

APPLICATION OF HOLLOW FIBER SUPPORTED LIQUID MEMBRANE FOR EXTRACTION OF COBALT BY CYANEX 272

Considering the advantages of hollow fiber supported liquid membrane (HFSLM), it has been applied for extraction of Co(II) with a motivation to extract cobalt from various waste resources. Extraction efficiency and transport behavior of Co(II) through HFSLM containing Cyanex 272 diluted in kerosene were investigated. Experiments were performed as a function of aqueous feed solution velocity (1000 mL/min) for both feed and strip, pH of feed solution in the range of 4.00-6.75, the carrier concentration of 25-1000 mol/m³, and acid concentration in strip solution of 1-500 mol/m³ on. The mass transfer rate or flux $J_{Co(II)}$, which is a function of metal concentration, volume of solution, and membrane area were analyzed. The optimum condition for extraction of Co(II) was pH of 6.00, Cyanex 272 concentration of 500 mol/m³ and H₂SO₄ concentration of 100 mol/m³.

Keywords: Cyanex 272; Hollow Fiber Supported; Cobalt recovery

1. Introduction

Hydrophobic carrier-mediated transport of metal through membrane is commonly known as supported liquid membrane processes (SLM) is a potential alternative technology for selective separation of toxic metals, enrichment of valuable metal and sequential separation of various metals. Membranes for the separation and concentration of metal ions have received considerable attention throughout the past four decades due to characteristics such as operational simplicity, energy, and selectivity advantages, lower solvent inventory factor and low-cost operation factors [1]. From an application point of view, membranes separation processes find applications in the various field such as separation of metal values from industrial waste [2-9], analytical applications [10-14], biomedical application [15-18] as well as in wastewater treatment [19-21].

Cobalt metal is relatively expensive and important because of its wide applications. Due to the scarcity of this metal, its recovery from secondary resources such as industrial wastes becomes essential. SLM has become an attractive alternative to conventional solvent extraction (SX) for selective separation of metal ions from dilute aqueous solutions because it combines extraction and stripping operation in a single stage. Out of two different SLM process like; flat sheet supported liquid membrane (FSSLM) and the hollow fiber supported liquid membrane (HFSLM) the latter one provide sufficient interfacial area makes it a better candidate for metal extraction. To achieve a sufficient interfacial area, the hollow fiber membrane module is used in

this study as a liquid membrane support device. In comparison to FSSLM, the HFSLM has several inherent advantages like; (i) comparatively higher surface area, (ii) provide rapid transport owing to the surface area and membrane thickness, (iii) The feed/strip phases are more easily recoverable than the FSSLM, and (iv) the entire source and receiving phase are not in contact with the membrane at any given instant.

HFSLM contains an extraction reagent incorporated into the organic phase is similar to those used in conventional SX, and their use in membranes results in a large decrease in solvent inventory. The metal extraction chemistry is identical to that found in SX but the overall process is governed by kinetic rather than equilibrium. The HFSLM technique has been used for extraction/separation of cobalt using different extractant such as HEP(EHP) [22], D2EPHA [23], Cyanex 272 with Ionquest[®] [24], dialkyl phosphinic acid [25]. A systematic study for extraction of cobalt using Cyanex 272 has never been reported yet. The present study examines the possibility of using an HFSLM technique to extract cobalt using Cyanex 272.

2. Experimental

2.1. Chemicals/Reagents

All chemicals used in this study namely; CoSO₄, H₂SO₄, NaOH, NH₄OH, CH₃COONa, and CH₃COOH etc., were of analytical reagent grade. Stock solutions of CoSO₄ (1000 Kg/m³)

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were prepared by dissolving cobalt sulfate in distilled water and standardized against EDTA solution. The required concentrations of solutions were prepared by dilution of stock solution. Cyanex 272 was used as extractant. Kerosene (bp 180-270°C) and Tri-*n*-butyl-phosphate (TBP) supplied by Junsei Chemicals Co., Ltd., Japan were used as a diluent and phase modifier, respectively for all sets of experiments.

2.2. Hollow fiber module

The hollow fiber module Liqui-Cel[®] Minimodule[®] contactor (1.25 in. × 9 in.) was purchased from Celgard. The module is made up of hollow fiber fabric, wrapped around a central distribution tube. Details of the module and fibers are presented in Table 1.

TABLE 1

Characteristics of the hollow fiber membrane

Module	Characteristics	Membrane	Characteristics
Material	Polysulfone	Fiber	X50 – polypropylene
Shellside	Standard Female Luer Lock	Pore size (μm)	0.03
Lumenside	½ inch Hosebarb	Porosity, ε (%)	40% Porosity
No of fibers	3600	Tortuosity, τ	

2.3. HFSLM preparation and methods

The schematic diagram for the HFSLM module used in this experiment is shown in Fig. 1. A hollow fiber module with an effective membrane area (geometrical membrane area × porosity) of 0.2 m² was used for the hollow fiber liquid membrane experiment. The effective membrane was considered because of only the pores not the surface of membrane involved in the transportation of metal ions. The feed solution was kept under agitation using a mechanical stirrer. Equal volumes of samples (1 cm³) were withdrawn from both the solutions at the desired time interval. Impregnation of the solvent on the polymeric support was carried out by pumping the organic solvents through the fiber bore for 1 h at a slow flow rate. Solvent flowed rapidly through the porous wall of the fibers and was collected in the outer shell. This probably indicates that the impregnation was completed in a few minutes. The module was operated in recycling mode. In this mode, feed containing Co(II) in acidic sulfate media and strip solutions of H₂SO₄ are circulated using the pump. The volumes of the strip solution and feed solution used were 2000 cm³ each. A buffer solution of CH₃COOH-CH₃COONa was used to maintain the required pH of the feed solution in the range of 4.00 to 6.75. Equal volumes of samples 1 cm³ each were withdrawn from both the solutions at the desired time interval. The samples were analyzed for Co(II) concentration using atomic absorption spectrophotometer.

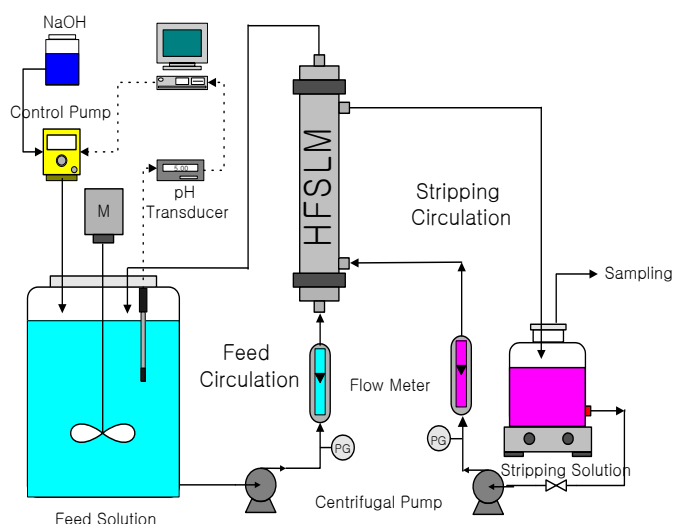
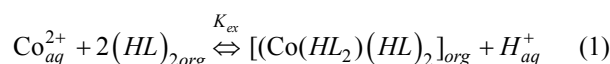


Fig. 1. Schematic diagram of the experimental apparatus for the hollow fiber liquid membrane

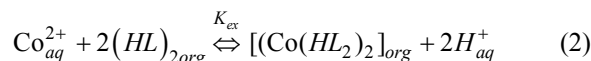
3. Results and discussion

3.1. Extraction mechanism and mass transfer phenomenon on HFSLM

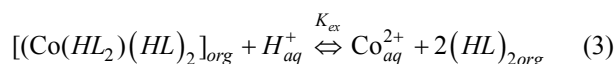
Co(II) extraction by Cyanex 272 using HFSLM mainly can be controlled in three important stages, i.e., (i) Co(II)-Cyanex 272 solvent extraction at feed-membrane interface, (ii) mass transfer of Co-Cyanex 272 complex through diffusion from the feed-membrane interface to membrane-strip interface, and (iii) dissociation of Co(II)-Cyanex 272 complex at membrane-feed interface. The solvent extraction mechanism by which cobalt ions is extracted from an aqueous phase using excess Cyanex 272 and stoichiometric (limited) amount of Cyanex 272 can be written as given in Equation 1 and Equation 2, respectively.

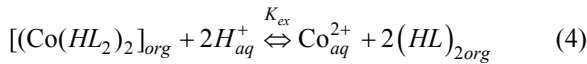


where the subscripts *aq* and *org* denote species in the aqueous and organic phases, respectively. The (HL)₂ stands for dimeric Cyanex 272 and HL stands for monomer Cyanex 272.



At the feed-membrane interface, the Co²⁺ can form the complex with Cyanex 272 (Co-Cyanex272) at appropriate pH, which then diffuses through membrane pores to membrane-feed interface. At membrane-strip interface using appropriate stripping solution at requisite concentration, Co-Cyanex 272 dissociates. The Co-Cyanex 272 dissociation chemistry can be explained using Equation 3 and 4 for extraction reaction Equation 1 and 2 given below, respectively.





Mass transfer of Co^{2+} in HFSLM happened following stages.

- (i) Diffusion of Co^{2+} from the bulk feed phase to feed-membrane interface and form Co-Cyanex 272 complex.
- (ii) Diffusion of Co-Cyanex 272 complex from the feed-membrane interface to the strip-membrane interface.
- (iii) At strip-membrane interface using strip acid dissociation reaction occurs then the Cyanex 272 diffuses back to the feed-membrane interface.
- (iv) From the strip membrane interface, Co^{2+} diffuses to bulk strip phase.

The relationship which correlates the membrane flux J_M , concentration of the feed solution $[M_f]$ at the time t , the concentration of the strip solution $[M_s]$ at the time t , the volume of the feed solution, V_{Sol} and the effective membrane area A_{Memb} (geometrical membrane area x porosity), is

$$J_M = \frac{V_{\text{Sol}}}{A_{\text{Memb}}} \frac{d[M_s]}{dt} = -\frac{V_{\text{Sol}}}{A_{\text{Memb}}} \frac{d[M_f]}{dt} \quad (5)$$

The permeation of cobalt through HFSLM at different times is shown in Fig. 2 for a typical experiment. $V/A[\text{Co}]$ was plotted against time “ t ” for each experiment, and from the slope of the initial straight line, flux of the metal ion ($J_{\text{Co(II)}}$) was calculated, where V = volume of the solution on each side of the membrane (m^3), A = effective membrane area (m^2) and t = time (s).

The relationship among flux J_M , pH, Cyanex 272 concentration and Co^{2+} concentration has been discussed elsewhere [26]. In the HFSLM, Co-Cyanex 272 dissociation is fast at the membrane-strip interface, diffusion in the membrane, thickness of the membrane, the porosity of the membrane, and tortuosity

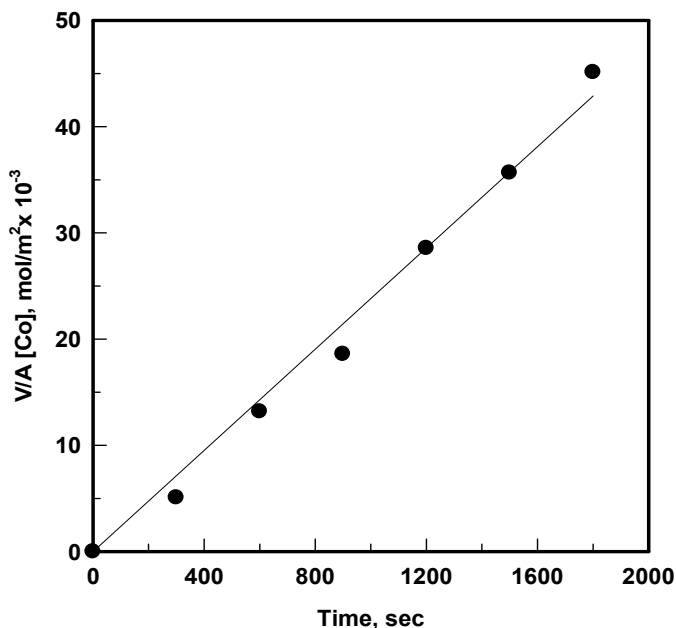


Fig. 2. Permeation of Co(II) through HFSLM at different time

of the supported membrane are constant [26]. Considering all these facts, using Fick's law and taking logarithms, Equation 5 can be expressed as Equation 6 [26].

$$\log J_M = npH + n \log (\text{HL})_{2\text{org}} + n \log ([\text{Co}]) + \log C \quad (6)$$

Where C is the constant for all the constants together explained above.

Hence, from least square slope value of $\log J_M$ versus pH, $\log J_M$ versus Cyanex 272 concentration, and $\log J_M$ versus Co^{2+} concentration, the extraction behavior can be analyzed.

3.2. Effect of flow rate

The boundary layer resistance plays determining a role for diffusion of metal ions from bulk solution phase to feed-membrane interface, feed-membrane interface to membrane-strip interface and finally from the strip-membrane interface to strip solution bulk phase. Resistance in a stirred diffusion liquid membrane contributed from hydrophobic membrane intrinsic resistance and boundary layer resistance at both sides of the membrane. The boundary layer resistance contributed by the hydrophobic membrane can be overcome by flow rate optimization. Effect of flow rate on the extraction of cobalt in HFSLM process was investigated. The feed phase was maintained at pH of 6.00, in membrane phase 750 mol/m^3 of Cyanex 272 was used. The strip acid concentration was 100 mol/m^3 . Using a feed solution with 10 mol/m^3 of cobalt, the effect of flow rate on the metal ion flux was studied in the range of 200-1500 mL/min, and the results are shown in Fig. 3. It was observed that cobalt flux increased with an increasing flow rate between 200 and 1000 mL/min and decreased slowly thereafter. As shown in figure the cobalt flux $J_{\text{Co(II)}}$ values varied from

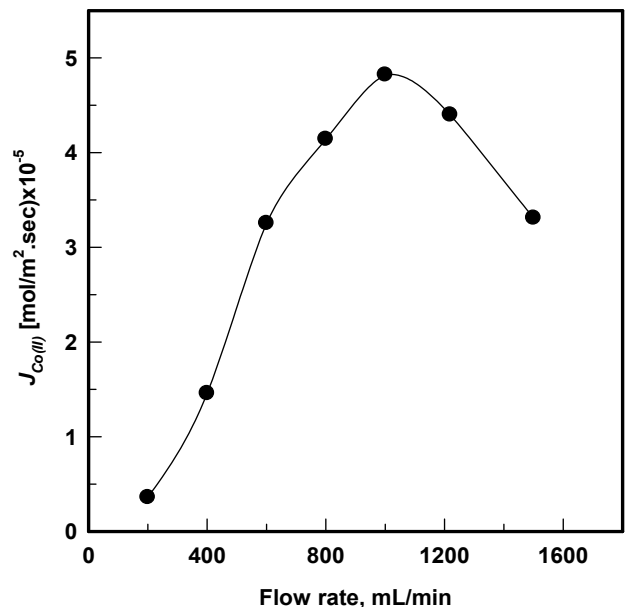


Fig. 3. Effect of flow rate on the flux of cobalt $J_{\text{Co(II)}}$

0.36×10^{-5} mol/m²s to 4.82×10^{-5} mol/m²s as flow rate increases from 200 to 1000 mL/min. Above the flow rate of 1000 mL/min up to 1500 mL/min the cobalt flux $J_{\text{Co(II)}}$ values decreased from 4.82×10^{-5} mol/m²s to 3.31×10^{-5} mol/m²s. Hence, the flow rate of 1000 mL/min is the optimum condition to overcome the boundary layer resistance. This decrease in cobalt flux $J_{\text{Co(II)}}$ at a flow rate higher than 1000 mL/min may be due to deterioration of extractant in the membrane phase at a higher flow rate. Therefore, in the present experimental set-up, a flow rate of 1000 mL/min was assumed to be sufficient to overcome the resistance due to the aqueous boundary layer, and this flow rate was maintained in all other studied parameters.

3.3. Effect of feed pH

Above explained chemical Equation 1 and 2 clearly indicates pH solution is determinant for the formation of Co-Cyanex 272 complex. Hence, the effect of feed pH was optimized through variation study. The extraction of cobalt from sulfate media containing 10 mol/m³ of Co(II) was studied using Cyanex 272 of 1000 mol/m³ within the pH range 4.00-6.75. Fig. 4(a) shows that the flux of cobalt $J_{\text{Co(II)}}$ increases from 0.39×10^{-5} mol/m²s to 2.39×10^{-5} mol/m²s as pH of the feed solution increases from 4.00 to 6.00. Above the pH 6.00 to 6.75 the flux values for cobalt decreases from 2.39×10^{-5} mol/m²s to 1.83×10^{-5} mol/m²s. In the case of HFSLM study pH of 6.00 in the feed solution is the best condition for extraction of cobalt. There was no flux detected below pH 4.00. Above the pH 6.75 is not suitable as there is precipitation of cobalt occurs. As excess Cyanex 272 was used in the membrane phase for extraction, the stoichiometry explained Equation 1 can be applied well to explain the effect of

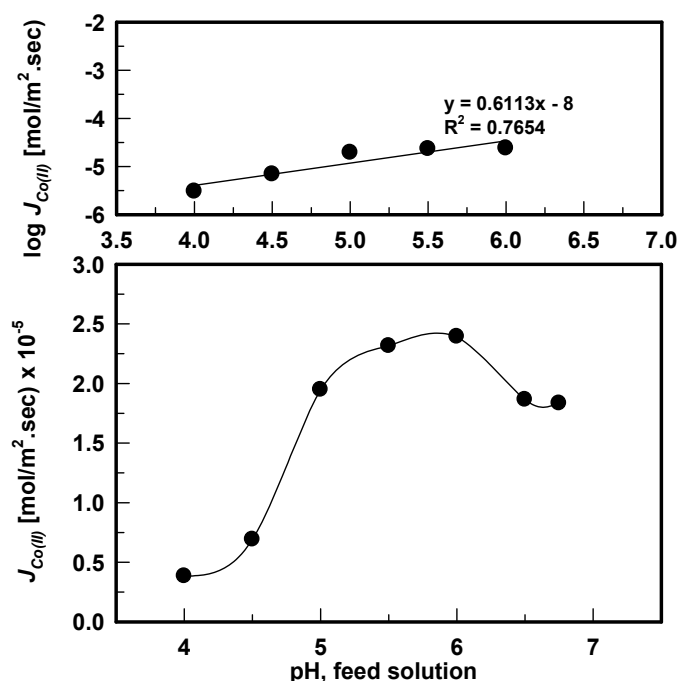


Fig. 4. (a) Effect of feed pH on the flux of Co(II) $J_{\text{Co(II)}}$ (b) Effect of feed pH on $\log J_{\text{Co(II)}}$ of Co(II)

pH on flux. The dependency of $\log J_{\text{Co(II)}}$ versus the equilibrium pH at a constant Cyanex 272 concentration 1000 mol/m³ was constructed in Fig. 4(b). From the least square slope value of $\log J_{\text{Co(II)}}$ versus the equilibrium pH (0.62) using Equation 6, it can reasonably be concluded the cobalt extraction occurs by the exchange of one mole of H⁺ per mole of Co(II).

3.4. Effect of extractant concentration

As solvent inventory, one of the important advantages, determining suitable extractant concentration for efficient mass transfer is essential. At the same time, since the mass transport in HFSLM is diffusion driven, eliminating adverse effect from viscosity optimum extractant concentration need to be determined. Hence, the effect of the concentration of Cyanex 272 in the membrane phase on the flux of cobalt $J_{\text{Co(II)}}$ was studied in the range 25-1000 mol/m³. The Co(II) concentration and pH of the feed solution were kept constant at 10 mol/m³ and 6.00, respectively. The flow rate for both feed and strip solution was kept constant at 1000 mL/min. Fig. 5(a) shows the effect of extractant on the flux of cobalt $J_{\text{Co(II)}}$. As shown in figure cobalt flux increases from 0.49×10^{-5} mol/m²s to 4.82×10^{-5} mol/m²s with increase in Cyanex 272 concentration up to 500 mol/m³. With further increases in extractant concentration, the permeation rate of cobalt decreases gradually from 4.82×10^{-5} mol/m²s to 2.39×10^{-5} mol/m²s. As per Equation 1; with an increase in Cyanex 272 concentration, the formation of Co(II)-Cyanex 272 complex increases at the feed side-membrane interface up to 500 mol/m³. Higher the extractant concentration, obviously the viscosity increases, which can affect the mass transfer. Fig. 5(a) shows above 500 mol/m³ of Cyanex 272, the flux for cobalt

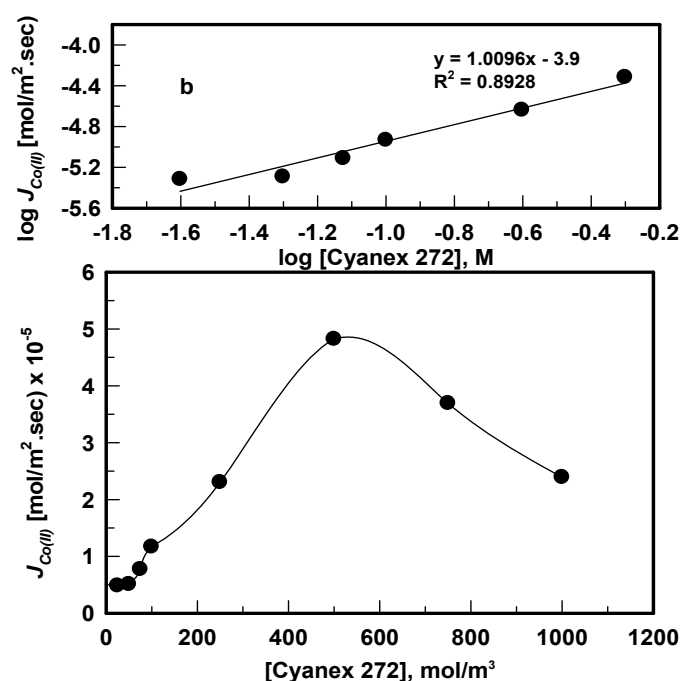


Fig. 5. (a) Effect of [Cyanex 272] on flux of Co(II) $J_{\text{Co(II)}}$ (b) Effect of $\log [\text{Cyanex 272}]$ on $\log J_{\text{Co(II)}}$

decreases because of the increase in viscosity of Cyanex 272 [22]. A slope of $\log J_{\text{Co(II)}}$ versus $\log [\text{Cyanex 272}]$ can justify stoichiometry involve in Co extraction using Cyanex 272. The dependency of the $\log J_{\text{Co(II)}}$ versus $\log [\text{Cyanex 272}]$ was plotted and shown in Fig. 5(b). Similarly using Equation 6, from the $\log J_{\text{Co(II)}}$ versus $\log [\text{Cyanex 272}]$ dependency is a straight line with slopes 1.009 for cobalt, specifying the relationship of one mole of the extractant requirement for extracted of one mole of cobalt ion.

3.5. Effect of cobalt ion concentrations in feed

Effect of cobalt sulfate concentration on the flux of cobalt was studied in the range of 2.5 mol/m^3 to 100 mol/m^3 . In the case of HFSLM study, the Cyanex 272 concentration in the membrane phase and pH of the solution were kept constant at 500 mol/m^3 and 6.00, respectively. The strip acid concentration was kept constant at 100 mol/m^3 and flow rate for both feed and strip solution was kept constant at 1000 mL/min . The results obtained are presented in Fig. 6(a). With increased concentration of cobalt sulfate in feed phase from 5 mol/m^3 to 100 mol/m^3 the flux value of cobalt $J_{\text{Co(II)}}$ increases from 2.84×10^{-5} to $5.30 \times 10^{-5} \text{ mol/m}^2\text{s}$. Within this concentration range of cobalt in the feed solution, the availability of cobalt ion at the feed side-membrane interface increased with the increase of cobalt concentration. So interfacial chemical reaction shifts forward direction presented in Equation 1, which leads to increase of $J_{\text{Co(II)}}$ from increases from 2.84×10^{-5} to $5.30 \times 10^{-5} \text{ mol/m}^2\text{s}$ (Fig. 6(a)). Fig. 6(b) shows the dependency of $\log J_{\text{Co(II)}}$ versus the $\log [\text{Co}]$ at constant Cyanex 272 concentration of 500 mol/m^3 . The least square slope value of the line for cobalt flux with respect to cobalt concentration in the aqueous phase is ~ 0.2 .

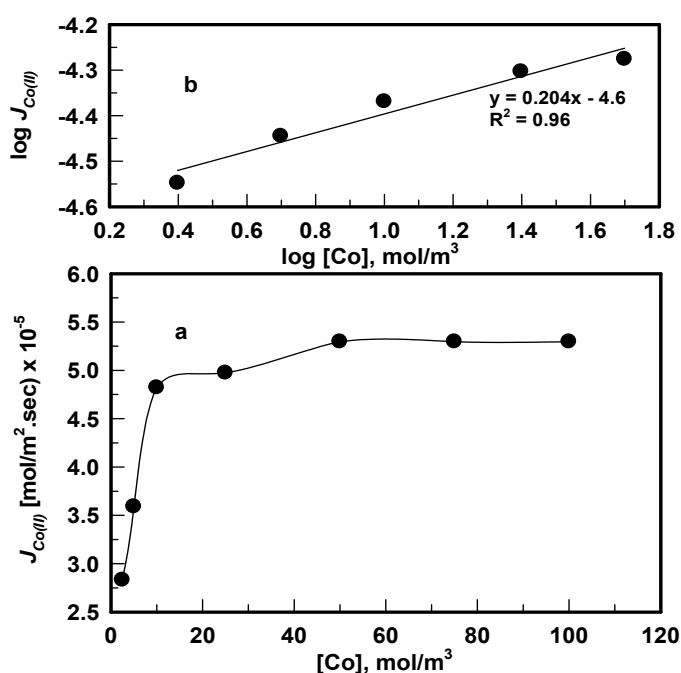


Fig. 6. (a) Effect of [cobalt] on flux of cobalt $J_{\text{Co(II)}}$ (b) Effect of $\log [\text{Co}]$ vs. $\text{Log } J_{\text{Co(II)}}$

3.6. Effect of strip acid concentration

In the HFSLM process, Co-Cyanex 272 diffused from feed-membrane interface to membrane-strip interface need to be stripped for Cyanex 272 to diffused back to the feed-membrane interface. For recovery of metals, the selective stripping of metals at the membrane-strip interface is an important phenomenon. To get efficient cobalt stripping, the stripping behavior was studied with different concentrations of strip acid solutions in the range of 1 to 500 mol/m^3 . All other parameters such as pH of feed at 6.00, Cyanex 272 concentration in membrane phase at 500 mol/m^3 , cobalt sulfate at 10 mol/m^3 were kept constant. The flow rate of feed phase as well strips phase was kept constant at 1000 mL/min . Fig. 7 shows the plot of $J_{\text{Co(II)}}$ against H_2SO_4 concentration. It indicates that $J_{\text{Co(II)}}$ increased from $0.89 \times 10^{-5} \text{ mol/m}^2\text{.s}$ to $4.82 \times 10^{-5} \text{ mol/m}^2\text{.s}$ with increase of acid concentration from 1 mol/m^3 to 100 mol/m^3 . Further increase of acid concentration to 500 mol/m^3 has no significant effect on metal ion flux. Hence, $100 \text{ mol/m}^3 \text{ H}_2\text{SO}_4$ can provide enough proton to back-extract Co^{2+} or dissociation of Co-Cyanex 272.

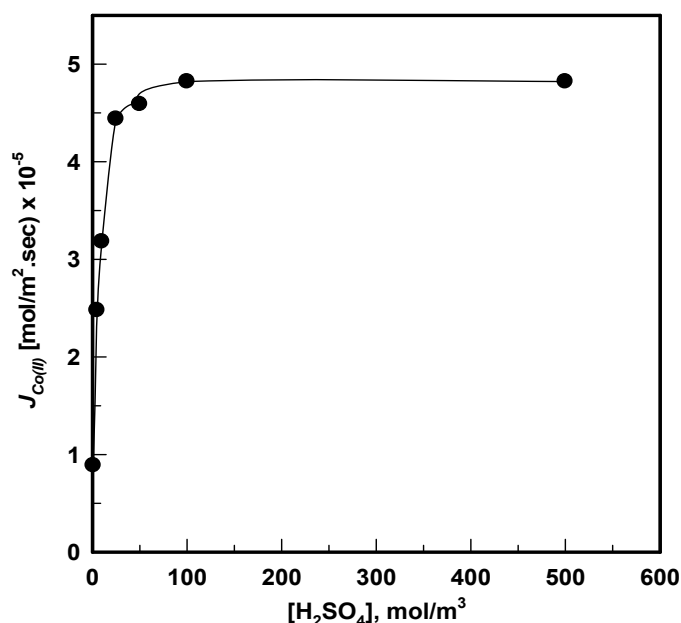


Fig. 7. Effect of $[\text{H}_2\text{SO}_4]$ on the flux of cobalt $J_{\text{Co(II)}}$

4. Conclusions

Studies for the extraction of Co(II) was carried out by HFSLM technique using Cyanex 272 as a mobile carrier. Following conclusions may be drawn from the studies.

- [1] The cobalt flux increases with increase in pH from 4.00 to 6.00. There was no extraction below pH 4.00.
- [2] Cobalt flux increases with increase Cyanex 272 concentrations in the membrane phase up to 500 mol/m^3 and then became saturated.
- [3] The stripping kinetic of cobalt with H_2SO_4 was very fast. $100 \text{ mol/m}^3 \text{ H}_2\text{SO}_4$ was found to be the suitable concentration for the stripping.

- [4] The optimum condition for extraction of cobalt was pH of 6.00, Cyanex 272 concentration of 500 mol/m³ and H₂SO₄ concentration of 100 mol/m³.

Acknowledgments

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