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Removal of Hexavalent Chromium and Some Organic Compounds Using Two Combined Photo-Fenton and Electrochemical Techniques

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Abstract: The tanning industries have been of great relevance in the economic sector of our country since the 17th century because they contribute to the export and manufacture of leather. From a socioeconomic standpoint, it is beneficial for society; however, this type of industry generates organic and inorganic pollutants that affect the effluents and the ecosystem of the sector. Therefore, advanced oxidation processes such as Fenton and photo-Fenton and electrochemical techniques were addressed in this research. For this, Fenton and photo-Fenton tests were carried out using samples of the effluents from the WWTP (wastewater treatment plant) of the tanneries and they were reacted with known concentrations of hydrogen peroxide and ferrous sulfate (Fenton Reagent) and in the case of photo-Fenton, additionally using an ultraviolet light lamp for 1 hour, obtaining 92.50% turbidity removal percentages, 100% color, 78% COD, and 66% TOC. In the case of electrochemical techniques, cyclic voltammetry, linear scanning voltammetry, and chronoamperometry techniques were used to remove the hexavalent chromium present in the wastewater. Solutions with concentrations within the range of real potassium dichromate wastewater in 0.5M H_2SO_4 solution were prepared using a graphite cloth as the working electrode, an Hg/$HgSO_4$ reference electrode, and a graphite rod counter electrode, obtaining a 99.54% hexavalent chromium reduction using these techniques. Finally, it can be concluded that the advanced Fenton and photo-Fenton oxidation processes were very efficient in the removal of organic compounds present in the effluents of the tanneries. In addition, when combined with electrochemical techniques, the decontamination process is optimized because it reduces the production of heavy metals such as hexavalent chromium, which are dangerous to human health and the ecosystem. This research provided a great achievement from the academic, economic, and environmental viewpoints since these processes are economical and environmentally friendly.

Keywords: tanneries, Fenton, photo-Fenton, electrochemical techniques, hexavalent chromium.

使用两种组合的光芬顿和电化学技术去除六价铬和一些有机化合物

摘要:

自17世纪以来，制革工业在我国的经济部门中一直具有重要意义，因为它们有助于皮革的出口和制造。从社会经济的角度来看，它对社会有益；然而，此类工业会产生影响该行业废水和生态系统的有机和无机污染物。因此，本研究涉及先进的氧化过程（例如芬顿和光芬顿）

以及电化学技术。为此，使用来自制革厂污水处理厂（废水处理厂）的废水样品进行芬顿和光芬顿测试，并将它们与已知浓度的过氧化氢和硫酸亚铁（芬顿试剂）反应，并且在光芬顿，另外使用紫外灯照射1小时，获得92.50%的浊度去除率.100%的颜色.78%的化学需氧量和66%的总有机碳。就电化学技术而言，循环伏安法、线性扫描伏安法和计时电流法技术用于去除废水中存在的六价铬。使用石墨布作为工作电极、汞/硫酸汞参比电极和石墨棒对电极，制备浓度在0.5中号硫酸溶液中的真实重铬酸钾废水浓度范围内的溶液，使用这些电极获得了99.54%的六价铬还原率。技术。最后，可以得出结论，先进的芬顿和光芬顿氧化工艺对于去除制革厂废水中存在的有机化合物非常有效。此外，与电化学技术相结合，净化过程得到优化，因为它减少了六价铬等重金属的产生，这些重金属对人类健康和生态系统有害。这项研究从学术、经济和环境的角度来看都取得了巨大的成就，因为这些过程既经济又对环境友好.

关键词：制革廠、芬頓、光芬頓、電化學技術、六價鉻.

1. Introduction

The leather industry and its manufactures have a long tradition in Colombia, dating back to the late seventeenth century, when the first exports were registered. Considering this, and the important participation that our country can achieve by developing leather production, it is necessary to consider new alternatives for wastewater degradation as a factor for its development. Worldwide, this industry is recognized as one of the most polluting waters due to the chemical processes involved. It is known that effluents from the leather industry constitute one of the most complex wastes for treatment because of the characteristics of their pollutant load [1].

The extensive use of heavy metals and their compounds by tanning industries has resulted in large amounts of this element being released into the environment. These inorganic micropollutants are of great concern because they are not biodegradable, highly toxic, and have a probable carcinogenic effect. If they are discharged directly into the sewage system, their presence decreases the efficiency of the biological treatment to which the wastewater is subjected and makes the activated sludge generated by the treatment unsuitable for application on agricultural land [2]. Chromium is one of the most important heavy metals, which is widely used in many industrial processes such as tanning, electroplating, printed circuit boards and metal finishing, metal processing, painting, and steel manufacturing [3]. Almost 80% of the tanneries in India and the world practice the chrome tanning process [4].

In the last 10 years, there has been a fairly rapid evolution of research activities dedicated to the protection of the environment due to the special attention paid to ecosystems by international social, political, and legislative authorities, which in some cases has led to the delivery of very serious regulations [5]. Compliance with strict quality standards is especially demanded for substances that exert toxic effects in the biological field, preventing the activation of biological degradation processes.

Therefore, there is a crucial need to develop efficient and ecologically friendly methods to treat polluted waters and reduce or completely eliminate contaminants. Among these methods, advanced oxidation processes were precisely defined as water treatment processes carried out at room temperature and normal pressure [6] and based on the in situ generation of a powerful oxidizing agent, such as hydroxyl radicals (•OH), in sufficient concentration to effectively decontaminate water. POAs have recently received increasing attention, as evidenced by the large body of fundamental and applied research [7]-[12]. In fact, they are promising, efficient, and environmentally friendly methods for removing persistent organic pollutants from water. Several types of AOP are based on the in-situ formation of •OH radicals through various chemical, photochemical, sonochemical, or electrochemical reactions.

The oldest and most widely used chemical AOP is the Fenton method, in which a mixture of a soluble Fe (II) salt and H_2O_2, known as Fenton reagent, is applied to degrade and destroy POPs [7]-[8], [12]. However, it is possible to greatly improve the oxidation efficiency and ease of use of this method by simultaneously irradiating the treated ambient water sample with ultraviolet light (photo-Fenton method) or sunlight (solar photo-Fenton method) [12]. In addition, other photochemical methods, such as heterogeneous photocatalysis using TiO_2 suspensions [11]-[13], as well as ozonolysis (O_3 + *UV* irradiation) [13], were reported. Another interesting improvement is based on combining the Fenton technique with electrochemical reactions.

On the other hand, electrochemistry is a technique based on the transfer of electrons, which makes it especially interesting from an environmental point of view, since it constitutes a clean and efficient way of producing hydroxyl radicals (•OH) in situ capable of destroying a wide variety of contaminants and POPs. These •OH radicals can be produced electrochemically either directly (via the AO process) or indirectly via electrocatalytically generated Fenton reagent in situ (electro-Fenton process). The efficiency of the process can be further increased by combining both electrochemical processes, namely the simultaneous AO with a diamond-doped boron anode and the classical EF process (carbon felt or gas diffusion cathodes) [14]-[15]. It is also widely used in the reduction and removal of heavy metals such as hexavalent chromium because it has various techniques that replace it with non-polluting ions in the metal reduction process.

For this reason, this research addresses the advanced oxidation processes of Fenton and photo-Fenton for the removal of organic material present in wastewater from tanneries in the department of Quindío, through the parameters of turbidity, color, BOD, COD, and TOC, obtaining very satisfactory results in the reduction of said contaminants. In addition, cyclic voltammetry, linear scanning voltammetry, and chronoamperometry techniques were used for the reduction of the hexavalent chromium present in the effluents, which turned out to be very economical, fast, efficient, and sensitive in the process of reducing this heavy metal.

2. Materials and Methods

2.1. Reagents and Preparation of Solutions

All reagents used in this work were of analytical reagent grade and were used without any further purification. Ferric sulfate hexahydrate ($FeSO_4.6H_2O$) 98%, hydrogen peroxide (30% w/w), not stabilized), and H_2SO_4 98% were purchased from Aldrich. All solutions were prepared in ultrapure water (Milli-Q water, Millipore). The 0.5 M H_2SO_4 used as the supporting electrolyte was prepared with 98% H_2SO_4 (J.T. Baker). A 10 mM $K_2Cr_2O_7$ (99%, Aldrich) solution was prepared as a stock solution.

2.2. Equipment

A brand METTLER TOLEDO ultraviolet-visible spectrophotometer was used to determine color and turbidity, and a set of jars for the realization of the Fenton process with ultraviolet lamp couplings (wavelength of 269nm) for photo-Fenton, another of the equipment used, was the equipment for the determination of total organic carbon (TOC - V CSH brand SHIMADZU).

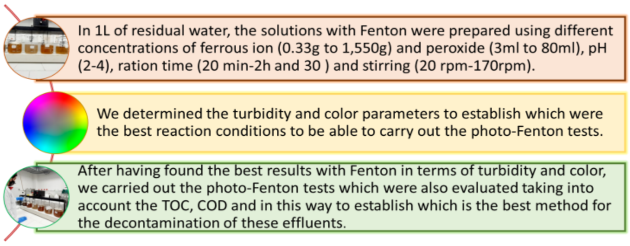
For electrochemical studies, a potentiostat/galvanostat (PINE, Wavenow AFP2, Durham, NC, USA), controlled by After Math software (v 1.610513, Durham, NC, USA), was used.

2.3. Methods

2.3.1. Fenton and Photo-Fenton Processes

All the experiments were carried out using 6 reactors with continuous stirring (jar test). For the reaction process with the Fenton reagent, the solutions of the real waters belonging to the tanneries of La María in the department of Quindío were homogenized, adjusting the pH to 4. Initially, different concentrations of Fe^{+2} and hydrogen peroxide were used [16].

When the best reaction ranges for Fenton were generated, the photo-Fenton process was subsequently carried out. For this, the solutions were exposed to ultraviolet light lamps (wavelength of 269 nm) for 2 hours.



In 1L of residual water, the solutions with Fenton were prepared using different concentrations of ferrous ion (0.33g to 1,550g) and peroxide (3ml to 80ml), pH (2-4), ration time (20 min-2h and 30) and stirring (20 rpm-170rpm).

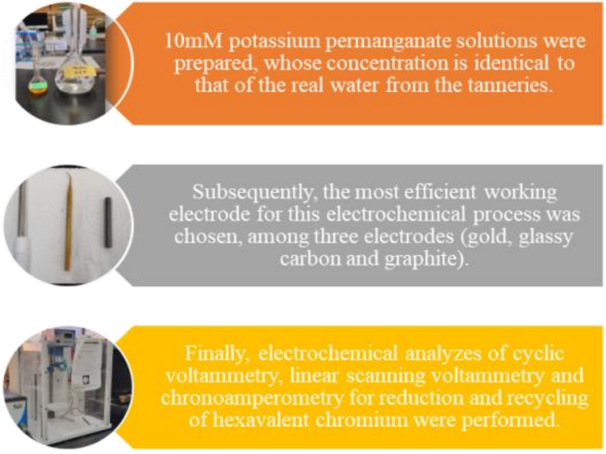
We determined the turbidity and color parameters to establish which were the best reaction conditions to be able to carry out the photo-Fenton tests.

After having found the best results with Fenton in terms of turbidity and color, we carried out the photo-Fenton tests which were also evaluated taking into account the TOC, COD and in this way to establish which is the best method for the decontamination of these effluents.

Fig. 1 Photo-Fenton process

2.3.2. Electrochemical Processes

Electrochemical studies were carried out in a three-electrode electrochemical cell using a carbon cloth as the working electrode, a reference electrode (Hg/Hg_2SO_4/0.5M H_2SO_4; 0.68 V/ NHE), and a graphite rod as the counter electrode. The potential values reported are referred to the normal hydrogen electrode (NHE). All studies were conducted at room temperature (25°C).



10mM potassium permanganate solutions were prepared, whose concentration is identical to that of the real water from the tanneries.

Subsequently, the most efficient working electrode for this electrochemical process was chosen, among three electrodes (gold, glassy carbon and graphite).

Finally, electrochemical analyzes of cyclic voltammetry, linear scanning voltammetry and chronoamperometry for reduction and recycling of hexavalent chromium were performed.

Fig. 2 Electrochemical processes

To determine the potential range where the Cr (VI) reduction-oxidation process takes place, cyclic voltammetry was used. Potential sweeps were performed for x cycles from a to b V/NHE at a sweep rate of w mV s^{-1}. The study was conducted with x mL of 0.5 M H_2SO_4, to which x mL of the stock solution of $K_2Cr_2O_7$ was added.

Once the potential at which Cr (VI) reduction was observed, the linear voltammetry technique was used to determine the cathodic peak current. For this purpose, E_i = x mV/ENH and E_f = x mV/ENH, respectively, at a $v = x$ mV s^{-1}.

3. Results and Discussion

3.1. Photo-Fenton Process

To perform the photo-Fenton analyses, the concentrations of Fe + 2 and hydrogen peroxide that had worked more efficiently in the Fenton process were chosen. Therefore, the assembly of the jar equipment was used and a box with ultraviolet light lamps with a wavelength of 269 nm was attached so that the solutions were irradiated for 2 hours and in this way to be able to compare the removal processes for both experiments. Figures 3 and 4 show the mounting for the photo-Fenton.

Fig. 3 Set of jars with samples for photo-Fenton

Fig. 4 Experimental setup for the photo-Fenton process

As can be seen in Figure 4, the assembly consists of a set of jugs with the reactors containing one liter of contaminated water from the tanneries, and the Fenton reagent is added according to the optimal conditions that resulted in the previous experiment. The variant is the irradiation of ultraviolet light at 269 nm for 2 hours.

After irradiating the samples, we analyzed four parameters to compare the effects of Fenton and photo-Fenton in the different samples evaluated. These parameters are color, turbidity, total organic carbon (TOC), and chemical oxygen demand (COD), obtaining that the samples that were treated with photo-Fenton achieved a better removal and reduction of organic contaminants with respect to Fenton, as shown in Fig. 5.

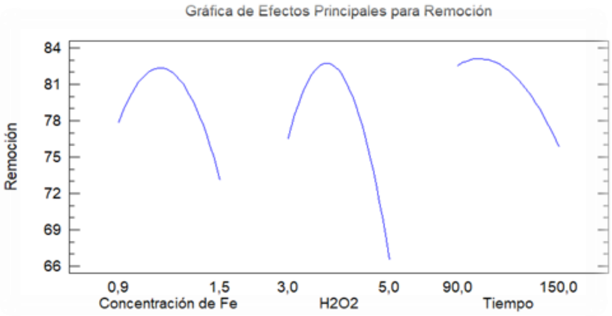


Fig. 5 Effects of photo-Fenton removal

The results obtained for photo-Fenton, according to the response surface analysis, demonstrate that the optimal ferrous ion concentration for good removal is 1.2g/L, since when we increase this concentration, removal begins to decrease. The same happens for the amounts of peroxide; an optimal volume for a good removal is 3 ml, and in the case of the reaction time, this is located in a maximum of 120 minutes.

Fig. 6 shows in a clearer and more concise way the effects of the physicochemical parameters evaluated for photo-Fenton.

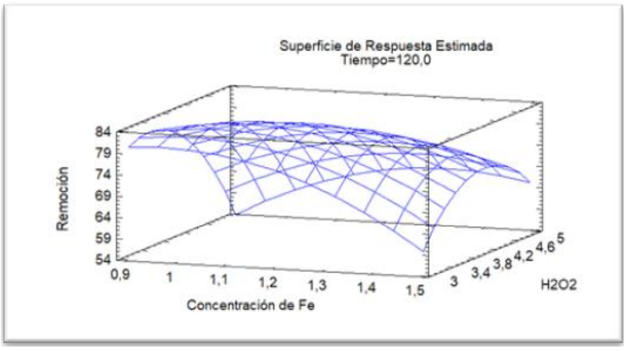


Fig. 6 Turbidity removal results using photo-Fenton

This graph shows the effects of turbidity removal from photo-Fenton-treated waters. Through these response surface analyses, the best concentrations of ferrous ions and peroxide were obtained, as well as the optimal removal time for the turbidity parameter, reaching removals above 90%, which is exactly a removal of 92%.

Table 1 shows the results obtained for color, where it is evidenced that there is a better removal using the photo-Fenton process, achieving color removals of more than 100%.

Finally, we compare the removal of total organic carbon (TOC) and chemical oxygen demand (COD) with respect to the Fenton and photo-Fenton processes, which revealed better COT and COD removal for the photo-Fenton process.

Table 1 Color results after using photo-Fenton

Samples in triplicate	Original Water	Photo F1	Photo F2	Photo F3	Photo F4
Wavelengths	436	436	436	436	436
Absorbance	1.388	0.02	0.113	0.033	0.02
Removal (%)		99.998	99.991	99.997	99.998
Wavelengths	525	525	525	525	525
Absorbance	1.034	-0.03	0.045	-0.025	-0.032
Removal (%)		100.002	99.995	100.002	100.003
Wavelengths	620	620	620	620	620
Absorbance	0.868	-0.037	0.028	-0.033	-0.039
Removal (%)		104.262	96.774	103.803	104.493

However, the removal levels were low for both processes because of the interference of some inorganic compounds and ions, which we will deal with in a future study using electrochemical techniques such as electro-photo-Fenton.

Table 2 Comparison of TOC values for Fenton and photo-Fenton processes

Water	TOC (mg/L)	Removal
AOF	643.46	
AOFF	645.5	
F1	270.325	57.98
F2	253.6	60.58
F3	260.36	59.53
F4	258.75	59.78
F5	249.56	61.21
F6	238.96	62.86
FOF1	244.9	62.06
FOF2	226.33	64.93
FOF3	222.2	65.57
FOF4	233.55	63.81
FOF5	224.8	65.17
FOF6	218.5	66.15

Notes: AOF - water original Fenton, AOFF - water original photo-Fenton, F – Fenton, FO - photo-Fenton

Table 3 Comparison of COD values for Fenton and photo-Fenton processes

Absorbance	COD	Water
0.156	681.75	FF1
0.157	681.75	FF2
0.158	731.75	FF3
0.159	636.75	FF4
0.16	669.25	FF5
0.161	795.75	FF6
0.162	994.25	COD AOFF
0.163	764.25	F1
0.164	656.75	F2
0.165	671.75	F3
0.166	734.25	F4
0.167	714.25	F5
0.168	796.75	F6
0.169	861.75	COD AOF

Notes: COD AOF - water original Fenton, COD AOFF - water original photo-Fenton, F – Fenton, FF - photo-Fenton

Figures 7 and 8 show comparison of the wastewaters before and after treatment with the photo-Fenton process.

Fig. 7 Wastewater before being treated with Fenton and photo-Fenton processes

Fig. 8 Wastewater after treatment with the Fenton and photo-Fenton processes

3.2. Electrochemical Results

A calibration curve was made for the concentrations of hexavalent chromium similar to the real waters of the tanneries, which were prepared with potassium dichromate, in order to determine the reduction peaks of said ion using the technique of preliminary cyclic voltammetry and a graphite bar as the working electrode. Initially, 5 complete cycles were carried out and subsequently 10 more, applying a potential from 0 V (reduction potential) to 1.44 V (oxidation potential) at a scanning speed of 50 mV/s. With this technique, it was possible to establish the optimal reduction signal in the cathodic potential for hexavalent chromium, as shown in Figure 9.

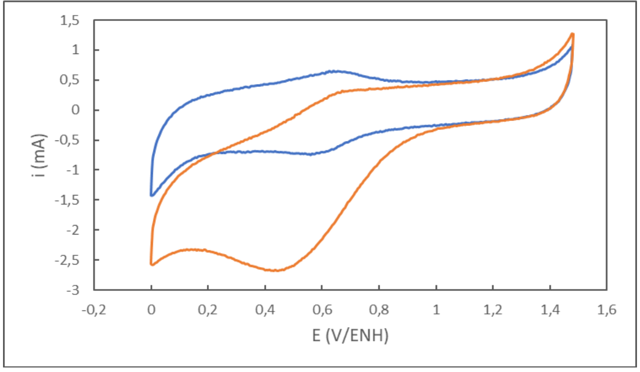


Fig. 9 Cyclic voltammogram using a graphite working electrode before (-) and after (-) the reduction of hexavalent chromium to a concentration of 10 mM with a potential window of 0–1.44 V and a sweep speed of 50 mV/s

After establishing the range of the hexavalent chromium reduction potential through the cyclic voltammetry technique, tests were also carried out with the linear sweep voltammetry (LSV) technique using reduction potentials ranging from a potential window of -0.1V to 1.24V as shown in Figure 10. In this way, it was possible to record the peak signal in which the hexavalent chromium begins to reduce.

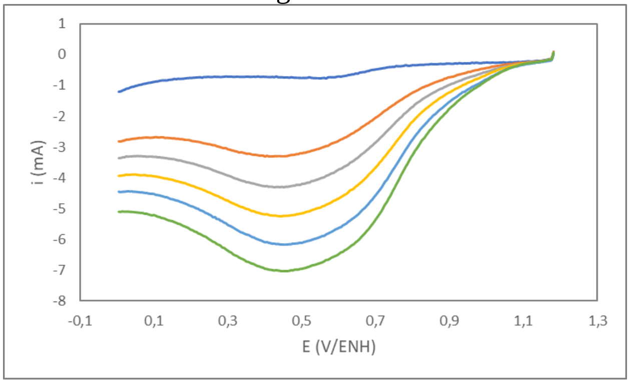


Fig. 10 Graphic of linear sweep voltammetry with a potential window of -0.1 V to 1.24 V with a sweep speed of 50 mV/s

Table 4 shows the data for the realization of the calibration curve using the linear sweep voltammetry (LSV) method. These processes were carried out in triplicate obtaining an R=0.995, with this table, the calibration curve was made, as shown in Figure 11.

Table 4 Hexavalent chromium calibration curve using linear scan voltammetry

Concentration C (mM)	**Current i (mA)**
0.38461538	1.46810936
0.56603774	2.12667049
0.74074074	2.82699386
0.90909091	3.59156732
1.07142857	4.09914138

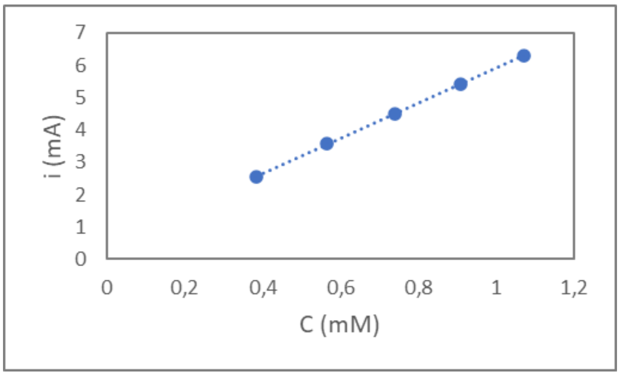


Fig. 11 Calibration curve for graphite electrode (LSV)

Figure 12 shows the results of the chronoamperograms that were performed at constant potential (0.46V), which was obtained from the peak signal that was shown both in the cyclic voltammograms and with the linear sweep voltammetry technique. This was done to ensure the reduction of hexavalent chromium by evaluating the currents obtained for a period of 10 seconds at the concentrations established according to the range of the real concentration of hexavalent chromium in the effluents of the tanning industry.

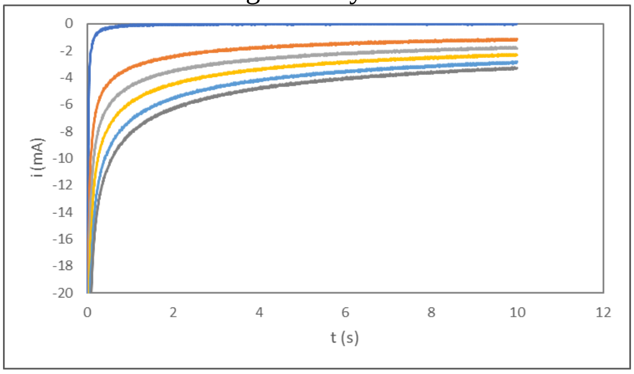


Fig. 12 Chronoamperometry graph to determine the correlation of the concentration with the current over a certain time

In the same way, a calibration curve was made as shown in Figure 8 with the data obtained through the chronoamperometry (CA) technique to monitor the current resulting from the faradic processes that occurred in the graphite electrode. depending on the time recorded in Table 5, these data were of vital importance to subsequently perform the reduction of hexavalent chromium using the potential and establishing the ideal currents for these concentrations obtained through both calibration curves.

Table 5 Hexavalent chromium calibration curve using chronoamperometry

Concentration C (mM)	Current i (mA)
0.38461538	1.46810936
0.56603774	2.12667049
0.74074074	2.82699386
0.90909091	3.59156732
1.07142857	4.09914138

3.2.1. Hexavalent Chromium Reduction Using Graphite Cloth

An analyte of known concentration of potassium dichromate was prepared to determine the reduction of chromium in terms of concentration at a given time. For this, linear scanning voltammetry and chronoamperometry techniques were used.

Figure 13 shows the hexavalent chromium reduction process using the linear sweep voltammetry method. For this process, graphite cloth was used because, by having a larger contact area, it allowed better diffusion of the electrons, establishing optimal conditions for the reduction of this heavy metal.

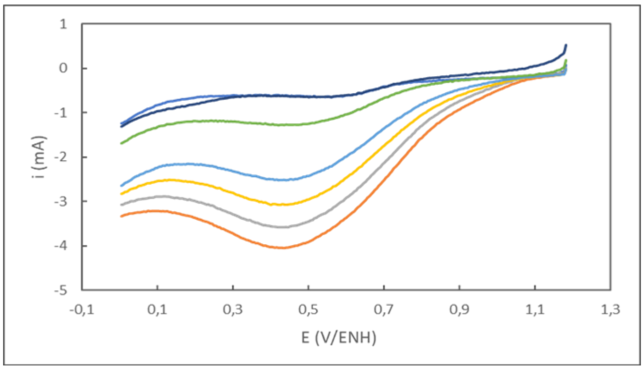


Fig. 13 Graphic of hexavalent chromium reduction using the LSV technique with a potential window of -0.1 V to 1.24 V with a sweep speed of 50 mV/s

The contact time of the solution with the graphite cloth was an average of 5 hours in which a reduction of hexavalent chromium of 99% was obtained, as shown in Table 6. The data were obtained after making the reduction curve for this process, as shown in Figure 14.

Table 6 Reduction percentage of hexavalent chromium

i (mA)	t (h)	i (mA)	% Reduction
-0.61049865			
-4.018954	0	3.40845535	100
-3.54350475	1	2.93300609	86.050888
-3.0552058	2	2.44470715	71.7247814
-2.49944464	3	1.88894599	55.4194143
-1.27548468	4	0.66498603	19.5098941
-0.6297736	5	0.01927494	0.56550376

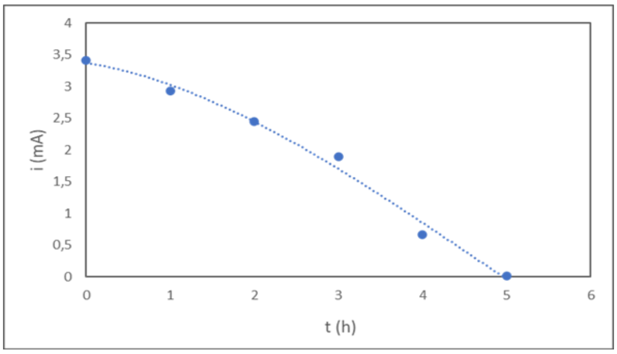


Fig. 14 Curve of hexavalent chromium reduction using LSV technique

Considering that hexavalent chromium is one of the most marked environmental problems in the effluents produced by the tanning industries, the linear sweep voltammetry technique turned out to be very efficient for the reduction of said metal, compared to [16] using this technique to reduce hexavalent chromium in some food additives, obtaining a 92% reduction of this metal. Therefore, by using graphite cloth as the working electrode, this material allowed us to increase the hexavalent chromium reduction percentage to 99.54%, making it more innovative and efficient.

In addition, we used the chronoamperometry technique to establish reduction parameters and thus verify that the graphite cloth reduced hexavalent chromium efficiently under the same reaction conditions that were used in the (LSV), obtaining very satisfactory results with this technique, as shown in Figure 15.

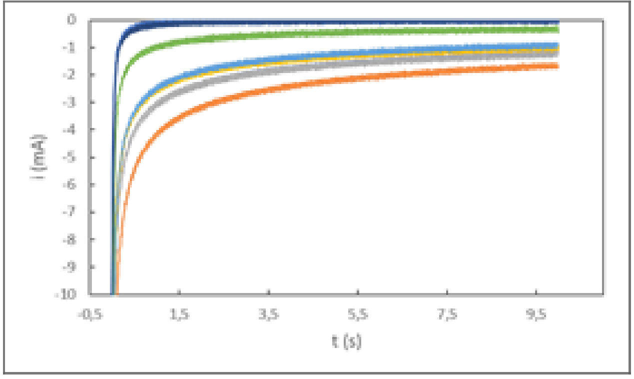


Fig. 15 Graphic of hexavalent chromium reduction using the CA technique

To obtain the reduction percentage, the following curve was constructed with the data obtained using the chronoamperometry method, as evidenced in Table 7 and Figure 16. This technique also turned out to be very novel for the reduction of hexavalent chromium in wastewater from the tanning industry; therefore, it could not be compared with other studies. In addition, very satisfactory results were obtained because a hexavalent chromium reduction of 97.88% was achieved, which makes these two electrochemical techniques economically viable and sensitive in the reduction of said heavy metal.

Table 7 Percentage reduction of hexavalent chromium in CA

i (mA)	t (h)	i (mA)	% Reduction
-0.08686228			
-2.1396454	0	2.05278312	100
-1.3847095	1	1.29784722	63.2237866
-1.29475968	2	1.2078974	58.8419397
-1.04097277	3	0.95411049	46.4788745
-0.41774908	4	0.3308868	16.118936
-0.13183718	5	0.0449749	2.19092306

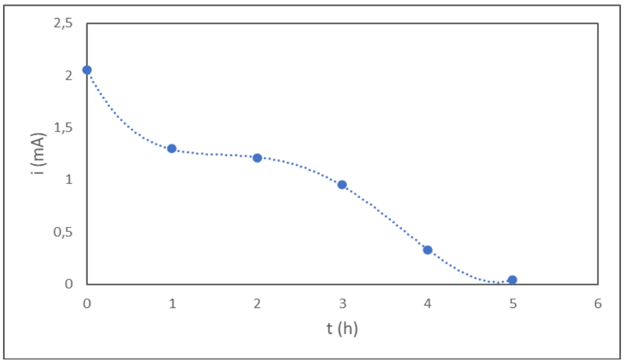


Fig. 16 Curve of the hexavalent chromium reduction using the CA technique

This technique also turned out to be very novel for the reduction of hexavalent chromium in wastewater from the tanning industry; therefore, it could not be compared with other studies. In addition, very satisfactory results were obtained since a reduction of hexavalent chromium of 97.88% was achieved, which makes these two electrochemical techniques economically viable and sensitive in the reduction of said heavy metal.

4. Conclusion

1. The main findings of this study are framed in the contribution that Fenton and photo-Fenton have to the environment, being very friendly techniques due to the minimum cost of the reagents and efficient in the removal of organic contaminants. Comparing both techniques, it turns out to be the most significant photo-Fenton in decontamination, showing turbidity removals greater than 92%, 100% color, and 78% TOC.
2. When comparing the advanced oxidation methods studied in this research, we can conclude that Fenton and photo-Fenton have been very little studied in this type of water produced by the manufacture of tanneries, so it is an innovative study, and they were also obtained removals. 100% color which has not been reported in other articles, as well as in the removal turbidity.
3. The evaluated techniques are very efficient in the elimination of organic contaminants in the wastewater produced by the tanneries and are also very economical and environmentally friendly.
4. The innovation of this research results in the type of water evaluated since with the study of these techniques, very good results were obtained in terms of the removal of organic contaminants, in addition to the positive impact on the ecosystem. The limitation of this study was the removal of COD because there were interferences from inorganic contaminants; therefore, 65% removal was obtained. To improve this, we want to combine electrochemical techniques such as electro-photo-Fenton.
5. We can also conclude that both advanced oxidation processes turned out to be very relevant and effective for the removal of organic contaminants in wastewater produced by tanneries, being the photo-Fenton treatment much more efficient, so it is recommended to use this process for These effluents are the product of industrial tanning water, and we propose a line of research in analytical chemistry where advanced oxidation and electrochemical processes are coupled to optimize the process and obtain better results.
6. Calibration curves were made using the techniques of cyclic voltammetry, linear scanning voltammetry, and chronoamperometry in wastewater simulated with hexavalent chromium, demonstrating that these techniques are very efficient in the removal of heavy metals.
7. When choosing the best working electrode, we found that the graphite electrode, in addition to being very efficient, is also very economical, which facilitates the realization and adaptation of said electrochemical techniques, in addition to being friendly to the environment since it does not generate recalcitrant or toxic products in the solution.
8. A 99.45% reduction of chromium was obtained when using graphite cloth as the working electrode, which indicates that these electrochemical processes are quite efficient for the removal of hexavalent chromium from the wastewater produced by the tanning industry.

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