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Separation of Co(II)/Ni(II) with Cyanex 272 using a flat membrane microcontactor: stripping kinetics study, upscaling and continuous operation

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Abstract

In the present paper, the impact of the acid concentration, Cyanex 272 concentration, and membrane wetting properties on the stripping kinetics of loaded Cyanex 272 with cobalt is studied in a flat membrane microcontactor. To reduce the environmental impact and to be ever economically viable, the extractant needs to be regenerated. From the observed results, a model was derived to describe the stripping kinetics, enabling to maximize throughput. Like for the extraction of cobalt, also for the reversed reaction (stripping of loaded Cyanex 272 with cobalt), pseudo-first order kinetics could be assumed. However, unlike the extraction of cobalt, the reaction kinetics for the stripping of loaded Cyanex 272 had to be taken into account. As a consequence, the concentration of sulphuric acid influences the stripping kinetics and consequently throughput as well. Furthermore, it was also shown that the concentration of Cyanex 272 affected the stripping rate, in contrast to the extraction of cobalt. While for extraction diffusion in the organic phase can be neglected, this was no longer the case for stripping. When the concentration of Cyanex 272 was increased, the stripping rate decreased severely. To increase throughput, a scale-up strategy was proposed, that could be realized without inducing a loss of efficiency. This was demonstrated by increasing throughput by a ten-fold. Moreover, also the separation efficiency is studied in a continuous operation set-up over a span of 5 hours.

Keywords

membrane microcontactor; cobalt; nickel; Cyanex 272; stripping; upscaling

List of Symbols

SX	solvent extraction
MMC	membrane microcontactor
C	concentration
H ⁺	proton
Co ²⁺	cobalt ion
HR	Cyanex 272 monomer in its acidic state
(HR) ₂	Cyanex 272 dimer in its acidic state
CoR ₂ .(HR) ₂	loaded Cyanex 272 with cobalt
r	reaction rate
k _{r, 1}	forward reaction rate constant
k _{r, 2}	backward reaction rate constant
k	local mass transfer coefficient
J	flux
K _{eq}	equilibrium constant
K _M	overall mass transfer coefficient
Sh	Sherwood number
h	channel height
D	diffusion coefficient
u	velocity
x	axial position
L	length channel
w	width channel
V	internal volume channel

H	partition coefficient
% Extracted	percentage extracted
% Stripped	percentage stripped
t	Residence time

Greek letters:

δ	membrane thickness
ε	membrane porosity
τ	membrane tortuosity

Subscripts:

F	feed
R	raffinate
E	extract
S	solvent
b	bulk
x	axial position
L	outlet MMC ($x = L$)
in	inlet
aq	aqueous
org	organic
i	interface
m	membrane
eff	effective
eq	equilibrium
H ⁺	proton

Co^{2+}	cobalt ion
$\text{CoR}_2(\text{HR})_2$	loaded Cyanex 272 with cobalt
$(\text{HR})_2$	Cyanex 272 dimer in its acidic state

Superscripts:

n	fitting constant
p	fitting constant

1 Introduction

Cobalt and nickel are important non-ferrous metals and its separation is primarily achieved by solvent extraction (SX) with bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) as extractant. 40% of the cobalt production in the western hemisphere is produced in this manner (Ayanda et al., 2013). To perform SX, membrane contactors are interesting tools as they omit the phase separation step, which is usually of prime importance in traditional SX equipment (e.g. packed columns, centrifugal extractors, mixer-settlers), as it dictates the overall throughput (Ritcey and Ashbrook, 1984). Downside of the membrane contactor is the slow mass transfer. This is generally based on diffusion and as a result such devices require residence times in the range of hours (Yeh et al., 2013a, 2013b).

Using microfabrication technology (Hessel et al., 2009), membrane microcontactors (MMC) with channel heights of 100 μm or less can be constructed, reducing the residence time to the minute range (Hereijgers et al., 2013; Willersinn and Bart, 2015). In previous work (Hereijgers et al., 2015d), we studied the effects on the extraction kinetics for the reactive extraction of cobalt with Cyanex 272 in a flat membrane microcontactor. We demonstrated that certain operating conditions can severely decrease the mass transfer rate and concomitantly the overall extraction rate. When, for instance, the cobalt concentration was increased above 17 mmol/L, saturation of the interface occurred. Consequently, when the cobalt concentration was increased with a factor of 6.7, the time needed to extract 99% of the cobalt, raised with a factor of 4.85 up to 4 min. Also saponification of Cyanex 272, instead of buffering the aqueous feed solution, strongly reduced the extraction rate. In that case, a reduction of the extraction rate up to a factor of 3.62 has been demonstrated by using saponified Cyanex 272.

A special application of the membrane contactor is the supported liquid membrane (SLM). In SLM typically the organic extractant fills up the pores and at opposite sides of the membrane flows an

aqueous non-wetting liquid (feed and stripping solution). Doing so, extraction and stripping can be executed with one single membrane contactor unit (Swain et al., 2007), (Swain et al., 2015).

Downside of the SLM approach is its limited stability (Yang et al., 2003), (Parhi, 2013). Unavoidably, organic solvent from the pores is lost, either by dissolution or drag forces. Consequently, a renewal strategy (e.g. replenishment of the organic solvent by dispersing it in the stripping phase (Ren et al., 2010)) is required to perform separation continuously.

While the extraction of cobalt with Cyanex 272 with different kinds of membrane contactors (e.g. hollow fiber (Soldenhoff et al., 2005), MMC (Hereijgers et al., 2015d)) has been thoroughly studied, the reversed reaction, stripping of loaded Cyanex 272, has to the best of our knowledge not yet been studied in membrane contactors. However, to reduce the environmental impact and to be economically viable, it is absolute necessary to regenerate the extractant, such that it can be reused. For Cyanex 272 this is accomplished by stripping the loaded organic phase with a strong acid. During stripping, protons are exchanged for cobalt ions, transferring the cobalt back to the aqueous phase, but more importantly regenerating Cyanex 272 such that it can be reused in the extraction stage. Preferably, this should be accomplished by flowing only once through the membrane contactor. With hollow fibers, for instance, the flow is often recirculated as mass transfer is then high (Aguilar and Cortina, 2008; Drioli et al., 2005; Yeh et al., 2013a, 2013b), but doing so the process becomes discontinuous.

While for extraction of cobalt with Cyanex 272 the extraction rate has been maximized, throughput still remained limited ($< 100 \mu\text{l}/\text{min}$) (Hereijgers et al., 2015d). Therefore, upscaling of the MMC is necessary. To do this, the internal volume has to be enlarged. Increasing the channel height, however, is not an option as it lowers throughput instead of increasing it (Hereijgers et al., 2013), due to the fact that the time needed to diffuse a distance scales with the power of two, while the volume scales linearly with the channel height. Therefore, upscaling can only be performed by

increasing the length or width. Elongating the MMC, however, is also limited as the axial pressure drop increases with the length and due to this also the pressure difference across the membrane will increase, potentially leading to breakthrough, where the non-wetting phase penetrates through the pores of the membrane and disperses into the wetting phase. This leaves only the width available for upscaling, but then some sort of strategy is required to avoid maldistribution of the liquid flow.

In the present work, the impact of the acid concentration, Cyanex 272 concentration, and membrane wetting properties on the stripping kinetics of loaded Cyanex 272 is studied for the MMC. From these results, a model is derived which allows for optimizing the stripping kinetics. Furthermore, throughput is increased by proposing a scaling-up strategy for the MMC. Subsequently, a set of up-scaled MMCs are used to continuously separate cobalt from nickel by regenerating and recycling Cyanex 272 in a closed loop, allowing to study the effect of a mid-term operation period.

2 Experimental

2.1 Chemicals

Cyanex 272 (45 wt% in escaid 110, 1260 mmol/L) from Cytec (NJ, US) was utilized as such, with no further purification. Sodium hydroxide, cobalt(II)sulfate heptahydrate, nickel(II)sulfate hexahydrate, sulfuric acid, n-heptane and acetic acid were purchased from Sigma-Aldrich (Belgium) with a purity of 99+%. To calibrate the atomic absorption spectroscopic analysis, commercial stock calibration solutions of 1000 mg/ml Co^{2+} and Ni^{2+} were obtained from Chem-Lab (Belgium), which were used to create calibration standards with a concentration of 1, 2.5, 5, 7.5 and 10 ppm Co^{2+} and Ni^{2+} . The water used in the experiments was prepared in the laboratory (Milli-Q-gradient, Millipore, MA, USA).

2.2 Construction of the MMC

Construction of the 50 μm deep MMCs (Fig. 1) with a micromill (Datron M7 CNC mill) was performed in similar manner as reported previously (Hereijgers et al., 2015d), using following membranes: (1) a tri-layered polypropylene/polyethylene/polypropylene membrane (Celgard 2320, $d_{\text{pore}} = 27 \text{ nm}$, $\delta = 20 \text{ }\mu\text{m}$, $\varepsilon = 39 \%$) and (2) a hydrophilized PTFE membrane (Advantec H010A293D, $d_{\text{pore}} = 100 \text{ nm}$, $\delta = 35 \text{ }\mu\text{m}$, $\varepsilon = 71 \%$). Besides the previously reported 37 μl MMC (Fig. 1a) (Hereijgers et al., 2015d), also a scaled-up MMC with an internal volume of 377 μl , which was 100 mm wide, 220 mm long and 50 μm deep was constructed (Fig. 1b).

Fig. 1: a) Schematic representation and fully assembled view of a) the 37 μl large MMC and b) the 377 μl large MMC. c) Comparison picture of one channel of the 37 μl and the 377 μl large MMC to a one euro coin.

2.3 Extraction and stripping experiments

For the extraction experiment the aqueous feed was prepared by dissolving 14 mmol/L cobalt(II)sulfate heptahydrate and 4 mmol/L nickel(II)sulfate hexahydrate in water. Subsequently,

500 mmol/L acetate buffer (pH = 7) was added and the pH was checked using a glass electrode (WTW Inolab) and adjusted with 10 mol/L NaOH if necessary. The organic solvent consisted of Cyanex 272 in escaid 110 (1260 mmol/L) and was diluted in n-heptane to the desired concentration. For the stripping experiments, the feed (loaded Cyanex 272) was prepared by mixing the aqueous feed used in the extraction experiments with Cyanex 272 in a flask and manually shaken for 5 min, forming Co-Cyanex 272 (14 mmol/L) and a small portion Ni-Cyanex 272 (0.2 mmol/L). This yielded a distribution factor of 167 for cobalt and 0.11 for nickel. As only a small portion of nickel was co-extracted, the separation factor (~1500) was also highest at a pH of 7 (Hereijgers et al., 2015d). Next, the loaded organic phase was separated from the aqueous phase and used as such as feed. The stripping solution was prepared by diluting concentrated sulfuric acid (98%) to the desired concentration. The feed solution and extraction solvent or stripping solution were fed with two HPLC pumps (Shimadzu, LC10AD) at equal flow rates into the MMC. For the continuous operation experiments, a third dual syringe pump (Hitec Zhang Syrdos 2), equipped with 1 ml syringes, was used to continuously recycle the organic phase. Steady-state condition was assumed after three times the internal volume of the entire system went through the set-up. At that point samples of the aqueous phase were collected at the outlet in an ice bath. Subsequently, these samples were diluted with 400 mmol/L hydrochloric acid solution and analyzed using atomic absorption spectroscopy (ICE 3000 AA Spectrometer Thermo Scientific). From these results the amount extracted and/or stripped was calculated using Eq. 1:

$$\% \text{ Extracted or Stripped} = \frac{C_{Co^{2+},F} - C_{Co^{2+},R}}{C_{Co^{2+},F}} * 100 \quad (1)$$

with C the concentration. Every sample was always visually checked for phase homogeneity to ensure a breakthrough-free operation. Before starting a new extraction campaign, all air was removed by flushing the set-up with isopropanol for 5 min at a flow rate of 5 ml/min.

3 Results

3.1 Reaction kinetics

When Cyanex 272 is in its acidic state, extraction (from left to right, Eq. 2) and stripping (from right to left, Eq. 2) proceeds by the following overall reaction (Eq. 2) (Devi et al., 1994; Parhi and Sarangi, 2008; Swain et al., 2015; Tait, 1993):

Performing the extraction in a membrane microcontactor, the overall extraction kinetics was mass transfer limited and reaction kinetics could be neglected (Hereijgers et al., 2015d). The flow inside the MMC was laminar and consequently the transport of cobalt towards the extraction solvent was solely due to diffusion, leading to a mass transfer limited regime. However, when 5 ml 15 mmol/L loaded Co-Cyanex 272 was vigorously mixed by hand with 5 ml 1000 mmol/L sulfuric acid, equilibrium was not instantaneously reached (Fig. 2). From this, it can be inferred that the reversed reaction (stripping) most likely is not only mass transfer limited, but that is also dependent on the reaction kinetics. This is also in accordance with literature (Fu and Golding, 1988) where di-(2-ethylhexyl)phosphoric acid (D2EHPA), also a phosphorus based extractant, was used. Likely, both phenomena should be incorporated into the model to describe the stripping kinetics in the MMC (see § 3.3), whereas for extraction this was not necessary (Hereijgers et al., 2015d).

Fig. 2: Amount of cobalt stripped as a function of the reaction time in a shake experiment with 15 mmol/L loaded Co-Cyanex 272, 252 mmol/L Cyanex 272 and 1000 mmol/L sulfuric acid.

3.2 Stripping kinetics model

It was shown (Hereijgers et al., 2015d) that for extraction pseudo-first order kinetics could be assumed under following conditions:

- The aqueous feed is buffered, allowing Cyanex 272 to be used in its acidic state.
- The cobalt concentration in the feed remains below 17 mmol/L.
- The concentration Cyanex 272 is at least 4.4 times higher than the cobalt concentration.

Under these conditions, an analytically solvable model could be derived, omitting the need for numerical simulations. For stripping under the same conditions, it is likely valid to assume pseudo-first order reaction kinetics. Only now no buffer is added, but instead sulfuric acid in a high concentration. With pseudo-first order reaction kinetics the concentration of protons and Cyanex 272 are assumed constant. In literature, however, no expression was found for the reaction rate. Therefore, to describe the reaction rate Eq. 3 is used, where the concentrations of loaded Co-Cyanex 272 and cobalt have an exponent of 1 as pseudo-first order kinetics is assumed.

$$-r_{CoR_2.(HR)_2} = k_{r,2} C_{CoR_2.(HR)_2} C_{H^+,in}^n - k_{r,1} C_{Co^{2+}} C_{(HR)_2,in}^p \quad (3)$$

with r the reaction rate and k_r the reaction rate constant. The exponents n and p will have to be determined experimentally. To describe the mass transfer of cobalt in the MMC, the following assumptions were made:

- The system operates in steady-state in terms of operating condition. This does not mean that the percentage stripped is constant in function of the residence time (or velocity), but instead that there is no concentration build-up inside the MMC.
- The solvents are immiscible.
- The pores of the membrane are completely filled by the wetting liquid.
- Axial diffusion can be neglected (Hereijgers et al., 2013).
- No saturation of the surface occurs.

To describe the different flux steps (Eqs. 4-10) from the feed towards the stripping phase, the film theory is used:

- At the feed side loaded Co-Cyanex 272 diffuses from the bulk towards the membrane (Eq. 4):

$$J_{CoR_2.(HR)_2,F} = k_{CoR_2.(HR)_2,F} (C_{CoR_2.(HR)_2,F,b,x} - C_{CoR_2.(HR)_2,F,i,x}) \quad (4)$$

with J the flux and k the local mass transfer coefficient. The subscript F denotes the feed, b the bulk, i the interface and x the axial position.

- Depending on the wetting properties of the membrane, the pores are filled with either the organic phase (hydrophobic membrane) or the aqueous phase (hydrophilic membrane). In case of a hydrophobic membrane, the loaded Co-Cyanex 272 diffuses from the interface with the membrane and the feed through the pores towards the interface with the membrane and the stripping solution (Eq. 5):

$$J_{CoR_2.(HR)_2,m} = k_{CoR_2.(HR)_2,m} (C_{CoR_2.(HR)_2,F,i,x} - C_{CoR_2.(HR)_2,m,i,x}) \quad (5)$$

The subscript m denotes the membrane. At this interface, equilibrium (Eq. 6) can no longer be assumed as was the case with the extraction of cobalt, which was only mass transfer limited.

$$K_{eq} = \frac{k_{r,1}}{k_{r,2}} = \frac{C_{CoR_2.(HR)_2,eq} C_{H^+,eq}^2}{C_{Co^{2+},eq} C_{(HR)_2,eq}^2} \quad (6)$$

With K_{eq} the equilibrium constant, which is equal to 3.27×10^{-11} (Hereijgers et al., 2015d).

Instead, the flux of cobalt that is transferred to the stripping side, is described by the reaction rate equation (Eq. 3), yielding Eq. 7 in combination with Eq. 6:

$$-r_{CoR_2(HR)_2} = k_{r,2} C_{H^+,in}^n \left(C_{CoR_2(HR)_2,m,i,x} - K_{eq} \frac{C_{(HR)_2,in}^p}{C_{H^+,in}^n} C_{Co^{2+},S,i,x} \right) \quad (7)$$

The subscript S denotes the stripping solution. In case of a hydrophilic membrane is used, the pores are filled with the stripping solution and transfer of cobalt to the stripping phase now occurs at the interface with the feed and the membrane (Eq. 8):

$$-r_{CoR_2(HR)_2} = k_{r,2} C_{H^+,in}^n \left(C_{CoR_2(HR)_2,F,i,x} - K_{eq} \frac{C_{(HR)_2,in}^p}{C_{H^+,in}^n} C_{Co^{2+},m,i,x} \right) \quad (8)$$

Next, the aqueous cobalt diffuses through the pores towards the interface where the stripping phase and the membrane meet (Eq. 9):

$$J_{Co^{2+},m} = k_{Co^{2+},m} (C_{Co^{2+},m,i,x} - C_{Co^{2+},S,i,x}) \quad (9)$$

- At the interface where the stripping phase meets the membrane the aqueous cobalt diffuses towards the bulk of the stripping phase (Eq. 10):

$$J_{Co^{2+},S} = k_{Co^{2+},S} (C_{Co^{2+},S,i,x} - C_{Co^{2+},S,b,x}) \quad (10)$$

Inside the MMC steady state condition applies. Consequently, the fluxes and reaction rate are equal to one another (Eq. 11):

$$J = J_{CoR_2.(HR)_2,F} = -r_{CoR_2(HR)_2} = J_{Co^{2+},S} = J_{CoR_2.(HR)_2,m} \text{ or } J_{Co^{2+},m} \quad (11)$$

Summarizing Eqs. 4-10 yields Eq. 12:

$$J = K_M \left(C_{CoR_2.(HR)_2,F,b,x} - \frac{K_{eq} C_{(HR)_2,in}^p}{C_{H^+,in}^n} C_{Co^{2+},S,b,x} \right) \quad (12)$$

with K_m the overall mass transfer coefficient. Depending on the membrane wetting properties, the overall mass transfer coefficient is described by Eq. 13 (hydrophobic membrane) or Eq. 14

(hydrophilic membrane):

$$\frac{1}{K_M} = \frac{1}{k_{CoR_2.(HR)_2,F}} + \frac{1}{k_{CoR_2.(HR)_2,m}} + \frac{1}{k_{r,2} C_{H^+,in}^n} + \frac{C_{(HR)_2,in}^p K_{eq}}{C_{H^+,in}^n} \left(\frac{1}{k_{Co^{2+},S}} \right) \quad (13)$$

$$\frac{1}{K_M} = \frac{1}{k_{CoR_2.(HR)_2,F}} + \frac{1}{k_{r,2} C_{H^+,in}^n} + \frac{C_{(HR)_2,in}^p K_{eq}}{C_{H^+,in}^n} \left(\frac{1}{k_{Co^{2+},m}} + \frac{1}{k_{Co^{2+},S}} \right) \quad (14)$$

The local mass transfer coefficients can be determined from the Sherwood number (Eq. 15), which is equal to 0.94 for a channel filled with diamond shaped pillars of AR 1 with an interpillar distance of 0.3 mm (Hereijgers et al., 2015d).

$$k = \frac{Sh D_{bulk}}{2 h} \quad (15)$$

with Sh the Sherwood number, D_{bulk} the bulk diffusion coefficient and h the channel depth. Diffusion inside the pores of the membrane is described by the effective diffusion coefficient (Eq. 16):

$$k_m = \frac{D_{eff}}{\delta} = \frac{\epsilon D_{bulk}}{\tau \delta} \quad (16)$$

with D_{eff} the effective diffusion coefficient inside the pores of the membrane, δ the thickness of the membrane, ε the porosity of the membrane and τ the tortuosity of the membrane, which is equal to 4.51 for the Celgard 2320 membrane (Cannarella and Arnold, 2013) for the Advantec H010A293D a value of 1 was taken (Hereijgers et al., 2013). Eq. 12 describes the mass transfer of cobalt from the feed phase to the stripping phase at an axial position x . However, the feed and stripping phase also flow co-axially along opposite sides of the membrane. To take this convective mass transport into account, the mass balance can be written at one side of the membrane (Eq. 17):

$$J = -u_F h_F \frac{\partial C_{\text{CoR}_2(\text{HR})_2, F, b, x}}{\partial x} \quad (17)$$

with u the velocity. As steady-state condition applies inside the MMC, Eq. 12 and 17 are equal to one another. With the boundary conditions in Eq. 18, Eqs. 19 and 20 are obtained describing the loaded Co-Cyanex 272 concentration in the feed (see supporting information for a detailed derivation):

$$x = 0 \rightarrow C_{\text{CoR}_2(\text{HR})_2, F, b, x} = C_{\text{CoR}_2(\text{HR})_2, F, \text{in}} \quad (18)$$

$$x = L \rightarrow C_{\text{CoR}_2(\text{HR})_2, F, b, x} = C_{\text{CoR}_2(\text{HR})_2, F, L}$$

$$C_{\text{CoR}_2(\text{HR})_2, F, L} = \frac{\frac{1}{\alpha} C_{\text{CoR}_2(\text{HR})_2, F, \text{in}} + C_{\text{CoR}_2(\text{HR})_2, F, \text{in}} e^{-\frac{K_M L}{u_F h_F} \left(1 + \frac{1}{\alpha}\right)}}{1 + \frac{1}{\alpha}} \quad (19)$$

$$\alpha = \frac{C_{H^+, \text{in}}^n}{K_{eq} C_{(\text{HR})_2, \text{in}}^p} \frac{u_S h_S}{u_F h_F} \quad (20)$$

with L the length of the MMC channel. Using Eq. 19 $C_{\text{CoR}_2(\text{HR})_2, F, b, L}$ can be calculated as a function of the velocity, which can be converted to the residence time using Eq. 21.

$$t = \frac{L}{u_F} \quad (21)$$

3.3 Influence of the concentration of sulfuric acid

The concentration of sulfuric acid had a distinct impact on the stripping kinetics (Fig. 3). With 1000 mmol/L sulfuric acid, equilibrium was reached after 3.7 min, stripping 95.7% of the loaded Cyanex 272. However, with 500 mmol/L and 250 mmol/L sulfuric acid concentration, only 91.0% and 82.6% of the loaded Co-Cyanex 272 was stripped after 7.4 min. This was in agreement with the batch experiment (Fig. 2) and with the assumption that the reaction rate had to be taken into account for stripping. For the reversed reaction (extraction), the mass transfer limited regime applied and consequently reaction kinetics could be neglected. This was observed when the concentration of Cyanex 272 was varied (Hereijgers et al., 2015d), which is for extraction the reagent instead of sulfuric acid. By varying the concentration of Cyanex 272 the overall extraction kinetics were not influenced, only the amount extracted at equilibrium, confirming that the reaction rate could be neglected for extraction.

The solid lines in Fig. 3 describe the model (Eq. 19) and coincide with the experimental data for 250 and 1000 mmol/L sulfuric acid concentration. For 500 mmol/L sulfuric acid concentration the fit was less satisfactory. At concentrations higher than 1000 mmol/L sulfuric acid concentration, breakthrough occurred, preventing a stable operation. Breakthrough occurs when the pressure difference across the membrane ($\text{Pressure}_{\text{non-wetting}} - \text{Pressure}_{\text{wetting}}$) is larger than a critical value, known as the breakthrough pressure (Hereijgers et al., 2015a). This breakthrough pressure is a function of a number of parameters, including the interfacial tension between the aqueous and organic liquid. The lower the interfacial tension, the lower that the breakthrough pressure will be. When the sulfuric acid concentration is increased, the interfacial tension is known to decrease (Guo et al., 2008) and concomitantly this will lower the breakthrough pressure. This explains why breakthrough was observed at sulfuric acid concentrations higher than 1000 mmol/L. Consequently, 1000 mmol/L is the preferred choice as it yields the highest stripping kinetics without inducing breakthrough. To calculate the models, a diffusion coefficient of $6.4 \times 10^{-10} \text{ m}^2/\text{s}$ for CoSO_4 in water

was taken from literature (Xiong et al., 1987) and the parameters from table 1 were determined by fitting Eqs. 1 and 19 by the sum of the least squared errors on the experimental data from Figs. 3-6. From this, a diffusion coefficient of $3.43 \times 10^{-10} \text{ m}^2/\text{s}$ for loaded Co-Cyanex 272 in n-heptane was obtained, which is close to the diffusion coefficient reported in literature (Parhi and Sarangi, 2008) with kerosene as solvent. The reaction rate constant was also determined from fitting and amounted to $1.62 \times 10^{-10} \text{ L}^{2.64}/(\text{mol}^{2.64} \text{ s})$. The exponent n in Eq. 3 was equal to 2.64 and the exponent p was set equal to 0 as it did not affect the stripping kinetics.

Fig. 3: Impact of the sulfuric acid concentration onto the stripping kinetics of loaded Co-Cyanex 272 with the following conditions: 14 mmol/L loaded Co-Cyanex 272, 224 mmol/L Cyanex 272, $h = 50 \mu\text{m}$, $w = 13 \text{ mm}$, Celgard 2320 membrane and 250, 500 or 1000 mmol/L sulfuric acid.

Table 1: The bulk diffusion coefficient of loaded Co-Cyanex 272 in n-heptane with 224 mmol/L Cyanex 272, reaction rate constant for stripping and the exponents n and p obtained by fitting the model (Eq. 3) by the sum of least squared errors onto the experimental data in Figs. 3-6.

$D_{\text{CoR}_2 \cdot (\text{HR})_2 \text{ in n-heptane with } 0.2236 \text{ mol/L Cyanex 272}}$	$3.43 \times 10^{-10} \text{ m}^2/\text{s}$
$k_{r,2}$	$1.62 \times 10^{-14} \text{ L}^{2.64}/(\text{mol}^{2.64} \text{ s})$
n	2.64
p	0

3.4 Influence of the concentration of Cyanex 272

With an increase of the Cyanex 272 concentration the viscosity is known to increase as well (Swain et al., 2007), lowering the diffusion coefficient and consequently the mass transfer kinetics. For extraction, this did not affect the extraction kinetics, as the mass transfer resistance contribution by the diffusion in the organic phase channel could be neglected (Hereijgers et al., 2015d). For stripping, however, the concentration of Cyanex 272 did influence the stripping kinetics (Fig 4a). This could be explained by the fact that for stripping now diffusion in the aqueous phase channel could be neglected but not in the organic phase channel (Eqs. 13 and 14). For a Cyanex 272 concentration of 224 mmol/L equilibrium was reached after 3.7 min, stripping 95.6% of the loaded Co-Cyanex 272, whereas for a Cyanex 272 concentration of 1232 mmol/L only 57.1% of the loaded Co-Cyanex 272 was stripped after 7.4 min. Measuring the amount of loaded Co-Cyanex 272 stripped after 3.7 min at various Cyanex 272 concentrations (Fig. 4b) the diffusion coefficient of the loaded Co-Cyanex 272 in the organic phase could be determined and dropped from $3.43 \times 10^{-10} \text{ m}^2/\text{s}$ to $3.09 \times 10^{-11} \text{ m}^2/\text{s}$ when increasing the Cyanex 272 concentration from 224 mmol/L to 1232 mmol/L. From the results in Fig. 3b, an empirical correlation between the Cyanex 272 concentration and the diffusion coefficient of loaded Co-Cyanex 272 in the organic phase was deduced (Eq. 22):

$$\ln(D_{CoR_2-(HR)_2} [m^2/s]) = -2.28 \times 10^{-3} C_{HR} [mmol/L] - 21.2 \quad (22)$$

Fig. 4: a) Impact of the Cyanex 272 concentration onto the stripping kinetics of loaded Co-Cyanex 272 with the following conditions: 14 mmol/L loaded Co-Cyanex 272, 1000 mmol/L sulfuric acid, $h = 50 \mu\text{m}$, $w = 13 \text{ mm}$, Celgard 2320 membrane and 224 or 1232 mmol/L Cyanex 272. b) The diffusion coefficient of loaded Co-Cyanex 272 as a function of the concentration of Cyanex 272.

3.5 Influence of the membrane wetting properties

From Eqs. 13 and 14 it was clear that the wetting properties of the membrane influenced the stripping kinetics (see supporting information for the characterization of the wetting properties of the membranes). Like with classical non-reactive solvent extraction it is desirable to have the extract phase (stripping solution) in the pores of the membrane rather than the raffinate phase (feed) when the partition coefficient is higher than one (Hereijgers et al., 2013). This can be understood by looking at the concentration gradient inside the membrane. With the extract phase inside the pores, the concentration gradient will be higher than with the raffinate phase inside the pores, enhancing mass transfer. This effect is translated in the overall mass transfer coefficient by the partition coefficient (non-reactive SX), which appears in the membrane resistance term when the pores are filled by the extract. Due to this, the overall mass transfer coefficient will increase. This effect is also observed with the stripping of cobalt (reactive SX) in case of a hydrophilic membrane. The stripping phase will then fill the pores and Eq. 14 applies, where the membrane resistance term is multiplied with the equilibrium constant instead of the partition coefficient, as it is a reactive SX. This strongly reduces the membrane resistance term and its contribution to the overall resistance in contrast with

a hydrophobic membrane (Eq. 13). As the model predicted, this was also observed experimentally (Fig. 5). When a hydrophilic membrane was used only a residence time of 0.9 min was needed to reach equilibrium instead of 3.7 min with a hydrophobic membrane.

Fig. 5: Impact of the membrane wetting properties onto the stripping kinetics of loaded Co-Cyanex 272 with the following conditions: 14 mmol/L loaded Co-Cyanex 272, 224 mmol/L Cyanex 272, 1000 mmol/L sulfuric acid, $h = 50 \mu\text{m}$, $w = 13 \text{ mm}$ and Celgard 2320 membrane (hydrophobic) or Advantec H010A293D membrane (hydrophilic).

3.6 Continuous operation

Using two MMC units for respectively extraction and stripping a feed solution containing nickel and cobalt can be separated continuously (Fig. 6). The organic phase (Cyanex 272) will primarily (Hereijgers et al., 2015d) extract cobalt from the feed, leaving a nickel rich raffinate behind. Subsequently, in the second MMC unit the loaded organic phase is stripped with sulfuric acid, yielding a cobalt rich stripping solution and regenerated Cyanex 272. The regenerated Cyanex 272 was collected in a small buffer vessel (2 mL) and fed again in the first MMC unit, closing the loop for the organic phase.

Fig 6: Flow diagram of continuous operation setup

However, to increase throughput and to lower the ratio of void volume of the connection tubing and pump over the flow rate, it is necessary to scale-up the MMCs. To scale-up the MMCs the preferred strategy is to increase the width. However, going from a small inlet gap (diameter: 1 mm) to a wide channel an entrance effect could arise, enlarging the residence time distribution and negatively affecting the extraction and stripping kinetics (Hereijgers et al., 2015b). This effect also becomes more significant with wider channels. By placing radially elongated pillars with an aspect ratio of 10 at the inlet and outlet of the channel, the incoming and outgoing liquid was distributed and collected over the entire width of the channel. In Fig. 7 the impact of upscaling is depicted for extraction and stripping. The extraction and stripping efficiency for the MMCs with a width of 13 mm ($V = 37 \mu\text{l}$) and 100 mm ($V = 377 \mu\text{l}$) is in general very similar. The apparent outliers (Fig. 7b) at a residence time of 1.9 and 3.8 min are most likely due to experimental variation as a value above 100% is physically impossible. As a consequence, the flow rate at which equilibrium was reached for extraction and stripping, could be respectively increased from 60 $\mu\text{l}/\text{min}$ to 600 $\mu\text{l}/\text{min}$ and from 40 $\mu\text{l}/\text{min}$ to 400 $\mu\text{l}/\text{min}$.

Fig. 7: a) The extraction kinetics of cobalt with Cyanex 272 for a 37 μl large MMC and a 377 μl large MMC under following conditions: 14 mmol/L CoSO_4 , 500 mmol/L acetate buffer ($\text{pH} = 7$), 252 mmol/L Cyanex 272, $h = 50 \mu\text{m}$ and Celgard 2320 membrane. b) The stripping kinetics of loaded Co-Cyanex 272 for a 37 μl large MMC and a 377 μl large MMC under following conditions: 14 mmol/L loaded Co-Cyanex 272, 224 mmol/L Cyanex 272, 1000 mmol/L sulfuric acid, $h = 50 \mu\text{m}$ and Advantec H010A293D membrane.

With the use of two 100 mm wide MMCs, according to the flow diagram in Fig. 6, cobalt and nickel was separated continuously during 5 hours. Every 20 minutes a sample of the Ni rich raffinate and Co rich stripping solution was collected and analyzed. During these 5 hours no decrease in efficiency was observed (Fig. 8). The aqueous feed that consisted of 14 mmol/L CoSO_4 , 4 mmol/L NiSO_4 and 500 mmol/L acetate buffer ($\text{pH} = 7$) and the organic phase that consisted of 252 mmol/L Cyanex 272 were fed into the first MMC unit at a flow rate of 100 $\mu\text{l}/\text{min}$. The raffinate solution that was collected at the outlet of the first MMC unit had an average concentration of 0.3 ± 0.2 mmol/L CoSO_4 and 4 ± 0.1 mmol/L NiSO_4 (Fig 8a). Concomitantly, 98.0 % of the cobalt and 14.8 % of the nickel was extracted from the feed (Fig 8b). Subsequently, the loaded organic phase flowed towards the second MMC, which was fed at the opposite side of the membrane with 1000 mmol/L sulfuric acid solution at a flow rate of 100 $\mu\text{l}/\text{min}$. The obtained stripping solution at the outlet of the second MMC unit had an average concentration of 13 ± 1.4 mmol/L for CoSO_4 and 0.4 ± 0.3 mmol/L for NiSO_4 (Fig. 8c), resulting in a complete stripping of the loaded organic phase (Fig. 8d). The amount nickel stripped seemed to increase over time, but the data were highly scattered, due to the fact that the

concentration of nickel and loaded Cyanex 272 with nickel was below the limit of quantification range of the AAS-system. Consequently, the error had a relatively large impact when the amount stripped was calculated with such low feed and raffinate concentrations (Eq. 1). For the extraction of cobalt (Fig. 8b) this limit of quantification range did not pose a problem as the feed concentration was large. Therefore, the error on the raffinate concentration had a relatively small impact when calculating the amount of cobalt extracted (Eq. 1).

From these results it can be concluded that the efficiency remained constant during the 5-hour operation. A minor breakthrough was observed at the stripping unit, most likely due to pressure pulsations of the pumps. 0.67ml aqueous stripping solution was collected at the organic phase outlet, which represents 1.87 % of the total processed volume. This did not pose a problem as these few water droplets settled at the bottom of the buffering tank and which can be easily removed if necessary. A possible solution to prevent breakthrough completely, is to use active backpressure regulation or internal pressure regulation by the use of an integrated diaphragm (Adamo et al., 2013).

Fig. 8: The extraction and stripping performance of the continuous operation setup over a period of 5 hours under following conditions: feed: 14 mmol/L CoSO_4 , 4 mmol/L NiSO_4 , 500 mmol/L acetate buffer ($\text{pH} = 7$); extraction solvent: 252 mmol/L Cyanex 272; stripping solvent: 1000 mmol/L sulfuric acid; $h = 50 \mu\text{m}$; $w = 100 \text{ mm}$; Celgard 2320 membrane for the extraction MMC unit and Advantec H010A293D membrane for the stripping MMC unit. a) The concentration of cobalt and nickel in the Ni rich raffinate as a function of the run time at the outlet of the extraction MMC. The dashed lines represent the concentration of the feed. b) The amount cobalt and nickel extracted as a function of the run time. The dashed lines represent the equilibrium obtained from a shake test. c) The concentration of cobalt and nickel in the Co rich stripping solution as a function of the run time at the outlet of the stripping MMC. The dashed lines represent the concentration of the loaded Co-Cyanex 272 and Ni-Cyanex 272 coming from the extraction MMC. d) The amount cobalt and nickel stripped as a function of the run time. The dashed line represents complete stripping at 100 %.

3.7 Countercurrent operation

Extraction and stripping were always conducted in cocurrent mode. Countercurrent mode, however, is theoretically a superior method as it allows to reach multiple stages. Then again for a stable operation, cocurrent mode is superior over countercurrent mode as the pressure difference over the membrane is larger in countercurrent mode, enlarging the possibility of breakthrough.

Plotting Eqs. 23-24 describing the extraction kinetics for co- and countercurrent mode for classical non-reactive extraction obtained from (Hereijgers et al., 2015c), it is seen that in terms of kinetics there is no difference between co- and countercurrent mode (Fig. 9).

For cocurrent mode the concentration in the raffinate is given by Eq. 23 and for countercurrent mode by Eq. 24 and in both cases the concentration at the inlet of the solvent side is equal to zero:

$$C_R = \frac{\frac{\alpha_R}{\alpha_E} C_F + C_F e^{-\frac{K_M L}{u_R h_R} \left(1 + \frac{\alpha_R}{\alpha_E}\right)}}{1 + \frac{\alpha_R}{\alpha_E}} \quad (23)$$

$$C_R = \frac{C_F \left(1 - \frac{\alpha_R}{\alpha_E}\right) e^{\left(\frac{1}{\alpha_E} - \frac{1}{\alpha_R}\right)}}{1 - \frac{\alpha_R}{\alpha_E} e^{\left(\frac{1}{\alpha_E} - \frac{1}{\alpha_R}\right)}} \quad (24)$$

The subscript R denotes the raffinate and E the extract. Eq. 23 is nearly identical to Eq. 19 and only differs in the definition of α_R and α_E (Eq. 25):

$$\alpha_R = \frac{u_R h_R}{K_M L} \quad \alpha_E = \frac{u_E h_E H}{K_M L} \quad (25)$$

with H the partition coefficient.

Fig. 9: The amount extracted as a function of the residence time for co- and countercurrent mode for non-reactive extraction with $H = 100$ and $K_M = 10^{-6}$ m/s.

For non-reactive extraction α_R / α_E depends on the partition coefficient, whereas α (Eq. 20) for reactive extraction depends on the equilibrium constant, the concentration of protons and of Cyanex 272. Nonetheless, a similar behavior for co- and countercurrent extraction is also expected for reactive extraction, which was indeed also observed experimentally both for extraction and stripping (Fig. 10). As all cobalt was extracted after one stage under the applied conditions, there was no need for multiple stages. Consequently, preference was given to the cocurrent mode.

Fig. 10: a) The amount cobalt extracted as a function of the residence time for the cocurrent and countercurrent mode under following conditions: 14 mmol/L CoSO_4 , 500 mmol/L acetate buffer ($\text{pH} = 7$), 252 mmol/L Cyanex 272, $h = 50 \mu\text{m}$ and Celgard 2320 membrane. b) The amount cobalt stripped as a function of the residence time for the cocurrent and countercurrent mode under following conditions: 14 mmol/L loaded Co-Cyanex 272, 224 mmol/L Cyanex 272, 1000 mmol/L sulfuric acid, $h = 50 \mu\text{m}$ and Celgard 2320 membrane.

4 Conclusions

It was shown that pseudo-first order kinetics could be assumed for stripping of loaded Cyanex 272 with cobalt and that a model could be derived allowing to maximize the stripping rate. However, whereas for extraction the concentration of Cyanex 272 did not influence the extraction rate, the concentration of sulfuric acid did affect the stripping rate of loaded Cyanex 272. This was caused by the reaction kinetics and consequently had to be taken into account. The highest stripping rate was obtained at the highest sulfuric acid concentration possible, which was 1000 mmol/L. At higher concentrations of sulfuric acid, breakthrough occurred. Furthermore, it was also shown that the concentration Cyanex 272 affected the stripping rate, in contrast to what occurs during the extraction of cobalt. With an increase of the Cyanex 272 concentration the diffusion coefficient of loaded Cyanex 272 in the organic phase dropped. For extraction this effect was to be neglected due to a lower mass transfer resistance contribution of the solvent (larger concentration gradient), which was not applicable for stripping. Next, the impact of the membrane wettability was demonstrated. Using a hydrophilic membrane instead of a hydrophobic one, the membrane mass transfer resistance term could be reduced, lowering the required residence time for complete stripping from 3.7 min to 0.9 min. Using distributor features, a scale-up strategy was demonstrated without loss of efficiency, increasing throughput by a ten-fold and allowing to operate continuously. During this continuous operation, the separation efficiency did not drop over the entire period of 5 hours. Operating in countercurrent mode did not affect the extraction and stripping rate, as predicted by the models.

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