Evaluation of electrocoagulation by Fenton reagent for the removal of turbidity and sulfides in wastewater from the process of depilation or liming in tanneries

Evaluación de la electrocoagulación por reactivo Fenton para la eliminación de turbidez y sulfuros en las aguas residuales del proceso de depilación o encalado en curtiembres

Avaliação da eletrocoagulação pelo reagente de Fenton para remoção de turbidez e sulfetos em águas residuárias do processo de depilação ou calagem em curtumes

Oscar Enrique Robayo Triana[1]
Diego Alberto Sánchez Pérez[2]
Rafael Nikolay Agudelo Valencia[3]

Received: January 20th, 2020
Accepted: March 30th, 2020
Available: May 4th, 2020

How to cite this article:
O. E. Robayo Triana, D. A. Sánchez Pérez, R. N. Agudelo Valencia, "Evaluation of electrocoagulation by Fenton reagent for the removal of turbidity and sulfides in wastewater from the process of depilation or liming in tanneries," *Revista Ingeniería Solidaria*, vol. 16, no. 3, 2020.
doi: https://doi.org/10.16925/2357-6014.2020.02.08

Artículo de investigación. https://doi.org/10.16925/2357-6014.2020.02.08

[1] Universidad Libre de Colombia, Carrera 70 #53-40 (Bogotá-Distrito Capital, Colombia)
ORCID: https://orcid.org/0000-0002-7033-4968
E-mail: oscare-robayot@unilibre.edu.co

[2] Universidad Libre de Colombia (Bogotá-Distrito Capital, Colombia)
ORCID: https://orcid.org/0000-0002-1252-1255
E-mail: diegoa-sanchezp@unilibre.edu.co

[2] Universidad Libre de Colombia (Bogotá-Distrito Capital, Colombia)
ORCID: https://orcid.org/0000-0002-6646-7725
E-mail: rafaeln.agudelov@unilibre.edu.co

Abstract

Introduction: This article is the result of the research "Evaluation of the intensified electrocoagulation in wastewater of the liming process in The Scorpion tannery in the municipality of Villapinzón-Cundinamarca with analysis at the Universidad Libre de Colombia-Sede Bosque Popular between 2018 and 2019.

Objective: To evaluate the Electro-Fenton strategy as an alternative for the treatment of wastewater from the skin tanning process.

Methodology: An experimental design of factorial type 3^3 is used in two phases, utilizing a Batch type reactor. In the first phase, the number of iron electrodes, H_2O_2 dosage and current intensity supplied is analyzed. For the second phase, the reaction time is varied, and with a number of plates defined, the parameters of sulfide concentration, total organic carbon (TOC) and both initial and final turbidity for a subsequent analysis of variance (ANOVA) were analyzed.

Conclusion: In the first stage of treatment, for a reaction time of 60 minutes, a turbidity removal of 96.2%, 65.4% sulfide and 52.3% of TOC was obtained. With these, it was determined that the greatest removal was obtained with 4 electrodes. In the second stage, with follow-up treatment in function of time, a removal of 99.2% for turbidity, 68.35% for sulfur and 53.5% for TOC was obtained.

Originality: An electrochemical system is used to treat wastewater from the tannery industry, based on previous research, in order to adapt the technology to the sector mentioned initially.

Limitations: The study is limited to the use of iron electrodes with current densities and doses of H_2O_2 used. In this type of system aluminum electrodes, stainless steel, graphite and doped materials can be used to maximize the reaction in the electrodes, as well as the use of ozone as an oxidizing agent.

Keywords: Electrocoagulation, Fenton, ElectroFenton, Lime or depilation, Turbidity

Resumen

Introducción: Este artículo es el resultado de la investigación "Evaluación de la electrocoagulación intensificada en aguas residuales del proceso de encalado en la curtiduría Scorpion en el municipio de Villapinzón-Cundinamarca, estudio realizado en la Universidad Libre de Colombia-Sede Bosque Popular entre 2018 y 2019.

Objetivo: evaluar la estrategia Electro-Fenton como alternativa para el tratamiento de aguas residuales del proceso de bronceado de la piel.

Metodología: Se utiliza un diseño experimental del factorial tipo 33 en dos fases, utilizando un reactor de tipo Batch. En la primera fase, se analiza el número de electrodos de hierro, la dosis de H2O2 y la intensidad de corriente suministrada. Para la segunda fase, el tiempo de reacción varía, y con una serie de placas definidas, se analizaron los parámetros de concentración de sulfuro, carbono orgánico total (TOC) y turbidez tanto inicial como final para un análisis posterior de varianza (ANOVA).

Conclusión: En la primera etapa del tratamiento, durante un tiempo de reacción de 60 minutos, se obtuvo una eliminación de turbidez del 96.2%, 65.4% de sulfuro y 52.3% de TOC. Con estos, se determinó que la mayor remoción se obtuvo con 4 electrodos. En la segunda etapa, con el tratamiento de seguimiento en función del tiempo, se obtuvo una eliminación del 99.2% para turbidez, 68.35% para azufre y 53.5% para TOC.

Originalidad: se utiliza un sistema electroquímico para tratar las aguas residuales de la industria de la curtiduría, basado en investigaciones previas, para adaptar la tecnología al sector mencionado inicialmente.

Limitaciones: El estudio se limita al uso de electrodos de hierro con densidades de corriente y dosis de H2O2 utilizadas. En este tipo de sistema, se pueden utilizar electrodos de aluminio, acero inoxidable, grafito y materiales dopados para maximizar la reacción en los electrodos, así como el uso de ozono como agente oxidante.

Palabras claves: electrocoagulación, Fenton, ElectroFenton, Cal o depilación, Turbidez.

Resumo

Introdução: Este artigo é o resultado da pesquisa “Avaliação da eletrocoagulação intensificada em águas residuais do processo de calagem no curtume The Scorpion no município de Villapinzón-Cundinamarca com análise na Universidade Libre de Colombia-Sede Bosque Popular entre 2018 e 2019.

Objetivo: Avaliar a estratégia Electro-Fenton como alternativa para o tratamento de efluentes do processo de bronzeamento da pele.

Metodologia: Um projeto experimental de fatorial tipo 33 é utilizado em duas fases, utilizando um reator do tipo Batch. Na primeira fase, são analisados o número de eletrodos de ferro, a dosagem de H2O2 e a intensidade da corrente fornecida. Para a segunda fase, o tempo de reação é variado e, com uma série de placas definidas, foram analisados os parâmetros de concentração de sulfeto, carbono orgânico total (TOC) e turbidez inicial e final para uma posterior análise de variância (ANOVA).

Conclusão: Na primeira etapa do tratamento, para um tempo de reação de 60 minutos, obteve-se uma remoção de turbidez de 96,2%, 65,4% de sulfeto e 52,3% de TOC. Com estes, determinou-se que a maior remoção foi obtida com 4 eletrodos. Na segunda etapa, com acompanhamento do tratamento em função do tempo, obteve-se remoção de 99,2% para turbidez, 68,35% para enxofre e 53,5% para COT.

Originalidade: Um sistema eletroquímico é utilizado para o tratamento de efluentes da indústria de curtumes, baseado em pesquisas anteriores, a fim de adequar a tecnologia ao setor mencionado inicialmente.

Limitações: O estudo limita-se à utilização de eletrodos de ferro com densidades de corrente e doses de H2O2 utilizadas. Nesse tipo de sistema eletrodos de alumínio, aço inoxidável, grafite e materiais dopados podem ser utilizados para maximizar a reação nos eletrodos, bem como a utilização do ozônio como agente oxidante.

Palavras-chave: Eletrocoagulação, Fenton, ElectroFenton, Cal ou depilação, Turbidez

Introduction

The municipality of Villapinzón, Cundinamarca, is recognized as a large producer of tanned skins nationwide. For this reason it is also considered responsible for a large part of the pollution load contributed to the upper Bogotá river basin [1]. The leather tanning process requires large amounts of water and chemical inputs, causing the generation of large volumes of industrial wastewater with a wide variety of pollutants such as sulfides, ammonium, fats and oils, organic matter, solids and chromium trivalent among others [2]. The majority of companies, dedicated to the tanning of leathers in the municipality of Villapinzón, execute their processes in an artisanal way. Added to these, some tanning companies do not carry out the adequate treatment of industrial wastewater. Therefore, the environmental authority established the option of changing and improving technologies in wastewater treatment in order to fulfill the water quality objectives for the upper Bogotá river basin [3].

Of all the processes that are carried out in the tanning of cattle skins, the liming or depilation process is recognized as being the one that provides the greatest polluting load in terms of BOD, COD, fats and oils, lime and sulfides [4]. It is considered that

70% of the pollutant load contributed by the tanning companies occurs or is generated in the liming or depilation process, that is to say, it is the stage of the processing of skins that can cause major impacts on aquatic ecosystems and the health of humans. The high pH, the considerable amount of organic matter and the presence of sulfides in the residual wastewater cause the decrease of dissolved oxygen in the receiving water bodies [5]. High concentrations of sulfur in the atmosphere can generate hydrogen sulfide in the atmosphere, in addition to the presence of sulfides in the environment causing problems in nitrogen uptake and plant growth due to problems in the enzyme oxidase present in plants [6]. According to the above, the need to look for alternatives that allow for the treatment of wastewater from the liming process, in order to minimize the environmental impacts generated by the tanning sector, can be appreciated. At present, the most acceptable treatment of lime or depilation wastewater is by catalytic oxidation of sulfides (using manganese as a catalyst), followed by clarification (using aluminum sulfate, aluminum polychloride or aluminum hydroxychloride), aerobic biological treatment and fine filtration in sand and activated carbon [7]. This configuration for the treatment of wastewater from lime has the need for different process units, operating times, energy consumption and demand for chemical inputs, achieving an effluent with low concentrations of BOD, COD and sulfides, but high concentrations of different dissolved ions (sulfates, nitrites, nitrates, chlorides) [8].

In this document, the use of the technique called intensified electrocoagulation is evaluated, which is based on the application of electric current to emulsify or dissolve contaminants present in water [9]. The reactor for this process usually consists of a container with iron electrodes, connected to a direct current power supply. This process has many advantages in terms of removing a wide range of contaminants such as heavy metals, ionic compounds and organic matter [10]. Electrocoagulation (EC) has low investment costs, simplicity of equipment and ease in process control [11]. Accordingly, the EC adapts to the need to oxidize sulfides, organic matter and remove dissolved solids in wastewater (clarification). This technique can also reduce the use of chemical inputs such as sulfate of manganese (catalyst for the oxidation of sulfides) and aluminum sulfate (coagulating agent of greater use), compounds that despite being part of the conventional treatment process, provide enough sulfates to affect the characteristics of the discharge and therefore lead to regulatory non-compliance regarding the sulfate concentration in the final effluent of the treatment system.

Within the electrochemical oxidation processes (EAOP), the electroFenton is based on the traditional Fenton reaction but complemented with iron electrodes. In this, the treatment process takes place directly on the plates along with the formation of the OH^* radicals [12]. The electroFenton process is characterized by energy consumption and the use of inputs that are not harmful to the environment. The electrodes in this type of systems can be iron, since they favor the reaction of Fenton. The treatment technique must have constant agitation and its most relevant problem is the cost of operation due to the high intensity of electrical current required. However, the electroFenton process helps reduce the amount of chemical inputs and the operating time when compared to the traditional treatment [13].

The electrically assisted Fenton reaction is known as the electroFenton process and is included among the advanced oxidation processes (AOPs), in which organic pollutants are oxidized by reaction with hydroxyl radicals. In the electroFenton process, hydrogen peroxide is added and Fe^{2+} is supplied by the sacrificial anode. This allows for better control in the generation of OH^* radicals in the reactor. The reactions in the electrocoagulation process with iron electrodes are:

In the anode.

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \tag{1}$$

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_2 \tag{2}$$

In the cathode.

$$H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \tag{3}$$

The Fenton reaction causes most of the carbonaceous organic compounds to be mineralized in CO_2 y H_2O in accordance with the following equations:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^* \tag{4}$$

$$Fe^{2+} + OH^* \tag{5}$$

$$OH^* + RH \rightarrow H_2O + R^* \tag{6}$$

$$R^* + Fe^{3+} \rightarrow R^+ + Fe^{2+} \tag{7}$$

Research background

Through the bibliographic review of the chemical and biological treatment of chemical products and wastewater, from tanning carried out in the United States in 2013 by Giusy Lofrano, the trend regarding the process of wastewater treatment is established with a view to future years. The implementation of biological treatments among the chemicals already established for the treatment of wastewater is proposed along with discussions regarding the trend for the integration of advanced oxidation techniques to the biological process in the water treatment process [14]. Simultaneously, Alberto Mannucci in 2010 demonstrated the effectiveness of the anaerobic treatment of wastewater loaded with a large amount of organic matter, achieving removals greater than 80% in a time of 8 hours in addition to presenting advantages in terms of sludge production and low energy consumption [15].

The most commonly used treatment method in the industry is catalytic oxidation with air and manganese. In research carried out by María Haidy Castillo in 2015, the effectiveness of the catalytic oxidation process, with cobalt and manganese for the removal of organic material, was demonstrated by the reduction of volatile material which was 95%, so the current treatment strategy in most of the tanneries in the Villapinzón sector is viable despite carrying a high energy cost [16]. In 2016, Md Abdul Hashem developed an investigation of treatment of residual water with hydrogen peroxide in which 99% of sulfur present in the water was removed in addition to the reduction of salinity of 87%; although the success of the reaction depends on the pH of the water [8].

In 2015, Yang Deng carried out a bibliographic review of advanced oxidation processes (AOPs). In this project, the effectiveness of AOPs as an alternative for the treatment of primary pollutants as part of the treatment for wastewater with a high concentration of organic material is highlighted [17]. Among the alternatives for advanced oxidation, the use of hydrogen peroxide and UV light are noteworthy. Salatiel Wohlmuth da Silva conducted an investigation in 2015 with hydrogen peroxide, titanium oxide and UV light in which 60% of the COD was achieved in 4 hours of reaction, in addition to oxidizing other pollutants such as sulfur, although in a smaller amount [18]. In a bibliographic review carried out by José Antonio Sánchez at the University of Almería in 2011, he postulated the combination of advanced oxidation processes with a biological treatment with the purpose of reducing operation and investment costs, which was demonstrated in works carried out in Mediterranean countries [19]. Blanco Llorca of the University of Barcelona in 2012, carried out an investigation for the removal of color in the water by means of electrochemical processes based on the photoFenton, managing to remove 99% of coloration in wastewater demonstrating a high efficiency for the removal of contaminants from dyes that are not degraded in conventional treatment [20]. Eloy Isarain-Chavez of the Universidad Autónoma of Barcelona conducted an investigation about electro oxidation, electroFenton and photoelectroFenton treatments in which 90% of the organic load was removed in a wastewater from skin tanning [21]. In the same field, Ayhan Sengil in the year of 2019 conducted an investigation about the treatment of tanning waters by electrocoagulation; 82%, 90% and 96% sulfide and oil removals were achieved respectively in 10 minutes of treatment at pH 3 [22]. Yabin Sun in 2007 and Amel Benhadji in 2011 used aluminum electrodes for the electrocoagulation process with sulfide removals greater than 90% sulfide in leather tanning wastewater [23][24].

Materials and methods

The residual water for the development of the tests was supplied by the tannery El Escorpión, located in the Reatova village of the municipality of Villapinzón, Cundinamarca. The water sample was collected and preserved according to what is established in the standard methods for the analysis of drinking and residual water, stored in amber plastic bottles and refrigerated at 4 °C for later analysis in the laboratory [25]. The initial characterization of the wastewater resulted in a concentration of 1428 mg/L of sulfur, pH of 12.4, turbidity of 1740 NTU, COT of 5675 mg/L. For the development of the experimental procedure, a container with a capacity of 2.4 liters was used, built in acrylic and 0.11 m long, 0.11 m wide and 0.2 m high. The container has slots 0.01 m thick for maximum installation of 6 plates or electrodes. The distance between slots is 0.05 m and there is a space of 0.05 m from the bottom of the electrocoagulation vessel or reactor to the base of the plates. The iron electrodes were 0.15 m high, 0.1 m wide and 0.001 m thick. The direct current supply was made with the help of a 12 V Power supply 0-24 V AC/DC Frederiksen source and 50% hydrogen peroxide was used to complete the reaction of Fenton.

Figure 1. Electrocoagulator design
Source: own work

The experimental process was carried out in two stages. Initially, each experiment was carried out over a period of 60 minutes and the dose of 50% hydrogen peroxide (1.5 ml, 2.5 ml and 4 ml), the number of iron plates or electrodes (2, 4 and 6) and the current intensity (4 A, 6 A and 8 A) were varied. The potential difference in each test was 12 V and from the ANOVA, the number of plates for which the greatest efficiency is achieved in terms of removal of the pollutants of interest was determined. In the second stage the number of plates or electrodes was kept constant (according to what was found in the previous stage), and the reaction time (30 min, 60 min and 90 min), the dose of hydrogen peroxide at 50% (3 ml, 4 ml and 5 ml) and current intensity (4 A, 6 A and 8 A) were varied. In each and every one of the tests carried out, the pH, sulfide concentration, turbidity and TOC were analyzed both at the beginning and at the end. The results were analyzed through analysis of variance (ANOVA) and the optimal conditions of the trials were found using the methodology known as the response surface (RS). Next, in Figure 2, the methodological design is summarized.

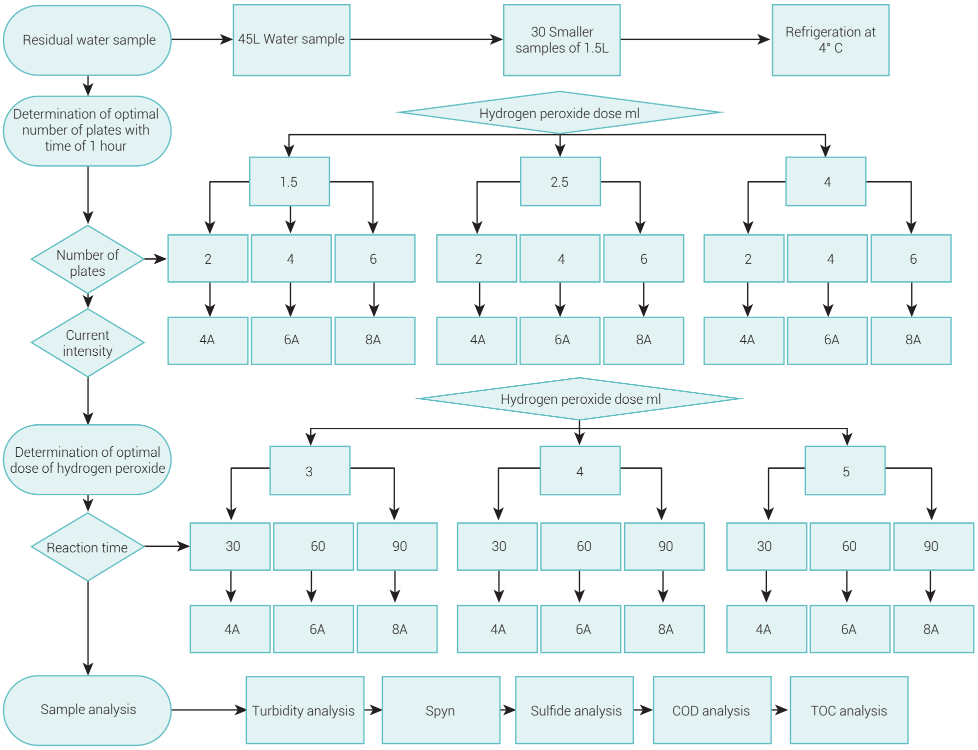


Figure 2. Diagram of the experimental design for the intensified electrocoagulation process carried out

Source: own work

In practice, one of the variables of greatest consideration for the design and operation of electrocoagulation systems is the current density, which is defined as the current intensity applied to the system divided by the total area of the plates in contact with water. The current density supplied in the process was determined by means of Equation 1.

$$\rho_I = \frac{Current\ Intensity\ (A)}{Area\ of\ the\ plates\ in\ contact\ with\ wastewater\ (m^2)} \tag{1}$$

The plates were submerged 0.1 m so that the contact area of each plate was 0.02 m^2, so that for every two plates used, the contact area will be 0.04 m^2. The current density reaches a value of 206.5 A/m^2 when 8 A is applied for every two plates or electrodes. The contact area was determined based on the characteristics of the reaction vessel, the height of plates submerged in the water and the number of plates used in the test, thus, Equation 2 corresponds to the calculation of the plate area or electrodes.

$$A_{p=2*h_p*b_p*n_p} \tag{2}$$

In Equation 2, h_p is the height of the plates submerged in m, b_p is the width of the plates in m^2, n_p is the number of plates in m. In the case of using 2 plates, the contact area for electrocoagulation was of 0.04 m^2, for 4 electrodes the treatment area is 0.08 m^2 and for 6 electrodes it is 0.12 m^2. The process of induction of electric current was obtained by means of Faraday's law, with which the number of grams of iron transferred from the anode to wastewater during the electrolysis process was calculated. The value was calculated according to equation 3.

$$n_Q = \frac{(I*t)}{F} * \frac{PM}{Z} \tag{3}$$

In Equation 3, t is the treatment time in seconds, F is the Faraday constant (96485 C mol^{-1}) and the variable I refers to the current intensity supplied in A. PM is the molecular mass of the material that conforms the electrodes and Z is the oxidation state of the oxidized iron. In accordance with the previous equation and given the conditions for carrying out the tests, 3.12 g of iron is supplied to the reaction for 4 A of current; for 6 A, 4.68 g is provided and for 8 A, 6.25 g.

Results

The results of the tests performed according to the experimental design for the first stage are presented in Figure 3. The data for constructing the graph and performing variance analysis are shown in Table 1.

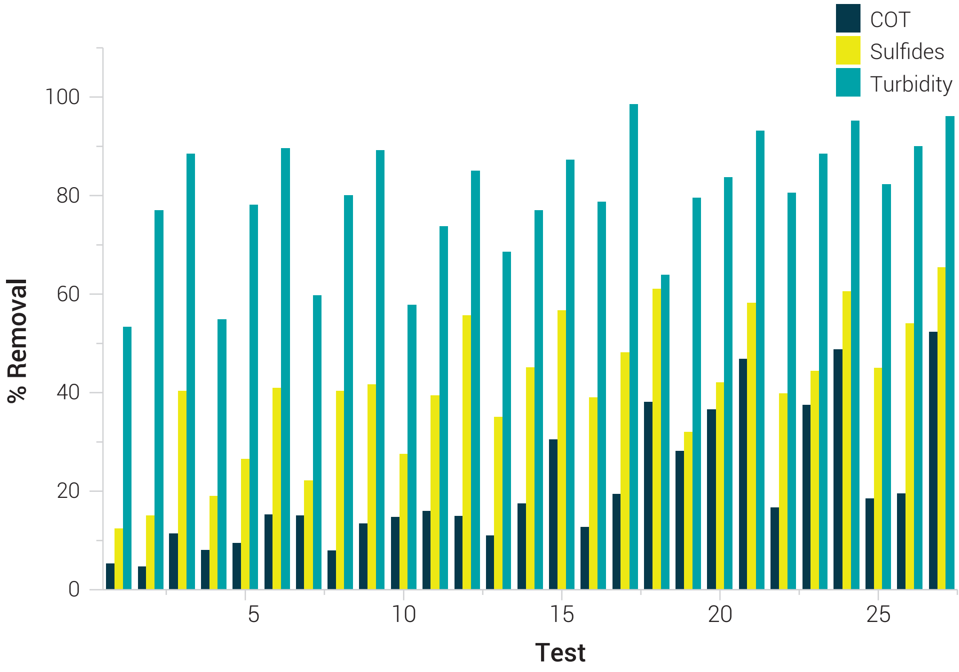


Figure 3. Diagrams of removal percentages
Source: own work

Table 1. Results for the first part of the experimental design

Experiment number	Current Intensity (A)	Number of plates	Dose of hydrogen peroxide (ml)	Percentage of removal Sulfides	Percentage of removal TOC	Percentage of removal Turbidity
1	4	2	1.5	12.46	5.29	53.4
2	4	4	1.5	15.12	4.76	77.0
3	4	6	1.5	40.41	11.45	88.5
4	6	2	1.5	19.02	8.12	54.9
5	6	4	1.5	26.61	9.46	78.2
6	6	6	1.5	40.99	15.28	89.6

(continúa)

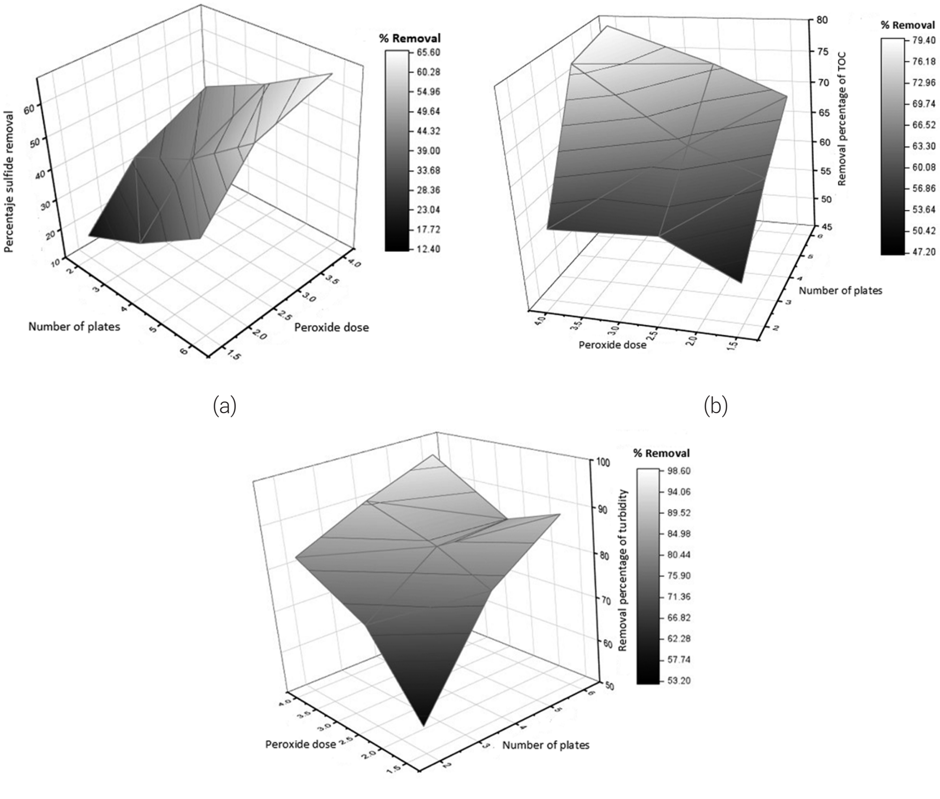
(viene)

Experiment number	Current Intensity (A)	Number of plates	Dose of hydrogen peroxide (ml)	Percentage of removal Sulfides	Percentage of removal TOC	Percentage of removal Turbidity
7	8	2	1.5	22.19	15.12	59.8
8	8	4	1.5	40.40	7.93	80.1
9	8	6	1.5	41.64	13.44	89.2
10	4	2	2.5	27.56	14.78	57.9
11	4	4	2.5	39.48	15.95	73.8
12	4	6	2.5	55.74	14.98	85.1
13	6	2	2.5	35.06	11.05	68.6
14	6	4	2.5	45.17	17.50	77.0
15	6	6	2.5	56.74	30.54	87.3
16	8	2	2.5	39.11	12.74	78.8
17	8	4	2.5	48.16	19.44	98.559
18	8	6	2.5	61.10	38.11	63.9
19	4	2	4.0	32.00	28.14	79.6
20	4	4	4.0	42.09	36.60	83.7
21	4	6	4.0	58.24	46.87	93.2
22	6	2	4.0	39.85	16.74	80.6
23	6	4	4.0	44.40	37.48	88.5
24	6	6	4.0	60.64	48.83	95.2
25	8	2	4.0	45.08	18.57	82.3
26	8	4	4.0	54.11	19.53	90.0
27	8	6	4.0	65.42	52.33	96.203

Source: own work

Based on the results of the Table 1, the ANOVA response surface was performed for determining variables within the treatment process. Figure 4 shows the response surfaces for each of the response variables analyzed. Table 2, 3 and 4 contain the results of variance analysis for percentage of sulfides, TOC and turbidity removed.

With the results obtained from the tests in the initial stage, the ANOVA response surface model was designed with the determining variables within the treatment process.



(a) (b)

(c)

Figure 4. Response surface of the effect of the variables or factors on the response variable, (a) sulfide removal, (b) COT removal, (c) turbidity removal. Reaction time 60 minutes

Source: own work

Table 2. Sulfur variance analysis for the first experimental part

Source	DF	Seq SS	Adj MS	F Value	P Value
Model	9	5070.97	563.44	53.24	0.000
Linear	3	3638.56	1212.85	114.60	0.000
Amperage	1	40.95	40.95	3.87	0.066
Number of plates	1	1821.62	1821.62	172.12	0.000
Dose of hydrogen peroxide	1	429.17	429.17	40.55	0.000
Square	3	167.53	55.84	5.28	0.009
Amperage * Amperage	1	2.56	2.56	0.24	0.629
Number of plates * Number of plates	1	32.92	32.92	3.11	0.096
Dose of hydrogen peroxide * Dose of hydrogen peroxide	1	115.36	115.36	10.90	0.004

(continúa)

(viene)

Source	DF	Seq SS	Adj MS	F Value	P Value
Interaction	3	57.52	19.17	1.81	0.183
Amperage * Number of plates	1	33.73	33.73	3.19	0.092
Amperage * Dose of hydrogen peroxide	1	22.12	22.12	2.09	0.166
Number of plates * Dose of hydrogen peroxide	1	0.12	0.12	0.01	0.916
Error	17	179.92	10.58		
Lack-of-Fit	11	144.15	13.10	2.20	0.173
Pure Error	6	35.76	5.96		
Total	26	5250.89			
R^2: 0.9657					

Source: own work

In the response surface model of Table 2, it is observed that the variables that have influence on the removal of sulfides are the applied current density and number of electrodes, leaving the supplied dose of peroxide in the background.

Table 3. TOC variance analysis for the first experimental part.

Source	DF	Seq SS	Adj MS	F Value	P Value
Model	9	3354.58	372.73	4.16	0.006
Linear	3	2278.78	759.59	8.47	0.001
Amperage	1	26.31	26.31	0.29	0.595
Number of plates	1	1427.94	1427.94	15.92	0.001
Dose of hydrogen peroxide	1	467.54	467.54	5.21	0.036
Square	3	163.01	54.34	0.61	0.620
Amperage * Amperage	1	18.81	18.81	0.21	0.653
Number of plates * Number of plates	1	78.47	78.47	0.87	0.363
Dose of hydrogen peroxide * Dose of hydrogen peroxide	1	46.04	46.04	0.51	0.483
Interaction	3	458.92	152.97	1.71	0.204
Amperage * Number of plates	1	16.68	16.68	0.19	0.672
Amperage * Dose of hydrogen peroxide	1	51.08	51.08	0.57	0.461
Number of plates * Dose of hydrogen peroxide	1	320.53	320.53	3.57	0.076
Error	17	1524.87	89.70		
Lack-of-Fit	11	330.64	30.06	0.15	0.996
Pure Error	6	1194.23	199.04		
Total	26	4879.45			
R^2: 0.8127					

Source: own work

Table 3 shows that the variables with the greatest influence on TOC removal are the dose of hydrogen peroxide and the number of plates, not including quadratic interactions between variables.

Table 4. Turbidity variance analysis for the first experimental part

Source	DF	Seq SS	Adj MS	F Value	P Value
Model	9	2736.22	304.024	3.50	0.013
Linear	3	1332.55	444.183	5.11	0.011
Amperage	1	2.97	2.971	0.03	0.856
Number of plates	1	833.70	833.704	9.59	0.007
Dose of hydrogen peroxide	1	150.26	150.258	1.73	0.206
Square	3	169.06	56.353	0.65	0.595
Amperage * Amperage	1	19.00	19.003	0.22	0.646
Number of plates * Number of plates	1	148.72	148.719	1.71	0.208
Dose of hydrogen peroxide * Dose of hydrogen peroxide	1	0.00	0.002	0.00	0.996
Interaction	3	343.98	114.661	1.32	0.301
Amperage * Number of plates	1	95.79	95.794	1.10	0.308
Amperage * Dose of hydrogen peroxide	1	1.89	1.891	0.02	0.884
Number of plates * Dose of hydrogen peroxide	1	154.09	154.094	1.77	0.201
Error	17	1477.43	86.908		
Lack-of-Fit	11	990.85	90.077	1.11	0.472
Pure Error	6	486.59	81.098		
Total	26	4213.65			
	R^2: 0.8439				

Source: own work

Table 4 shows that the only determining response variable within the turbidity removal process, is the number of plates in the treatment system. However, with a greater number of plates or electrodes, it becomes necessary to intensify the power supply, so as to maintain current intensity, generating higher operating costs.

The second experimental stage was performed according to the results of the first experimental part, so that 4 electrodes were used in all other tests. In this new stage, the reaction time, current intensity and peroxide dose were varied; the same response variables were maintained in order to analyze the treatment process as a function of time. In other words, the number of plates was kept constant, along with the electrocoagulation time of reaction, with the aim of establishing the shortest time to achieve the greatest efficiency. The reaction time was varied from 30 to 90 minutes at 30 minute intervals, the dose of peroxide was varied in a greater range than in the previous stage (3 ml, 4 ml and 5 ml) and the current intensity applied was varied in the same way as in the preceding tests (4 A, 6 A and 8). The results attained sulfide, TOC and turbidity removals of 68.35%, 75.75% and 99.29% respectively. The experimental results are presented in Figure 5 and the experimental data for constructing the graph and performing variance analysis are shown in Table 5.

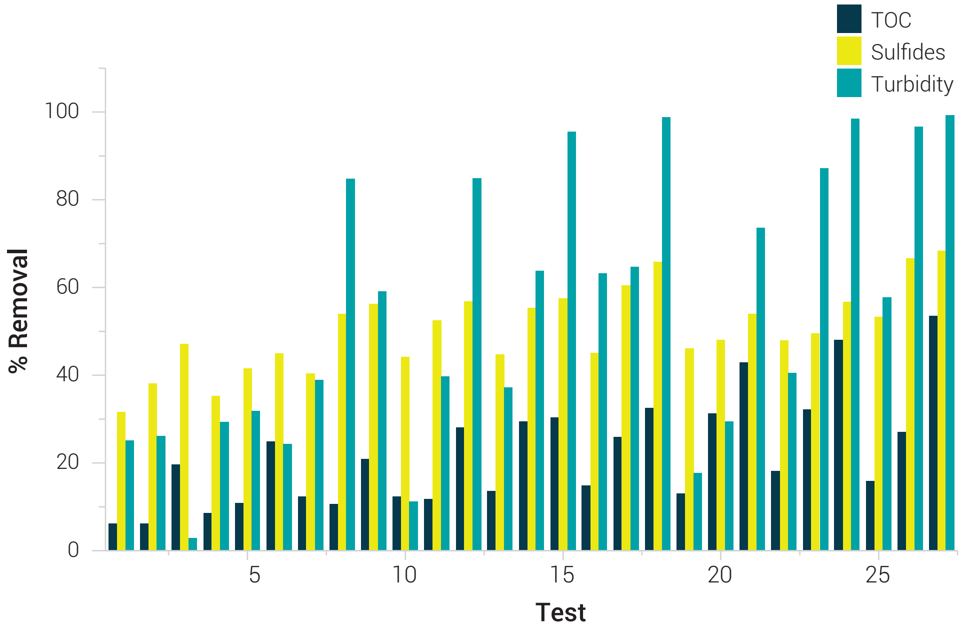


Figure 5. Percentage of removal of response variables in the second experimental stage

Source: own work

Table 5. Results first part of the experimental design

Experiment number	Current Intensity (A)	Number of plates	Dose of hydrogen peroxide (ml)	Percentage of removal Sulfides	Percentage of removal TOC	Percentage of removal Turbidity
28	4	30	3	31.68	6.26	25.2
29	4	60	3	38.14	6.26	26.2
30	4	90	3	47.15	19.62	2.9
31	6	30	3	35.29	8.65	29.4
32	6	60	3	41.53	10.87	31.9
33	6	90	3	45.02	24.97	24.4
34	8	30	3	40.40	12.41	39.0

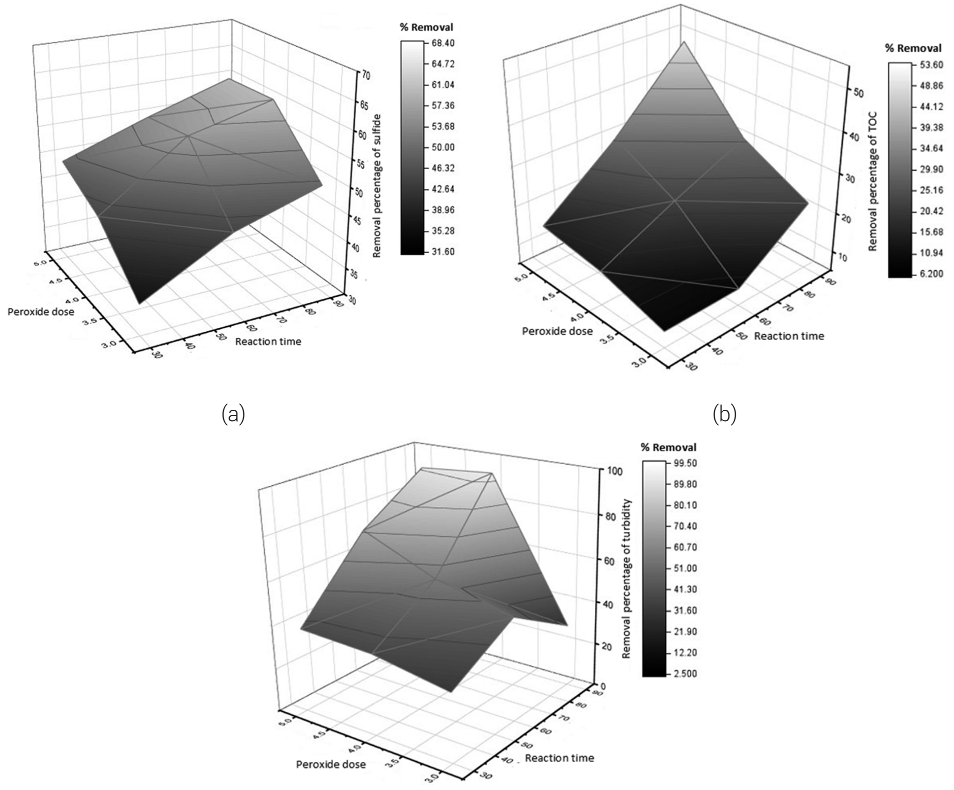
(continúa)

(viene)

Experiment number	Current Intensity (A)	Number of plates	Dose of hydrogen peroxide (ml)	Percentage of removal Sulfides	Percentage of removal TOC	Percentage of removal Turbidity
35	8	60	3	54.08	10.66	84.8
36	8	90	3	56.23	20.94	59.1
-	-	-	-	-	-	-
37	4	30	4	44.24	12.34	11.2
38	4	*60*	*4*	52.56	11.81	39.8
39	4	*90*	*4*	56.87	28.09	85.0
40	6	30	*4*	44.78	13.62	37.2
41	6	*60*	*4*	55.38	29.48	63.8
42	6	*90*	*4*	57.50	30.36	95.5
43	8	30	4	45.08	14.93	63.3
44	8	*60*	*4*	60.55	25.96	64.7
45	8	*90*	*4*	65.84	32.62	91.8
-	-	-	-	-	-	-
46	4	30	5	46.13	13.07	17.7
47	4	*60*	*5*	48.13	31.25	29.5
48	4	*90*	*5*	54.08	43.00	73.6
49	6	*30*	*5*	47.93	18.17	40.6
50	6	*60*	*5*	49.52	32.21	87.2
51	6	*90*	*5*	56.79	48.05	98.5
52	8	30	5	53.32	15.96	57.8
53	8	*60*	*5*	66.65	27.13	96.7
54	8	*90*	*5*	68.35	53.53	99.2

Source: own work

The experimental results were again analyzed by means of ANOVA and response surface. From these analyses the most favorable conditions for the process and the variables of greatest influence for this were determined. The response surfaces are presented in Figure 6. The results obtained from the response surface model identified the variables or determining factors in the process, depending on the treatment time. Variance analysis results for the percentage of sulfide removal, TOC and turbidity are recorded in Tables 6, 7 and 8, respectively.



(a) (b)

(c)

Figure 6. Response surfaces of the effect of the variables or factors on the response variables, (a) sulfide removal, (b) TOC removal, (c) turbidity removal. 4 plates or electrodes

Source: own work

Table 6. Sulfide variance analysis for the second experimental part

Source	DF	Seq SS	Adj MS	F Value	P Value
Model	9	2083.20	231.467	25.93	0.000
Linear	3	1822.67	607.557	68.07	0.000
Amperage	1	465.23	465.232	52.13	0.000
Time of Reaction	1	786.53	786.528	88.12	0.000
Dose of hydrogen peroxide	1	570.91	570.911	63.97	0.000
Square	3	230.01	76.669	8.59	0.001
Amperage * Amperage	1	71.13	71.126	7.97	0.012
Time of Reaction * Time of Reaction	1	24.56	24.559	2.75	0.115
Dose of hydrogen peroxide * Dose of hydrogen peroxide	1	134.32	134.322	15.05	0.001

(continúa)

(viene)

Source	DF	Seq SS	Adj MS	F Value	P Value
Interaction	3	30.53	10.176	1.14	0.361
Amperage * Time of Reaction	1	20.25	20.253	2.27	0.150
Amperage * Dose of hydrogen peroxide	1	3.24	3.243	0.36	0.555
Time of Reaction * Dose of hydrogen peroxide	1	7.03	7.031	0.79	0.387
Error	17	151.73	8.925		
Total	26	2234.93			
R^2:0.9321					

Source: own work

The response surface model shows the process variables or factors that directly influence the removal of sulfides in the wastewater; also shown are the reaction times, the dose of hydrogen peroxide at 50% and the current intensity. The quadratic function of the peroxide doses and the reaction time is also of valid significance for the removal of the response variable.

Table 7. TOC variance analysis for the second experimental part

Source	DF	Seq SS	Adj MS	F Value	P Value
Model	9	3844.47	427.16	28.25	0.000
Linear	3	3470.79	1156.93	76.52	0.000
Amperage	1	100.07	100.07	6.62	0.020
Time of Reaction	1	1453.09	1453.09	96.11	0.000
Dose of hydrogen peroxide	1	1917.63	1917.63	126.83	0.000
Square	3	79.30	26.43	1.75	0.195
Amperage * Amperage	1	40.82	40.82	2.70	0.119
Time of Reaction * Time of Reaction	1	0.39	0.39	0.03	0.874
Dose of hydrogen peroxide * Dose of hydrogen peroxide	1	38.08	38.08	2.52	0.131
Interaction	3	294.39	98.13	6.49	0.004
Amperage * Time of Reaction	1	0.56	0.56	0.04	0.850
Amperage * Dose of hydrogen peroxide	1	1.88	1.88	0.12	0.729
Time of Reaction * Dose of hydrogen peroxide	1	291.95	291.95	19.31	0.000
Error	17	257.03	15.12		
Total	26	4101.50			
R^2: 0.8214					

Source: own work

In the response surface model studied, it is observed that the variables that have the greatest influence on the sulfide removal process are current, density and dose of hydrogen peroxide.

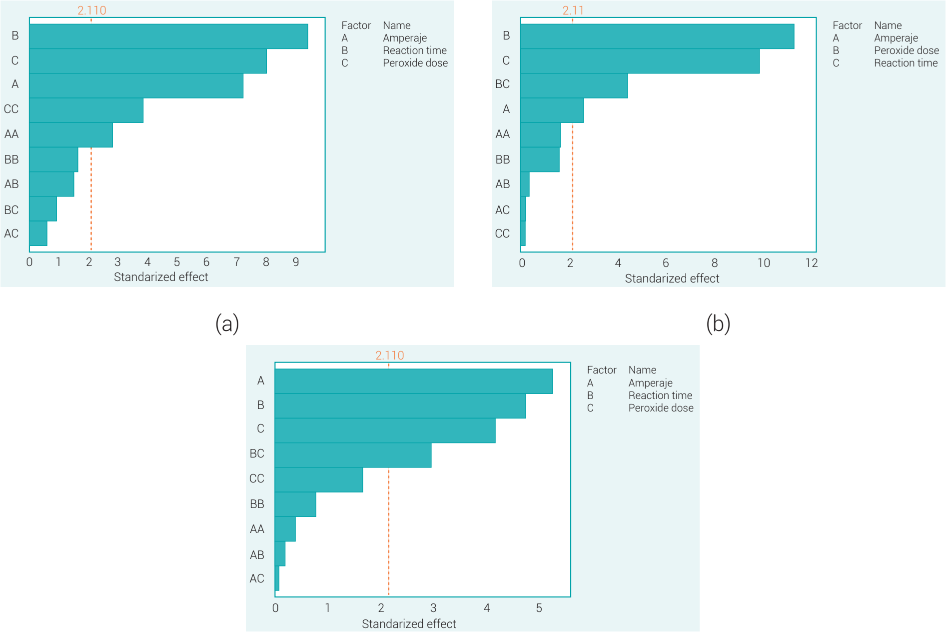
Table 8. Turbidity variance analysis for the second experimental part

Source	DF	Seq SS	Adj MS	F Value	P Value
Model	9	19836.8	2204.09	8.74	0.000
Linear	3	16736.5	5578.85	22.12	0.000
Amperage	1	6902.2	6902.19	27.36	0.000
Time of Reaction	1	4294.1	4294.14	17.02	0.001
Dose of hydrogen peroxide	1	5540.2	5540.22	21.96	0.000
Square	3	889.0	296.33	1.17	0.349
Amperage * Amperage	1	33.2	33.24	0.13	0.721
Time of Reaction * Time of Reaction	1	703.7	703.70	2.79	0.113
Dose of hydrogen peroxide * Dose of hydrogen peroxide	1	152.1	152.07	0.60	0.448
Interaction	3	2211.2	737.08	2.92	0.064
Amperage * Time of Reaction	1	1.6	1.61	0.01	0.937
Amperage * Dose of hydrogen peroxide	1	8.7	8.72	0.03	0.855
Time of Reaction * Dose of hydrogen peroxide	1	2200.9	2200.90	8.73	0.009
Error	17	4288.1	252.24		
Total	26	24124.9			
	R^2: 0.8568				

Source: own work

The response surface model concludes that the 3 variables have a direct influence on the percentage of turbidity removal as well as the quadratic interaction between the reaction time and the 50% hydrogen peroxide dose.

The Pareto chart presented in Figure 7 allows us to observe the effect of each response or factor in addition to the interactions between them.



(a)

(b)

(c)

Figure 7. Pareto chart to determine the effect of the variables or factors on the response variables, (a) sulfide removal, (b) TOC removal, (c) turbidity removal. 4 plates or electrodes

Source: own work

Discussion

Based on what is observed in Figure 3, it can be noted that the highest removal percentages for sulfides and TOCs are achieved for a current intensity of 8 A, 6 plates or iron electrodes and a dose of 4 mL of 50% hydrogen peroxide. However, an important part of the process is to achieve clarification of wastewater without the use of coagulating agents. The use of 6 plates means that there are 3 sacrificial anodes in the process. In this way, the amount of iron added causes the water to become cloudy and red, along with a greater wear of electrodes (anodes), which increases the cost of the process due to the replacement of the anodes. In order to achieve maximum turbidity removal, it was decided to slightly sacrifice the removal of the other response variables. The complementary tests were carried out with 4 plates or electrodes, with current experimental conditions achieving 48.15% removal rates, 38.11% and 98.54% for sulfide, TOC and turbidity respectively; this, under the optimal conditions for current intensity and hydrogen peroxide doses defined with the experimental results.

In the first experimental part and using ANOVA, it was determined that the variables that have the greatest influence on the response variables, sulfur concentration and TOC are the applied current density and the hydrogen peroxide dose. With respect to turbidity, the number of plates turns out to be the variable with the greatest influence on the process. The correlation coefficient (R^2) for the RS in Figure 4, corresponding to sulfides, TOC and turbidity, reach values of 0.96, 0.81 and 0.84 respectively. It can be seen that the increase in the number of plates and peroxide dose increases the percentage of sulfide and TOC removal, due to the increase in the contact area between the water and the electrodes and because of the greater amount of oxidizing agents present in the water, as well as increased formation of OH^* radicals.

In the second part of the experimental design, through ANOVA, it was determined that all the variables or factors studied have an influence on the removal percentages of the pollutant under study. It is clear that, as reaction times increase, the hydrogen peroxide dose and the current intensity increase the removal percentages of the three response variables. This is due to an increase in oxidizing agent, reaction time and a higher rate of radical formation in the electrodes. The RSs presented correlation coefficients of 0.93 for sulfur, 0.82 for TOC and 0.82 for turbidity. The values of the correlation coefficients are considered acceptable to delineate the analyzed process. The Pareto chart presented in Figure 7, allow us to observe the effect of each factor and interactions between them, on the response variables.

With the Pareto chart represented by means of Figure 7 (a) it is observed that all the variables or factors influence the sulfur removal percentage, although the reaction time is the variable with the greatest influence. Figure 7 (b) denotes that the percentage of TOC removal depends mainly on the reaction time and the dose of peroxide and the interaction between these two variables. Finally, from Figure 7 (c) it is observed that the interaction between reaction time and dose of peroxide are the variables with the greatest effect on the percentage of turbidity removal.

It should be noted that the use of 4 electrodes provides an acceptable area for contact between the water and the power supply plates. This results in a current density of 154.87 A/m^2 with a potential difference of 12 V. Increasing the number of electrodes reduces the current density but maximizes the contact area, a situation that facilitates the reactions that take place at each electrode; this includes the oxidation of the iron that forms the anode, which reduces the life of those electrodes and results in turbidity due to excess iron in the wastewater.

Conclusions

Electrocoagulation with Fenton's reagent is used as a technique for the treatment of wastewater from the liming process in tannery wastewater It constitutes as an alternative that allows for the clarification of wastewater without the use of chemical inputs such as coagulants and polymers for flocculation. Moreover, it allows for the oxidation of Sulfides and organic material. This process was achieved with a reaction time and clarification lower than that actually attained with conventional techniques performed in the tanning sector of Chocontá and Villapinzón, Cundinamarca. The process was executed with 4 iron plates or electrodes, a current density of 8A and 5ml of the 50% hydrogen peroxide (in 1.5 L of waste water) and 90 minutes of reaction time. As a result, a percentage removal of 68.35 % of sulfides, 75.75 % of TOC and 99.29 % of turbidity was achieved.

From the first experimental stage, it is determined that the use of 6 electrodes allows for a greater removal of sulfides and TOC, but the oxidation of iron in the anode affects the removal of turbidity due to excess iron in the clarified water, that is, a greater number of electrodes reduces the current density and increases the turbidity of the treated wastewater. This affects the aesthetic appearance of the wastewater and increases the solids load for the filters, causing greater operational effort.

The sulfur, TOC and turbidity removal process in lime wastewater was evaluated by electrocoagulation and intensified with the Fenton reaction. The efficiency of the process regarding the removal of sulfur, TOC and turbidity takes place over a reaction time of 90 minutes, with 4 iron electrodes and a dose of 5 mL of hydrogen peroxide, achieving removals of 68% for sulfur, 53% for TOC and 99% for turbidity.

The treatment by intensified electrocoagulation by the Fenton reagent, increases the total cost of the treatment compared to the conventional treatment, however, the time of treatment and use of chemical inputs is reduced so that the ionic charge of the treated wastewater is reduced; a fact that represents an efficient alternative for the treatment of wastewater from liming processes.

References

[1] S. Y. Martinez Buitrago and J. A. Romero Coca, "Revisión del estado actual de la industria de las curtiembres en sus procesos y productos: un análisis de su competitividad," *Rev. Fac. Ciencias Económicas*, vol. 26, no. 1, pp. 119-120, 2017. [Online]. doi: https://doi.org/10.18359/rfce.2357

[2] D. Saranya and S. Shanthakumar, “Green microalgae for combined sewage and tannery effluent treatment: Performance and lipid accumulation potential,” *J. Environ. Manage.*, vol. 241, no. April, pp. 1-2, 2019. [Online]. doi: 10.1016/j.jenvman.2019.04.031

[3] R. V. Numpaque P. and S. E. Viteri R., “Biotransformación del pelo residual de curtiembres,” *Rev. Ciencias Agrícolas*, vol. 33, no. 2, pp. 96-97, 2016. [Online]. doi: dx.doi.org/10.22267/rcia.163302.56.

[4] G. Durai and M. Rajasimman, “Biological treatment of tannery wastewater - A review,” *Journal of Environmental Science and Technology*. 2011. pp. 1-2 [Online]. doi: 10.3923/jest.2011.1.17

[5] E. E. Gerek, S. Yılmaz, A. S. Koparal, and N. Gerek, “Combined energy and removal efficiency of electrochemical wastewater treatment for leather industry,” *J. Water Process Eng.*, vol. 30, 2019. [Online]. doi: https://doi.org/10.1016/j.jwpe.2017.03.007

[6] M. F. Umbarila-Ortega, J. S. Prado-Rodríguez, and R. N. Agudelo-Valencia, “Remoción de sulfuro empleando ozono como agente oxidante en aguas residuales de curtiembres,” *Rev. Fac. Ing.*, 2019. [Online]. doi:https://doi.org/10.19053/01211129.v28.n51.2019.9081

[7] A. Portada Mamani, *Tratamiento de las aguas residuales del proceso de curtido en pieles por procesos fisico-quimico de la curtiembre de la facultad de Ingenieria Quimica de la UNA Puno*, Tesis, 2016.

[8] M. A. Hashem, M. S. Nur-A-Tomal, and S. A. Bushra, “Oxidation-coagulation-filtration processes for the reduction of sulfide from the hair burning liming wastewater in tannery,” *J. Clean. Prod.*, vol. 127, pp. 1-2. 2016. [Online]. doi : 10.1016/j.jclepro.2016.03.159

[9] H. W. Lin *et al.*, “Electrochemical oxidation of iron and alkalinity generation for efficient sulfide control in sewers,” *Water Res.*, vol. 118. [Online]. doi: https://doi.org/10.1016/j.watres.2017.02.069}

[10] S. U. Khan, D. T. Islam, I. H. Farooqi, S. Ayub, and F. Basheer, “Hexavalent chromium removal in an electrocoagulation column reactor : Process optimization using CCD , adsorption kinetics and pH modulated sludge formation,” *Process Saf. Environ. Prot.*, vol. 122, pp. 118–119, 2019. [Online]. doi: https://doi.org/10.1016/j.psep.2018.11.024

[11] K. P. Papadopoulos *et al.*, “Treatment of printing ink wastewater using electrocoagulation,” *J. Environ. Manage.*, vol. 237, no. November, 2019. [Online]. doi: https://doi.org/10.1021/ie202809w

[12] E. Sociedad Química de México., *Revista de la Sociedad Química de México.*, vol. 58, no. 3. Sociedad Química de México, pp 4-6, 2014. [Online]. doi: https://www.redalyc.org/articulo.oa?id=47532759001

[13] A. Cruz-Rizo, S. Gutiérrez-Granados, R. Salazar, and J. M. Peralta-Hernández, "Application of electro-Fenton/BDD process for treating tannery wastewaters with industrial dyes," *Sep. Purif. Technol.*, vol. 172, 2017. [Online]. doi:https://doi.org/10.1016/j.seppur.2016.08.029

[14] G. Lofrano, S. Meriç, G. E. Zengin, and D. Orhon, "Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: A review," *Sci. Total Environ.*, vol. 461–462, 2013. [Online]. doi: https://doi.org/10.1016/j.seppur.2016.08.029

[15] A. Mannucci, G. Munz, G. Mori, and C. Lubello, "Anaerobic treatment of vegetable tannery wastewaters: A review," *Desalination*, vol. 264, no. 1–2, 2010. [Online]. doi: https://doi.org/10.1016/j.desal.2010.07.021

[16] M. H. Castaño, R. Molina, and S. Moreno, "Cooperative effect of the Co-mn Mixed oxides for the catalytic oxidation of VOCs: Influence of the synthesis method," *Appl. Catal. A Gen.*, 2015 pp. 48-49. [Online]. doi: https://dx.doi.org/10.1016/j.apcata.2014.12.009

[17] Y. Deng and R. Zhao, "Advanced Oxidation Processes (AOPs) in Wastewater Treatment," *Current Pollution Reports*. 2015. [Online]. doi: https://dx.doi.org/10.1007/s40726-015-0015-z

[18] T. P. Sauer, L. Casaril, A. L. B. Oberziner, H. J. José, and R. de F. P. M. Moreira, "Advanced oxidation processes applied to tannery wastewater containing Direct Black 38-Elimination and degradation kinetics," *J. Hazard. Mater.*, vol. 135, no. 1–3, pp. 274–275, 2006. [Online]. doi: https://dx.doi.org/10.1016/j.jhazmat.2005.11.063

[19] I. Oller, S. Malato, and J. A. Sánchez-pérez, "Science of the Total Environment Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination — A review," *Sci. Total Environ.*, vol. 409, no. 20, 2011. [Online]. doi: https://dx.doi.org/10.1016/j.scitotenv.2010.08.061

[20] A. Blanco Llorca, "Procesos Electroquímicos De Oxidación Avanzada Aplicados a La Recuperación De Aguas Contaminadas Con El Colorante Azoico Direct Yellow - 4.," *Análisis Interdisciplinario Y Gestión Sostenible*, 2012. pp 2-3. [Online]. doi: http://diposit.ub.edu/dspace/handle/2445/32177

[21] E. Isarain-Chávez, C. De La Rosa, L. A. Godínez, E. Brillas, and J. M. Peralta-Hernández, "Comparative study of electrochemical water treatment processes for a tannery wastewa-

ter effluent," *J. Electroanal. Chem.*, vol. 713, 2014. [Online]. doi: https://dx.doi.org/10.1016/j.jelechem.2013.11.016

[22] I. A. Şengil, S. Kulaç, and M. Özacar, "Treatment of tannery liming drum wastewater by electrocoagulation," *J. Hazard. Mater.*, vol. 167, no. 1–3, 2009. [Online]. doi: https://dx.doi.org/10.1016/j.jhazmat.2009.01.099

[23] J. wei FENG, Y. bing SUN, Z. ZHENG, J. biao ZHANG, S. LI, and Y. chun TIAN, "Treatment of tannery wastewater by electrocoagulation," *J. Environ. Sci.*, vol. 19, no. 12, 2007. [Online]. doi: https://dx.doi.org/10.1016/S1001-0742(07)60230-7

[24] A. Benhadji, M. Taleb Ahmed, and R. Maachi, "Electrocoagulation and effect of cathode materials on the removal of pollutants from tannery wastewater of Rouïba," *Desalination*, vol. 277, no. 1–3, 2011. [Online]. doi: https://dx.doi.org/10.1016/j.desal.2011.04.014

[25] APHA/AWWA/WEF, *Standard Methods for the Examination of Water and Wastewater*, 23rd ed., American Public Health Association, Washingto, DC, USA: Am. Public Heal. Assoc. Washingto, DC, USA, 2017. [Online]. doi: https://dx.doi.org/ISBN%209780875532356