

Article

Enhanced UV/H₂O₂ System for the Oxidation of Organic Contaminants and Ammonia Transformation from Tannery Effluents

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Abstract: In this work, a UV/H₂O₂ system in real tannery wastewater was evaluated by an experimental design with optimal stage 2-level I-optimal reaction surface using Design Expert software to analyze the effects of temperature, pH, UV lamp power (W), and H₂O₂ concentration on COD removal and nitrification. It was found that pH and temperature were the variables that affected the process the most. It was found that an acidic pH of 4.5–5.5 and temperatures between 50 and 70 °C favored improved COD and ammonium oxidation. The process conditions—temperature 54.6 °C, pH 4, pW-UV 60 W and hydrogen peroxide 0.5—were confirmed in the next phase of the study using a one-way statistical analysis ANOVA. Under these conditions, the nitrite removal rate was 98.4%, ammonium 94.53%, chromium 92.3%, chlorides 62.4%, BOD 67.4%, COD 44.5%, and color 48%.

Keywords: tannery wastewater; advanced oxidation processes; COD; nitrification; photocatalysis



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1. Introduction

Tanneries are significant businesses that create high-quality leather goods utilized in various industries, including apparel, automobiles, footwear, and furniture. However, since the production process uses a lot of water, wastewater with high levels of organic and inorganic pollutants, including heavy metals, salts, and tannins, is produced. Due to its detrimental effects on aquatic life and human health, this wastewater from tanneries is a significant environmental issue [1]. In a global context, Asia, Latin America and Europe are the leading leather producers in the world; Italy is the leading leather producer in the European continent, owning 60% of the companies and exporting more than 70% of the total production in Europe; in Latin America, Brazil and Argentina stand out in the sector; they have a significant number of emerging companies with great competitiveness in the market, exporting their products to countries such as China, Hong Kong, Vietnam and the United States. Colombia has a 5% share in the production of the tanning industry worldwide and is the sixth largest producer in this sector in Latin America [2]. Production in the tanning industry consumes an average of 10–25 m³ of water in its various stages and can generate an average of 8 to 20 m³ of wastewater; this amount can vary depending on the technological development of each industry. According to estimates, the tanning industry produces roughly 22 billion liters of wastewater annually, most of which takes place in

underdeveloped nations because the process requires little technological advancement. These effluents are reported to typically contain biodegradable substances such as fats, proteins, and carbohydrates as well as contaminants such as solvents, additives, and toxic heavy metals that are typical of the process and, in addition to changing the characteristics of the ecosystems into which they are discharged, also influence human health. They also contain pollutants such as solvents, additives, and toxic heavy metals [3], which, in addition to altering the properties of the ecosystems into which they are discharged, also impact human health by causing, among other things, liver and kidney damage, skin irritation, chronic bronchitis, nasal irritation, cancer, and DNA damage [4,5].

Several studies have described using physical, chemical, biological, and advanced oxidation processes (AOPs) to treat tannery wastewater. Concerning physical treatment systems, processes such as sedimentation, filtration, and centrifugation have been used to remove suspended solids and other particulates from tannery wastewater. The advantages of physical treatment systems are low cost and ease of use, but their effectiveness in removing dissolved contaminants is limited [6]. Chemical processes have shown that chemicals such as coagulants and flocculants are used to remove suspended solids and dissolved organics from tannery wastewater. The advantages of chemical treatment systems include their effectiveness in removing pollutants, but they can generate large amounts of sludge and require careful handling of the chemicals [7]. The use of micro-organisms to biodegrade organic matter in tannery wastewater has been reported; studies of these processes have used biological agents, including bacteria, microalgae, and some fungi. Batch reactor (SBR) systems have been used to treat tannery wastewater, reducing concentrations of COD and BOD by 70–88% [8,9]. Activated sludge systems show exciting results in BOD₅ and COD removal of 90% and 80%, respectively, with specific suspended solids in the mixed liquor (MLVSS) operating requirements of 3500 mg/L while maintaining an aeration time of 12 h [10]. The advantages of biological treatment systems include their efficiency in removing pollutants and their potential for energy recovery. Still, they require longer treatment times and are sensitive to variations in wastewater composition, especially concentrations of fats and oils and recalcitrant compounds that can lead to cell death of the micro-organisms used in these processes [11].

AOPs have become very important in recent years in treating wastewater-containing dyes [12], especially from the tanning industry [13]. Strongly oxidizing radicals, primarily the free hydroxyl radical (OH), are produced and used in these procedures with the goal of selectively reducing stubborn contaminants to a less hazardous state. One of the most crucial processes is the Fenton process, which employs iron (Fe²⁺) to break down hydrogen peroxide and create an OH radical before it is reduced again. According to reports, this system can remove up to 62% chromium, 98% BOD, and 93% COD from effluent from tanneries. A photo-Fenton system, a cyclic mechanism that regenerates the Fe²⁺ ion, might be used to address this technique's fundamental limitation—the disposal of significant amounts of iron ions in the sludge—even if it raises treatment costs [14,15]. Because of its capacity to reduce dyes, synthetic aromatic compounds, and persistent organic pollutants, ozone oxidation is another method used in the treatment of tannery wastewater; removal rates of 90–98% COD, 96% dyes, and 90% ammonium have been reported, though the effectiveness of the process primarily depends on pH. Molecular ozone dominates the reaction and is selective at acidic values (pH 4.5) where the process is direct; however, at pH > 7, the reaction decomposes and creates OH, which is less selective and has a greater oxidation potential [16]. As for photocatalytic processes, photo-Fenton is one of the most studied processes in tannery effluents and achieves a removal rate of 70–90% of COD, 86–98% of color and 90% of Cr. The efficiency of the process depends largely on the pH of the solution, with the optimal range for higher catalytic activity being 2.8–3.0. Iron hydroxides are formed at a pH of >5, which reduces the reactivity of OH, while at values below 2, complex iron species are formed, which react more slowly with H₂O₂ and reduce the efficiency of the process [17,18].

The UV/H₂O₂ system is very important for treating tannery effluents, as it allows no sludge production and significant COD removal in short reaction times [19]. Recent studies have brought significant insight into the treatment of wastewater with this process, evaluating individually the effects of pH, peroxide dosage, and UV intensity [20]; the use of catalysts such as TiO₂ and Fe₂O₃ has been employed to improve the performance of the UV/peroxide system. Although these catalysts increase the degradation rate and reduce the amount of peroxide to be used, the cost of the process rises, and its use in large-scale applications may limit its use, the UV absorption range is limited, and finally, the recovery of the catalyst from the treated wastewater is still a challenge [21]. As can be seen, the UV/H₂O₂ system is of great importance in treating tannery effluents. However, the effects of parameters such as temperature, pH, and UV intensity and their correlation with peroxide concentration still need to be determined, as they have yet to be analyzed in depth in real tannery effluents. This work sought to contribute scientifically to the optimization of operating conditions of the UV/peroxide photocatalytic process for the treatment of real tannery wastewater using a statistical design with response surface analysis, where the effect of temperature, pH, peroxide concentration and lamp potential was evaluated. The optimization conditions were validated with 10 replicates. This research contributes to the scientific understanding of advanced photocatalytic oxidation processes on the role of pH, temperature, UV lamp potential, and peroxide concentration in the generation of reactive species such as hydroxyl radical and their role in pollutant degradation contributing to the development of sustainable tannery wastewater treatment strategies that can be adapted to specific pollutants and environmental regulations.

2. Materials and Methods

2.1. Tannery Wastewater

The effluent came from a cattle hide tannery in the city of Cúcuta (Norte de Santander, Colombia). The samples were collected 60 min apart during the working day (by duplicate), with a volume of 300 mL per sample up to a total volume of 20 L. The samples were slightly acidified with H₂SO₄ and kept at 4 °C before COD analysis.

2.2. Physicochemical Characterization of the Tannery Effluents

The tannery wastewater was physiochemically characterized according to the 23rd edition of Standard methods for examining water and wastewater (Table 1).

Table 1. Physicochemical characterization.

Parameter	Units	Standard Methods Number
COD		5220C
BOD		5210B-4500-OG
Nitrates		4500-NO ₃ B
Nitrites		4500-NO ₂ B
Ammonia nitrogen		4500-NH ₃ F
Phosphates	mg·L ⁻¹	4500-P C
Total Suspended Solids		2540D
Cr		3111D
Sulfides		4500-S2 F
Chlorides		4500-CIB
pH	pH units	4500B
Conductivity	μS·cm ⁻¹	2510B

2.3. Experimental Analysis

An experimental design with three levels of I-optimal reaction area (Table 2) was used and analyzed with Design-Expert[®] software version 22.0.2 (Stat-Ease, Inc., Minneapolis, MN, USA). The variables evaluated were temperature, initial pH, UV lamp power, and hydrogen peroxide concentration, and the reaction variables were COD, NO₃, and

color. The experimental design resulted in 40 experiments performed in triplicate, giving 120 experiments.

Table 2. Experimental design.

Parameter	Factor		
	Lower Level (−1)	Medium Level (0)	Higher Level (+1)
H ₂ O ₂ (M)	0.3	0.5	0.7
Lamp power (W)	30	45	60
pH	4	5	6
Temperature (°C)	50	65	80

The wastewater was passed through a grease trap for 10 min and then segmented for 30 min in a pilot plant located at the laboratory of operational units of Universidad Francisco de Paula Santander (Cúcuta, Colombia). A photocatalytic reactor with a 500 mL overall volume and an operating volume of 200 mL was used, with temperature and pH control (Figure 1). Circulation was performed at 550 rpm. HCl and NaOH at a concentration of 0.1 M were used for pH control. The H₂O₂ concentration was 35%, from which the concentrations used in the experimental design were calculated. Finally, 254 Nm UVC lamps with a power of 15 W were used, providing a light intensity of 44 $\mu\text{W}\cdot\text{cm}^{-2}$.

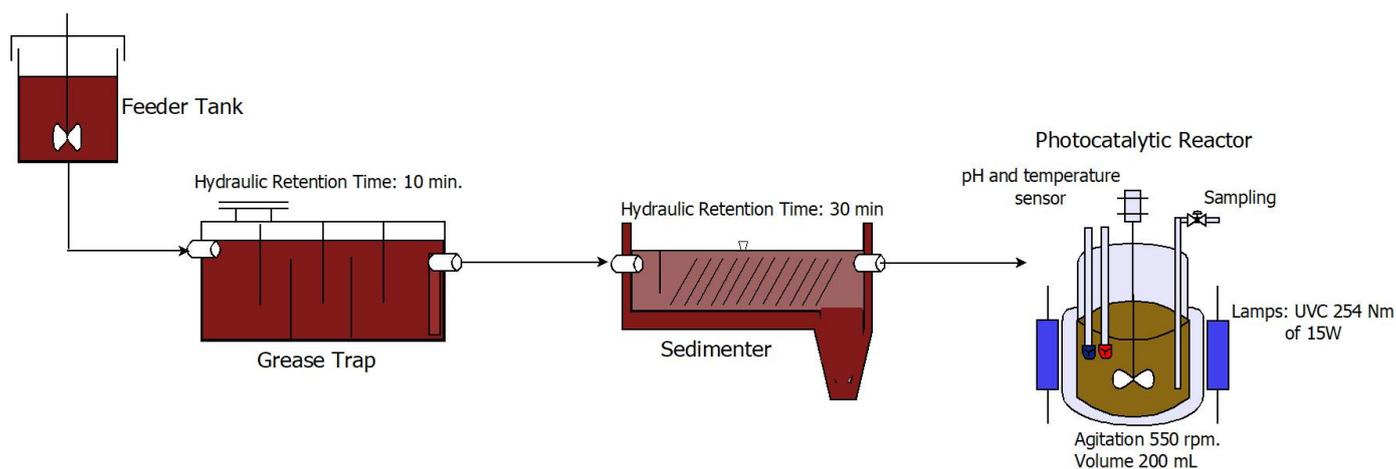


Figure 1. Experimental setup for the UV/Hydrogen Peroxide process.

2.4. Analytical Methods

Total organic carbon (TOC) was determined using a TOC analyzer (Thermo Fisher Scientific, Waltham, MA, USA). Operating conditions were a sample volume of 0.5 mL, water chase volume 1.0 mL, injection line purge on, injection line purge of 0.5 mL, acid volume of 0.5 mL, ICS loading flow 200 mL·min^{−1}, carrier gas delay time of 0.40 min, ICS loading time 50 min, detector sweep flow 500 mL·min^{−1}, oven sweep time 1.0 min, and system flow 200 mL·min^{−1}. The measurement of nitrates was carried out according to the method described (SM-4500-NO₃-C), following the standard procedure indicated in the commercial kits for these compounds of HANNA Instruments UK; a calibration curve was elaborated from 0 to 10 mg·L^{−1}, obtaining the Equation (1) with which the concentrations were determined.

$$C = \frac{A - I}{S} \quad (1)$$

where:

C = concentration (mg·L^{−1})
 A = absorbance

I = intercept of the regression line.

S = slope of the regression line.

The quantification of the COD was determined by the method 5220 C-Closed reflux of the standard methods edition 23, using potassium dichromate as an oxidant agent in an acid medium. For this, its digestion was carried out by adding 1.5 mL of digester solution and 3.5 mL of catalyst solution to 2.5 mL of sample; it was stirred in the vortex, heated for 2 h at 150 °C, and allowed to cool to room temperature (25 °C). The sample was then transferred to a larger vessel, and 0.05 to 0.10 mL (1 to 2 drops) of ferroin indicator was added and stirred rapidly on a magnetic stirrer while titrating with standardized 0.10 mol L⁻¹ FAS. The endpoint was an abrupt color change from blue–green to reddish brown. The calculation was performed using the Equation (2). The COD calibration curve was generated from five patterns of potassium acid phthalate, made up of five concentrations: 0, 50, 100, 250, and 500 mol·L⁻¹. Each experiment was carried out in triplicate.

$$COD \text{ mg } O_2/L = \frac{(B - A) * M * 8000}{mL \text{ sample}} \quad (2)$$

where:

B = mL FAS used for sample

A = mL FAS used for blank

M = molarity of FAS

8000 = milliequivalent weight of oxygen × 1000 mol·L⁻¹

To determine color removal, a spectrophotometric scan was performed using a THERMO GENESYS10 spectrophotometer from the Environmental Quality Laboratory, Bayamon, PR, USA. The scan was performed for each sample in a wavelength range from 200 to 750 nm at a temperature of 25 °C, and the peaks of the absorbance values in the curve were determined. The separation interval of the measurement was calibrated to 1 nm. Deionized water was used to measure the baseline of the sweeps.

3. Results and Discussions

3.1. Physicochemical Characterization of Tannery Wastewaters

Table 3 shows the physicochemical characterization of the tannery effluents evaluated in this study. The results of the physicochemical characterization show that the COD concentration is $6180.45 \pm 3.24 \text{ mg}\cdot\text{L}^{-1}$ and the BOD is $2128.27 \pm 2.86 \text{ mg}\cdot\text{L}^{-1}$, which allows detection of a high pollutant load of these effluents, as well as a high concentration of total suspended solids $1184.65 \pm 1.12 \text{ mg}\cdot\text{L}^{-1}$, chlorides $2100.38 \pm 1.73 \text{ mg}\cdot\text{L}^{-1}$ and conductivity $1102 \pm 0.56 \mu\text{S}\cdot\text{cm}^{-1}$. The pH of the effluents evaluated showed an acid pH (5.18 ± 0.1); the concentration of chromium was $1.2 \pm 0.04 \text{ mg}\cdot\text{L}^{-1}$, a value close to the levels allowed by current regulations for Colombia. It has been reported that tannery effluents have a pollutant organic load resulting from the chemicals used in the tanning and dyeing process, a higher number of suspended solids (SS), a fluctuating pH (4–7), and a high concentration of COD [22,23]; these characteristics are similar to those found in this study. Studies have reported that a BOD/COD ratio > 0.6 shows that effluents are biodegradable and, therefore, can be degraded by biological processes; lower values imply recalcitrant wastewater that must be treated by other oxidative processes such as those found in this study [24]. BOD shows biodegradable organic compounds, unlike the COD value related to organic and inorganic constituents [25]; changes in the BOD/COD ratio may be related to the degree of changes in the structure of organic compounds after oxidation [3].

Table 3. Physicochemical characterization of tannery effluents.

Parameter	Units	Average Value
COD		6180.45 ± 3.24
BOD		2128.27 ± 2.86
Nitrates		74.56 ± 0.67
Nitrites		0.64 ± 0.08
Ammonia nitrogen	mg·L ⁻¹	18.32 ± 0.23
Phosphates		21.8 ± 0.48
Total Suspended Solids		1184.65 ± 1.46
Cr		1.2 ± 0.04
Sulfides		47.34 ± 0.54
Chlorides		2100.38 ± 1.73
pH	pH units	5.18 ± 0.03
Conductivity	µS·cm ⁻¹	928.5 ± 1.12

3.2. COD

The results of the ANOVA analysis for COD removal (Table 4) using the UV/H₂O₂ system show that the model F-value of 2.78 implies that the model is significant. There is only a 1.34% chance that such a large F-value is due to noise. *p*-values less than 0.0500 indicate that the model terms are significant. It can be demonstrated that pH, temperature-pW, and pH-pW interactions are significant terms in the model. Finally, the F-value for lack of fit of 0.22 implies that the lack of fit is not significant relative to the pure error. There is a 97.62% chance that such a large F-value of lack of fit is due to noise.

Table 4. ANOVA analysis of 2-level I-optimal Response Surface design for COD removal.

Source	Sum of Squares	Df	Mean Square	F-Value	<i>p</i> -Value	
Model	188.50	14	13.46	2.78	0.0134	significant
A-Temperature	2.09	1	2.09	0.4321	0.5172	
B-pH	64.75	1	64.75	13.38	0.0012	
C-Hydrogen Peroxide	1.01	1	1.01	0.2091	0.6516	
D-pW	0.2136	2	0.1068	0.0221	0.9782	
AB	1.66	1	1.66	0.3427	0.5637	
AC	8.94	1	8.94	1.85	0.1867	
AD	76.36	2	38.18	7.89	0.0023	
BC	20.37	1	20.37	4.21	0.0513	
BD	50.94	2	25.47	5.26	0.0127	
CD	7.10	2	3.55	0.7338	0.4906	
Residual	116.16	24	4.84			
Lack of Fit	9.54	7	1.36	0.2174	0.9762	not significant
Pure Error	106.62	17	6.27			
Cor Total	304.66	38				

Figure 2 shows the effects of pH and temperature on COD removal. Studies have reported high COD levels in tannery effluents, a typical average characterization may be in the range of 1500–12,000 ppm, a product of the various dyes used in the process as well as salts, organic acids, and other compounds that interfere with treatment and degradation [26–29]. COD, the removal of pollutants, depends on the amount of OH available for oxidation; therefore, the generation of OH is crucial, and this process is affected by the pH of the wastewater. As observed in this work, an acidic pH favors the generation of OH and its reaction with the oxidation of the pollutant load, while high pH values decrease the COD removal rate; studies have shown that at high pH (9–12) the dissociated form of hydrogen peroxide acts as a scavenger of the generated OH*, which affects the reduction of COD removal due to the loss of carbon oxidation potential [20,30]. Temperature affects the rate of peroxide degradation, the generation of hydroxyl radicals, and the solubility of the target impurity, among other factors that contribute to the effectiveness of the UV/H₂O₂

oxidation process. Studies have shown that the ideal temperature for tannery fluids can vary from 30 to 70 °C to eliminate organic contaminants. Generally, higher temperatures favor quicker reactions but can also result in the peroxide degrading itself [31]; similar values were found in this study. Another factor that can affect the efficiency of the UV peroxide oxidation process is the concentration of contaminants in the tannery effluent. Chen et al. [32] revealed that greater starting COD concentrations resulted in a slower removal rate for organic pollutants from tannery effluent by UV/peroxide oxidation; this aspect may account for the removal findings attained in our investigation.

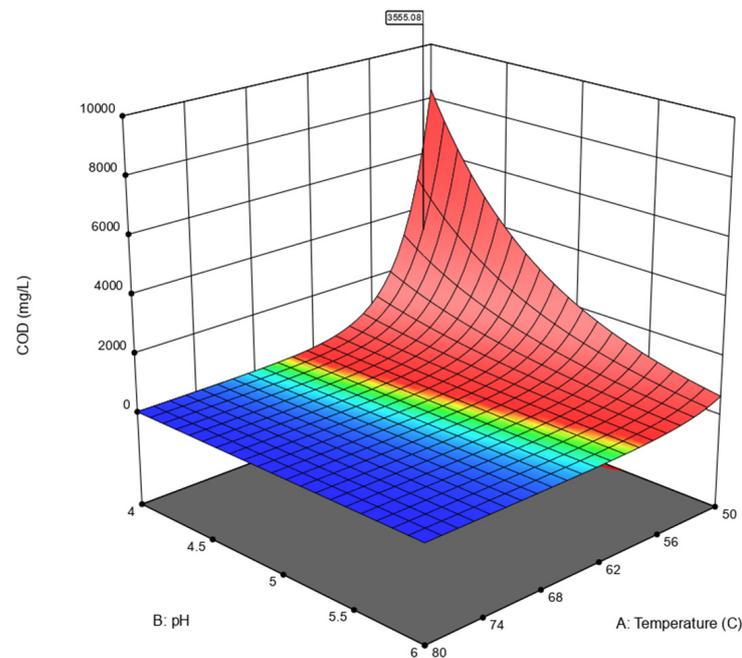


Figure 2. Response Surface Graphical for COD removal. Red color show high COD removal, while blue color shows low COD removal.

3.3. Nitrification

The results of the ANOVA analysis on nitrification (Table 5) using the UV/H₂O₂ system show that the model F-value of 8.65 is significant; there is only a 0.01% chance that such a large F-value is due to noise. *p*-values less than 0.0500 indicate that the model terms are significant. In this case, pH is the significant variable in the model; the remaining variables evaluated are not significant as they obtained values greater than 0.1000. Finally, the F-value of 0.53 implies that the lack of fit is not significant concerning the pure error; there is an 89.49% chance that such a large F-value of lack of fit is due to noise.

Table 5. ANOVA analysis of 2-level I-optimal Response Surface design for Nitrification.

Source	Sum of Squares	Df	Mean Square	F-Value	<i>p</i> -Value	
Model	158.33	5	31.67	8.65	<0.0001	significant
A-Temperature	1.77	1	1.77	0.4825	0.4921	
B-pH	119.48	1	119.48	32.63	<0.0001	
C-Hydrogen Peroxide	6.22	1	6.22	1.70	0.2014	
D-pW	15.91	2	7.95	2.17	0.1300	
Residual	120.84	33	3.66			
Lack of Fit	40.18	16	2.51	0.5293	0.8949	not significant
Pure Error	80.66	17	4.74			
Cor Total	279.17	38				

Figure 3 shows the response surface analysis of the interaction between pH and temperature on nitrate generation. Nitrification is a crucial step in wastewater treatment [11]; pH and temperature can significantly impact the efficiency of the nitrification process in a UV/H₂O₂ system. The pH affects the availability of hydroxyl radicals, which are the vital oxidizing species in the process. Singh et al. [33] reported that at low pH values (lower than 3.5), the concentration of hydroxyl radicals could decrease, resulting in lower nitrification rates; similarly, at higher pH values (higher than 9.5), the concentration of hydroxyl radicals is also reduced due to the formation of peroxide radicals, which are less reactive than hydroxyl radicals. Similarly, it was pointed out that at an initial pH above 9, photo-oxidation converts ammonium to NO₂ and NO₃, and it is also possible that at a pH above 9 and in the presence of UV, photoreduction of NO₃ to NO₂ occurs. The inability of natural waters to convert NO₃ to NO₂ by UV photolysis may be due to the rates of NO₂ photo-oxidation being significantly quicker in the presence of H₂O₂ than those of NO photo-oxidation, NO₃ photoreduction, and NO₂ photo-oxidation in the absence of H₂O₂ [34], a situation demonstrated in this study. In this work, the optimal pH range was found to be 4.5–5.8. Temperature is another critical factor affecting the nitrification process in the UV/H₂O₂ system [26]; the reaction rate usually increases with increasing temperature, up to a certain point, after which it starts to decrease; it has been reported that the optimum temperature range for the UV/peroxide nitrification process is between 35 °C and 60 °C for tannery wastewater [13], similar to those found in this study; at room temperature or below 35 °C the reaction rate decreases, requiring thermal boosting, while at higher temperatures (above 80 °C), the reaction rate decreases due to OH* recombination, and the scavenging effect (OH* acts as an antioxidant) dominates over the thermal decomposition of H₂O₂ present in tannery waste effluents [30].

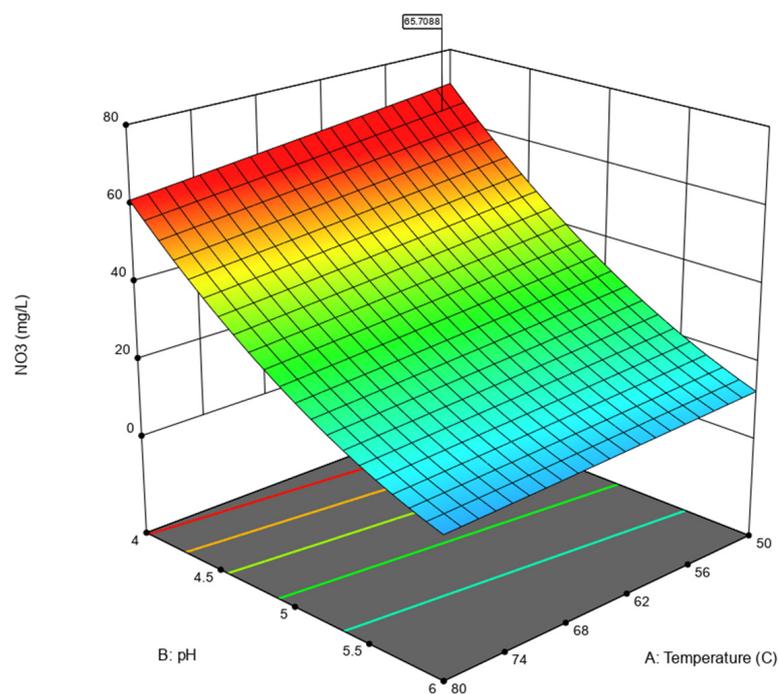


Figure 3. Surface response of the interaction between pH and hydrogen peroxide concentration. Red shows high NO₃ content, while blue shows low content.

3.4. Optimization and Validation of UV/H₂O₂ Operating Conditions

To optimize the operational variables, a new experimental design was developed based on the findings of the previous experimental design, and an ANOVA analysis was developed with a 2-stage I-optimal response surface design (Table 6).

Table 6. 2-level I-optimal response surface design.

Factor	Parameter	Units	Minimum	Maximum
A	H ₂ O ₂	M	0.2000	0.8000
B	Lamp Power	W	30.00	60.00
C	pH		4.50	7.50
D	Temperature	°C	50.00	80.00

Table 7 shows the result of the ANOVA design for the removal of COD, the conditions were volume: 300 mL, reaction time 1 h, stirring 550 rpm, and the lamps were UVC 254 nm.

Table 7. ANOVA Results of COD removal.

Source	Sum of Squares	Df	Mean Square	F-Value	<i>p</i> -Value	
Model	1428.27	14	102.02	19.12	<0.0001	significant
A-H ₂ O ₂	98.85	1	98.85	18.52	0.0016	
B-Lamp Power	642.49	1	642.49	120.40	<0.0001	
C-pH	62.48	1	62.48	11.71	0.0065	
D-Temperature	51.80	1	51.80	9.71	0.0110	
AB	10.53	1	10.53	1.97	0.1904	
AC	10.91	1	10.91	2.04	0.1832	
AD	0.2993	1	0.2993	0.0561	0.8176	
BC	14.75	1	14.75	2.76	0.1274	
BD	17.68	1	17.68	3.31	0.0988	
CD	5.26	1	5.26	0.9864	0.3441	
A ²	15.26	1	15.26	2.86	0.1218	
B ²	165.37	1	165.37	30.99	0.0002	
C ²	106.68	1	106.68	19.99	0.0012	
D ²	8.14	1	8.14	1.52	0.2451	
Residual	53.36	10	5.34			
Lack of Fit	31.86	5	6.37	1.48	0.3383	not significant
Pure Error	21.50	5	4.30			
Cor Total	1481.63	24				

As for the removal of COD, the model results show that it is significant, as the F value of the model is 19.12. There is only a 0.01% chance that such a large F value is due to noise. *p*-values of less than 0.0500 indicate that the model terms are significant. In this case, the linear behaviors of H₂O₂, lamp power, pH, and temperature are not significant. Similarly, the quadratic behaviors of lamp power and pH are also significant. Values above 0.1000 indicate that the model terms are not necessary. The F-value for the lack of fit of 1.48 means that the lack of fit is not significant relative to the pure error. There is a 33.83% chance that such a large F-value for lack of fit is due to noise.

Table 8 shows the result of the ANOVA design for nitrate formation; the conditions were: volume 300 mL, reaction time (1 h), stirring 550 rpm, and the lamps were UVC 254 nm.

The model's F-value of 80.79 indicates that the model is significant; there is only a 0.01% chance that such a large F-value is due to noise. *p*-values less than 0.0500 indicate that the model terms are significant. In this case, the variables with linear behavior: H₂O₂, lamp power, pH, and temperature are significant; likewise, the linear interactions of H₂O₂—lamp power, lamp power—temperature, pH-temperature, as well as the quadratic behavior of lamp power, pH and temperature are significant terms in the model. The F-value for the lack of fit of 4.13 implies a probability of 7.28% that such a significant F-value is due to noise.

Table 8. ANOVA Results for nitrification.

Source	Sum of Squares	Df	Mean Square	F-Value	<i>p</i> -Value	
Model	5457.47	14	389.82	80.79	<0.0001	significant
A-H ₂ O ₂	327.04	1	327.04	67.78	<0.0001	
B-Lamp Power	2380.42	1	2380.42	493.36	<0.0001	
C-pH	123.41	1	123.41	25.58	0.0005	
D-Temperature	298.50	1	298.50	61.87	<0.0001	
AB	107.82	1	107.82	22.35	0.0008	
AC	12.03	1	12.03	2.49	0.1454	
AD	2.96	1	2.96	0.6126	0.4520	
BC	23.82	1	23.82	4.94	0.0505	
BD	32.10	1	32.10	6.65	0.0275	
CD	113.57	1	113.57	23.54	0.0007	
A ²	1.65	1	1.65	0.3418	0.5717	
B ²	706.58	1	706.58	146.44	<0.0001	
C ²	172.05	1	172.05	35.66	0.0001	
D ²	88.53	1	88.53	18.35	0.0016	
Residual	48.25	10	4.82			
Lack of Fit	38.85	5	7.77	4.13	0.0728	not significant
Pure Error	9.40	5	1.88			
Cor Total	5505.72	24				

Figure 4 shows the response surface plots for COD removal and nitrate formation (nitrification). Treatment of tannery effluent is a complex process and may require combining multiple treatment techniques to achieve effective contaminant removal [12]. According to the study's experimental methodology, various parameters affect how well the UV/H₂O₂ process removes COD. (Figure 4a). The H₂O₂ concentration, the temperature, the pH of the process, the UV radiation applied, and the contact time between the wastewater and the light are variables that need to be optimized for each type of tannery wastewater [31]. The amount of organic pollutants in the effluent, including phenols, aromatics, dyes, and other organic compounds, may increase competition for the hydroxyl radicals produced by the UV/H₂O₂ process, which could lower the effectiveness of pollutant removal because some organic pollutants might not receive enough -OH radicals for oxidation [30]. The major source of OH* formation is H₂O₂, hence the higher the COD concentration, the more peroxide must be used; however, too much H₂O₂ contributes to effluent COD since any remaining H₂O₂ acts as an OH* scavenger, which reduces the effectiveness of COD removal [1]. UV light intensity also affects the UV/H₂O₂ reaction to decolorize dyes in tannery effluents. It has been reported that decolorization efficiency is very low when only H₂O₂ without UV is used, and that the use of UV light causes degradation of the pollutants but requires too long exposure times; the rates of dyeing and degradation of the pollutants increase with increasing lamp intensity, with pseudo-first order reaction rates occurring in relation to UV power [35]; However, the disadvantage of the UV/H₂O₂ process is the low absorption of H₂O₂ in the UV range, so the amount of UV radiation is reduced. In this study, it was discovered that both the degradation rate of COD and the oxidation of ammonium to nitrate increased with increasing lamp power, which is explained by the fact that theoretically higher pollutant discoloration and oxidation rates occur at higher UV powers due to the faster formation of free radicals and also depend on the initial conditions [36]. Concerning the photo-oxidation of ammonium to nitrate, it has been pointed out that an optimal concentration of H₂O₂ is required to achieve effective photo-oxidation [12]. There have been no reports demonstrating direct photolysis of NH₃/NH₄ to NO₃ by UV254nm, thus requiring the addition of H₂O₂; in this study, the low concentrations of H₂O₂ were found to have a better effect on the photo-oxidation of nitrogen compounds to nitrate than high concentrations. It has been reported that high concentrations of H₂O₂ do not always increase the photo-oxidation of ammonium to nitrate because UV and OH can

rapidly degrade H_2O_2 . High amounts of H_2O_2 may be ineffective for the photo-oxidation of ammonium and increase COD concentrations in wastewater [34].

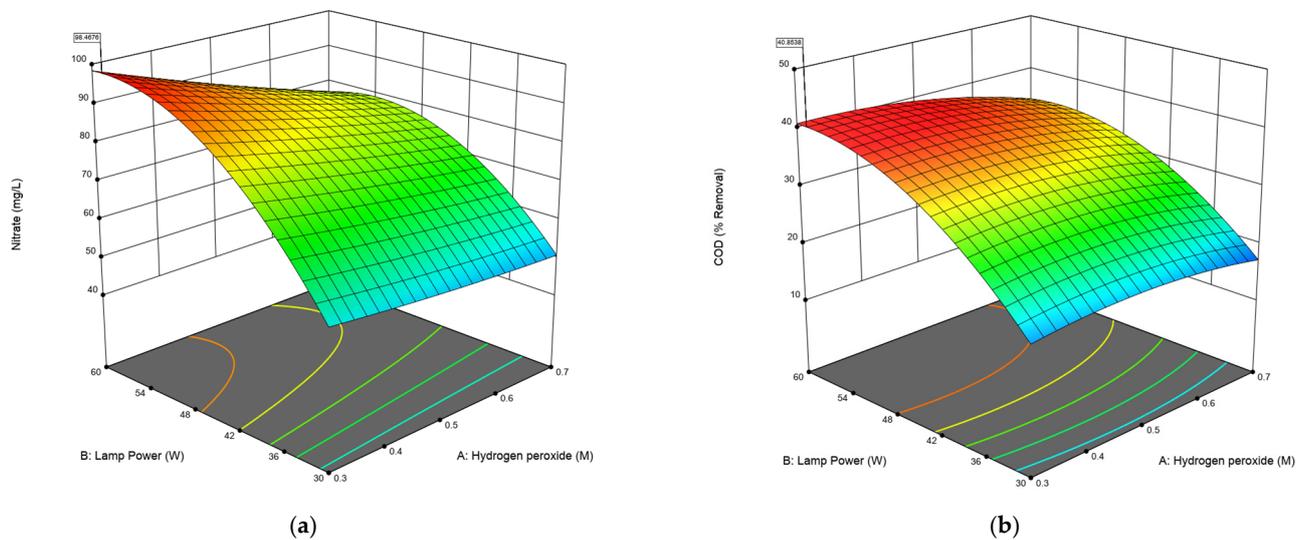


Figure 4. Surface response of optimization and validation of UV/ H_2O_2 operating conditions (a) nitrate formation. (b) COD removal. Red color shows high removal, while blue color shows low removal.

The findings from the response surface and experimental design in this study enabled the identification of the variables needed to validate the process conditions. Temperature, pH, and pW values were 65.5 ± 0.2 °C, 5.5 ± 0.1 , and 0.3 M, respectively, of peroxide. Experiments were repeated 10 times to verify these conditions. The results were analyzed using a One-sample *t*-test on GraphPad Prism software version 10.1.0 for Mac (GraphPad Software, Boston, MA, USA). Figure 5 shows the results of the verification of the optimal conditions. In the case of DOC, there are no significant differences between the observed and expected values. In contrast, in the case of nitrates, there are significant differences between the experimentally determined value and the expected value, although the predicted value was higher.

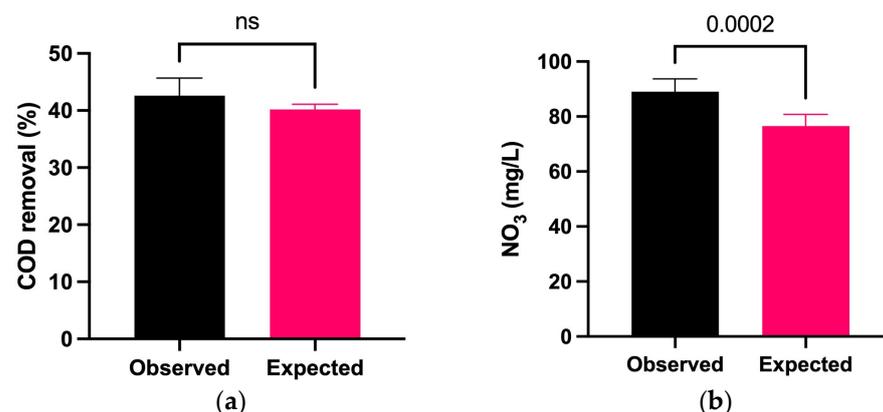


Figure 5. The One sample *t*-test between predicted and expected results of (a) COD removal and (b) nitrate generation.

Figure 6 shows the removal percentages achieved using the optimum values with the UV/ H_2O_2 process. Most of the pollutant parameters evaluated had removal rates above 70%; COD achieved a removal rate of 44.5%, BOD 67.4%, chromium 92.3%, and color 48%.

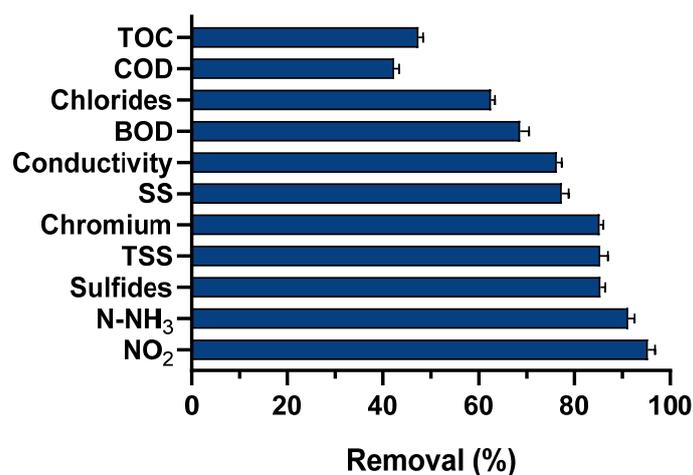


Figure 6. Removal of contaminants. Process conditions: reaction time: 60 min., temperature: 52.5 ± 0.2 °C, pH: 4.2 ± 0.1 , and pW: 60.

In a UV/peroxide process, the removal of COD and BOD occurs through a combination of oxidation and biodegradation processes. The hydroxyl radicals produced by the UV/peroxide reaction attack and oxidize the organic pollutants, breaking them down into simpler, biodegradable compounds [37], yielding an effluent that microorganisms can potentially use as the pollutant load has decreased to a level where biodegradation processes can occur, further reducing the pollutant load [38]. Table 9 shows the removal percentages achieved in this research compared to other AOPs used for tannery water treatment.

Table 9. Pollutant removal rates of the UV/H₂O₂ process compared to other AOPs.

Parameters (% Removal)	This Research (UV/H ₂ O ₂)	[39]	[40]	[41]		[19]	
				UV/H ₂ O ₂	TiO ₂ / H ₂ O ₂ /UV	FENTON	UV/H ₂ O ₂
COD	43.34 ± 1.04	64.3	30.2	18.8	68.3	63.06	45.2
TOC	46.5 ± 0.67	n.r	n.r	n.r	n.r	60	57.7
BOD	68.65 ± 1.35	n.r	30.2	n.r	n.r	52.5	46.18
Color	43.4 ± 0.16	56	n.r	67.36	91.5	n.r	
N-NH ₃	77.5 ± 0.28	16.45	n.r	78.8	90.7	12	0.5
Cr	85.23 ± 0.78	68.02	65.7	n.r	n.r	n.r	n.r
TSS	83.5 ± 1.55	9.21	49	n.r	n.r	n.r	n.r
Chlorides	62.5 ± 0.84	n.r	43	n.r	n.r	n.r	n.r

n.r.: no register.

According to studies, COD and BOD removal rates typically range from 40 to 80%. In this study, COD and color removal results were relatively lower than those of Saranya et al. [39], while removal rates for Cr, N-NH₃, and TSS were lower than those attained in this study; [40] applied a UV//H₂O₂ process in the fluxes of a tannery and found COD removals of 18.8%, BOD 30.2%, TSS 49%, Cr 65.7%, and chlorides 43%, which were lower than those reported in this study; nevertheless, color removal was greater compared to that achieved in this research; [41] reported the implementation of two AOPs (UV/H₂O₂ and TiO₂/H₂O₂/UV) in which they evaluated the removal of COD, color, and N-NH₃ showing removals of 18.8%, 67.36%, and 78.8%, respectively, for the UV/H₂O₂ process and 68.3% for COD, 91.5% for color and 90.7% for N-NH₃ in the TiO₂//H₂O₂/UV system, it can be seen that comparing the results with this study, the UV//H₂O₂ process obtained lower efficiencies while the TiO₂ mediated system obtained removals above the system evaluated

in this study. Finally, Schrank et al. [19] examined the removal rates of a Fenton system with a UV/H₂O₂ photocatalytic system and discovered that the Fenton system performs better. However, there are not many noticeable changes between them. When comparing those results to the ones from this study, it was also discovered that the Fenton system performs marginally better in terms of COD and TOC removal, whereas the UV/H₂O₂ system in this study performed marginally better in terms of BOD removal. Although systems such as Fenton or photo-Fenton can have removals above the range established in this research, the results reported in the literature for various AOPs for the treatment of tannery wastewater clearly show that the photocatalytic system implemented in this research is within the established ranges for the removal of different pollutants, given the expense of employing reagents and other equipment, the UV/peroxide system has a lower energy cost than Fenton, ozone, and photo-Fenton [8,42]. The concentration of the pollutant load and the physicochemical characteristics of the wastewater determine the clearance rate [43]. As observed in this study, chlorides can also be removed by the UV/peroxide system. This process can occur because chlorides can react with -OH to form hypochlorous acid (HOCl) and hydrochloric acid (HCl), which are subsequently oxidized to chloride ions and water [44]. Concerning chromium, removal in a UV/peroxide system can be achieved by oxidation followed by precipitation. Chromium in wastewater can exist in various oxidation states, with hexavalent chromium (Cr (VI)) being the most toxic. -OH, can oxidize Cr (VI) to trivalent chromium (Cr (III)), which can then precipitate as hydroxide or oxide salts [45].

4. Conclusions

A UV peroxide system can effectively remove various pollutants from wastewater, including organic pollutants, COD, BOD, chlorides, chromium and ammonium. The removal efficiency of each pollutant depends on several factors, such as the initial concentration of the pollutant, the pH of the system, and the amount of H₂O₂ used. According to this study, the degradation process is influenced by the pH, temperature, and UV radiation intensity, and their optimization results in faster degradation rates. The application of a catalyst can increase removal rates; integrating bicarbonate or carbonate in the UV/peroxide system as a catalyst can be a promising strategy to improve the removal times, removal efficiency, and oxidation rates of the organic compounds. However, it is necessary to investigate additional strategies to improve the removal of COD and TOC using the photocatalytic process examined in this work. The results of the final physicochemical properties allow evaluation of the potential of the UV/peroxide system's integration with the cultivation of microalgae and cyanobacteria as a culture medium and as a source of biomass with industrially relevant metabolites that would allow development of a sustainable strategy for the implementation of these treatments for the tanning industry in the future.

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