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Extraction separation of Co(II) from Ni(II) in H_2SO_4 solutions with carriers in hollow-fiber contactors

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ABSTRACT

The separation of Co(II) from Ni(II) in H_2SO_4 solution across a hollow fiber membrane containing D_2EHPA carriers dissolved in kerosene was studied. The Co(II) was simultaneously re-extracted to a strip phase containing H_2SO_4. Experiments were conducted to determine the effects of the feed pH (4–5), carrier concentration (0.1–0.5 mol/dm^3), strip acidity (0.1–2 mol/dm^3), and flow rates of the three phases (200–600 cm^3/min). The extraction efficiency for each metal ion was found to increase with increasing flow rate of the feed phase, feed pH, and D_2EHPA concentration in the extraction module. Co(II) was preferentially extracted over Ni(II) by D_2EHPA under the same extraction conditions. In the extraction module, the separation factor $\beta_{Co/Ni}$ increased with increasing flow rate of the feed phase and D_2EHPA concentration but decreased with increasing feed pH. In the re-extraction module, the recovery of Co(II) increased with increasing the feed pH, D_2EHPA concentration, and flow rate of the strip phase but decreased with increasing the strip acidity. At a feed pH of 4, the percent extraction and recovery of Co(II) were 81% and 26.4% (Ni/Co–11% in strip phase), respectively. The percent extraction and recovery for Co(II) using one-stage HFMCs were better than those using two-stage HFMCs.

Keywords: Cobalt/nickel separation; D_2EHPA; Hollow fiber contactor

1. Introduction

Cobalt and nickel are among the most important non-ferrous metals, and increasing demand for these metals is leading to a rapid depletion of previously rich sources [1]. Cobalt demand has recently risen due to its use in superalloy materials, catalysts, the nuclear field, chemical applications (most notably rechargeable batteries), and other industrial fields. The separation of Co/Ni in sulfate and chloride solutions has been of practical interest to researchers for a long time. Using classical methods, such as chemical precipitation and oxidation, it is difficult to separate Co/Ni in a simple

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and economic way due to their similar physicochemical properties [2–4]. However, the recovery and separation of Co and Ni in aqueous solutions through solvent extraction is of great interest due to its significant capital and operating cost savings [5,6].

In the past two decades, microporous membrane-based solvent extraction has been developed to avoid many of the problems associated with common solvent extraction. These problems include phase separation, solvent loss, and emulsion formation, as well as shortcomings that arise from loading and flooding in both conventional mixer-settlers and column contactors (e.g. packed towers) [7,8]. Although, due to the resistance of membranes, such dispersion-free processes may result in a slower rate of mass transfer compared with traditional column operations [9,10], they could possess possible advantages such as the increased mass transfer offered by the higher surface/volume ratio associated with microporous hollow fiber membranes. Membrane contactors possess additional advantages, such as the capability of continuous treatment of large amounts of dilute solutions without directly mixing aqueous and organic phases, as well as reductions in equipment volume and space.

Emulsion liquid membrane, a novel type of extraction method, effectively eliminates the equilibrium limitation, but the demulsification step renders the operation rather difficult [11,12]. Another technique employs two hollow fiber modules– one for extraction and the other for re-extraction–thereby eliminating the equilibrium limitation and imparting high efficiency [13]. A systematic examination of the performance of solvent extraction in hollow fiber membrane contactors (HFMCs) would advance this method.

In this work, extraction separation of Co(II) from Ni(II) in sulfate solutions using two hollow fiber extractors with D_2EHPA reagents was experimentally investigated. Commercially available D_2EHPA was selected as a mobile carrier because it is cheaper, than Cyanex reagents and because the equilibrium and kinetic parameters for the extraction of Co(II) and Ni (II) could be obtained from the literatures [14,15]. Experiments were performed to determine the effects of the feed pH, carrier concentration, strip acidity, and flow rates of the fluids. The extraction efficiency and recovery for Co(II) using one-stage and two-stage HFMCs experiments were also discussed.

2. Experimental

2.1. Apparatus, modules, and solutions

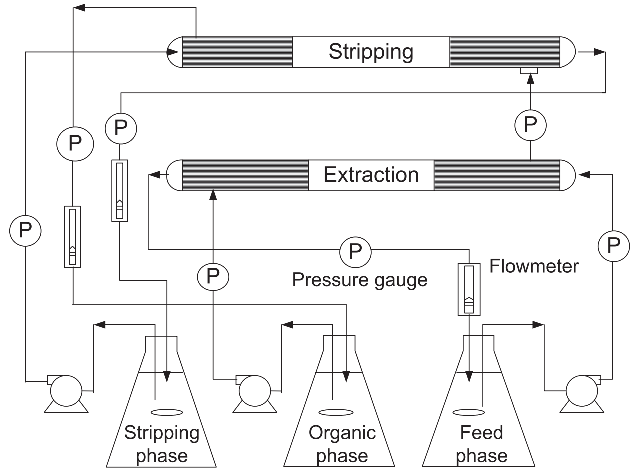

Fig. 1. Schematic representation of experimental setup for extraction and re-extraction in hollow fiber contactors.

Fig. 1 shows the experimental set-up for the extraction and re-extraction processes. The microporous hollow fiber modules subject to analysis were Hoechst Celanese Liqui-Cel Extra-Flow 2.5 × 8 Membrane Contactors (Model 5PCG 261, Table 1). These modules are small laboratory-scale versions equipped with three 0–1 $\mathrm{dm^3/min}$ pumps and flow meters that are specifically designed for experimental purposes. D_2EHPA was supplied by Aldrich Co. Kerosene, obtained from Union Chemical Works Ltd., Taiwan, was washed twice with 20 vol.% H_2SO_4 to remove aromatics and then was washed with deionized water three times. The metal salts ($CoSO_4$, $NiSO_4$) and other inorganic chemicals were supplied by Merck Co. (analytical reagent grade). The organic (membrane)

Table 1
Characteristics of the microporous hollow fiber modules

Description	Hoechst Celanese Liqui-Cel Extra-Flow 2.5 × 8 membrane contactor (Model 5PCG-261)
1. Shell characteristics	
Material	Polypropylene
Length	20.3 cm
Inner diameter, $2R_o$	6.3 cm
Outer diameter, $2R_i$	7.7 cm
2. Fiber characteristics	
Material	Celgard X-30 240 polypropylene hollow fiber
Number of fibers, N	10,200
Effective length, L	19.8 cm
Inner diameter, $2r_i$	240 μm
Outer diameter, $2r_o$	300 μm
Effective surface area, A	1.4 m
Effective area/volume	29.3 $\mathrm{cm^2/cm^3}$
Average pore size, d_p	0.03 μm
Membrane porosity, ε	0.4
Membrane tortuosity, τ	2.6

phase was prepared by the addition of D_2EHPA to kerosene (concentration 0.1–0.5 M). The aqueous feed was prepared by dissolving the metal salts ($CoSO_4$, $NiSO_4$) in deionized water. The feed pH was adjusted by adding small amounts of either H_2SO_4 or NaOH. A pH control device was used to keep the pH of the feed solution in the HFMCs constant. The aqueous strip phase was prepared by the addition of H_2SO_4 to deionized water (0.1–2.0 M).

2.2. Experimental procedures

In all HFMCs experiments, including one-stage (feed/organic/strip) and two-stage (feed/organic and organic/strip), both phases were contacted in a countercurrent and re-circulating mode. In both modules, the aqueous phases (1 L, 500 ppm Co and Ni in 0.1 mol/dm^3 Na_2SO_4) flowed through the tube side (200–600 cm^3/min), while the organic phase (1 L, 0.1–0.5 mol/dm^3 D_2EHPA in kerosene) circulated through the shell side of fibers (200–600 cm^3/min), wetting the pores of hydrophobic fibers. Pressure gauges and valves were used to control the flow rates and to ensure that a positive pressure of about 2–5 psi g was maintained on the aqueous side of the membrane [9,13]. The aqueous–membrane interface is stabilized by holding a pressure higher on the non-wetting liquid than that maintained on the wetting liquid, but lower than that necessary for the non-wetting liquid to displace the wetting liquid from the pores.

Prior to operating the modules, the organic phases of interest and deionized water were fed into each side of the modules for 30 min. The flow rates of aqueous and organic phases were fixed at required values and stabilized by controlling pressure gauges. The strip phase (1 L) then was replaced by the H_2SO_4 solution, and the feed phase was replaced by the solution containing different concentrations of solute. The extraction and re-extraction then was started. Aqueous feed and strip samples (1 cm^3) were taken at preset time intervals, and the concentrations of metallic ions were determined by using an atomic absorption spectrophotometer (Varian Model 220FS). The concentrations of Co(II) and Ni(II) in the organic phase were obtained by mass balance. The feed pH was measured by using a pH meter (Horiba Model F-23).

In this study, the extractability of metal ion was determined by the percentage of extraction:

$$\text{Percent extraction} = (C_{M,f,0} - C_{M,f})/C_{M,f,0} \times 100 \qquad (1)$$

where $C_{M,f,0}$ and $C_{M,f}$ are the metal ion concentrations in feed phase at $t = 0$ and t, respectively.

The percentage of recovery of metal was calculated by:

$$\text{Recovery} = C_{M,s}/C_{M,f,0} \times 100 \qquad (2)$$

where $C_{M,s}$ is the metal ion concentration in strip phase at $t = t$.

To express the separation quantitatively in extraction module, the separation factor, β, was defined as follows:

$$\beta_{(\mathrm{Co/Ni}),f} = (C_{\mathrm{Co},f}/C_{\mathrm{Co},f,0})/(C_{\mathrm{Ni},f})/C_{\mathrm{Ni},f,0}) \qquad (3)$$

3. Results and discussion

3.1. Batch solvent extraction equilibrium of metallic ions

The extraction reaction of Ni(II) or Co(II) ions in aqueous solutions with an organic solution containing a cation-exchange extractant of D_2EHPA may be represented as [16] follows:

$$\mathrm{M}^{2+}_{\mathrm{aq}} + \overline{2(\mathrm{HR})_2} \Leftrightarrow \overline{MA_2(\mathrm{HR})_2} + 2H^+_{\mathrm{aq}} \qquad (4)$$

The term $(HR)_2$ refers to the dimeric form of the extractant (D_2EHPA) in the organic phase. It has been reported elsewhere that this extractant exists as a dimer under these experimental conditions [3]. The batch solvent extraction was carried out in a pH range of 2–7 using 0.1 M D_2EHPA as shown in Fig. 2. The extraction efficiencies for Co(II) increase from 30% to 100% as the equilibrium pH_e increases from 4 to 5.5, but the efficiency remains constant thereafter. However, the extraction efficiencies for Ni(II) increase from 3.5% to 83% as the pH_e increases from 4 to 5.5. The pH_{50} of Co (II) and Ni(II) are 4.5 and 5.5, respectively (pH_{50} is defined as the pH at which 50% recovery of metal is achieved). Therefore, we investigated extraction separation using the HFMCs in the pH range of 4–5.

3.2. Effect of operational variables on extraction efficiency and recovery in HFMCs

To evaluate the performance of hollow fiber membrane contactors (HFMCs) as extraction devices, the initial metallic concentration of 500 ppm was selected. The impact of the feed pH, D_2EHPA concentration, strip acidity and flow rates of the fluids on the extraction efficiency, and recovery are shown in Figs. 3–8. The effect of the feed pH on percent extraction and recovery for metals in HFMCs at various time points is shown in Fig. 3(a)–(c). The extraction efficiencies for both metals increase with increasing feed pH. Co(II) is preferentially extracted relative to Ni(II) with D_2EHPA as the extractant. Such trend was found by the previous

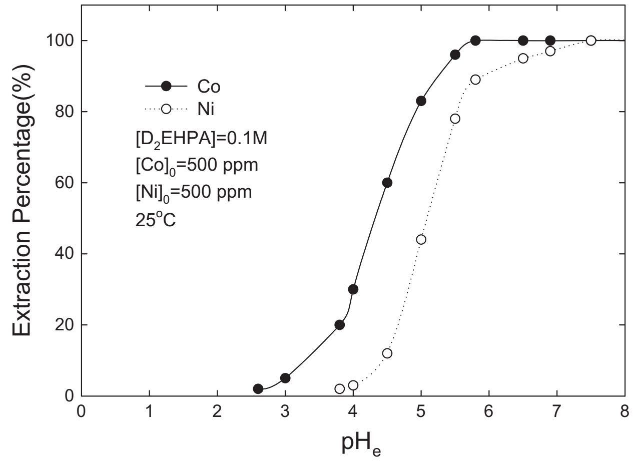

Fig. 2. Effect of pH$_e$ on the extraction efficiencies of Co and Ni(II) in H_2SO_4 using 0.1 mol/dm^3 D_2EHPA.

literature [17]. Ribeiro Jr. et al. studied the cobalt/nickel separation by liquid surfactant membranes (SLM) using Cyanex 302 as carrier. They found that the percentages extraction of Co(II) and Ni(II) increased with pH by the SLM technique [17]. It can be seen in Fig. 3(c) that the recovery for Co(II) in the re-extraction module increases from 26.4% to 30% with co-extraction for Ni (II) from 3.0% to 5.3% as the feed pH increases from 4 to 5 (2-h operation).

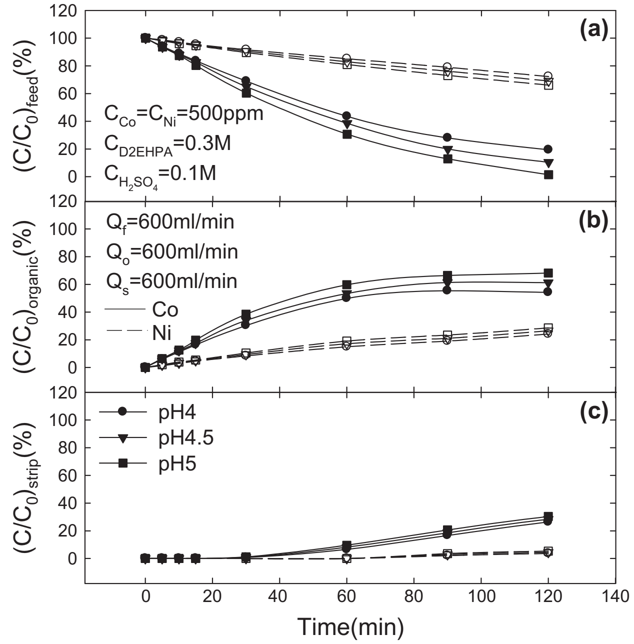

Fig. 3. Time profiles of the extraction and re-extraction for Co(II) and Ni(II) with D_2EHPA in HFMCs at different feed pH: (a) feed phase, (b) organic phase, and (c) strip phase.

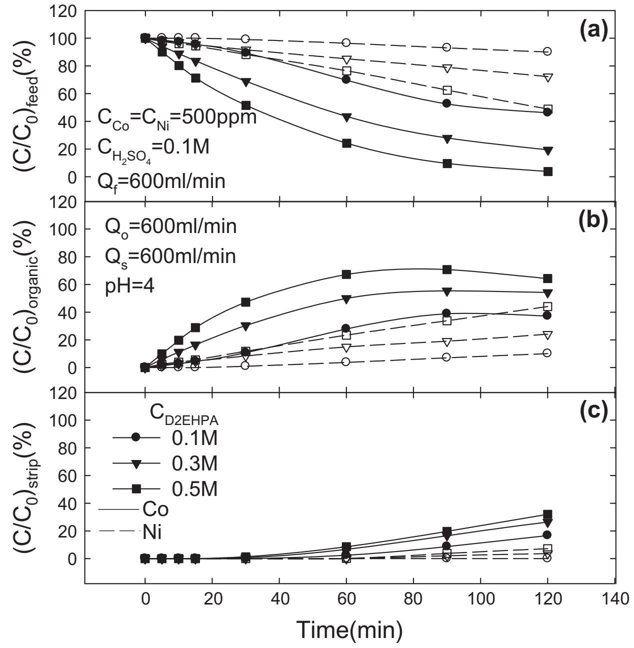

Fig. 4. Time profiles of the extraction and re-extraction for Co(II) and Ni(II) in HFMCs at different D_2EHPA concentrations: (a) feed phase, (b) organic phase, and (c) strip phase.

The effects of carrier concentrations on extraction efficiency and recovery in HFMCs are shown in Fig. 4 (a)–(c). Increasing the D_2EHPA concentration increases the extraction efficiencies for both metals in the extraction module. Devi et al. reported that the percentage extraction for Co(II) and Ni(II) increased with increasing the Na-D_2EHPA concentration [18]. Juang studied the competitive permeation of Co(II) and Ni(II) in SLM containing D_2EHPA in kerosene and reported that the fluxes of Co(II) and Ni(II) increased with increasing D_2EHPA concentration [19]. In this work, the percent extraction for Co(II) is only 54% using 0.1 M D_2EHPA solution but is 97% using 0.5 M D_2EHPA solution (2-h extraction). The co-extraction efficiency for Ni(II) is 10% using 0.1 M D_2EHPA solution but the efficiency is 51% using 0.5 M D_2EHPA solution (2-h extraction). The higher carrier concentration (0.5 M) would result in higher extraction efficiencies of both metal ions at pH 4 and would lead to a lower separation factor in the extraction modules. It can be seen in Fig. 4(c) that the recovery of Co(II) increases from 16.6% to 31.9% with co-re-extraction of Ni(II) from 0.0% to 7.1% as D_2EHPA concentration increases from 0.1 M to 0.5 M. For concerning about extraction efficiency and recovery, the operation condition in HFMCs with 0.3 M D_2EHPA was chosen for further studies. Here, using 0.3 M D_2EHPA, the percent extraction of Co(II) is 81% and the recovery of Co(II) is 26.4% (Ni/Co—11% in strip phase).

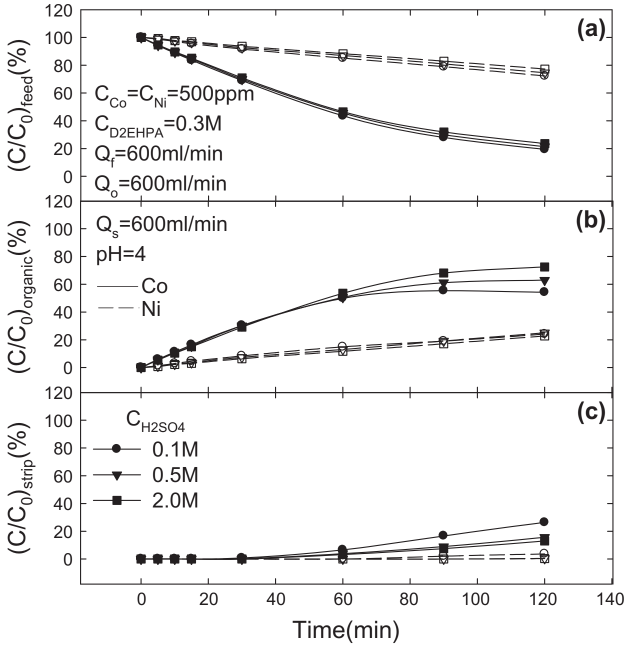

Fig. 5. Time profiles of the extraction and re-extraction for Co(II) and Ni(II) with D_2EHPA in HFMCs at different strip acidity: (a) feed phase, (b) organic phase, and (c) strip phase.

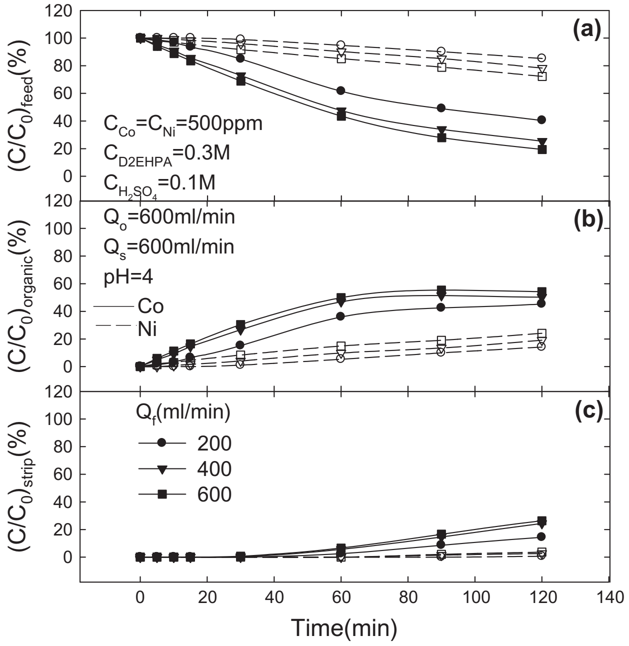

Fig. 6. Time profiles of extraction and re-extraction of Co (II) and Ni(II) in HFMCs at different flow rates of feed phase: (a) feed phase, (b) organic phase, and (c) strip phase.

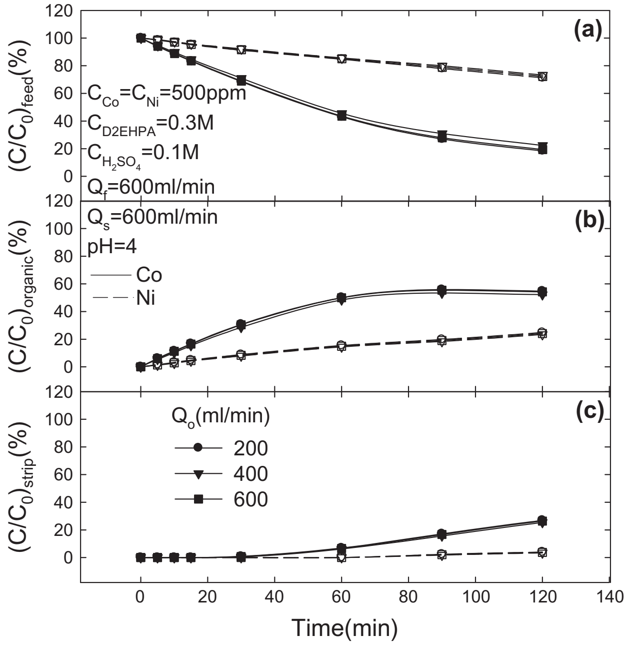

Fig. 7. Time profiles of extraction and re-extraction for Co (II) and Ni(II) in HFMCs at different flow rates of organic phase: (a) feed phase, (b) organic phase, and (c) strip phase.

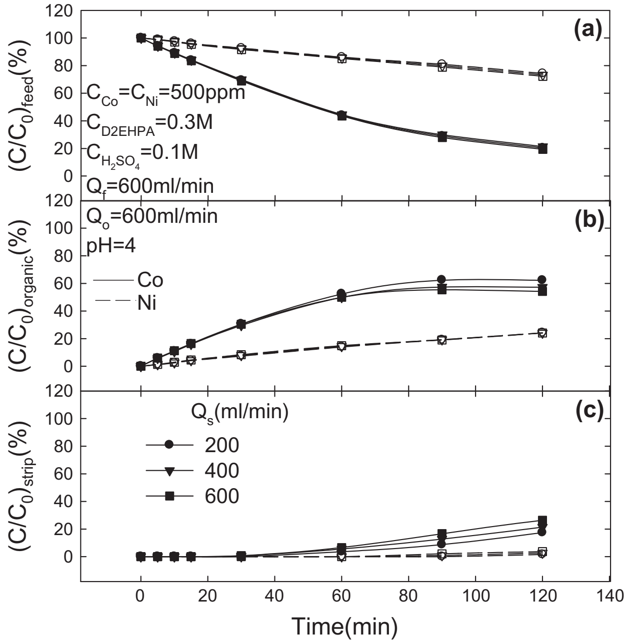

Fig. 8. Time profiles of extraction and re-extraction for Co (II) and Ni(II) in HFMCs at different flow rates of strip phase: (a) feed phase, (b) organic phase, and (c) strip phase.

The influence of strip acidity on extraction efficiency and recovery in HFMCs is shown in Fig. 5(a)–(c). The percent extraction for Co(II) increases slightly with increasing strip acidity in the extraction module. The recovery of Co(II) in the re-extraction module increases from 3.6% to 26.4% as the strip concentration increases from 0.1 to 2 M.

The effects of flow rates of three phases on the extraction efficiency and recovery are shown in Figs. 6–8. In the extraction modules, the extraction efficiencies and recoveries for both metals increase when the flow rates of feed phase increase (Fig. 6(a) and (c)). This observation is in agreement with earlier results [8,9]. It is likely that a higher fluid flow rate could reduce the resistance of the stagnant layer to diffusion under laminar flow and increase the complete use of the fiber area. However, the effect of flow rate of the organic phase on the percent extraction and recovery of Co(II) is ignored (Fig. 7). It can be observed that flow rate of the strip phase on the percent extraction of Co(II) is neglected, but the recovery of Co(II) slightly increases with increasing strip flow rates as shown in Fig. 8.

To compare with one-stage HFMCs, two-stage HFMC experiments were performed. The extraction percentages and recovery of Co(II) using HFMC in two stages (2 or 4 h of operation) under the condition of 0.3 M D_2EHPA and feed pH 4 are shown in Fig. 9 (a) and (b). In the same operating time (2-h), the percent extraction of Co(II) using two-stage HFMC (52%) (Fig. 9(a)) is smaller than that using one-stage HFMC (81%) (Fig. 9(c)). Besides, it could be also observed that the percent extraction and recovery of Co(II) in one-stage (2-h) operation (percent extraction: 81%, recovery: 26.4%) are the better than those in two-stage operation (Fig. 9(b), 4-h operation: 2-h extraction and 2-h re-extraction) (percent extraction: 76%, recovery: 23.5%). It should be noted that the later takes the double operating time compared with the former. It is due to the fact that this novel type of extraction method (employing two hollow fiber modules–one for extraction and the other for re-extraction) effectively eliminates the equilibrium limitation and imparts high efficiency.

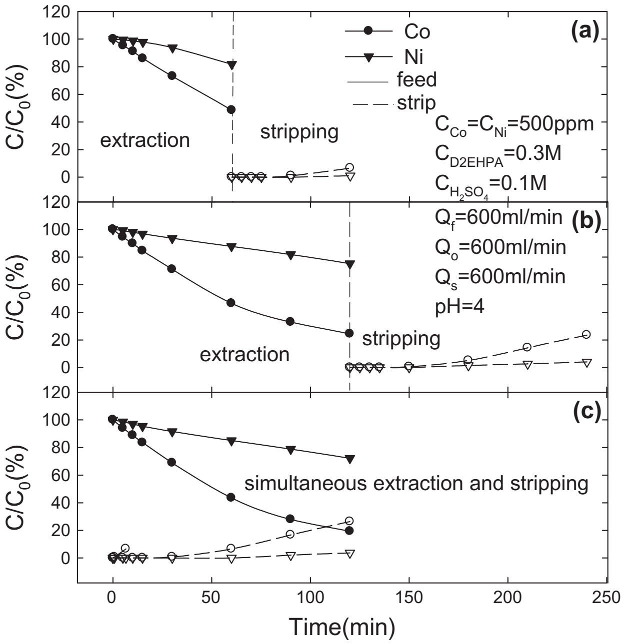

Fig. 9. Time profiles of the extraction and re-extraction for Co(II) and Ni(II) in HFMCs (a) using two-stage (2 h operation), (b) using two-stage (4-h operation), and (c) one-stage (2-h operation).

4. Conclusions

The non-dispersive extraction and separation of Co(II) from Ni(II) in sulfate solution to a kerosene solution of D_2EHPA with simultaneous re-extraction to a strip solution using two hydrophobic hollow fibers contactors have been studied. We found that the extraction efficiency and recovery for both Co(II) and Ni(II) increased with increasing feed pH, carrier concentration and the flow rate for the feed phase. However, the separation factor of the extraction module decreases with increasing feed pH. The extraction efficiency and recovery of Co(II) using one-stage HFMCs were better than those using two-stage HFMCs. It is feasible to separate Co(II) from Ni(II) in H_2SO_4 solution under appropriate conditions by HFMCs. The novel type of extraction method with HFMCs is a good alternative for extractive separation processes.

References

[1] B. Gupta, A. Deep, V. Singh, S.N. Tandon, Recovery of cobalt, nickel, and copper from sea nodules by their extraction with alkylphosphines, Hydrometallurgy 70 (2003) 121–129.

[2] P.E. Tsakiridis, S. Agatzini-Leonardou, Process for the recovery of cobalt and nickel in the presence of magnesium from sulphate solutions by Cyanex 272 and Cyanex 302, Miner. Eng. 17 (2004) 913–923.

[3] K. Sarangi, B.R. Reddy, R.P. Das, Extraction studies of cobalt (II) and nickel(II) from chloride solutions using Na–Cyanex 272. Separation of Co(II)/Ni(II) by sodium salts of D_2EHPA, PC-88A and Cyanex 272 and their mixtures, Hydrometallurgy 52 (1999) 253–265.

[4] D. Darvishi, D.F. Haghshenas, E.K. Alamdari, S.K. Sadrnezhaad, M. Halali, Synergistic effect of Cyanex 272 and Cyanex 302 on separation of cobalt and nickel by D_2EHPA, Hydrometallurgy 77 (2005) 227–238.

[5] B. Ramachandra Reddy, D. Neela Priya, Chloride leaching and solvent extraction of cadmium, cobalt and nickel from spent nickel–cadmium, batteries using Cyanex 923 and 272, J. Power Sources 161 (2006) 1428–1434.

[6] B. Ramachandra Reddy, D. Neela Priya, K.H. Park, Separation and recovery of cadmium(II), cobalt(II) and nickel(II) from sulphate leach liquors of spent Ni–Cd batteries using phosphorus based extractants, Sep. Purif. Technol. 50 (2006) 161–166.

[7] S.H. Lin, R.S. Juang, Simultaneous extraction and stripping of EDTA-chelated metallic anions with Aliquat 336 in hollow fiber contactors, Chem. Eng. Sci. 57 (2002) 143–152.

[8] S.H. Lin, C.N. Chen, R.S. Juang, Kinetic analysis on reactive extraction of aspartic acid from water in hollow fiber membrane modules, J. Membr. Sci. 281 (2006) 186–194.

[9] S.H. Lin, R.S. Juang, Kinetic modeling of simultaneous recovery of metallic cations and anions with a mixture of extractants in hollow-fiber modules, Ind. Eng. Chem. Res. 41 (2002) 853–861.

[10] Z. Ren, W. Zhang, H. Meng, J. Liu, S. Wang, Extraction separation of Cu(II) and Co(II) from sulfuric solutions by hollow fiber renewal liquid membrane, J. Membr. Sci. 365 (2010) 260–268.

[11] M. Matsumoto, K. Knodo, F. Nakashio, Extraction of copper with liquid surfactant membranes containing chelating reagent in a stirred tank, Proc. Solv. Extr. Conf., ISEC'83, Denver, AIChE, New York, 1983, p. 55.

[12] K. Lee, D. Evans, E. Cussler, Selective copper recovery with two types of liquid membranes, AIChE J. 24 (1982) 860–868.

[13] S.H. Lin, R.S. Juang, Mass-transfer in hollow-fiber modules for extraction and back-extraction of copper(II) with LIX64N carriers, J. Membr. Sci. 188 (2001) 251–262.

[14] R.S. Juang, Modelling of the competitive permeation of cobalt and nickel in a di(2-ethylhexyl)phosphoric acid supported liquid membrane process, J. Membr. Sci. (1993) 157–166.

[15] R. Mohapatra, S.B. Kanungo, P.V.R.B. Sarma, Kinetics of transport of Co(II) from aqueous sulfate solution through a supported liquid membrane containing di(2-ethylhexyl) phosphoric acid in kerosene, Sep. Sci. Technol. 27 (1992) 765–781.

[16] K. Soldenhoff, M. Shamieh, A. Manis, Liquid–liquid extraction of cobalt with hollow fiber contactor, J. Membr. Sci. 252 (2005) 183–194.

[17] C.P. Ribeiro, Jr., O.S. Costa, Andrea, P.B. Lopes Iluska, F. Campos Frederico, A. Ferreira, Alessandro, A. Salum, Cobalt extraction and cobalt–nickel separation from a simulated industrial leaching liquor by liquid surfactant membranes using Cyanex 302 as carrier, J. Membr. Sci. 241 (2004) 45–54.

[18] N.B. Devi, K.C. Nathsarma, V. Chakravortty, Separation and recovery of cobalt(II) and nickel(II) from sulphate solutions using sodium salts of D_2EHPA, PC 88A and Cyanex 272, Hydrometallurgy 49 (1998) 47–61.