Korean Chem. Eng. Res., 57(3), 313-320 (2019)
https://doi.org/10.9713/kcer.2019.57.3.313
PISSN 0304-128X, EISSN 2233-9558

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Extraction/Separations of Cobalt by Supported Liquid Membrane: A Review

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(Received 19 February 2019; Received in revised form 19 March 2019; accepted 22 March 2019)

Abstract – Extraction/separation of cobalt by supported liquid membrane has been reviewed. The review discusses various directions associated with the supported liquid membrane process, such as the kind of supported liquid membrane, the principle of supported liquid membrane, transport mechanism involved, and the advantages and disadvantages of the supported liquid. Finally, extraction and separation of cobalt from other metals using extractant through supported liquid membrane have been reviewed. Separation of cobalt using various reagents and cobalt recovery from scrap using commercial extractant can be a potential perspective from the application of supported liquid membrane application.

Key words: Cobalt, supported liquid membrane, commercial extractant, Hollow fiber

1. Introduction

Efficient and selective separation/recovery of metal ions from industrial wastes, primary recourses, and secondary recourses has gained significant attention due to increasing demand for high purity products and also for environmental concerns. Various hydrometallurgical techniques are available for separation, purification and concentration of metals such as liquid-liquid extraction or solvent extraction (SX), precipitation, cementation, adsorption, ion exchange, and chromatography. These techniques have some disadvantages related to heterogeneous reactions (e.g., longer operation times), and in the majority of the cases the process is really a removal, and not a recovery, of metals [1-8]. Concerning the recovery of valuable metals from waste, separation, purification, and concentration of metals from its mixed solution the solvent extraction processes are efficient, versatile and flexible to a variation in the metal content and different metals in wastes, compared with other processes. Solvent extraction (SX) is a well-established technology used widely in extractive metallurgy for the production of metals in the industry. SX is a well-established technology for the production of metals from the relatively concentrated feed. However, industrial dilute effluents, feed solution poses an important challenge, as the solvent extraction technique is not cost effective for the separation of metals from the dilute solution. Supported liquid membrane (SLM) extraction is emerging as an alternative to conventional solvent extraction due to its high selectivity, operational simplicity, low solvent inventory, low energy consumption, zero effluent discharge, and the combination of extraction and stripping into one single stage.

Grand View Research has reported that the global membrane separation technology market is expected to reach $42 billion by 2024 and is supposed to grow at a compound annual growth rate (CAGR) exceeding 10% from 2016 to 2024 [9]. The major applications of membrane separation technology include water treatment where nanofiltration, microfiltration, reverse osmosis, and ultrafiltration [9]. But as far as the SLM market, size is not quite clear. Although much research effort has been made for metal extraction by SLM, an industrial application for metal recovery is very limited. The potential applications of SLM are listed below.

(i) Treatment, removal, and recovery of metals from wastewaters and industrial effluents.

(ii) Recovery of metals from the process stream of an industry.

(iii) Selective recovery/separation of metals from low metal-bearing secondary resources.

(iv) Removal of an organic contaminant like phenols and ammonia from wastewaters.

2. Supported Liquid Membrane

The supported liquid membrane (SLM) is a separation technique in which an organic extractant or carrier is soluble in organic solvent or diluent and immiscible in water, selective toward the desired species, is immobilized in a thin microporous hydrophobic membrane and interposed between two aqueous phases (feed and strip solutions). Whereas, the same chemistry is involved in both the SX and SLM processes. The SLM technique involves the impregnation of a porous membrane with a water-immiscible organic solvent. In a carrier-facilitated SLM, extraction with acidic extractants is performed by the diffusion of metal ion from the feed phase toward the membrane, where it forms the metal-complex and then it will be back-extracted into the strip phase due to a proton gradient between the strip and

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‡ This article is dedicated to Prof. Yong Kang on the occasion of his retirement from Chungnam National University.

feed phase, which provides the driving force for the mass transfer [10]. Also, co-transport exists because the different metal ions present in feed solution can be transported according to their affinity with the selected carrier. High selectivity can be obtained if the extractant is specific or very selective for one solute. In fact, every specific solute needs its own specific extractant or specific experimental condition, which makes this selection very important but also very difficult [11-13].

2-1. Advantages of the supported liquid membrane extraction process

Several beneficial features make it an attractive alternative [14-16]:

- Modest energy requirement: In the liquid fiber filtration process, no phase change is involved. Consequently, need no latent heat. This makes the SLM have the potential to replace some unit operations which consume heat, such as distillation or evaporation column.
- No waste products: Since the basic principle of the SLM is filtration, it does not create any waste from its operation except the unwanted component in the feed stream. This can help to decrease the cost of operation to handle the waste.
- Low operation cost: Requires lower initial capital costs and operating costs.
- The capability of treating a variety of elements and compounds in industrial settings.
- At greater speed and with a high degree of effectiveness, with varying contaminant concentrations and volume requirements.
- Low solvent inventory: because of low solvent inventory, tailor-made extractants can be used.
- Low energy consumption.
- Simple operational unit.
- High separation can be obtained in a single step.
- Extraction and stripping can be obtained in one step.
- Environmentally safe technology.
- Total recovery is possible.
- No sludge production.
- Meets EPA Common Sense Initiative (CSI) guidelines and zero discharge.
- Meet regulations for effluent discharge.
- No post-treatment cost improves process quality.

2-2. Disadvantages of the supported liquid membrane extraction process

Due to some disadvantages, SLM extraction leads to application constraints:

- Membrane fouling: Membrane fouling is a general problem dealt with membrane processes.
- Lack of research: Membrane technology is a new technology, and so far, research done on it is less compared to other hydrometallurgical fields. Hence, more research will be done in the future because of its potential.
- Physical and chemical constraints: Polymeric liquid membrane support made of the polymer cannot be used on corrosive substances and high-temperature condition.

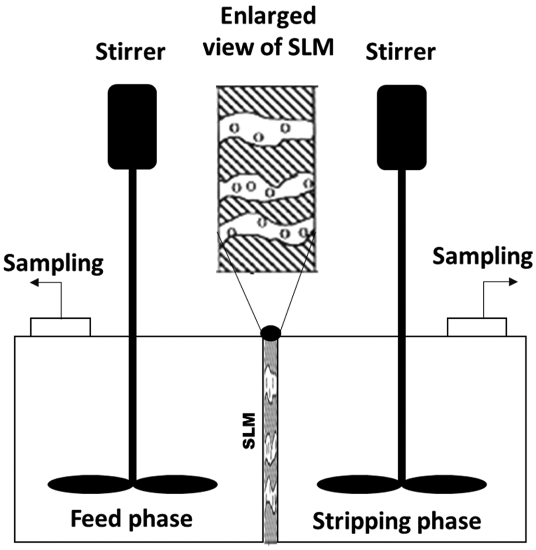


Fig. 1. Schematic for Flat Sheet Supported Liquid Membrane.

Supported liquid membrane (SLM) processes basically are two types [17].

(i) Flat sheet supported liquid membranes (FSSLM)
(ii) Hollow fiber supported liquid membranes (HFSLM)

2-3. Flat sheet supported liquid membranes

The most simplistic in design, the FSSLM can be utilized for laboratory scale but cannot be scaled up for industrial use. A schematic diagram for the FSSSLM module used in this experiment is shown in Fig. 1. A two-compartment cell separated by a flat sheet porous membrane impregnated with a solvent. Like SX, in the SLM the extractant solution is made from diluting the active extractant with a diluent and phase modifier. The feed and strip solution is usually kept under agitation using mechanical stirrer during the separation process. Combination of physical and chemical process help extraction/separation of metal selectively from feed to strip phase. Essentially, a porous polymer membrane whose pores are filled with the organic liquid and carrier, set in between our source phase and receiving phases, which are being gently stirred shown Fig. 1. A common mechanism which works for metal extraction in both the FSSLM and HFSLM process is explained in a separate section.

2-4. Hollow fiber supported liquid membranes

The design of the HFSLM is like a large electrical cable. It has an outer shell, which is a single nonporous material, through which the materials inside cannot be transported. Inside that shell, there are many thin fibers running the length of the shell, all in parallel, neat rows. What occurs is that the source phase is piped through the system from top to bottom, and the pores in the fibers themselves are filled with the organic phase. The carriers in that phase then transport the source across to the receiving phase, and then the receiving phase is

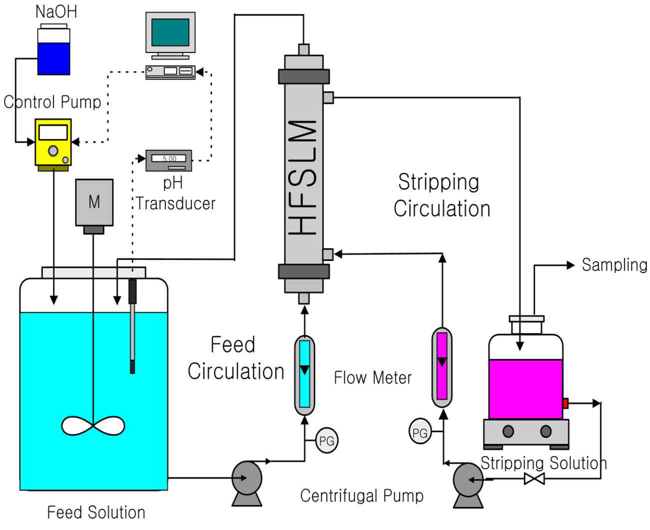
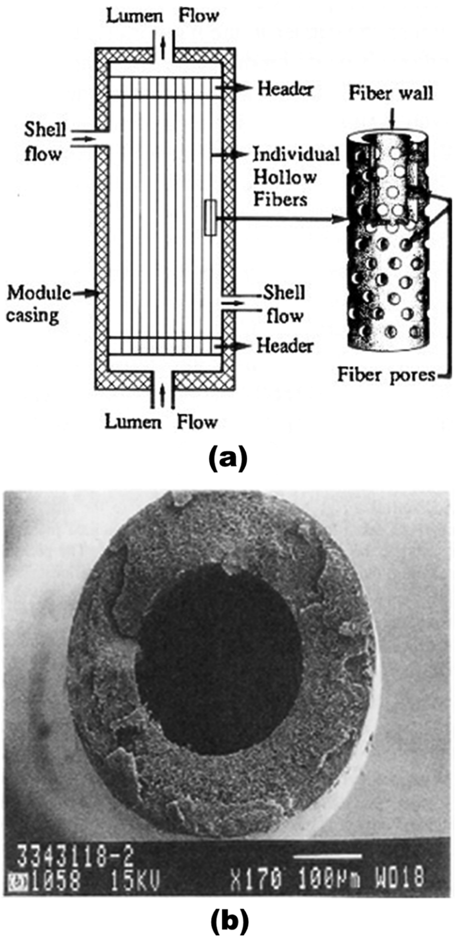


Fig. 2. Schematic for Hollow Fiber Supported Liquid Membrane process.



(a)

(b)

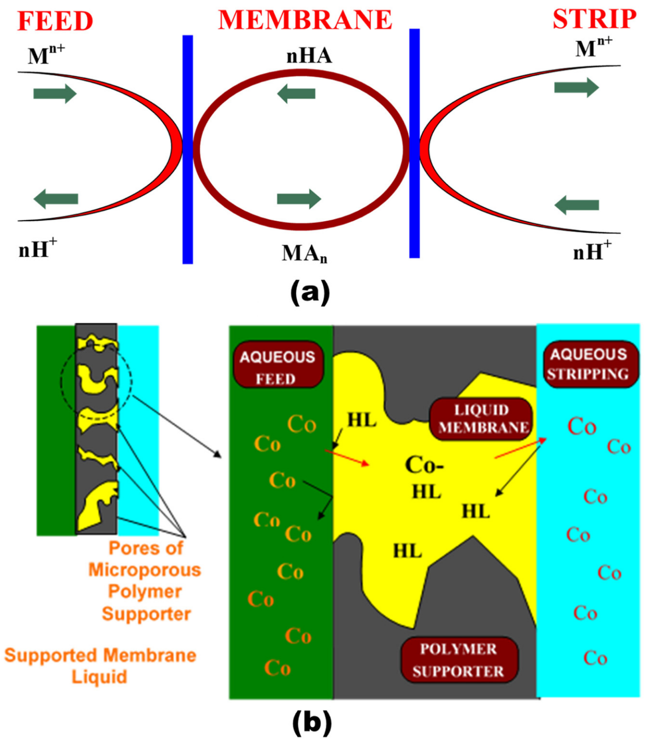
Fig. 3. (a) Hollow fiber supported liquid membrane set up, (b) Close-up cross-section of a hollow fiber membrane.

forced out through the sides of the shell. Fig. 2 represents this system. Fig. 3(a) shows schematic for only hollow fiber module and Fig. 3(b) shows a close-up cross-section of a hollow fiber membrane.

- There are several inherent advantages to using the hollow fiber system.
- The surface area and membrane thickness provide rapid transportation.
- The source/receiving phases are more easily recoverable than the FSSLM.
- The entire source and receiving phase are not in contact with the membrane at any given instant.
- Leakage and contamination are easily contained.
- Likewise, there are a few problems associated with this system.
- Very hydrophobic membrane solvents are required to maintain integrity.
- Hollow fiber system must be cleaned between uses or there will be aqueous and contaminant buildup.
- Pore fouling, causing caking in filters, often occurs due to surface effects and particles in the system.

3. Extraction/Separations Principles of Supported Liquid Membranes

SLM employs a thin microporous membrane that has been impregnated with an organic solvent to separate the feed and stripping solutions. Fig. 4(a) shows that at the feed/membrane interface, the extraction takes place and the formed metal complex diffuses to the membrane/stripping interface where the stripping occurs. The features of the SLM compared to the conventional solvent extraction are that the extraction and stripping are simultaneously carried out in such a way



(a)

(b)

Fig. 4. (a) Mechanism for metal ions transport through SLM, (b) Schematic presentation for transportation of metals through pores of the active liquid membrane.

that equilibrium limitation is not applicable, no limitations of the aqueous/organic ratio are required, and emulsification, flooding and loading limits, phase disengagement and large solvent inventory are avoided. Fig. 4(b) shows the active transport of metals through membrane pores. The metal ions come in contact with the interface of the feed-membrane-pore interface, then metal atom forms an organometallic complex. Then the metal extractant complex diffuses through membrane pore from the feed-membrane interface to strip membrane interface. At the membrane-pore-strip interface, the organometallic complex dissociates in the presence of strip acid. The mechanism continues as explained in Fig. 4(b). The general extraction mechanism by which a divalent metal ion is extracted from an aqueous phase using organic extractant can be written as [18,19].

$$M^{n+}_{aq.} + n(HL)_{org.} \Leftrightarrow ML_{n\,org.} + nH^{+}_{aq.} \tag{1}$$

where the subscript aq. is the aqueous phase and org. is the organic phase. The equilibrium constant, K of the reaction can be written as:

$$K = \frac{[ML_n]_{org.}[H^+]^n_{aq.}}{[M^{n+}]_{aq.}[HL]^n_{org.}} \tag{2}$$

where, distribution ratio, $D = [ML_n]_{org.}/[M^{n+}]_{aq.}$

$$K = \frac{D[H^+]^n_{aq.}}{[HL]^n_{org.}} \tag{3}$$

Taking logarithms, using the relation $pH = -\log [H^+]$ and re-arranging Equation (3).

$$\log D = \log K + n \log[HL]_{org} + n\,pH \tag{4}$$

Consequently,

$$(\partial \log D/\partial pH)_{[HL]org} = (\partial \log D/\partial \log[HL]_{org})_{pH} = n \tag{5}$$

The separation factor for liquid-liquid extraction (b_{sx}) is calculated using Equation (6).

$$b_{sx} = D_{Co} / D_{Li} \tag{6}$$

where, D_{Co} = distribution coefficient of the cobalt and D_{Li} = distribution coefficient of the lithium.

Analyzing the experimental value of distribution ratio (D) as a function of equilibrium pH and extractant concentration at a constant value of other parameters allows estimation of the number of extractant molecules associated with the extractant metal complex.

The relationship which correlates the membrane flux J, concentration of the feed solution [M], the volume of the feed solution V, and the effective membrane area A, is

$$J = (V/A)\, d[M]/dt \tag{7}$$

To discuss and describe the permeation of metal species through the combined SLM/strip dispersion process, a new permeability coefficient, *P*, of the metal species removed from the feed solution can be defined by the following formula:

$$J = [M]_{initial} \mathbf{x} P \tag{8}$$

The permeability coefficient of the membrane, P, is defined as in Equation 8.

$$P = J / [M]_{initial.} \tag{9}$$

Considering and integrating Equations (7) and (9), we can get the permeability coefficient in SLM related as:

$$Ln[M_f]_t / [M_f]_0 = -(A/V)\, P.t \tag{10}$$

$M_f(t)$ and $M_f(o)$ are the concentrations of metal ions in feed solution at time $t = t$ and $t = o$, respectively.

The mass transfer co-efficient otherwise similar to permeability coefficient is related as:

$$Ln[M_f]_t / [M_f]_0 = -(A/V)\, K.t \tag{11}$$

The mass transfer coefficient in membrane phase K for carrier and the complex can be approximated as [19-21]:

$$K = \varepsilon D_{diff.} / \tau d \tag{12}$$

$D_{diff.}$, diffusion coefficient for studies were calculated using these two equations (Equation (12) and Equation (13)).

Where, $D_{diff.}$ = diffusion coefficient for metal through the membrane
d = thickness of the membrane
ε = porosity of the membrane
τ = tortuosity of membrane

Dependencies of viscosity on flux can be calculated derived from the study. According to the Wilke Chang relation [22]:

$$D_{diff.} = kT/\eta \tag{13}$$

where *k* is constant, *T* the absolute temperature and η is the viscosity. By combining Equations (12) and (13), we can get

$$K = \varepsilon\, kT/\eta.d.\,\tau \tag{14}$$

Two or more metal ion species present in the feed solution can be separated when their permeability coefficient values are different. The separation factor SLM_{SLM} is defined by the following equation:

$$\beta_{SLM} = P_1/P_2 = (J_{M1} / [M_1]_f) / (J_{M2} / [M_2]_f) \tag{15}$$

where, J_{M1} and J_{M2} are the fluxes for the major and the minor transporting components, respectively, and $[M_1]_f$ and $[M_2]_f$ are their feed concentrations.

The extraction % and recovery % were calculated by

4. Extraction/Separations of Cobalt by Supported Liquid Membranes

Carrier-mediated transport through SLM is currently recognized as a potentially valuable technology for selective separation and concentration of toxic and valuable metal ions. Membranes for the separation and concentration of metal ions have received considerable attention throughout the past three decades due to characteristics such as operational simplicity, energy, and selectivity advantages, lower solvent inventory factor and low-cost operation factors [24]. From an application point of view, membrane separation processes find applications in the various field such as separation of metal values from industrial waste [25-32], analytical applications [33-37], biomedical application [38-41] as well as in wastewater treatment [42-44].

Transport study of different metal ions using supported liquid membranes (SLMs) has applications in both industrial and analytical fields for their separation, pre-concentration, and removal from wastewater [45,46]. The SLM technique is used for the extraction of different metal ions such as Cu, Zn, Cr, Al, Ce, Au, Pt, and Fe(III). The same SLM technique has been used for separation of various metals such as Cd-Zn, Co-Zn, Au(I)-Au(II), Fe-Cu, Ag-Cu, Nb-Ta, In-Ga, Yt-Fe, Pd-Pt, Au-Ag, Ce-La, Ga-As from binary solution, Fe-Cu-Ni, Cu-Ni-Zn-Mn, Ag-Cu-Zn, V-Cr-Mo. Several extractants such as Cyanex 923, Aliquat 336, D2EHPA and LIX84 are used for the extraction and separation of metals. Separation of cobalt in the presence of different media using various extractant has been investigated. The separation systems like Co-Ni [14,47-49], Co-Zn [50], Mn-Co [51,52], Co [51,52,53,54-56] have been reported using the SLM technique. Gega et al. [47] studied the competitive transport behavior of Co(II) and Ni(II) using di-2-ethylhexylphosphoric acid (D2EHPA) as well as commercial extractants, i.e., Cyanex® 272, 301, and 302 from sulfate media. For all studied ionic carriers, i.e., D2EHPA, Cyanex® 272, Cyanex® 302 and Cyanex® 301, transport of Co(II) cations much better than Ni(II). With pH of the aqueous feed phase increase, the initial fluxes of Co(II) and Ni(II) grow, and in all cases these fluxes are higher for the SLM process. The values of both metal fluxes were increased in the following order of applied ionic carriers: Cyanex® 272 < Cyanex® 302 < D2EHPA < Cyanex 301.

Bukhari et al. [39] studied extraction and transport behavior of cobalt through SLMs; based on triethanolamine (TEA), as a carrier in cyclohexanone diluent, supported in polypropylene hydrophobic microporous film has been carried out. Effect of different parameter Co(II) ions, HCl (in feed) and TEA (in membrane) concentrations have been investigated, viscosity has been investigated. The optimum flux value of 8.19×10^{-7} mol/m^2 s at 3.75 M TEA (membrane phase) for Co(II) In 1 M HCl feeds medium. Association of TEA molecules with cobalt ions as $LH\cdot CoCl_3$ and $(LH)_2\cdot CoCl_4$, with a major contribution by the former ~80% and ~ 20% by the later depending on HCl concentration in the feed has been reported.

Youn et al. [53] studied the permeation behavior of cobalt using HEH (EHP) as a carrier in sulfate media. A mathematical model considering the transfer resistance of the counterion was developed to analyze the cobalt permeations for the system where the cobalt concentration in a feed phase varies over a wide range and validity of the model was verified.

Prakorn et al. [64] studied the transport behavior of Co(II) in chloride media through HFSLM using di-(2-ethylhexyl) phosphoric acid (D2EHPA) diluted in kerosene. They studied the effect of various parameters like the effect of flow rate, pH of feed solution, carrier concentration and metal ions concentration. In their study, resistance in the series model was proposed, and validity of the model along with a variation of the different parameter was verified. From their study, the model has good potential for the prediction of permeability of Co(II). Campderros et al. also reported the same kind of study.

Wang et al. [56] investigated the transport behavior of Co(II) from an aqueous acetic acid media at approximately pH 6.00 using bis(2-ethylhexyl) phosphinic acid as a mobile carrier. The microporous polypropylene membrane was used as a solvent. The effects of pH value in the feed solution, the concentration of BEHPA in the membrane, experimental temperature and initial concentration of Co(II) in the feed on the transport rate of Co(II) were investigated. The transport kinetic equation was derived in terms of the law of mass diffusion and interface chemistry. Campderros et al. [57] did the same kind of study for cobalt using of D2EHPA as an extractant. The rate of cobalt transport through an SLM using P 507 as a mobile carrier was studied by He et al. [58] The limiting thickness of the aqueous diffusion film is the same order of magnitude as the membrane thickness (2×10^{-3} cm); the order of magnitude of the diffusion coefficient of the Co-extractant complex in the SLM was 10^{-7} cm^2/s.

Mohapatra et al. [59] studied the permeation rate of Co^{2+} from its aqueous sulfate solution through a solid SLM using D2EHPA in kerosene as a mobile carrier. The author studied the permeation as a function of hydrodynamic conditions, the concentration of Co(II) (0.17~4.25 mol/m^3), pH 3.5~6.0 in the feed solution, the carrier concentration in the range of 20~400 mol/m^3 in the membrane. The permeation factor was observed at a higher concentration of Co(II) or a lower concentration of H^+ due to carrier saturation.

Lee et al. [60] investigated the separation of cobalt and nickel from a mixed sulfate solution by using an HFSLM. The 2-Ethylhexyl-phosphonic acid mono-2 ethylhexyl ester [HEH(EHP)] was used as a solvent, which was diluted in kerosene. The permeation rate of cobalt was 10^{-6} to 10^{-7} mol/m^2.s, and the separation factor of Co(II) over Ni(II) was 10-220. By recirculation of the stripping solution, a tenfold enrichment of cobalt was possible, and cobalt with 95% purity was recovered from the low-concentrated solution. Jeong et al. [47], Choi et al. [61] and Youn et al. [62] investigated the same separation system and a model based on the continuity equation and considered not only the co-transport of cobalt and nickel but also the counter-transport of hydrogen ions. The concentrations in the stripping solution were taken into account in the model as well as the concentration in the feed solution and liquid membrane. The experimental results were in agreement with the model.

Juang et al. [48] investigated the separation of Co(II) from Ni(II) from sulfate solution through SLMs which contain D2EHPA dissolved in kerosene as a carrier. The permeation rate equations were derived considering the aqueous film diffusion of metal ions toward and out of the membrane and diffusion through the membrane of D2EHPA and its metal complexes. The mass transfer coefficients of the metal ions were determined using a permeation cell. The calculated permeation rates are in good agreement with the measured ones. Higher selectivity in the separation of cobalt and nickel is obtained when the diffusional resistance in the membrane phase is dominant. He, et al. [58] and Huang et al. [63] also reported the same kind of separation in their investigation using D2EPHA and P 507 (HEH(EHP)), respectively.

Alguacil et al. [64] and Mohapatra et al. [65] studied the selective transport of cobalt(II) from zinc(II) sulfate solution using the SLM technique using DP-8R as a mobile carrier. The suitable conditions for the separation of both metals were established aqueous feed pH 3.0, [Co]/[Zn] molar concentration ratio near 22, receiving phase 0.5 M sulfuric acid and membrane phase DP-8R 10 vol.% in Exxsol D100. Alguacil et al. [52] and Mohapatra et al. [63] also studied the transport of manganese and cobalt ions from sulfate solution through an SLM containing DP-8R acidic extractant dissolved in Exxsol D100 as a mobile carrier. Higher selectivity in the separation of manganese and cobalt was obtained when the source phase had high [Co]/[Mn] concentration ratios.

Yildiz et al. [66] investigated Co/Ni separation by SLM using a mixture of Alamine 308 (tri-isooctylamine) and TBP where extracted metals were stripped using complexing reagent (NH_4SCN). Verbeken et al. [67] investigated cobalt removal from waste-water by SLM using a mixture of di-2-ethyl-hexyl phosphonic acid (D2EHPA) and 5-dodecylsalicylaldoxime (LIX 860-I). Verbeken et al. also indicated that the above mixture synergizes and provides superior extractability compared to individual extractant. Surucu et al. [68] reported separation of Co/Ni by FSSLM using Alamine 300 as a carrier where NH_4SCN was used as stripping solution. Surucu et al. indicated selective extraction with an efficiency of 99.9%, and the separation factor was 506.

Swain et al. [18] investigated the extraction of Co (II) by supported liquid membrane using Cyanex 272 as an extractant. Cobalt extraction was from dilute sulfate solution by a supported liquid membrane (SLM) and compared with solvent extraction (SX). The mass transfer behavior in the FSSLM process and distribution coefficients in SX was compared in a sulfate solution. Complete extraction of cobalt from dilute sulfate solution at pH of 6.00, using 750 mol/m^3 of Cyanex 272 and strip acid concentration of 25 mol/m^3 was achieved by FSSLM process. Swain et al. [69-71] also investigated the separation of Co and Li by FSSLM and HFSLM. Separation of Co (II) and Li (I) by FSSLM using Cyanex 272 as a mobile carrier was reported by Swain et al., where the permeation rate of Co(II) and Li(I) from a sulfate media was focused [69]. The report indicated optimum separation could be achieved in the pH range of 4.0 to 6.0 using Cyanex 272 by FSSLM process. Synergistic separation behavior of Co (II) over Li (I) by FSSLM using Cyanex 272 and DR-8R was studied Swain et al. [70]. Separation behavior was investigated using individual Cyanex 272, DR-8R and also a mixture of both. Optimum separation behavior was implicated in the range of pH 5-6. Quantitative extraction behavior of Co(II) and Li(I) using above extractants can be compared as Cyanex 272 and DP-8R mixture $\approx 3 \times$ Cyanex 272 $\approx 15 \times$ DP-8R [70]. Swain et al. [71] also investigated the separation of Co (II) and Li (I) by HFSLM using Cyanex 272 as an extractant and also compared its behavior with FSSLM. The study revealed that the optimal process parameter for FSSLM and HFSLM was very close or similar. At optimal condition the separation factor was found to follow the order as: FSSLM > HFSLM > dispersive SX [71].

5. Conclusion

The SX technique is a well-established process, but SLM extraction is an emerging alternative field of research; it has a new dimension to search and find a techno-economical solution. FSSLM technique inherited with a problem like small surface area can be overcome by HFSLM technique. Complete purification of cobalt is possible by SLM process using organic extractant as a mobile carrier even at 99.99% purity. The SLM process leads to no effluent discharge in the whole process; hence, the process can be environment-friendly. In contrast, SX can be applied for the same purpose, but it is limited by high volume solvent investment, emulsification, tedious multi-step extraction, stripping and scrubbing. But in the SLM process the drawbacks can be overcome and separation of cobalt with requisite purity can be achieved in a single stage.

Acknowledgment

This study was supported by the R&D Center for Valuable Recycling (Global-Top R&D Program) of the Ministry of Environment (Project No.: 2016002250005).

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