



Review Paper

Supported Liquid Membrane in Metal Ion Separation: An Overview

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Article info

Received 2017-05-13
Revised 2017-08-09
Accepted 2017-09-18
Available online 2017-09-18

Keywords

Supported liquid membrane
SLM
Metal ion
Carrier
Organic solvent
Stripping phase
Feed phase

Highlights

- Liquid membrane principles investigation
- Literature review on metal ions removal using flat sheet and hollow fiber SLM since 2000
- Mechanism of facilitated transport and Complex transportation in the SLM
- Factors affecting the efficiency of the SLMs in the separation of metal ions

Abstract

Using liquid membrane and, in particular, supported liquid membrane (SLM) is a novel method of separation in comparison to other methods such as adsorption, extraction and ion exchange. SLM is a combination of simultaneous extraction and disposal whose high efficiency and capability is proven by many studies. So far, many researchers have utilized SLM in various scientific fields including analytical chemistry, organic and inorganic chemistry, chemical engineering, biotechnology and bio pharmaceuticals. Dynamic transfer, high selectivity, possibility of expensive carrier usage, low energy consumption and low operational costs are part of the advantages attributed to SLM. In the present paper, previous studies and the latest achievements in designing various modules for metal ions separation by SLM are reviewed.

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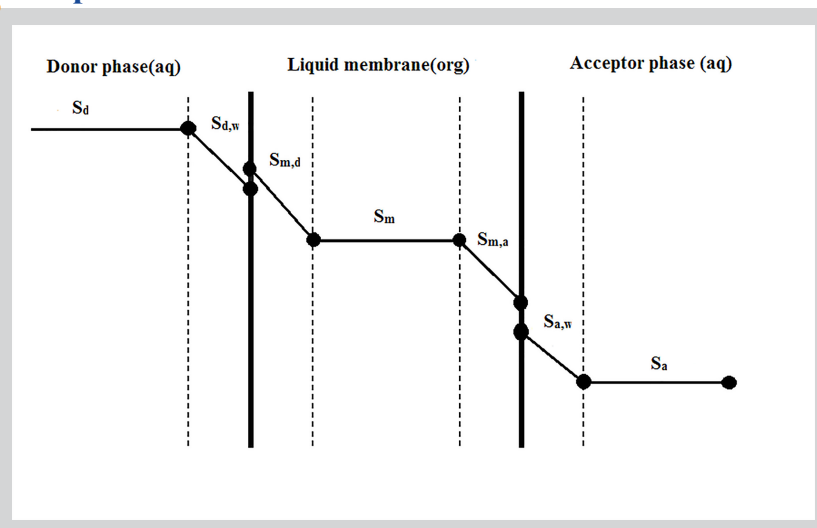
1. Introduction

With the growth of modern technologies, the amount of industrial wastewater discharged into the environment is progressively getting larger. Pollutants contained in the produced wastewaters have devastating effects on human health and other living creatures. Metal ions are one of the most toxic contaminants present in the wastewater discharged into the environment and therefore, the environmental protection agencies around the world put strict restrictions on the amount of metal pollutants contained in the industrial effluents. To remove the metal ions from wastewater, various methods such as Liquid-Liquid extraction, adsorption, ion exchange, electrodialysis and membrane processes are developed among which the use of SLM is becoming

more popular for researchers due to its high pollutant removal efficiency even at very low concentrations of metal ions. Liquid membrane is known as a green technology because of its green characteristics such as being eco-friendly and its low consumption of organic solvent [1]. The main features of this technology are its low start-up and operating costs, low carrier, solvent and energy consumption, easy capability of commercialization and high selectivity [2-3].

In general, liquid membrane is divided into three categories in terms of manufacturing technology: supported liquid membrane (SLM), emulsion liquid membrane (ELM) and bulk liquid membrane (BLM). Figure 1 indicates

Graphical abstract



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a schematic representation of different types of liquid membranes [4, 5]. BLM usually consists of a bulk aqueous feed and one receiving phase separated by a bulk organic water-immiscible liquid phase in a U-shaped tube. BLMs are usually used for studying a new carrier and evaluation of its transmission characteristics. Since the mass transfer surface of BLM is not considerable, it is unfavorable to be commercialized [4]. In the ELM, the receiving phase is emulsified in a liquid membrane. The emulsion is then dispersed in the feed solution and mass transfer from the feed to the emulsified receiving phase takes place. Liquid membranes can be either aqueous or organic, however, the majority of publications have considered them to be organic [5-7]. In SLM, the organic phase which plays the role of the liquid membrane fills the pores of a porous polymer support and stabilizes by means of capillary forces. In the next step, the polymer saturated with organic solution is located between the receiving and the feed phases and then, mass transfer between two phases occurs. Since the membrane phase is usually hydrophobic, an extraction agent is added as a carrier to make a complex at the interface of the membrane and feed phase. The carrier facilitates the mass transfer between the receiving and the feed phases. To adjust the membrane phase viscosity, another organic material is sometimes added to the membrane phase as a diluent. In some cases, a special material is added to the membrane as a phase modifier to prevent emulsion layer formation at the interfaces. So far, only a few review papers have been published in liquid membrane field. In 1999, Gyves et al. [8] published a review paper on SLM. They explained the concept of SLM and investigated the development of theoretical models validated by the experimental results. Furthermore, they gave a concise report of most research accomplished in the field of SLM for metal removal until 1999.

Kocherginsky et al. [4] have investigated all types of liquid membranes in terms of the technology. In another study, Agreda et al. [9] have specifically investigated supported liquid membrane technologies in the field of metal removal. They explained the modules that have been used in SLM and have given a brief explanation about their transport mechanisms.

In this review, the importance of removing metals from industrial wastewater is expressed and more detailed explanations on SLM and its application on the metal ions removal and recovery are given. In addition, a brief report of nearly all research papers published in metal separation by SLM since 2000 is presented.

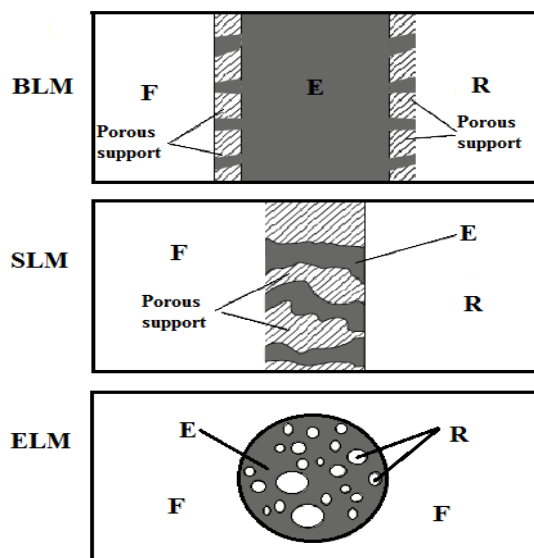


Fig. 1. Types of liquid membranes [10].

2. The importance of removing metals from wastewater

The production and accumulation of contaminants such as heavy metals (chromium, copper, lead, cadmium, zinc, nickel, etc.) are one of the most concerning factors in environmental problems and destruction of ecosystems. Heavy metal contaminants are dangerous and non-biodegradable pollutants. Nevertheless, the presence of some of these metals in low concentrations is essential for the environment [11]. Zinc is one of the metals, a small amount of which is essential for life because it is a main component of over 200 enzymes. However, its concentration has to be maintained below a safe threshold in nature [12, 13]. Chromium is one of the most toxic metals whose exceeded amounts may cause irrecoverable effects on humans and other living organisms. This metal has a considerable impact on the development of

cancerous and non-cancerous tumors. Symptoms of chromium poisoning is kidney failure, liver diseases and the weakness of the respiratory system [14].

Controlled levels of ferrous metals are also essential for the environment. Iron is present in the structure of hemoglobin, myoglobin and other proteins. Nevertheless, excessive concentration of this metal in living organisms initially causes nausea and diarrhea and at higher doses, it can cause cardiovascular problems, anemia and weakness of the nervous system [15].

Copper is also one of the metals which is involved in the structure of many vital enzymes, but high concentrations of copper cause problems such as jaundice, mental retardation, liver and kidney disorders and skin diseases [3].

Lead has been cited as one of the three most toxic heavy metals that have latent long-term negative impacts on the health, causing anemia, encephalopathy, hepatitis and nephritic syndrome [16].

Cadmium is another metal of which its non-permissible values promote cancerous tumors and damaged kidney tissues [17].

Among other metals, arsenic, aluminum, mercury, manganese and molybdenum are counted as toxic metals and their excessive amounts can be a threat to human health and other living organisms [18].

3. Supported liquid membrane

3.1. Transfer mechanisms and kinetics

When an immiscible phase separates two other phases, the difference in the concentration of any species in the separated phases causes mass transfer. The mass transfer efficiency of each depends on the mass transfer coefficient. Any species extracted easier by the membrane phase from the feed phase and repulsed better to the receiving phase is transferred faster. So it can be said that the rate of mass transfer of species depends on their physicochemical characteristics [5].

Entropy reduction and the consequent increase in the free energy occur alongside the separation and enrichment processes. Therefore, these processes are not spontaneous. So, for transferring components and running a continuous separation system, the energy source and difference in chemical potential on both sides of the membrane is required. These requirements are prepared by changing the solubility and penetration of mixture components on both sides. Determining the solubility of a component in a mixture is very complicated due to the presence of other species. Also, the diffusion coefficient of a component depends on the concentration of other components. Therefore, a large number of complicated mathematical models such as solution diffusion, network model, etc. are presented by researchers for mass transfer description.

3.2. The transmission driving force

SLM mass transfer occurs on both sides of the membrane due to the presence of the chemical potential gradient. This chemical potential difference is expressed by Eq. (1):

$$d\mu = RTd\ln C_i + RTd\ln \gamma_i \quad (1)$$

where C_i represents the concentration of activity coefficient of component i . Concentration profile has been schematically reported in Figure 2.

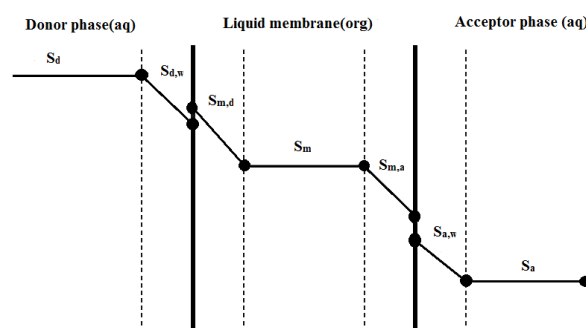


Fig. 2. Profile concentration in SLM [5].

As shown in Figure 2, transferring the desired part of the feed phase includes the following steps:

1. Diffusion of molecule S across the boundary layer at the feed phase
2. Extraction of molecule on the feed/membrane interface
3. Diffusion of molecule across the membrane boundary layer on the feed side
4. Convective transport of the molecule in the liquid membrane zone
5. Diffusion of molecule across the membrane boundary layer on the strip side
6. Re-extraction of molecule on the membrane/strip interface
7. Diffusion of molecule S across the strip phase boundary layer

Based on the solution-diffusion model, the component transmission mechanism through the membrane can be done in two simple ways, simple transport and facilitated transport and both of them obey Fick's law [8, 19].

3.3. Simple transport

This mechanism is based on the solubility of the component into the membrane phase and then, penetration through the membrane to the other side and finally stripping into the acceptor phase. Stripping is done through chemical reaction, which results in increasing the mass transfer rate. For instance, in the metal separation, extraction agents such as EDTA, thiosulfate, cyanide, thiocyanate and iodide are added to the acceptor phase to enhance the selectivity and the mass transfer rate.

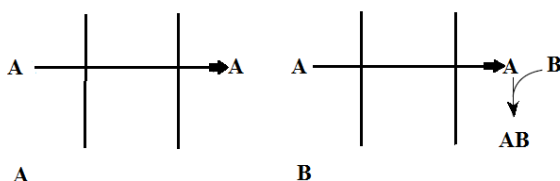
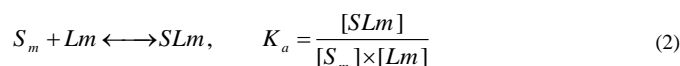


Fig. 3. Types of simple transport [5].

3.4. Facilitated transport

For components such as metal ions, amino acids, peptides and so forth whose solubility into the membrane phase is very low, additives named carriers are added to the organic phase (membrane), which enhances the solubility of the component. The carrier makes a complex with the solute and then passes across the membrane and on the other side of the membrane, the component is stripped into the acceptor phase due to reasons such as gradient in the specific solute or H^+ concentration. In carrier selection, it must be noted that the carrier and its complex with the solute must be soluble in the organic phase and immiscible in the aqueous phase. In the facilitated transport mechanism, the process can be controlled by two ways: complex formation and complex diffusion through the membrane. In many cases, the facilitated transport mechanism is very complicated and is explained based on the kinetics of complex formation and penetration into the membrane. It is usually assumed that the carrier is completely hydrophobic and therefore, the complex formation and complex dissociation reactions take place only at the membrane-aqueous phase interfaces. This transport mechanism is called small Carrousel [20]. This is a very restricting item that prevents SLM from being widely utilized in the real technical purposes, since there are few selections for the carrier.

In small carrousel, if a ligand (L_m) makes a complex with the component S at the membrane surface, the equilibrium constant is defined as follows:



If the complex formation and dissociation happen quickly, the process will be controlled by diffusion and the mass flux will be calculated according to Fick's law.

As indicated in Figure 4, three forms of transport mechanisms may occur depending on the carrier type [5]:

- A simple transport: In this mechanism, the solute makes a complex with the carrier, passes across the membrane phase and is stripped into the receiving phase.
- Co-current coupled transport (co-transport): In this transport

mechanism, another component in accompaniment with the component (i.e. two components) makes a complex with the carrier and passes across the membrane and both components are released into the receiving phase.

- Counter-current transport: In this case, the specimen in the feed phase makes a complex with the carrier, passes across the membrane and is released into the receiving phase; simultaneously, another component in the receiving phase makes a complex with the carrier, passes across the membrane in the opposite direction and is stripped into the feed phase.

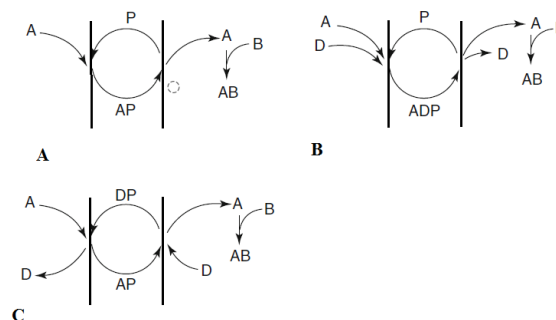


Fig. 4. Transport mechanisms: (a) simple transport, (b) co-current coupled transport and (c) counter-current transport.

3.5. Liquid membrane efficiency

Many advantages such as high selectivity, high separation factor and low operational costs have been attributed to liquid membranes and in particular to supported liquid membranes. In contrast, instability and low permeability are the biggest disadvantage of liquid membranes. These factors are largely linked to the form of membrane structural modules. For instance, hollow fiber modules are used to enhance the stability of the liquid membranes and contribute to their industrialization. Thus, in recent decades, most research has been focused on improving the permeability, stability and selectivity of the liquid membranes. Addressing these three factors is essential in evaluating any novel liquid membranes.

Permeability: Permeability is defined as the amount of component transported through a specific surface area of the membrane at a given time. It is related to the permeation flux J as follows [3, 20]:

$$J = P C \quad (3)$$

Selectivity: Selectivity means separation of the solute within a multi-component mixture. Selectivity widely depends on the support pore size and the transport mechanism in the membrane. High selectivity is not achievable in the simple transport mechanism since the selectivity is only controlled by the solubility in the organic phase and diffusion while adding a carrier to the organic phase, which makes a complex only when the solute enhances the selectivity significantly.

Stability: Despite many advantages of supported liquid membranes, the major reason for not using supported liquid membranes at a large scale is their low stability and life time [19, 21]. Instability in the membrane phase occurs by the separation of solvent or carrier from the organic phase to the aqueous phases due to the formation of emulsion at the interfaces of organic and aqueous phases. Solvent evaporation is also another reason for the liquid membrane instability [5]. Despite SLM high selectivity and effective separation due to the possibility of producing value added products in relatively small amounts by SLM, it can be attractive technology in the chemical and pharmaceutical industry, but recent development in forming a stable liquid has not resulted in commercialization yet [4]. The main reason for membrane instability is loss of carrier and/or solvent from the membrane phase, which decreases membrane selectivity and separation performance [1, 4]. Through the experiment, it has been shown that after which instability phenomena are observed, the membrane performance vary from less than one hour to several months [4]. The pressure difference across the membrane and emulsification or displacement of liquid membrane components, e.g., carriers to the feed or stripping phase, blockage of support pores by precipitation of carrier (increasing carrier concentration reduces organic phase interfacial tension and it makes membrane less stable) and support pores wetting (water enters pores and replaces the organic liquid membrane phase) are the challenges against these components being fixed in the support [19, 21]. The minimum transmembrane pressure, which is necessary for pushing the liquid membrane out of the largest pores can be calculated via equation (4):

$$P_c = 2\gamma \cos \frac{\theta}{r} \quad (4)$$

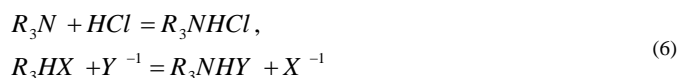
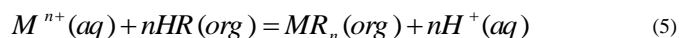
where γ is interfacial tension between feed or strip solution and SLM phase and θ is the contact angle between pores and the liquid membrane and r is the pore radius. If transmembrane pressure becomes larger than P_c it results in SLM degradation which is a challenge against carrier fixing, than the immobilizing carrier into the support by using continuous reimpregnation of support with the liquid membrane [4], reducing surface shear, gelling the immobilized liquid [8] and making barrier layers on the membrane surface by interfacial polymerization or physical deposition [4] or nanoporous coating on the SLM as major ways for immobilizing carrier and organic solvent into the support. In addition, the kinds of carriers and solvents are important factors for SLM stability. Moreover, support thickness and pore size are important factors in membrane stability and control mass transport rate in the membrane. Since the membrane phase is held in the support only by the capillary forces, the solid support pore size highly affects the SLM stability and higher thickness and smaller pores result in a more stable and less permeable membrane and therefore adequate balance between stability and permeability should be intended [19]. Since membrane stability is the biggest barrier to the membrane industrialization, releasing the rate of carrier and organic solvent into the feed or permeate phase during bench/industrial units is one of the main factors that should be intended for future researches on SLM industrialization and providing stable membranes at a large scale.

Organic solvent immiscibility with the aqueous feed and strip phase and capillary force is the main reason for holding solvent in the support pores [4, 19]. Surface tension between organic solvent and support pores is necessary for membrane stability, but on the other hand the solvent should wet the supporting membrane by forming near-zero contact angle for having good transportation. Therefore, low surface tension between solvent and supports should be desired [19]. The SLM support should be chemically stable on exposure to impregnating the solvent and any chemical interactions which destroy the support should be prevented [22].

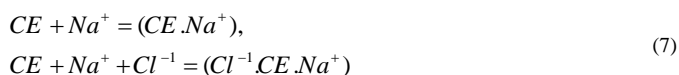
3.6. The mechanism of metal ions transport and association/dissociation reaction through organic membrane/feed and acceptor phase

Since carrier is a hydrophobic complex formation (association) that takes place through the organic membrane/feed interface, the solute makes a complex with the carrier, passes across the membrane phase and is stripped into the receiving phase [4]. Since the extraction/releasing of metal ions by carriers is performed via association/dissociation reaction in the SLM [8], the difference in the extraction/stripping mechanism is equivalent to different association/dissociation reactions. Association reaction in the SLM is done by compound formation or ion-pair formation or solvation. Equations (5), (6) and (7) show samples of the association reaction by compound formation, ion-pair formation and solvation, respectively. In extraction by compound formation and solvation, in which association reaction is performed via forming compound and solvate as their name indicates. Cyanex 272 is an example of carrier used in extraction by compound formation and crown ethers are an example of solvating extractants.

In extraction by ion-pair formation: the amine based extractants, e.g., Aliquate 336 and Alamine 304, are the carrier of this kind of extraction and due to their basic property these carriers can extract acid from aqueous solution and then metal ions (which are trapped in anionic complexes) can be extracted via anion exchange reactions [22].

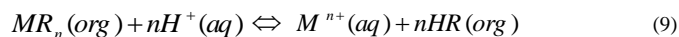
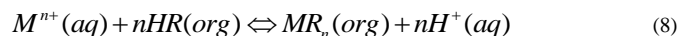


R= alkyl or H, Y^{-1} is a metal ion anionic complex, X^{-1} is an anion such as Cl^{-1} .

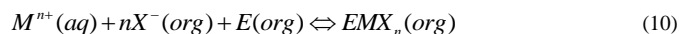


CE= crown ether

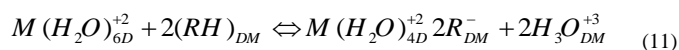
Perhaps, Bloch was the first person who used the liquid membrane with a carrier for metal ion recovery in 1970 [21]. In general, the difference in the carrier pH results in a different association/dissociation mechanism.



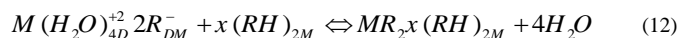
and follows equation (6) if a basic carrier is used.



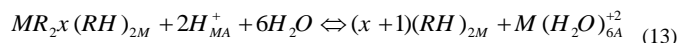
In fact H^+ concentration difference is used as a driving force for the extraction and directs metal ion transport, for example, it transfers carrier-ion complex from feed to a more acidic strip phase on the other side of the membrane. There dissociation reaction takes place and the carrier complex misses its ion and becomes protonated (equation (9)) and returns towards the feed phase. Since by this mechanism the metal ion is transported against its concentration gradient, coupled counter-transport takes place. However, when the basic carrier is used, association reaction through the organic membrane/feed phase follows the equation (10) and coupled coextraction takes place [4]. Equations (8), (9) and (10) are simplified modes of association/dissociation reactions. However, in reality the mechanisms are more complex. Komasawa [23] investigated the extraction of metal ions using DEHPA as carrier. During the hydrated metal ion reaction with carrier at the feed-membrane neutral species are made:



Then DEHPA (RH) is replaced instead of neutral species coordinated water molecules and results in solubility of the ion in the membrane phase:



Again, on the other side of the membrane, hydrated cation is formed and at the membrane-acceptor phase:



The subscripts D, M, A, refer to the bulk donor, membrane and acceptor phase, respectively. DM and MA represent the donor/membrane and the membrane/acceptor interfaces.

3.7. SLM configurations

There are three types of modules for SLM processes; flat sheet SLM (FSSLM), hollow fiber SLM (HFSLM) and spiral wound SLM (SWSLM). Many studies have been focused on the first two modules (i.e. FSSLM and HFSLM) while there are very few works on the last one (i.e. SWSLM). Therefore, the first two modules are taken into consideration. Due to the higher surface to volume ratio of HFSLM compared to that of the FSSLM, it possesses higher permeability and extraction capacity. In addition, HFSLM provides high mass transfer rate, continuous flow, lower capital and operating costs, less energy consumption, low extractant inventory, high stability and hence, is more beneficial in the separation of metal ions, making it a better and more efficient choice for industries [24].

Many studies have been focused on metal ions separation using SLM since 1984. Gyves et al. [8] reviewed the published papers on SLM for metal ion removal until 1999. A brief report of studies in the separation of metal ions using FSSLM and HFSLM from 2000 onward is presented in Table 1 and Table 2, respectively.

3.8. Factors affecting the efficiency of the SLMs in the separation of metal ions

3.8.1. Feed phase pH

Vankatsowaran et al. [72] tried to recover the copper ions by SLM in 2007. They used coconut oil as the membrane phase and Di (2-ethylhexyl) phosphoric acid (D2EHPA) as the acidic carrier. The importance of their research was that instead of using toxic, non-biodegradable and expensive chemicals as the solvent, they used an inexpensive and environment-friendly solvent like coconut oil whose vapor pressure is close to zero. The use of this type of solvent with low vapor pressure can cause membrane stability. They showed that feed phase pH affects the quality of copper separation (Figure 5). They indicated that copper transport starts from a pH of 2 and increases with an increase in the pH up to 4 and decreases at a pH above 5, which is due to the formation and precipitation of $Cu(OH)_2$.

Table 1
Literature review on metal ion removal using flat sheet SLM since 2000.

Ion	Solvent/Carrier	Stripping agent	Feed Solution	Reference
Ag(I)	Toluene/DC18C6	Na ₂ S ₂ O ₃	HNO ₃	Altin et al. 2010 [25]
Ag(I) Hg(II)	NPOE/PhenS ₂ O, TT12C4	Na ₂ S ₂ O ₃ , EDTA	Picric acid	Shamsipur et al. 2006 [26]
Ag(I)	Kerosene , NPOE/ Calix[4]Pyrroles	Na ₂ S ₂ O ₃ + EDTA	Picric acid	Amiri et al. 2008 [27]
Ag(I)	Cyclohexane/TDDA	HNO ₃	HNO ₃	Rehman et al. 2012 [28]
Ag(I) Cu(II)	Chloroform/DB18C6	Distilled water	Thiourea	Gherrou et al. 2001 [29]
Ag(I)	Chloroform/Cryptand2.2.2	Distilled water	Synthetic Wastewater	Arous 2004 [30]
Am(III)	n-dodecane+1-Octanol/ n-Pr-BTP	EDTA	NaNO ₃	Bhattacharyya et al. 2011 [31]
Am(III)	n-dodecane/TODGA	Oxalic acid, Citric acid, distilled water	HNO ₃ +NaNO ₃	Ansari et al. 2006 [32]
Am(III)	n-dodecane/TEHGA	HNO ₃	HNO ₃	Panja et al. 2008 [33]
Au(I) Pd(II) Pt(II)	Chloroform/ P-tetra-butylthiacalix[4]jaren	HCl+ thiourea	HCl	Fontas et al. 2006 [34]
As(V)	Dodecane+dodecanol/ Aliquate 336	NaCl	HCl	Guell et al. 2011 [35]
Au(I)	Xylene/Cyanex 923+ Primene JMT	NaCl	NaCN	Alguacil et al. 2004 [36]
Au(I)	Cumene/LIX79	NaOH	NaCl	Sastre et al. 2000 [37]
Au(III) Au(I)	Xylene/Cyanex 921	Natural Water	Lithium Salt	Alguacil et al. 2005 [38]
Au(III)	n-dodecane/ Cyanex 923	NaSCN+NaCl	HCl	Alguacil et al. 2001 [39]
Cd(II)	Kerosene/Aliquat336	EDTA	HCl	Lv et al. 2007 [40]
Cd(II)	Solvesso100/Cyanex923	Distilled water	NaCl	Alguacil et al. 2005 [41]
Cd(II)	Exsol 100/Cyanex 923	Distilled water	HCl	Rathore et al. 2009 [42]
Cd(II) Pb(II)	Chloroform/TBP,TOPO, D ₂ EHPA,TEHP	Distilled water	HNO ₃	Azzoug et al. 2014 [43]
Cd(II)	Kerosene/ D2EHPA	H ₂ SO ₄	H ₂ SO ₄	Parhi et al. 2009 [44]
Cd(II)	NPOE/ thiacalix[4]arene	HCl	HCl	Zaghbani et al. 2005 [45]
Cd(II)	Kerosene/TOA	CH ₃ COONH ₄	HCl+NaCl	Gu et al. 2006 [46]
Cd(II)	Xylene/ Cyanex 923	Distilled water	HCl+H ₃ PO ₄	Alguacil et al. 2001 [47]
Cd(II)	Cyclohexane/TBP	EDTA	HCl	Nowier et al. 2000 [48]
Cd(II) Ni(II)	Kerosene/ D2EHPA+ M2EHPA	H ₂ SO ₄	Synthetic Wastewater	Mahmoodi et al. 2014 [49]
Cd(II)	Toluene/Aliquat 336	EDTA	HCl	Altin et al. 2011 [50]
Cd(II) Zn(II)	Kerosene/ M ₂ EHPA+D ₂ EHPA, Cyanex302	H ₂ SO ₄	Synthetic Wastewater	Peydayesh et al. 2013 [51]
Co(II)	Chloroform/Alamine336	NH ₃ +TEA	CH ₃ COOH	Sürtücü et al. 2010 [52]
Co(II)	Exsol D100/DP8R,Acorga M5640	H ₂ SO ₄	H ₂ SO ₄ +NH ₄ OH	Alguacil et al. 2011 [53]
Co(II) Li (I)	Kerosene/DP-8R	H ₂ SO ₄	H ₂ SO ₄	Swain et al. 2010 [54]
Co(II)	Chloroform/ Alamine300	NH ₃ +TEA	NH ₄ SCN	Sürtücü et al. 2012 [55]
Co(II)	Cyclohexanone/TEA	HCl	HCl	Bukhari et al. 2004 [56]
Co(II) Li (I)	Kerosene/ Cyanex 272	H ₂ SO ₄	Sulfate media	Swain et al. 2007 [57]
Co(II)	Paraffin/Cyanex 272	H ₂ SO ₄	Synthetic Wastewater	León et al. 2013 [58]
Co(II) Ni(II)	Kerosene/ D2EHPA, Cyanex302,301,272	H ₂ SO ₄	H ₂ SO ₄	Gega et al. 2001 [59]
Co(II)	Commercial paraffin / Cyanex 272	H ₂ SO ₄	Synthetic Wastewater	Leon et al. 2016 [60]
Cr(III)	NPOE/Lasalocid A	HNO ₃	NaOH	Tayeb et al. 2007 [61]
Cr(III)	Cyclohexanone/TEA	H ₂ SO ₄	Na ₂ SO ₄	Chaudry et al. 2007 [62]
Cr(VI)	Chloroform/Alamine336	NaOH	H ₂ SO ₄	Eyupoglu 2011 [63]
Cr(VI)	Toluene/ CYPHOS IL 101	NaOH	HCl	Miguel et al. 2014 [64]
Cr(VI)	Dichloromethane +5%NPOE/ Calix[4]jarene	NaOH	Synthetic Wastewater	Solangi et al. 2013[65]
Cr(VI)	Xylene/ Cyanex 923	NaCl	HCl	Alguacil et al. 2000 [66]

Cr(VI)	Toluene/ TOPO	diphenyl Carbozide(DPC) + H ₂ SO ₄	H ₂ O ₂	Nawaz et al. 2016 [67]
Cs(I)	Nitrobenzene+Toluene/ DTBB18C6	HNO ₃	HNO ₃	Mohapatra et al. 2004 [68]
Cu(II)	Diphenylether/ P-morpholinomethyl Calix[4]arene	Distilled water	HCl	Minhas 2013 [3]
Cu(II)	Kerosene/2H5DBA	H ₂ SO ₄	Synthetic Wastewater	Molinari et al. 2006 [69]
Cu(II)	Chloroform / HPBI	HNO ₃	Acidic media	Mitiche et al. 2008 [70]
Cu(II)	Kerosene/LIX841	H ₂ SO ₄	Chalcopyrite Leach Liquor	Adebayo et al. 2008 [71]
Cu(II)	Coconut Oil/ D2EHPA	H ₂ SO ₄	H ₂ SO ₄	Venkateswaran 2007 [72]
Cu(II)	Iberfluid/ MOC-55 TD	H ₂ SO ₄	Synthetic Wastewater	Alguacil et al. 2001 [73]
Cu(II)	Various diluent/Acorga M5640	HNO ₃	Synthetic Wastewater	Alguacil et al. 2002 [74]
Cu(II)	- /Aliquat 336 , TBP	Distilled water	KCN , CH ₃ COONH ₄	Medjahed et al. 2014 [75]
Cu(II)	Dihexylether/ DbzDA18C6+Oleic acid	Na ₂ S ₂ O ₃	HNO ₃	Romero et al. 2005 [76]
Cu(II)	Nonane /4-ethyl-1-Phenyl-1, 3- octadione	H ₂ SO ₄	(NH ₄) ₂ SO ₄	Peng et al. 2015 [77]
Cu(II) Zn(II)	Kerosene/TOPO-99+ TBP	H ₂ SO ₄	Synthetic Wastewater	swain et al. 2004 [78]
Eu(III)	Kerosene/D ₂ EHPA, Cyanex272	H ₂ SO ₄	HNO ₃	Zaheri et al. 2015 [79]
Eu(III)	Kerosene/ D2EHPA	HNO ₃	Synthetic Wastewater	Pei et al. 2011 [80]
Fe(II) Fe(III)	Kerosene/TOA	HClO ₄	HCl	Mahmoud 2012 [81]
Fe(III)	Xylene/3-phenyl-4-acyl -5-isoxazolnes	HCl	HCl	Buonomenna et al. 2002 [82]
Fe(III) Cu(II)	Kerosene/Alamine336, LIX84	HCl	NaCl	Gill et al. 2000 [83]
Fe(III) Cu(II)	n-dodecane/ D2EHPA	H ₃ PO ₄	H ₃ PO ₄	Zhang et al. 2003 [84]
Fe(III)	n-dodecane/ D2EHPA	H ₃ PO ₄	H ₂ SO ₄	Zhang et al. 2002 [85]
Hg(II)	Coconut Oil/ TOA	NaOH	HCl	Chakrabarty et al. 2010 [86] Kumric et al. 2006 [87]
Lu(III)	Hexane/ D2EHPA	HCl	Synthetic Wastewater	
Mn(II)	Cyclohexane/TEA	H ₂ SO ₄	H ₂ SO ₄	Rehman et al. 2011 [88]
Mn(II)	Kerosene/ D2EHPA+ TOPO	HNO ₃	Biological Fluids	Soko et al. 2003 [89]
Mn(II) Co(II)	Exxsol D100/DP-8R	H ₂ SO ₄	Synthetic Wastewater	Alguacil et al. 2002 [2]
Mo(VI)	Kerosene/ Alamine336	Na ₂ CO ₃	H ₂ SO ₄	Marchese et al. 2004 [90]
Mo(VI)	Kerosene/Alamine336	Na ₂ CO ₃	H ₂ SO ₄	Basualto et al. 2003 [91]
Nb(V)	- / TBP	HCl	HCl	Campderrós et al. 2000 [92]
Nd(III)	Kerosene/ D2EHPA	HNO ₃	Synthetic Wastewater	Pei et al. 2012 [93]
Nd(III)	Petrofin/ DNPPA+TOPO	H ₂ SO ₄	HCl	Anitha et al. 2013 [94]
Ni(II)	Kerosene/ D ₂ EHPA	H ₂ SO ₄	Synthetic Wastewater	Talebi et al. 2015 [95]
Ni(II)	Cyclohexanone/TEA	NaOH	HCl	Bukhari et al. 2006 [96]
Pb(II)	Kerosene, Dichloroethane/ Octylsulfanylacetic acid	HNO ₃	Synthetic Wastewater	Oberta et al. 2011 [97]
Pb(II)	Coconut Oil/ D ₂ EHPA	Na ₂ CO ₃	HCl	Bhatluri et al. 2015 [98]
Pb(II) Cd(II)	Coconut Oil/ Aliquat336	Na ₂ EDTA	Seawater	Bhatluri et al. 2014 [17]
Pb(II)	Kerosene/(benzyl amino)-26,28-dihydroxy Calix[4]arene	HCl	Synthetic Wasetwater	Kaya et al. 2013 [99]
Pb(II) Cd(II)	NPOE/Lasalocid A	HCl,HNO ₃	TEA+Tricine	Canet et al. 2002 [100]
Pd(II)	n-dodecane/DTDGA	HNO ₃	HNO ₃	Panja et al. 2014 [101]
Pd(II) Au(III)	NPOE/Thiacalix[4]arene bearing three amide	NaSCN	HCl+NaCl	Zaghbani et al. 2007 [102]
Pt(IV)	NPOE/Aliquat 336	NaClO ₄	HCl+NaCl	Fontas et al. 2005 [103]
Pt(IV) Rh(III)	Kerosene/HDEHP	HCl	HCl	Bhandare et al. 2002[104]
Pu(IV)	n-dodecane/TODGA	Oxalic acid	HNO ₃	Panja et al. 2010 [105]
Sr(II)	Chloroform/ DTBCH18C6	Distilled water	HNO ₃ +Al(NO ₃) ₃	Mohapatra et al. 2006 [106]
Sr(II)	1-Octanol/	Distilled water	Nuclear Wastewater+	Rawat et al. 2006 [107]

	DtBuCH18CG		HNO ₃ +Al(NO ₃) ₃	
Tb(III)	Kerosene/ P507	HCl	HCl	Pei et al. 2010 [108]
Th(IV)	n-dodecane/ TODGA	HNO ₃	HNO ₃	Panja et al. 2010 [109]
Tm(III)	Kerosene/PC-88A	HCl+ CH ₃ COONa	HCl	Pei 2009 [110]
U(VI)	Dichloromethane /D2EHFA+TOPO	Distilled water	HNO ₃ +KNO ₃	A.Kadous 2009 [111]
U(VI)	n-dodecane/ D ₂ EHIBA	HNO ₃	HNO ₃	Shailesh et al. 2006 [112]
U(VI)	n-dodecane/T ₂ EHDGA	HNO ₃	HNO ₃	Panja et al. 2012 [113]
U(VI)	n-Paraffin/DNPPA	H ₂ SO ₄	HNO ₃	Biswas et al. 2012 [114]
U(VI)	n-Paraffin/DNPPA	Oxalic acid	HNO ₃	Biswas et al. 2013 [115]
U(VI)	n-dodecane/TODGA	HNO ₃	HNO ₃	Panja et al. 2009 [116]
U(VI)	Toluene/ Alamin 336	Distilled water	HCl	Lakshmi et al. 2004 [117]
V(II)	Xylene/ D ₂ EHPA,TOPO	Distilled water	HNO ₃	Hor et al. 2010 [118]
V(V)	Toluene/Alamine336, Cyanex923	NH ₃	H ₂ SO ₄	Lozano et al. 2005 [119]
V(V)	TOMAC	NH ₃	H ₂ SO ₄	Nosrati et al. 2013 [120]
V(V)	Cyclohexane/ TOA	HNO ₃	HCl	Chaudry et al. 2007 [121]
Zn(II)	Kerosene/ D ₂ EHPA	H ₂ SO ₄	Na ₂ SO ₄	He et al. 2006 [122]
Zn(II)	Kerosene/ PC-88A	CH ₃ COONa	HCl	Tarditi et al. 2008 [123]
Zn(II)	Kerosene/TOPS-99	Distilled water	Acidic media+NaX	Swain et al. 2005 [124]
Zn(II)	Exxsol D100/DP-8R	H ₂ SO ₄	Synthetic Wastewater	Alguacil et al. 2005 [125]

D₂EHPA=bis(2ethylhexyl) Phosphoric acid. TOPO= triethylphosphine oxide. TOA= tri-n-octyl amine. HEHEPA=(2-ethylhexyl)phosphoric acid. DTBCH18C6=di-tert-butylcyclohexano 18 crown 6. TODGA= N,N, N'N'-tetraoctyl diglycolamide. DP8R=di(2-ethylhexyl) phosphoric acid derivation. T₂EHDGA= N,N,N',N'-tetra-2-ethylhexyl-3-pentane-diamide. DNPPA= di-n-pentylphosphoric acid. DC18C6=dicyclohexano-18-crown-6. TBP= tributyl phosphate. TEHP= tris(2-n-butoxyethyl)phosphate. N-Pr-BTP= 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine. PC88A= (2-ethylhexyl)phosphoric acid mono-2-ethylhexyl ester. JMT=long-chain primary alkylamine(t-C₁₈H₃₇NH₂ to t-C₂₂H₄₅NH₂). TOMAC=tri-n-octyl methyl ammonium chloride. DTBB18C6=di-t-butyl benzo 18 crown 6. TEA= triethanol amine. TOPS-99=di-2-ethylhexyl phosphoric acid. DtBuCH18CG=4,4'(5?)Di-t-butyl-cyclohexano-18-crown-6. 2HSDBA=2-hydroxy-5-dodecylbenzaldehyde. TT12C4=tetrathia-12-crown-4. HPBI=3-phenyl-4-benzoylisoxazol-5-one. DTDGA=N,N,N',N'-tetra-(2-ethylhexyl)dithiodiglycolamide. TDDA=tri-n-dodecylamine. DB18C6=dibenzo-18-crown-6. HDEHP=bis(2-ethylhexyl)phosphoric acid. CMPO=octylphenyl-N,N'-diisobutylcarbamoylmethylenephosphine oxide. DbzDA18C6=1,10-dibenzyl-1,10-diaza-18-crown-6. D2EHIBA=Di(2-ethylhexyl)isobutyramide. TiOAC=triisooctylammonium chloride. P507=2-ethyl hexyl phosphonic acid-mono-2-ethyl hexyl ester.DA₁₈C₆=diaza-18- crown-6. [C₄MIM]PF₆=1-butyl-3-methylimidazolium hexafluorophosphat.

Table 2

Literature review on metal ion removal using hollow fiber SLMs since 2000.

Ion	Solvent/Carrier	Stripping agent	Feed Solution	References
Ag(I)	Kerosene/ LIX84-I	Na ₂ S ₂ O ₃ · 5H ₂ O	Synthetic Wastewater	Wongsawa et al. 2014 [126]
As(V)	Toluene/ Aliquat 336,	NaOH, DI Water,		
Hg(II)	Bromo-PADAP,Cyanex923-471	HNO ₃ , H ₂ SO ₄ , CH ₄ N ₂ S	H ₂ SO ₄	Lothongkum et al. 2011 [127]
Au(I)	n-heptane/LIX79, LIX79+TOPO	NaOH	NaCN	Kumar et al. 2000 [128]
Cd(II)	Decaline/Aliquat336	HCl+NaNO ₃	NaCl Solution	Fontas et al. 2006 [129]
Cd(II)	Exxsol D100/TiOAC	NH ₄ OH	HCl	Alguacil et al. 2016 [130]
Cd(II)	[C ₄ MIM]PF ₆ / DA ₁₈ C ₆	Na ₂ S ₂ O ₃	Synthetic Wastewater	Mao et al. 2016 [131]
Ce (IV)	Toluene/D2EHFA	H ₂ SO ₄	Synthetic Wastewater	Ramakul et al. 2012 [132]
La(III)	Dodecane/TBP,CMPO	Na ₃ CA	HNO ₃ +NaNO ₃	Fu et al. 2004 [133]
Co(II)	Benzene/Alamine300	NH ₃	HCl+Thiocyanate	Leepipatpiboon et al. 2013 [134]
Ni(II)	Kerosene/Cyanex272	H ₂ SO ₄	Synthetic Wastewater	Swain et al. 2015 [135]
Co(II)	Kerosene/D ₂ EHPA	H ₂ SO ₄	HNO ₃	Vernekar et al. 2013 [23]
Li(I)	Dodecan+4%dodecanol	HNO ₃ , HSO ₄ ,NaNO ₃	Synthetic Wastewater	Guell et al. 2008 [136]
Cr(VI)	Kerosene/ Aliquat 336 , TOA	NaCl , NaOH	Industrial wastewater	Usapein et al. 2009 [137]
Cs(I)	NPOE+n-dodecane/CNC	Distilled Water	HNO ₃	Kandwal et al. 2011 [138]
Cs(I)	n-dodecane+NPOE/ Calix[4] arene- bis-naphtho Crown-6	Distilled water	HNO ₃	Kandwal et al. 2010 [139]
Cu(II)	Acetone/Aliquat336	NaOH	HCl	Eshaghi et al. 2010 [140]
Cu(II)	Kerosene/ D2EHFA	HCl	Synthetic Wastewater	Zhang et al. 2010 [141]
Cu(II)	Kerosene/ Aliquat 336 , LIX84-1	NaOH,		
Cr(III)		H ₂ SO ₄	Synthetic Wastewater	Prakorn et al. 2004 [142]

Cu(II)	Kerosene/LIX841,				
Zn(II)	TOPO-99 , Cyanex272	H ₂ SO ₄	Synthetic Wastewater	Parhi et al. 2008 [143]	
Cd(II)					
Ni(II)					
Hg(II)	Kerosene/TOA	NaOH	HCl	Uedee et al. 2008 [144]	
Hg(II)	Toluene/Aliquat336	Thiourea	HCL	Chaturabul et al. 2015 [24]	
Hg(II)	Cumene/N-benzoyl-N-N-diheptadecylthiourea	CH ₄ N ₂ S	Synthetic Wastewater	Fontas et al. 2005 [145]	
Cd(II)					
Pb(II)					
Hg(II)	Toluene/TOA	NaOH	Synthetic Wastewater	Pancharoen et al. 2010 [146]	
Nd(II)	Octane/HEHEPA	H ₂ SO ₄	HNO ₃	Wannachod et al. 2014 [147]	
Nd(III)	Octane/PC88A	H ₂ SO ₄	H ₂ SO ₄	Wannachod et al. 2014 [148]	
Ni(II)	Kerosene/ LIX 860-I + Cyanex 302	H ₂ SO ₄	H ₂ SO ₄	Voorde et al. 2004 [149]	
Ni(II)	Kerosene/ LIX860I	H ₂ SO ₄	Industrial wastewater	Lothongkum et al. 2009 [150]	
Pb(II)	Toluene/D2EHPA	HNO ₃ ,H ₂ SO ₄ , HCl	Synthetic Wastewater	Suren et al. 2014 [151]	
Pb(II)	1-phenylhexane/ Kelex 100	HCOOH	Synthetic Wastewater	Flores et al. 2010 [152]	
Pb(II)	n-heptane,kerosene/ D ₂ EHPA	HCl	Acetic acid/acetate + NaCl , Formic acid/Formate	Escobar et al. 2004 [153]	
Cd(II)					
Pd(II)	Hexane/Nonyl thiourea	NaSCN+NaCl	HCl	Uheida et al. 2004 [154]	
Pd(II)	chloroform/ Oleic acid	NaNO ₂	Thionidazine+ Oleic acid	Chaturabul et al. 2012 [155]	
Pu(IV)	n-dodecane/TBP	NH ₂ OH- HCl + HNO ₃	HNO ₃	Rathore et al. 2001 [156]	
Rh(III)	Dodecane/Aliquat336	NaHSO ₃ + NaSCN	HCl	Fontas et al. 2000 [157]	
Sr(II)	n-dodecane/TODGA	Distilled water	HNO ₃	Jagdale et al. 2013 [158]	
U(VI)	Kerosene/ Aliquat 336+ TBP	HNO ₃	Na ₃ PO ₄	Lothongkum et al. 2009 [159]	
U(VI)	Kerosene/Aliquat 336+ TBP	HNO ₃	Trisodium phosphate	Pancharoen 2011 [160]	
U(VI)	Kerosene/ TBP	NaOH	Yellow Cake +HNO ₃	Leepipatpaiboon 2014 [161]	
V(V)	Kerosene/Lix 84			Rout et al. 2014 [162]	
Y(III)	Toluene/PC-88A	HCl	Synthetic Wastewater	Gaikwad et al. 2010 [163]	
Y(III)	n-dodecane/ PC88A, D ₂ EHPA	HNO ₃	HNO ₃	Kandwal et al. 2011[164]	

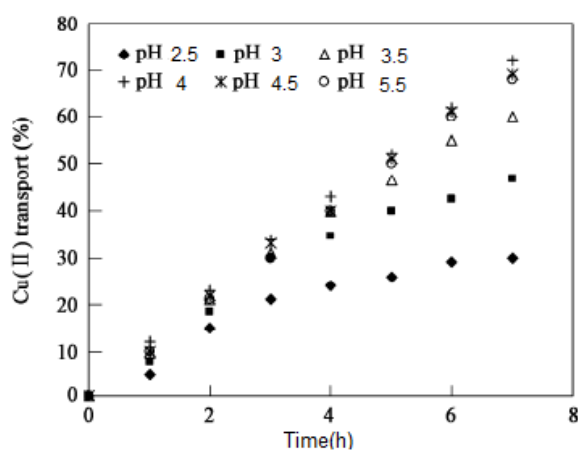


Fig. 5. The impact of feed phase pH on the quality of Copper (II) separation [72].

In 2015, Zaheri et al. [79] recovered europium metal by carbon nanotubes and the acidic carrier (Cyanex 272) in the SLM system and investigated the effect of feed pH on the quality of separation (Figure 6). In 2013, Rout et al. [162] attempted to separate the vanadium metal by HFSLM (hollow fiber supported liquid membrane) using an acidic carrier (Lix-84). They indicated that when pH increases over the optimal point, metal ion transportation is decreased due to the formation of metal hydroxide (Figure 7).

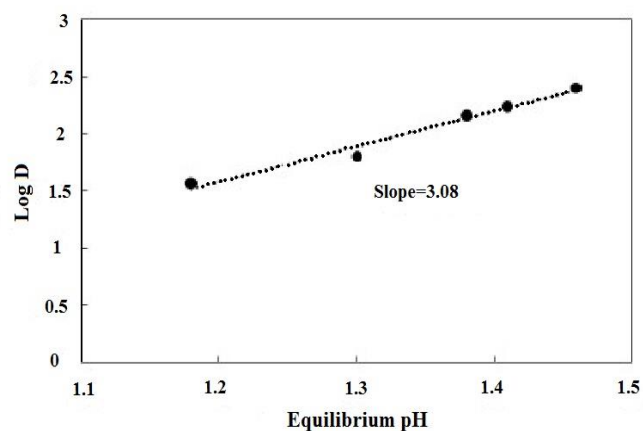


Fig. 6. Feed phase pH effects on the quality of Europium (III) separation [79].

In 2011, Güell et al. [35] recovered As (V) ion by dodecane solvent and alkaline carrier (Aliquate 336) in the SLM system. They investigated the impact of various parameters on the recovery efficiency and stated that by increasing pH to 10 the recovery is enhanced and exceeds the optimum pH results in a decrease of recovery efficiency due to the metal hydroxide formation. They justified this conclusion by indicating that since the carrier is alkaline, hence for Arsenate transfer, it must be in the form of anion (HASO_4^{2-}) in the feed phase, which occurs only at high feed phase pH. Therefore, by increasing feed phase pH, the transport rate is increased. On the other hand, if the feed phase pH becomes very high, the transport rate will be decreased due

to the hydroxide arsenic deposits formation (Figure 8).

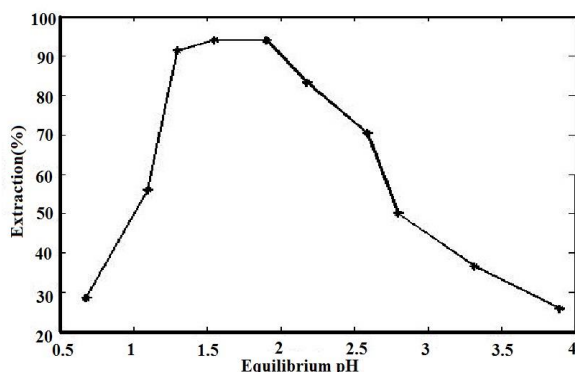


Fig. 7. The effects of feed phase pH on the quality of Vanadium (V) separation [162].

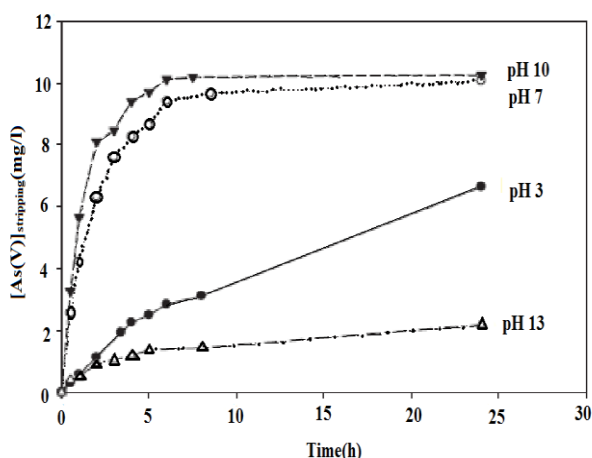


Fig. 8. The impact of the feed phase pH on the quality of As (V) separation [35].

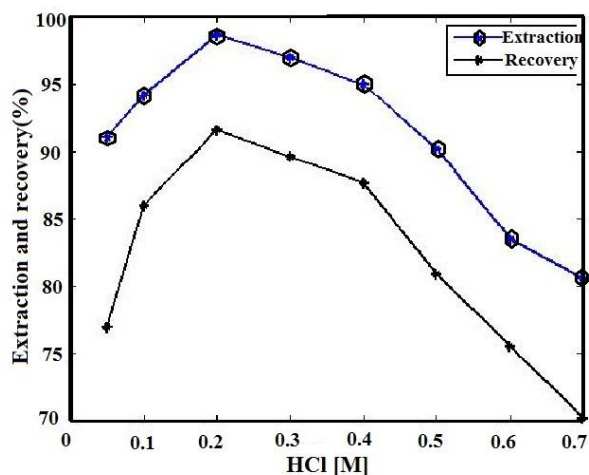


Fig. 9. Solvent (HCl) concentration effects on the quality of Mercury(II) separation [24].

In 2015, Bhatlari et al. [98] investigated cadmium and lead removal from an aqueous feed by coconut oil as the solvent and Aliquate 336 as the carrier. They increased the mass transfer flux by adding EDTA to the acceptor phase. In general, it was indicated that the impact of the feed phase pH on the separation of metal ions in SLMs depends on the type of carrier (in terms of acidity or alkalinity), and also the form of metal ion transport. If the carrier is acidic, it releases H^+ in the feed phase and therefore, by increasing the feed phase pH, the transport rate is enhanced due to the increased metal ion-carrier complex formation [122, 148]. If the carrier is alkaline, the metal ion must turn into an anion form and then cross the membrane. The anion formation

occurs only at high feed phase pH. On the other hand, if the feed phase pH exceeds an optimum value, the transport rate is decreased due to the hydroxide metal precipitation [75, 86, 121]. In some cases where neutral or alkaline carriers are used, due to the co-transport mechanism, by increasing the acid concentration in the feed, mass transfer increases. Chaturabul et al. [24] used this mechanism in the separation of mercury from water dispersed in oil. In Figure 9, the effect of pH on the extraction rate of mercury from the feed phase is indicated. Strestha Chaturabul et al. used toluene as the solvent and an alkaline carrier named Aliquate 336. They stated that due to the release of Cl^- from HCl and formation of a complex with a metal ion, mass transfer is enhanced by decreasing the pH; however, decreasing the pH below an optimum value results in lowered mass transfer.

3.8.2. Solvent

Solvent in the SLM system plays a key role in the recovery of metal ions [3]. Minhas et al. [3] investigated five characteristics of the solvent including polarization, viscosity, water solubility, volatility and surface tension. They indicated that high polarity, low viscosity, high surface tension, low volatility and low water solubility are essential specifications for an appropriate solvent to reach an appropriate stability.

3.8.3. Carrier

In the SLM systems, selecting a proper carrier is necessary for the metal ion separation. The carrier forms a complex with the component in the feed phase and carries it to the other side of the membrane. Generally, carrier selection is based on kinetics and thermodynamics knowledge. A suitable carrier and its complex should be soluble in the membrane phase and immiscible in the feed and receiving phases. In addition, any precipitation should be avoided. Most carriers used in the liquid membrane systems for metal ion recovery are macro-cyclic polymers such as crown ether, calixarene, calix-crown, etc. and macromolecule polymers such as acyclic polyethers. The extraction mechanism by carriers is based on the ion exchange mechanism or complex formation without exchanging the ion. All carriers are divided into four categories: anionic (alkaline), cationic (acidic), neutral and chelate [5]. According to the recent studies within the last decade, using macro-cycle and macromolecule polymers as the carriers results in an efficient metal ion recovery with high selectivity. Venkateswaran et al. [72] investigated the effect of carrier concentration on the mass transfer flux for the copper (II) separation. They reported that by increasing the carrier concentrations, the copper ion extraction rate is enhanced due to the elevated complex formation, but with a further increase in the carrier concentration, the mass transfer is lowered due to the increase in membrane viscosity (see Figure 10).

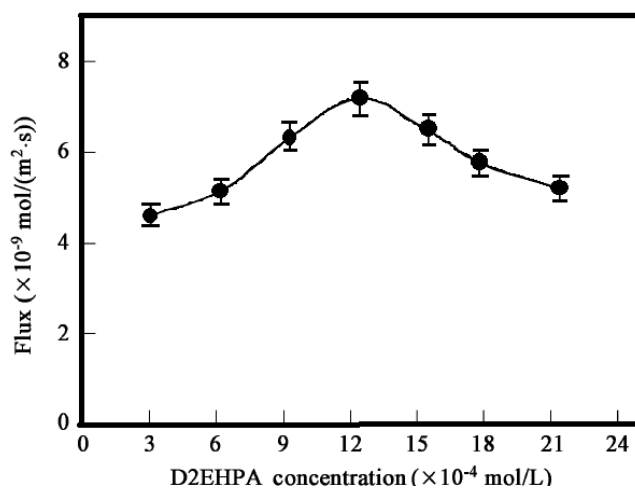


Fig. 10. The carrier (D₂EHPA) concentration effects on the quality of Copper (II) separation [72].

Rout et al. [162] reported the effect of the carrier concentration on the mass transfer flux for vanadium separation. According to Figure 11, since the applied carrier (LIX-841) did not indicate a significant impact on the membrane phase viscosity, a successive increase of the carrier concentration continually enhances the mass transfer flux.

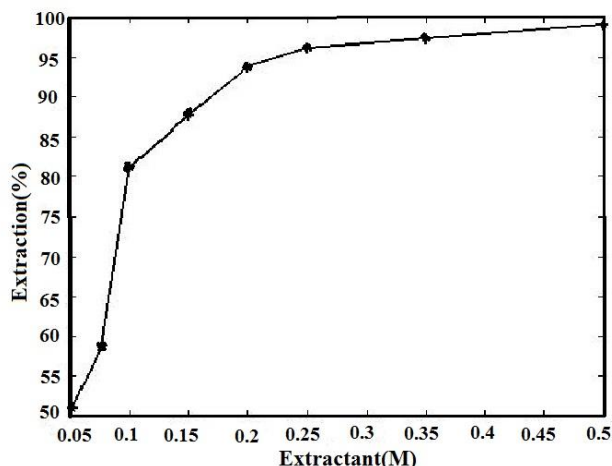


Fig. 11. The effect of carrier concentration on extraction of vanadium [162].

3.8.4. Metal ion concentration

The impact of copper (II) concentration on the feed phase has been studied by Venkateswaran et al. [72]. According to their results, at low metal ion concentrations, by increasing the copper (II) concentration, mass transfer flux increases; however, at high metal ion concentrations, the copper ions extraction percentage is not enhanced remarkably by increasing the copper (II) concentration due to the saturation of the organic phase. Swain et al. [54] presented similar results during the separation of cobalt(II) by HFSLM. The results of these two studies are indicated in Figures 12 and 13. Other studies which investigated the ion concentration effect in metal ion transport reported similar results [40, 96, 111, 152].

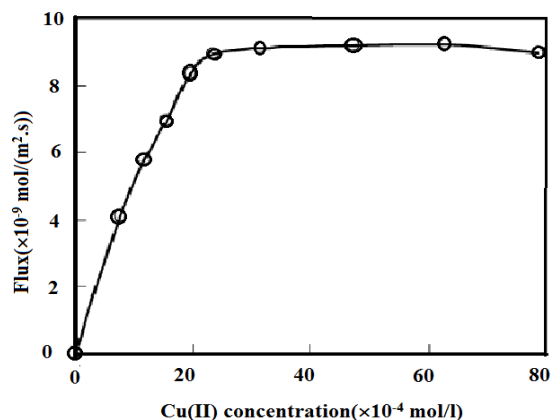


Fig. 12. The impact of copper (II) concentration in the feed on the mass transfer flux [72].

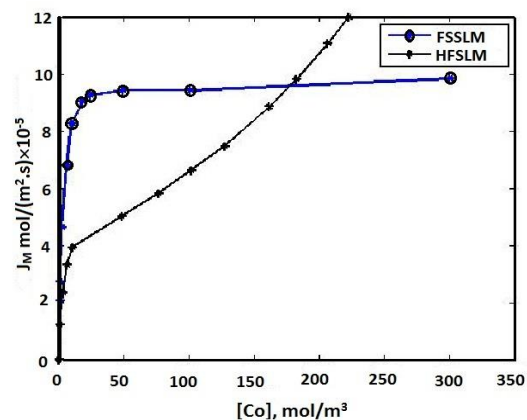


Fig. 13. The impact of cobalt (II) concentration in the feed on the mass transfer flux [54].

3.8.5. Flow rate of feed and receptor phases

Chaturabul et al. [24] investigated the effect of the feed and acceptor phases flow rates on the mass transfer flux in the hollow fibers supported liquid membrane (see Figure 14). According to studies which investigated the flow rate effect, at low flow rates, the ion extraction is enhanced by increasing the flow rate due to the increase in turbulence; however, by further increasing the flow rate, residence time and consequently the extraction percentage decreases [148, 165]. Kandwal et al. [139], Wannachod et al. [166] and Kandwal et al. [138] also obtained similar results through working on cesium and neodymium.

3.8.6. Stirring speed

From several investigations done by various researchers, it can be concluded that at low stirring speed, the influence of agitation on the removal of metal ions is directly proportional, but excessive stirring speed over an optimum value leads to the membrane phase destruction due to the presence of high turbulence at the interfaces and consequent partial separation of membrane phase and entrance to the aqueous phases in the form of emulsified droplets (see Figure 15) [27, 40, 41, 72, 88, 111, 135].

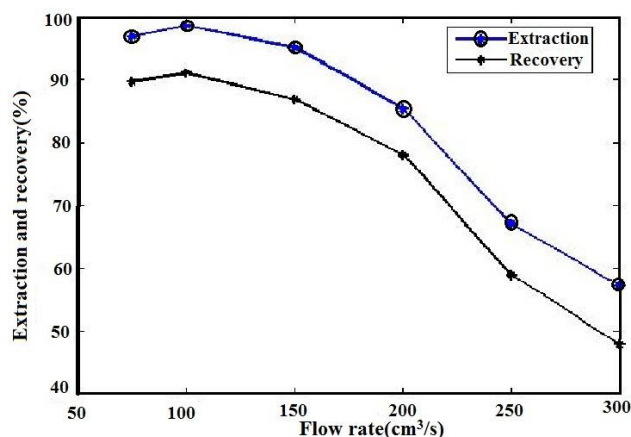


Fig. 14. Feed and receptor phases flow rate effect on the extraction percentage [24].

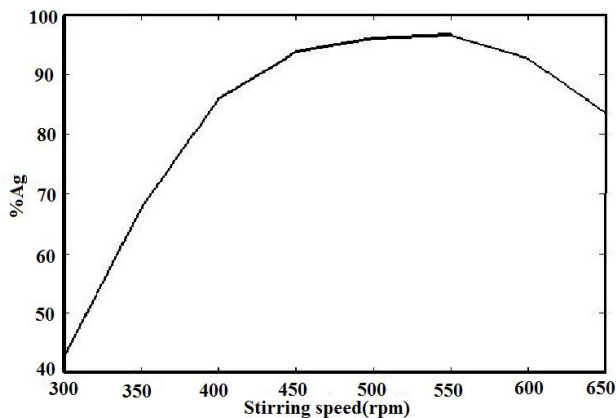


Fig. 15. Stirring speed effect on extraction percentage of silver [27].

3.8.7. Pore size

Pore size effects on the mass transfer flux were examined by Panja et al. [113] and Lakshmi et al. [117] for the uranium (IV) separation system and Zaheri et al. [79] for the separation of europium. According to their reports, by decreasing the membrane pore sizes, mass transfer flux and selectivity are enhanced (Figure 16). In another study by Nosrati et al. [120], the effect of pore size on vanadium (IV) separation was dynamically investigated (see Figure 17). They indicated that the membrane with a smaller pore size results in faster removal of vanadium ions for the first 20 hours of the separation process, but the removal efficiency of the membrane with bigger pore size surpasses that of the other membrane after 20 hours of the process due to membrane fouling. Also, Bhtacharyya et al. [31] reported that, membrane

pore size increasing, usually results in a decrease in the permeability, which was attributed to lower capillary forces and higher leachability of the carrier solvent with membranes of higher pore size.

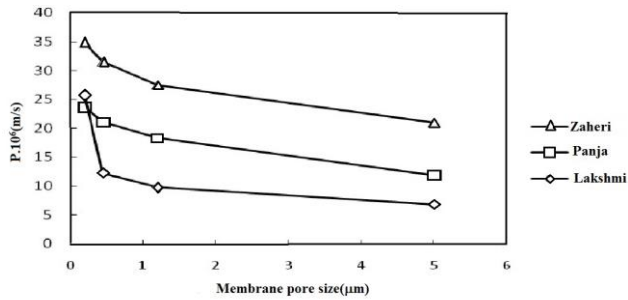


Fig. 16. The membrane pore size effect on mass transfer flux for europium (III) separation [79].

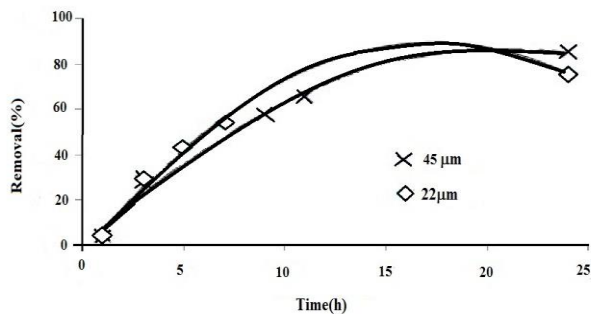


Fig. 17. The membrane pore size effect on vanadium (IV) removal percentage [120].

3.8.8. Support thickness

Panja et al. [113], Bansal et al. [165] and Kadous et al. [111] studied the influence of membrane thickness on the flux of mass transfer. They reported that the membrane thickness is inversely proportional to the mass transfer flux. Zaheri et al. [79] also investigated this issue as shown in Figure 18.

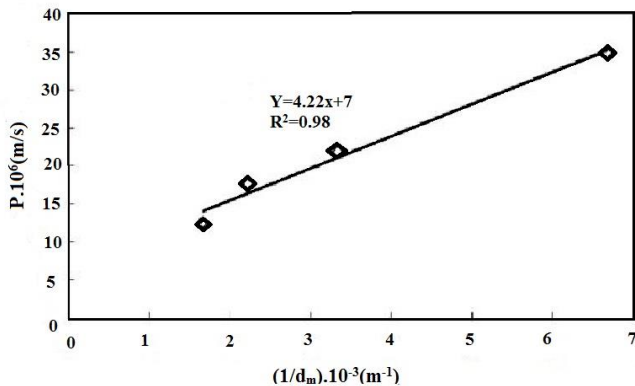


Fig. 18. The membrane thickness effect on the mass transfer flux for europium (III) separation; d_m =support thickness [79].

3.8.9. Temperature

Temperature does not play a key role in the membrane separation efficiency because the majority of membranes are used at low temperatures. However, it can be expected that an increase in the separation temperature results in higher solubility of phases which causes the formation of emulsion layers at the interfaces. This leads to the liquid membrane degradation and the consequent efficiency decrement [152, 167, 168] (see Figure 19).

3.9. Combination of mobile and fix carrier

There are two types of carriers used in the liquid membrane: mobile carrier in which the complex moves freely across the membrane and releases the specific component into the receiving phase and fixed carrier which has

limited mobility around its equilibrium and moves via the "hopping" mechanism [169-170]. It is obvious that the mobile carriers are more permeable and the fixed carriers are more stable [169-172]. Therefore, an optimal combination of these two types of carriers is of great importance to the overall membrane performance (provides high stability and specially high permeability) [171]. Since crosslinked poly(vinyl alcohol) (PVA) has a good compatibility with both mobile and fixed carriers, it can be a good choice for being used as the matrix of the active layer [170]. In addition, PVA has a strong interaction with nonvolatile mobile carriers which increase their stability [171]. Zou et al. [170], Hot et al. [173] and Huang [171] studied this method. All of them used crosslinked PVA as the matrix of the active layer. In their investigations, Poly(allylamine) and polyethylenimine were used as the fix carriers and dimethylglycine (DMG) salts, AIBA-K and KHCO_3 - K_2CO_3 were used as the mobile carriers [170, 171, 173].

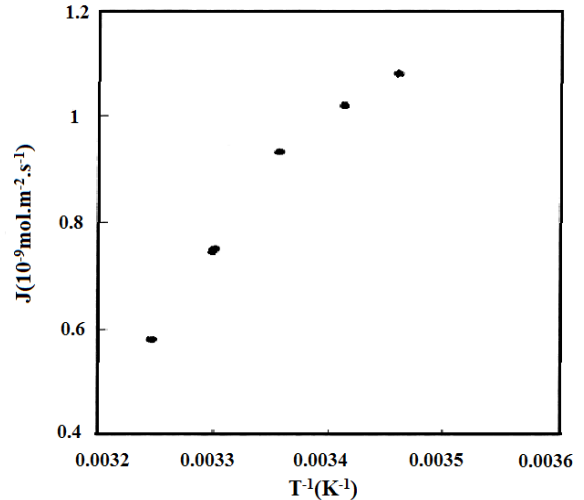


Fig. 19. The temperature effect on the mass transfer flux [168].

4. Conclusions

- Due to the advantages expressed for the liquid membrane such as efficient separation, cost-effectiveness and high selectivity, SLM is one of the most popular options for metal ion separation. In general, SLM has a great potential in the separation and recovery of metals and its efficiency is dependent on the pH of feed, metal ion concentration, carrier type, carrier concentration, pore size, stirring speed and strip solution. In addition, due to the low carrier consumption rate, using expensive carriers is economical.
- Changing the pH of the feed phase to enhance the performance of SLMs is dependent on the carrier used in the process.
- In general, increasing the carrier concentration to a specific point increases the membrane permeability increase; however, exceeding the concentration over that point decreases the permeability due to the elevated viscosity of the liquid membrane.
- In terms of the flow rate effect, increasing the feed flow rate to a certain point leads to enhanced ion extraction; however, with further increasing the flow rate, residence time and consequently the extraction percentage decreases.
- The agitation speed is directly proportional to the metal ion extraction efficiency; however, excessive stirring speed over an optimum value leads to the membrane phase destruction.
- Temperature does not play a key role in the membrane separation efficiency; however, it can be expected that an increase in the separation temperature results in higher solubility of phases which causes the formation of emulsion layers at the interfaces.
- In terms of physical characteristics of the membrane, the membrane thickness is inversely proportional to the mass transfer flux and decreasing the membrane pore size leads to enhanced mass transfer flux and selectivity.
- The effect of metal ion concentration on extraction efficiency has an optimum value below which the extraction efficiency is directly proportional to the ion metal concentration and above which the membrane is saturated and no more enhancements are achieved.
- In spite of the many advantages of SLM, the only disadvantage of SLM for separating heavy metals is their low stability due to the solvent

evaporation and their membrane phase degradation due to the loss of the solvent and/or the carrier from the support pores. To achieve an appropriate stability, the selected solvent must be attributed by high polarity, low viscosity, high surface tension, low volatility and low water solubility. In addition, the carrier must have low solubility in the aqueous feed and strip phases to avoid carrier transport into the aqueous phases. Further studies for enhancing stability should be done in the future.

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