

## Electrochemical Reduction of Hexavalent Chromium in the Tannery Effluents in the Quindío Department, Colombia

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**Abstract:** Considering the essential participation of Colombia in leather production, it is necessary to consider new alternatives for wastewater degradation as a factor for its development. This industry is recognized worldwide as one of the most polluting water due to the chemical processes. The effluents of the leather industry constitute one of the most complex residues for their treatment due to the characteristics of their contaminant load. Thus, an adequate treatment of such wastewater is essential from an environmental and health viewpoint. This study aims to reduce hexavalent chromium in the tannery effluents of the Quindío Department. This study applied different electrochemical methods to simulated wastewater with hexavalent chromium concentrations similar to those of tannery effluents in the Quindío Department, such as cyclic voltammetry, linear sweep voltammetry, and chronoamperometry, using graphite rod and carbon cloth as working electrodes. Obtaining a chromium reduction of around 99.45% is a very satisfactory result considering that the tanning industries in Colombia do not comply with the legislation for eliminating chromium in their effluents. Finally, the electrochemical techniques employed proved to be very efficient and reliable for remediating industrial wastewater, specifically with the effluents treated in this study, since they have economically sustainable characteristics in terms of operating costs, in addition to being environmentally friendly.

**Keywords:** tanneries, electrochemical methods, carbon cloth, hexavalent chromium, wastewater.

## 哥倫比亞金迪奧省制革廠廢水中六價鉻的電化學還原

**摘要：**考慮到哥倫比亞對皮革生產的重要參與，有必要考慮將廢水降解的新替代品作為其發展的一個因素。由於化學過程，該行業被全世界公認為污染最嚴重的水行業之一。由於其污染物負荷的特點，皮革工業的廢水構成了最複雜的處理殘留物之一。因此，從環境和健康的角度來看，對此類廢水進行充分處理是不可避免的。本研究旨在減少金迪奧省制革廠廢水中的六價鉻。本研究採用循環伏安法、線性掃描伏安法和計時電流法等不同的電化學方法，使用石墨棒和碳布作為工作電極，模擬六價鉻濃度與金迪奧省制革廠廢水相似的廢水。考慮到哥倫比亞的製革工業不遵守消除廢水中鉻的立法，獲得約 99.45% 的鉻減少是一個非常令人滿意的結果。最後，事實證明，所採用的電化學技術對於修復工業廢水非常有效和可靠，特別是本研究中處理的廢水，因為它們除了對環境友好外，還具有運營成本方面的經濟可持續特徵。

**关键词：**制革廠、電化學方法、碳布、六價鉻、廢水。

## 1. Introduction

The leather industry and its manufacturers have a long tradition in Colombia, dating back to the end of the 17th century, when the first exports were recorded. Such industry is recognized worldwide as one of the most water polluting, due to the chemical processes. Effluents from the leather industry are one of the most complex wastes to treat due to the characteristics of their contaminant load, including heavy metals, which are considered as micropollutants or inorganic contaminants.

Inorganic micro-pollutants are of great concern because they are non-biodegradable, highly toxic, with a potential carcinogenic effect. If discharged directly into the sewage system, their presence decreases the effectiveness 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 [1–5].

Among heavy metals, chromium is most important as it is widely used in many industrial processes, such as tanning, electroplating, printed circuit boards, metal finishing, metal processing, painting, manufacturing steel [6–9]. Nearly 80% of Indian tannery practices the chrome tanning process [10]. Most chromium is discharged in aqueous waste as Cr(III) and Cr(VI). Cr(VI), which is more toxic of the two, is present as dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) or as chromate ( $\text{CrO}_4^{2-}$ ) [11].

Some leather industries treat chromium-containing wastewater by aerobic or anaerobic, precipitation, or ion exchange methods [12]. Other methods also used to remove chromium, are adsorption [13] and reverse osmosis [14]. However, all these methods generate much mud and have a high cost. Electrochemical treatment, on the other hand, is a promising technique that offers several advantages over other remediation techniques; furthermore, electrochemical remediation offers a terminal process for the recovery of metals from contaminated effluents or wastewater [15, 16].

Taking into account that an adequate treatment of said wastewater is essential from the environmental and sanitary viewpoint, in this study an economic, viable and low-cost solution is proposed with the use of three electrochemical techniques such as cyclic voltammetry, linear sweep voltammetry and chronoamperometry to reduce the hexavalent chromium present in the waters of the tanneries in the department of Quindío-Colombia and thus remedy a serious environmental problem in that area.

## 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 further purification. The 0.5 M  $\text{H}_2\text{SO}_4$  used as the supporting electrolyte was prepared with 98%  $\text{H}_2\text{SO}_4$  (J.T. Baker).

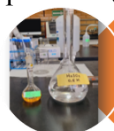
A 10 mM  $\text{K}_2\text{Cr}_2\text{O}_7$  (99%, Aldrich) solution was prepared as a stock solution.

### 2.2. Equipment

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. Methodology

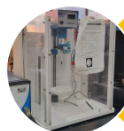
Electrochemical studies were performed out in a three-electrode electrochemical cell, using a carbon cloth as work electrode, a reference electrode ( $\text{Hg}/\text{Hg}_2\text{SO}_4/0.5\text{M H}_2\text{SO}_4$ ; 0.68 V/NHE), and a graphite rod as counter electrode. The potential values reported are referred to the normal hydrogen electrode (NHE). All studies were performed 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. 1 Methodology flowchart

To determine the potential range where the Cr(VI) reduction-oxidation process occurs, the cyclic voltammetry technique was used. Potential sweeps were performed for  $x$  cycles, from  $a$  to  $b$  V/NHE at a sweep rate of  $w$   $\text{mV s}^{-1}$ . The study was conducted with  $x$  mL of 0.5 M  $\text{H}_2\text{SO}_4$ , to which  $x$  mL of the stock solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  was added.

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

## 3. Results and Discussion

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, 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 50mv/s. With this technique, it was possible to establish the optimal reduction signal in the cathodic potential for hexavalent chromium, as shown in Fig. 2.

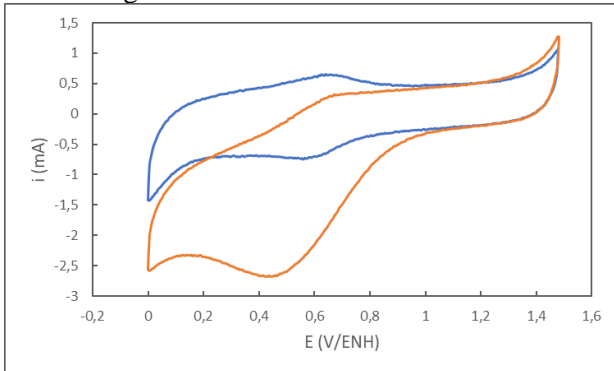


Fig. 2 Cyclic voltammogram using graphite working electrode before (-) and after (-) the reduction of hexavalent chromium to a concentration of 10 mM with a potential window of 0 V to 1.44 V with a sweep speed of 50 mv/s

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 A 1.24 V as shown in Fig. 3 and in this way, it was possible to record the peak signal in which the hexavalent chromium begins to reduce.

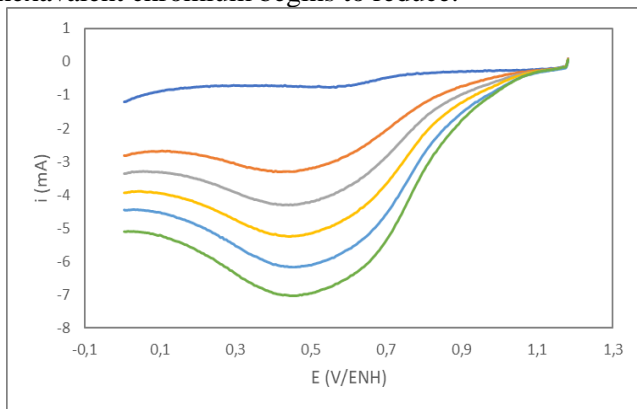


Fig. 3 Graphic of Linear sweep voltammetry with a potential window of -0,1 V to 1.24 V with a sweep speed of 50 mv/s

Table 1 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

Table 1 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 Fig. 4.

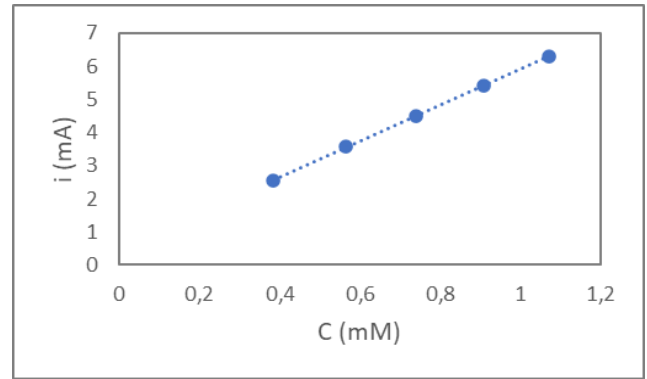


Fig. 4 Calibration curve of the graphite electrode (LSV)

Fig. 5 shows the results of the chronoamperograms that were performed at a 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 belonging to the effluents of the tanning industry.

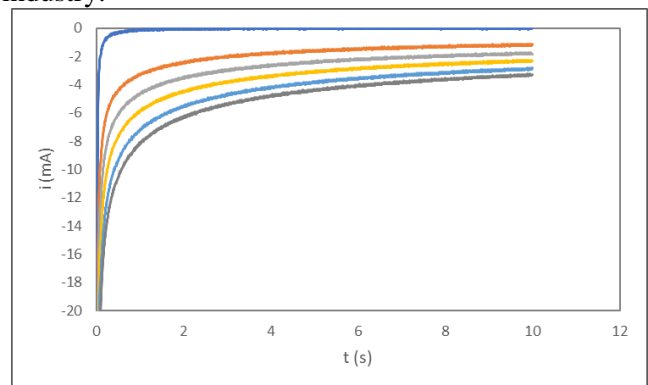


Fig. 5 Chronoamperometry graph to determine the correlation of the concentration with the current over a certain time

A calibration curve was made as shown in Fig. 4 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 2. These data were of vital importance to subsequently conduct the reduction of hexavalent chromium using the potential and establishing the ideal currents for these concentrations obtained through both calibration curves.

Table 2 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

### 3.1. 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, and for this, linear scanning voltammetry and chronoamperometry techniques were used.

Fig. 6 shows the hexavalent chromium reduction process through the linear sweep voltammetry method. For this process, graphite cloth was used since, by having a larger contact area, it allowed better diffusion of the electrons, establishing optimal conditions for the reduction of this heavy metal.

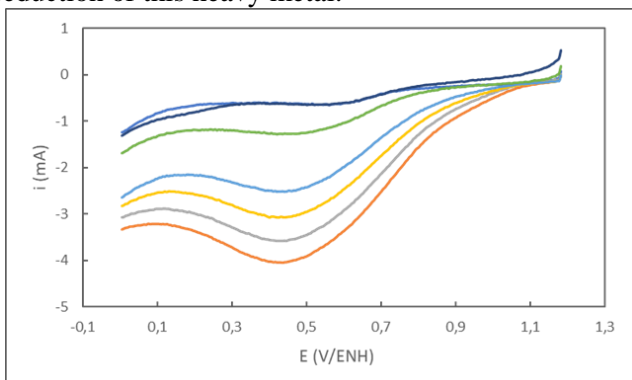


Fig. 6 Graphic of hexavalent chromium reduction using the LSV technique with a potential window of -0.1 V to 1.24 V with a sweep speed of 50 mv/s

The contact time of the solution with the graphite cloth was an average of 5 h in which a reduction of hexavalent chromium of 99% was obtained as shown in Table 3 whose data were obtained after making the reduction curve for this process as shown in Fig. 7.

Taking into account 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 with studies by [16] who used 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.

Table 3 Reduction in the percentage of hexavalent chromium

<i>i</i> (mA)	<i>t</i> (h)	<i>i</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

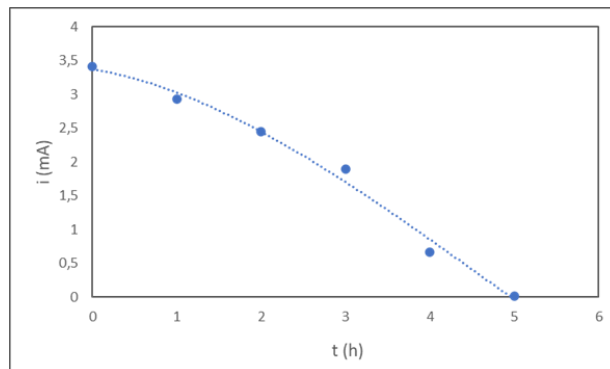


Fig. 7 The curve of hexavalent chromium reduction using the LSV technique

Additionally, 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 Fig. 8.

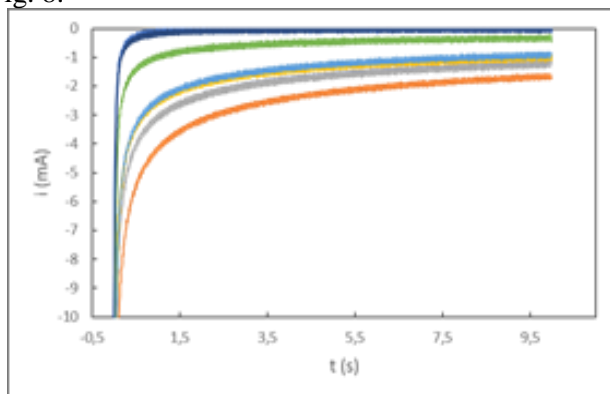


Fig. 8 Graphic of hexavalent chromium reduction using the CA technique

To obtain the reduction percentage, the following curve was made, with the data obtained using the chronoamperometry method, as evidenced in Fig. 9 and Table 4. This technique also turned out to be very novel for the reduction of hexavalent chromium in wastewater from the tanning industry, so it could not be compared with other studies. Additionally, very satisfactory results were obtained since 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 4 The percentage reduction of hexavalent chromium for CA

<i>i</i> (Ma)	<i>t</i> (h)	<i>i</i> (mA)	% <i>i</i> (mA)
-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



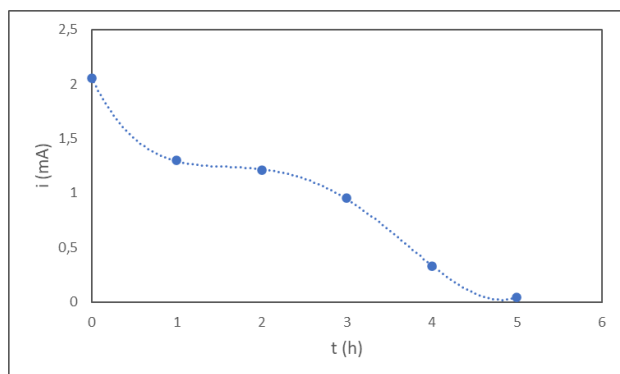


Fig. 9 Curve of hexavalent chromium reduction using the CA technique

This technique also turned out to be very novel for the reduction of hexavalent chromium in wastewater from the tanning industry, so it could not be compared with other studies. Additionally, 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

In this research, we use electrochemical methods to standardize hexavalent chromium reduction processes in wastewater present in the tanning industry; therefore, the authors conclude the following.

Electrochemical analyzes such as cyclic voltammetry, linear sweep voltammetry and chronoamperometry were performed on simulated wastewater with hexavalent chromium, demonstrating that these techniques are very efficient in heavy metal removal.

When choosing which was 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 they do not generate recalcitrant or toxic products in the solution.

A 99.45% chromium reduction 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.

Compared to other studies, this was very efficient with respect to the reduction of hexavalent chromium, reaching reductions of almost 100%. It is recommended to conduct these studies coupled with techniques such as Fenton or photo-Fenton to optimize the processes of decontamination of residual waters produced by the tanning industry.

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