

Chromium Removal from Tannery Effluent by Electrodialysis

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Tannery effluents contain high chromium concentrations, posing a significant environmental and public health risk. Most electrodialysis studies for chromium removal have used synthetic solutions; therefore, this study investigates total chromium removal from actual tannery effluents using an electrodialysis system with titanium electrodes and an MA-MK-MA membrane configuration. Preliminary tests with a synthetic basic chromium sulfate solution (1,521 mg/L) at three voltages (12.2 V, 15 V, and 9 V) yielded reductions of 66.42%, 44.06%, and 32.21%, respectively. The progressive current decrease between tests, attributed to membrane fouling, prompted a cleaning procedure by recirculating 0.05 M HCl for 20 minutes, which restored system efficiency. The actual effluent (2,363 mg/L), due to its high suspended solids content, underwent preliminary coagulation-flocculation, reducing chromium to 1,301 mg/L. The final test at 15 V for 5 hours achieved 99.79% reduction, yielding a final effluent of 2.64 mg/L total chromium. The results demonstrate that electrodialysis is an efficient alternative for treating actual tannery effluents, and that HCl cleaning effectively restores system performance.

1. Introduction

The leather tanning industry is among the manufacturing activities with the greatest environmental impact worldwide, generating effluents with chromium concentrations ranging from 10 to 1,000 mg/L (El-Gawad et al., 2023), far exceeding international discharge limits, such as the European Union's (0.1–3.0 mg/L) (Vaiopoulou & Gikas, 2020). This poses a serious environmental and health risk (Luo et al., 2022), as Cr(VI) is a classified human carcinogen (Group 1) (Zhigalenok et al., 2025), and Cr(III), approximately 500 times less toxic, can cause contact dermatitis and rhinitis (Hartati et al., 2024). Between 30% and 40% of the basic chromium sulfate used in tanning is released into the effluent (Hossain et al., 2023), making chromium the sector's most significant pollutant (UNIDO, 2023). In response, various treatment strategies have been proposed, including adsorption (Hashem et al., 2021), electrocoagulation (Valdiviezo-Gonzales et al., 2023), electrochemical reduction (Wan et al., 2024), ion exchange (Kocaoba et al., 2022), chemical reduction (Lian et al., 2024), and reverse osmosis (Kapepula & Luis, 2024), among others. Each alternative, however, has limitations in operational complexity, by-products, scalability, or cost that hinder industrial implementation. Electrodialysis (ED) emerges as a promising alternative given these limitations. This technology applies an electric field between an anode and a cathode to induce selective ion transport through alternating cation exchange membranes (CEM) and anion exchange membranes (AEM), which allow selective passage of cations and anions, respectively (Rosentreter et al., 2025), separating dilute and concentrate compartments (Hopsort et al., 2024). Metal accumulation in the concentrate compartment enables potential reuse (Latinis et al., 2021), and its continuous operation, scalability, and low reagent consumption establish it as viable for treating metal-containing industrial effluents (Arana Juve et al., 2022). However, most previous studies used synthetic solutions, limiting their direct applicability to actual tannery effluents, whose complex composition and high chromium content remain little studied in such systems. Therefore, this study evaluates the applicability of ED with actual tannery effluent using a laboratory-scale module with an MA–MK–MA membrane configuration and titanium electrodes, assessing system performance with synthetic chromium solutions at different voltages, the effect of HCl cleaning on system recovery, and total chromium removal from pretreated actual effluent.

2. Materials and Methods

2.1 Feed solutions

Two tannery effluent samples were collected from the discharge tank of a tannery in Lima, Peru, during different production batches and stored in high-density polyethylene containers at 4 °C until analysis. The first sample, used for initial characterization, contained 1,393 mg/L of total chromium, whereas the second, used in the final test, contained 2,363 mg/L. For each of the three preliminary tests, 2,400 mL of synthetic solution was prepared by dissolving 13.48 g of 25% basic chromium sulfate in distilled water to match the chromium concentration of the characterized effluent. The solution was divided into three 800-mL portions for the dilute and concentrate containers and for initial chromium determination, which confirmed an actual concentration of 1,521 mg/L.

2.2 Reagents and ion-exchange components

A 25% basic chromium sulfate solution (Tamkron) was used to prepare the synthetic solution, while 0.5 M NaCl and 0.09 M Na₂SO₄ (analytical grade) were used for membrane conditioning and electrode protection, respectively. Coagulation-flocculation was performed using Servifloc 2256 (10,000 ppm), Servifloc 2170 (1,000 ppm), and Servifloc 2120 (1,000 ppm), with TecnoClean 417 for pH adjustment. Membranes were cleaned with 0.05 M HCl (37% purity). All reagents were supplied by CIMATEC S.A.C., Lima, Peru. Two MA-41P anion exchange membranes and one MK-40 cation exchange membrane (Shchekinoazot, Russia) were conditioned in 0.5 M NaCl for 40 h before use, each with a contact area of 86.44 cm². Their characteristics are listed in Table 1. Two titanium electrodes (10 × 5 cm, 1.5 mm thick) served as the anode and cathode.

Table 1: Characteristics of ion-exchange membranes

Membrane	Type	Thickness (mm)	Electric resistance ($\Omega \cdot \text{cm}^2$)	Transport number
MK-40 (Cationic)	Heterogeneous	0.5 ± 0.03	< 10	> 0.98
MA-41P (Anionic)	Heterogeneous	0.5 ± 0.03	< 10	> 0.94

2.3 Analytical methods

The total chromium concentration in all samples was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer, model AVIO 500), following EPA Method 200.7 Rev. 4.4 (United States Environmental Protection Agency, 1994). Results were expressed in mg/L. During the experiments, pH and conductivity were monitored every 30 minutes in the dilute and concentrate containers, using a pH meter (Hanna Instruments, model HI98107) and a conductivity meter (Hach, model HQ40D), respectively.

2.4 Preliminary coagulation-flocculation treatment

Due to the high suspended solids content of the actual effluent, which could foul the ion exchange membranes, given that organic matter and colloidal solids are recognized causes of membrane fouling in electrodialysis systems (Malalagama et al., 2025), a preliminary coagulation-flocculation treatment was performed before electrodialysis. This technique has gained broad acceptance in industrial effluent treatment for its ease of application and low operating cost, effectively targeting colloidal particles and organic matter, and performs optimally at pH values between 6.5 and 7.5 (Badawi et al., 2023). Three reagent dosage combinations were evaluated using jar tests in a portable flocculator at 300 rpm for 30 minutes with 100 mL of effluent per test, as shown in Table 2. The pH was adjusted to 6.5 using TecnoClean 417 neutralizer, within this optimal range.

Table 2: Reagent combinations evaluated in the jar test

Test	Servifloc 2256 (ppm / mL)	Servifloc 2170 (ppm / mL)	Servifloc 2120 (ppm / mL)
Test 1	100 / 1 mL	20 / 2 mL	50 / 5 mL
Test 2	100 / 1 mL	30 / 3 mL	100 / 10 mL
Test 3	300 / 3 mL	50 / 5 mL	200 / 20 mL

2.5 Electrodialysis system configuration

The experimental module consisted of 3 cylindrical acrylic containers (1.24 L capacity, 800 mL effective volume) storing the dilute, concentrate, and electrode rinsing solutions, circulating through corresponding compartments separated by membranes in an MA-MK-MA configuration. Membranes were separated by two mesh-type spacers (0.5 cm thickness) that promoted turbulence and membrane contact while preventing mechanical damage, in a plate-and-frame configuration. Electrodes were housed within two 1 cm-thick perforated acrylic supports allowing circulation of the electrode rinsing solution, with an electrode-to-electrode distance of 3 cm, and connected to a DC power supply (Uni-T, model UTP-3704S, 0-32 V, 5 A). Recirculation used three peristaltic pumps (P1, P2, P3) of 15 W, 41 L/h, at room temperature. Figure 1 shows a schematic representation.

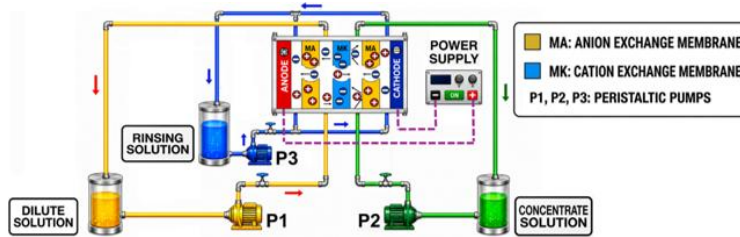


Figure 1: Electrodialysis module with an MA-MK-MA configuration

2.6 Experimental design

Three experimental tests were conducted using synthetic solutions containing 1,521 mg/L Cr, evaluating applied voltages of 12.2, 15, and 9 V and operating times of 4 and 5 h. The selected voltage range was based on previous electrodialysis studies under comparable conditions using the same DC power supply model (0–32 V, 5 A), where Medina Collana et al. (2024) identified voltage as a key operational parameter and reported higher removal efficiency within a 7–15 V range, with the best performance near 15 V. Additionally, Arana Juve et al. (2022) indicated that increasing voltage improves ion transport but may increase energy consumption and concentration polarization. Therefore, the selected voltages allowed chromium removal performance to be evaluated under suitable membrane operating conditions. Between the preliminary tests and the final test, a membrane cleaning procedure was performed using 0.05 M HCl, and the voltage yielding the highest current after cleaning was selected for the final test with pretreated actual effluent (1,301 mg/L Cr) for 5 hours. The parameters are summarized in Table 3. Each test was performed once ($n=1$).

Table 3: Experimental design parameters

Variable	Unit	Test 1	Test 2	Test 3	Final test
Voltage	V	12.2	15	9	15
Time	h	4	5	5	5

The process efficiency was evaluated as the total chromium reduction percentage (Equation 1):

$$R = \frac{C_i - C_f}{C_i} \cdot 100\% \quad (1)$$

where R is the reduction (%), and C_i and C_f are the initial and final Cr concentrations in the dilute solution (mg/L). The specific energy consumption (SEC) was calculated according to Equation 2:

$$E = \frac{U \int_0^t I dt}{V} \quad (2)$$

where E : SEC (Wh/L); U : voltage (V); $\int I dt$: current-time integral (A·h); V : dilute volume (0.8 L).

2.7 Experimental procedure

The dilute and concentrate containers were loaded with synthetic solution (1,521 mg/L Cr) and the electrode rinsing container with 0.09 M Na_2SO_4 (800 mL each). Voltages of 12.2 V, 15 V, and 9 V were applied for the first, second, and third tests, respectively, recording pH, conductivity, voltage, and current every 30 minutes and extracting a dilute sample at the end of each test for total chromium determination. After the three tests, a progressive current decrease due to membrane fouling prompted a cleaning procedure by recirculating 0.05 M HCl for 20 minutes through all compartments, measuring current at 12.2 V, 15 V, and 9 V at the beginning and end, and selecting the highest-current voltage for the final test. For the final test, HCl was replaced by pretreated actual effluent (1,301 mg/L Cr) in the dilute and concentrate containers and the electrode rinsing solution was renewed; the system operated for 5 hours at the selected voltage, recording pH, conductivity, voltage, and current every 30 minutes and extracting a dilute sample at the end for total chromium determination.

3. Results and Discussion

3.1 Results of the preliminary coagulation-flocculation treatment

Test 3 of the jar test, as shown in Table 2, was selected as the optimal reagent combination, achieving the highest solids sedimentation, as indicated by a more compact sediment and clearer supernatant compared with Tests 1 and 2. The reagent doses were proportionally scaled from 100 mL to 5 L, using 150 mL of Servifloc 2256, 250 mL of Servifloc 2170, and 1,000 mL of Servifloc 2120. This pretreatment reduced chromium concentration from 2,363 mg/L to 1,301 mg/L (44.94%), confirming its effectiveness before electrodialysis.

3.2 Chromium reduction in preliminary tests

As shown in Table 4, a directly proportional relationship between initial current and chromium removal efficiency was observed: Test 1 recorded the highest current (0.19 A) and removal (66.42%), followed by Test 2 (0.07 A, 44.06%) and Test 3 (0.04 A, 32.21%), consistent with the literature where higher current density is associated with greater metal removal in electrodialysis (Arana Juve et al., 2022). Despite Test 2 operating at higher voltage (15 V) than Test 1 (12.2 V), its efficiency was lower due to cumulative membrane fouling, which increased electrical resistance and limited effective current and Cr^{3+} migration (Malalagama et al., 2025), as indicated by the progressive current decrease from 0.19 A to 0.07 A and 0.04 A. Specific energy consumption followed the same pattern: 10.41, 6.75, and 2.70 Wh/L for Tests 1, 2, and 3, respectively, as higher membrane resistance reduced effective current, ionic transfer, energy consumption, and chromium removal.

Table 4: Summary of results from preliminary tests with synthetic solution ($C_0 = 1,521 \text{ mg/L Cr}$)

Test	Voltage (V)	Time (h)	Current (A)	Chromium reduction (%)	Final dilute concentration (mg/L)	Specific energy consumption (Wh/L)
Test 1	12.2	4	0.19	66.42	510.6	10.41
Test 2	15	5	0.07	44.06	850.7	6.75
Test 3	9	5	0.04	32.21	1,031	2.70

3.3 pH and conductivity evolution in preliminary tests

The synthetic solution in the dilute and concentrate containers showed initial pH values of 3.40–3.89, attributable to Cr^{3+} hydrolysis releasing protons (Islam et al., 2023). As shown in Figure 2a, all three tests exhibited an initial pH decrease followed by progressive recovery: Cr^{3+} migration toward the concentrate reduced H^+ generation in the dilute, most evident in Test 1, where the final dilute pH (3.54) exceeded the initial value (3.40), consistent with its higher removal (66.42%). In the electrode rinse container, pH decreased from 6.56–7.78 to 2.78, 2.98, and 3.16 in Tests 1, 2, and 3, due to H^+ generation by water oxidation at the anode (Abdipour et al., 2024), with more acidic values at higher currents, consistent with higher current densities increasing H^+ generation (Arana Juve et al., 2022). Regarding conductivity (Figure 2b), the concentrate showed a sustained increase confirming effective Cr^{3+} accumulation through the CEM, while the dilute showed a continuous decrease in Test 1 and stable or transiently increasing conductivity in Tests 2 and 3 due to fouling, and the electrode rinse container maintained stable conductivity (17.42, 14.78, and 11.53 mS/cm), confirming the protective role of Na_2SO_4 .

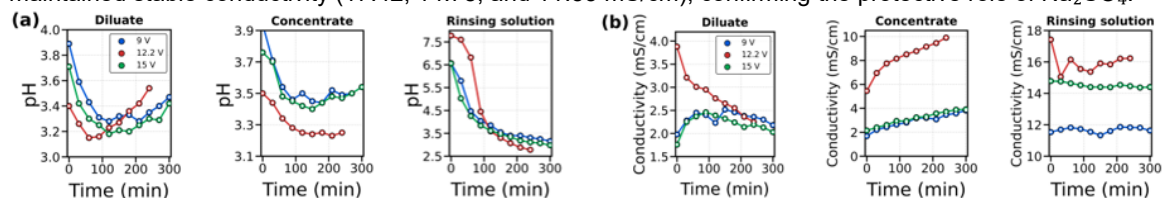


Figure 2: pH (a) and conductivity (b) evolution in dilute, concentrate, and rinse containers for preliminary tests

3.4 System recovery after cleaning with HCl

Due to the cumulative fouling observed in the preliminary tests, a cleaning procedure was performed by recirculating 0.05 M HCl for 20 minutes through all compartments, measuring the current at 9 V, 12.2 V, and 15 V at the beginning and end of the procedure. The results are shown in Table 5.

Table 5: Current before and after cleaning with 0.05 M HCl

Voltage (V)	Initial (A)	Final (A)	Increase (%)
9	0.03	0.22	633
12.2	0.05	0.46	820
15	0.09	0.59	556

The current increase (556 to 820%) after HCl cleaning indicates a notable recovery of the system, consistent with previous studies on acid cleaning of ion exchange membranes (Tiago et al., 2022). Although the pH of the dilute compartment remained below 4, considerably lower than the 5.5 operational pH limit applied by Pilco Núñez et al. (2018) in a similar tannery electrodialysis system to avoid chromium (III) hydroxide precipitation, a localized layer of chromium hydroxide may have formed at the membrane–solution interface, promoted by local pH changes resulting from concentration polarization at elevated current densities (Arana Juve et al., 2022). This could explain the high effectiveness of the observed acid cleaning, as acidic solutions are particularly effective at dissolving chromium hydroxide deposits and other inorganic scales.

3.5 Chromium removal from actual effluent

Following membrane recovery by HCl cleaning, the final test using pretreated actual tannery effluent (1,301 mg/L Cr) evaluated applied voltages of 9, 12.2, and 15 V. The highest current (2.50 A) was obtained at 15 V (Figure 3a). This current was significantly higher than that obtained with the synthetic solution, since solution conductivity directly influences the effective current density (Wu et al., 2025). At 15 V, the current initially increased and then progressively decreased over the 5 h of operation (Figure 3b), in agreement with concentration polarization caused by ion depletion in the dilute compartment, as reported by Arana Juve et al. (2022). The pH of the dilute compartment increased up to 9.25, above pH 6, the point above which $\text{Cr}(\text{OH})_3$ becomes the predominant chromium species in solution (Kocaoba et al., 2022). Consequently, the decrease in chromium concentration in the dilute compartment may have resulted both from electromigratory transport toward the concentrate compartment and from $\text{Cr}(\text{OH})_3$ precipitation. The alkaline conditions reached may also have favored the deposition of $\text{Cr}(\text{OH})_3$ precipitates on the membrane surface, potentially contributing to system fouling. Since chromium was only quantified in the dilute compartment, a complete mass balance could not be established. Future studies should quantify chromium in the concentrate compartment, in precipitated solids, and in possible membrane deposits to determine the relative contribution of each removal mechanism. ICP-OES analysis confirmed a chromium removal of 99.79% (from 1,301 to 2.64 mg/L), with an SEC of 133.87 Wh/L, approximately twelve times higher than the 10.8 Wh/L reported by Pilco Núñez et al. (2018). However, that study required 60 h to achieve a chromium removal of 98.13%, whereas the present work achieved a removal of 99.79% in only 5 h, evidencing the trade-off between process intensification and energy consumption when considering industrial scale-up. These results indicate that ED is a promising technology for treating actual tannery effluents with high chromium concentrations. However, industrial implementation will require further system optimization to improve energy efficiency, minimize membrane fouling, and validate continuous operation at pilot scale, which remain key challenges for large-scale ED processes (Hopsort et al., 2024). Furthermore, evaluating chromium recovery from the concentrate stream could promote resource recovery, consistent with the capability of ED to recover valuable ions through optimized operation (Latinis et al., 2021).

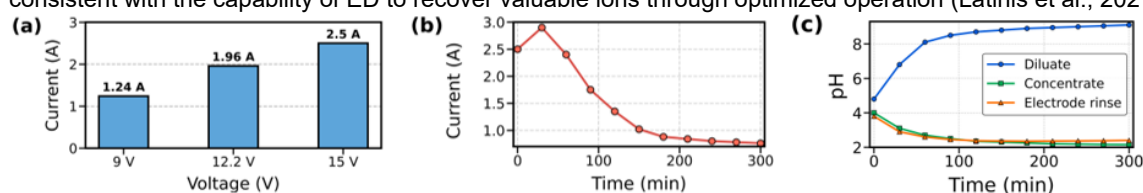


Figure 3: Voltage selection (a), current (b), and pH (c) evolution during the final test with actual effluent

4. Conclusions

This work demonstrated that ED is an effective technology for total chromium removal from actual tannery effluents, unlike most previous studies focused on synthetic effluents. Current density was confirmed as the determining operational parameter, with a directly proportional relationship between initial current and removal efficiency (66.42%, 44.06%, and 32.21% at 0.19 A, 0.07 A, and 0.04 A, respectively). Membrane fouling during the preliminary tests was one of the main challenges observed, and cleaning with 0.05 M HCl proved effective in restoring system performance, increasing current by 556% to 820%. Preliminary coagulation-flocculation treatment played a key role in conducting electrodialysis with actual effluent, reducing chromium concentration from 2,363 mg/L to 1,301 mg/L (44.94%) and achieving a final removal efficiency of 99.79% with an SEC of 133.87 Wh/L. The elevated pH observed during this final test points to an additional contribution of chromium hydroxide precipitation to the removal achieved, and raises the possibility of membrane fouling at this stage. As each test was performed once, data reproducibility could not be statistically assessed; future studies should incorporate replicated trials to confirm these results, quantify chromium in the concentrate compartment, assess membrane fouling following this test, optimize operational parameters, and evaluate industrial scalability.

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