Influence of Pt, Ag and Au electrodes on Cr (III) electrofiltration with current density

Influencia de los electrodos de Pt, Ag y Au en la electrofiltración de Cr (III) con densidad de corriente

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ABSTRACT
The metals Pt, Au and Ag as electrodes were studied at electrofiltration Cr³⁺ ion. The system of three half-cells were used. The Cr²⁺ migration from the central half-cell to the others half-cells where are electrodes was evaluated. Current density and the configurations of metals such as anode - cathode, is determined. The electrodes activity varies with current density as well as cathode or anode. The Cr³⁺ electromigration to cathodic half-cell increase when anode activity to generate H3O⁺ ions was higher than cathode (OH⁻ ions). Instead, the migration of Cr³⁺ to the anode is by electroosmosis. The presence of Au as an electrode generates greater electromigration of the chromium ion to the cathode.

Keyword: Electrofiltration, electrode, chromium, Au, Ag, Pt, electromigration.

RESUMEN
Se estudiaron los metales Pt, Au y Ag como electrodos en la electrofiltración del ion Cr³+. Se utilizó un sistema de tres semiceldas. Se evaluó la migración de Cr³⁺ desde la semicelda central a las otras
semiceldas donde se encuentran los electrodos. Se determinó la densidad de corriente y las configuraciones de los metales como ánodo - cátodo. La actividad de los electrodos varía con la densidad de corriente, así como con el cátodo o el ánodo. La electromigración de Cr3+ hacia la semicelda catódica aumenta cuando la actividad del ánodo para generar iones H3O+ es mayor que la del cátodo (iones OH-). En cambio, la migración de Cr3+ al ánodo se produce por electroósmosis. La presencia de Au como electrodo genera una mayor electromigración del ion cromo hacia el cátodo.

**Palabra clave:** Electrofiltración, electrodo, cromo, Au, Ag, Pt, electromigración

### 1 INTRODUCTION

Tannery effluents are characterized by their complex composition, which creates extreme pHs between alkaline and acidic, high suspended solids concentrations, BOD, chromium, COD, and sulfates, all of them with low biodegradability (Deghles & Kurt, 2016).

In leather industry, 90% of the tanneries use basic chromium salt Cr(OH)SO₄ for economic savings, quality, and market (Ortega et al., 2005). By the process, hides absorb just 60 to 70% of chromium, residuary water is discharged as effluent (Rey de Castro, 2013).

Different methods are used to treat effluents with chromium: coagulation-flocculation (Golbaz et al., 2014), precipitation (Mijaylova et al., 2003), electrocoagulation (Zongo et al., 2009), electrodialysis (Tamersit et al., 2018), etc. Although precipitation method is widely used due to its effectiveness for higher chromium concentrations than 1000 mg/L (Religa et al., 2011), this process requires addition of chemical reagents that increase pH significantly, requiring tertiary treatments.

Electrochemical technologies are investigated in environmental applications for wastewater treatment because they work at 25 °C and 1 atm, low current densities and reduce significantly the use of reagents (Du et al., 2013).

Electrofiltration (EF) is a clean technology, a hybrid one that combines membrane filtration and electrochemistry. Indeed, an applied electric field attracts charged species through a membrane (Fan et al., 2015). Ions, suspended solids, and microorganisms have electrical charges and can be transported by applying a potential difference between two electrodes. Therefore, filtration kinetics is improved and prevent membrane fouling (Mostafazadeh et al., 2016).

There are some factors that influence EF: current density, conductivity, particle concentration, operation time, as well as the nature of the electrodes and membrane material (Mahmoud et al., 2010). An electrochemical electrode must have good electrical conductivity, chemical and electrochemical stability under a wide range of conditions, and prompt electron transfer (Swain, 2007). Electrode design parameters for EF, such as improved materials, types, and configuration, allow lower operating costs (Weber et al., 2002; Mahmoud et al., 2010).
The application of EF to wastewater treatment has been putted into practice to separate different types of pollutants: phenol (Hakimhashem et al., 2010), calcium salts (Quin et al., 2011), organic matter (Tsai et al., 2011), UV filters (benzophenone-3) (Chen & Deng, 2013), pharmaceutical substances (Bakr & Rahaman, 2016) humic substances and metal ions (Wei et al., 2015).

Investigations on electrofiltration technologies such as electrodialysis, studied the separation of Cr3+ ions and other metal ions (Korzenowski et al., 2008). However, EF studies have only investigated the electro-separation of As3+ and As5- ions (Hsieh et al., 2007).

Useful electrodes in electrofiltration to separate different pollutants, correspond to materials such as platinum, stainless steel, titanium in alloy with different oxides (rutile, iridium), aluminum (Mostafazadeh et al., 2016) and raw titanium (Hsieh et al., 2007).

Scientific and industrial interest have been focused on the use of EF as a tertiary wastewater treatment that separate chromium ions. Accordingly, the present work investigates the behavior of the metals Ag, Pt, Au, and Graphite as electrodes to separate Cr3+ from aqueous solutions by EF, as well as the influence of current density.

2 MATERIALS AND METHODS
2.1 MATERIALS

Synthetic solution of 200 (mgCr3+/L) was prepared using Cr(OH)SO4 (tanning agent) of commercial grade. The solution was adjusted to pH = 1 with analytical grade H2SO4.

Nanofiltration membrane, Synder NTE brand, with 600-800 TFC cut off.

Electrodes of 99.99% silver, 18 karat gold, 99.99% pure platinum and commercial graphite, with contact areas of 1.43 cm², 1.92 cm², 1.77 cm² and 5.06 cm² respectively.

2.2 ELECTROFILTRATION SYSTEM

The experiments were carried out in a polypropylene Batch electrochemical system, composed of three 200 cm³ half-cells divided by two nanofiltration membranes (Figure N°1). The electrodes were located in the extreme compartments attached to the system through a support, with a separation distance of 10 cm.

Electric energy was supplied by a direct current power source. A digital multimeter, PRASEK PREMIUM model PR-45ª, was used to measure voltage and amperage applied to the system. The amperage was measured in series using a 1300 ohm rheostat.

Applied current density was between 150-320 mA/cm². The operation time was 5 hours for all experiments.
2.3 ANALYSIS
Cr3 concentrations were analyzed using the EPA 7196A colorimetric method with diphenylcarbazide, where the Cr3 ion was oxidized to Cr6. The absorbance of the samples was measured in an Orion AquaMate 8000 UV-Vis spectrophotometer at 540 nm.

2.4 STATISTICAL ANALYSIS
A factorial design was used, considering the variables of current density, Cr3 concentration, and electrodes. Three replicates of the experiment were performed. The data obtained was subjected to an analysis of variance (ANOVA).

3 RESULTS AND DISCUSSION
The nature of the electrodes is a fundamental property that impacts the EF performance, which determines the electrons transference and oxidation-reduction reactions (Weber et al., 2002). The metals behavior: Ag, Au, and Pt, have been studied as EF electrodes and their function as anodes and/or cathodes. Previous academic works concluded that current density of 220 and 270 mA / cm2 was appropriate to analyze their process influence. The pairs of electrodes were written in order, e.g. Pt – Ag: where the first one (Pt) corresponds to the anode and the second one (Ag) to the cathode.

3.1 INFLUENCE OF ELECTRODE PAIRS
When electrical current is applied into the electrofiltration process, electrolysis of water happens in the electrodes half cells. This generate H3O+ and OH− ions, being crucial in the electrofiltration process. The reactions which take place in the process are:

Anode
The results for 220 (mA / cm²) current density are presented in Graph N ° 2, indicate:

1. Electromigration is the migration of positive metal ions towards opposite charges electrons in electrofiltration process, it is an electrokinetic phenomenon due to the effect generated by the \( \text{H}_3\text{O}^+ \) ions, which are produced in the anode by electrolysis of water (Mahmoud et al., 2010, Dalla et al., 1998). At using different pairs of metals in the electromigration of the \( \text{Cr}^{3+} \) ion from the central compartment towards the cathodic half-cell no significant differences are observed, thus, \( \text{Cr}^{3+} \) ion concentration was in the range of 11.8 to 13.9 (mgCr\(^{3+}\)/L). The exceptions were: Ag - Pt system with a maximum of 17.1 (mgCr\(^{3+}\)/L) and Au - Ag with a minimum of 7.1 (mgCr\(^{3+}\)/L). These results show: with current density of 220 (mA / cm²) the generation of \( \text{H}_3\text{O}^+ \) ions for each system is similar, therefore, the separation of the \( \text{Cr}^{3+} \) ion does not change substantially with the type of pair metal electrode used. Likewise, there is no correlation between the standard potentials of cells formed by each pair of electrodes with the electromigration of the \( \text{Cr}^{3+} \) ion.

2. Indeed, the \( \text{Cr}^{3+} \) ion with positive charge must migrate toward the cathodic half-cell and not into the anodic one. However, the results show that regardless of the pair of electrodes used, there is always a \( \text{Cr}^{3+} \) quantity present in the anodic half-cell. When an electric field is applied to the system, the membranes that separate half cells become electrically charged and the double electrical layer on their surface becomes unbalanced, generating some ions diffusion through the membrane, an electrokinetic phenomenon called electroosmosis (Mahmoud et al., 2010; Wiley & Weihs, 2015; Weber & Stahl, 2002). This phenomenon would cause the diffusion of the chromium ion from the electric double layer through the membrane towards the anode half-cell. Average quantity of \( \text{Cr}^{3+} \) which passes to the anode by electroosmosis is 3.1 (mgCr\(^{3+}\)/L). Ebbers et al. (2015) make a similar system to this, and less than 5% of chromium passes to the anode.
3.2 INFLUENCE OF CURRENT DENSITY

Generally, the chromium migration is a function of the electrodes electrochemical activity and current density. According to the Evans diagrams (Pedeferri, 2019), variation of current intensity can change the electrode activity from oxidative to reductive behavior or vice-versa.

**Pt – Ag and Ag – Pt Systems**

**Pt-Ag:**

The migration of the Cr\(^{3+}\) ions towards cathodic cell oscillates between 9.8 - 13.3 (mgCr\(^{3+}\)/L) as seen in (Figure N°3). The Cr\(^{3+}\) ion electromigration toward cathode increases with the flux of H\(_3\)O\(^+\) ions generated at the anode. Therefore, there is not a tendency to increase the Cr\(^{3+}\) separation with the current density in the range of 140 to 336 (mA/cm\(^2\)), it implies that the activity of Pt at the anode to generate H\(_3\)O\(^+\) ions tends to remain constant under the range of current density studied.

At the anodic half-cell, an amount of Cr\(^{3+}\) which migrates to the anode cell increases from 0.7 to 11.9 (mgCr\(^{3+}\)/L) for current densities between 210 and 336 (mA/cm\(^2\)). Being the last value similar to the one obtained by Cr\(^{3+}\) electromigration to the cathodic cell. In the system, the H\(_3\)O\(^+\) ions generated in the anode migrate to the cathodic cell and OH\(^-\) ions produced in the cathode towards the anodic cell (Acar et al., 1995, Dalla et al., 1998), creating a pH gradient between both half-cells (Aziz et al., 2006). At current densities higher than 210 (mA/cm\(^2\)) the reductive activity of Ag (Diagram of Evans, Betts et al., 2005) strongly increased, generating hydroxyl ions, whereas the oxidizing activity of Pt is almost constant. That generates a greater flow of OH\(^-\) groups than H\(_3\)O\(^+\) in the system. Thus, the membrane of the cathode cell
will have a higher concentration of $\text{OH}^-$ ions on its surface than the anode membrane with $\text{H}_3\text{O}^+$ ions, as seen in Figure N°4. The high concentrations of $\text{OH}^-$ in the cathodic cell membrane would stabilize the chromium ion on its surface as $\text{Cr}^{3+}(\text{H}_2\text{O})_6$ (Rollinson, 1975, p. 103). Due to the coupling of water molecules to the ion, the phenomenon of dielectric exclusion is produced, (Roy et al., 2017) reason why the Cr$^{3+}$ ion cannot pass into the cathodic half-cell. In the central cell, to balance the system there would be an increase in Cr$^{3+}$ ion concentration on the anode membrane, which by electroosmosis passes to the anodic cell. In this case, current density increases as well Cr$^{3+}$ concentration increases in the anodic half-cell.

Figure N° 3. Influence of current density on Cr$^{3+}$ electrofiltration for the Pt - Ag electrode system.

Figure N° 4. Electroosmosis and electromigration of the Cr$^{3+}$ ion and its counterions.

**Ag-Pt:**
In the cathodic half-cell, two different Cr\(^{3+}\) electromigration behaviors are observed (Figure N° 5): An increase in chromium quantities from 4.1 to 20.3 (mgCr\(^{3+}/L\)) for current densities of 113 to 220 (mA/cm\(^2\)) respectively. At current densities higher than 220 (mA/cm\(^2\)) there is no significant increase of chromium ion that passes through the half-cell, being almost constant at 18.2 (mgCr\(^{3+}/L\)). The Cr\(^{3+}\) electromigration depends on the activity of the Ag anode, which generates H\(_3\)O\(^+\) ions and corrosion on Ag was observed in the essays (Figure N° 6) at current densities higher than 220 (mA/cm\(^2\)). According to the Evans diagram (Betts et al., 2005), Ag tends to be unstable and oxidize with an increase of the current intensity:

$$\text{Ag} \rightarrow \text{Ag} + +1 \text{e}^-$$

As Ag is oxidized, its ability to generate H\(_3\)O\(^+\) ions decrease, therefore, chromium ion electromigration towards the cathode is not increased.

The Cr\(^{3+}\) concentration in the anodic cell does not vary substantially with the current density between 110 to 260 (mA/cm\(^2\)), being on average 3.2 (mgCr\(^{3+}/L\)). As previously mentioned, chromium ion migrates to the anodic half-cell by the electroosmosis mechanism.

![Figure N° 5. Influence of current density on Cr\(^{3+}\) electrofiltration for the Ag - Pt electrode system](image)
Figure N° 6. Ag electrode corrosion at 220 (mA / cm2)

Au - Pt and Pt - Au systems

Au-Pt:

The electromigration of chromium to the cathodic half-cell (Figure N° 7) has an inflection point at 181 (mA/cm²), with the lowest chromium concentration: 7.9 (mg Cr³⁺/L). At this current density, the activities of Pt and Au electrodes in both half-cells are similar, also the H₃O⁺ and OH⁻ ions generation. Therefore, the Cr³⁺ electromigration to the cathode is minimal: 7.9 (mg Cr³⁺/L). However, at higher current densities, Pt activity predominates producing more H₃O⁺ ions compared to OH⁻ production by Au electrode. This generates a higher chromium electromigration reaching 18 (mg Cr³⁺/L) to 270 (mA/cm²).

The Cr³⁺ migration towards the anodic half-cell changes with current density, as shown in Figure N° 6. Initially, the Cr³⁺ concentration decreases from 11.9 to 3.3 (mg Cr³⁺/L) for 113 and 181 (mA/cm²) respectively. And at current densities above 181 mA / cm², the Cr³⁺ concentration remains constant in the range of 3.4 to 4.0 (mg Cr³⁺/L). At low current densities, Pt electrode is more active than Au, therefore a higher concentration of OH⁻ ions than H₂O³⁺ would be produced. This phenomenon, previously described, induces the electroosmosis of the Cr³⁺ ion towards the anodic half-cell, reaching 11.9 (mg Cr³⁺/L) for 113 (mA/cm²). As the current density increases, the activity of Pt decreases and also the OH⁻ generation. As a consequence, the chromium electroosmosis declines and remains at an average of 3.5 (mg Cr³⁺/L) in the range of 181 to 270 (mA/cm²).

The chromium migration to the anode and cathode are mainly related to the change on electrodes activity with current density. Observing that the Au electrode corrodes (Figure N° 8) at current densities lower than 181 (mA/cm²).
Pt-Au:

Moreover, chromium electromigration toward cationic half-cell increases from 167 (mA/cm²), reaching a concentration of 20.1 (mgCr³⁺/L) for 271 (mA/cm²), as seen in Figure N° 9. For this system, when current densities are higher than 167 (mA/cm²), Pt anode has higher activity than Au cathode, so this generates a higher concentration of H₃O⁺ ions. In contrast, the Au activity is constant in the studied range of current density, hence OH⁻ ions generated do not vary substantially.

In this system, the chromium migration towards the anodic half-cell is generally less than 4.3 (mgCr³⁺/L) in the entire range of current density studied, mainly due to the electroosmosis phenomenon.
Figure N° 9. Influence of current density on Cr\(^{3+}\) electrofiltration for the Pt - Au electrode system.

Au - Ag and Ag - Au systems

Au-Ag:

The Cr\(^{3+}\) migration towards the cathodic half-cell, in a system with Au - Ag electrodes is shown in Figure N° 10. It was observed that with higher current densities as 224 (mA/cm\(^2\)) the Cr\(^{3+}\) migration increases exponentially from 6 to 32.9 (mgCr\(^{3+}\)/L) for 224 and 308 mA/cm\(^2\) respectively.

In contrast, the Cr\(^{3+}\) migration to the anodic cell, mainly by the electroosmosis mechanism, remains at an average of 4.3 mgCr\(^{3+}\)/L, for different current densities worked.

The electromigration of Cr\(^{3+}\) is related to the H\(_2\)O\(^+\) concentration in the system, which is a function of the metal activity that performs the anode function. In this case, when the Au activity increases exponentially at current densities higher than 224 (mA / cm\(^2\)), Cr\(^{3+}\) ion increase and also the cathodic half-cell migration. In contrast, the Ag activity as a cathode is not influenced by current density.
Ag-Au:

The results for the Ag - Au system, are presented in Figure N° 11. The chromium electromigration to the cathodic cell increases linearly with current density from 161 to 270 (mA/cm²), reaching 4.6 to 21.7 (mgCr³⁺/L) respectively. However, chromium ions which pass into anodic cell, do not vary substantially with current density along the range of 140 to 308 (mA/cm²).

In general, when Ag and Au are used as electrodes in the system, the current density variation does not considerably influence in the reducing activity of the cathodic metal, being the chromium concentration that passes into the anodic cell by electroosmosis less than 4.3 (mgCr³⁺/L). On the other hand, the Cr³⁺ electromigration increases linearly (Ag - Au) or exponentially (Au - Ag) from certain current density values, where the differences in activities between the pairs of electrodes begin, and which is observed with a higher chromium separation towards the cathodic cell.
2. Au and Ag systems.

Systems that have the same material as electrodes are studied: Ag - Ag and Au - Au. The results show that:

**Ag-Ag**

The Ag activity to separate Cr$^{3+}$ changes with current density (Figure N° 12). At low densities, there is a higher Cr$^{3+}$ concentration which migrates to the anode cell. As mentioned, the electroosmosis mechanism occurs when the cathodic electrode has higher activity than the anodic one. In consequence, there is a higher electrolysis of the water, with a superior increase in OH$^-\$ concentration than H$_3$O$^+$ produced at the anode. But, by increasing current density, the electrodes activities are reversed, and the activity of anode begins to predominate, generating a higher H$_3$O$^+$ concentration, promoting the chromium electromigration toward cathodic cell, being in evidence that Ag activity varies according to current density. The result supports the comments about the Ag activity with other metals in the system to separate Cr$^{3+}$ ions.
Au-Au

In this system, the amount of Cr$^{3+}$ ions which passes into the cathodic cell increases with current density (Figure N° 13). Therefore, the transport mechanism of Cr$^{3+}$ towards that half-cell would be by electromigration. It means that H$_3$O$^+$ generation is higher than OH$^-$ produced at the cathode. Consequently, the predominant activity of Au as an electrode in the system is mainly oxidant in the electrolysis of water. By contrasting this behavior with the other systems studied, it is observed that the presence of Au as an electrode promotes the chromium separation by electromigration towards the cathode.
4 CONCLUSIONS

It has been observed that the Pt, Ag, and Au activities as electrodes vary with current density and with their function as cathode or anode. The Cr$^{3+}$ migration toward the cathodic cell could transport by the electromigration mechanism and when it passes to the anode cell by electroosmosis mechanism. Likewise, in systems where Au is present as an electrode, a higher Cr$^{3+}$ concentration migrates to the cathodic cell.

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