EVALUATION OF KINETIC CONSTANTS AND TRANSPORT EFFICIENCIES AT MEMBRANE INTERFACES TO OPTIMIZE Co(II) RECOVERY BY BULK LIQUID MEMBRANES

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Abstract — The harms of heavy metals to the environment and public health joined to their character of valuable resource, have lead to an increasing interest in the search of efficient processes for their removal/recovery. In this paper we study the optimization of cobalt(II) recovery by bulk liquid membranes through a carrier facilitated counter transport mechanism, using DP8R as carrier and H2SO4 as stripping agent (protons as counter-ions), by analyzing the influence of different operational parameters (carrier concentration in the membrane, stripping agent concentration in the product phase, stirring rate and organic phase volume) on both the extraction/stripping kinetic constants and the Co(II) transport efficiencies through the feed/membrane and the membrane/product interfaces.

Keywords — Cobalt recovery, bulk liquid membranes, DP8R, facilitated counter-transport.

I. INTRODUCTION

Its many potential applications in both scientific and technological fields have made cobalt one of the most sought after heavy metals on earth. The strategic and industrial importance of cobalt derives from its application in many technological fields such as alloying additive to steels, component of magnetic alloys, catalyst, glass and ceramics making, medicine, manufacture of batteries, and production of paints and lacquers (Cote, 2000). This has lead to a steadily growth in cobalt production in the last two decades, from 23207 Mg in 1995 to 56635 Mg in 2005 (Kapusca, 2007) and to around 98113 Mg in 2015 (Cobalt Development Institute, 2016). This exploitation has lead to a gradual decrease in primary cobalt resources and an increase in cobalt-wastes. Therefore, the recovery of cobalt from raw materials and secondary sources must be considered an interesting research field from both economic and environmental viewpoints.

Different techniques have been described for the recovery of cobalt from water solutions, including chemical precipitation (Gómez-Lahoz et al., 1993), adsorption (Ghaly et al., 2016; Ligandimine et al., 2016), biosorption (Kyzas et al., 2016; Dabbagh et al., 2016), solvent extraction (Wieszczyk et al., 2015), ion exchange (Vaughan et al., 2016), electrowinning (Sharma et al., 2005), micellar enhanced ultrafiltration (Kumar and Marathe, 2011), nanofiltration (Gherasim et al., 2015), forward osmosis (Liu et al., 2017), liquid membranes (Alguacil et al., 2011; León et al., 2013, León et al., 2016a) and combined methods (Sadyrbaeva, 2014).

Liquid membranes have shown great potential as a separation method since they combine the process of extraction and stripping (removal and recovery) into a single unit operation (Sastre et al., 1998). The extraction chemistry is basically the same as that for liquid-liquid extraction, but transport is governed by kinetic rather than equilibrium parameters, that is, by a non-equilibrium mass transfer.

To improve the effectiveness of the removal/recovery process facilitated transport mechanisms have been described (León, 2016). In carrier mediated transport an ion exchange reagent is incorporated in the membrane phase to carry the diffusing species across the membrane to the product phase, a process that is usually accompanied by the transport of other chemical species from the product to the feed phase. In this study, DP8R (bis-2-ethylhexyl phosphoric acid) has been used as carrier due to its chemical stability, fast extraction and stripping of Co(II) and low solubility in the aqueous phases (Sadyrbaeva, 2014).

To optimize the recovery of Co(II) by bulk liquid membranes containing DP8R as carrier and protons (H2SO4) as counter-ions, an analysis of the effect of different operational parameters (carrier concentration in membrane phase, stripping agent concentration in product phase, stirring rate and organic phase volume) on the extraction/stripping kinetics constants and on the Co(II) transport efficiencies through the feed/membrane and membrane/product interfaces, is carried out in this paper.

The transport mechanism is illustrated in Fig. 1. The carrier DP8R, (HR)2, diffuses from the bulk membrane phase to the feed membrane interface where, due to its high interfacial reactivity (Vandergrift and Horowitz, 1980), a dimerized molecule undergoes acid dissociation (Komasawa et al., 1981) and reaction with cobalt (II) according to the chemical equation:

\[
\text{Co}^{2+} \text{(aq) +2(HR)2 (org)} \leftrightarrow \text{CoR2(HR)2 (org) + 2H}^+ \text{(aq)}
\]

The cobalt (II)-DP8R complex formed (CoR2(HR)2) diffuses through the membrane to the membrane product interface where, by reversing the above reaction, protons are exchanged for cobalt (II) ions, which are re-
the product phase. DP8R is regenerated, thus initiating a new separation cycle. The cobalt (II) transport mechanism is therefore a coupled countertransport mechanism, with Co (II) and H⁺ travelling in the opposite direction.

This mechanism involves two consecutive reactions, the extraction and stripping reactions, and it is interesting because it offers the possibility of transporting a component against its own concentration gradient (De Gyves and Rodríguez, 1999).

**II. METHODS**

**A. Transport Experiments**

Experimental studies were carried out applying the bulk liquid membrane technique, using a stirred transfer Lewis type cell with bulk liquid membrane layered over feed and product phases (Fig. 1). The feed phase contained a 0.025 M cobalt (II) sulphate solution in formiate buffer, pH 4, the membrane phase consisted in solutions of different concentrations of DP8R (1% to 10%) in kerosene and the product phase comprised sulfuric acid solutions of different concentrations (0.05 M to 2 M). The effect of stirring speed (50 to 250 rpm) and membrane phase volume (12.5 to 50 cm³) were also analyzed. Typical experimental conditions were: 6% DP8R, 1 M H₂SO₄, 200 rpm stirring speed, 25 mL membrane phase volume, time 24 hours.

**B. Methods**

Samples of feed and product phases were taken at intervals and Co(II) ion concentration was determined by UV spectrophotometry using an Unicam UV2 instrument, measuring the absorbance of the colour developed by the product of the reaction between Co(II) and xylenol orange (Chaudry et al., 1990; Basher and Ehtayeb, 2014). All experiments were carried out in duplicate and the relative standard deviation between replicate samples was less than 4%.

Efficiency percentages of Co(II) extracted from the feed to the membrane phase (F/M) and stripped from the membrane to the product phase (M/P), at 24 hours, were calculated from the following equations (Ng et al., 2011):

\[
F/M = \frac{C_{f0} - C_{f}}{C_{f0}} \times 100
\]  

(1)

\[
M/P = \frac{C_{p0} - C_{p}}{C_{p0}} \times 100
\]  

(2)

where \(C_{f0}\) is the initial concentration of cobalt (II) ions in the feed phase and \(C_{f}\) and \(C_{p}\) are the concentrations of cobalt (II) in the feed and product phases, respectively, at a time \(t\).

The carrier facilitated counter-transport of Co (II) ions through bulk liquid membranes has been analyzed by the kinetic laws of two consecutive irreversible first-order reactions, the removal or extraction reaction and the recovery or stripping reaction.

\[
k_e \quad \text{Co(II)}_f \rightarrow \text{Co(II)}_m \rightarrow \text{Co(II)}_p
\]

where \(k_e\) and \(k_s\) are the apparent pseudo first order constants for the global transport process from the feed phase to the membrane phase and from the membrane phase to the product phase, respectively.

This kinetic behaviour can be described according to the following equations (Szpakowska, 1994; He et al., 2000; León et al., 2016b).

\[
R_f = \exp(-k_e t),
\]  

(3)

\[
R_m = \frac{k_s}{k_e - k_s} \left[ \exp(-k_s t) - \exp(-k_e t) \right],
\]  

(4)

\[
R_p = 1 - \frac{1}{k_s - k_e} \left[ k_s \exp(-k_s t) - k_e \exp(-k_e t) \right].
\]  

(5)

Dimensionless reduced concentrations of cobalt (II) in the feed \((R_f)\), membrane \((R_m)\) and product phases \((R_p)\) were used \((R_f=C_f/C_{f0}, R_m=C_m/C_{m0} \text{ and } R_p=C_p/C_{p0})\), the sum of \(R_f+R_m+R_p\) being unity. In the experiments with different membrane volumes, a “corrected concentration”, related to feed volume, was defined in the membrane phase \((C_{m0}=V_mC_m/V_f)\) in order to use the relation \(R_f+R'_m+R_p=1\).

Numerical analysis, by non-linear curve fitting, of the variation with time of Co(II) reduced concentration in the feed, in the membrane and in the product phase, permits
III. RESULTS AND DISCUSSION

The influence of carrier concentration in the membrane phase on cobalt(II) removal/recovery is shown in Fig. 3. The increase in carrier concentration in the membrane phase up to 6% leads to an increase in the extraction kinetic constant, but to a decrease in the stripping kinetic constant. This produces an increase in the Co(II) transport efficiency through the feed/membrane and membrane/product interfaces, being the latter much less significant. Higher values of carrier concentration in the membrane phase facilitates the formation of the CoR₂(HR)₂ complex, that is, the extraction of cobalt(II) from the feed to the membrane phase, but also increases the mass transfer resistance due to the increase in the viscosity of membrane phase, which causes a reduction on the diffusivity of CoR₂(HR)₂ complex through the membrane phase. Further increase in carrier concentration has no significant influence due to both, the saturation of the feed membrane interface by the carrier and the increase in membrane phase viscosity.

The influence of stripping agent concentration in the product phase on Co(II) removal/recovery is shown in Fig. 4. The increase in sulphuric acid concentration in the product phase from 0.05M to 1.00M leads to an increase in both the extraction and the stripping kinetic constants, being the latter much more significant. This, produces a slightly increase in the transport efficiency through the feed/membrane interface, but an important increase in the transport efficiency through the membrane/product interface, because the acidity of the product phase enhanced the stripping reaction at that membrane/product interface and, consequently, the driving force for the transport of Co(II) ions through the membrane phase. A further increase in sulphuric acid concentration to 2.00M has no so significant effect on Co(II) removal/recovery due to both the saturation of the membrane/product interface by the stripping agent and the increase in the product phase viscosity.

The influence of the stirring rate on Co(II) removal/recovery is shown in Fig. 5. A higher stirring rate leads to a noticeable increase in cobalt removal/recovery. The increase in the stirring rate leads to the increase in both, the extraction and the stripping kinetic constants, which produces, obviously, an increase in the transport efficiencies through the feed/membrane and the membrane/product interfaces. These results can be explained by the decrease in the size of the boundary layers at both sides of the feed/membrane and membrane/product interfaces (with no alteration of their hydrodynamic stability) resulting from the increase in stirring speed, which enhanced both the effectiveness and the speediness of the Co(II) transport through the liquid membrane. These variations are important between 20 and 150 rpm but they are much less significant between 150 and 250 rpm.

The influence of the membrane phase volume on Co(II) removal/recovery is shown in Fig. 6. The increase in the volume of membrane phase, without modifying cobalt concentration in the feed phase and carrier concent
the number of carrier molecules that accompanied the
increase in membrane volume. The decrease in the
stripping kinetic constant is due to the diminution of the
concentration of CoR₂(HR)₂ complex in membrane
phase, which diminishes the diffusivity of the complex
through that membrane phase and, consequently, the
effectiveness and the speediness of the cobalt (II) stripping
reaction at the membrane/product interface. The global
result is a slightly increase in the Co(II) transport effi-
ciency through the feed/membrane interface, but an im-
portant decrease in transport efficiency through the
membrane/product interface.

According to the described results, optimal experi-
mental/economic conditions for Co(II) removal/recovery by bulk liquid membranes using DP8R as
carrier are as follows: 6% DP8R concentration in mem-
brane phase, 1M sulfuric acid concentration in product
phase, 150 rpm stirring speed and 12.5 mL volume of
membrane phase.

III. CONCLUSIONS
A study to optimize the recovery of Co(II) from aque-
sous solutions by bulk liquid membranes, through a car-
er facilitiated countertransport mechanism, using
DP8R, as mobile carrier, and sulphuric acid, as stripping
agent (protons as counter ions), by analyzing the effect
of different operational variables (carrier concentration
in membrane phase, stripping agent concentration in
product phase, stirring rate and organic phase volume)
on the extraction and stripping kinetics constants and on
the transport efficiencies through feed/membrane and
membrane/product interfaces, is carried out in this pa-
ter. The increase in DP8R concentration in the
membrane phase, in sulphuric acid concentration in the
product phase and in stirring rate in the three phases,
and the decrease in the volume of the membrane phase
leads to an increase in the Co(II) recovery in the prod-
uct phase. Optimal experimental/economic conditions
for Co(II) recovery are as follows: 6 % DP8R concen-
tration in membrane phase, 1M sulphuric acid concen-
tration in product phase, 150 rpm stirring speed and
12.5 mL volume of membrane phase.

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REFERENCES
Alguacil, F.J., M. Alonso, F.A. López and A. López-
Delgado, “Active transport of cobalt (II) through a
supported liquid membrane using the mixture
DP8R and Acorga M5640 as extractant,” Desalina-
Addition Method for Simultaneous Spectrophoto-
metric determination of Co(II) and Zn(II) ions,”
Chaudry, M.A., M.T. Malik and A. Ali, “Transport of
Co(II) ions through di(2-ethylhexyl) phosphoric ac-
id-CCl₄ supported liquid membrane,” Sep. Sci.
Cobalt Development Institute, “2015 Production Statis-
Cote, G., “Hydrometallurgy of strategic materials,”
Dabbagh, R., Z.A. Moghaddam and H. Ghaforian,
“Removal of cobalt (II) ion from water by adsorp-
tion using intact and modified Ficus carica leaves as
low-cost natural sorbent,” Des. Wat. Treat., 57,
19890-19902 (2016)
De Gyves, J. and E. Rodríguez, “Metal Ion Separations
Ghaly, M., F.M.S.E. El-Dars, M.M Hegazy and A.R.O.
Rahman, “Evaluation of synthetic birnessite utili-
zation as a sorbent for cobalt and strontium remov-
al from aqueous solution,” Chem. Eng. J., 284,
1373-1385 (2016).
Gherasim, C.V., K. Hancková, J. Palarčík and P.
Mikulášek, “Investigation of cobalt (II) retention
from aqueous solutions by a polyamide nanofiltra-
Gómez-Lahoz, C., F. García-Herruzo, J.M. Rodríguez-
Maroto and J.J. Rodríguez, “Cobalt(II) removal
from water by chemical reduction with sodium bo-
He, D., M. Ma and Z. Zhao, “Transport of cadmium
ions through a liquid membrane containing amine
extractants as carriers,” J. Membr. Sci., 169, 53-59
(2000).
Kapusca, J.P.T., “Cobalt production and markets: A
Komasawa, I., T. Otake and Y. Higaki, “Equilibrium
studies of the extraction of divalent metals from ni-
trate media with di-(2-ethylhexyl) phosphoric acid,”
Kumar, V.A. and K.V. Marathe, “Selective separation
of copper (II) and cobalt (II) from wastewater by
using continuous cross-flow micellar-enhanced ul-

Figure 6. Influence of membrane phase volume on the remov-
al/recovery kinetic constants (kₑ, kₛ) and on the transport effi-
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