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# Electrochemical reduction of Cr(VI) in the presence of sodium alginate and its application in water purification

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## ABSTRACT

Chromium (Cr) is used in many manufacturing processes, and its release into natural waters is a major environmental problem today. Low concentrations of Cr(VI) are toxic to human health and living organisms due to the carcinogenic and mutagenic nature of this mineral. This work examined the conversion of Cr(VI) to Cr(III) via electrochemical reduction using gold electrode in an acidic sodium alginate (SA) solution and subsequent removal of the produced Cr(III)-SA by the polymer-enhanced ultrafiltration (PEUF) technique. A solution of SA in nitric acid was used both as an electrolytic medium during the voltammetric measurements and bulk electrolysis and as an extracting agent during the PEUF technique. The electroanalysis of Cr(VI) was performed by linear sweep voltammetry in the presence of acidic SA solution to study its voltammetric behavior as a function of the Cr(VI) concentration, pH, presence of Cr(III), SA concentration and scan rate. In addition, the quantitative reduction of Cr(VI) to Cr(III) was studied through the bulk electrolysis technique.

The results showed efficient reduction with well-defined peaks at approximately 0.3 V vs. Ag/AgCl, using a gold working electrode. As the pH increased, the reduction signal strongly decreased until its disappearance. The optimum SA concentration was 10 mmol/L, and it was observed that the presence of Cr(III) did not interfere in the Cr(VI) electroanalysis. Through the quantitative reduction by bulk electrolysis in the presence of acidic SA solution, it was possible to reduce all Cr(VI) to Cr(III) followed by its removal via PEUF.

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## Introduction

Chromium is considered a raw material for industrial development. This mineral is valuable in the manufacturing process of surface plates and chrome electroplating (decorative and hard coating), manual work of stainless steel and other alloys,

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and the manufacture of inks, concrete, bricks, photography, paints, plastics and textiles (Codd et al., 2001; Sánchez and Rivas, 2011; Wang et al., 2013).

The main industries that contribute to the release of chromium to natural waters are leather, mining, galvanoplasty, etc. (Monteiro et al., 2002). Variations ranging from 4 to 1000 mg/L Cr(VI) have been reported in industrial effluents (Jobby et al., 2018). In water, chromium ions are stable in the trivalent oxidation state, Cr(III), and in the hexavalent oxidation state, Cr(VI). Cr(III) is essential for life, but at a low concentration, however, Cr(VI) is toxic, highly mobile in the environment, non-biodegradable, cumulative, and presents adverse effect on human health and living organisms, due to its carcinogenic and mutagenic nature (Aroua et al., 2007; Uysal and Ar, 2007; Zhao et al., 1998). Cr(VI) is mainly present in oxygenated waters, whereas Cr(III) is predominantly found in anoxic conditions (Padan et al., 2019). In solution, different species of Cr(VI) ( $\text{H}_2\text{CrO}_4$ ,  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , and  $\text{CrO}_4^{2-}$ ) and Cr(III) ( $\text{Cr}^{3+}$ ,  $\text{Cr}(\text{OH})^{2+}$ , and  $\text{Cr}(\text{OH})_3$ ) coexist in different proportions depending on the concentration and pH of the medium (Hu et al., 2016).

Chromium can usually be measured in aqueous solutions mainly by spectroscopic techniques. However, several research works have focused on the electroanalysis of Cr(VI) in aqueous solution to simplify the analysis, save time, and have continuous "in situ" measurement (Jin et al., 2016). Compton et al. used carbon electrodes modified with gold nanoparticles in inorganic acidic media for the reduction of toxic Cr(VI) into Cr(III) and its analytical determination (Kachooosangi and Compton, 2013; Welch et al., 2005).

On the other hand, the separation of Cr from the aqueous environment is important. Several methods to directly remove Cr(VI) from waters have been conducted, as well as the reduction of Cr(VI) to the less toxic Cr(III), prior to its removal. Among these methods include bio-reduction (Pradhan et al., 2017), chemical reduction (Alidokht et al., 2011), nanofiltration and microfiltration (Zolfaghari and Kargar, 2019), reverse osmosis (Gao et al., 2013), physical adsorption (Liu et al., 2019), and photocatalytic reduction (Chen et al., 2017; Sane et al., 2018). Nevertheless, most of these methods are complex and expensive, restricting their use. Accordingly, electrochemical reduction could be an attractive alternative since it can be selective, efficient, cleaner and cost effective, and the use of reducing reagents is not necessary (Almaguer-Busso et al., 2009).

Lately, indirect electroreduction has been proven in Cr(VI) reduction. In this method, the cathode, usually Fe, Cu, Al or Ti, among others, releases metal ions into the solution due to the anodic polarization that, in turn, acts as a reduction agent for Cr(VI) in the bulk of the solution (Barrera-Díaz et al., 2011). After direct or indirect electroreduction, the Cr(III) generated is precipitated by the increase of the solution pH to form  $\text{Cr}(\text{OH})_3$  or by complexing into the bulk solution via different complexing agents. However, these methods produce the deposition of precipitates on the electrode surface, impairing the electroreduction process (Yang et al., 2019; Yao et al., 2020).

The polymer enhanced ultrafiltration (PEUF) technique uses high molecular weight water soluble polymers to separate the ionic species from the aqueous solution. Indeed, some studies have shown that this technique is capable of removing Cr(VI) and Cr(III) (Sánchez et al., 2018, 2017).

There is great interest in using naturally occurring polymers for water remediation due to their biocompatibility. In this context, alginates are biopolymers from seaweed, consisting of an unbranched copolymer of (1→4)-linked  $\beta$ -D-mannuronic acid and  $\alpha$ -L-guluronic acid residues. If the uronic acid groups are in the acid form ( $-\text{COOH}$ ), the polysaccharide, called alginic acid, is insoluble in water. Otherwise, the sodium salt of alginic acid ( $-\text{COONa}$ ), or sodium alginate (SA), is soluble in water (Masuelli and Illanes, 2014).

SA has been used to remove metals such as Cs (Cho et al., 2018), Pb (Ren et al., 2016), Cu (Shuo et al., 2019), Ag, and Fe, among others (Li et al., 2013; Lu et al., 2015). This was possible due to the carboxyl groups of the SA molecular chain which can adsorb these metals (Karthik and Meenakshi, 2015; Li et al., 2019). The other characteristic that has been reported in the literature is its electrochemical properties. Recent studies have used SA to improve the electrochemical behavior of lithium batteries, obtaining excellent results because of its good charge transfer capacity (Liu et al., 2019; Zhang et al., 2019). Zhang et al. (2019) used SA as a binder solution for organic lithium ion batteries, obtaining excellent electrochemical performance when SA was used in different electrodes. This excellent performance was attributed to the presence of carboxylic and hydroxylic functional groups in the SA structure, which would promote faster electron transfer and facilitate lithium ion diffusion within the organic electrode. On the other hand, we have previously studied the electrochemical oxidation of arsenic species and its subsequent removal, using water-soluble polymers containing quaternary ammonium groups coupled with the PEUF technique. These water-soluble polymers were used as supporting electrolytes in the electro-oxidation of arsenic and as arsenic extracting agents in the PEUF technique (Sánchez et al., 2016, 2015).

In this work, we propose for the first time the use of acidic SA solution as an electrolytic medium for the electroreduction of Cr(VI) to Cr(III) using gold electrode and the subsequent removal of electro-reduced Cr(III)-SA aqueous solution using the PEUF technique.

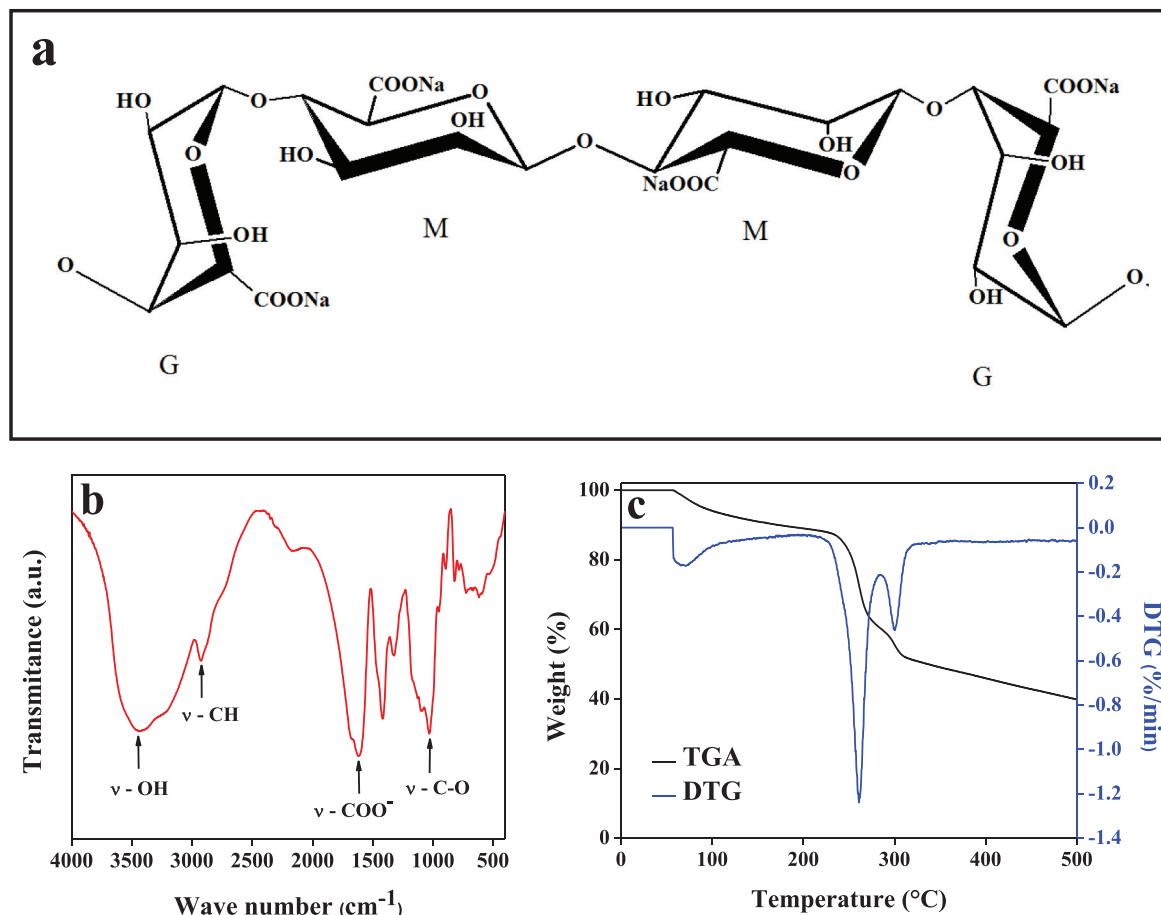
## 1. Materials and methods

### 1.1. Fractionation of SA by membranes

The SA (Fig. 1a) was obtained commercially (Sigma-Aldrich, USA). A sample of 10 mmol/L of SA was dissolved in 20 mL of milli-Q water and then fractionated by an ultrafiltration membrane with a molecular weight cut-off (MWCO) of 10 kDa (Merck-Millipore, Germany). The polymer fraction solutions were lyophilized (Liobras L101, Brazil).

### 1.2. Characterization of SA

The freeze-dried SA samples were analysed by Fourier Transform Infrared Spectroscopy (FT-IR, Bruker Tensor 27, USA) in the range of 4000–400  $\text{cm}^{-1}$ . The obtained absorption spectra were analysed with Origin 8 software (Origin Lab Corp., USA). The thermogravimetric analysis (TGA) was carried out on a Star System 1 thermo balance (Mettler Toledo, USA) in the range of 25 °C to 500 °C at a heating flow rate of 10 °C/min



**Fig. 1 – (a) Chemical structure of sodium alginate, where M corresponds to D-mannuronic acid and G corresponds to L-guluronic acid, (b) FT-IR spectrum of SA, and (c) thermogram of SA.**

under inert atmosphere (N<sub>2(g)</sub>, Linde, Chile). Subsequently, the first derivative of the TGA curve (DTG) was plotted to determine the inflection points which allowed a better interpretation of the results.

### 1.3. Electrochemical reduction of Cr(VI)

The electrochemical reduction of Cr(VI) was performed using a CHI 660B electrochemical analyser (CH Instruments, USA), using a conventional three-electrode system. The reference electrode was an Ag/AgCl electrode in 3 mol/L of KCl. A platinum wire and a platinum plate were used as the counter electrodes in linear sweep and bulk electrolysis, respectively. A gold disc (3 mm diameter, CH Instruments, USA) was used as the working electrode in linear sweep voltammetry, which was polished after each measurement to a mirror-like surface, using a standard electrode polishing kit (CH Instruments, USA). In bulk electrolysis, a gold plate working electrode (1 cm<sup>2</sup>) was used.

Linear sweep voltammetry was used for the reduction of Cr(VI) (Merck, Germany) in acidic SA solution using HNO<sub>3</sub> (Merck, Germany). The potential range used was -0.1 V to +0.80 V at a scan rate of 50 mV/sec. Different variables were studied to optimize the electroreduction process, such

as pH (2.0, 3.0, 4.0, and 5.0) and SA concentration (7.5, 10, and 25 mmol/L). Then, using the best conditions, a calibration curve from 0.10 to 0.60 mmol/L of Cr(VI) was performed. Additionally, the effect of the presence of Cr(III) (Merck, Germany) as an interferer at different Cr(VI):Cr(III) molar ratios (0.6:0.0; 0.6:0.2; 0.6:0.3; 0.6:0.4; 0.6:0.6) was studied. Finally, the effect of the scan rate on Cr(VI) reduction was analysed using different scan rates (10, 50, 100, 200, and 300 mV/sec). The quantitative reduction of Cr(VI) to Cr(III) was also studied through the bulk electrolysis technique in acidic SA solution. A solution containing 10 mmol/L of Cr(VI) and SA at pH 2.0 was submitted to exhaustive electroreduction ( $E_{\text{appl}} = 0.3$  V). The electrolysis was conducted in a one-compartment cell, without separation between the working electrode (gold, 1 cm<sup>2</sup>) and the auxiliary electrode (platinum, 1 cm<sup>2</sup>). After the electrolysis, the pH of the solution was monitored. Samples were taken at different time intervals and the remaining Cr(VI) in the solution was determined by linear sweep voltammetry. The calculation of the complete conversion of Cr(VI) to Cr(III) was obtained according to Faraday's law of electrolysis (Eq. (1)), resulting in a total applied charge of 3.00 Coulombs (Sánchez et al., 2015).

$$\text{Applied Charge} = n^{\circ}e^{-} \times \text{mol Cr} \times F \quad (1)$$

where  $n^{\circ}e^{-}$  corresponds to the number of electrons exchanged in the reduction reaction and  $F$  is Faraday's constant corresponding to 96,500 C.

The limit of detection (L.O.D.) and the limit of quantification (L.O.Q.) were calculated for linear sweep voltammetry of Cr(VI) according to Eqs. (2) and (3), respectively:

$$\text{L.O.D.} = (3 \times \sigma_{\text{Blank}})/m \quad (2)$$

$$\text{L.O.Q.} = (10 \times \sigma_{\text{Blank}})/m \quad (3)$$

where  $\sigma$  corresponds to the standard deviation of the blank and  $m$  is the slope of the calibration curve.

#### 1.4. Polymer-enhanced ultrafiltration

The PEUF equipment and procedure used in this work have been previously described (Sánchez et al., 2017, 2016; Sánchez and Rivas, 2011). In this work, the washing method was used, which consisted of a batch-like procedure wherein washing was performed with water at constant pH. After bulk electrolysis, the pH of the SA-Cr(III) solution was monitored and adjusted, and then, the solution was stirred for 1 hr at 20 °C, placed in the ultrafiltration cell, and washed with water at the same pH. PEUF was performed under a total pressure of 2.0 bars using an ultrafiltration membrane of regenerated cellulose (Merck-Millipore, Germany) with a MWCO of 10 kDa. The total volume in the cell was kept constant during the filtration process. Fractions of 10 mL were collected at different time intervals until a total volume of 100 mL. The chromium concentration in the filtrate was determined by atomic absorption spectrometry (AAS) using a Thermo M Series AA spectrometer (Thermo Scientific, USA). A blank analysis was performed using an acidic solution of SA (10 mmol/L) with Cr(VI) (0.60 mmol/L) that was not electrochemically reduced. The Cr(VI) uptake was systematically presented as the percentage of retention, i.e.,  $R$  (%), denoting the fraction of Cr(VI) remaining in the ultrafiltration cell (Eq. (4)).

$$R = (\text{Cr}_{\text{cell}}/\text{Cr}_i)100\% \quad (4)$$

where  $\text{Cr}_{\text{cell}}$  (mmol/L) is the concentration of Cr retained in the cell, and  $\text{Cr}_i$  (mmol/L) is the initial concentration of Cr. Otherwise, the filtration factor ( $Z$ ) was calculated according to Eq. (5):

$$Z = V_p/V_r \quad (5)$$

where  $V_p$  (L) corresponds to the permeate volume and  $V_r$  (L) is the retentate volume. Using the experimental data, we can plot a graph of the retention profile, in which  $R$  is represented as a function of  $Z$ .

## 2. Results and discussion

### 2.1. Characterization of SA

Fig. 1a shows the chemical structure of SA and Fig. 1b depicts the characteristic FT-IR signals of SA biopolymer. Accordingly, the absorption bands at  $3450\text{ cm}^{-1}$  correspond to the tension vibration of  $-\text{OH}$  groups. At  $2930\text{ cm}^{-1}$ , the C-H stretching of SA

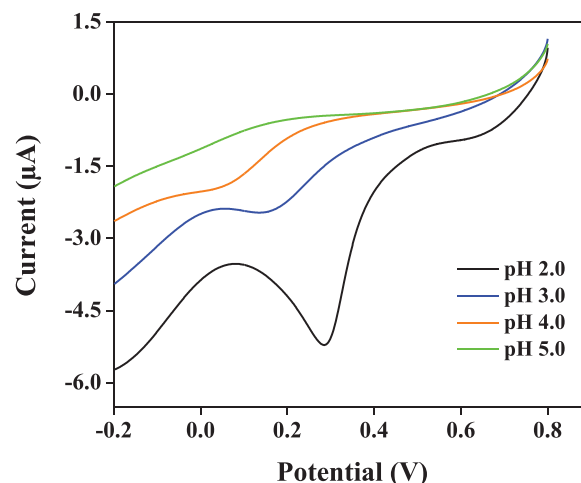


Fig. 2 – Linear sweep voltammetry of Cr(VI) in 10 mmol/L SA at different pH values and scan rate of 50 mV/sec.

appears, and two tension-vibration bands occur at  $1618\text{ cm}^{-1}$  and  $1440\text{ cm}^{-1}$ , corresponding to  $-\text{COO}$  groups. Additionally, a vibrational band associated with  $-\text{C}-\text{O}$  groups is observed at  $1050\text{ cm}^{-1}$  (Hu et al., 2018). This characterization confirms the purity of the SA polymer after fractionation by ultrafiltration. On the other hand, TGA analysis of SA shows three decomposition zones (Fig. 1c). The first decomposition zone, from 38 °C to 98 °C, corresponds to the loss of adsorbed water present in the SA sample. As the temperature increases, decarboxylation of the  $-\text{COOH}$  groups present in the biopolymer occurs, at a temperature range of 226 °C to 278 °C. The third decomposition zone, from 292 °C to 314 °C, corresponds to the cleavage of the SA polymer chains. The peaks displayed on the DTG curve show the maximum temperature at which each decomposition step occurs (69, 261 and 300 °C). This thermal behavior is characteristic of SA biopolymer (Tripathy and Singh, 2001).

### 2.2. Electrochemical methodology

#### 2.2.1. Optimization of electrochemical conditions

To determine the effect of pH on the electrochemical reduction of Cr(VI) in the presence of 10 mmol/L of SA,  $\text{HNO}_3$  was used to adjust the pH (Fig. 2). The choice of  $\text{HNO}_3$  was based on the work of Kachoosangi et al., 2013, wherein the authors compared different inorganic acids ( $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HClO}_4$ , 0.3 mol/L) in the electrochemical reduction of Cr(VI) by linear sweep voltammetry. They did not observe any signal in the presence of  $\text{HCl}$ , demonstrating that the chloride anion acts as an interferent in the reduction of Cr(VI). On the other hand, in the presence of  $\text{HNO}_3$ , they obtained a sharper signal and higher sensitivity compared to the other acids (Kachoosangi and Compton, 2013).

Fig. 2 shows the voltammograms of Cr(VI) reduction in the presence of SA at different pH values. These results showed that the lower the pH, the sharper and better defined the Cr(VI) reduction peak. Therefore, the increase of pH reduced the size of the peak until its disappearance. This effect of pH on Cr(VI) electroreduction is in concordance with the results previously reported by Kachoosangi et al., confirming that SA



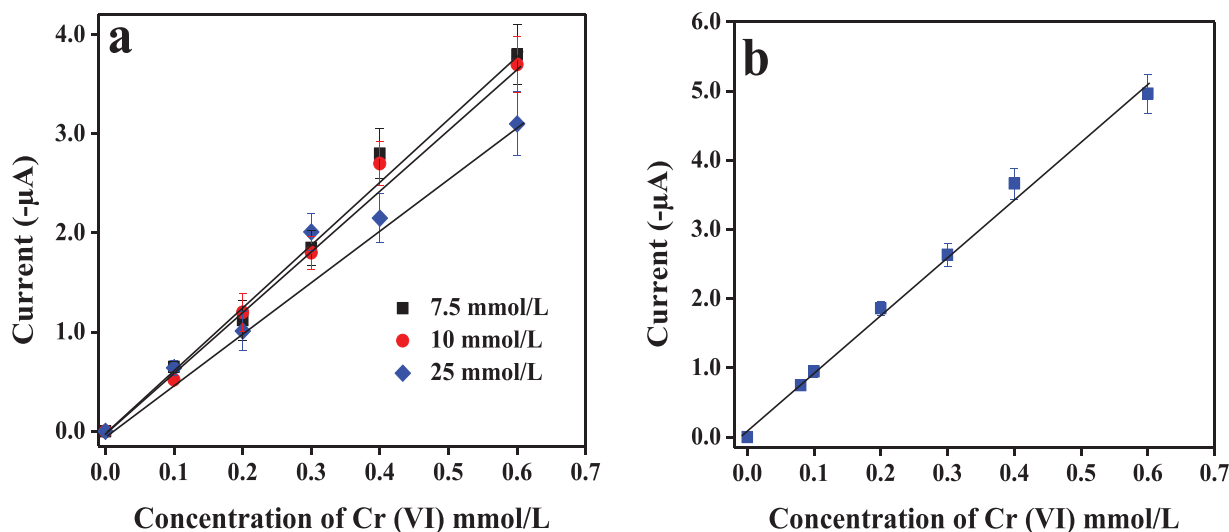
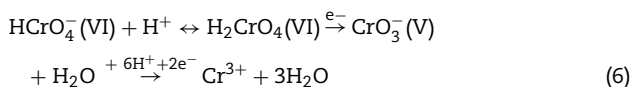


Fig. 3 – (a) Effect of SA concentration on Cr(VI) electro-reduction and (b) calibration curve in the range of 0.08 to 0.60 mmol/L Cr(VI).

solution with nitric acid is a good electrolytic medium and does not interfere in the electrochemical reduction of Cr(VI) (Kachooangi and Compton, 2013).

As was established, the reduction of hexavalent chromium is strongly influenced by the pH of the medium as well as the concentration of Cr(VI). There are different species of hexavalent chromium in solution:  $\text{H}_2\text{CrO}_4$ ,  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , and  $\text{CrO}_4^{2-}$ , depending on the two factors aforementioned. In alkaline pH, the dominant species in solution is  $\text{CrO}_4^{2-}$ ; in acidic medium, the dominant species is  $\text{HCrO}_4^-$ ; and at higher Cr(VI) concentration (above 5 mmol/L) in acid medium,  $\text{Cr}_2\text{O}_7^{2-}$  begins to predominate (Weng et al., 2007). Accordingly,  $\text{HCrO}_4^-$  is the predominant hexavalent chromium species present at the concentrations of this work (lower than 0.60 mmol/L). On the other hand,  $\text{HCrO}_4^-$  species can undergo protonation, generating molecular chromic acid ( $\text{H}_2\text{CrO}_4$ ). The reduction of hexavalent chromium could proceed with the uptake of  $1\text{e}^-$  forming pentavalent chromium ( $\text{CrO}_3^-$ ), and then with the uptake of 2 more  $\text{e}^-$ , the complete reduction into Cr(III) is reached, as suggested by Eq. (6) (Kachooangi and Compton, 2013).



To study the influence of the SA as the electrolytic medium, three different concentrations were used in the electroreduction of Cr(VI) (Fig. 3a). For all the studied concentrations (7.5, 10, and 25 mmol/L), it was possible to obtain well-defined reduction peaks with good linear regressions ( $R^2 = 0.995$ ,  $0.993$ , and  $0.988$ , respectively).

Considering that the SA polymer is poorly soluble in water (Masuelli and Illanes, 2014), which would cause fouling of the membrane in PEUF technique, low SA concentrations were chosen to favor the correct performance. Accordingly, 10 mmol/L of SA it was chosen to perform this work. Finally, under the optimal conditions (pH 2.0 and 10 mmol/L of SA), a calibration curve of Cr(VI) was performed in the range of 0.08 to 0.60 mmol/L, (Fig. 3b). The linear equation obtained was

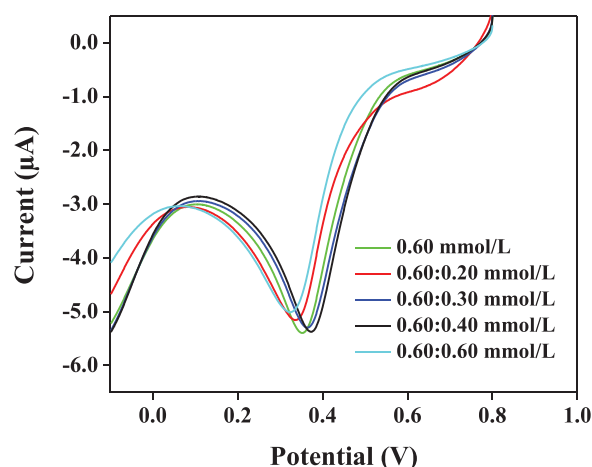


Fig. 4 – Effect of Cr(III) as an interferent in Cr(VI) analysis.

$y = 8373.6x + 107.8$  with a  $R^2$  of 0.995, and the calculated L.O.D. and L.O.Q. were 0.020 mmol/L and 0.068 mmol/L, respectively.

#### 2.2.2. Interference of Cr(III) on Cr(VI) detection

The interfering effect on the electroreduction of Cr(VI) in the presence of chromium Cr(III) was studied (Fig. 4). In nature, Cr(III) is found at a ratio up to 100 times higher than Cr(VI) (Welch et al., 2005), for this reason Cr(III) was considered as a possible interferent on the analysis of Cr(VI). It was possible to observe that Cr(III) did not interfere on the reduction of Cr(VI), demonstrating this analysis is specific for Cr(VI).

#### 2.2.3. Scan rate effect

To determine the effect of scan rate on the Cr(VI) electroreduction, a study in the range of 10 to 300 mV/s was performed. A solution of 0.60 mmol/L of Cr(VI) in the presence of 10 mmol/L SA at pH 2.0 was prepared. Fig. 5a shows that as the scan rate increases, the reduction current increases, and the potential

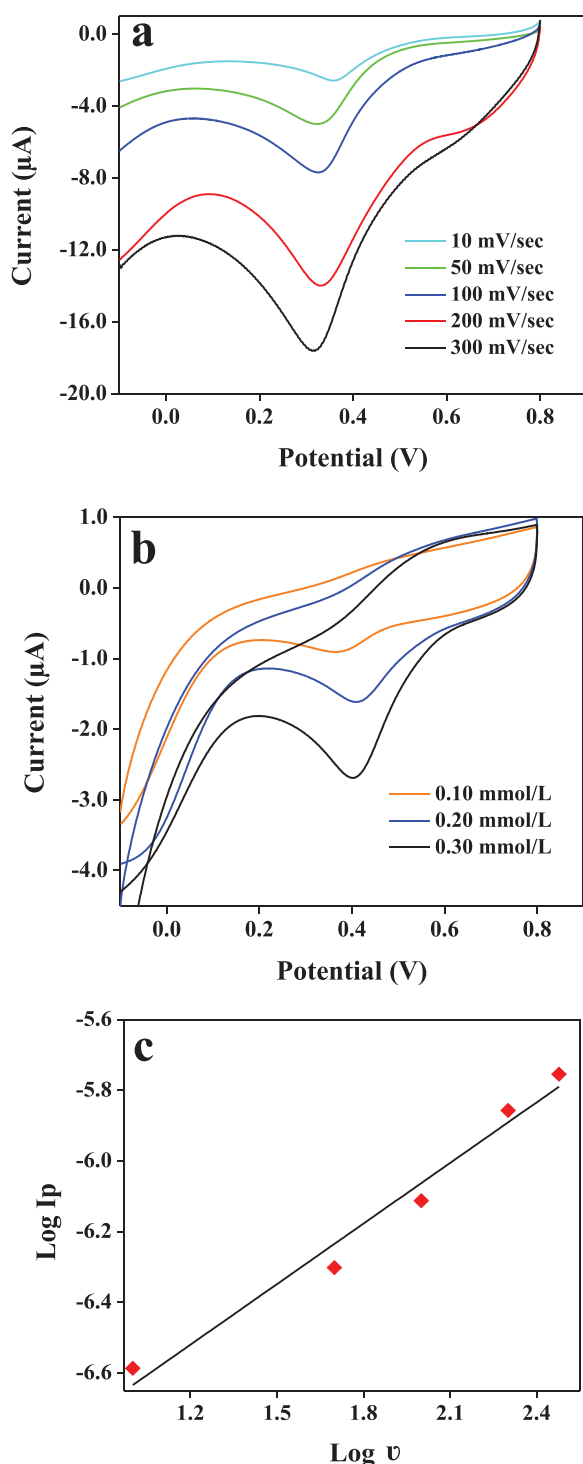


Fig. 5 – (a) Linear sweep voltammetry at different scan rates (10–300 mV/s). (b) Cyclic voltammetry at pH 2.0 in the presence of 10 mmol/L SA at a scanning rate of 50 mV/s. (c) Logarithmic plot of maximum current vs. scan rate for SA-Cr(VI).

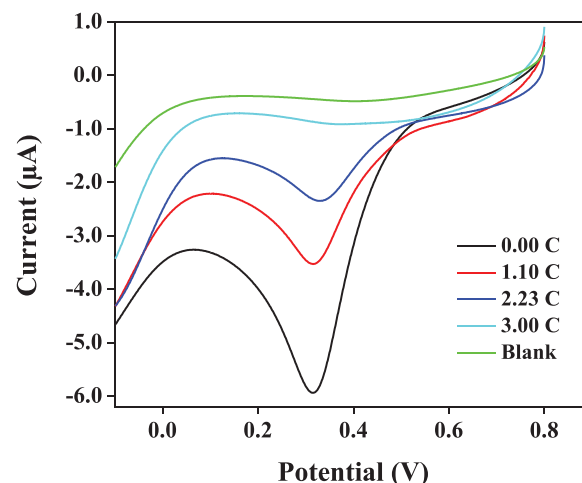


Fig. 6 – Voltammetric measurements of remnant Cr(VI) during bulk electroreduction study at a scan rate of 50 mV/sec. Blank is the signal obtained without Cr(VI).

is slightly shifted to lower values. The small change in potential could be due to adsorption or the formation of a double layer on the electrode surface, showing an irreversible nature of the reduced species (Purushothama et al., 2018). This irreversible behavior is demonstrated with the cyclic voltammetry technique at different Cr(VI) concentrations, which shows a reduction peak without the presence of an oxidation peak (Fig. 5b).

It has been reported that the slope value of the  $\log I_p$  versus  $\log v$  plot can establish the nature of the mass transport, i.e., equal to 0.50 and 1.0 for diffusional and adsorptive processes, respectively (Costa et al., 2017). The linear regression equation for the plot of  $\log I_p$  vs.  $\log v$  (Fig. 5c) is given by Eq. (7), with a slope of 0.571 and an  $R^2=0.974$ . The previous result indicates that the reduction reaction process is controlled by diffusion (Kingsley et al., 2016).

$$\log I_p (\mu A) = 0.571 \log v (mV/s) - 7.205 \quad (7)$$

### 2.3. Electroreduction of Cr(VI) to Cr(III) by bulk electrolysis

An exhaustive reduction of hexavalent chromium to trivalent chromium was performed by electrolysis, using a gold macro-electrode (1 cm<sup>2</sup>). A solution of 0.60 mmol/L Cr(VI) was prepared in the presence of 10 mmol/L SA in nitric acid as the electrolytic medium (pH 2.0). The electrolysis was performed at a potential of 0.3 V vs. Ag/AgCl electrode, which is the potential of maximum reduction. The reduction from Cr(VI) to Cr(III) was followed in situ by linear sweep voltammetry (Fig. 6). The pH of the SA-chromium solution during the process was monitored, without showing important variations. This could be due to the presence of carboxyl and hydroxyl functional groups in the SA polymer which interact with the protons of the solution keeping the pH constant. During the progress of the electrolysis, the time to reach the theoretical charge (C) for the complete conversion of Cr(VI) to Cr(III) was recorded (Table 1). The faradaic efficiency was determined from the theoretical and experimental applied charge, showing a value of approximately 0.9. This value demonstrates excellent efficiency in the conversion of Cr(VI) to Cr(III), reaching

**Table 1 – Evolution of the parameters during the electrolysis of SA-Cr(VI) solution in acidic media.**

Experimental concentration Cr(VI) (mmol/L)	Theoretical applied charge (C)	Experimental applied charge (C)	Total time of electrolysis (min)	% conversion Cr(VI) to Cr(III)	Faraday efficiency
0.64	0.0	0.0	0.0	0	0.00
0.35	1.7	1.1	152	45	0.66
0.21	2.5	2.2	437	67	0.90
0.05	3.4	3.0	680	92	0.88

92% of conversion (Table 1). During the electrolysis, the slight deposition of a precipitate was also observed on the golden macroelectrode surface, with the characteristic green color of Cr(III). This phenomenon would correspond to the formation of chromium hydroxide ( $\text{Cr}(\text{OH})_3$ ), due to a possible increase of the pH near the electrode surface, as a consequence of the electroreduction of water (Hu et al., 2017). The formation of this precipitate produces a decrease in the area available for the reduction reaction, which could explain the increase in the time of electrolysis and that the faradaic efficiency does not reach the unity value (van Genuchten et al., 2017; Yang et al., 2019).

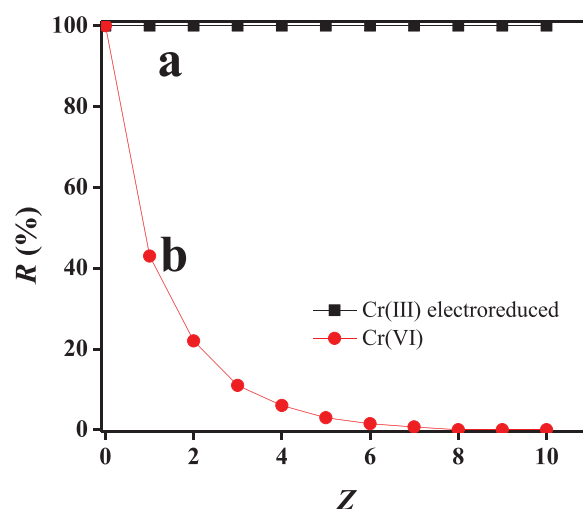
#### 2.4. Removal of electroreduced chromium by PEUF technique

Previous studies have reported the efficient extraction of arsenic species using various water-soluble poly-quaternary ammonium salts as an electrolytic medium in bulk electrolysis, and as complexing reagents in the PEUF technique (Sánchez et al., 2015, 2010; Sánchez and Rivas, 2010). In the present study, we developed a novel chromium remediation strategy, combining the electroreduction of Cr(VI) to Cr(III) in the presence of SA in acidic media with the PEUF technique. In this work, it was demonstrated that the acidic solution of SA is a good electrolytic medium, as well as an adsorbent agent for the removal of chromium ions. This behavior could be explained by the presence of  $\text{COO}^-$  groups in its structure, making SA a good alternative as the extracting polymer in the PEUF technique. Fig. 7 shows the retention percentage (R%) of chromium as a function of filtration factor (Z). As it is possible to observe, Cr(III) (produced during the electrolysis) was almost completely retained, while Cr(VI), in its oxy-anionic form, did not interact with the polymer and therefore, not retained during the PEUF process.

These preliminary experiments confirm that the combination of the electroreduction of Cr(VI) to Cr(III) with the PEUF technique represents an efficient and promising approach to remove chromium in contaminated water.

### 3. Conclusions

Cr(VI) was successfully electroreduced to Cr(III) in acidic SA solution as the electrolytic medium. The effect of different variables on Cr(VI) reduction was studied. The acidic pH favored the electrochemical reduction of Cr(VI) probably due to the large presence of protons, which could contribute to the ionic driving force for the chromium electroreduction. The electrochemical analysis showed that the current intensity



**Fig. 7 – (a) Removal profile of electroreduced chromium in acidic SA solution as the electrolytic medium and extracting agent. (b) Removal profile of Cr(VI) in acidic SA solution which was not electroreduced.**

was proportional to the Cr(VI) concentration, and the process was irreversible and controlled by diffusion. Linear sweep voltammetry allowed to determine the Cr(VI) concentration without the interference of Cr(III), showing that this method can be a selective alternative for Cr(VI) determination. SA solution with nitric acid proved to be a good electrolytic medium to reach the complete reduction of Cr(VI) by electrolysis and an excellent extracting agent for the removal of Cr(III) by the PEUF technique.

This work demonstrated that combining electrochemistry and membrane separation techniques could be a promising tool for water remediation on a larger scale.

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