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Electro-Fenton method for dye removal of agro-industrial wastewater from flower production

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ABSTRACT

Removal of recalcitrant dyes from agroindustrial wastewater produced in flower processes represents a significant environmental challenge for flower industries worldwide. Advanced oxidation processes (AOPs) emerge as a clean and effective costly alternative for removing dye contaminants in wastewater. This study used an electro-Fenton technique as an alternative for the treatment of colored wastewater from flower-producing crops in Colombia. Initially, the physicochemical characterization of the wastewater was carried out by Chemical Oxygen Demand (COD), color, pH, conductivity, temperature, and oxidation-reduction potential. Subsequently, an electrochemical process was carried out through a power source and six iron electrodes. Variables, such as hydrogen peroxide concentration (500 and 700 mg/l H_2O_2), amperage (1 and 2 A), and treatment time (60 and 90 minutes), were controlled. Based on a desirability function for multiple response analysis, the electro-Fenton process allowed a maximum COD removal of 80.9% and 88.5% for color (desirability criterion of 86%). Residence time in the reactor, voltage, current density, and concentration of hydrogen peroxide were the most significant variables. Finally, the role of other physicochemical variables involved during the dye degradation process was explained.

1. Introduction

The increase in population density and industrial production has caused a high generation of polluting liquid and solid waste. This type of waste is usually discharged with little or no treatment into surface water currents, deteriorating its quality. For this reason, there is a pressing need for the development and adaptation of new technologies that allow the conservation of water resources through the effective treatment of wastewater. Over the years, the agroindustrial sector has become one of the fundamental bases for the Colombian economy, bringing together the labor activities of most of the country's population. It is estimated that 25% of the Gross Domestic Product for exports comes from this sector [1]. Flower-

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producing companies are among Colombia's most critical sectors; the type of soil and the Colombian climate have positioned the country as the second largest exporter of flowers after the Netherlands [1]. To respond to market needs, commercialized flowers are dyed with artificial colors; however, these practices generate wastewater that contains dissolved recalcitrant organic substances, heavy metals, organic and inorganic pigments, and surfactants, among others [2,3]. The dyeing process is carried out through the absorption of the dye into the flower. The stem is submerged in a solution colored with pigments, and the petals gradually absorb the color. Once the process is finished, the unabsorbed wastewater should be treated before it can be discharged into surface water currents. In this sense, many companies in the flower growing sector carry out inadequate or no treatment before discharging raw effluents, causing high concentrations of toxic substances in the rivers and streams in the region. The dumping of this waste not only visually deteriorates the environment but also impacts the dynamic balance of the ecosystem, causing a decrease in the penetration of solar radiation, oxygen renewal, and flora and fauna present in the environment. Similarly, some of these compounds have shown toxic, mutagenic, and carcinogenic properties with harmful repercussions for human health [4]. Given the properties of these discharges, conventional wastewater treatment systems are not effective enough when treating them, making it necessary to look for other strategies, such as AOPs. These processes have successfully treated industrial wastewater, highlighting their high effectiveness in removing recalcitrant pollutants [5-7]. AOPs allow the total or partial elimination of compounds resistant to conventional treatments, reduce toxicity, and destroy pathogenic microorganisms [8]. AOPs used for wastewater remediation are often used alone or in combination with conventional methods. Its principle is based on the generating and using transient oxygen species with high oxidative power, mainly the hydroxyl radical (OH•) [9]. Interest in AOPs has increased since it is reported that these processes are friendly to the environment, and their chemical, photochemical, and electrochemical principles consist of the temporary generation of hydroxyl radicals as their primary oxidizing agent [10]. In addition to the hydroxyl radical, other reactive oxidizing species, such as H_2O_2, contribute to the removal of persistent pollutants [11]. In this sense, technologies based on electrochemistry offer significant advantages over traditional technologies since this method reduces the concentration of pollutants in wastewater [10,12]. Among the systems studied, those based on the reaction of hydrogen peroxide (H_2O_2) with ferrous ion (Fe^{+2}) (Fenton), leading to the formation of hydroxyl radicals, were emphasized (Equations 1, 2, 3). Fenton has a high oxidation-reduction potential and can oxidize organic species regardless of their complexity and structure. Equation 4 presents the oxidation reaction of organic species through a Fenton process [13]:

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+2} + OH\bullet + HO- \quad (1)$$

$$H_2O_2 + OH\bullet \rightarrow HO_2\bullet + H_2O \quad (2)$$

$$HO_2\bullet \leftrightarrow O_2-\bullet + H+ \quad (3)$$

$$OH\bullet + [Cn\ Hn\ On\ Nn] \rightarrow CO_2 + H_2O \quad (4)$$

he presence of toxic and recalcitrant compounds is a significant problem for conventional treatments [14]; in this sense, OH• radicals can modify the chemical structure of recalcitrant organic compounds, converting them into simpler compounds with less molecular mass, less toxic and, consequently, more biodegradable [12]. Among the most popular advanced oxidation processes, electro-Fenton stands out. It is based on generating the Fenton reaction through electrochemical systems, whose principle is using electrogenerated ions in wastewater and adding a particular concentration of peroxide of hydrogen (H_2O_2) for pollutant reduction. The electric current that circulates between the diodes destabilizes the contaminants suspended or dissolved in the aqueous medium, and the addition of H_2O_2 generates reactive oxygen species that mineralize them. These variable processes, such as treatment time and hydrogen peroxide concentration, increase the efficiency and optimization of the treatment system [15]. Authors such as Barrera and others [16] reported significant reductions in the concentration of recalcitrant pollutants in wastewater, represented by a decrease in COD through a Fenton reaction with electrogenerated H_2O_2. On the other hand, Gil-Pavas et al. [17] obtained COD degradation percentages close to

50.67% in approximately 60 min. The parameters that significantly influenced the increase in removal efficiency were the distance between electrodes, agitation, initial concentration, and voltage, which were inversely proportional to the contaminant removal. The electro-Fenton process offers some advantages in the removal of recalcitrant contaminants. However, the operating conditions in which the process is carried out depend on parameters such as pH, the concentration of the oxidizing agent, the composition of the wastewater, and the treatment time, which substantially affect the efficiency and speed of the oxidation process [18]. As previously described, the focus of this study was to establish the conditions under which an electro-Fenton process allows the effective treatment of colored wastewater generated in a flower-producing company. During the process, operational variables such as treatment time, amperage, and hydrogen peroxide concentration were controlled to demonstrate the efficiency of the reaction and the percentage of removal of contaminants and color. Additionally, the behavior of the physicochemical variables involved in the process was monitored. The optimal conditions for eliminating this type of contaminant were found using a multiple response model through the desirability function. In this study, the use of electro-Fenton was proposed as a clean alternative for the treatment of wastewater from flower-producing companies. This study contributed to new knowledge in the treatability of colored wastewater from the flower agroindustry in Colombia. Implementing Electro-Fenton AOP using iron electrodes is a novel way to eliminate dye wastewater from flower production. Significant color and COD removals were achieved through this AOP, which implied that this technique could be successfully applied in reducing the pollutant load of wastewater from flower crops (mainly hydrangea crops) located in the east of Antioquia (Colombia).

2. Materials and methods

2.1. Materials and measurements

The treated industrial wastewater samples were obtained from a flower-producing company in northwestern Colombia. The physicochemical parameters of pH, electrical conductivity (mS/cm), total dissolved solids (mg/l), temperature (°C), and oxidation-reduction potential (mV) were measured using a Hach brand multiparameter reference HQ40D. The electrode was introduced into a representative sample of 10 ml of wastewater for physicochemical measurements at the beginning and end of each treatment. The closed reflux method and colorimetry were used according to the procedures established in the standard methods to determine the COD. Finally, with the COD results of each sample, the COD removal percentage was calculated as expressed in Equation 5:

$$\%\ \text{COD remotion} = \frac{(\text{CODinitial} - \text{CODfinal})}{\text{CODinitial}} * 100 \qquad (5)$$

Color determination was made from absorbance measurements at wavelengths λ = 436–525-620 nm, as stipulated in Colombian regulations [19] and as proposed by Martínez and Osorio [20]. This process was carried out using a Spectroquant® Prove 600 UV-VIS spectrophotometer, equipped with a 1 cm path length quartz cell and a 190-1100 nm wavelength spectrum. The removal percentage was established using Equation 6:

$$\%\ \text{Color remotion} = \frac{(\text{Abs.initial}\lambda - \text{Abs.final}\lambda)}{\text{Abs.initial}\lambda} * 100 \qquad (6)$$

The results of the initial characterization of the colored wastewater from the flower industry are presented in Table 1. All analyses were performed following the procedures established by the Standard Methods for the Examination of Water and Wastewater, 24th edition [21]. All measurements were made in the environmental monitoring laboratory of the Universidad Católica de Oriente.

2.2. Electrochemical process

For the electrochemical process, a perfectly stirred (120 rpm) batch reactor (1000 ml) was used, equipped with six rectangular-shaped iron electrodes of dimensions 3 cm X 8 cm X 0.3 cm (18 cm^2 effective area). These electrodes were placed in suspension with respect the bottom of the container. Each electrode represented an anode and a cathode held with electrical clips attached to transmitter cables and connected to a 10 V power source. The amperage was varied for the experimental runs between a 1 A and 2 A current density of 5.5 and 11.11 mA/cm^2, respectively. The current density was derived from the relationship between the amperage and the effective area of the electrodes. The range employed in this study was established based on the findings published by researchers engaged in the electro-Fenton dye wastewater treatment processes [23, 33, 39]. Each of the electrodes was located at a distance of 1 cm. After each treatment, the electrodes were cleaned and rinsed with 1 M HCl and deionized water. Figure 1 shows the assembly scheme used.

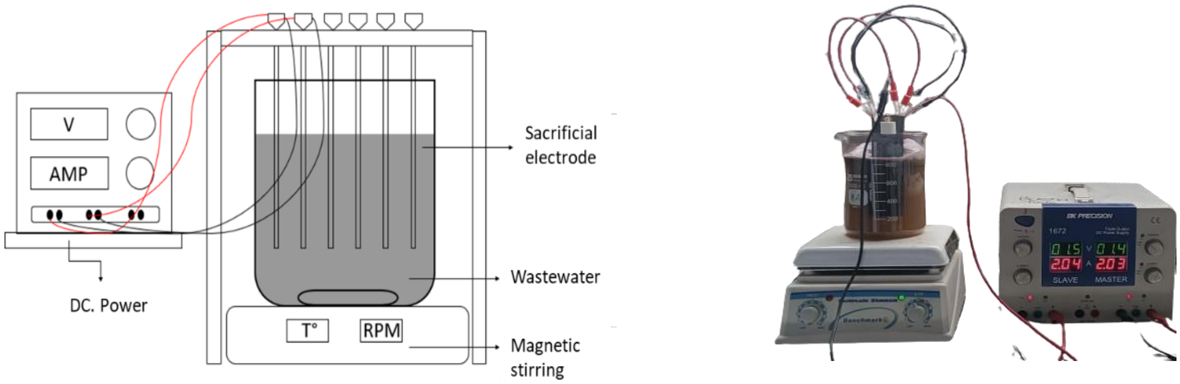

Fig. 1. Schematic diagram of the electro-Fenton reactor. Source: self-made.

2.3. Experimental design and data analysis

A 2^3 Factorial Design was implemented. The factors considered were residence time in the reactor (60 and 90 minutes), amperage (1 and 2 A- current density 5.5 and 11.11 mA/cm^2), and H_2O_2 concentrations (500 and 700 mg/L at an H_2O_2/COD ratio 1.2 and 1.6, respectively). The reason for implementing this factorial design was to discover the operation region in more detail. Knowing the optimal conditions, performing an optimization design such as a composite design or Box and Benkhen is adequate. This research tried to implement the second step in an optimization methodology, exploring the operational parameter to find the region where the optimal could be present; in this case, it was better to use a factorial design than a composite design or Box and Benkhen. The % of COD and % of color removal of the different treatments were considered as response variables. In the same way, variables of interest, such as pH, conductivity, and oxidation-reduction potential, were monitored. All treatments were replicated three times. Table 2 shows the experimental runs carried out. For the definition of the H_2O_2 concentration, the H_2O_2/COD ratio was taken, which has been shown to have a marked influence on response variables such as color and COD when working in the range between 0.5 and 2 [22,23]. The data obtained after the experimental process were analyzed using Excel, R Commander, and R Wizard software. Descriptive central tendency and dispersion measures were used to characterize each treatment and its replicates. In the same way, an analysis of variance (ANOVA) was used to establish which factors and treatments significantly affected the removal of COD and color. Through a response surface methodology, the operating conditions that maximized the removal percentage of COD and color were selected simultaneously [24]. For this, the data was modeled using a second-order polynomial function. The general form can be described by this polynomial function according to Equation 7:

$$Y_i = \beta 0 + \sum_{i=1}^{3} \beta\mathrm{iXi} + \sum_{i=1}^{3} \beta\mathrm{iiXi}^2 + \sum_{i=1}^{3}\sum_{j}^{3} \beta\mathrm{ijXiXj} \tag{7}$$

where Yi is any of the two stated response variables, Xi and Xj are the experimental factors, β_0 is the intercept coefficient, βi is the linear coefficient for factor i, βij is the quadratic coefficient for its corresponding factor i, and βij is the coefficient of interaction between factor i and j. These coefficients were adjusted through statistical software using the results obtained in the experimental design. All hypothesis tests were established with 95% confidence [25]. In the same way, a desirability function was used to find the simultaneous best point [24].

3.Results and discussion

This study evaluated the effect of treatment time, hydrogen peroxide concentration, and amperage to determine the efficiency of an electro-Fenton (EF) wastewater removal system. The data obtained demonstrated effective and representative results regarding removing contaminants from the water sample. Table 1 shows the physicochemical parameters studied during the EF process and the initial values of the colored effluent.

Table 1. Initial physicochemical parameters and values of the colored residual water.

Parameter	Initial value		
COD (mg/L)		424	
BOD_5 (mg/L)		46	
Color λ (436–525-620 nm) α (436–525-620 m^{-1})	3,11 311	2,91 291	3,48 348
pH (pH units)		4	
Conductivity (mS/cm)		5,36	
(Total Dissolve Solids) SDT (g/L)		3,67	
Temperature (°C)		21,07	
Redox Potential (mV)		221,38	

The effluent sample presents a dark color with a predominantly blue tone, mainly due to the combination of dyes used in the flower staining process. In the same way, the results obtained in the absorbed wavelengths corroborate a dominant presence of this tonality in the area of the most significant absorbance (620 nm). The initial BOD5/COD ratio was 0.11 (<0.4), indicating that this type of colored agroindustrial effluent was not biodegradable according to regulations. Additionally, the presence of a high content of salts and the dissolved material was evident, quantified under the parameters of conductivity (mS/cm) and total dissolved solids (SDT mg/l) typical of the staining and postharvest process of the flower. The initial pH value was within the appropriate range (2 to 4 pH) for EF-related advanced oxidation processes [26]. It should be noted that the efficiency decreases rapidly at higher pH values (pH > 5) because H_2O_2 is unstable under basicity conditions. The increase in pH during the EF process favored electrocoagulation; in this process, contaminants were removed by complexation and electrostatic attraction [27].

3.1. Effect of operational factors on COD and color reduction (%CODR and %ColorR)

Details of the experimental runs and the data obtained (expressed as %CODR and %ColorR) are presented in Table 2. The %CODR ranged from 53.2 to 80.9%, and the %ColorR ranged from 74.6 to 88.5%. The standard deviation (SD) for the different runs in the %CODR and %ColorR presented a maximum of 3.6 and 2.3, respectively (Table 2).

Table 2. Experimental results of the treatments applied for the variables %CODR and %Color R.

				%CODR				%ColorR			
Tt.	Time	Amp	H_2O_2/COD	Med	DE	Min	Max	Med	DE	Min	Max
T1	90	2	1.2	72	3.6	69.2	76	78.9	2.3	76.2	80.3
T2	90	2	1.6	79.1	1.9	76.9	80.2	88.3	0.2	88.1	88.5
T3	90	1	1.2	73.6	2.6	70.3	76.5	75.7	0.3	75.5	76
T4	90	1	1.6	80.2	0.8	79.3	80.9	87.7	0.1	87.6	87.7
T5	60	2	1.2	55.2	2.5	53.4	58.1	80.6	0.4	80.3	81.1
T6	60	2	1.6	59.2	0.6	58.6	59.7	87.3	1.1	86.1	88.2
T7	60	1	1.2	54.5	1.5	53.2	56.5	75.3	0.6	74.6	75.8
T8	60	1	1.6	59.2	0.6	58.6	59.7	85.8	0.2	85.5	85.9

The data collected during the experimental process were correlated for each response variable through second-order polynomial models. The results obtained from the estimated coefficient, the *P value*, and the adjustment of R^2 for the response variables are presented in Table 3. The statistical analysis of the models using an ANOVA test is shown in Table 4 for %CODR and %ColorR, respectively. It can be established, by the significance value (*$p<0.05$*) for the response variable %CODR, that the treatment time (*p<0.001*) and the H_2O_2 concentration (*p<0.001*) played a determining role in the removal of the polluting load. On the other hand, regarding color removal, the amperage (*p<0.001*) and the H_2O_2 concentration (*p<0.001*) had the most significant influence on color removal. Additionally, the interactions Time: Amperage (*p=0.0332*); Time: H_2O_2/COD (p= 0.0117); Amperage: H_2O_2/COD (*p= 0.000267*) also had a positive influence on the degradation process of this variable.

Table 3. Estimated values and probability (P) of the second-order COD and Color removal model.

	%CODR		%ColorR	
	Estimate	Pr(>|t|)	Estimate	Pr(>|t|)
Intercept	14.54444	0.398	38.19167	0.0000811
Time	0.43474	0.037	-0.1368	0.136803
Amperage	4.22222	0.541	17.96833	0.0000129
H_2O_2/COD	-1.19444	0.919	23.61042	0.000253
Time: Amperage	-0.05763	0.286	-0.05473	0.033239
Time: H_2O_2/COD	0.20870	0.128	0.16622	0.011704
Amperage: H_2O_2/COD	-0.29167	0.942	-7.99687	0.000267
Adjusted R^2	0.9629		0.9719	

Table 4. Analysis of variance (ANOVA) for the %CODR and %ColorR in the Electro-Fenton process.

		Sum Cua	Df	Valor F	Pr(>F)
%CODR	Time	2392.32	1	601.0823	<0.001
	Amperage	1.64	1	0.4110	0.5291
	H_2O_2/COD	202.48	1	50.8743	<0.001
	Time: Amperage	4.8	1	1.2070	0.2857
	Time: H_2O_2/COD	10.08	1	2.5327	0.128
	Amperage: H_2O_2/COD	0.02	1	0.0055	0.9418
	Residuals	75.62	19		
%ColorR	Time	1.04	1	1.2699	0.273822
	Amperage	49.48	1	60.1851	<0.001
	H_2O_2/COD	609.78	1	741.7036	<0.001
	Time: Amperage	4.33	1	5.2706	0.033239
	Time: H_2O_2/COD	6.39	1	7.7777	0.011704
	Amperage: H_2O_2/COD	16.37	1	19.9131	0.000267
	Residuals	15.62	19		

The treatment time is an essential variable in %CODR and %ColorR; the highest efficiencies occurred with longer treatment times (90 min). Removal efficiency was higher with time, which could be associated with decantating dissolved organic compounds. The number of hydroxide flocs increased with increasing current density and the treatment time of the electrochemical process, and likewise with the release of metals from the electrodes [28,29]. Similar results were presented by Can-Güven [23], where the highest removals were obtained after 45 min of treatment with 54.8% and 88.1% for COD and color removal, respectively, for dyes from the textile industry. A similar case was presented by Guvenc et al. [30], where the maximum removal occurred at 30 min, with 69.4% for COD removal. Both results presented lower removals than the values obtained by this investigation. The %ColorR had a more significant influence at the treatment time; its elimination gradually increased as the treatment time increased. After one hour of the electrolytic process, the color removal percentage remained constant. In this way, the efficiency in color reduction was directly related to the concentrations of the hydroxyl radical and metal ions released by the electrodes, with which the longer treatment time led to a more significant generation of ions [31]. The H_2O_2 concentration directly influenced the removal of contaminants for both COD and color (Table 2 and Table 4), which was directly related to the generation of the hydroxyl radical. It was

observed how better removal results were gradually obtained with the increase in concentration, with maximums of 80.2% and 88.5% for %CODR and %ColorR, respectively. These results agree with those reported by Guvenc et al. [30,32]; they found that by applying this reagent in an H_2O_2/COD ratio of 0.4–2 in the EF process, higher COD and color removal efficiencies were obtained. Likewise, in this investigation, with an increase in the ratio from 1.2 to 1.6, there was an increase in the removal of 4.2% and 8.2% for the removal of COD and color for treatment times of 90 minutes and a current of 2 A. However, removal may decrease when there is an excess of H_2O_2 concentration because the hydroxyl radical is less oxidizing, in addition to the self-destruction of H_2O_2 [22]. Current is one of the relevant variables in the EF process due to its relationship with the formation of H_2O_2 at the cathode through the reduction of oxygen at the anode. Additionally, higher applied amperage is related to a higher electrical production of ferrous ions from ferric ions [27]. For the %CODR, the current did not present significant differences in the treatment (Table 4). However, there were good removals of this contaminant for 1 A and 2 A, with 80.9% and 80.2% removal for COD, respectively. For its part, the response variable %ColorR presented removal variations between 74.6% and 88.5% for the current applied between 1 A and 2 A. The efficiency in the removal increased when the current increased, which can be associated with a more outstanding production of hydroxyl radicals during the process. Something similar was observed by Mohajeri et al. [33], who suggested a similar effect in the current range from 0.75 to 4.25 A, with a treatment time of 0 to 30 min. On the other hand, Can-Güven [23] found the optimal removal for a current density of 21 mA/cm^2 with 46.1% and 74% in removals for COD and color, which contrasts with the present investigation where higher removals were obtained with a maximum current density of 11.11 mA/cm^2 for both response variables (Table 2).
coefficients, β_{11}, β_{22}, and β_{33} are the quadratic coefficients, and β_0 is a constant coefficient [20]. In the current article, the Box-Behnken method with three factors in three levels was applied using Design-Expert software (version 7). Each variable was coded at three various levels between –1 and +1 in the ranges determined by the preliminary experiments. According to screening tests, the factors and their selected levels are presented in Table 2.

3.2. Response surface plots and best treatment

The response surfaces in 2 and 3 dimensions were built with the results of the adjusted second-order model. These figures observe the influence of the factors studied and their relationship, as well as the reductions in pollutant %CODR (Figure 2) and %ColorR (Figure 3). According to the surfaces (Figure 2a and 2b), the highest reductions for COD were obtained with the highest peroxide ratio (1.6), which referred to 700 mg/l of this reagent. Additionally, it was associated with more prolonged treatment (90 min). Under this combination, average removals of up to 80% were obtained as COD (Table 2). The release of Fe+2 ions in the EF process and their reaction with OH• radicals influenced COD removal through direct oxidation of organic compounds on the anode surface. This process was also favored by the high initial conductivity of the contaminant (5.36 mS/cm), which allowed a better performance of the electrolytic process under an adequate current density (1 A). In the case of COD removal, Espinoza-Quiñones [34] reported similar results, where a higher current density and lower electrical conductivity presented the optimum for removing dyes in an EF process. Figure 3 presents the response surfaces associated with the factors studied and their interactions for color removal (%ColorR, Y axis).
The treatments with the highest values of amperage (2 A.) and peroxide concentration (H_2O_2/COD 1.6; concentration [H_2O_2] 700mg/l) presented the optimal color removal conditions. This research used T2 and T6 (Table 2) with %ColorR averages of 88.5% and 88.2%, respectively (Figure 3 a, b, e, f). The applied current density (11.11 mA/cm^2; 2 A) played a vital role because it favored the formation of Fe^{+2} ions in the sacrificial iron anode and, in parallel, reduced water in the cathode. Subsequently, adding H_2O_2 in the appropriate ratio provided a favorable environment for the Fenton reactions and the production of OH• radicals responsible for discoloring the aqueous solution. However, it has been found that when the current density rises disproportionately, the removal efficiency decreases due to competitive

reactions between the electrodes of the EF process [27]. In this sense, Guvenc et al. [32] found optimal removal values for an amperage of 2.75 A and an H_2O_2/COD ratio of 1.25 for color removal of 87.6%, which is similar to our findings. Additionally, in color removal, the longer treatment times (90 min) and peroxide concentration (H_2O_2/COD 1.6; concentration [H_2O_2] 700mg/l) presented the highest removal conditions. In this way, the treatments T2 and T4 (Table 2) with %ColorR averages of 88.5% and 87.7%, respectively (Figure 3 c, d, e, f), were optimal. This behavior can be explained by the fact that iron electro-dissolution increases with time in EF processes. In this way, the efficiency of color removal depends directly on the concentrations of Fe^{+2} ions and OH● radicals produced by the electrodes. A longer electrolysis time will generate a more significant amount of ions. What has been seen so far is consistent with the fact that the removal of pollutants increases with the increase in the concentration of H_2O_2. However, this efficiency decreases for a concentration higher than the optimal values due to the OH● radical scavenging effect of H_2O_2 and their recombination (Nidheesh and Gandhimathi, 2012). The results of the present investigation contrast with those obtained by Davarnejad et al. [35], who reported a 71.58% color removal for a treatment time of 73.19 min and an H_2O_2 ratio of 1.23 for a volume of 250 ml of water problem.

3.3. *Desirability multiple response analysis*

In order to establish the levels of the factors that maximize the percentage of COD removal and color removal in the process simultaneously, multiple response optimization techniques were used from the desirability analysis. In Figure 4, by locating the red dots, it is possible to establish that the optimal process conditions to maximize the percentage of Color and COD removal are located at 1.6 for the H_2O_2.COD factor, the value of 1 in the Amperage conditions, with a duration of 90 minutes. For future experiments, it is suggested to increase the concentration of H_2O_2 and decrease the amperage. After the multiple optimization analysis, the optimum of the response variables and the optimal desirability of the treatment were obtained. The results are presented in Table 5. Under these conditions, an optimal COD removal of 80.38% was expected, and a color removal of 87.84% 86% of the time the treatment was carried out.

Table 5. Multiple Response according to desirability model.

Best Amperage	1 A
Best H_2O_2/COD	1.6
Best resident Time (min)	90
%CODR prediction	80.38
%ColorR prediction	87.84
%Optimal desirability	86

Multiple authors have used the desirability function to obtain the best treatment with multiple responses in electro-Fenton processes.

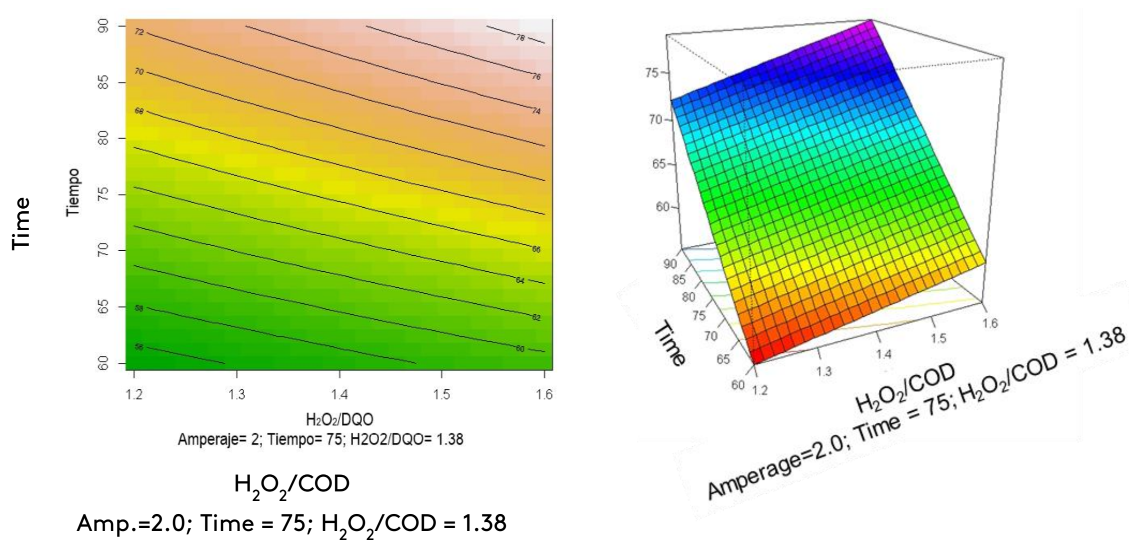

Fig. 2. Response surface for COD reduction (%CODR, Y axis).

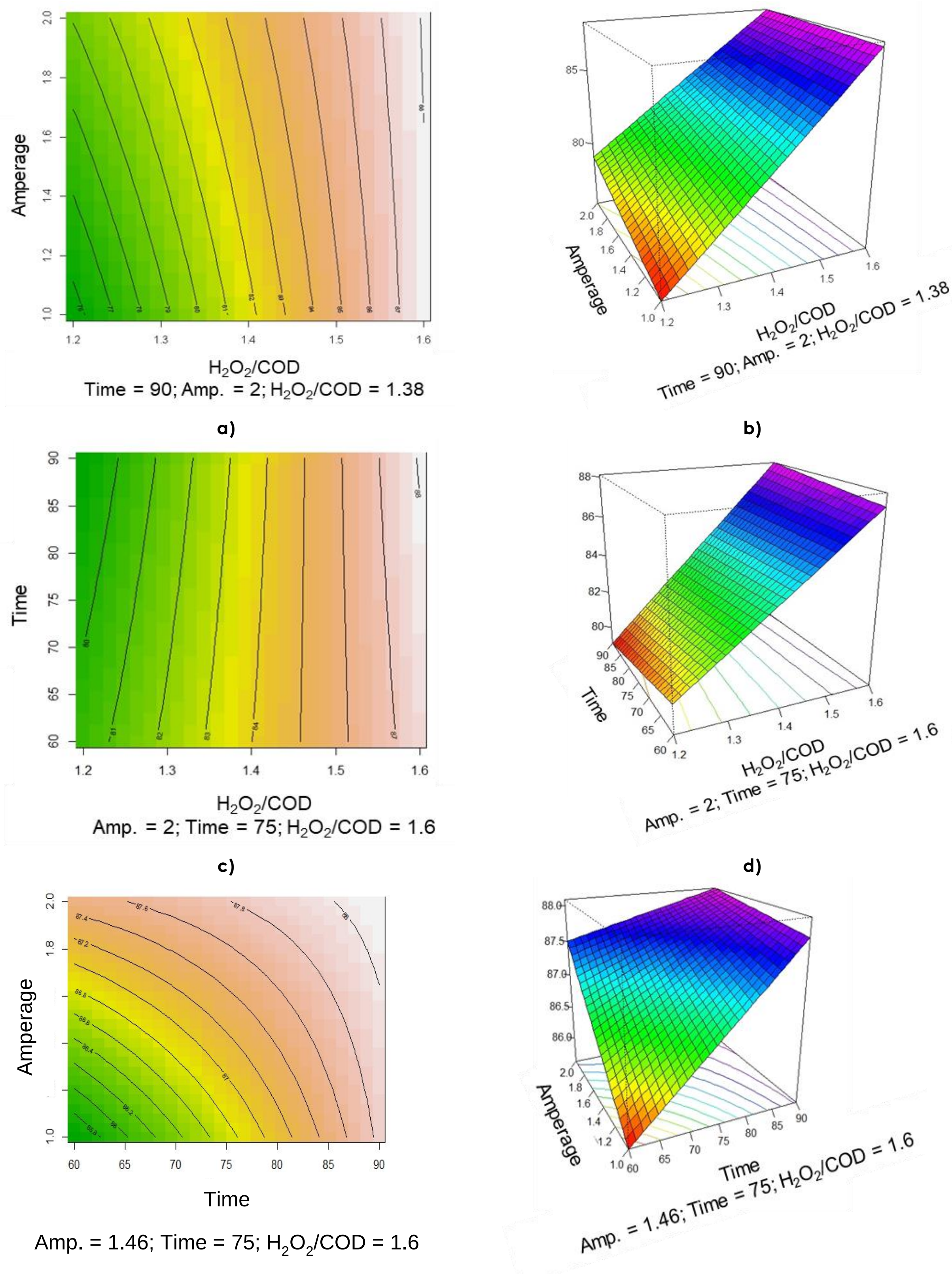

Fig. 3. Color removal response surface (%ColorR, Y axis) 2D a) and 3D b) H_2O_2/COD factors and Amperage; 2D c) and 3D d) H_2O_2/COD and Time factors; 2D e) and 3D f) Time and Amperage factors.

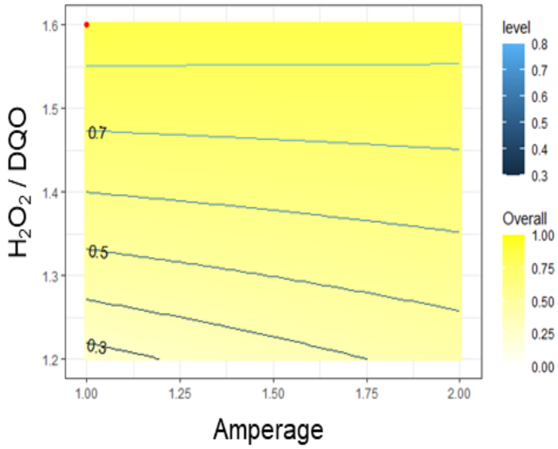

Fig. 4. Multiple response optimization results for percent COD removal and color removal.

Bhatnagar et al. [36] optimized the removal process of wastewater contaminated with textile dyes based on four experimental factors. The authors optimized the removal of COD and, simultaneously, the removal of color, minimizing the consumption of electrical energy in the process. This way, the optimal conditions were obtained with an initial pH of 4.0, a current density of 27.78 A/^{m2}, an initial concentration of the pollutant of 2 g/L, and a treatment time of 110 minutes. Under these conditions, the desirability of 90.78% was achieved for energy consumption, 96.27% for color removal, and 23.58 23.58 kWh/kg removal. This technique proved to be adequate when the validation of the experiment was carried out. For their part, Wan et al. [37] used a desirability model to obtain the optimal conditions for the removal of the Acid Black 2 dye, which is highly toxic to humans, using an electrochemical technique. The authors obtained a total desirability of 93.8 % under a current density of 53.36 mA/cm^2, a reaction time of 99.50 min, and an initial pH of 5.68. Under these conditions, 90.01% of COD was removed; an energy efficiency of 80.71% was achieved. Ultimately, the authors proposed a validation test for the results that closely coincided with those obtained by the desirability model. Similarly, Hiwarkar et al. [38] used a desirability function and an electrochemical oxidative degradation process; they obtain the optimal simultaneous conditions for the mineralization of pyrroline, a recalcitrant heterocyclic compound. They found a current density of 175 A/m^2, an initial pH of 8.7, and a treatment time of 150 minutes. They achieved an optimal COD removal of 69.30% and complete mineralization of the polluting agent. The desirability obtained for the multiple optimizations of this process was 97.5%, also considering minimizing energy consumption. These referents demonstrate the convenience of using multiple response optimization to find the optimal conditions for electrochemical processes when several response variables are to be evaluated simultaneously. These results contrast those found in this research where, through multiple response optimization, lower treatment time (90 min) was obtained for COD and color degradation very close to those reported (80.38% and 87.84%, respectively). Additionally, through this technique, a desirable optimum of lower current density (55.5 A/m^2) was found for the colored wastewater effluent from the flower agroindustry. These results imply a lower expenditure in terms of time and energy, which ultimately translates into economic savings for treating effluents contaminated with industrial dyes.

4.Conclusions

The removal of chemical oxygen demand and the color of wastewater from the process of dyeing flowers in crops in Colombia were evaluated using the electro-Fenton process. The main findings of the optimal removal process were related to the treatment time, the H_2O_2/COD ratio, and the current density with values of 90 minutes, 5.5 mA/cm^2 (1 A), and 1.6 (700 mg/l H2O2), respectively. Through these optimal treatment values, COD and color removals of 80.38 and 87.84%, respectively, would be obtained. These results were obtained using iron electrodes spaced at a sample distance of 1 cm and under the initial pH (4 pH units) and conductivity (5.36 mS/cm) conditions of the colored wastewater. According to the experimental processes, it is possible to conclude that the electro-Fenton is an effective technique for the removal of contaminant loads such as COD and color in effluents from the floriculture agroindustry, with maximum removals of 80.9 and 88.5%, respectively. However, it is essential to evaluate other techniques and a combination of different advanced oxidation techniques (photo Fenton, ozone peroxide, ozone-

UV, and other physicochemical properties) that remove this type of wastewater to find higher efficiencies depending on the pollutant load.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that would influence this paper.

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