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Study of the effects of the applied current regime and the concentration of chromic acid on the transport of Ni^{2+} ions through Nafion 117 membranes

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ABSTRACT

In the present work galvanostatic experiments are conducted with an electrodialysis cell in order to study the passage of Ni^{2+} ions present in chromic acid solutions through a Nafion cation-exchange membrane. The competing transport between H^+ and Ni^{2+} ions through the membranes has been studied under the imposition of under- and overlimiting currents. Results show an increasing competence between both ions when the concentration of protons exceeds that of the Ni^{2+} ions. Increased nickel removal rates and current efficiency values were achieved with intensive current regimes due to the onset of electroconvection. However, at low values of the $[Ni^{2+}]/[H^+]$ ratio, this improved transfer through the membrane implies high values of specific energy consumption due to increased membrane voltage drops, thus decreasing the convenience of applying overlimiting currents. The obtained results are related to the values of plateau length calculated from the polarization curves of this membrane/electrolyte system and prove that Ni^{2+} ions promote the arising of electroconvective vortices, whereas H^+ ions hamper electroconvection.

1. Introduction

The metal finishing industry constitutes one of the most intensive consumers of hexavalent chromium [1–3]. During chromium plating operations, chromic acid is reduced at the surface of metallic objects in order to prevent their oxidation [4]. Once the plating process is finished, the plated pieces are rinsed. The configuration of the rinsing technology is generally a multiple step cascade rinse [5,6]. In this stage spent rinse waters, which contain a significant concentration of Cr(VI) and cationic impurities such as Ni^{2+}, Fe^{3+} or Cr^{3+} ions, are generated. Therefore, an important amount of chromic acid can be recovered from these effluents in order to be reused in the plating operations and high volumes of water can be decontaminated for their reuse in the rinsing operations [7].

The hazards associated with hexavalent chromium encourage the finding and development of effective solutions for the treatment of these contaminated effluents. Several studies have proven the toxicity and carcinogenic effects of Cr(VI) species in different organs of the human body, inducing specially lung cancer [8,9]. Among the available technologies for the treatment of spent rinse waters, electrodialysis seems to offer many advantages with respect to other methods. Chemical precipitation implies the addition of chemicals and the production of large quantities of sludge [10,11], the use of ion-exchange resins involves further operations in order to regenerate ion exchangers, and reverse osmosis does not allow the separation of cationic contaminants from anionic species of Cr(VI). By contrast, electrodialytic techniques allow the simultaneous separation of ions of different charge and can make feasible the reutilization of chromic acid free from cationic impurities in the plating baths, thus maintaining the efficiency of the process. It would also permit the recirculation of water without chromic acid and cationic impurities to the washing step [3,7,10,12–15].

So far, the development of resistant, high conductive and selective membranes remains as one of the main challenges for the improvement of electrodialysis applied to the heavy metal removal from industrial wastewaters [16,17]. Though polymeric homogeneous membranes posses good transport properties, they are exposed to a fast ageing when used with strong acidic and oxidizing mixtures as those effluents coming from plating industries [17]. Alternatively, some efforts must be done in order to develop ceramic ion-conducting membranes with transport properties comparable to those of the organic ones [18]. Nafion membranes combine the good transport properties of homogeneous organic membranes with excellent thermal, chemical and mechanical stability [19]. However, as occurs with all ion-exchange membranes, operating conditions are usually restricted by the so-called limiting current densities (i_{lim}). When i_{lim} values are surpassed, concentration polarization becomes intensive and the counter-ion concentration at the membrane surface on the depleting solution side vanish, thus leading to a mass transfer limitation and high cell voltages [20].

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Traditionally, overlimiting currents have been attributed to the dissociation of water as a consequence of high electric fields, implying a waste of energy without the implication of an additional transport of other counter-ions. On the contrary, different authors recently observed in experimental results that the fact of having water splitting products cannot be the only effect responsible for the notable increase in current density obtained beyond the limiting value [21–23]. After the development of electroconvection theory by Rubinstein and Maletzki [24], electroconvection has been considered as one of the main mechanisms contributing to overlimiting current regimes. In agreement, recent studies pointed out the interest of working at overlimiting current regimes, since an improved ionic transport through the membranes has been verified due to an additional supply of counter-ions apart from water splitting products to the membrane surface [25,26].

In membrane separation processes, several factors are responsible for their performance [27], namely the membrane characteristics, the concentration and properties of the species present in the composition of the baths, as well as the operating conditions involved in the process. Besides this, the properties of the electrolyte, such as the conductivity, may change significantly depending on the concentration of species. This could imply changes in the predominance of different mass transfer mechanisms, which affect the performance of the process for a given energy input. In particular, overlimiting current regimes can be promoted for specific compositions of the electrolyte [28–30], hence being the energy usage associated with the transition from under- to overlimiting conditions also dependent on the composition of the effluents. Moreover, various studies have proven that depending on the type of cations their transport properties and interactions with the Nafion membranes can change significantly [31–35]. In electrodialytic processes, in contrast to other membrane processes, current transport above the limiting value dictated by concentration polarization can be achieved if the driving force is increased beyond a critical voltage drop. The fact that this increased ionic flux would be carried by the ions of interest, which occurs when electroconvection is one of the mechanisms promoting overlimiting currents, broadens the possibilities of this technique to new procedures such as the utilization of intensive current regimes [28,30,36].

Nevertheless, not much work has been carried out with galvanostatic experiments planned in this direction. Therefore, the scope of the present study is to investigate the performance of a cation-exchange membrane (CEM) under different regimes of imposed current with varying electrolyte concentrations. Thereby, the experiments will serve to check if higher rates of mass transfer of target ions under intensive current regimes are achieved and ascertain the associated repercussion on the current efficiency and specific energy consumption values. For this purpose, Ni^{2+} ions are selected as the target ions to remove from chromic acid solutions, since this is one of the most common contaminants in spent chromium plating rinse waters. In addition, the effect of H^+ ions on the Ni(II) removal is studied. Simulated spent rinse waters of variable concentrations of CrO_3 and $NiSO_4$ are used to analyze the influence of the electrolyte composition on the performance of an electrodialysis operation by means of the calculation of the figures of merit.

2. Experimental

2.1. Membranes

The CEM employed in the experiments is a Nafion® 117 (Du Pont) membrane. The Nafion membrane is a homogeneous membrane made of tetrafluoroethylene with sulphonic ionizable groups acting as the fixed ion-exchanging sites. The anion-exchange membrane (AEM) is a heterogeneous Ionics AR-204-SZRA-412 (from Ionics Inc.) membrane prepared from vinyl monomer and acrylic fiber with $-N^+(CH_3)_3$ attached fixed groups [37]. The transport of Ni^{2+} ions through the CEM will be the main issue of the present work while the utilization of the AEM will serve to facilitate the transport of Cr(VI) present in the rinse waters in the form of anionic species towards the anodic compartment. Before performing each experimental test, membranes were equilibrated during 24 h under stirring immersed in the solutions of the same concentration as those required in the experiments.

2.2. Materials and reagents

Synthetic solutions with varying concentrations of CrO_3 (99%, Panreac) and $NiSO_4 \cdot 6H_2O$ (99%, Panreac) were prepared. For the preparation of solutions, distilled water was employed. The range of concentrations of $NiSO_4$ and CrO_3 was selected from previous works concerning the treatment of chromium plating rinse waters [7,15,38]. The concentrations used in the experiments were 10^{-3} and 10^{-2} M for $NiSO_4$ and 0, 10^{-3} and 10^{-2} M in the case of CrO_3. The evolution of nickel concentration with time was analyzed using a Perkin-Elmer AA Analyst 100 atomic absorption spectrometer with a lamp current of 17 mA and a wave length of 351.5 nm.

2.3. Experimental setup

The experimental setup is composed of an electrodialytic cell consisting of three cylindrical compartments, between which the AEM and the CEM were clamped (see Fig. 1). Each compartment has a volume of 130 ml and the effective area of the membranes was 12.56 cm^2. All the experiments were carried out at room temperature (25 °C) and without recirculation. The three compartments were filled with the same solution, so as to reduce the effect of diffusive transport between different compartments. A constant current is imposed between two graphite electrodes by a potentiostat/galvanostat (Autolab, PGSTAT 20). During the experimental tests, the imposed current promotes the motion of different ions due to the electric field created within the electrodialytic cell. The ions with electronegative sign (CrO_4^{2-}, $HCrO_4^-$, $Cr_2O_7^{2-}$ and SO_4^{2-}) move from the central towards the anodic compartment crossing the AEM. At the same time, the AEM impedes the passage of the protons generated in the anode as a consequence of water oxidation, which allows the regeneration of chromic acid for its reintroduction in the plating baths. SO_4^{2-} ions take part at the composition of the plating baths as catalyst, so that their recovery in the same compartment where chromic acid is concentrated does not imply a disadvantage for the process. On the other hand, nickel is present in the cationic Ni^{2+} form at the acidic pH of the solutions. Additionally, when CrO_3 is dissolved in aqueous solutions chromic acid is generated and consequently, the released

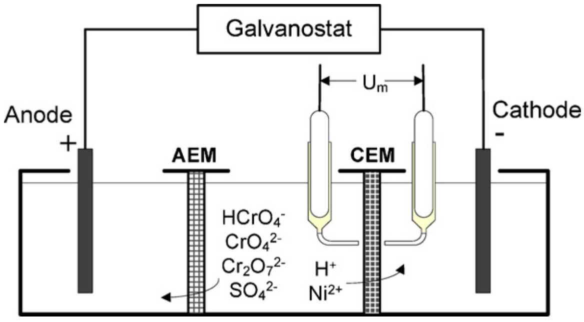

Fig. 1. Schematic diagram of the three-cell electrodialysis reactor used for the recovery of chromic acid and purification of spent rinse waters. (AEM, anion-exchange membrane; CEM, cation-exchange membrane; U_m, membrane voltage drop.)