

Received: December 15, 2014; reviewed; accepted: March 12, 2015

SEPARATION OF COBALT FROM NICKEL USING NOVEL ULTRASOUND-PREPARED SUPPORTED LIQUID MEMBRANES CONTAINING CYANEX 272 AS CARRIER

Gerardo LEON*, Guillermo MARTINEZ*, Loreto LEON**,
María Amelia GUZMAN*

* Departamento de Ingeniería Química y Ambiental, Universidad Politécnica de Cartagena, 30203 Cartagena, Spain. gerardo.leon@upct.es

** Departamento de Ciencias Politécnicas, UCAM, Campus de los Jeronimos, Guadalupe, 30107 Murcia, Spain

Abstract: The demand for cobalt has increased significantly in recent years due to its use in a wide variety of products and processes. Cobalt and nickel often accompany each other in nature and close physicochemical properties of both metals make their separation a complicated practical problem. Organophosphorous extractants have been widely used to separate cobalt from nickel. This paper presents the preliminary results obtained for separation of cobalt from nickel using Cyanex 272 containing supported liquid membranes prepared by a novel ultrasound-assisted method. The results show that this novel supported liquid membrane preparation method leads to higher separation factors than those described in the literature under similar separation conditions.

Keywords: cobalt, nickel, separation, supported liquid membranes, ultrasound, facilitated counter-transport, Cyanex 272

Introduction

Cobalt is a metal of high economic value and strategic importance due its potential application in both scientific and technological fields. Cobalt is widely used in a variety of products and processes including alloys, hard materials (carbines), magnets, batteries, catalysts, glass, ceramics, pigments and lacquers (Cote, 2000). Its production has grown steadily over the last two decades, from a total production of 23.2 gigagrams (Gg) in 1995 to 56.6 Gg in 2005 (Kapusca, 2007) and to 77.2 Gg in 2012 (Cobalt Development Institute, 2013). Cobalt and nickel often accompany each other in nature and their separation is a complicated practical problem. As they have very close physicochemical properties, classical separations methods are not applicable and search for a new separation technologies has led to many achievements in solvent

extraction (Flett, 2005; Reddy et al., 2009; Sun et al., 2010), ion exchange (Mendes and Martins, 2004; Li et al., 2012) and liquid membrane (Gega et al., 2001; Kumbasar, 2012) techniques.

Liquid membranes have shown great potential as a separation method, especially in cases where solute concentrations are relatively low and other techniques cannot be applied efficiently. They offer a potentially attractive alternative in that they combine the processes of extraction and stripping (removal and recovery) into a single unit operation (Sastre et al., 1998).

As cobalt is usually recovered from nickel, to improve the selectivity of the liquid membrane separation process, a carrier reagent is incorporated in the membrane phase to preferentially transfer Co(II), rather than Ni(II), from the feed to the receiving phase across the membrane. Widely used carriers are organophosphorus compounds (Juang, 1993; Youn et al., 1997; Gega et al., 2001; Ribeiro et al., 2004; Kumbasar, 2009a; Kumbasar, 2009b), though, other extractants such as Alamine 300, (Kumbasar and Tutkun, 2008; Surucu et al., 2012) and 8 hydroxyquinoline (Kumbasar, 2012) have also been used. Though Cyanex 272 has been widely used in separation of Co(II) from Ni(II) by extraction (Gandhi et al., 1993; Lindell et al., 2000; Evans et al., 2012), its use in the liquid membrane processes is not so common.

Three kinds of liquid membranes have been described: bulk, supported and emulsion liquid membranes (Sastre et al., 1998). Supported liquid membranes are obtained when a rigid porous substrate is filled with the organic solution of the carrier. Most of the studies on Co(II)/Ni(II) separation by liquid membranes has been carried out using emulsion liquid membranes (Longquan et al., 1997; Ribeiro et al., 2004; Kumbasar, 2009a; Kumbasar, 2009b; Kumbasar, 2012). Only a few studies have used supported liquid membranes (Juang, 1993; Youn et al., 1997; Gega et al., 2001; Surucu et al., 2012) and only one of them have used Cyanex 272 as the carrier (Gega et al., 2001).

The object of this paper is to present the preliminary results obtained for separation of cobalt from nickel using supported liquid membranes prepared by a novel ultrasound-assisted method (León et al., 2013). This novel method enables higher values of transport efficiency, flux and permeability than other classical preparation methods (Leon et al., 2013). This is due to the modifications introduced in the structure of the polymeric support (increasing its pore radius and its pore density (Masselin et al., 2001; León et al., 2013)), and to increase in pore filling on the part of the organic solution of the carrier (Leon et al., 2013). These effects result from acoustical streaming and cavitation, generated when ultrasound passes through the organic solution (Leon et al., 2013), which decrease the viscosity of solution. It is due to higher temperature (Masselin et al., 2001), and high speed liquid jets directed at the support surface, which appear when cavitation occurs near the surface of the polymeric support used to prepare the supported liquid membrane (Kyllonen et al., 2005).

A carrier mediated counter-transport mechanism of Co(II) and Ni(II) ions through the supported liquid membrane, using Cyanex 272 as the carrier and H^+ as counter

ions, is presented in Fig.1. The carrier diffuses from the bulk membrane phase to the feed membrane interface, where metal(II) ions are exchanged for protons. Due to the high interfacial reactivity of Cyanex 272 (Vandergrift and Horowitz, 1980), a dimerized molecule undergoes acid dissociation and reacts with metal(II). During the process each metal(II) ion is exchanged for two protons (Reddy, Priya, 2006). The metal(II) carrier complexes formed diffuse through the membrane to the membrane receiving phase interface, where, by reversing the above reaction, protons are exchanged for metal(II) ions, which are released into the product phase; the carrier is regenerated, thus beginning a new separation cycle. The metal(II) transport mechanism is a coupled counter ion transport mechanism, with metal(II) and H^+ travelling in opposite directions.

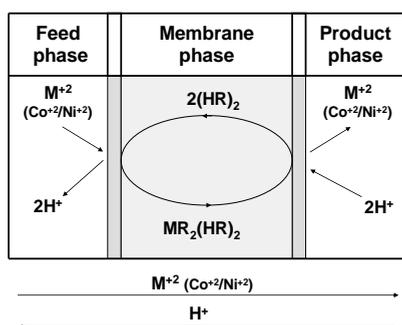


Fig. 1. Schematic representation of carrier-mediated counter-transport mechanism of Co(II) and Ni(II) through supported liquid membrane

Experimental

Experimental studies were carried out using two compartment permeation cells, which consisted of a feed phase (250 cm^3) separated from a receiving phase chamber (250 cm^3) by a supported liquid membrane with an effective area of 15 cm^2 . A schematic illustration of the experimental cell is shown in Fig. 2a.

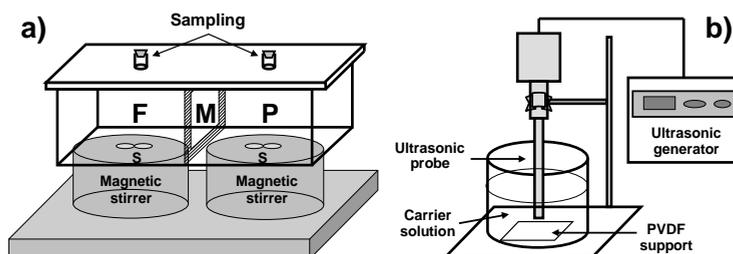


Fig. 2. Schematic representations of experimental transport cell (a) and sonication system (b)

Mixtures of cobalt(II) and nickel(II) at different concentrations ($8.5 \cdot 10^{-4}$ – $8.5 \cdot 10^{-3}$ M) in acetate buffer at different values of pH (3–6) were used as a feed phase. Aqueous sulphuric acid solutions (0.05–0.5 M) were used as a receiving phase. Both feed and receiving phases were mechanically stirred (50–300 rpm) at room temperature. A microporous hydrophobic PVDF GVHP film (20 cm² geometrical area) from Millipore Durapore (porosity 75%; pore dimension 0.22 μm; thickness 125 μm) was used as a solid porous support. The liquid membrane phase was formed of Cyanex 272 solutions of different concentrations (0.0689–0.6890 M) in commercial paraffin. The typical experimental conditions were: initial metal ion concentrations in the feed phase $3.4 \cdot 10^{-3}$ M, feed pH 5.5, carrier concentration in the membrane phase 0.344 M, sulphuric acid concentration in the receiving phase 0.2 M, and stirring speed in both feed and receiving phases 200 rpm.

The pores of micro porous support were filled with the organic solution of Cyanex 272 by soaking the polymeric support in the organic solution, at atmospheric pressure, assisted by ultrasound, using a Labsonic M (Sartorius) ultrasound equipment (titanium probe 10 mm diameter, sound rating density 130W/cm²), at 30 KHz, 150 μm, for 30 minutes (three times, 10 minutes each time at 5 minute intervals). The active layer of polymeric support was positioned perpendicularly to the direction of ultrasound and at a distance of 16 mm from the ultrasound probe (Fig. 2b).

Samples from the receiving phase compartment were taken at given time intervals and Co(II) and Ni(II) concentrations were measured by flame atomic absorption spectrophotometry using a Shimadzu AA-2600 equipment. Significant separation factor values were obtained after times of 120 minutes, which was selected as the end time. The experiments were carried out in duplicate and the results obtained showed less than 3% deviation.

Membrane fluxes (J) were determined by monitoring cobalt(II) and nickel(II) concentrations in the receiving phase as the function of time, based on the following equation (Hor et al., 2010):

$$J = \frac{V}{A} \frac{dC}{dt} \quad (1)$$

where V is volume of the product phase, A effective surface area of the membrane (geometrical area multiplied by porosity (Parhi, Sarangi, 2008)), C metal(II) concentration in the receiving phase, and t time elapsed. The metal(II) fluxes were calculated from the slope of straight line obtained, when plotting the metal concentration in the product phase as a function of time.

The Co/Ni separation factor (α), under different experimental conditions, was calculated by the following equation (Youn et al., 1997).

$$\alpha = \frac{\frac{J_{\text{Co}}}{[\text{Co}]_{f,0}}}{\frac{J_{\text{Ni}}}{[\text{Ni}]_{f,0}}} \quad (2)$$

where $[\text{Co}]_{f,0}$ and $[\text{Ni}]_{f,0}$ are the initial concentrations of Co(II) and Ni(II) in the feed phase, and J_{Co} and J_{Ni} are de initial fluxes of Co(II) and Ni(II), respectively.

Results and discussion

Cobalt-nickel separation by Cyanex 272 containing supported liquid membranes prepared by an ultrasound-assisted method leads to Co(II) fluxes that are about one hundred-folds higher than the fluxes of Ni(II) under all the experimental conditions assayed and to cobalt/nickel separation factors ranging from 20 to 200 (Figs. 3–7).

The effect of initial feed phase pH on the initial fluxes of Co(II) and Ni(II) and on their separation factor is shown in Figs. 3a and 3b. The Co(II) initial flux increases from pH 3 to 5.5 and then remains constant. The Ni(II) initial flux increases over the studied range of pH, although the increase between pH 3 and 5.5 is slightly lower than that observed for Co(II). The result of these flux variations with feed pH is increase in the separation factor above pH 3, which reaches a maximum at pH 5.5.

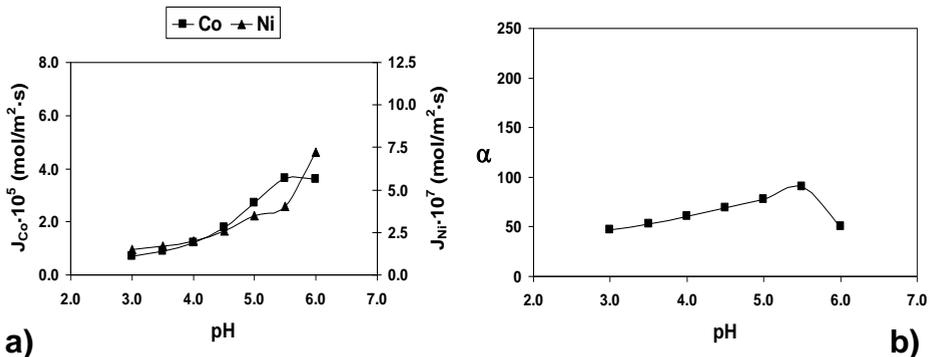


Fig. 3. Variation of initial fluxes of Co(II) and Ni(II) (a) and separation factor (b) with initial feed pH

The effect of carrier concentration in the membrane phase on the initial fluxes of Co(II) and Ni(II), and on their separation factor is shown in Figs. 4a and 4b. It can be seen that two metals behave differently. While the Co(II) initial flux increases with carrier concentration between 0.0689 and 0.344 mol/dm³ and then remains constant, the Ni(II) flux increases over the whole range of studied Cyanex 272 concentration. It leads to continuous decrease in the separation factor as the Cyanex 272 concentration increases.

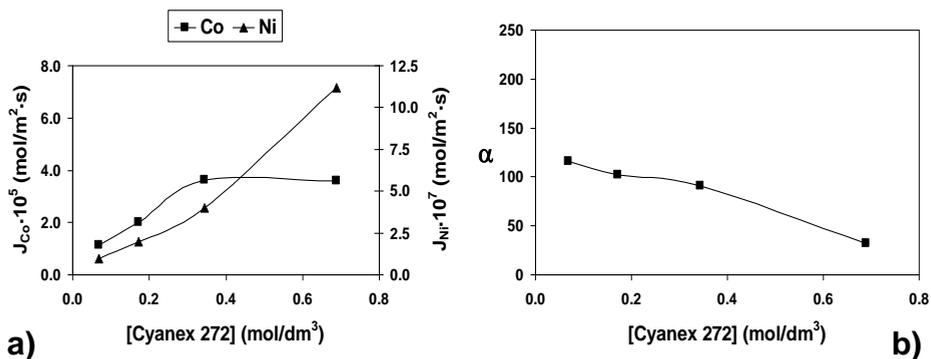


Fig. 4. Variation of initial fluxes of Co(II) and Ni(II) (a) and separation factor (b) with Cyanex 272 concentration in membrane phase

The effect of sulphuric acid concentration in the receiving phase on the initial fluxes of Co(II) and Ni(II), and on their separation factor is shown in Figs. 5a and 5b. Both metals behave similarly, their initial flux increasing as the sulphuric acid concentration increases from 0.05 to 0.20 M, while the initial fluxes of both metals remain constant above this concentration (a slight increase of Ni(II) initial flux is observed). It leads to gentle decrease in the Co/Ni separation factor, as the sulphuric acid concentration increases.

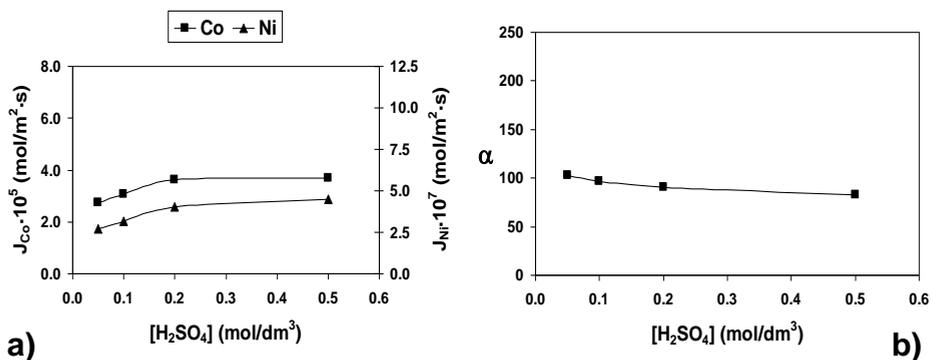


Fig. 5. Variation of initial fluxes of Co(II) and Ni(II) (a) and separation factor (b) with H₂SO₄ concentration in receiving phase

The effect of stirring rate on the initial fluxes of Co(II) and Ni(II), and on their separation factor is shown in Figs. 6a and 6b. For both metals, the initial flux increases when the stirring rate increases from 50 to 200 rpm (the increase is higher for the Ni(II) flux), and remains constant at higher stirring rates. It leads to decrease in the separation factor between 50 and 200 rpm and to a constant value above this stirring rate value.

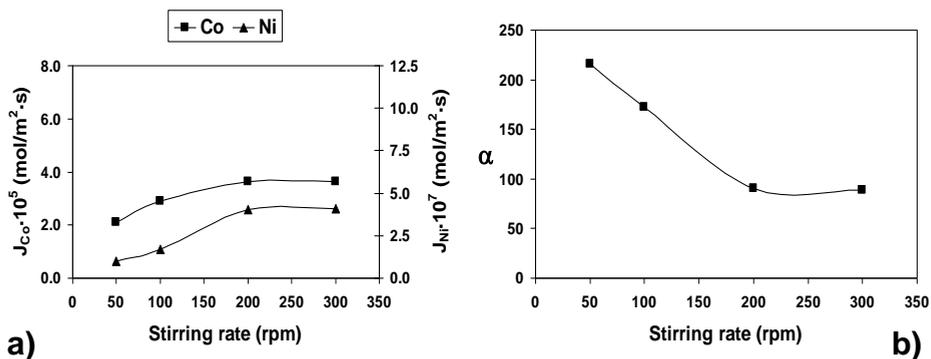


Fig. 6. Variation of initial fluxes of Co(II) and Ni(II) (a) and separation factor (b) with stirring rate

The effect of feed concentration on initial fluxes of Co(II) and Ni(II) and on their separation factor is shown in Figs. 7a and 7b. The flux of both metals increases with the metal concentration in the feed phase, although the increase in the Ni(II) flux is greater. It leads to decrease in the separation factor as the metal concentration in the feed phase increases (this decrease is four-fold when the metal concentration decreases ten-fold).

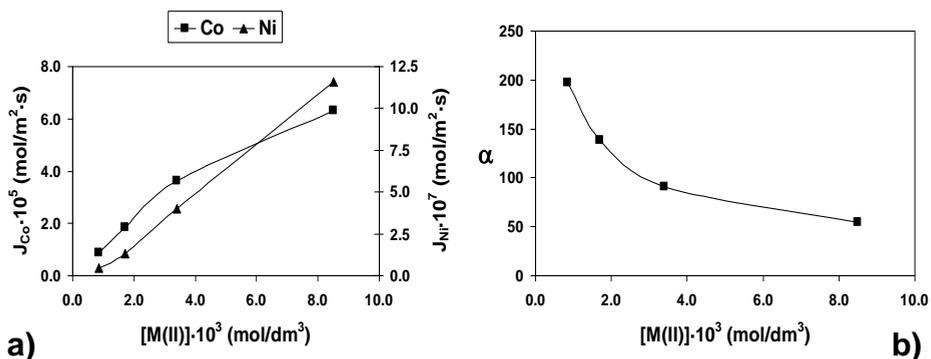


Fig. 7. Variation of initial fluxes of Co(II) and Ni(II) (a) and separation factor (b) with Co(II), Ni(II) concentrations in feed phase

According to these results, higher Co(II)/Ni(II) separation factors were obtained with a feed pH of 5.5, Cyanex 272 concentration in the membrane phase of 0.0689 M, sulphuric acid concentration in the receiving phase of 0.05 M, 50rpm stirring rate and $8.5 \cdot 10^{-4}$ M metallic ion concentration in the feed phase. Comparison of the results obtained in this work with those related with separation of cobalt(II) and nickel(II) by liquid membranes mentioned in the literature is difficult due to different experimental conditions used, that is different type of liquid membrane, carrier nature, receiving

phase nature, polymeric support, etc. Only Gega et al. (2001) used the same carrier and receiving phase (but different polymeric support), and a classical liquid membrane preparation method (soaking the polymeric support in the organic solution during 12 hours) can be compared. The separation factors obtained using our ultrasound-assisted method are about twenty-fold higher than those obtained by Gega et al. (2001). A possible explanation is that the supported liquid membrane prepared by the ultrasound-assisted method increases the preferential transport of Co(II) over Ni(II), due to higher pore size and porosity of the polymeric support, and to the greater degree of pore filling by the Cyanex 272 organic solution derived from the ultrasound-assisted preparation method.

Conclusions

In this work we present the preliminary results obtained for separation of cobalt from nickel through supported liquid membranes prepared by a novel ultrasound-assisted method. Separation was carried out through a carrier mediated counter-transport mechanism by using Cyanex 272 as the carrier and protons (H₂SO₄) as the counter-ions, under different experimental conditions. The supported liquid membrane was prepared by filling the pores of the microporous support with the organic solution of Cyanex 272 through soaking the polymeric support in the organic solution, at atmospheric pressure, assisted by ultrasound. The supported liquid membranes prepared by the ultrasound-assisted method led to fluxes of Co(II) that they are about one hundred-folds higher than the fluxes of Ni(II) under any of the experimental conditions assayed, and the cobalt-nickel separation factors ranging from 20 to 200. The highest Co(II)/Ni(II) separation factors were obtained at pH 5.5, at Cyanex 272 concentration in the membrane phase of 0.0869 M, 0.051 M sulphuric acid concentration in the receiving phase, 50 rpm stirring rate and 8.5·10⁻⁴ M metallic ion concentration in the feed phase. The Co(II)/Ni(II) separation factors obtained in this work are about twenty-fold higher than those described in the literature (Gega et al., 2001) using the same carrier and receiving phase. This is due to increase in the preferential transport of Co(II) over Ni(II) through the supported liquid membrane prepared by the ultrasound-assisted method, derived from the higher pore size and porosity of the polymeric support and from the greater degree of pore filling by the Cyanex 272 organic solution.

References

- COBALT DEVELOPMENT INSTITUTE, 2013. *First Half Production Statistics*. Cobalt News. 13, 3-4.
- COTE G., 2000. *Hydrometallurgy of strategic materials*, Solv. Extr. Ion Exch. 18, 703-727.
- EVANS H.A., VU L., BAHRI P.A., BARNARD K.R., 2012. *Development of an integrated model for cobalt solvent extraction using Cyanex 272*. Comput. Aid. Chem. Eng. 31, 550-554.
- FLETT D.S., 2005. *Solvent extraction in hydrometallurgy: The role of organophosphorus extractants*. J. Organometallic Chem. 690, 2426-2438.

- GANDHI M.N., DEORKAR N.V., KHOPKAR S.M., 1993. *Solvent extraction separation of cobalt(II) from nickel and other metals with cyanex 272*. *Talanta* 40, 1535-1539.
- GEHA J., WALKOWIAK W., GAJDA B., 2001. *Separation of Co(II) and Ni(II) ions by supported and hybrid liquid membranes*. *Sep. Purif. Technol.* 22-23, 551-558.
- HOR M., RIAD A., BENIJJAR A., LEBRUM L., HLAÏBI M., 2010. *Technique of supported liquid membranes (SLMs) for the facilitated transport of vanadium ions (VO₂⁺)*. *Parameters and mechanism on the transport*. *Desalination* 255, 188-195.
- JUANG R.S., 1993. *Modelling of the competitive permeation of cobalt and nickel in a di(2-ethylhexyl)phosphoric acid supported liquid membrane process*. *J. Membr. Sci.* 85, 157-166.
- KAPUSCA J.P.T., 2007. *Cobalt production and markets: A brief overview*. *Cobalt News* 7, 9-12.
- KUMBASAR R.A., 2009a. *Selective extraction and concentration of cobalt from acidic leach solution containing cobalt and nickel through emulsion liquid membrane using PC-88A as extractant*. *Sep. Purif. Technol.* 64, 273-279.
- KUMBASAR R.A., 2009b. *Cobalt-nickel separation from acidic thiocyanate leach solutions by emulsion liquid membranes (ELMs) using TOPO as carrier*. *Sep. Purif. Technol.* 68, 208-215.
- KUMBASAR R.A., 2012. *Selective transport of cobalt (II) from ammoniacal solutions containing cobalt and nickel by emulsion liquid membranes using 8-hydroxyquinoline*. *J. Ind. Eng. Chem.* 18, 145-151.
- KUMBASAR R.A., TUTKUN O. 2008. *Separation of cobalt and nickel from acidic leach solutions by emulsion liquid membranes using Alamine 300 (TOA) as a mobile carrier*. *Desalination* 224, 201-208.
- KYLLONEN, H.M., PIRKONEN, P., NYSTROM, M., 2005. *Membrane filtration enhanced by ultrasound: a review*. *Desalination* 181, 319-335.
- LEÓN G., MARTÍNEZ G., GUZMÁN M.A., MORENO J.I., MIGUEL B., FERNÁNDEZ-LÓPEZ J.A., 2013. *Increasing stability and transport efficiency of supported liquid membranes through a novel ultrasound-assisted preparation method: Its application to cobalt(II) removal*. *Ultrason. Sonochem.* 20, 650-654.
- LI B., LIU F., WANG J., LING C., LI L., HOU P., LI A., BAI Z., 2012. *Efficient separation and high selectivity for nickel from cobalt-solution by a novel chelating resin: Batch, column and competition investigation*. *Chem. Eng. J.* 195-196, 31-39.
- LINDELL E., JÄÄSKELÄINEN E., PAATERO E., NYMAN B., 2000. *Effect of reversed micelles on Co/Ni separation by Cyanex 272*. *Hydrometallurgy* 56, 337-357.
- LONGQUAN L., CHENG W., YADONG L. 1997. *Separation of cobalt and nickel by emulsion liquid membrane with the use of EDTA as masking reagent*. *J. Membr. Sci.* 135, 173-177.
- MASSELIN I., CHASSERAY X., DURAND-BOURLIER L., LAINE J.M., SYZARET P.Y., LEMORDANT D., 2001. *Effect of sonication on polymeric membranes*. *J. Membr. Sci.* 181, 213-220.
- MENDES F.D., MARTINS A.H., 2004. *Selective sorption of nickel and cobalt from sulphate solutions using chelating resins*. *Int. J. Min. Proc.* 74, 359-371.
- PARHI P.K., SARANGI K., 2008. *Separation of copper, zinc, cobalt and nickel ions by supported liquid membrane technique using LIX 84I, TOPS-99 and CYANEX 272*. *Sep. Purif. Technol.* 59, 169-174.
- REDDY B.R., PRIYA D.N., 2006. *Chloride leaching and solvent extraction of cadmium, cobalt and nickel from spent nickel-cadmium batteries using Cyanex 923 and 272*. *J. Power Sources* 161, 1428-1434.
- REDDY B.R., RAO S.V., PARK K.H., 2009. *Solvent extraction separation and recovery of cobalt and nickel from sulphate medium using mixtures of TOPS 99 and TIBPS extractants*. *Min. Eng.* 22, 500-505.

- RIBEIRO C.P., COSTA A.O.S., LOPES I.P.B., CAMPOS F.F., FERREIRA A.A., SALUD A., 2004. *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, 45-54.
- SASTRE A.M., KUMAR A., SHUKLA J.P., SINGH R.K., 1998. *Improved techniques in liquid membrane separations: An overview*. Sep. Purif. Meth. 27, 213-298.
- SUN X., JI Y., ZHANG L., CHEN J., LI D., 2010. *Separation of cobalt and nickel using inner synergistic extraction from bifunctional ionic liquid extractant (Bif-ILE)*. J. Hazard. Mater. 182, 447-452.
- SURUCU A., EYUPOGLU V., TUTKUN O., 2012. *Selective separation of cobalt and nickel by flat sheet supported liquid membrane using Alamine 300 as carrier*. J. Ind. Eng. Chem. 18, 629-634.
- VANDERGRIFT C.F., HOROWITZ E.P., 1980. *Interfacial activity of liquid-liquid extraction reagents-I: Dialkyl phosphorous based acids*. J. Inorg. Nucl. Chem. 42, 119-125.
- YOUN I.J., LEE Y., JEONG J., LEE W.H., 1997. *Analysis of Co-Ni separation by a supported liquid membrane containing HEH(EHP)*. J. Membr. Sci. 125, 231-236.