

CURRENT-VOLTAGE CURVES FOR TREATING EFFLUENT CONTAINING HEDP: DETERMINATION OF THE LIMITING CURRENT

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Abstract - Membrane separation techniques have been explored for treating industrial effluents to allow water reuse and component recovery. In an electrodialysis system, concentration polarization causes undesirable alterations in the ionic transportation mechanism. The graphic construction of the current voltage curve is proposed for establishing the value of the limiting current density applied to the cell. The aim of this work was to determine the limiting current density in an electrodialysis bench stack, the function of which was the treatment of an electroplating effluent containing HEDP. For this, a system with five compartments was used with a working solution simulating the rinse waters of HEDP-based baths. The results demonstrated correlation between the regions defined by theory and the experimental data.

Keywords: Electrodialysis; Current-voltage curve; Limiting current density; Effluent treatment; HEDP.

INTRODUCTION

Superficial finishing processes by electroplating are employed to confer aesthetic or strength properties to products in the automotive, aeronautic, bathroom metal fixtures, and jewelry sectors, among others. The procedure consists of immersing the parts in a sequence of electrolytic baths, which contain metallic ions. In the case of strike baths, metal cyanide complexes are used so as to reduce the cation's redox potential (Panossian, 1997). However, the toxicity associated with cyanide has stimulated the development of alternative raw materials. That is the case of alkaline copper baths based on 1-hydroxyethane-1,1-diphosphonic acid (HEDP), used as an intermediary layer in decorative chrome deposition on Zamak parts (Vargas, 2008). The replacement of the cyanide compounds with HEDP should over-

come two disadvantages: the generation of a new effluent, since the cyanide treatment methods are already commercially disseminated, and the cost of the raw material. Hence, to make the HEDP compounds technically and economically viable, it is necessary to consolidate a methodology for treating the effluent, recovering components and reusing water in the industrial flow.

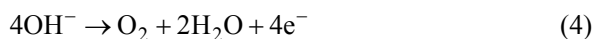
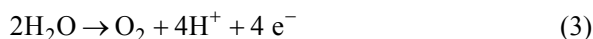
Electrodialysis (ED) has been explored for treating plating effluents (Marder *et al.*, 2004; Korzenowski *et al.*, 2008; Frenzel *et al.*, 2005; Chiapello and Gal, 1992), acid mine drainage (Buzzi *et al.*, 2013), and effluents containing organic compounds, such as organic acids (Severo Júnior, Alves e Ferraz, 2014), effluents of tanneries (Rodrigues *et al.*, 2008) and of refineries (Machado, 2008). As it can be seen, several studies were developed involving the application of the ED, or ED along with other techniques, such as

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ion exchange resins (Gayathri and Senthil Kumar, 2010). Its attractiveness lies in the possibility of recovering water and ions present in it, dispensing with the phase changes and with the addition of components required by some treatment processes (Noble and Stern, 1995). The technique involves the use of an electric current applied perpendicularly to ion-selective membrane surfaces. The action of this electric field promotes the separation of the ionic species present in the original solution. New solutions may be generated as a result, more concentrated or more diluted than the initial ones (Galuchi, 2010).

Three driving forces act on mass transport: convection, electromigration and diffusion. The convective portion usually results from a difference in hydrostatic pressure difference and acts mainly in the core of the solution. Electromigration results from the electric potential gradient and predominantly influences ionic mobility. The non-dissociated species are taken from one compartment to the other by diffusion, due to the difference in concentrations (Rodrigues *et al.*, 2008; Galuchi, 2010).

Apart from ion migration, the redox reactions occur in the electrode compartments. In the cathode compartment, hydrogen (H_2) is formed (Equations (1) and (2)) and in the anode compartment, oxygen (O_2) is formed (Equations (3) and (4)) (Benvenuti, 2012).



One of the factors that may affect the system performance is the fact that the radius of the proton is smaller than that of other ions, which gives it greater mobility. The preferred proton transport can cause changes in the pH of the solution being treated and increase the resistivity of the solution (Streit, 2011). To minimize the effect of these reactions, contact between the working solution and the electrode solution is avoided. Therefore, the anode and cathode compartments receive saline solutions that maintain conductivity and guarantee the stability of the system, without interfering with the process (Benvenuti, 2012). The process efficacy may be determined by the assessment of parameters such as percent extraction, current efficiency, electrochemical behavior of membranes and limiting current density (Streit, 2011; Marder *et al.*, 2006).

A cell limiting current density is related to the concentration polarization phenomenon, which occurs when there are alterations in mass transport, harming the process efficiency (Machado, 2008). If a current greater than the limiting current is applied to the system, the number of ions at one of the interfaces of the membrane tends to zero, since the ions are conducted within the matrix at a speed higher than their speed in solution. As a counterpart, an accumulation of charges will occur on the opposite interface when the transference rate is above the speed at which cations or anions manage to diffuse to the core of the solution (Streit, 2011). As a consequence, the salt concentration in the concentrate can exceed the solubility limit and precipitate, causing membrane clogging and an increase in the system's resistivity. In the dilute solution, the number of ions available to transport the current will be reduced. The process starts to be limited by the ion diffusion and the current value will reach the limiting current (Korzenowski *et al.*, 2008; Rodrigues *et al.*, 2008; Machado, 2008).

Among the techniques for determining the limiting current density, the current-voltage curve (CVC) method consists in the graphic construction of a polarization curve, characterized by three distinct regions, as shown in Figure 1 (Machado, 2008).

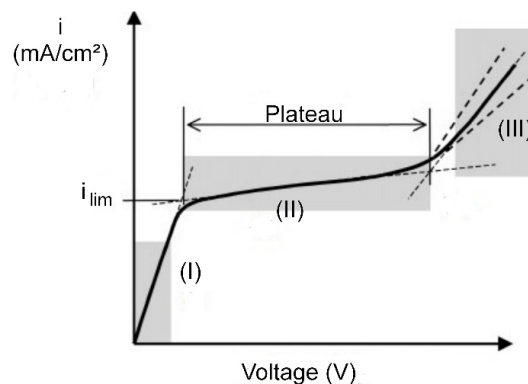


Figure 1: Typical current voltage curve and transition between regions I and II to determine the limiting current density (Machado, 2008).

The first linear region is governed by Ohm's law for the electrolyte and membrane resistivity. The second region is characterized by a plateau resulting from the reduction of the number of ions in the layer adjacent to the membrane surface. In the third region, another linear increase in current is observed, this time above the limiting current. The polarization curve is obtained by means of applying successive current increments at a constant ratio, recording the

corresponding membrane potential. The value of the limiting current density is determined by the intersection of the curves tangent to regions I and II (Korzenowski *et al.*, 2008; Rodrigues *et al.*, 2008).

Studies were performed in order to elucidate the concentration polarization mechanism (Tanaka, 1991; Bouhidel and Oulmi, 2000; Mavrov *et al.*, 1993). However, the construction of current-voltage curves applied to a system containing organic acids such as HEDP must be evaluated. The aim of this work is to determine the value of the limiting current density of an electro dialysis cell used for treating effluent containing HEDP, by constructing polarization curves.

MATERIALS AND METHODS

For constructing the polarization curves, a system was used with 5 compartments and cationic (HDX 100, pink color) and anionic (HDX 200, green color) commercial membranes of Chinese origin with 16 cm² in area. The characteristics of the membranes used in this study are presented in Table 1.

In the central container, denominated diluted, 1000 mL of working solution simulating washing waters containing HEDP complexing agent at a 1% concentration were added. 1000 mL of potassium chloride were added to the other compartments – denoted as cathode, concentrate cathode, anode and concentrate anode – for maintaining the system conductivity. Commercial titanium electrodes coated with titanium oxide and ruthenium oxide (70TiO₂/30RuO₂) were used at the ends as cathode and anode. The circulation of the solutions in the compartments was performed by independent pumps connected to the containers. A direct current source was employed for applying the electric current. To ensure the stability of the electrical current and the accuracy of the measurements, the system was continuously monitored with the aid of a multimeter connected to the power supply, as shown in the schematic drawing of Figure 2. Initially, a 5 mA direct current was applied to the system for 5 minutes. After this period, the current value was gradually increased in 2 mA increments, maintaining such current for 2 minutes and interspersing with periods of 3 minutes with no current application. The anionic and cationic membrane potentials were measured with the aid of multimeters connected to platinum wires placed at the membranes interfaces. This method has been used by other researchers (Buzzi *et al.*, 2013; Benvenuti *et al.*, 2012), since it allows the determination of the membrane potential in a filter-press assembly. At the end of each interval, the data of applied current,

membrane potential and total cell potential were recorded. The system assemblage is illustrated in Figure 2 and in Figure 3.

Table 1: Characteristics of cationic (HDX100) and anionic (HDX200) membranes.

Parameter	HDX100 - Cationic	HDX200 - Anionic	Unity
Ionic group attached	-SO ₃ ⁻	-NR ₃ ⁺	-
Water content	35 – 50	30 – 45	%
Ion exchange capacity	≥ 2.0	≥ 1.8	mol/kg (dry)
Membrane surface resistance (0.1 mol NaCl)	≤ 20	≤ 20	Ω · cm ²
Permselectivity (0.1 mol KCl/0.2 mol KCl)	≥ 90	≥ 89	%
Burst strength	≥ 0.6	≥ 0.6	MPa
Dimensional change rate	≤ 2	≤ 2	%
Water permeability	≤ 0.1 (< 0.2 MPa)	≤ 0.2 (< 0.035 MPa)	mL/h · cm ²

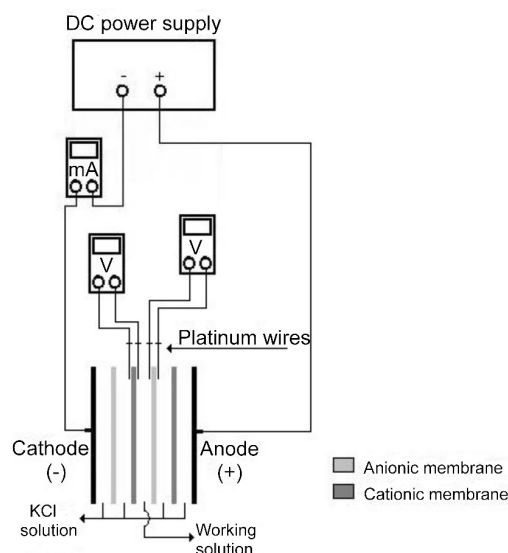


Figure 2: Schematic diagram of the system assemblage.

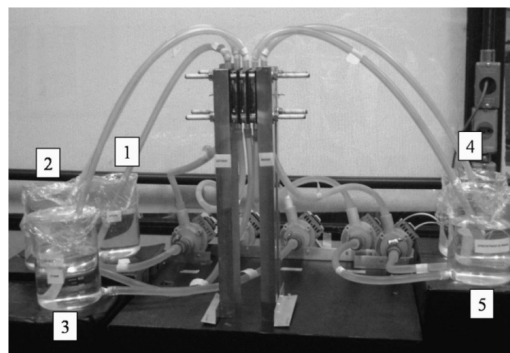


Figure 3: Electro dialysis cell containing 5 compartments.

RESULTS AND DISCUSSION

The assays for obtaining the polarization curves were conducted in triplicate and the results were reproducible. The current results versus membrane potential are depicted in Figure 4. The left column refers to the results obtained for the anionic membrane and the right column is related to the curves for the cationic membrane.

In the curves for the cationic membrane, the third

region was not reached. All curves showed the existence of a linear stage. In Figures 4(b) and 4(d), a change of slope is noted, indicating the limiting current region. For the cationic membranes, the intersection of the tangents to the first and second regions determines a limiting current between 41.6 and 59.2 mA. Considering the superficial area of the membrane equal to 16 cm², the system limiting current density is 2.6 mA.cm⁻², limited by the cationic membrane.

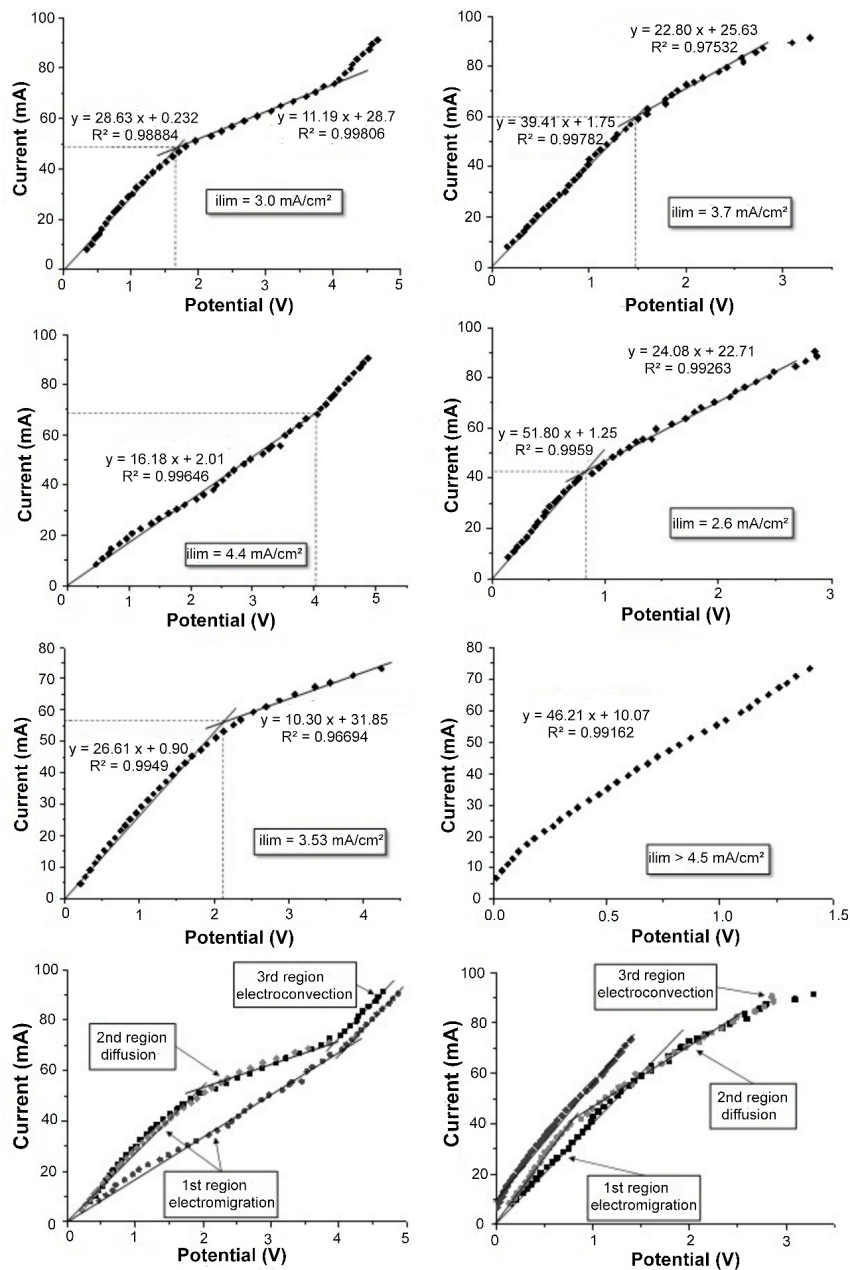


Figure 4: Polarization curves in triplicate for the cationic membrane are shown in (a), (c), (e) and for the anionic membrane are shown in (b);(d);(f). Overlapping of cationic curves is shown in (g) and of anionic curves is shown in (h).

As stated by Machado (2008), the current applied must remain between 70% and 80% of the limiting current in order to avoid concentration polarization phenomena. This margin, applied to the system proposed, results in values between 29.4 mA and 33.6 mA, (1.8 mA.cm^{-2} to 2.1 mA.cm^{-2}). The results indicate that, in a similar ED system, the application of currents of this magnitude over definite times prevents the occurrence of concentration polarization, and the process may be an alternative for treating rinsing waters containing HEDP.

CONCLUSIONS

The methodology for graphical construction of current-voltage curves was used to determine the limiting current density of an electrodialysis system. A correlation was observed between the three regions defined by theory and the experimental curves, obtaining results between 1.8 mA.cm^{-2} and 2.1 mA.cm^{-2} . The application of the results to an electrodialysis system may enable further investigation of HEDP acid and metallic cation recovery.

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