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Transport of Trivalent and Hexavalent Chromium through Different Ion-Selective Membranes in Acidic Aqueous Media

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ABSTRACT

The aim of this work was to evaluate the transport of trivalent and hexavalent chromium through anion- and cation-selective membranes using two- and three-compartment electrodialysis cells. Tests were done with acidic solutions of trivalent chromium ions, Cr^{3+} , and hexavalent chromium ions, $\text{Cr}_2\text{O}_7^{2-}$. In each situation the transport of metallic ions through the membrane was evaluated. In the tests with trivalent chromium, Nafion 417 and Selemion CMT cation-selective membranes were used, and in the tests with hexavalent chromium, Selemion AMT membrane was used. The influence of SO_4^{2-} ions and of the concentration of H^+ ions in the solutions was also analyzed. Results showed the oxidation of the Cr^{3+} ion at the anode and the reduction of the $\text{Cr}_2\text{O}_7^{2-}$ ion at the cathode. The maximum yield in the process was reached when hexavalent chromium solutions were used in the absence of sulfate ions and a Selemion AMT membrane in a three-compartment cell.

INTRODUCTION

Electrodialysis is a membrane separation technique based on the selective migration of aqueous ions through ion-selective membranes, using a direct current electrical potential as the driving force. This technique accomplishes

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the deionization of an aqueous stream producing a deionized stream (dialysate) and a concentrated stream (concentrate). Electrodialysis, as well as other membrane separation techniques, has been employed in a variety of industrial applications in the past few decades. Some proposed applications of electrodialysis include desalination of sea and brackish waters and concentration of sea water prior to evaporation (1–3), removal of salts and acids from solutions in the pharmaceutical (4) and food-processing (5) industries, separation and reconcentration of acids (6, 7), water cleanup (8, 9), recovery of metals and salts from industrial wastewater (10–15) and from radioactive wastes (16).

The application of electrodialysis in wastewater treatment seems promising since the technique allows not only the separation but also the recuperation of particular kinds of contaminants present in the wastes, such as metallic ions. On the other hand, the utilization of precipitating agents as in ordinary waste disposal techniques is not necessary, thus avoiding the production of sludge. Of course, electrodialysis is limited to eliminating only ionic species from wastes. Audinos (17) presented a broad discussion on the application of electrodialysis in this field. The use of electrodialysis in wastewater treatment, however, is constrained by specific requirements concerning the solutions. These requirements include the absence, or at least an adequate level, of fouling and scaling substances, suspended particulate matter and oxidizing material, and an adequate range of concentration of the total ions in solution (15, 18).

Literature suggests the application of electrodialysis in the recovery of such metals as nickel (14), copper (15), chromium (19, 20), zinc (12), and gold (21) from spent metal plating baths and from metal plating rinsewaters. In some situations a modified electrodialysis system is proposed, where the electrodialysis stack has a limited number of membranes and the electrodes are in contact with the solutions under treatment. Audinos (17) defined this technique as electroelectrodialysis rather than electrodialysis. Gavach (13) suggested the use of electroelectrodialysis to obtain reconcentrated acid from a mixture of acid and metal salt. He also pointed out some disadvantages of electroelectrodialysis compared to electrodialysis, including the higher investment costs. However, when dealing with metals in solution, electroelectrodialysis has the advantage of allowing the recuperation of the metal as a metallic electrodeposit.

The purpose of this work was to investigate some aspects of the use of ion-selective membranes in the separation and concentration of trivalent and hexavalent chromium in acidic aqueous media. To accomplish this, different ion-selective membranes were tested and different sets of electroelectrodialysis cells were proposed. The transport of chromium was evaluated in terms of current efficiency (c_e) and percent extraction (% extraction) defined as:

$$c_e = F \frac{(eq_0 - eq_f)}{it} \times 100 \quad (1)$$

$$\% \text{ Extraction} = \frac{(eq_0 - eq_f)}{eq_0} \times 100 \quad (2)$$

where F is Faraday's constant, i is the current, t is the elapsed time of the experiment, and eq is the number of ionic equivalents of chromium in the cathodic compartment of the two-compartment cell used in the experiments with trivalent chromium, in the anodic compartment of the two-compartment cell used in the experiments with hexavalent chromium, and in the intermediate compartment in the experiments with a three-compartment cell. The subscripts 0 and f denote the corresponding values at the beginning and at the end of the experiment, respectively.

EXPERIMENTAL

Materials

The chemicals were all reagent grade and were used without further purification. The acidic solutions were prepared from distilled and deionized water with sulfuric acid (Vetec). Basic chromium(III) sulfate (Fluka) and chromic anhydride (Merck) were used in the preparation of trivalent and hexavalent chromium solutions, respectively. Two different cation-selective membranes [Nafion 417 (a registered trademark of E. I. du Pont de Nemours & Co.) and Selemion CMT (a registered trademark of the Asahi Glass Co)] and one anion-selective membrane (Selemion AMT) were used. The electroelectrodialysis cell was made in transparent acrylic and was modular, thus allowing the use of two or three compartments, as shown in Fig. 1. The cathode

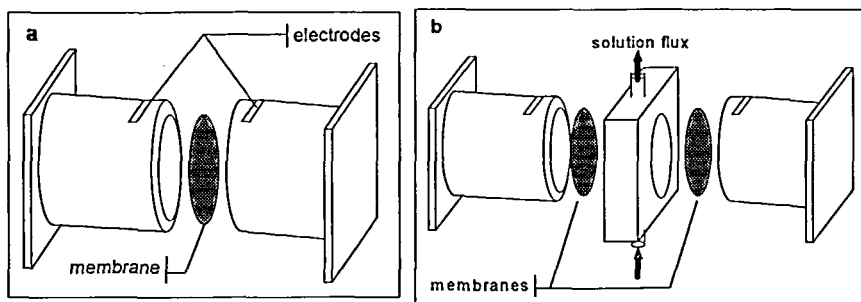


FIG. 1 Two (a) and three (b) compartment electrodesdialysis cells used in the experiments with trivalent and hexavalent chromium.

was made from a brass foil in order to allow the visual inspection of an eventual chromium electrodeposition, and had the same area as the membrane. The anode was a platinum sheet. A direct current supply was employed in all the experiments. When necessary, pumping of the solutions was made with a diaphragm pump having a flow rate of $220 \text{ mL}\cdot\text{min}^{-1}$.

Methods

Trivalent Chromium

In the first stage of the work, the transport of trivalent chromium in both cationic membranes (Nafion 417 and Selemion CMT) was evaluated. Trivalent chromium solutions were 3.0 or $1.7 \text{ g}\cdot\text{L}^{-1} \text{ Cr}^{3+}$ in dilute sulfuric acid at different concentrations. All the experiments were galvanostatic, with current densities of 40 or $20 \text{ mA}\cdot\text{cm}^{-2}$. The temperature was kept at $25 (\pm 3)^\circ\text{C}$. Two different electroelectrodialysis cells were used, as shown in Fig. 1.

In the two-compartment cell, the $0.1 \text{ N H}_2\text{SO}_4$ solution containing Cr^{3+} was placed in the anodic compartment of the cell and the cathodic compartment was filled with $0.1 \text{ N H}_2\text{SO}_4$ without chromium in order to promote the migration of Cr^{3+} ions toward the cathode during the experiment. In this situation, stirring of the solutions possibly occurred due to gas evolution at both electrodes. The initial chromium concentration in the anodic compartment was $3.0 \text{ g}\cdot\text{L}^{-1}$ and the current density was $40 \text{ mA}\cdot\text{cm}^{-2}$. The membrane used in this cell was Nafion 417.

In the three-compartment cell, the solution containing chromium was pumped through the intermediate compartment and the anodic and cathodic compartments contained sulfuric acid solutions without chromium. In this situation, the concentration of chromium in the intermediate compartment solutions was $1.7 \text{ g}\cdot\text{L}^{-1}$. Current density was reduced from 40 to $20 \text{ mA}\cdot\text{cm}^{-2}$ and the duration of the experiment was doubled in order to minimize heating of the solution due to the Joule effect. These values of current density and concentration of chromium were kept unchanged in all further experiments. Different concentrations of sulfuric acid were tested, and Nafion 417 and Selemion CMT cation-selective membranes were employed.

Hexavalent Chromium

The preparation of hexavalent chromium solutions was done by dissolving anhydrous chromic acid both in 0.1 N sulfuric acid or directly in distilled water. The chromium concentration was $1.7 \text{ g}\cdot\text{L}^{-1}$ and the current density used in all the experiments was $20 \text{ mA}\cdot\text{cm}^{-2}$. Since hexavalent chromium is an anion ($\text{Cr}_2\text{O}_7^{2-}$), the Selemion AMT anion-selective membrane was used in these experiments. Two- and three-compartment electroelectrodialysis cells

were used. In the two-compartment cell, hexavalent chromium was placed in the cathodic compartment in order to promote its migration toward the anode and the anodic compartment initially contained pure dilute sulfuric acid. As in the experiments with trivalent chromium, when using the three-compartment cell, the solution containing chromium was pumped through the intermediate compartment, and pure dilute sulfuric acid was used in the anodic and cathodic compartments.

RESULTS AND DISCUSSION

Trivalent Chromium

Figure 2 shows the transport of ions expected to occur with trivalent chromium in the two- and three-compartment cells. Of course, transport of protons through the membrane also occurs, since membranes do not distinguish between Cr^{3+} and H^+ . This fact implies a lower current efficiency in the process.

In the two-compartment cell, percent extraction of trivalent chromium after 180 minutes was 12.5% and the current efficiency in the process was 10.9%. In the two-compartment cell, the Cr^{3+} ions are directly in contact with the anode. This promotes the oxidation of the trivalent chromium to hexavalent chromium. The appearance of a typical yellow coloration in the solution during the experiment confirmed the occurrence of oxidation. This reaction is undesirable since it limits the amount of trivalent chromium available for migration through the cation-selective membrane. As a consequence, the current becomes predominantly transported by protons and the current efficiency becomes still lower.

As can be seen in Fig. 2, the three-compartment cell avoids the contact of trivalent chromium with the anode. The experiments in which the three-compartment cell was used showed no oxidation of chromium to the hexavalent state. As a consequence, higher values of percent extraction and current

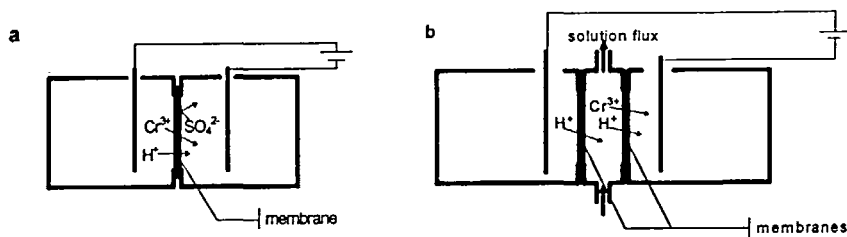


FIG. 2 Schematic transport of ions expected to occur in the experiments with trivalent chromium in two (a) and three (b) compartment electrochemical cells.

TABLE 1
Percent Extraction and Current Efficiency in Electrodialysis of Trivalent Chromium in a Three-Compartment Cell (after 360 minutes with a current density of $20 \text{ mA}\cdot\text{cm}^{-2}$)

Acidic solution	Nafion 417 membrane		Selecion CMT membrane	
	% Extraction	c_e (%)	% Extraction	c_e (%)
H ₂ SO ₄ , 1.0 N	3.37	3.62	0	0
H ₂ SO ₄ , 0.1 N	24.4	23.8	14.9	14.6
H ₂ SO ₄ , pH 2.6	16.7	16.6	—	—

efficiency were obtained. Table 1 presents data obtained from the three-compartment cell. Different concentrations of sulfuric acid were used, in order to analyze the effect of the concentration of the protons in the solution.

The highest values of current efficiency and percent extraction were obtained when using 0.1 N H₂SO₄ and Nafion 417 membranes, with a decrease in both the parameters in more concentrated and more diluted sulfuric acid. This point leads to the question of trivalent chromium solubility in aqueous media. As the pH of an acidic aqueous solution of trivalent chromium is increased, its solubility decreases with the precipitation of different oxides and hydroxides. There is still a question whether chromium hydroxide is a definite compound or a mixture of hydrates (22). Furthermore, Cr(III) is characterized by a tendency to form polynuclear complexes in neutral or slightly acidic solutions. These complexes range from dimers through polymers of colloidal dimensions to precipitated Cr(III) hydroxide (22). This suggests that the decrease in the transport of chromium through the membrane when the proton concentration is lowered may be due to the formation of these complexes of hydroxides, which can have a fouling or scaling effect on the membrane. On the other hand, a very high concentration of protons could show a strong competitive effect with the chromium due to its high ionic mobility, thus also decreasing the transport of the metal ions through the membrane. Sundstrom and Klei (23) commented that the preferential removal of one ionic species over others is a common phenomena in electrodialysis and is a complex function of pH, membrane nature, and polarization.

Hexavalent Chromium

The transport of ions expected to occur in the two-compartment cell for hexavalent chromium is shown in Fig. 3. This configuration follows the model proposed by Audinos (17) for the recuperation of chromium from effluents of chroming baths by electrodialysis. This cell configuration would permit the concentration of chromic acid in the anodic compartment because

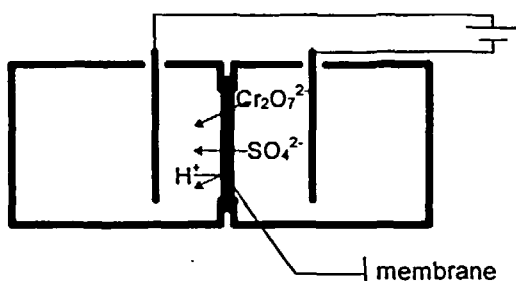


FIG. 3 Schematic transport of ions expected to occur in the experiments with hexavalent chromium in the presence of sulfate ions in a two-compartment electro dialysis cell.

oxygen evolution takes place at the anode with proton production. The electro-deposition of metallic ions eventually present in the cathodic solution would also be expected. Results showed, however, that the cathode promoted reduction from hexavalent to trivalent chromium and no electrodeposition of the metal, thus leading to an accumulation of Cr^{3+} ions in the cathodic solution. In analogy to experiments with the two-compartment cell for trivalent chromium, this effect impedes further transport of chromium through the membrane. In spite of this, the Selemion AMT membrane seems more permeable to $\text{Cr}_2\text{O}_7^{2-}$ ions than either the Nafion 417 or the Selemion CMT membranes to Cr^{3+} ions. After 240 minutes, the percent extraction of hexavalent chromium in the cathodic compartment was 61.0%. From then on, the cell voltage

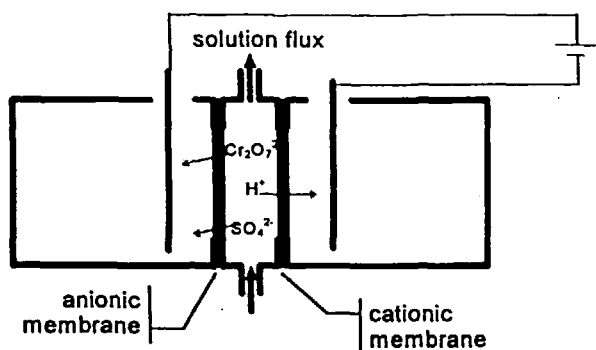


FIG. 4 Schematic transport of ions expected to occur in the experiments with hexavalent chromium in the presence of sulfate ions in a three-compartment electro dialysis cell.

TABLE 2
Percent Extraction and Current Efficiency in Electrodialysis
of Hexavalent Chromium in a Three-Compartment Cell
with a Selemion AMT Anion-Selective Membrane
(after 360 minutes with a current density of $20 \text{ mA}\cdot\text{cm}^{-2}$)

Acidic solution	% Extraction	c_e (%)
CrO_3 in 0.1 N H_2SO_4	54.6	17.9
CrO_3 in distilled water	82.3	25.3

began to rise since most chromium remaining in the cathodic compartment was in the trivalent state.

The three-compartment cell was also used with hexavalent chromium in order to avoid electrode reactions of chromium. Figure 4 shows the transport of ions in this cell. The use of one cation-selective membrane is necessary to avoid the depletion of protons in the cathodic compartment due the hydrogen evolution reaction, which leads to an increase in the pH and a rise in the electrical resistance of the system. Table 2 presents percent extraction and current efficiency after 360 minutes of experiment for CrO_3 dissolved both in 0.1 N sulfuric acid and in distilled water.

The transport of chromium is clearly more effective in the absence of sulfate ions. As in the case of trivalent chromium, competitive migration of sulfate ions and dichromate ions seems to be the reason for this behavior.

CONCLUSIONS

The drawback of using two-compartment cells instead of three-compartment cells for both trivalent and hexavalent chromium has been clearly demonstrated because electrode reactions of oxidation and reduction of the chromium inhibits further transport of the metal ions through the respective membranes. The efficiency of electrodialysis of trivalent chromium markedly decreases when the pH decreases due to the fact that the protons in solution have a significantly higher transport number than chromium ions. In the same way, the transport of the hexavalent chromium is more effective in the absence of sulfate ions. Transport of hexavalent chromium in an anion-selective membrane is more effective than transport of trivalent chromium in either of the cation-selective membranes tested.

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