

Research Article

Study of Chromium Removal by the Electrodialysis of Tannery and Metal-Finishing Effluents

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The metal-finishing and tannery industries have been under strong pressure to replace their current wastewater treatment based on a physicochemical process. The electrodialysis process is becoming an interesting alternative for wastewater treatment. Electrodialysis is a membrane separation technique, in which ions are transported from one solution to another through ion-exchange membranes, using an electric field as the driving force. Blends of polystyrene and polyaniline were obtained in order to produce membranes for electrodialysis. The produced membranes were applied in the recovery of baths from the metal-finishing and tannery industries. The parameter for electrodialysis evaluation was the percentage of chromium extraction. The results obtained using these membranes were compared to those obtained with the commercial membrane Nafion 450.

1. Introduction

Over the past few decades, there has been increased concern for the preservation of water resources. Industrial activities have led to widespread heavy metal contamination of soils and natural waters. Among the various sources of water contamination, the electroplating industry stands out as one of the most important, because it generates a considerable volume of effluents containing high concentrations of metal ions and, often, high concentrations of organic matter [1]. Another aggravating factor is that the traditional process for the treatment of these effluents, not very efficient and in some cases totally inefficient, produces dangerous solid waste (electroplating sludge), which should, therefore, be disposed of in appropriate landfills.

The most commonly used technology for the treatment of effluents is the physicochemical one, followed by units of biological treatment, usually consisting of activated sludge or aerated lagoon systems [2]. These conventional treatments are generally not able to reduce all the polluting parameters. Chemical Oxygen Demand (COD), chlorides, sulfates, and chromium often do not reach the required limits [3].

In this context, the leather and metal-finishing industries urge researchers to investigate new technologies for the recovery or recycling of chemical wastewater [4]. Because of their toxicity, these effluents cannot be rejected without pretreatment in the environment [5, 6].

Membrane technology has become increasingly attractive for wastewater treatment and recycling [7]. The main advantage of a membrane process is that concentration and separation are achieved without changing the physical state or using chemical products. Because of their modularity, membrane techniques in general and electromembrane techniques in particular are very well adapted to pollution treatment at its source; within this process, the electrodialysis process is becoming a good alternative when compared to the traditional methods of wastewater treatment [8, 9].

Electrodialysis (ED) is a membrane separation process based on the selective migration of aqueous ions through an ion-exchange membrane as a result of an electrical driving force. The transport direction and rate for each ion depend on a number of conditions, such as, its charge, mobility, relative concentrations, and applied voltage. Ion separation

is closely associated with the characteristics of the ion-exchange membrane, especially its permselectivity. ED was first used for the desalination of saline solutions, but other applications, such as, the treatment of industrial effluents, have gained importance [10, 11].

The purpose of this study is the investigation of the transport of some ions through synthesized membranes and a commercial one by electro dialysis. For the tannery effluents, photoelectrochemical oxidation (PEO) processes were previously used to degrade organic matter [12–14].

2. Experimental

For this study, two different real effluents were collected at two industries in the Southern Brazil. One effluent was collected at the discharge point of the conventional effluent treatment plant (CET) of a tannery plant. This plant carries out all the industrial processes from raw hides to finished leather. This effluent was then photoelectrooxidized for 24 hours and then treated by ED. A scheme of the PEO system used in this work is shown in Figure 1. It is made up of two serial, one liter PVC electrolytic reactors.

A 400 W high-pressure mercury-vapor lamp was used as a light source. Before each experiment, the UV light was turned on for 15 min to allow the UV energy to become stable. Two pairs of electrodes were used. The cathode and anode were DSA (70TiO₂/30RuO₂). The electrode area inside the cell was 118 cm². During the experiments, the reactor was operated in a batch recirculation mode. The effluent was recirculated at a flow rate of 4 L·h⁻¹, and 50 L effluent was treated by PEO for each experiment. The photoelectrochemical oxidation experiments were carried out using a DC power supply with an applied current density of 20 mA cm⁻².

In the metal-finishing plant, the effluent was also collected at the discharge point of the conventional effluent treatment plant (CET). The chromium concentrations were 0.5 ppm for the tannery effluent and 60 ppm for the metal-finishing effluent.

2.1. Membranes. The membranes were prepared by mixing conventional polymer (HIPS) with conducting polymers polyaniline (PAni). Two different mixing methods were tested to evaluate the effect of the production method. Dopants for polyaniline (PAni), camphorsulfonic acid (CSA), and p-toluenesulfonic acid (p-TSA) were also used.

HIPS and PAni were dissolved in 20 mL of tetrachloroethylene. After dissolution, PAni was dispersed in an HIPS polymeric matrix for 30 minutes. This dispersion was performed at 1,000 rpm in a mixer (Fisaton). The membranes were molded on glass plates using a laminator to keep thickness constant, and the solvent evaporated slowly for 24 hours under room temperature. The membranes were referred to as MCS and MTS.

2.2. Membrane Characterization

2.2.1. Infrared Spectroscopy. The samples were prepared with potassium bromide (KBr) powder. All of the samples were

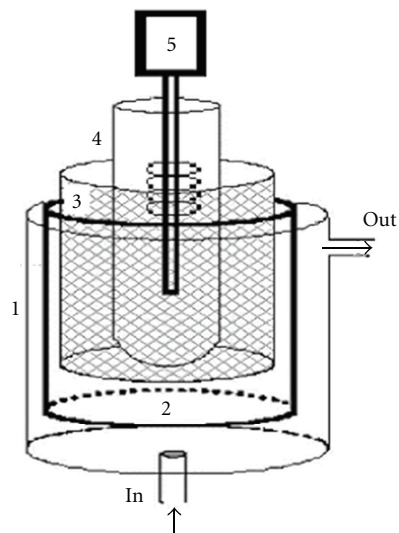


FIGURE 1: Schematic representation of PEO system: (1) PVC reservoir; (2) titanium oxide cathode; (3) titanium oxide recovered with TiO₂/RuO₂ anode; (4) quartz tube; (5) mercury steam lamp.

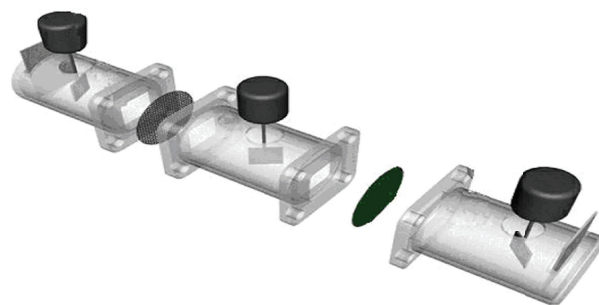


FIGURE 2: Three-compartment cell used for electro dialysis.

analyzed using an FTIR Perkin Elmer spectrometer model Spectrum 1000. The spectra were recorded in the spectral range of 400–4,000 cm⁻¹.

2.2.2. Swelling. Excess water was removed with a paper filter, and the membranes were weighed and kept in the oven at 80°C for 10 hours and then weighed again. The uptake of water was determined by the mass difference between the wet and the dried membranes (after heating at 80°C). Water absorption is expressed in percentage.

2.2.3. Morphology. Scanning electron micrographs of the membranes' surface were obtained using a microscope (Philips XL20) after the samples were sputter-coated with gold.

2.2.4. Electro dialysis. The membranes were synthesized (MTS and MCS) [15–17] and the commercial membrane (Nafion 450) was used as a cation selective membrane. Selemion AMV was used as an anion selective membrane. All of the membranes were maintained in contact with the solutions for 48 h in order to achieve equilibrium.

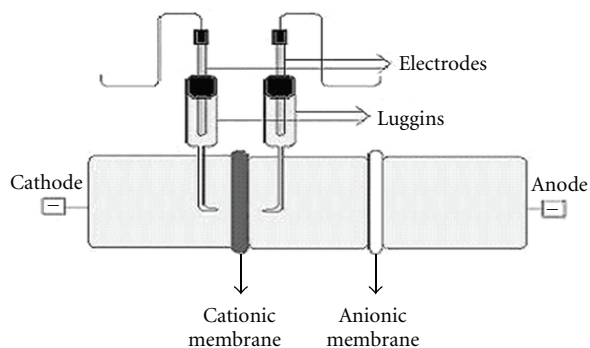


FIGURE 3: Three-compartment cell used to determine polarizations curves.

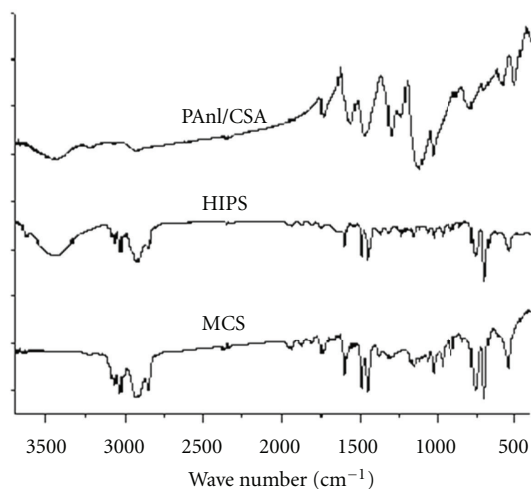


FIGURE 4: FTIR spectrum of PANi/CSA, HIPS sample, and MCS membrane.

The membranes were also equilibrated in deionized water at room temperature for 24 hours, with the aim of testing the hydrophilic behavior of $-\text{SO}_3^-$ from the doping acid that was used in polyaniline.

The electro dialysis experiments were performed using a three-compartment cell with a capacity of 200 mL each, as shown in Figure 2. A platinumized titanium electrode was used as the anode and cathode. A Selmion AMT anionic membrane was utilized and the cationic membranes were the synthesized membranes (MCS and MTS) and Nafion 450. The area of the membranes was 16 cm^2 and all the experiments were galvanostatic, with a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$. All of the electro dialysis experiments were carried out during 180 minutes.

The evaluation of the electro dialysis process was expressed in percent extraction, that is, how much of the ion in question was transferred from the diluted to the concentrated compartment:

$$\text{Pe \%} = \frac{M_i - M_f}{M_i} \times 100, \quad (1)$$

where Pe is the percent extraction (%), M_i is the ion concentration considered in the diluted compartment in

TABLE 1: Solutions used in electro dialysis tests for recovery of metals tannery and metal-finishing effluents.

Experiment	Cathodic compartment	Intermediary compartment	Anodic compartment
1	0.1 M Na_2SO_4	Tannery effluent photoelectro-oxidized with 20 A and 5 h	0.1 M Na_2SO_4
2	0.1 M Na_2SO_4	Metal-finishing effluent	0.1 M Na_2SO_4

TABLE 2: Thickness and swelling of the membranes.

Membrane	Thickness (mm)	Swelling (%)
MCS	0.20–0.25	13.6
MTS	0.20–0.25	12.9
Nafion 450	0.40	28.6

time zero, and M_f is the ion concentration considered in the diluted compartment at the final time.

Table 1 shows the solution's distributions that were used in the experiments.

2.2.5. Polarization Curves. Current-voltage curves (CVCS) were obtained in galvanostatic mode using a classical three compartment cell [18, 19]. This cell was composed of three symmetrical 200 cm^3 half cells. These compartments were separated by gaskets, which clamp the membrane. In the geometrical center of the gaskets there was a cylindrical hole. The working area of the AMV membrane was 16 cm^2 . Two Ag/AgCl electrodes, immersed in Luggin's capillaries, allowed the measurement of the potential difference between the two sides of the membrane. Mechanical stirrers were placed in each compartment. The same solutions were used on both sides of the membrane. The electrical current was supplied with two platinum electrodes (Figure 3). Electric current was applied using a DC power source for 120 seconds. The curves were obtained by potential measurements through the membrane corresponding to the applied current.

3. Results and Discussion

3.1. Thickness and Swelling. Table 2 shows the thickness and swelling of the membranes produced for this study and of the Nafion 450 membrane.

The swelling capacity of the membrane affects not only its dimensional stability but also its selectivity, electric resistance, and hydraulic permeability. Dimensional stability increases as the polymer affinity for water decreases. Conversely, as the polymer affinity for water increases, ionic transport resistance decreases [20].

Membranes that use CSA as a doping acid show slightly greater swelling than other membranes. However, the Nafion 450 membrane showed much greater swelling than the synthesized membranes. This difference may be associated with the fact that Nafion is a supported membrane and is thicker than the membranes under study.

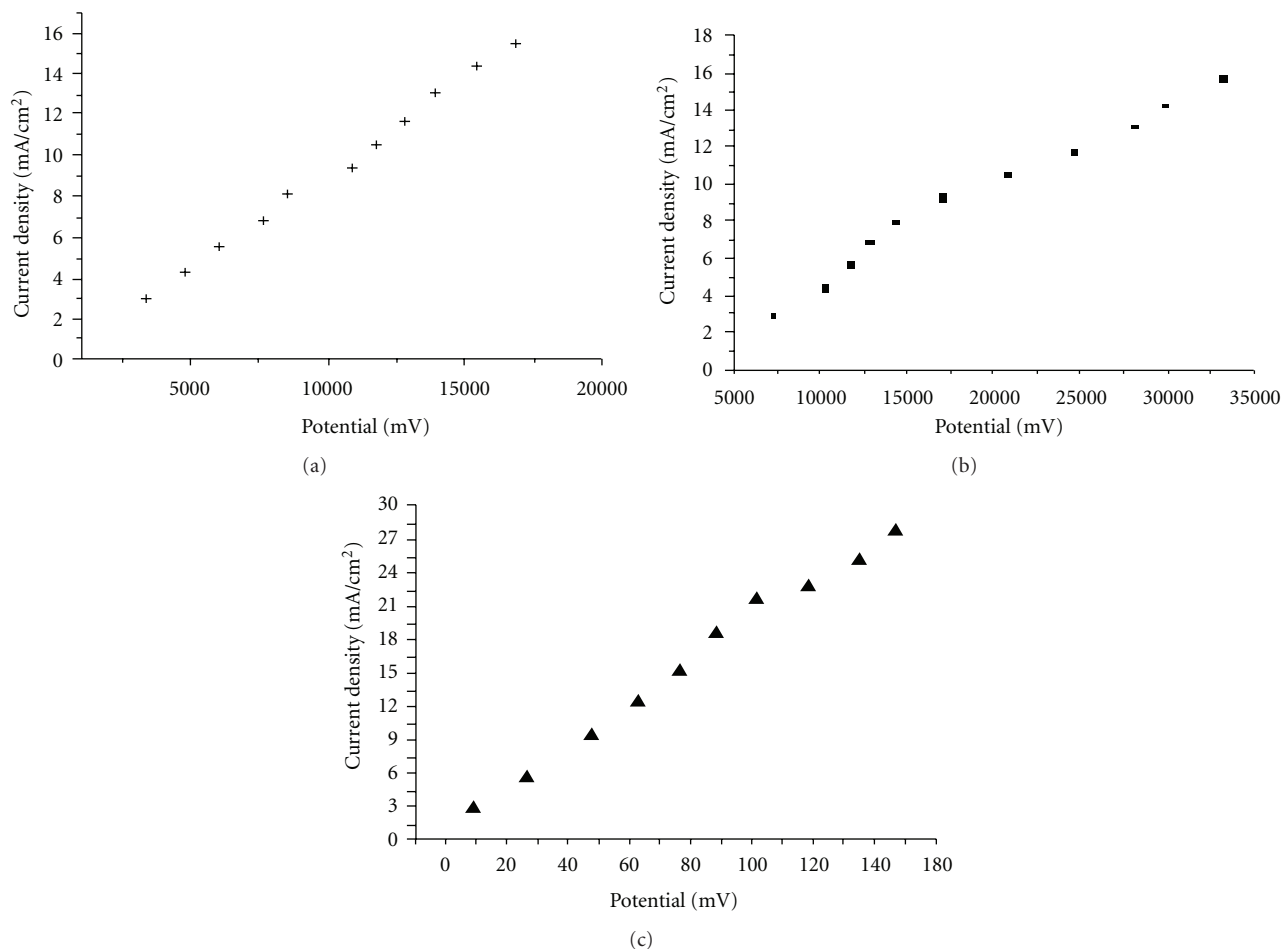


FIGURE 5: Polarization curves of the synthesized membranes and commercial membrane using the metal-finishing effluents. (a) MCS, (b) MTS, and (c) Nafion 450.

MPC for HIPS membrane with polyaniline doped with camphorsulfonic acid (CSA), MPT for HIPS membrane with polyaniline doped with p-toluenesulfonic acid (TSA). This difference between the transport numbers may be related to the structure of polyaniline dopant acid because its dopant (CSA) is more hydrophilic than the other one (p-TSA).

3.2. Infrared Spectroscopy. To ensure incorporation into the polymeric matrix, samples of PANi/CSA, HIPS, and MCS membrane were analyzed. Figure 4 shows the FTIR spectra of these samples.

In Figure 4, HIPS spectrum and different peaks were observed. The peak at $2,948\text{ cm}^{-1}$ corresponds to an angular deformation of CH_3 . At $1,731\text{ cm}^{-1}$, there is a peak attributed to the stretching of $\text{C}=\text{O}$ groups. The peaks at $1,645\text{ cm}^{-1}$ and $1,554\text{ cm}^{-1}$ correspond to N_2H stretching. The peaks at $1,075\text{ cm}^{-1}$ and $1,140\text{ cm}^{-1}$ are associated to the stretching of $\text{C}-\text{O}-\text{C}$ groups [17].

The MCS membrane spectrum displays peaks of PANi and HIPS spectra, thus showing the incorporation of PANi into the plastic matrix. Some of the peaks are overlapped, as seen in the stretching of $\text{N}-\text{H}$ groups, in approximately $3,430\text{ cm}^{-1}$.

3.3. Polarization Curves. Figure 5 presents the polarization curves of the synthesized membranes and commercial membrane Nafion 450 using the metal-finishing effluents.

According to the classical theory [21, 22] of concentration polarization for ion-exchange membranes, the current-voltage response shows three regions. The shape of current-voltage curves can be distinguished. In the first region, a linear relationship is obtained between the current and voltage drop that is referred to as the ohmic region. In the second region, the current varies very slightly with voltage, denoting an almost unrelated current applied voltage, corresponding to the so-called limiting current. In the region III is an over-limiting current region, and then current intensity increases again with the applied voltage.

The MCS and MTS membranes presented a higher electric resistance than the Nafion 450 membrane and the limit current density was around $11\text{ mA}\cdot\text{cm}^{-2}$. For the Nafion 450 membrane, the limit current density was around $20\text{ mA}\cdot\text{cm}^{-2}$, thus showing that electric resistance is lower.

Figure 6 presents the polarization curves of the synthesized membranes and commercial membrane Nafion 450, using the tannery effluents.

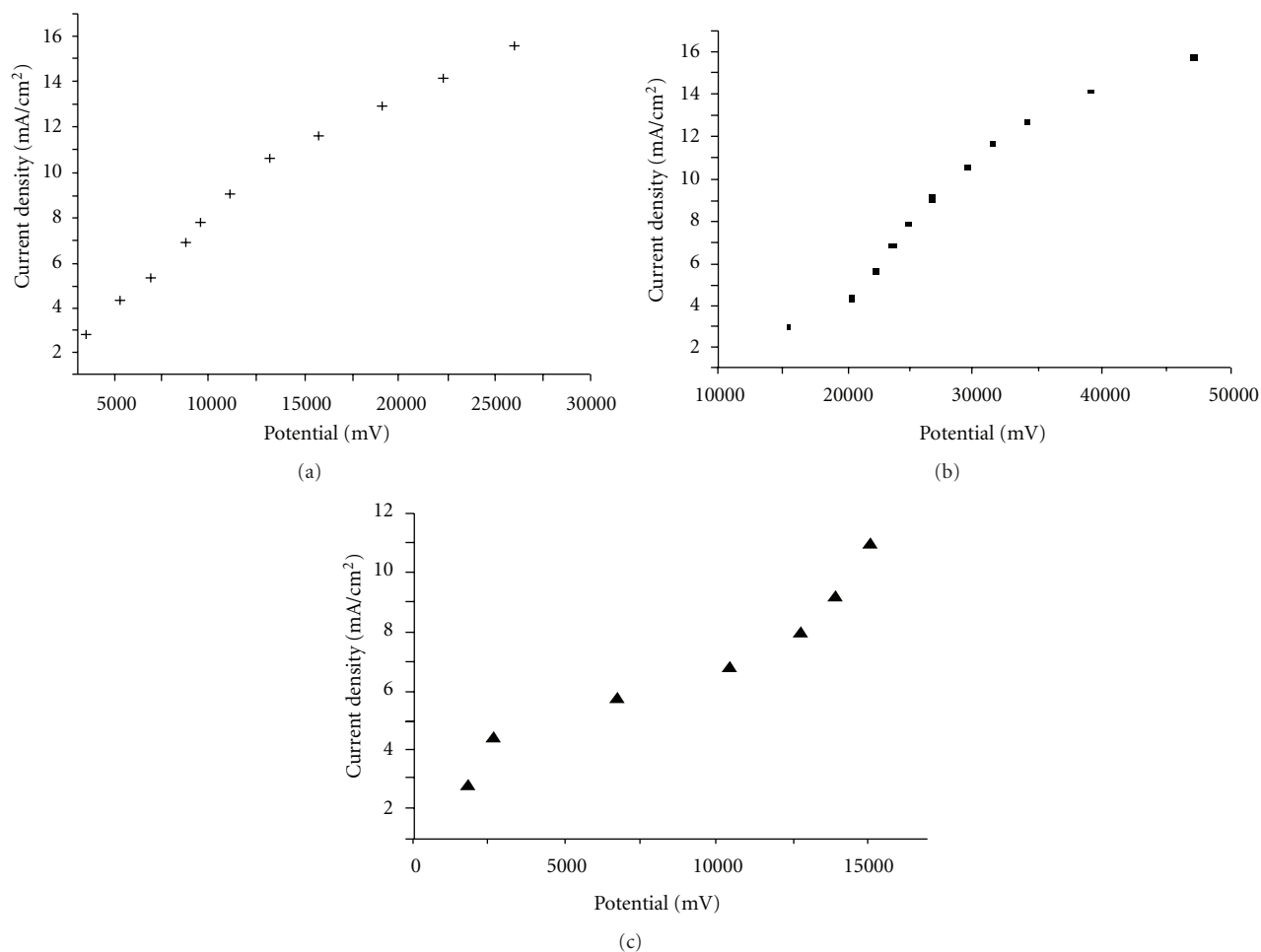


FIGURE 6: Polarization curves of the synthesized membranes and commercial membrane using the tannery effluents (a) MCS, (b) MTS, and (c) Nafion 450.

In Figure 6, it is possible to observe the current-potential curves of the membranes used for the treatment of the tannery effluents after photoelectrochemical oxidation. It is verified that the curves present the same behavior as the curves obtained with the metal-finishing effluent.

The membranes had higher resistance due to the residual organic matter present in the effluent, which might have caused the membranes fouling, hindering the transport, and consequently increasing electric resistance. This phenomenon was also observed for the commercial membrane Nafion 450.

3.4. Electrodialysis. Table 3 shows the chromium transport from metal-finishing effluents through the synthesized membranes and the commercial membrane. It is possible to verify that the Nafion 450 membrane presented better results when compared to the synthesized membranes (MTS and MCS).

The analysis of chromium in the tannery effluent is shown in Table 4. The MCS membrane had better chromium transport than the MTS membrane. The commercial Nafion membrane showed a better result, once again. Transport results confirmed the effect of the acid structure used

TABLE 3: Chromium percent extraction through membranes using the metal-finishing effluents.

Membrane	Pe Cr ³⁺ (%)
MCS	18.7
MTS	19.3
Nafion 450	37.9

as polyaniline dopant. TSA (toluenesulfonic acid) is an aromatic acid and CSA (camphorsulfonic acid) is a cyclic acid; this difference may affect the interactions between the (HSO₃⁻) groups from the dopant acid and nitrogen from polyaniline, which may, in turn, affect ionic transport through the membrane.

3.5. Morphology. Regarding the morphology of membranes (Figure 7), it is possible to observe the MTS (A) and MCS (B) surfaces. The addition of polyaniline clearly promoted changes in the morphology of the HIPS polymeric matrix. The main differences between the MCS and MTS membranes were observed in the polyaniline structure. The morphology

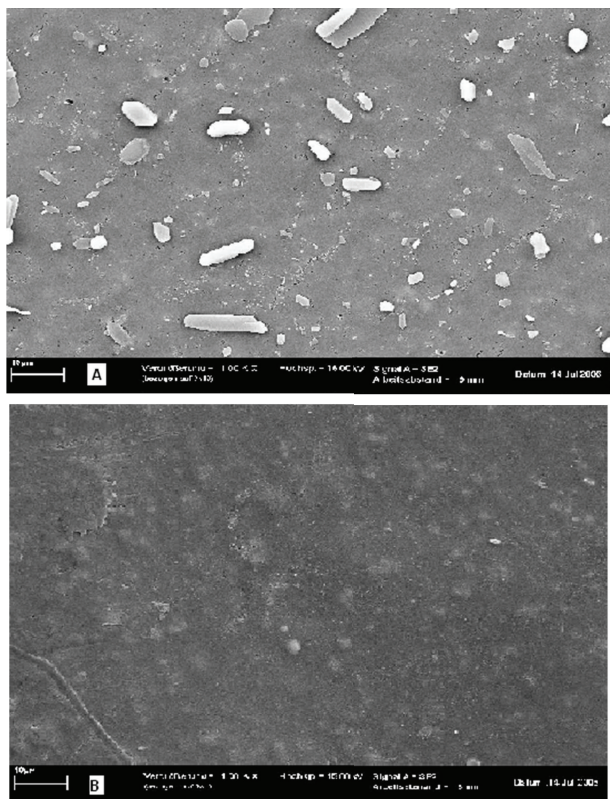


FIGURE 7: Microscopy (A) MTS and (B) MCS membrane surface.

TABLE 4: Chromium percent extraction through membranes using tannery effluents.

Membrane	Pe Cr ³⁺
MTS	95
MCS	96
Nafion 450	100

of the MTS membrane resembles needles; such a difference is due to the fact that during the synthesis of polyaniline doped with p-toluenesulfonic acid (p-TSA), the complete oxidation reaction of the aniline took place.

4. Conclusions

Infrared spectroscopy showed characteristic bands of PANi in the spectra of the membranes, especially the peak at $1,034\text{ cm}^{-1}$ regarding the S=O group. The synthesized membranes presented similar chromium transport to that observed in the Nafion 450 membrane using the tannery effluent. Electric resistance was higher in the synthesized membrane than in the commercial membrane.

Using the metal-finishing effluent, it was possible to verify that the MCS and MTS membranes presented similar results in chromium transport. The Nafion 450 membrane, however, presented better results, because its electric resistance is lower.

The study proved the feasibility of using an alternative technology in the treatment of tannery and metal-finishing effluents, bringing great advantages to water reuse.

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