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Competitive transport of hydrochloric acid and zinc chloride through diffusion dialysis and electrodialysis membranes. Recovery of spent pickling solutions

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Hot-dip galvanizing consists of covering the surface of iron or steel pieces with a reactive zinc layer that provides oxidation protection. This process is carried out by immersion of the metallic pieces in a bath of molten zinc. During the whole process, spent pickling solutions (SPS) coming from stages such as washing, pickling or galvanizing itself are generated. Among other substances, SPS contain high concentrations of zinc, iron and HCl. The increasingly stringent regulations regarding the discharge of acids and metals into the environment, and the increasing demand upon the recycling/reuse of these effluents after proper treatment, have focused the interest of the research community on the development of new approaches for the recovery of acid and metals from these industrial wastes [1,2].

The difficulty underlying the development of recovery processes is associated to the physicochemical complexity usually encountered in hydrochloric acid effluents, where the main species are present as anionic species, such as zinc chlorocomplexes; as a result it is difficult to select one universal method for the treatment of this type of effluents. Membrane techniques are considered to be simple, effective and sustainable because of large and well-defined area of contact, compactness and reduced size of equipment, no need of chemicals addition, easy scale-up [3]. Among them, Diffusion Dialysis (DD) and Electrodialysis (ED) are membrane separation processes with demonstrated applications in the recovery of valuable compounds from liquid matrices. The basic element of these technologies is an ion-exchange membrane having in its structure electrically charged sites, which facilitate the transport of counter-ions while the co-ions are rejected. If an anion-exchange membrane is used, the anions can permeate the membrane freely but the cations will be retained by the membrane. The protons, however, can pass the anion-exchange membrane in spite of their positive charge because they are transported by a tunnelling mechanism. Thus, the acid could be removed from the complex solutions [4].

Diffusion dialysis (DD), using anion exchange membranes, is an attractive method for acid recovery that was first applied industrially in the late 1950s. The driving force for this process relies on the difference in chemical potential of the species on either side of a membrane and as such the only external power required is that needed to circulate the solutions [4,5]. Electrodialysis membrane technology is an electromembrane process where combinations of ionic membranes are placed between a pair of electrodes. Under the influence of an applied dc electric field, ions move in the direction of the opposite charged electrode. Electrodialysis membrane technology enables not only separation of acid but also its concentration to high enough values to recycle the acid to be further used in the pickling bath [6].

This work reports the comparative study of the recovery of hydrochloric acid from SPS by means of DD and ED. First, the comparison of the efficacy of both technologies has been carried out after the experimental evaluation of the acid flux and selectivity in the individual technologies as a function of the operational variables, i.e., initial concentration of acid and metals, permeate phase composition and current density. Maximum flux values obtained in the DD study were $1.5 \cdot 10^{-3}$ mol/m^2·s and $2.5 \cdot 10^{-4}$ mol/m^2·s for HCl and Zn respectively. When ED

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was used the HCl flux increased four times with respect to the values obtained with DD for similar concentrations and the total zinc flux was three times lower, thus leading to a significant improvement in the separation selectivity. It was also observed that the flux of HCl decreases with the increase of current density, due to the existence of negatively-charged complexes, so that a correct optimization of the operation conditions must be carried out.

Next the membrane transport of HCl and Zn species in both technologies was described after the development of mass balances that led to the mathematical models and characteristic parameters. The overall mass transfer coefficient in DD, defined as the ratio between the species diffusivity and the membrane thickness, through dialysis membranes has been calculated by using the Michaels equation [7]. On the other hand, the Nernst–Planck equation that accounts for the contributions of the concentration driving force and the migration of ions as a result of the electric field, has been used to describe the results obtained through ED membranes. The diffusion coefficients of zinc and protons did not remain constant within the whole range of experimental variables, and their variation was described by means of an exponential equation $D_i = D_0 \cdot \exp(-\tau \cdot Cm)$, that was incorporated into the mathematical model [6]. The mathematical model that also incorporates the distribution of zinc chloride (cationic and anionic) species as a function of process conditions is a useful tool in the comparison of the performance of both membrane separation technologies.

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