Short communication

Continuous multistage electrodialytic treatment of copper smelter wastewater

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ABSTRACT

In this work, a continuous multistage electrodialytic technique is evaluated as a possible treatment of copper smelter wastewater. Six experiments with different values of feed flow rate, current density and treatment time were carried out. It was possible to concentrate copper during experiments and a maximum recovery of 10% was achieved. The experiment with a feed flow rate of 30 mL min^{-1}, current density of 300 A m^{-2} and a treatment time of 2 h was the most efficient, with a copper recovery of 5.1%. In sections where copper was concentrated, a solution with mCu/mAs ratio around 2 was obtained, this value is substantially higher than 0.1, which is the value for a mining wastewater.

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1. Introduction

Chile is one of the main copper manufacturers in the world. During the processing and concentration of the minerals considerable amounts of residues and wastewaters are produced. During the smelting of copper sulphides and the subsequent gas treatment, considerable volumes of wastewater are generated containing mainly copper, arsenic and other inorganic species in concentrations that exceed the local legal threshold values (Gutiérrez et al., 2010). Different treatment alternatives exist such as chemical precipitation, electrodialysis, ion exchange, and adsorption (Hansen et al., 2010). At present the wastewater is processed by chemical precipitation to meet the environmental regulations (Chilean Republic, 2000). Wastewaters are treated with Ca(OH)$_2$ to increase the pH to approximately 10, which favors the precipitation of heavy metals as hydroxides but also precipitates calcium sulphate. The Ca(OH)$_2$ addition produces a great volume of sludge, owing to the fact that initial pH of the wastewater is very acidic (pH < 1) Núñez et al., 2011. The sludge contains a mix of inorganic elements including Cu and As. This methodology has the disadvantage that great quantity of sludge is produced and requires a subsequent treatment (Gutiérrez et al., 2015). Other alternatives or complementary techniques for treatment of acid effluents from smelting as electrodialysis are used. Electrodialysis is utilized to transport, separate and concentrate ions according to their electrical charge, by means of ion exchange membranes,

under the action of electrical field (Sadrzadeh and Mohammadi, 2009). The advantage of this technique is the recovery and separation of the copper present in the arsenic-rich wastewater (Hansen et al., 2015; Caprarescu et al., 2011, 2014).

The overall aim of this work is to study copper and arsenic separation, both elements contained in mining wastewater, by means of continuous electrodialytic technique, in order to achieve this (i) a electrodialytic cell in laboratory scale will be designed, (ii) the influence of feed flow rate, current density and treatment time will be analyzed and (iii) the energy consumption and its relation with copper recovery will be studied.

2. Experimental

The main equipment for the wastewater treatment is the electrodialytic cell. It is designed to clean the wastewater as a continuous process mainly and is showed on Fig. 1. The solution to be treated is first pumped into section 3. After leaving this section, the solution is pumped into section 7 and then, it will be passed through section 11, and finally the solution abandons this last section with a lower charge of ions. The application of an electrical field in the cell produces the migration of ionic species present in the wastewater to the electrodes with opposite charge. The ions with positive charge cross the cationic membrane to enter to the section where cations are concentrated (cation sections 4, 8 and 12) and become trapped due to the anionic membrane which impedes their pass to the following section. The same applies to negative ions, which migrate to the opposite direction (to anion sections 2, 6 and 10), crossing the anionic membrane and
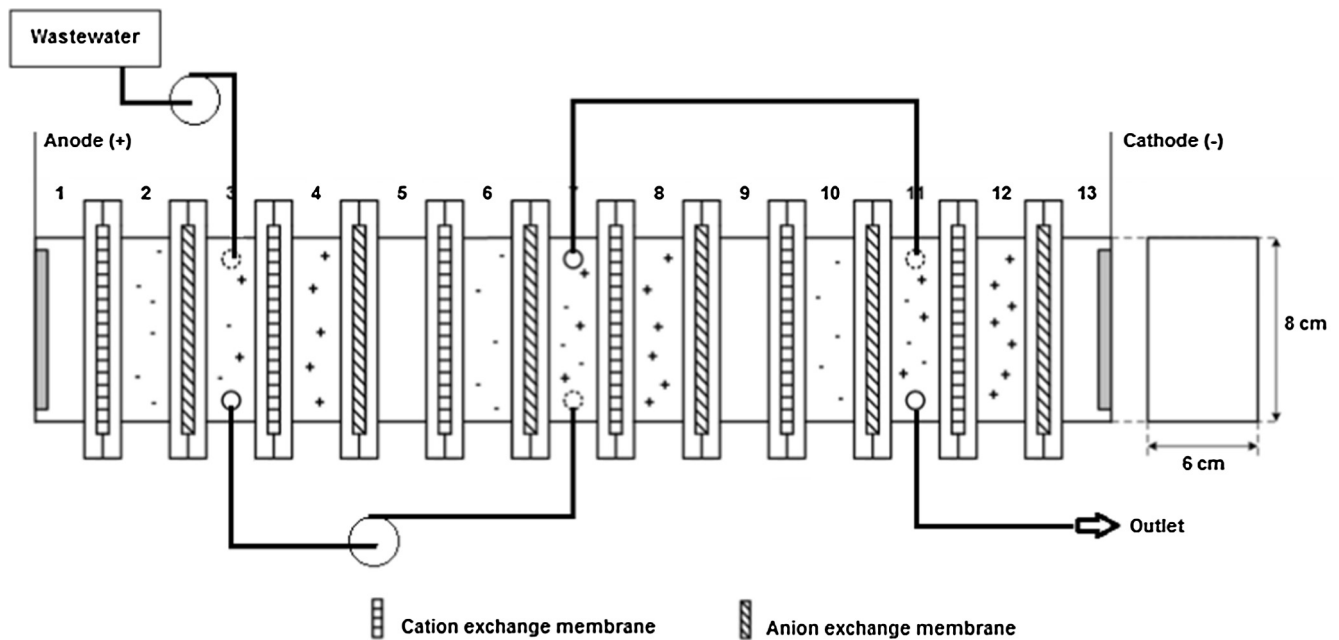

Fig. 1. Electrodialytic cell.

becoming trapped here because the cationic membrane blocks their passage to the following section. In consequence, there is a constant flow of ions from the wastewater to the cationic and anionic sections. Copper would be present as cations and would end in sections 4, 8 and 12, whereas arsenic would either by negatively charged or neutral at the actual pH, and therefore remain in the wastewater (neutral) or enter sections 2, 6 and 10 (negatively charged). Therefore, a separation of Cu and As is feasible.

During the continuous passage of the wastewater through the three sections of the cell, ions are recovered from the wastewater batch wise in this design; but sections 2, 6 and 10 could be combined via a continuous separate flow where copper is recovered without mixing with arsenic. The same could be the case with sections 4, 8 and 12. To avoid the mixing between copper and arsenic recovered in two consecutive stages, an additional section between anionic and cationic section of two consecutive stages will be considered placed between an anion and a cation exchange membrane (sections 5 and 9). In this way these act as bipolar membranes, and ions cannot pass these sections.

In summary, the electrodialytic cell consists of thirteen sections; between each section an ion exchange membrane was placed. The electrodes were installed at each end of the cell. All sections of the cell have dimensions of 6 cm (W) × 3 cm (D) × 8 cm (H), and a total volume of 157.5 mL for sections 2–12 was used. The electrodes were made of stainless steel with dimensions of 6 cm height, 3.8 cm width and 0.3 cm thickness. The ion exchange membranes used were AMI-7001 and CMI-7000 from "Membrane International INC".

The mining wastewater was provided by CODELCO, Ventanas Smelter and Refinery, located in V Region of Chile. The pH of the wastewater was adjusted to 2, using a solution of calcium hydroxide (Ca(OH)$_2$ 17.5%). Sections 1, 2, 4, 5, 6, 8, 9, 10, 12 and 13 were filled with 0.5 M sulphuric acid (H$_2$SO$_4$) and sections 3, 7 and 11 were filled with the wastewater.

The analysis of arsenic and copper was based on Chilean Official Standard NCh 2313/10 Of. 96. Copper and arsenic in sections 5 and 9 were not analyzed, because, in a previous experiment, arsenic was not detected and the copper concentration was lower than 0.5 mg L^{-1} in these sections. All experiments were carried out in duplicate and the error was always lower than 5%.

3. Results and discussion

Experimental conditions and results are shown in Table 1. Copper was recovered in sections 4, 8 and 12, whereas arsenic was detected in sections 2–12.

When working with different feed flow rates in concentrate sections, the overall copper recovery is lower when higher flow rates are used, due to the lower residence time in the cell. Moreover, when the current density increases, so does the copper recovery too. This is because with the increase of current density, a higher amount of energy is available to move copper ions to the concentrate section. In dilute sections the overall recovered mass of copper is negligible (<1 mg) independently of the increase in the flow rate and current density, due to the effectiveness of anion membrane, which avoids the passage of copper ions to dilute sections. The overall recovery of copper in dilute sections is lower than 1%.

Additionally, the presence of arsenic in the concentrate and dilute sections is primarily due to the existence of this element in a neutral molecule as H$_3$AsO$_3$ and H$_3$AsO$_4$ at the pH level used here and for that reason arsenic cannot be retained in a specific way by membranes. Therefore, mass transfer is taking place due to the permeability of membranes and diffusion. On the other hand, in the three concentrate solutions, m$_{Cu}$/m$_{As}$ ratio was increased to around 2 from 0.1 initially – indicating the potential of electrodialysis to separate copper from arsenic.

No clear trend was observed for the energy consumption with the change in current densities, due to the ratio between the recovered mass of copper and energy consumption was very close for the studied values of current density. A higher efficiency in copper removal for 300 A m^{-2} compared to 500 A m^{-2} with a flow rate of 30 mL min^{-1} was observed. However, when the flow rate was 60 mL min^{-1} this trend was reversed with values close to each other. Moreover, the energy can be better used with lower feed flow rates, i.e. 30 mL min^{-1}.

When comparing experiments 1, 5 and 6, in sections 4, 8 and 12 (corresponding to the concentrate sections), the optimum copper