OPPORTUNITIES AND CHALLENGES IN SUPPORTED LIQUID MEMBRANE TECHNOLOGY FOR METAL EXTRACTION: A SHORT REVIEW

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ABSTRACT

Generation of liquid effluents containing heavy metal leftovers from chemical and metallurgical industries pose threats to the environment and human health. Increasing demand for energy efficient and economical processes to eliminate and as well to retrieve metals from effluents lead to development of various chemical engineering separation and recovery processes. Supported liquid membrane (SLM) has been gaining popularity for its high separation factors and low energy requirements. This paper presents an overview of the recent SLM configurations and the key issues related to their implementations with the performance efficiency, their apparent limitations, fouling occurrence and potential challenges faced. Substantial progress and breakthroughs to promote improvement of SLM are discussed. SLM technology has been proven with promising potential over other methods, by combination of extraction, transport and re-extraction of heavy metals in one continuous system. This paper gives an outlook on future applications of SLM technology and promotes opportunities to integrate this technology for better metal extraction and recovery processes.

Keywords: Heavy metals; metal extraction; metal recovery; supported liquid membrane.

INTRODUCTION

Heavy metals are ubiquitously distributed, easily accumulated in the biosphere and penetrated into living organisms through food chain [1]. Environmental and health concerns have been raised globally as non-biodegradable heavy metals exceeding their toxicity level are released and thereby, causing the deterioration of human health and alteration of biochemical life cycle. Some heavy metals are known to be hazardous even at low concentrations like As, Ca, Cr, Pb, Ni and Hg [2]. Whereas, other heavy metals required by living organisms in low amount like Co, Cu, Fe, Mn, Zn and etc. will only lead to toxic effects at higher concentrations [3]. Innovations and modifications in treatment technologies are highly demanded to develop more reliable and environmentally sound techniques for separation and recovery of heavy metal ions.

New breakthroughs in creation of membranes made from less conventional materials have led to greater and cleaner technologies for the selective separation of heavy metal ions. Liquid membrane (LM) is a leading-edge separation system that involves selective permeation of solutes through the liquid barrier between two fluid phases [4]. Immiscible liquids are studied widely as semipermeable phase separators in the treatment of metal-bearing effluents, to urge the replacement of existing separation techniques such as solvent extraction [5], ion exchange [6], reverse osmosis [7], adsorption [8] and so forth. Along with reliable and significant results in achieving high separation factors with minimal energy demand [9], LM technology has continuously undergone numerous modifications and developments into several configurations.

There are three main design configurations of LM, namely bulk liquid membrane (BLM), emulsion liquid membrane (ELM) and supported liquid membrane (SLM). BLM consists of a layer of bulk LM that separates the feed and the strip phases, whereas in ELM, the LM forms an emulsion with the strip phase. SLM is developed in which the membrane phase containing organic solvent is impregnated in different geometries of hydrophobic microporous solid supports. Unlike BLM and ELM, SLM possesses unique properties whereby constraints such as emulsification, phase disruption and large solvent inventory could be prevented. The advantages possessed by SLMs, such as less capital and low operating cost, considerable potential for energy-saving, minimal use of expensive carriers, simple operation, and easy scale-up, favor their use in experimental studies [10]. The initial approach was reported by Scholander [11] who applied SLM for the transport of oxygen by using thin cellulose acetate filters impregnated with an aqueous hemoglobin solution. Since then, SLMs have been applied to solve an increasing number of separation problems by applying simultaneous extraction and re-extraction in one technological step.

This short review presents the SLM technology in the treatment of effluents containing heavy metals with the intention of furthering research and industrial applications. Technical challenges faced by SLM are highlighted and the scope for future work is briefly discussed. This review provides a clear outline for researchers on the recent developments in SLM technology.

SLM – PRINCIPLE AND ITS COMPONENTS

In brief, SLM system consists of a membrane phase where immobilized organic solvent is held by capillary forces in the pores of a hydrophobic microfiltration support, separating the aqueous feed phase containing the targeted species and the strip phase where the targeted species are selectively transported and recovered. When two miscible fluids are isolated by an immiscible liquid, this process encourages a mass transfer between these fluids. The driving force for the selective separation is the difference in concentration of the compounds between the phases [12]. Efficiency of membrane transport will be influenced by the partition coefficients of compounds whereby only compounds which are easily extracted from the feed phase into the membrane phase and easily re-extracted from the membrane to the strip phase, are transported within the system. Thus, the separation of different compounds in SLM is based on the same principle as liquid-liquid extraction followed by a back extraction.

Constitution of the feed and stripping phases plays an essential role in determining the degrees of extraction and the recovery of extracted substances. Effective extraction processes in SLM depends on the equilibrium pH, inert salt composition, and reagent concentrations in both feed and strip phases. The pH of feed solution is a parameter with great significance because the transport of metal is proportional to the degree of complexation [13] and thus, it influences a reaction's equilibrium constant at the liquid membrane/feed solution interface. Stripping process at the membrane-strip solution also determines the success of transfer of metal ion from the feed to strip side. Therefore, the types of stripping agents and their concentration determine the strength of the stripping process for transportation of target metal species. EDTA [14], hydrochloric acid [15], nitric acid [16], sodium hydroxide [17], sulfuric acid [18] and thiourea [19] have been used as stripping agents for extraction of various metals.

The membrane phase usually contains an extractant which acts as solute carrier, a diluent which is an inert organic solvent as viscosity adjuster and a modifier to prevent the third phase formation. Impregnation of organic solvent that contains a carrier by wetting in porous solid supports, makes considerably stable solid-liquid membranes by rejecting the aqueous phases. A carrier, also known as the complexation agent can selectively bind with compounds and separate the compounds from the aqueous feed phase through the membrane phase. As hydrated ion in aqueous solution, metal ion usually has little or no tendency to transfer into an organic phase. Thus, carrier in the organic phase allows the complexation reaction between metal ions and other coordinating species to achieve the desired extraction. Electrochemical potential difference of the component over both sides of the SLM drives back extraction to the other side of the membrane into the strip phase.

Various types of carriers have been applied in the SLM transport for heavy metal extraction processes and they are categorised into several different groups. The first group is large number of organic acids with their derivatives and related proton donors. Di(2-ethylhexyl)phosphoric acid familiarly known as D2EHPA or DP8R has been extensively applied in SLM for separation of Hg [20], Co [21], Cu [22], Ca [23] and Cr [24]. The dipolar phosphorus-oxygen bond promotes the binding of this compound to metal ions due to their high polarity. Acidic extractants able to promote stable emulsions with basic solutions and their extraction kinetics are quite rapid [25].

Second group is the chelating extractants used to extract metals by compound formation with the presence of hydroxyoximes, quinolines and β-diketones. They tend to be more selective but with slower extraction kinetics than organic acid or ion-pair extractants. Chelating extractants like Acorga M5640 [26], LIX 973N [27], and XI-55 [28] are used for the extraction of Cu and they often have excellent operating characteristics with both acid and ammonia leach solutions.

The third group is the water-immiscible primary, secondary, tertiary amines, and their derivatives, quaternary amine salts and other proton acceptors. Amines allow extraction to take place by ion-pair formation from acidic to near-neutral solutions with specific pH range. They can extract acid as free basic extractants, and then extract metal ions by anion exchange reaction. Aliquat 336 is used to extract As [29], Cr [30] and Hg [20], whereas tertiary amine like TOA extracts Fe [31] and TEA also exhibit rapid extraction and stripping kinetics in extraction of Pb [32] and Co [33].

The forth group is the solvating carriers or water-immiscible organic species with electron donor or acceptor properties. The weak basic solvating extractants can extract neutral metal complexes or acids. Most commonly used solvating extractants are phosphine oxides such as Cyanex 923 [34] and TOPO [35] and also phosphorus esters such as TBP [36, 37]. Solvating extractants can act as antagonists, synergists or phase modifiers when they are used in combination with other extractants. TBP is used as phase modifier in the extraction of Cu [38].

There is a grown interest of many researchers in metal selectivity of macrocycle carriers in SLM. Several macrocyclic compounds like crown and lariet ethers, calixarenes, calix crowns and cyclodextrins were used as ion carriers in liquid membrane for selective removal of metal ions [39]. Recently, investigations on calixarene compounds in liquid membranes to form carrier-metal complexes have increased [40]. The calixarenes tend to have distinctive organizational characteristics in forming large ligating sites to recognize assorted species of neutral ions, cations and anions. SLM containing a solution of calixarene derivative, was used for the selective recovery of chromium from nitric acidic medium [41].

The main component in SLM organic phase is the diluent. Generally, diluents must be inert toward the extraction system and they are used to prepare various concentrations of the organic phase by solubilizing the extractant and metal-extractant complexes. Diluents have significant effect on the metal extraction because they exhibit both physical and chemical interactions with the extractants for a better dispersion and coalescence performance. A good choice of diluent must have a broad range of miscibility with the extractant and it must be insoluble in the aqueous phase. They should also be chemically stable with low solvent losses caused by volatilization and degradation. Diluents should have low surface tension and viscosity to ease phase separation. By lowering the viscosity of the organic phase, it allows the diffusion of the solute complex within the liquid membrane. In most hydrometallurgical processes, petroleum-based diluents are generally used as they are readily available at a low cost. Environmental friendly green solvents such as vegetable oils [42] and ionic liquids [43] are introduced in the membrane separation to substitute petroleum-based diluents as they are toxic, flammable and non-biodegradable.

The solid support in SLM must be hydrophobic so that the organic solvent is retained in the membrane pores by capillary action. Support materials with good mechanical strength, chemical stability and thermal resistance are selected to withstand prolonged exposure to the impregnating solvents and the feed and strip phases. Stability of SLM depends on the porosity and the size, shape and curvature of the pores of the membrane support. There are a few suitable materials for the preparations of SLM supports and they are commercially available in the form of films or tubular. Polymers such as polypropylene [35], polyvinylidene difluoride [18] and polytetrafluoroethylene [4] are generally used for SLM for the removal of heavy metals.

SLM – CONFIGURATIONS

There are two commonly used designs of SLM-based membranes namely flat sheet supported liquid membrane (FSSLM) and hollow fiber supported liquid membrane (HFSLM). FSSLM is the simplest design whereby microporous solid support is used after impregnated with carrier and is clamped between two half cells using gaskets thus creating two separated compartments as shown in Figure 1. One compartment is filled with feed solution and the other compartment is meant for the strip solution. Mechanical stirrers are used to stir the solutions in both compartments. With the minimum usage of solvent, highly selective expensive carriers such as ionic liquids are used in FSSLM to minimize toxic effects, rate of pollution and instability separation processes [44]. FSSLM is identified to be good membrane at lab scale, however, scalability is expected to be the main obstacle for commercialization. Loss of membrane, diluent and/or carrier to the both aqueous phases and short lifetime are the main reasons where FSSLM based processes have not been exploited industrially due to their poor durability [45].

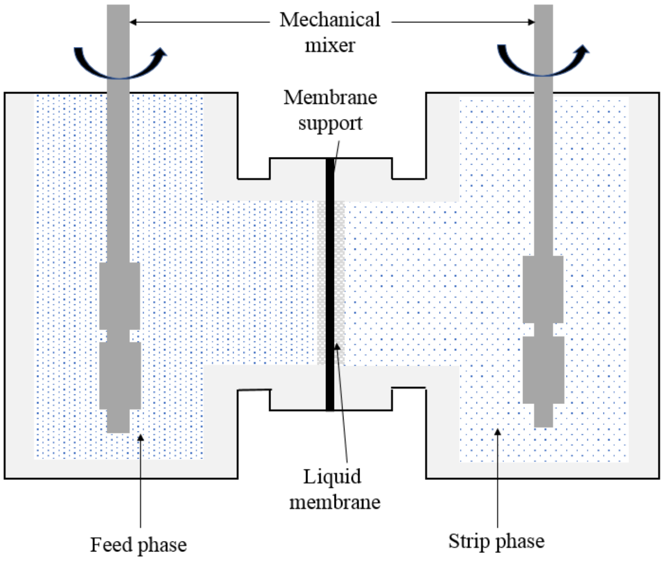

Figure 1. Schematic presentation of FSSLM

In HFSLM, a hollow fiber module shown in Figure 2(a) is used for extraction of metal ions. The outer cell of the module is a single nonporous material through which the solution present inside cannot be transported. Inside the shell, many thin fibers are packed in nice and neat rows. The feed phase passes the fibers and the strip phase through the shell side with the help of pumps as shown in Figure 2(b). The hollow fiber system provides excellent solute transportation from its large surface area and membrane thickness. Benefits of HFSLM over other separation techniques are low energy and extractant consumption, higher fluxes compared to solid membranes, ease of scaling up and suitable for operations with high pressure. HFSLM is a promising technique, notably in the areas of recovery of precious metals or removal of heavy metals from industrial activities. Several studies were conducted by Lothongkum to remove trace metal ions via HFSLM for produced waters [19, 46] and industrial wastewaters [47].

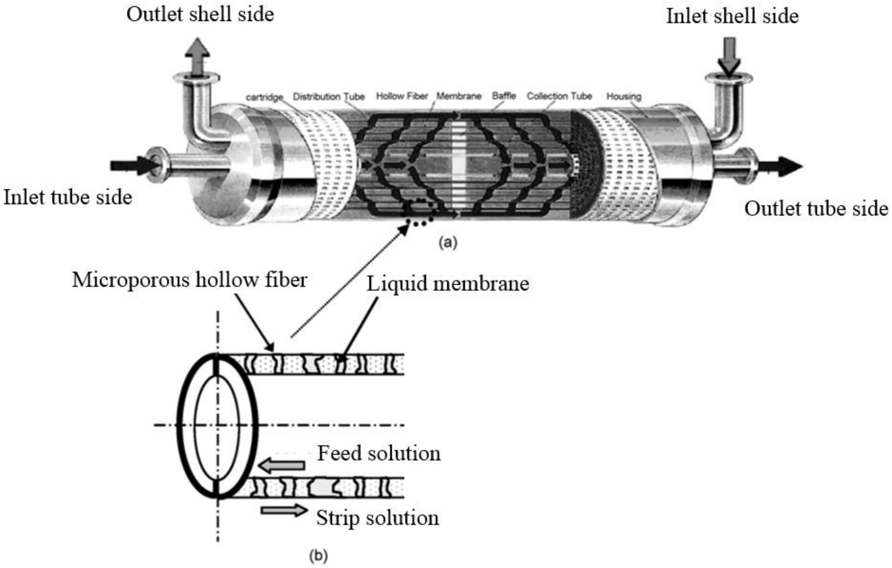

Figure 2. (a) Schematic presentation of HFSLM (b) flow pattern in HFSLM

SLM – RECENT APPLICATIONS IN HEAVY METAL EXTRACTION

The increase number of studies and knowledge in analysis, design and application of SLMs opens new prospects for SLM-based membranes in heavy metals separation and recovery for reuse as valuable byproducts. Existing SLM techniques have yet to find commercial applications whereby most applications only focus on the selective separation of one targeted metal ion in a single unit. In fact, there are numerous metal ions that could be recovered or separated simultaneously. A new strategy was developed by Duan et al. based on the SLM system for the simultaneous separation of several heavy metals from a mixed feed in using a two-membrane-three-compartment cell (sandwich SLM). Simultaneous separation of Cu, Co, and Ni from ammonia/ammonium chloride solution using a sandwich SLM was investigated, whereby the separation experiments indicated that more than 99.5% of Co, 98.0% of Ni, and 98.9% of Cu were separated into three different compartments from a mixed feed solution [48]. By extraction and stripping of different metals simultaneously, sandwich SLM will provide a wider scope in separation technology.

On the other hand, an integration of SLM with *in-situ* electrodeposition module has been invented to facilitate simultaneous separation of targeted heavy metals and expedite the recovery of precious metals. This study has proven that the process of combining electrodeposition with SLM for enhanced recovery and separation of Ca and Pb from industrial effluent is feasible by applying electric potential on the electrode, having desired pH in the feed phase for maximum extraction of metal into the membrane phase containing combination of selected carriers and solvent for the selective separation of the targeted heavy metal from mixed feed, and selecting stripping agent that enables dissociation of the stripped metal carbonate salt to yield electrodeposited pure metal [49]. With the application of electric field across SLM, transportation and deposition of heavy metals from polluted source phase will be enhanced to produce value added products.

SLM - OPPORTUNITIES AND CHALLENGES

Even though SLM technology surpasses many separation methods, there are lack of evident developments and applications at large scale. The main challenge faced during its implementation was instability of SLM. Poor stability of the membrane caused the performance to deteriorate over time, thus affecting both the flux and the selectivity. Emulsion formation in the membrane phase, loss of the carrier and/or the solvent in the membrane, continuous penetration of aqueous phase into membrane support pores, and the mutual solubility of compounds from the aqueous to the membrane phase, are the most common causes for SLM degradation [10]. Pressure differences over the membrane and membrane support pores blockage by complex precipitation of carrier at the membrane surface, lead to the destruction and replacement of a new membrane support.

To enhance the SLM stability, research on the preparation of membranes using ultrasound-assisted method was proposed. By allowing the ultrasound to pass through the extractant in the membrane, pore radius and pore density of the support will increase and therefore, increase in pore filling as a result of acoustical streaming and cavitation from the ultrasound [50] The use of ultrasound to prepare SLM for removal of Co from aqueous solutions has proven to achieve higher transport efficiency, flux, permeability and better stability after several runs of operation, as compared with soaking and vacuum preparation methods [51].

Increasing the interfacial tension between membrane and aqueous phase by adding electrolyte in the aqueous phases increases the stability of the SLM. Electrolyte such as sodium chloride is added both in the feed and stripping phases helps to improve the efficiency of SLM. One of the reasons for the instability of the SLM is the gradient of the surface tension between the feed and stripping phases and the SLM is more stable when this gradient is zero [52].

Regeneration of membrane phase was studied and a periodic reimpregnation of fresh liquid membrane into SLM managed to compensate for the loss of extractant. However, the feed and/or strip solution will be polluted with excessive emulsification of membrane liquid and also a decrease in permeation flux and selectivity [53]. To reduce the loss of membrane solutions in the support, coating SLM membrane surfaces with plasma polymerization [54]. This technique could stabilize the SLM but at the same time could minimize the pore size in the membrane surface and reduce the membrane permeability.

Dispersion SLM technology was newly developed with liquid membrane added into stripping phase to form a dispersion system to reduce the loss of carrier. PC-88A-kerosene-HCl dispersion SLM was proven to achieve stable membrane system, higher metal transmission efficiency and longer membrane lifespan for migration of Pb from Zn borne wastewater [55].

New SLM with carbon nanotubes (CNT) has received growing attention whereby oxidized CNTs could adsorb different inorganic and organic chemicals. Unique structural, chemical and physical properties of CNTs makes them attractive for transport of heavy metals [56]. Stability of SLM was proven to be satisfactory at 10 cycles of operation when multi-walled CNTs were dispersed in kerosene and Cyanex 272 and were held in the pores of membrane by ultrasonic agitation and capillary forces [57].

CONCLUSION

This short review has briefly explained the potential of SLM for high performance heavy metal separation. Even with various modifications to improve its stability, there are other hurdles for its implementation such as time, labor and reagent consuming, sensitive operation procedures and the large usage of environmentally unsafe solvents. New designs and modifications of SLM are needed to allow breakthroughs towards reusable, cost effective, pollution-free and high effectiveness in selective separation of heavy metals. Simultaneous separation for more-complex concurrence of two or more species of heavy metals by SLM technique is worth investigating for the real-time operation from the actual wastewater. Practical application of multi-stage SLM in industry may not be very close and development of truly functional membranes will probably require several years. Simple, cheaper and high-yield synthesis methods are required to prepare SLM on the large scales. These ideas will inspire researchers to conduct an extensive review on heavy metal removals by SLM separations.

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