentage removal of phenols, COD and BOD₅.

$$\%Removal = (C_i - C_f / C_i) * 100$$

Equation 6

Where C_i y C_f are the initial and final concentrations of phenols (mg L⁻¹), COD (mg O₂ L⁻¹) y BOD₅ (mg O₂ L⁻¹) before and after PF treatment.

2.4. Optimization of experimental conditions

The experimental data were used to determine the optimal operating conditions by RSM using Minitab® 21.4.2.0 software. For this purpose, the COD (mg O₂ L⁻¹) and sludge production (g L⁻¹) response variable data were fitted to an empirical statistical model with the general form presented in Equation (7). Additionally, the best response was found for electrical conductivity, color and turbidity; however, the effect of the independent variables on these parameters was not taken into account in the last tests, since the Colombian wastewater discharge regulations do not require them as control or quality parameters. The mathematical model was represented by a three-dimensional surface and contour plot developed in Matlab® to show the relationship between the studied factors and each response variable.

$$Y = \beta_0 + \sum_j^k \beta_j q_j + \sum_j^k \beta_j q_j^2 + \sum \sum_{i < j}^k \beta_{ij} q_i q_j + \varepsilon$$

Equation 7

Where Y corresponds to the response variable (COD and sludge), β_0 is a coefficient, β_i and β_j are linear coefficients, β_{ij} represents the interactive effect of the study factors q_i and q_j ;, k is the number of independent variables, and ε is the experimental error. For the response surfaces, a high coefficient of determination (R^2 greater than 0.80) and a low root mean square error (RMSE) were considered as performance metrics to determine the robustness of the model and its predictive ability, respectively [37]. This allowed the

theoretical definition of the best operating conditions, considering the Colombian regulations.

After using the RSM to determine the optimum operating condition, a new test was conducted with three replicates to validate the predicted results. Analysis of BOD₅, COD and phenols was performed on a composite sample formed by the combination of the effluent from the three replicates, while pH, conductivity, color, turbidity and amount of sludge were measured on each sample and the results averaged.

2.5. Photo-fenton operating cost

The operating cost of the PF treatment was estimated in US\$ per liter of treated wastewater, considering only the costs related to the acquisition of inputs and electricity according to the Colombian context. The prices used were: for hydrogen peroxide (US\$ 3.86 per L H₂O₂ 30 % v/v), iron sulfate heptahydrate (US\$ 4.1 per kg Fe₂SO₄·7H₂O), hydrochloric acid (US\$ 79.04 per L HCL 37 % v/v) and electrical energy (US\$ 0.07 per kWh). The costs were made to treat approximately 300 L, which corresponds to what the company that manages the portable toilets collects in a week. The cost methodology applied was carried out according to what was suggested by Trigueros et al. [38].

3. Results and discussion

3.1. Raw WWPT characteristics

Table 2 shows the physical and chemical characteristics of the untreated WWPT and the measured *In-situ* parameters. From the characterization the BOD₅ was found in the range of 500–3000 mg O₂ L⁻¹, which classifies the water as highly polluted, and the COD was in the typical values for an industrial wastewater, between 2000 and 5000 mg O₂ L⁻¹ [39]. The discharge of this untreated wastewater into a receiving water body would result in the depletion of oxygen used by microorganisms to oxidize biodegradable organic matter, which in turn would affect the supply of oxygen necessary for the development of aquatic fauna and flora, leading to their disappearance and ultimately to the eutrophication of the receiving water body due to organic matter inputs [40].

The concentration of COD and BOD₅ in untreated wastewater exceeded the limits established by Resolution 631 of 2015 for public sewerage service providers, with values for COD (150 mg O₂ L⁻¹) and BOD₅ (90 mg O₂ L⁻¹). Similarly, for industrial, commercial or other service activities, with limits for COD of 50 mg O₂ L⁻¹, BOD₅ of 50 mg O₂ L⁻¹ and phenols of 0.20 mg L⁻¹. Total phenols also exceeded the concentration of 0.20 mg L⁻¹ established for mining, hydrocarbon, manufacturing and production of goods and activities associated with services. This indicates that the untreated WWPT does not meet the requirements for discharge to surface water bodies or public sewers. If this were to occur, water quality would be adversely affected, particularly by chemical compounds such as phenols, which cause problems such as suffocation, gill necrosis, and slime production in aquatic animals such as fish, and interfere with the endocrine system, disrupting the oxidative phosphorylation reaction and ATP production [41]. Especially considering that phenols in wastewater in this study had a concentration of 9.2 mg L⁻¹ and concentrations above 5 mg L⁻¹ can damage cells [42].

The presence of inorganic anions such as chloride (Cl⁻) and sulfate (SO₄²⁻) ions could have an individual or combined effect on the degradation of the contaminants, thus affecting the efficiency of the PF process [43,44]. Especially because of the significant chloride concentration of 716 mg Cl⁻ L⁻¹. Chloride ions generate radicals (Cl[·]) less reactive than •OH and other radicals such as HClOH[·], ClOH⁻, Cl₂⁻ (Equations (10)–(13)), which complement the oxidation of the contaminant molecules [40,41]. However, these ions also react with Fe³⁺ to form Fe(Cl)²⁺ (Equation (8) and 9), a complex that affects the distribution and reactivity of iron ions, such as their concentration [43,44].



Table 2
Raw wastewater characteristics.

Parameter	Result
BOD ₅ (mg O ₂ L ⁻¹)	1957
COD (mg O ₂ L ⁻¹)	3660
Total phenolic content (mg L ⁻¹)	9.24
Total alkalinity (mg CaCO ₃ L ⁻¹)	1596
Chlorides (mg Cl ⁻ L ⁻¹)	716
Sulfates mg SO ₄ ²⁻ L ⁻¹	<10
pH	8.41
Electrical conductivity (mS cm ⁻¹)	10.48
Color (PCU)	4910
Turbidity (NTU)	195



The same occurs with sulfate ions, which form a sulfate ($SO_4^{\bullet -}$) radical upon exposure to UV light (Equation (14)) [43,44]. The sulfate radical is an oxidizing species with a higher redox potential at neutral pH (2.5–3.1 V) compared to $\bullet OH$ (1.8–2.7 V), which contributes to the reaction mechanism of pollutant degradation [43,44]. In addition, the sulfate anion can react with a hydrogen and a $\bullet OH$ to form $SO_4^{\bullet -}$, which reacts with a water molecule and H_2O_2 to form $\bullet OH$ and $HO_2^{\bullet}$ (Equations (15)–(18)) [43,44]. Other chemical reactions also occur (Equations (19)–(22)) [43,44]. However, it is possible that because of the low sulfate concentration found (<10 mg SO_4 L $^{-1}$), few such radicals were generated, with a low contribution to the efficiency of the PF process.



Table 3
WWPT characteristics after PF for the different treatments.

Treatment	Parameter	$\bar{X} \pm S$
T ₁	pH	2.43 ± 0.16
	Electrical conductivity (mS cm ⁻¹)	18.17 ± 0.79
	Color (PCU)	18680 ± 178
	Turbidity (NTU)	6.14 ± 3.85
T ₂	pH	3.82 ± 0.48
	Electrical conductivity (mS cm ⁻¹)	16.37 ± 1.02
	Color (PCU)	1398 ± 707
	Turbidity (NTU)	36.17 ± 28.4
T ₃	pH	2.79 ± 0.14
	Electrical conductivity (mS cm ⁻¹)	15.17 ± 0.25
	Color (PCU)	11796 ± 8582
	Turbidity (NTU)	1.37 ± 0.87
T ₄	pH	2.08 ± 0.08
	Electrical conductivity (mS cm ⁻¹)	18.42 ± 2.74
	Color (PCU)	6056 ± 7410
	Turbidity (NTU)	3.35 ± 0.62
T ₅	pH	2.24 ± 0.062
	Electrical conductivity (mS cm ⁻¹)	16.30 ± 0.21
	Color (PCU)	15872 ± 3052
	Turbidity (NTU)	3.05 ± 1.63
T ₆	pH	2.65 ± 0.09
	Electrical conductivity (mS cm ⁻¹)	14.70 ± 0.20
	Color (PCU)	4900 ± 127
	Turbidity (NTU)	1.37 ± 0.58
T ₇	pH	2.62 ± 0.03
	Electrical conductivity (mS cm ⁻¹)	15.76 ± 0.47
	Color (PCU)	7190 ± 3346
	Turbidity (NTU)	4.31 ± 1.92
T ₈	pH	4.59 ± 0.86
	Electrical conductivity (mS cm ⁻¹)	13.43 ± 0.21
	Color (PCU)	848 ± 661
	Turbidity (NTU)	21.63 ± 17
T ₉	pH	2.39 ± 0.02
	Electrical conductivity (mS cm ⁻¹)	16.20 ± 0.08
	Color (PCU)	13490 ± 1260
	Turbidity (NTU)	3.77 ± 2.21
T ₁₀	pH	7.73 ± 0.15
	Electrical conductivity (mS cm ⁻¹)	11.57 ± 0.38
	Color (PCU)	2663 ± 850
	Turbidity (NTU)	186 ± 61.9
T ₁₁	pH	8.25 ± 0.02
	Electrical conductivity (mS cm ⁻¹)	9.54 ± 0.24
	Color (PCU)	3440 ± 108
	Turbidity (NTU)	28.10 ± 1.13



On the contrary, a significant number of chlorinated radicals and surfactants can reduce and eliminate $\bullet\text{OH}$ generated during PF reactions [43,44]. In addition, Cl^- and SO_4^{2-} ions cause the pH of the wastewater to decrease during PF [43,44]. It should be noted that no studies were found that analyzed the effect of alkalinity in the treatment of real or synthetic wastewater by PF, since this parameter usually has a greater impact on biological treatments. A high alkalinity was obtained with a value of $1596 \text{ mg of CaCO}_3 \text{ L}^{-1}$, indicating a good capacity of the WWPT to neutralize acids, as well as the presence of basic substances characterized by ions such as OH^- , CO_3^{2-} and HCO_3^- [45]. Although the biodegradability index (BOD_5/COD) of 0.53 in the untreated WWPT indicates that biodegradation of organic matter is possible prior to physicochemical treatment [3], the presence of phenols highlights the need for their degradation by PF treatment. This is because the biological toxicity and chemical stability of phenolic substances inhibit the biodegradation, growth and reproduction of microorganisms [7]. In addition, a higher efficiency of AOPs compared to biological methods has been reported for the degradation of refractory contaminants [46].

3.2. WWPT characteristics treated with PF

A decrease in pH and an increase in conductivity of the effluent were observed, as shown in Table 3. These changes can be attributed to the fact that Fe^{2+} is an oxysalt, resulting in the release of salt ions and acids during its reaction. In addition, it is possible that both Fe^{2+} and Fe^{3+} reacted with chemical compounds present in the WWPT to form acids that contributed to the pH decrease. It was also possible that the pH was lowered by the effect of hydrogen ions (H^+) formed during the PF process [9]. Although various chemicals are available to correct water acidity, sodium bicarbonate could be used to increase the pH of the WWPT. This substance tends to be a widely applied option to ensure buffer capacity in wastewater because of its cost, availability, and effectiveness.

There was a minimum average increase in conductivity from 13.43 mS cm^{-1} to a maximum of 18.42 mS cm^{-1} at T_8 and T_4 . The pH was the factor with the greatest influence on the conductivity result, with a p-value of less than 0.05. As shown in T_4 and T_6 with the same dosage of H_2O_2 of 148.91 g L^{-1} and pH of 3.37 and 5.53 UNT. The same behavior was shown in T_8 and T_9 using 87.24 g L^{-1} of

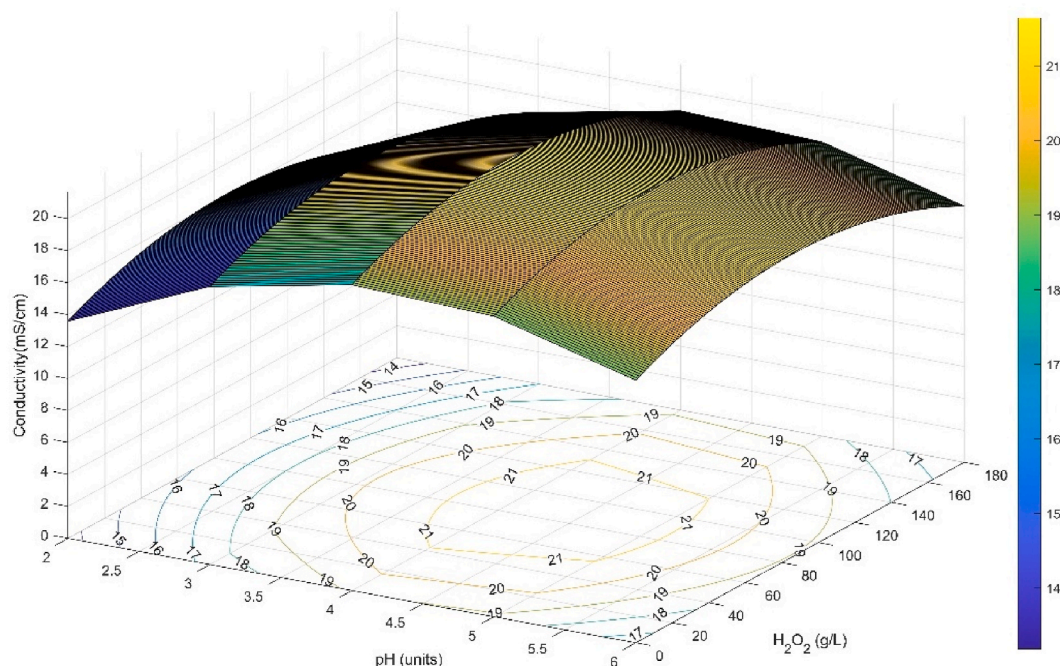


Fig. 4. Response Surface and Contour Plot for Conductivity (mS cm^{-1}): Effect of pH and H_2O_2 , at a Fe^{2+} concentration of 1.79 g L^{-1} , a UV-C irradiance of 6 Watts and a reaction time of 240 min.

H₂O₂ with pH of 6.00 and 2.80 UNT, and in T₁ and T₇. The best relationship between the factors studied and the final conductivity of the effluents treated with PF was found with a linear least squares model, as shown in Fig. 4.

A color reduction of less than 4910 PCU was obtained with 0.019, 87.24, and 148.91 g L⁻¹ H₂O₂ in the presence of 4.40, 6.00, and 5.53 UNT pH. While the color increased when the pH of the wastewater was conditioned below 4.40 UNT. There was a minimum color peak of 705 PCU and a maximum of 19920 PCU, as shown in Fig. 5, with pH being the most significant operating variable in the color changes, with a p-value of 0.001 in a linear plus interaction model. Colors ranging from green to various shades of yellow and orange were present in the PF-treated water (Fig. 2-Supplementary) after 1 h of treatment. This phenomenon was also reflected in the color of the settled sludge at the end of the process. These color changes indicate that the present pollutants were removed from the wastewater due to the decomposition of H₂O₂ by iron ions (Equations (1) and (2)) [28].

On the other hand, it is inferred that iron concentration has a strong effect on color removal and the orange color is attributed to the turbidity of iron ions in the effluent [19]. It was also observed that the effluent maintained a dark brown color after the addition of H₂O₂, which became lighter as the treatment time progressed (Fig. 3-Supplementary). It has been mentioned that this color is caused by the production of hydroquinone as an intermediate in the degradation of phenol, as well as the formation of carboxylic acids [9]. It is also important to note that the iron ions acted as coagulants by forming flocs among the sedimented pollutants, which allowed the reduction of suspended and dissolved solids, which in turn contributed significantly to the reduction of turbidity in the final effluent. The decrease in turbidity is also associated with the precipitation of ferric ions and ferric hydroxides formed in solution and degraded pollutants [47]. The turbidity of the treated water decreased with the increase in H₂O₂ concentration, which increased the availability of hydroxyl radicals to degrade the untreated WWPT particles and the intermediates formed. As observed when comparing T₂ and T₃ with a decrease of 81.54 % and 99.3 % at pH 4.40 UNT, T₁ and T₄ with 96.86 % and 98.28 % reduction at pH 3.27 UNT, and T₆ and T₇ with a turbidity reduction of 97.8 % and 99.29 % at pH 5.53 UNT. There was an increase in turbidity reduction at pH greater than 4.40 UNT. Turbidity removal had an optimal stable behavior with the experimental conditions used (Fig. 6), where H₂O₂ was the most influential factor with a p-value of 0.027.

3.3. Effect of pH and H₂O₂ dosage on COD removal

The variation of pH unit and H₂O₂ dosage showed a significant effect on the removal of COD from WWPT, achieving a reduction of this response variable in different percentages, as detailed in Table 4. A higher average removal efficiency of 82.10 % was obtained with a pH of 5.53 UNT and an H₂O₂ dosage of 148.91 g L⁻¹, as well as an average removal of 81.34 % with a pH of 4.40 UNT and 174.45 g L⁻¹ H₂O₂. On the other hand, by maintaining the previous pH values and reducing the dosage of H₂O₂, a decrease in COD removal efficiency was observed, specifically at a pH of 4.40 UNT and 0.019 g L⁻¹ H₂O₂, with a minimum average removal of 41.33 %. Therefore, an increase in the dose of H₂O₂ improved COD removal. These results indicate a higher oxidation potential of •OH in this type of wastewater, above the optimum pH of 2.80 suggested in the literature [11,19,27]. However, the efficiency of PF in wastewater

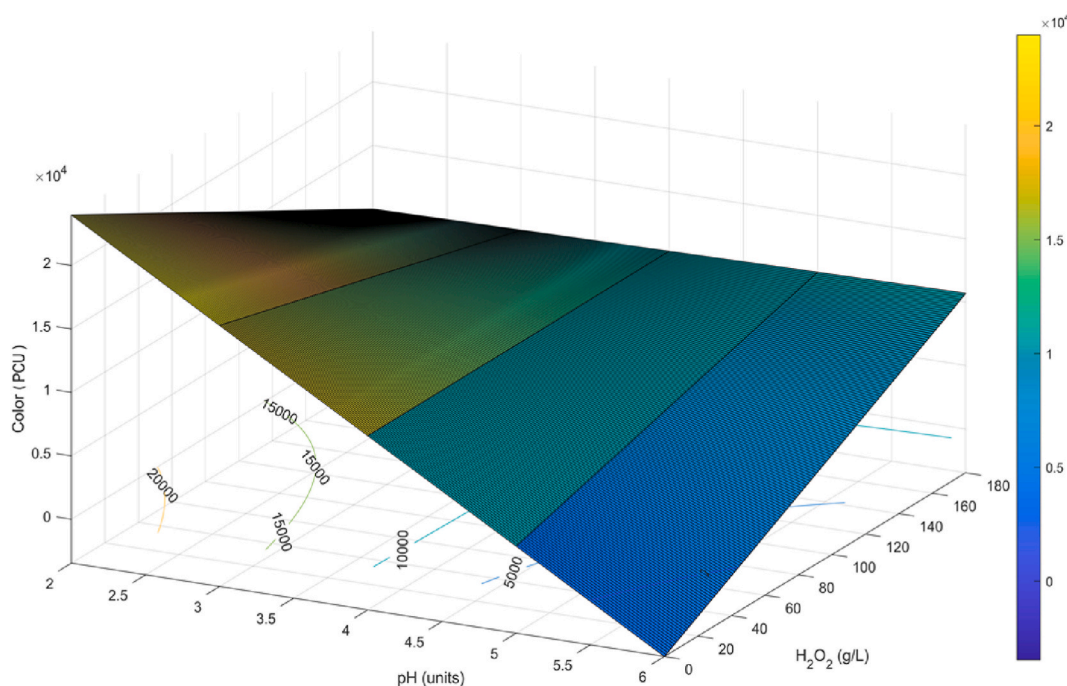


Fig. 5. Response Surface and Contour Plot for Color (PCU): Effect of pH and H₂O₂, at a Fe²⁺ concentration of 1.79 g L⁻¹, a UV-C irradiance of 6 W and a reaction time of 240 min.

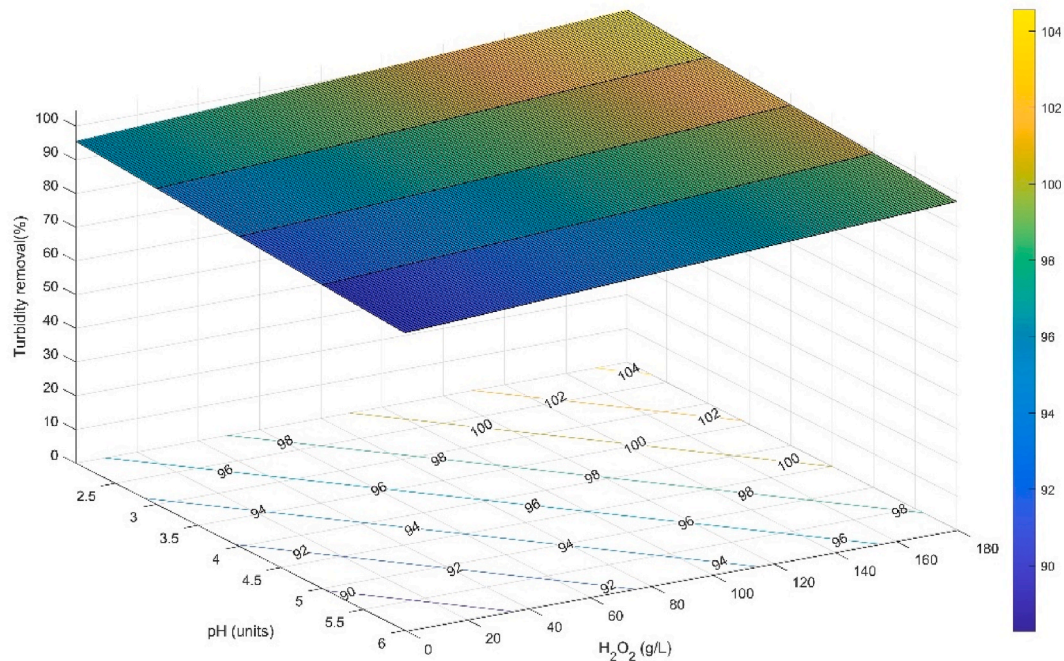


Fig. 6. Response Surface and Contour Plot for Turbidity (%): Effect of pH and H₂O₂, at a Fe²⁺ concentration of 1.79 g L⁻¹, a UV-C irradiance of 6 W and a reaction time of 240 min.

Table 4
COD removal (mg O₂ L⁻¹) in WWPT after PF.

Treatment	Initial value	$\bar{X} \pm S$	%RCOD ^a
T ₁	3660	1208 ± 116	66.10
T ₂	3660	2147 ± 47	41.33
T ₃	3660	683 ± 159	81.34
T ₄	3660	1014 ± 237	72.27
T ₅	3660	823 ± 48	77.49
T ₆	3660	655 ± 14	82.10
T ₇	3660	784 ± 53	78.56
T ₈	3660	883 ± 275	75.85
T ₉	3660	725 ± 80	80.17
T ₁₀	3660	1393 ± 678	61.93
T ₁₁	3660	1252 ± 37	65.79

^a COD Removal Percentage.

treatment at neutral pH without iron complexing agents has also been studied, showing good performance [48,49]. On the other hand, to avoid a decrease in PF efficiency due to iron precipitation under alkaline conditions, it has been recommended to use natural or chemical chelating agents that keep iron soluble and allow the Fenton reaction to take place at neutral or near-neutral pH [23,50,51]. Likewise, it has been mentioned that quinone derived from phenolic compounds from industrial wastewater can act as a chelating agent, allowing the Fenton reaction to take place at a high pH range [52].

It was found that the effect of pH and H₂O₂ dosage on COD removal followed a first order predictive model (Equation (23)). According to the regression analysis performed, the model explains the interaction between the independent variables and the response variable with a p-value of 0.024. The factor [H₂O₂] was the most significant factor in the reduction of COD within the 95 % confidence interval, with a p-value of 0.003. However, the interaction of pH and pH-[H₂O₂] had a low significance with a p-value greater than 0.05. The significant effect of H₂O₂ on COD removal is because this reagent is the main source to produce the •OH and also because it is an oxidant with a potential of 1.78 V [24,34].

$$\%RCOD = 0.761 - 0.027 \text{ pH} - 0.00088 \text{ H}_2\text{O}_2 + 0.00096 \text{ pH} * \text{H}_2\text{O}_2 \quad \text{Equation 23}$$

The %RCOD reached its maximum value, 84.75 %, when a pH of 4.40 UNT and 174.45 g L⁻¹ of H₂O₂ were used. The optimum range to obtain COD removals higher than 80 % is at a pH higher than 4.40 UNT together with a dosage of H₂O₂ higher than 87.24 g L⁻¹ (Fig. 7).

It was observed that the increase in H₂O₂ dosage did not negatively affect the treatment efficiency. Therefore, the maximum

concentration of this reagent remained within the optimal range, as a concentration above its limit leads to the consumption of $\bullet\text{OH}$ and triggers secondary reactions. This results in the formation of $\text{HO}_2^\bullet$ with a lower oxidative capacity of the contaminants (Equations (26) and (29)), which would result in a decrease in the efficiency of the process [10,26]. The same principle applies to the iron ion concentration (Equation (30)) [53], which remained stable. Therefore, an excess of the two reagents can induce low pollutant degradation efficiency, increase sludge formation, and raise COD in the effluent [28].

The efficiency of the process was enhanced by the absorption of UV radiation by H_2O_2 molecules at wavelengths shorter than 300 nm, which resulted in the production of $\bullet\text{OH}$ [54]. Additionally, the recovery of ferrous ions at wavelengths ranging from 250 to 400 nm contributed to the overall process [55]. The decomposition of hydrogen peroxide by ultraviolet radiation occurs in a series of phases. In the initial phase, the ionized form of hydrogen peroxide (HO_2^-) decomposes to produce a $\bullet\text{OH}$ and an anion radical ($\text{O}^\bullet$), which generates another radical upon reaction with water (Equations (24) and (25)). The second phase is the propagation phase (Equations (26) and (27)), followed by the final phase involving the recombination of $\bullet\text{OH}$ (Equations (28) and (29)) [18].



The concentration of 1.79 g L^{-1} of Fe^{2+} in combination with UV radiation and in the absence of H_2O_2 at an average pH of 8.14 UNT was found to reduce COD by 61.93 % (T_{10}); there was also a removal when only UV radiation was used. This is due to the coagulating power of the iron ions, and the direct chemical reaction of the UV radiation with the molecules present in the WWPT. The adsorption of UV energy by the molecules results in their breakdown into intermediates and total mineralization [24]. However, the type of pollutant and wavelength influence the process because pollutants absorb UV radiation differently and some are photostable [56]. In addition, when UV radiation reduces the size of molecules it is easier to degrade them by $\bullet\text{OH}$ s. UV photons also transmit energy to water molecules, breaking them apart and increasing the number of $\bullet\text{OH}$ available to react with contaminants, as presented in Equation (31) [22,24].

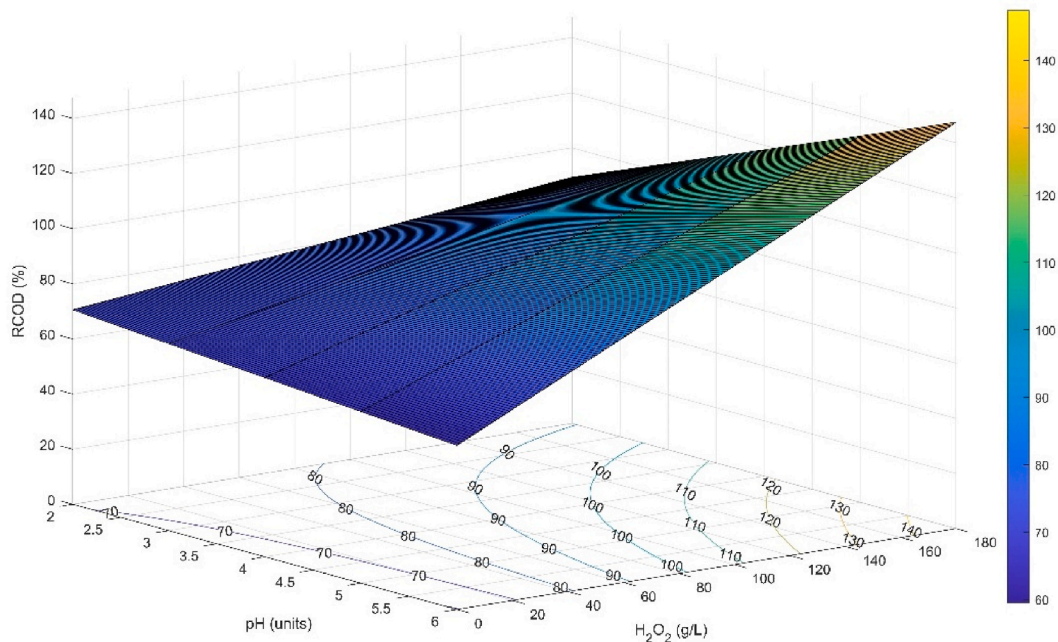


Fig. 7. Response surface and contour plot for %RCOD: Effect of pH and H_2O_2 , at a Fe^{2+} concentration of 1.79 g L^{-1} , UV-C irradiance of 6 W and 240 min of reaction.



On the other hand, the removal of COD was not affected by the presence of Cl^- and SO_4^{2-} in the WWPT. The reduction in COD is ultimately attributed to hydroxyl radicals and hydroperoxides formed during the Fenton reaction (Equations (1) and (2)) [26]. The radicals decompose organic substrates (RH) by subtracting hydrogen, transferring electrons, and forming a double bond (C=C) with the organic molecules (Equations (32)–(34)) [21]. The reduction in COD is also attributed to the mineralization of phenols by hydroxyl radicals ($\bullet OH$), which initiates the first redox reaction. This process results in the formation of benzoquinone and hydroquinone. The oxidative opening of the six rings produces low molecular weight carboxylic acids, such as maleic, oxalic, and formic acids [9,17]. These acids may contribute to a decrease in pH, as evidenced in this study. Direct photolysis of the pollutants also improves the COD of the effluent. Furthermore, the hydroxyl radical ($\bullet OH$) formed by the photodecomposition of hydrogen peroxide (Equation (9)) and photosensitization of ferrous and ferric complexes (Equations (5) and (35)) reduces the organic matter content, resulting in enhanced efficiency of the treatment system [24,26,27].



Although the effect of Fe^{2+} was not analyzed, the concentration used had a significant contribution in the production of $\bullet OH$, which is a key factor in the reduction of COD as pointed out by Ref. [9].

3.4. Effect of pH and H_2O_2 dosage on sludge production

The combinations of pH and H_2O_2 evaluated in the experiments resulted in the precipitation of particles expressed as settleable solids and then as sludge, as detailed in Table 5. A minimum average sludge production of 2.09 g L^{-1} was observed when using pH 3.27 and 4.40 UNT together with H_2O_2 doses of 148.91 and 174.45 g L^{-1} , respectively. In contrast, a higher sludge production of 2.86 g L^{-1} was recorded when using a pH of 6.00 UNT and H_2O_2 dosage of 87.24 g L^{-1} . The deviation results indicate that there were no significant variations in sludge production when the Fe^{2+} dosage was kept constant, with minimal differences ranging from 0.03 g L^{-1} to 0.21 g L^{-1} compared to the mean.

The formation of sludge in wastewater treatment with iron ions is directly related to the oxidation of Fe^{2+} to Fe^{3+} under pH conditions higher than 2.80 UNT, which deactivates the catalytic capacity of Fe^{3+} [27]. The above triggers a series of hydrolysis reactions and the formation of chemical complexes (Equations (36)–(39)), which are unable to participate in the Fenton reaction [52]. These reactions are dominated by ionic species such as Fe^{3+} , $Fe(OH)^{2+}$, $Fe^2(OH)_2^{4+}$, $Fe(OH)_2$, $Fe(OH)_3$, $Fe(OH)_4$ and $Fe(OH)_6^{3-}$, which favor the partial coagulation of macromolecules present in the wastewater [57]. In particular, ferrous ($Fe(OH)_2$) and ferric ($Fe(OH)_3$) hydroxides play a crucial role in the coagulation-flocculation process due to their higher charge density compared to the other iron(II) species [28,58]. Precipitated iron does not react with H_2O_2 , nor is Equation (5) carried out, and $Fe(OH)_3$ decomposes H_2O_2 into water and oxygen, reducing the amount of this reagent to produce $\bullet OH$ [28,51].



Table 5
Sludge production (g L^{-1}) in WWPT after PF.

Treatment	$\bar{X} \pm S$
T ₁	2.26 ± 0.03
T ₂	2.83 ± 0.20
T ₃	2.09 ± 0.07
T ₄	2.09 ± 0.06
T ₅	2.66 ± 0.08
T ₆	2.40 ± 0.10
T ₇	2.60 ± 0.14
T ₈	2.86 ± 0.06
T ₉	2.29 ± 0.21
T ₁₀	3.11 ± 0.04
T ₁₁	2.69 ± 0.07

On the other hand, the absence of H_2O_2 produced the highest amount of sludge with a value of 3.11 g L^{-1} , because no radicals are generated that can mineralize the particles present in the water, favoring their accumulation. On the contrary, an increase in the dose of H_2O_2 led to a decrease in the amount of sludge produced, as evidenced in T_2 and T_3 with a reduction of 74 %, where 0.019 and 174.45 g L^{-1} of H_2O_2 were used together with a pH of 4.40 UNT, an effect that was also registered between T_1 and T_4 with a 17 % reduction in the amount of sludge, with a pH of 3.27 UNT and doses of H_2O_2 of 25.56 and 148.91 g L^{-1} .

The first order model (Equation (40)) describes the relationship between pH, H_2O_2 dosage and sludge production with a p-value of 0.003 for a linear plus interaction model. Excluding the effect of del Fe^{2+} on sludge formation, the model shows that pH is the most significant variable, with a p-value of 0.002 within the 95 % confidence interval. Meanwhile, H_2O_2 and the interaction pH- $[\text{H}_2\text{O}_2]$ had low significance with a p-value greater than 0.05. The major influence of pH on sludge production is due to the reciprocal relationship between the oxidation potential of $\bullet\text{OH}$ and pH, as pH controls the chemical stability of H_2O_2 [28].

$$\text{Sludge (g / L)} = 0.208 + 0.1437 \text{ pH} + 0.00725 \text{ H}_2\text{O}_2 - 0.00207 \text{ pH} * \text{H}_2\text{O}_2 \quad \text{Equation 40}$$

Sludge production achieved its minimum value of 0.42 g L^{-1} at a pH of 3.00 UNT and $40.67 \text{ g L}^{-1} \text{ H}_2\text{O}_2$. The optimum range to obtain a sludge production lower than 0.70 g L^{-1} occurs at a pH higher than 3.00 UNT and an H_2O_2 dosage higher than 25.56 g L^{-1} (Fig. 8).

When using a pH higher than 3.00 UNT, it is likely that species such as $[(\text{H}_2\text{O})_8(\text{OH})_2]^{4+}$, $[(\text{H}_2\text{O})_7(\text{OH})_3]^{3+}$ and $[(\text{H}_2\text{O})_7(\text{OH})_4]^{5+}$ were formed, favoring the precipitation of iron [20]. As well as the precipitation of $\text{Fe}(\text{OH})_3$ at pH higher than 3.05–4.00 UNT [28,55]. The above decreases the availability of Fe^{2+} catalyst, the regenerative cycle of Fe^{3+} to Fe^{2+} and increases the formation of sludge [19, 28], as observed in the results obtained.

However, sludge formation also occurred at pH lower than 3.00 UNT, specifically at 2.80 UNT, which was not suggested by some studies [22,27]. Nevertheless, it could not be confirmed whether the precipitation of iron species, especially $\text{Fe}(\text{OH})_3$, increases the amount of sludge, decreases the degradation of pollutants and reduces the efficiency of the process at pH higher than 6.00 UNT, as stated in the literature [28,58]. However, it was found that the amount of sludge was higher when combining a low dose of H_2O_2 with a pH higher than 4.40 UNT, due to the fact that the precipitation of iron species was favored in this medium, which reduced the regeneration of Fe^{2+} , resulting in a lower production of $\bullet\text{OH}$ radicals and a reduced efficiency in the removal of COD, as detailed in Table 5.

Since the sludge characteristics were not determined, analyzing the physical, chemical, and biological properties of sludge from WWTP treated with the PF is necessary. This includes macro and micronutrients, pathogens, and organic and inorganic contaminants. Sludge composition varies with wastewater pollution load and treatment processes. Based on this analysis, it can be decided if the sludge can be used for agricultural or forestry purposes or must be disposed of in sanitary landfills.

3.5. Optimization of pH and H_2O_2 dosage and validation of the predictive model

It was found that using a pH of 4.72 UNT and 174.45 g L^{-1} of H_2O_2 , i.e., a molar ratio of $0.032 \text{ Fe}^{2+}/5.13\text{H}_2\text{O}_2$ a COD removal of 84.75 % could be achieved with a desirability (d) of 1.0 and a minimum sludge production of 0.73 g L^{-1} with a (d) of 0.57 as shown in Fig. 9.

After the validation of the composite optimization, an average sludge production of 0.73 g L^{-1} was obtained, which met the minimum requirement estimated by the model. In addition, a 95.49 % removal of COD was obtained, reducing it to $165 \text{ mg O}_2 \text{ L}^{-1}$ compared to the initial $3660 \text{ mg O}_2 \text{ L}^{-1}$, therefore the validation for this parameter exceeded the predicted %RCOD of 84.75 %, confirming the validity of the predictive model and the effectiveness of the optimal treatment condition. The characteristics of the effluent treated at the optimum conditions are presented in Table 6.

Under the same optimum operating conditions, a 97.83 % reduction in phenol concentration was achieved, from 9.24 mg L^{-1} to less than 0.20 mg L^{-1} . Similarly, a 98.01 % removal of BOD_5 was achieved, from $1957 \text{ mg O}_2 \text{ L}^{-1}$ to $38.90 \text{ mg O}_2 \text{ L}^{-1}$. This resulted in a reduction of the biodegradability index of 0.23 compared to the untreated WWPT, which had a value of 0.53. The biodegradability behavior is theoretically attributed to the residual presence of H_2O_2 in the PF-treated water at the time of COD and BOD_5 analysis, which masked the actual behavior of these two parameters [59]. This occurs because H_2O_2 consumes potassium dichromate, which increases the COD value (Equation (41)) [60]. Furthermore, in his research, Gilpavas [28] increased the BOD_5/COD ratio from 0.13 to 0.54 after eliminating the H_2O_2 residue in the treated effluent.



The composite optimization allowed to comply with the BOD_5 limit concentration ($90 \text{ mg O}_2 \text{ L}^{-1}$) for public sewerage service providers and the standards established for industrial, commercial, or service activities other than those contemplated in Chapters V and VI with BOD_5 limits ($50 \text{ mg O}_2 \text{ L}^{-1}$) and phenols of 0.20 mg L^{-1} . Also, the phenol concentration limit of 0.20 mg L^{-1} was met for mining, hydrocarbon, manufacturing and production of goods and service activities. On the other hand, the effluent did not meet the limits of $150 \text{ mg O}_2 \text{ L}^{-1}$ and $50 \text{ mg O}_2 \text{ L}^{-1}$ for COD. The results obtained in this study demonstrate the effectiveness of PF in the reduction of COD, elimination of phenols and significant removal of BOD_5 from WWPT. However, a typical characteristic of homogeneous PF, sludge formation, caused by coagulation of pollutant molecules and precipitation of iron ions and their species, was present [15].

On the other hand, it was identified that the cost of wastewater treatment under optimization conditions corresponds to US\$ 1.15 per liter. Although this value is lower than that reported by Poblete et al. [61] who found costs close to US\$ 24 in the treatment of

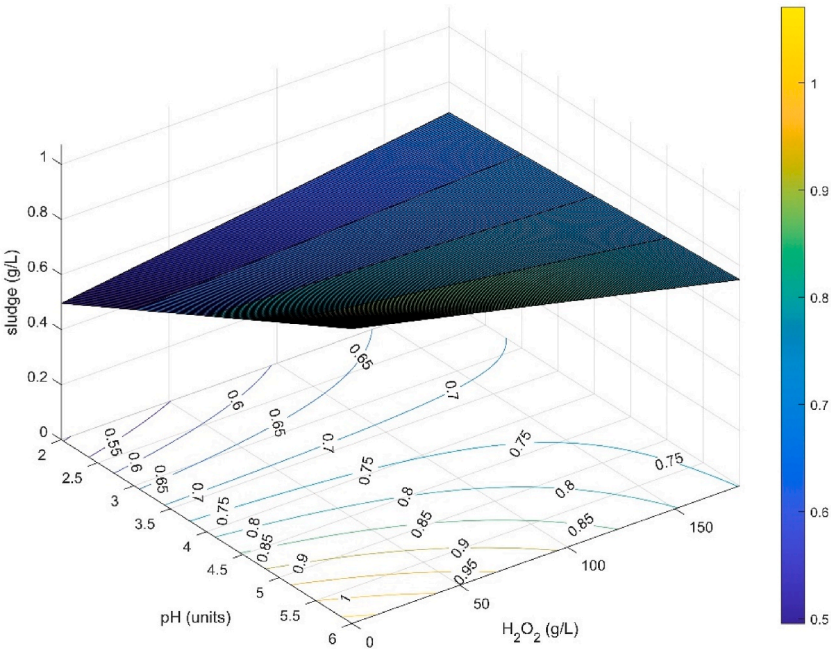


Fig. 8. Response and contour surface for sludge formation: effect of pH and H₂O₂, at Fe²⁺ concentration of 1.79 g L⁻¹, UV-C irradiation power of 6 W, and 240 min reaction time.

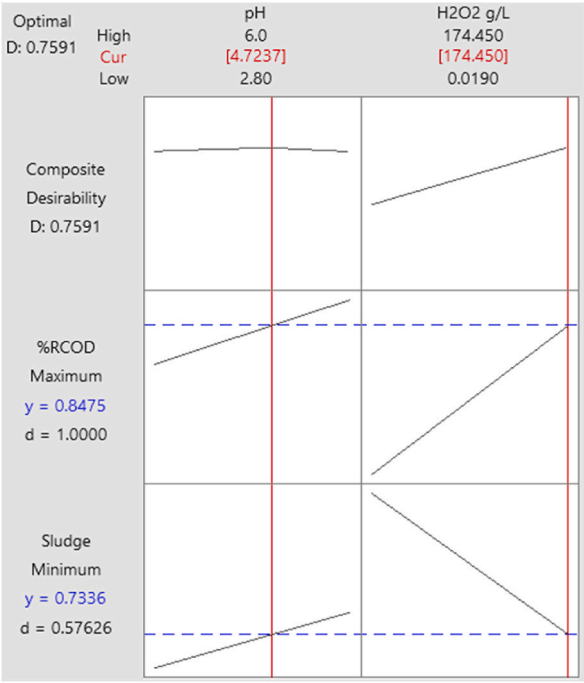


Fig. 9. Interaction plots between independent variables (pH and H₂O₂) and output responses.

vinasse waters which are characterized by their high phenol content. It is necessary to carry out a much more detailed economic analysis considering operational aspects and maintenance on a larger scale. In addition, the environmental taxes that are governed in Colombia for the discharge of wastewater must be considered.

Table 6
Characteristics of treated WWPT using the optimal pH and H₂O₂ dosage.

Parameter	Value
BOD ₅ (mg O ₂ L ⁻¹)	38.90
COD (mg O ₂ L ⁻¹)	165
Total phenolic content (mg L ⁻¹)	<0.20
pH	2.20
Electrical conductivity (mS cm ⁻¹)	13.30
Color (PCU)	4859
Turbidity (NTU)	5.48
Sludge (g L ⁻¹)	0.73

4. Conclusions

Under the established experimental conditions, the average COD removal varied from a minimum of 41.33 % to a maximum of 82.10 % in the different treatments. Similarly, sludge production ranged from 2.09 g L⁻¹ to 3.11 g L⁻¹. Under optimum conditions, with a pH of 4.72 UNT and a molar ratio of 0.032 Fe²⁺/5.13H₂O₂, a maximum COD removal of 95.49 %, a phenol reduction of 97.83 % and an average sludge production of 0.73 g L⁻¹ were achieved. These results demonstrate the efficiency of the PF in both removing organic matter and reducing the presence of phenols in the WWPT.

It was found that the dose of H₂O₂ was the most influential factor in the reduction of COD, with better results obtained as its concentration increased. While pH had a greater effect on sludge production when Fe²⁺ concentration was kept constant, sludge production increased with a low dose of H₂O₂ in the company of a pH higher than 4.40 UNT. It was clear that by keeping the treatment time, Fe²⁺ dosage and UV intensity constant, the amount of hydroxyl radicals depended directly on the variation of the H₂O₂ dosage; therefore, by increasing the amount of oxidant, the generation of radicals involved in the decomposition of the molecules also increased. On the other hand, the presence of chlorine and sulfate anions in the WWPT did not harm the removal of COD, phenols and BOD₅ when using the PF. The residual fraction of organic matter in the WWPT treated under optimal conditions highlights the need to consider PF treatment in combination with a conventional unit operation or other AOP to obtain an effluent that complies with the COD limit concentration established in the Colombian regulatory framework.

Finally, this study shows the importance of treating wastewater from portable toilets, which are treated as if they were domestic wastewater, however, they present emerging contaminants such as phenols that conventional treatments are not able to eliminate. Therefore, the application of Photo-Fenton in this type of water establishes an opportunity to continue analyzing this process, little explored in real wastewater. It is also necessary to investigate the process using indicators of sensitive organic matter such as TOC and analyze the possible excess of iron ions in the effluent or sludge. Furthermore, in the future it is necessary to evaluate the effect of increased exposure to UV radiation on the degradation of emerging contaminants such as phenols and sludge production.

Data availability statement

All data generated or analyzed during this study are included within the article.

CRedit authorship contribution statement

Yorgi San Juan-Garisado: Writing – original draft, Software, Methodology, Formal analysis, Data curation. **Francisco Luna-Guevara:** Writing – review & editing, Conceptualization. **Pablo Alberto Herrera:** Writing – original draft, Software, Methodology, Formal analysis, Data curation. **Jonathan Soto-Paz:** Writing – review & editing, Investigation. **Jesus David Alvarez-Trujillo:** Writing – review & editing, Investigation. **Cristian Mejia-Parada:** Writing – review & editing. **Brayan Alexis Parra-Orobio:** Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Francisco Luna-Guevara reports was provided by Universidad de Santander. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2024.e35286>.

References

- [1] Portable Sanitation Association International, About Portable Sanitation [Internet], United States, 2024. Available from: <https://www.psai.org/>.
- [2] L. Supo-Quispe, Degradación del fenol en aguas residuales de baños químicos portátiles del sector construcción mediante *Pseudomonas aeruginosa* [Tesis doctoral]. Puno, Perú: Universidad Nacional del Altiplano de Puno 10 (1) (2021) 1–97. http://repositorio.unap.edu.pe/bitstream/handle/20.500.14082/13838/Luis_Alberto_Supo_Quispe.pdf?sequence=1&isAllowed=y.
- [3] C. Yun-Young, B. Seung-Ryong, K. Jae-In, C. Jeong-Woo, J. Hur, L. Tae-U, et al., Characteristics and biodegradability of wastewater organic matter in municipal wastewater treatment plants collecting domestic wastewater and industrial discharge, *Water (Basel)*. 9 (6) (2017) 409, <https://doi.org/10.3390/w9060409>.
- [4] R.H. Perry, *Manual del Ingeniero Químico*. 6ta edición (3r edición en español), Tomo V. México. Editorial Mac Graw Hill, 1994 [Consultado el 22 de febrero de 2024], https://www.academia.edu/51039907/Manual_del_Ingeniero_Qu%C3%ADmico_Tomo_VI_Perry.
- [5] J.K. Wong, H.K. Tan, S.Y. Lau, P. Yap, M.K. Danquah, Potential and challenges of enzyme incorporated nanotechnology in dye wastewater treatment: a review, *J. Environ. Chem. Eng.* 7 (4) (2019) 103261, <https://doi.org/10.1016/j.jece.2019.103261>.
- [6] J. Ahmed, M.M. Rahman, I.A. Siddiquey, A.M. Asiri, M.A. Hasnat, Efficient hydroquinone sensor based on zinc, strontium and nickel based ternary metal oxide (TMO) composites by differential pulse voltammetry, *Sens. Actuators. B. Chem.* 256 (2018) 383–392, <https://doi.org/10.1016/j.snb.2017.10.076>.
- [7] H. Zhang, Z. Ling, J. Ma, Y. Nie, Biodegradability enhancement of phenolic wastewater using hydrothermal pretreatment, *Bioresour. Technol.* 367 (2023) 128199, <https://doi.org/10.1016/j.biortech.2022.128199>.
- [8] T. Chen, Q. Zeng, M. Cao, L. Zhang, B. Adyari, C. Ma, et al., Fate of contaminants of emerging concern in two wastewater treatment plants after retrofitting tertiary treatment for reduction of nitrogen discharge, *Environ. Res.* 118344 (2024) 118344, <https://doi.org/10.1016/j.envres.2024.118344>.
- [9] N. Kavian, G. Asadollahfardi, A. Hasanbeigi, M. Delnavaz, A. Samadi, Degradation of phenol in wastewater through an integrated dielectric barrier discharge and Fenton/Photo-Fenton process, *Ecotoxicol. Environ. Saf.* 271 (115937) (2024) 115937, <https://doi.org/10.1016/j.ecoenv.2024.115937>.
- [10] E.M. Jiménez-Bambague, C.A. Madera-Parra, M.F. Rangel-Delgado, I. Quintero-Martínez, D. Miranda-Mosquera, J.S. Aristizabal-Apolinar, et al., Photo-Fenton and Electro-Fenton performance for the removal of pharmaceutical compounds in real urban wastewater, *Electrochim. Acta* 442 (141905) (2023) 141905, <https://doi.org/10.1016/j.electacta.2023.141905>.
- [11] L. Rizzo, S. Malato, D. Antakyali, V.G. Beretsou, M.B. Dolić, W. Gernjak, et al., Consolidated vs new advanced treatment methods for the removal of contaminants of emerging concern from urban wastewater, *Sci. Total Environ.* 655 (2019) 986–1008, <https://doi.org/10.1016/j.scitotenv.2018.11.265>.
- [12] R. Montes, S. Méndez, J. Cobas, N. Carro, T. Neuparth, N. Alves, et al., Occurrence of persistent and mobile chemicals and other contaminants of emerging concern in Spanish and Portuguese wastewater treatment plants, transnational river basins and coastal water, *Sci. Total Environ.* 885 (163737) (2023) 163737, <https://doi.org/10.1016/j.scitotenv.2023.163737>.
- [13] S. Feijoo, M. Kamali, R. Dewil, A review of wastewater treatment technologies for the degradation of pharmaceutically active compounds: carbamazepine as a case study, *Chem. Eng. J.* 455 (140589) (2023) 140589, <https://doi.org/10.1016/j.cej.2022.140589>.
- [14] J.B. Adeoye, Y.H. Tan, S.Y. Lau, Y. Tan, T. Chiong, N.M. Mubarak, et al., Advanced oxidation and biological integrated processes for pharmaceutical wastewater treatment: a review, *J. Environ. Manage.* 353 (120170) (2024) 120170, <https://doi.org/10.1016/j.jenvman.2024.120170>.
- [15] S. Xavier, R. Gandhimathi, P.V. Nidheesh, S.T. Ramesh, Comparison of homogeneous and heterogeneous Fenton processes for the removal of reactive dye Magenta MB from aqueous solution, *Desalination Water Treat.* 53 (1) (2015) 109–118, <https://doi.org/10.1080/19443994.2013.844083>.
- [16] Y. Baba, T. Yatagai, T. Harada, Y. Kawase, Hydroxyl radical generation in the photo-Fenton process: effects of carboxylic acids on iron redox cycling, *Chem. Eng. J.* 277 (2015) 229–241, <https://doi.org/10.1016/j.cej.2015.04.103>.
- [17] P.J. Espinoza-Montero, R. Vasquez-Medrano, J.G. Ibanez, B.A. Frontana-Urbe, Efficient anodic degradation of phenol paired to improved cathodic production of H₂O₂ at BDD electrodes, *J. Electrochem. Soc.* 160 (7) (2013) 3171–3177, <https://doi.org/10.1149/2.027307jes>.
- [18] J. Monserrat-Castañeda, L. Castillo-Suárez, I. Linares-Hernández, F. Avendaño-Sanjuán, *Procesos Fenton en el tratamiento de aguas*, Editorial Universidad Autónoma del Estado de México, México, 2020, pp. 201–217 [Consultado el 22 de febrero de 2024], <http://hdl.handle.net/20.500.11799/109361>.
- [19] J.P. Ribeiro, H.G.M.F. Gomes, L. Sarinho, C.C. Marques, M.I. Nunes, Synergies of metallic catalysts in the Fenton and photo-Fenton processes applied to the treatment of pulp bleaching wastewater, *Chem. Eng. Process* 181 (109159) (2022) 109159, <https://doi.org/10.1016/j.cep.2022.109159>.
- [20] S. Rahim-Pouran, A.R. Abdul-Aziz, W.M.A. Wan Daud, Review on the main advances in photo-Fenton oxidation system for recalcitrant wastewaters, *J. Ind. Eng. Chem.* 21 (2015) 53–69, <https://doi.org/10.1016/j.jiec.2014.05.005>.
- [21] M.S. Lucas, J.A. Peres, Removal of COD from olive mill wastewater by Fenton's reagent: kinetic study, *J. Hazard Mater.* 168 (2–3) (2009) 1253–1259, <https://doi.org/10.1016/j.jhazmat.2009.03.002>.
- [22] I. Oller, S. Malato, Photo-Fenton applied to the removal of pharmaceutical and other pollutants of emerging concern, *Curr. Opin. Green. Sustain. Chem.* 29 (100458) (2021) 100458, <https://doi.org/10.1016/j.cogsc.2021.100458>.
- [23] L. Clarizia, D. Russo, I. Di-Somma, I. R. Marotta, R. Andreozzi, Homogeneous photo-Fenton processes at near neutral pH: a review, *Appl. Catal., B* 209 (2017) 358–371, <https://doi.org/10.1016/j.apcatb.2017.03.011>.
- [24] C. di Luca, J. García, D. Ortiz, M. Muñoz, J. Carbajo, Z.M. De Pedro, J. Casas, Mineralization of polystyrene nanoplastics in water by photo-Fenton oxidation, *J. Environ. Chem. Eng.* 11 (5) (2023) 110755, <https://doi.org/10.1016/j.jece.2023.110755>.
- [25] G.D. Harris, V.D. Adams, D.L. Sorensen, M.S. Curtis, Ultraviolet inactivation of selected bacteria and viruses with photoreactivation of the bacteria, *Water Res.* 21 (6) (1987) 687–692, [https://doi.org/10.1016/0043-1354\(87\)90080-7](https://doi.org/10.1016/0043-1354(87)90080-7).
- [26] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the fenton reaction and related chemistry, *Crit. Rev. Environ. Sci. Technol.* 36 (1) (2006) 1–84, <https://doi.org/10.1080/10643380500326564>.
- [27] E. Martín del Campo, R. Romero, G. Roa, E. Peralta-Reyes, J. Espino-Valencia, R. Natividad, Photo-Fenton oxidation of phenolic compounds catalyzed by iron-PILC, *Fuel* 138 (2014) 149–155, <https://doi.org/10.1016/j.fuel.2014.06.014>.
- [28] E. Gilpavas, *Procesos Avanzados de Oxidación para la degradación de índigo y materia orgánica de aguas Residuales de una Industria textil* [Tesis doctoral], Universidad Nacional de Colombia, Manizales, Colombia, 2020. <https://repositorio.unal.edu.co/handle/unal/78505>.
- [29] Y. Lei, J. Hou, C. Fang, Y. Tian, R. Naidu, J. Zhang, et al., Ultrasound-based advanced oxidation processes for landfill leachate treatment: energy consumption, influences, mechanisms and perspectives, *Ecotoxicol. Environ. Saf.* 263 (115366) (2023) 115366, <https://doi.org/10.1016/j.ecoenv.2023.115366>.
- [30] L.R. Rad, M. Irani, F. Divsar, H. Pourahmad, M.S. Sayyafan, I. Haririan, Simultaneous degradation of phenol and paracetamol during photo-Fenton process: design and optimization, *J. Taiwan Inst. Chem. Eng.* 47 (2015) 190–196, <https://doi.org/10.1016/j.jtice.2014.10.014>.
- [31] A. Faggiano, M. De Carluccio, A. Fiorentino, M. Ricciardi, A. Proto, et al., Photo-Fenton like process as polishing step of biologically co-treated olive mill wastewater for phenols removal, *Sep. Purif. Technol.* 305 (122525) (2023) 122525, <https://doi.org/10.1016/j.seppur.2022.122525>.

- [32] L. Carvalho-Neves, J. Beber de Souza, C. de Souza-Vidal, L.T. Herbert, K.V. de Souza, K. Geronazzo-Martins, et al., Phytotoxicity indexes and removal of color, COD, phenols and ISA from pulp and paper mill wastewater post-treated by UV/H₂O₂ and photo-Fenton, *Ecotoxicol. Environ. Saf.* 202 (110939) (2020) 110939, <https://doi.org/10.1016/j.ecoenv.2020.110939>.
- [33] S. Yıldız, I. Şentürk, G.T. Canbaz, Degradation of phenol and 4-chlorophenol from aqueous solution by Fenton, photo-Fenton, sono-Fenton, and sono-photo-Fenton methods, *J. Iran. Chem. Soc.* 20 (1) (2023) 231–237, <https://doi.org/10.1007/s13738-022-02663-z>.
- [34] J. Tejera, A. Hermosilla, R. Gascó, V. Miranda, V. Alonso, C. Negro, et al., Treatment of mature landfill leachate by electrocoagulation followed by Fenton or UVA-LED photo-Fenton processes, *J. Taiwan Inst. Chem. Eng.* 119 (2021) 33–44, <https://doi.org/10.1016/j.jtice.2021.02.018>.
- [35] F. Çiner, Ö. Gökkuş, Treatability of dye solutions containing disperse dyes by Fenton and Fenton-solar light oxidation processes, *Clean* 41 (1) (2013) 80–85, <https://doi.org/10.1002/clen.201000500>.
- [36] Ö. Gökkuş, F. Çoşkun, M. Kocaoğlu, Y.Ş. Yıldız, Determination of optimum conditions for color and COD removal of Reactive Blue 19 by Fenton oxidation process, *Desalination Water Treat.* 52 (31–33) (2014) 6156–6165, <https://doi.org/10.1080/19443994.2013.812523>.
- [37] D.C. Montgomery, Design and Analysis of Experiments, eighth ed., John Wiley & Sons, 2019 [Consultado el 22 de febrero de 2024], <https://industri.fatek.unpatti.ac.id/wp-content/uploads/2019/03/181-Design-and-Analysis-of-Experiments-Douglas-C.-Montgomery-Edisi-8-2013.pdf>.
- [38] D.E.G. Trigueros, L. Braun, C.L. Hinterholz, Environmental and economic feasibility of the treatment of dairy industry wastewater by photo-Fenton and electrocoagulation process: multicriteria optimization by desirability function, *J. Photochem Photobiol A. Chem.* 427 (113820) (2022) 113820, <https://doi.org/10.1016/j.jphotochem.2022.113820>.
- [39] O. Thomas, M.F. Thomas, Industrial wastewater. In: UV-Visible Spectrophotometry of Waters and Soils (Third Edition). Elsevier, 2022, pp. 385–416. <https://doi.org/10.1016/B978-0-323-90994-5.00013-7>.
- [40] E. Raffo-Lecca, E. Ruiz-Lizama, Caracterización de las aguas residuales y la demanda bioquímica de oxígeno, *Datos industriales* 17 (1) (2014) 71–80. <https://www.redalyc.org/articulo.oa?id=81640855010>.
- [41] S.B.M. Radziff, S.A. Ahmad, N.A. Shaharuddin, F. Merican, Y.Y. Kok, A. Zulkarnain, et al., Potential application of algae in biodegradation of phenol: a review and bibliometric study, *Plants* 10 (12) (2021) 2677, <https://doi.org/10.3390/plants10122677>.
- [42] S. Mohammadi, A. Kargari, H. Sanaeepur, K. Abbassian, A. Najafi, E. Mofarrah, Phenol removal from industrial wastewaters: a short review, *Desalination Water Treat.* 53 (8) (2015) 2215–2234, <https://doi.org/10.1080/19443994.2014.883327>.
- [43] L.G. Devi, C. Munikrishnappa, B. Nagaraj, K.E. Rajashekhar, Effect of chloride and sulfate ions on the advanced photo Fenton and modified photo Fenton degradation process of Alizarin Red S, *J. Mol. Catal. A. Chem.* 374–375 (2013) 125–131, <https://doi.org/10.1016/j.molcata.2013.03.023>.
- [44] F.E. Titchou, H. Zazou, H. Afanga, E.G. Jamila, R. Ait Akbour, M. Hamdani, et al., Comparative study of the removal of direct red 23 by anodic oxidation, electro-Fenton, photo-anodic oxidation and photoelectro-Fenton in chloride and sulfate media, *Environ. Res.* 204 (112353) (2022) 112353, <https://doi.org/10.1016/j.envres.2021.112353>.
- [45] C. Sierra-Ramírez, Calidad del agua, Evaluación y Diagnostico [Internet]. Bogotá, Colombia: Universidad de Medellín [Consultado 2024 abril 25], <http://hdl.handle.net/11407/2568>, 2011.
- [46] A. Babu-Ponnusami, S. Sinha, H. Ashokan, M.V. Paul, S.P. Hariharan, J. Arun, et al., Advanced Oxidation Process (AOP) combined biological process for wastewater treatment: a review on advancements, feasibility and practicability of combined techniques, *Environ. Res.* 237 (116944) (2023) 116944, <https://doi.org/10.1016/j.envres.2023.116944>.
- [47] N. Villota, J.M. Lomas, L.M. Camarero, Study of the paracetamol degradation pathway that generates color and turbidity in oxidized wastewaters by photo-Fenton technology, *J. Photochem. Photobiol. A. Chem.* 329 (2016) 113–119, <https://doi.org/10.1016/j.jphotochem.2016.06.024>.
- [48] C. Santos, M. Herraiz-Carboné, E. Lacasa, C. Sáez, R. Montes, J. Benito-Quintana, et al., Continuous-flow titration of low iron doses to promote photo-Fenton and photo-Fenton-like processes at neutral pH, *Chem. Eng. J.* 476 (146655) (2023) 146655, <https://doi.org/10.1016/j.cej.2023.146655>.
- [49] G.D. Silva, E.O. Marson, L.L. Batista, C. Ueira-Vieira, M. Starling, A.G. Trovó, Contrasting the performance of photo-Fenton at neutral pH in the presence of different organic iron-complexes using hydrogen peroxide or persulfate as oxidants for naproxen degradation and removal of antimicrobial activity, *Process Saf. Environ. Prot.* 147 (2021) 798–807, <https://doi.org/10.1016/j.psep.2021.01.005>.
- [50] N. López-Vinent, A. Cruz-Alcalde, C. Gutiérrez, P. Marco, J. Giménez, S. Esplugas, Micropollutant removal in real WW by photo-Fenton (circumneutral and acid pH) with BLB and LED lamps, *Chem. Eng. J.* 379 (122416) (2020) 122416, <https://doi.org/10.1016/j.cej.2019.122416>.
- [51] Y. Liu, H. Zhou, K. Wei, C. He, Y. Du, Y. Liu, et al., Extending semiconductor-based photo-fenton reaction to circumneutral pH using chelating agents: the overlooked role of pH on the reduction mechanism of Fe³⁺, *Chem. Eng. J.* 450 (138109) (2022) 138109 <https://doi.org/10.1016/j.cej.2022.138109>.
- [52] I. Vallés, I. Sciscenko, M. Mora, P. Micó, A.M. Amat, L. Santos-Juanes, et al., On the relevant role of iron complexation for the performance of photo-Fenton process at mild pH: role of ring substitution in phenolic ligand and interaction with halides, *Appl. Catal., B* 331 (122708) (2023) 122708, <https://doi.org/10.1016/j.apcatb.2023.122708>.
- [53] L.Z. Huang, M. Zhu, Z. Liu, Z. Wang, H.C.B. Hansen, Single sheet iron oxide: an efficient heterogeneous electro-Fenton catalyst at neutral pH, *J. Hazard Mater.* 364 (2019) 39–47, <https://doi.org/10.1016/j.jhazmat.2018.10.026>.
- [54] C.H. Liao, M.D. Gurol, Chemical oxidation by photolytic decomposition of hydrogen peroxide, *Environ. Sci. Technol.* 29 (12) (1995) 3007–3014, <https://doi.org/10.1021/es00012a018>.
- [55] M.D.G. de Luna, J.I. Colades, C.C. Su, M.C. Lu, Comparison of dimethyl sulfoxide degradation by different Fenton processes, *Chem. Eng. J.* 232 (2013) 418–424, <https://doi.org/10.1016/j.cej.2013.07.107>.
- [56] I. Sánchez-Montes, I. Salmerón-García, G. Rivas-Ibañez, J.M. Aquino, M.I. Polo-López, S. Malato, et al., UVC-based advanced oxidation processes for simultaneous removal of microcontaminants and pathogens from simulated municipal wastewater at pilot plant scale, *Environ. Sci.* 6 (9) (2020) 2553–2566, <https://doi.org/10.1039/d0ew00279h>.
- [57] J. Bratby, Coagulation and flocculation in water a wastewater treatment – third edition, *Water Intell. Online* 5 (0) (2015), <https://doi.org/10.2166/9781780402321>, 9781780402321–9781780402321.
- [58] A. Gürses, M. Yalçın, C. Doğan, Electrocoagulation of some reactive dyes: a statistical investigation of some electrochemical variables, *Waste Manag.* 22 (5) (2002) 491–499, [https://doi.org/10.1016/s0956-053x\(02\)00015-6](https://doi.org/10.1016/s0956-053x(02)00015-6).
- [59] L. Wang, X. Jiang, Unusual catalytic effects of iron salts on phenol degradation by glow discharge plasma in aqueous solution, *J. Hazard Mater.* 161 (2–3) (2009) 926–932, <https://doi.org/10.1016/j.jhazmat.2008.04.037>.
- [60] S.H. Do, B. Batchelor, H.K. Lee, S.H. Kong, Hydrogen peroxide decomposition on manganese oxide (pyrolusite): kinetics, intermediates, and mechanism, *Chemosphere* 75 (1) (2009) 8–12, <https://doi.org/10.1016/j.chemosphere.2008.11.075>.
- [61] R. Poblete, J. Bakit, Technical and economical assessment of the treatment of vinasse from Pisco production using the advanced oxidation process, *Environ. Sci. Pollut. Res. Int.* 30 (27) (2023) 70213–70228, <https://doi.org/10.1007/s11356-023-27390-7>.