Membrane-Based Solvent Extraction for Cobalt(II) Separation Using Cyanex 272

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Membrane-based solvent extraction of cobalt(II) from sulfuric waste solutions and model solutions containing nickel(II) and cobalt(II) sulfates was analyzed. Hollow fiber membrane contactor was used for the process. Solvent extraction was conducted using commercial extractant Cyanex 272. Organic phase was passed through the tube side while the acidic feed containing metals was passed through the shell side in counter-current mode. Simultaneous back extraction with sulfuric acid and its influence on the separation process was also tested. Pseudo-emulsion of stripping solution and Cyanex 272 was prepared in a tank and transferred to the membrane contactor.

1. Introduction

The main sources of Ni and Co are located in Ni-Co laterites that contain around 2.5% and 0.15% of each metal, respectively [1]. Both metals are essential for the electronic industry responsible of manufacturing electrodes for lithium ion batteries [2]. Different types of stainless steels contain high quantities of nickel. As a result, as much as 65% of extracted nickel, is consumed in steel production [3]. Some types of steel, made for use in fuel cells are coated with cobalt [4]. Due to their increasing demand, raw metals begin to be insufficient to meet industry needs and therefore, it is crucial to promote the use of secondary materials after the convenient separation process. In this process metals are leached from solid wastes and then are separated from the pregnant leaching liquor to obtain pure products for further reuse. Solvent extraction (SX) allows obtaining high quality products from mixtures of nickel and cobalt, regardless the metal concentration in the solution [5].

For sulfuric waste solutions and pregnant leaching liquors of nickel and cobalt, some commercial extractants have been proposed, including 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (PC-88A) [6], bis(2-ethylhexyl)phosphoric acid (D2EHPA) [7] and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) [8-10]. The latter currently finding the most interest. Looking for possibilities to reduce the costs of reagents, some synergistic mixtures of extractants have been proposed [11, 12].

2. Experimental

2.1 Materials

Cyanex 272 supplied by Cytec Industries (USA) was used as a metal carrier. Shellsol D70 supplied by Shell Chemicals was a diluent for the organic phase. Sodium hydroxide solutions

(5-10 M) were used to adjust the pH of feed mixtures at 5.2-5.5, which theoretically provides the maximum selectivity. 1 M sulfuric acid was employed as a stripping agent. Model sulfuric solutions were prepared by dissolving cobalt(II) and nickel(II) sulfates in deionized water. Real waste solution was obtained from stainless steel leaching industry. The hollow fiber membrane contactor used for the process was characterized by the parameters presented in Table 1.

Table 1. Parameters characterizing hollow fiber contactor Liqui-Cel (Celgard)

Parameter	Value/Description
Fiber material	Polypropylene
Shell material	Polypropylene
Type of fiber	X-50
Inner diameter (fibers)	240 µm
Thickness (fibers)	30 µm
Average pore size	0.03 µm
Porosity	40%
Effective length (fibers)	0.15 m
Effective membrane area	1.4 m^2
Number of fibers	10200

2.2 MBSX process

Membrane-based solvent extraction (MBSX) using a hollow fiber contactor with an effective membrane area of 1.4 m^2 has been analyzed as a way to improve the conventional SX process employed in the separation of nickel(II) and cobalt(II). This technology combines the advantages of SX, such as facilitated transport and selectivity, with the non-dispersive contact provided by polymeric hollow fibers. Solutions containing cobalt(II) and nickel(II) sulfates (3-15 g/L Co(II) and 3-25 g/L Ni(II)) were treated by MBSX using 0.6 M Cyanex 272 as selective extractant. 1 M solution of sulfuric acid was used as a stripping phase. A magnetic stirrer was used in the feed solution to ensure even distribution of the inflowing solution and added NaOH. A schematic view of the operation system is shown in Figure 1.

Two main issues were investigated: i) kinetics of cobalt(II) extraction and, ii) selectivity of the separation process that is essential to provide high quality products for their further recovery by electrowinning.
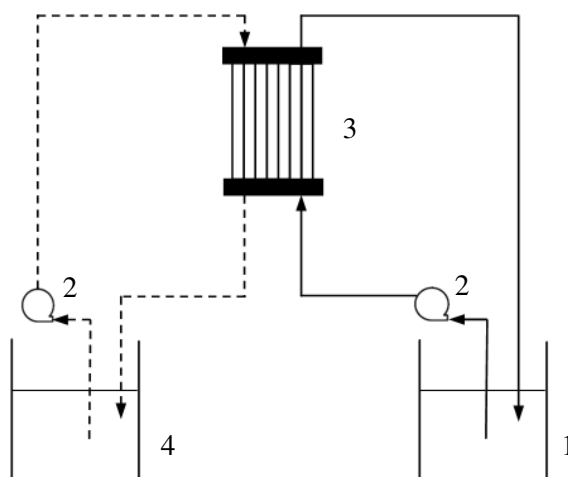
Figure 1. Schematic view of MBSX operation system. (1) Feed solution in the shell side, (2) pump, (3) hollow fiber membrane contactor, (4) organic phase or pseudo-emulsion (solutions of Cyanex 272 and H_2SO_4) in the tube side.

3. Results and Discussion

3.1 Extraction of cobalt and nickel

Preliminary results were obtained with synthetic solutions that contained around 2.5 g/L of cobalt and nickel. As depicted in Figure 2, after two hours of experimental running, cobalt extraction achieved yields above 95%. The extraction of nickel was in the range between 30-36% being this yield higher than the value theoretically expected (<20%) under the selected pH conditions. These differences might be initially attributed to two different reasons: i) the local pH increases as consequence of the non-instantaneous perfect mixing when NaOH was discontinuously dosed to the feed tank and, ii) the uncontrolled pH conditions in the membrane contactor.
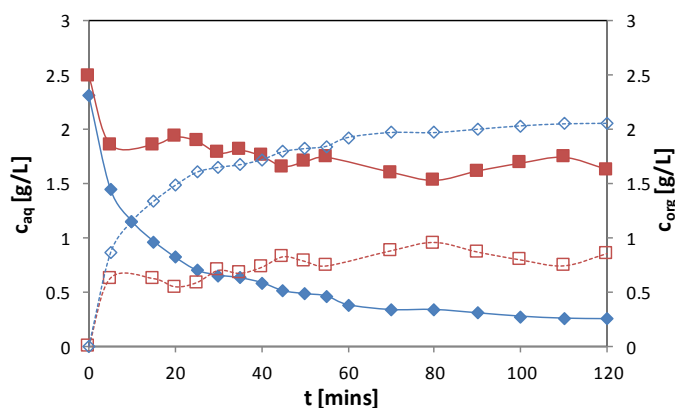

Figure 2. Evolution with time of (◊,♦) cobalt(II) and(□,■) nickel(II) concentration in the aqueous (continuous) and organic phase (discontinuous).

3.2 Influence of simultaneous back extraction

Simultaneous back extraction was conducted by introducing pseudo-emulsion of solutions of Cyanex 272 and sulfuric acid into the tube side of the membrane contactor. Pseudo-emulsion of

organic and stripping solution forms temporarily as long as the mixture is stirred. After stopping the stirrer, phases separates [13]. The volume ratio of organic to stripping phase was 5:1, thus, it allowed to concentrate the resulting aqueous solution. Figure 3 shows that simultaneous back extraction during the process allows to obtain higher yields of cobalt extraction. It also influences the kinetics of the process, which is then quicker than with back extraction conducted outside the system.
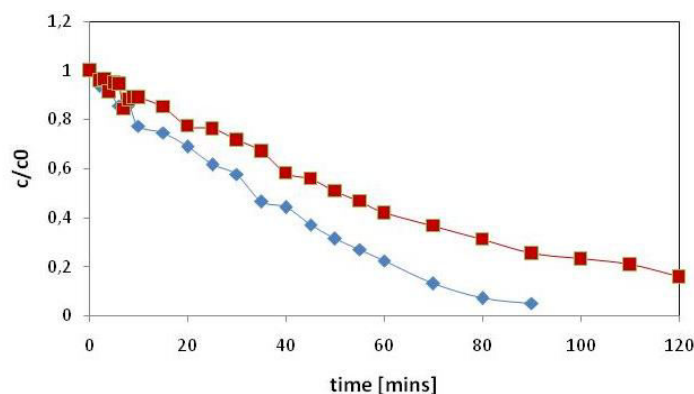

Figure 3. Evolution with time of cobalt(II) concentration in the aqueous solution. Process conducted (♦) with and (■) without simultaneous back extraction.

4. Conclusion

The preliminary results allow to conclude that MBSX ensures high efficiency and selectivity in the removal of cobalt from its sulfate solutions containing nickel(II). Further work will be focused on the improvement of pH controlling, the analysis of the back extraction stage and the evaluation of the stripping requirements to carry out the selective electrochemical recovery of cobalt. Back extraction included in the MBSX process reduces the time needed to achieve the limit of cobalt extraction. It also ensures constant regeneration of the organic phase, thus, influences positively selectivity, reducing co-extraction of nickel to less than 20%.

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