

Review Article

Supported Liquid Membrane Principle and Its Practices: A Short Review

P. K. Parhi

*Mineral Resources Research Division, Korea Institute of Geoscience and Mineral Resources (KIGAM),
Daejeon 305-350, Republic of Korea*

Correspondence should be addressed to P. K. Parhi; parhi_pankaj@yahoo.co.in

Received 20 June 2012; Revised 7 September 2012; Accepted 2 October 2012

Academic Editor: Lorenzo Cerretani

Copyright © 2013 P. K. Parhi. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The present paper on the supported liquid membrane (SLM) deals with the general principles and applications, followed by the uphill transportation characteristic of SLM. The liquid-liquid extraction with supported liquid membrane is one of the best alternate and promising technologies for the extraction of metal ions from solutions over other hydrometallurgical separation processes. The salient features of the supported liquid membrane (SLM) technique such as simultaneous extraction and stripping, low solvent inventory, process economy, high efficiency, less extractant consumption, and operating costs are discussed in detail. The supported liquid membrane of hollow fiber type provides high interfacial surface area for achieving maximum metal flux. Also the use of different organic extractants for SLM has been discussed.

1. Introduction

In hydrometallurgical several conventional methods are being used to remove and recover heavy metals from aqueous solutions. These methods include chemical precipitation [1], reverse osmosis [2], adsorption [3], ion exchange [4], solvent extraction processes [5], and so forth. These techniques have their own inherent limitations such as less efficiency, sensitive operating conditions, production of secondary sludge, high capital, and operating costs, and further the disposal is a costly affair [6, 7]. Hence, more efficient and cost-effective removal and recovery methods are sought after to overcome these difficulties. Of all these techniques, liquid membrane (LM) has been given considerable attention by the researchers for removal and recovery of heavy metals from aqueous solutions. Some of the pronounced advantages of LM over the traditional separation methods are: low capital and operating costs, low energy and solvent consumption, high concentration factors, and high fluxes [8].

The membrane separation techniques, namely, microfiltration, ultrafiltration, reverse osmosis, electrodialysis, and so forth, are being used in the industrial scale for separation of different components from solutions [2, 5, 9–11]. In

all the membrane separation process, membrane used is basically a thin film and porous in nature, which acts as a semipermeable barrier for allowing certain component to transport and others to reject. Depending on the feed and the process the product may be permeated or may be rejected by the membrane. In recent years these membrane separation processes are paid considerable attention because of their energy efficiency. Such a typical process membrane separation process with the transport behaviour of solute and solvents in feed as well as in permeate and the membrane phase is shown in Figure 1. All the membrane separation processes are dependent on molecular size, charge, and charge density and do not have selectivity [9, 11] for some particular ion.

Supported liquid membrane process is being applied for the extraction/separation/removal of valuable metal ions from various resources. It is one of the promising technologies for possessing the attractive features such as high selectivity and combine extraction and stripping into one single stage. It is also acts on nonequilibrium mass-transfer characteristics where the separation is not limited by the conditions of equilibrium. The limitations like aqueous/organic phase ratio, emulsification, flooding and loading limits, phase

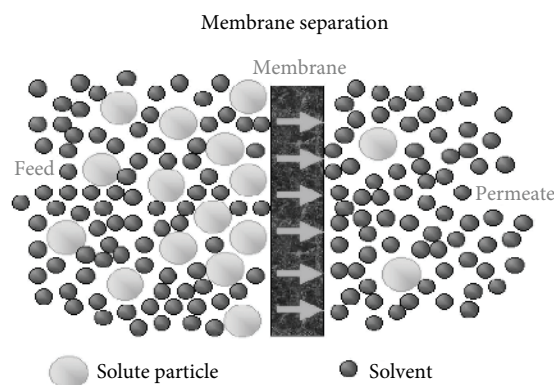


FIGURE 1: A view on transport behaviour of solute and solvent in membrane separation process.

disengagement, large solvent inventory, and so forth, can be avoided [11]. The supported liquid membranes (SLM) have applications in both industrial and analytical fields for separation, preconcentration, and treatment of waste water [8–13]. Thus SLM technology has been considered as an attractive alternative over conventional unit operations for separation and concentration of metal ions in the hydrometallurgical process [11–16].

2. Supported Liquid Membrane: In General

A liquid membrane is formed by a thin layer of organic phase (usually with dissolved reagents) between two aqueous phases of different compositions. This thin layer of organic phase can be immobilized onto a suitable inert microporous support, which when interposed in between two aqueous solutions is termed supported liquid membrane (SLM). In this three-phase extraction technique and analytes are extracted from a continuously flowing aqueous sample through an organic liquid phase into another usually temporally stagnant, aqueous phase [12–16, 19–26].

Liquid membrane (LM) is a relatively new and prospective separation system consisting of a liquid film through which selective mass transfers of gases, ions, or molecules occur via permeation and transport processes. Owing to its advantages over the solid membranes and solvent extraction [27, 28], LM has become the subject of intensive studies all over the world ever since its invention by Li and coworkers in the 1960s [29]. Different types of liquid membranes used for separation of metal ions are (i) emulsion liquid membranes (ELM), (ii) bulk liquid membrane (BLM), and (iii) supported liquid membrane (SLM). The emulsion liquid membrane and bulk liquid membranes are nonsupported liquid membrane and flat sheet liquid membrane and hollow fiber liquid membranes are supported liquid membrane. In supported liquid membrane microporous films are used as the solid support.

SLM is a nondispersive type LM, whose membrane phase is immobilized in the pores of a porous polymer. The

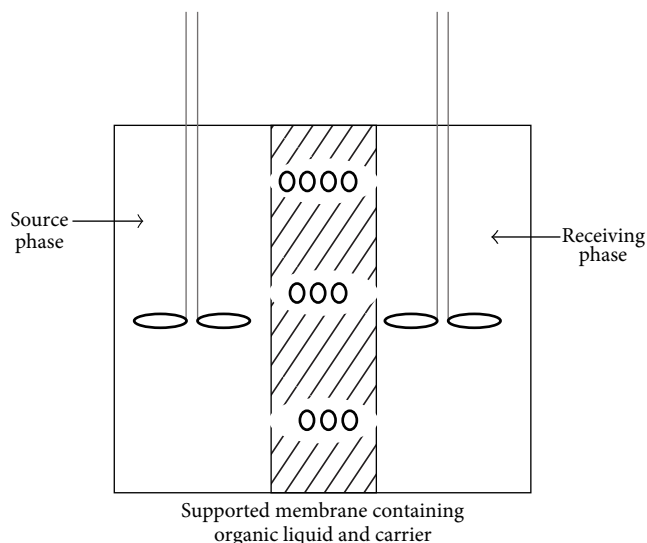


FIGURE 2: Schematic diagram of flat sheet supported liquid membrane (FSSLM) in membrane separation process.

polymeric support, which usually consists of microporous hydrophobic polymers, does not play an active role in the separation, but provides a structural support for the membrane phase (organic extractants) which is the active component in the separation [30]. These membranes can be configured either as a flat sheet or a cylindrical type (so as to avail maximum surface area) in which it does not just let the membrane liquid to rest on its surface but also allows the membrane liquid to penetrate into its pores. Based on the size, shape, surface area, and applications supported liquid membranes can be categorized into two major classes, namely, flat sheet supported liquid membrane (FSSLM) and hollow fiber supported liquid membrane (HFSLM).

2.1. Flat Sheet Supported Liquid Membrane (FSSLM). The flat sheet supported liquid membrane uses a microporous solid support for the liquid membrane and is the simplest form of the liquid membrane. The solid support is impregnated with the extractant and is clamped between two half cells using gaskets thus forming two compartments (Figure 2). One compartment is for feed solution and the other compartment for the strip solution. Both the phases are stirred by mechanical stirrers.

2.2. Hollow Fiber Supported Liquid Membrane (HFSLM). In hollow fiber supported liquid membrane, a hollow fiber module 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 (Figure 3) [17]. The source phase passes through the fibers and the receiving phase through the shell side with the help of pumps.

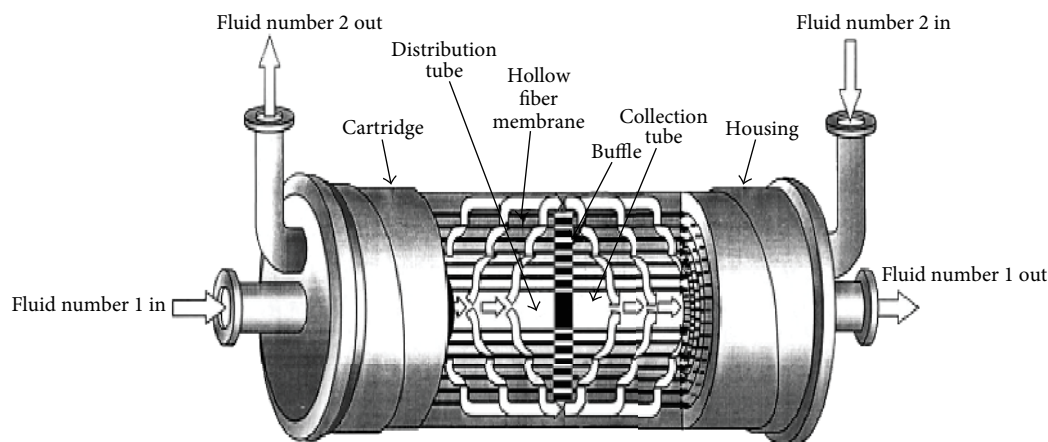


FIGURE 3: Hollow fiber supported liquid membranes (HFSLM), extra flow membrane contactor [17].

3. Components Used in Supported Liquid Membrane Separation

3.1. Supports. The solid support in LM is a polymer of hydrophobic/hydrophilic nature, which can be heterogeneous or homogeneous, symmetric or asymmetric in its structure, and may be either neutral or may carry positive or negative charges or both. It includes a variety of materials and structures depending on its use. But the SLM in particular the support material must be hydrophobic in nature so that it can retain the organic solvent in the membrane pores by capillary action. It is a prerequisite of the support material chosen that it should be thermally and chemically stable on exposure to the feed and the receiving phases and the impregnating solvents. There are a number of suitable support materials for the preparations of supported liquid membranes and those are available commercially in the form of films or tubular shapes [27].

The polymers such as PTFE, polypropylene, and polysulphones (repeat units of $\text{R-SO}_2\text{-R}'$ -, where R and R' may be mono and bisphenyl or phenoxy groups) are generally used for supported liquid membrane. The polymeric films are to provide an optimum balance between the membrane stability and solute flux lies in micro filtration range, that is, $0.1\text{--}10\text{ }\mu\text{m}$ [11]. The film materials are also available as a composite membrane where the films are laminated to a coarse material and often same polymer [31].

The membranes are made by a patented process in which an impervious PTFE film is converted to an expanded and mechanically stronger film. This film consists of a number of small nodules interconnected by a mass of very fine fibrils. The pore size of this kind membrane can be varied by careful process control.

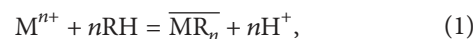
The polypropylene films are available from cleanse corporation under trade name Celgard and are manufactured by a multistage process including extrusion, annealing, and stretching of isotactic polypropylene to induce the formation of elongated pores. The specifications of Celgard-2500 and Celgard-2400 have been described recently and these films have demanding application for the recovery of heavy metals

in hydrometallurgical processes [32]. The polypropylene membranes in tubular form are also produced by thermal phase inversion process [33].

Polysulphone membranes are also prepared by phase inversion process in which polysulphone is mixed with a solvent to form a solution. The membrane is cast or spun in a case of hollow fiber and the solvent was removed by evaporation, precipitation, and annealing. The fibers obtained are asymmetric having very fine pores on inside of the fiber lumens [33, 34].

3.2. Extractants. The extractant used for supported liquid membrane is basically an organic solvent which has been chosen based on selectivity of the components present in the feed phases. This organic phase is supported by the solid support and acts as an immobilized phase. The chemistry of metal ion transfer through supported liquid membrane is same as it is for liquid-liquid extraction and most of the extractants used are familiar to the liquid-liquid extraction chemist. The extractions are classified as (i) extraction by compound formation, (ii) extraction by ion-pair formation, and (iii) extraction by solvation in terms of the mechanism of extraction involved.

Extraction by Compound Formation. The general extraction mechanism for extraction by compound formation is:

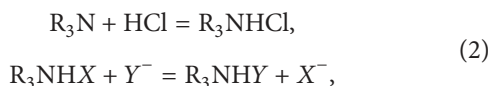


where M^{n+} is an n -valent cation, RH is a monobasic acid, and bar represents organic or membrane phase species. The most significance feature of the reaction is the degree of the extraction of the respective extractant at a particular concentration.

The extractants used for extraction by compound formation may be chelating such as LIX 84-I, LIX 64N, LIX 62N, LIX 860, and so forth, or may be acidic such as D2EHPA, PC88A, Cyanex 272 (phosphoric acid derivatives), and so forth, [14–16, 19–22]. These extractants are quite familiar in the hydrometallurgical process for the extraction/separation of various metal ions that is, Cu, Zn, Co, Ni, Fe, Mn, Mo

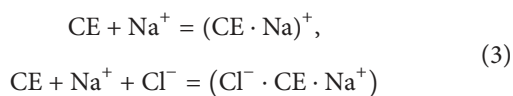
(VI), and so forth from the leach liquor (obtained from primary/secondary resources) [7, 8, 15, 16, 27].

Extraction by Ion-Pair Formation. Due to the basic property of the amine components the inorganic components in the solution can be extracted by ion-pair. The amine based extractants have two modes of action during ion pair formation reaction. Initially as a free base form they are able to extract acid from the aqueous solution, and then by anion exchange reaction these amines extract the metal ions. The extractants Alamine-336, Aliquat-336, Alamine-304, and so forth, are being used in SLM process for extraction of Mo, Cr, V, and so forth from the chloride solutions [8, 35–37]:



where R = alkyl or H.

Extraction by Solvation. The solvating extractants are weakly basic in nature and thus they extract either neutral metal complexes or acids by forming a solvate. It includes crown ethers which are cyclic polyether. These crown ethers are the best suit extractants for the extraction of the alkali or alkaline earth metal and it can be designed to show selectivity for one alkali metal over another. But these crown ethers were not applied in SLM because of their high cost and high water solubility. During extraction process the neutral crown ether reacts with the metal ion to form a charged complex. The suggested chemical reaction is presented in:



But the other extractants like TOPO, TBP, MIBK, and so forth, are being used most often for the extraction of valuable precious metal ions like Au by SLM technique [24, 25, 36].

3.3. Diluents. The diluents are generally used for preparation of various concentrations of the organic extractants used for the extraction of the metal ion. The nature of the diluents preferred is the same as it is for the solvent extraction process and so the diluents should have high dielectric constant, low viscosity, should be cheap, and so forth. However the primary requirements in the membrane formulation are to lower the solvent viscosity which leads to the diffusivity of the solute complex within the membrane. The effect of the diluents is quite significant on the extraction of metals because both physical and chemical interactions exist in between diluent and extractant. The diluents, namely, kerosene, xylene, toluene, hexane, cyclohexane, and so forth, are generally used in hydrometallurgical processes [38].

4. Different Steps Involved for Metal Extraction by SLM

In this process, the membrane is often formed by immobilizing a suitable extractant in the pores of polymeric support. The SLM thus formed is interposed between the feed and the strip phase and different steps such as extraction,

stripping, and extractant regeneration are combined to a single step [11, 39, 40]. The liquid membrane process can, therefore, be considered as an advanced variant of the traditional solvent extraction process. The SLM eliminates the equilibrium limitation inherent to solvent extraction and makes it economically feasible to use tailor-made expensive extractants.

In general the mass transfer process in the SLM process consists of seven important steps.

- (1) Diffusion of metal ions from the bulk of the feed phase to the inner surface of the membrane.
- (2) Diffusion of hydrogen ions from the inner surface of the membrane to the bulk of the feed phase.
- (3) Upon reaching the membrane feed phase interface, the metal ions are assumed to be divalent. Then, overall chemical reaction can be represented as given in (1).
- (4) Diffusion of the complex from the inner to the outer surface of the membrane phase. Again upon reaching the membrane-strip phase interface, the strip reaction takes place, regenerating the carrier and liberating the metal ions.
- (5) Diffusion of the regenerated carrier back to the inner surface of the membrane.
- (6) Diffusion of the liberated metal ions from the outer surface of the membrane to the strip bulk phase.
- (7) Diffusion of hydrogen ions from the bulk of the strip phase to the outer surface of the membrane phase.

5. Transport of Metals (II) Ions through SLM

The transport of metal from the feed phase to the strip phase by supported liquid membrane in this studied system is a coupled counter current transport. By this mechanism M^{n+} and H^+ move by diffusion in opposite direction through the membrane by the carrier RH [41]. The transportation of the lithium ion in particular from the feed phase to the strip phase where both the phases are separated by liquid membrane supported with the relevant carrier acting as the barrier is as shown in the Figure 4 [18].

At the feed solution-membrane interface, the carrier reacts with M^{n+} and releases H^+ to form MR_n complex. The complex diffuses through the membrane to the membrane-strip solution interface where it reacts with H^+ to release M^{n+} while the H^+ bind the carrier molecule. RH is then regenerated and “shuttles” back to the feed interface and the process begins again. If there is a proton gradient (such that $pH_{\text{feed}} > pH_{\text{strip}}$), then M^{n+} will diffuse across the membrane against its concentration gradient [41, 42].

The general extraction mechanism by which n -valent metal ion is extracted from an aqueous phase using phosphoric acid derivative as an extractant can be written as given in (1) and from which the extraction constant (K_{ex}) can be

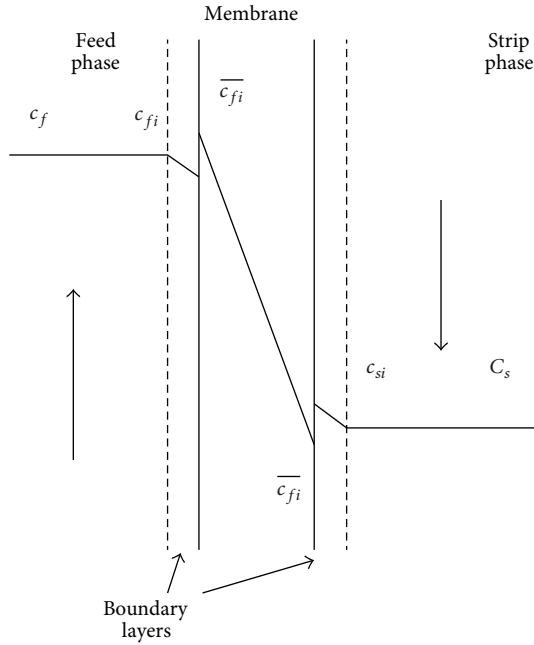


FIGURE 4: Transport mechanism of the metal ions across the supported liquid membrane (SLM) [18].

written as a function of molar concentration provided in which ionic strength of the aqueous solution is constant.

$$K_{\text{ex}} = \frac{[\text{MR}_n]_{\text{org.}} [\text{H}^+]_{\text{aq.}}^n}{[\text{M}^{n+}]_{\text{aq.}} [\text{RH}]_{\text{org.}}^n}, \quad (4)$$

where, distribution ratio, $D = [\text{MR}_n]_{\text{org.}} / [\text{M}^{n+}]_{\text{aq.}}$.
Thus,

$$K_{\text{ex}} = D \frac{[\text{H}^+]_{\text{aq.}}^n}{[\text{RH}]_{\text{org.}}^n}. \quad (5)$$

The transfer of the species is due to a proton potential gradient (the driving force of the process) existing between the two opposite sides of the supported liquid membrane. The molar fluxes J ($\text{mol/m}^2 \cdot \text{s}$) of the M^{n+} ions through the membrane from the feed side to the strip side can be determined by applying the following:

$$J = \frac{V [\partial M]}{A [\partial t]}. \quad (6)$$

The flux, J , of metal ions through the membrane, assuming that it follows Fick's first law [43], is given by

$$J = \frac{\bar{D}\epsilon (D_f [\text{M}^{n+}]_f - D_s [\text{M}^{n+}]_s)}{l}, \quad (7)$$

$$D_f = \frac{[\text{MR}_n]_{\text{org.}}}{[\text{M}^{n+}]_f}, \quad (8)$$

$$D_s = \frac{[\text{MR}_n]_{\text{org.}}}{[\text{M}^{n+}]_s}.$$

If $D_s \rightarrow 0$, that is, MR_n complex breaks on the strip side of membrane immediately after reaching there, depleting the concentration inside the membrane, then (7) becomes

$$J = \frac{D_f [\text{M}_{\text{aq}}^{n+}]_f \bar{D}\epsilon}{l}. \quad (9)$$

In this case $D_f = D$ and (9) becomes

$$J = \frac{\bar{D}\epsilon K_{\text{ext.}} [\text{RH}]^n [\text{M}^{n+}]_f}{l \cdot [\text{H}^+]^n}. \quad (10)$$

The diffusion coefficient, \bar{D} , through Chang-Wilkie equation is

$$\bar{D} = \frac{k^i T}{\eta}, \quad (11)$$

where η is the viscosity of the organic phase, T is the temperature, and k^i is a constant.

Taking into consideration the value of \bar{D} from (10), (11) becomes

$$J = k^i K_{\text{ext}} T \epsilon \frac{[\text{RH}]^n \cdot [\text{M}_{\text{aq}}^{n+}]_f}{\eta l [\text{H}^+]^n}. \quad (12)$$

For particular membrane, K^i , K_{ext} , ϵ , and l are constants, therefore,

$$J = \frac{K^i T [\text{RH}]^n [\text{M}_{\text{aq}}^{n+}]_f}{\eta l [\text{H}^+]^n}. \quad (13)$$

Taking logarithm of (13)

$$\log J = \log T + 2 \log [\text{RH}] + \log [\text{M}_n^{2+}]_f - \log \eta - n \log [\text{H}^+], \quad (14)$$

it can deduce that the flux, " J ", is directly proportional to the operating temperature (T), concentration of the carrier (RH), concentration of metal in feed solution, and inversely proportional to the viscosity of the liquid membrane (η) and acid concentration. The permeability coefficient [38] of the membrane, P , is defined as

$$P = \frac{J}{[M]}. \quad (15)$$

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

$$\alpha = \frac{P_1}{P_2} = \frac{(J_{\text{M}_1} / [\text{M}_1]_f)}{(J_{\text{M}_2} / [\text{M}_2]_f)}, \quad (16)$$

where J_{M_1} and J_{M_2} are the fluxes for the major and the minor transporting components, respectively, and $[\text{M}_1]_f$ and $[\text{M}_2]_f$ are the concentration of metal ions (initial) feed solutions.

6. Advantages and Disadvantages of Supported Liquid Membrane

Despite of the high removal efficiency of metal ions by various techniques such as chemical precipitation [44], coagulation-flocculation [45], flotation [46], membrane filtration [47–49], and biosorption [50–58], there is little emphasis on the recovery of the removed heavy metals by these techniques. Removal and recovery of heavy metals from aqueous solutions are attainable by techniques like solvent extraction (SX), ion exchange, and electrochemical treatment, but the recovery process is normally carried out in a separate unit by elution with suitable reagents [6]. SX technique appears to be one of the well-established techniques which is widely used in the industries to remove and recover heavy metals from aqueous solutions [41, 59]. Nonetheless, there has been an increasing demand on the use of SLM in place of SX in recent years owing to its unique configuration which offers several remarkable advantages which are discussed in detail.

6.1. Extraction and Stripping Processes in Single Unit. The ability of SLM to facilitate mass transfer between immiscible phases leads to the possibility of coupling what are typically distinct process steps in SX, that is, extraction and stripping processes, into a single unit [42]. This combination allows a simultaneous extraction and stripping of components from the aqueous feed into the membrane (organic liquid) phases and finally into the aqueous strip phase in single stage. The maximum driving force can be achieved with such a combination and the use of multistage and countercurrent processes, which is an inevitable trait in the classical SX, is not required [60]. By coupling the extraction and stripping processes in a single unit, LM is less complex, smaller in size, cheaper in cost, and more energy saving than the classical SX systems [61].

6.2. Uphill Transport Characteristic. In SX process the ultimate separation is limited by the conditions of equilibrium [60]. But LM which combines the extraction and stripping processes into a single stage gives rise to a nonequilibrium mass transfer, that is, uphill transport, in which the solutes can move from low to high concentration solutions and the ultimate separation is not limited by the conditions of equilibrium [62]. Venkateswaran et al. [59] reported an uphill transport characteristic exhibited by an LM system in the removal and recovery of Cu (II) and claimed that a concentration factor of more than five could easily be achieved. This finding is consistent with that obtained by Venkateswaran and Palanivelu [63] who investigated the transport of Pb (II) through a similar LM system.

6.3. High Interfacial Area per Unit Volume. SLM of hollow fiber type tends to provide a much higher interfacial area per unit volume for mass transfer than the SX columns, particularly in nondispersive SLM where the use of porous membrane support can provide up to several orders of magnitude higher interfacial area per unit volume than the classical SX systems [64]. This high interfacial area per unit

volume of SLM aids to increase its process efficiency [61], as well as to reduce the required equipment volume for a given separation, which sometimes may achieve more than five hundred times smaller than that of the classical SX systems [64].

6.4. Low Solvent Loss. As there is no entrainment of the organic solvents in the SLM the solvent loss is much less [60]. But the solvent can still be lost due to solubility of organic phase in aqueous phase [60].

6.5. Low Solvent Inventory. As the solvent used in SLM is a short-term mediator only, its extraction efficiency is of not much essential importance. The amount of solvent required for SLM is much less than conventional SX systems. In SLM, for instance, 10 cm³ of solvent is sufficient to impregnate 1 m² of a membrane of 20 μm thickness and 50% porosity [27]. The small solvent inventory, coupled with the significant lower solvent loss leads to the much lower solvent costs than SX. So expensive solvents can be used for SLM. Also more variety of insoluble inert and harmless organic liquids can be used as an intermediate liquid containing only a small amount of highly selective carriers.

6.6. No Loading and Flooding Limitations. For dispersion-free LM where separation is accomplished readily without phase dispersion, for instance the SLM; the loading of each liquid phase in such LM can be adjusted independently without any constraint while maintaining the same interfacial area per unit volume at high and low loadings [27, 60]. This property is particularly useful in applications having a required membrane to aqueous feed, or membrane to aqueous strip, phase ratio that is very high or very low [64]. Whereas the traditional SX columns are always subject to flooding at high flow rates and no loading at low flow rates [60].

6.7. Efficient in Application over Other Liquid Membrane Techniques. BLM is one of the simplest forms of LM system which is easy to manipulate while offering good membrane stability. However, the low flux of BLM is due to its small specific interface area and long transportation path of solutes encumbered its application in the actual separation systems [11, 30]. In addition, the use of large amount of organic solvents (membrane liquids) increases its capital and maintenance cost as well as poses a serious threat to the environment in case of solvent loss, particularly when the solvent used is of toxic in nature. Hence, the application of BLM is only restricted to laboratory studies such as studies of kinetics of mass transfer processes and reaction mechanisms [11]. On the other hand, ELM provides highest flux due to of its extremely high interfacial area. Also the concentration factor is very high due to the relatively small volume of strip solution used in a highly irreversible system. But unfortunately, unsolved difficulties with emulsion stability and other shortcomings such as feed and water occlusion, secondary emulsification, and necessity of controlling many parameters decreases the process selectivity. SLM, in contrast, is a

continuous process which tends to yield more predictable, reliable, and repetitive results than the single- and three-step batch processes of BLM and ELM, respectively, for which scaling up is difficult and uncertain [11].

On the other hand, supported liquid membranes also have a few drawbacks (given below).

6.8. Disadvantages of SLM

- (1) Instability of supported liquid membrane: in spite of its number of uses of SLM and its potential such as SLM high selectivity and effective separation of desired metal ion component or organic species, some disadvantages are also encountered whilst scaling up its operation in industrial scale. The major concern of the rare applications of SLM in industrial scale is attributes to the membrane instability in terms of long time performance [65], leads to the reduction of solute flux and membrane selectivity [66]. The consequence of loss of solvent from the supporting membrane, either by evaporation or dissolution/dispersion into the adjacent phases, is taking place [67]. On the other hand, organic solvents which are used as the solid support are generally volatile in nature and have some toxic effects. Thus, the volatility of the solvent increases that subsequently causes its loss and that renders the SLM more unstable. The toxicity caused by these volatile solvents is never desirable for apparent reasons. Therefore, membranes have the finite life and hence the cost of periodic membrane replacement needs to be considered while comparing the membrane process with the conventional solvent extraction processes.
- (2) The membrane introduces another resistance to mass transfer which is due to the membrane itself. However, this resistance is not always important, and steps can be taken to minimize it.
- (3) Lack of research: the membrane technology is a new technology and so far research done on it is less compared to other hydrometallurgical processes.

Looking into the several advantages and few disadvantages, SLM have attracted the attention of many interested workers from both academia and industry for a diverse range of applications. Some of the applications are discussed in the following section.

7. Potential Uses of Supported Liquid Membrane

The supported liquid membrane uses have yet to find commercial applications. Membrane transport of a variety of solutes has been examined and its potential uses in the process application has been demonstrated here. The depressed state of world economy in recent years has not encouraged the investment in new extraction technology.

7.1. Hydrometallurgical and Waste Recycling Process. The use of supported liquid membranes for the separation and concentration of metal ions has received considerable attention since last three decades due to characteristics such as easy operation, high selectivity, low operating cost, and so forth [40]. SLM is being used for recovery of metals from industrial process streams, not only because the metals are valuable, but also to meet increasingly stringent regulatory requirements. A number of literatures are available for the recovery of metal using membrane contactors reported. The use of membrane contactors for simultaneous extraction of metals such as Cu, Zn, and Ni and anions like Cr (VI), Hg, and Cd, respectively, from contaminated wastewaters is reported by authors [68].

The supported liquid membrane process has been tested on pilot scale for recovery of copper and uranium from sulphate leach liquors, for the recovery of uranium from wet phosphoric acids, and recently for the recovery of zinc from the waste liquors [16, 37]. The cost of uranium extraction has been compared on the basis of minimum plant capacities for the profitable operations. The recovery of uranium from the acidic sulphate leach liquor has been examined using a supported liquid membrane process. The performance of a supported liquid membrane process in long term field trials has been examined [37]. Copper has been recovered from the acidic sulphate solution on bench scale in a brief field trial [69]. However the supported liquid membrane process could prove more attractive for the small scale plant for the recovery of valuable metals from the dilute leach liquors. The SLM process can contribute for reduction of environmental pollution by metal finishing industry [4]. Application of SLM is dependent on the availability of lower cost support materials, preferably tubular form (hollow fiber liquid membranes), and the demonstration of the long effective membrane life. Hollow fiber modules are usually more expensive but they offer much higher surface area per unit of module volume up to 500 m^{-1} . Commercially available modules can be big enough and have up to 220 m^2 membrane area [17].

Selective permeation of plutonium is clearly demonstrated from real waste solutions containing other fission products such as Cs-137, Ru-106, and Eu-154 and it was possible to achieve an efficient separation of Pu in presence of fission products. This is advantageous in HFSLM system to treat real waste streams for recovery of Pu (IV) from the acidic wastes [70]. Octyl (phenyl)-N,N-diisobutylcarbamoylmethyl-phosphine oxide (CMPO) mixed with TBP supported on an inert matrix is capable of sorbing all alpha-emitting nuclides and fission products in their hexa-tetra- and trivalent states leaving behind a waste containing mainly the β -emitters ^{90}Sr and ^{137}Cs with trace amounts of ^{106}Ru and ^{125}Sb [71]. A generator system has been developed by using the extractant 2-ethylhexyl-2-ethylhexyl phosphonic acid (KSM-17 equivalent to PC 88A) supported on a polytetrafluoro ethylene (PTFE) membrane; a generator system has been developed for the preparation of carrier-free ^{90}Y from ^{90}Sr present in the high level waste (HLW) of the Purex process [72].

7.2. Waste Water Treatment. The supported liquid membrane has been used for removal of phenols and ammonia from waste waters and extensive experimental investigations [73] have been done. Removal of these contaminants from waste waters is dictated by environmental constraints and there is an incentive to reduce the cost of water treatment which is usually carried out biologically although resin adsorption can be used for the removal of phenol [59]. Separation and recovery of copper [35, 74], zinc [15, 16], nickel [20, 21], precious metals [75, 76], rare earth metals [36, 77, 78], alkali metals [18], and so forth, from aqueous solutions using SLM have been extensively studied.

8. Concluding Remarks

Supported liquid membrane is a promising and potential technology leading to its numerous applications especially in hydrometallurgical separation process. Owing to its several advantages, such as (i) ease of operation, (ii) no phase contamination, (iii) low energy consumption, (iv) high selectivity, and (v) low cost operation factors, this is being considered as one of the suitable alternate processes to the existing conventional separation process in recent days. In addition, supported liquid membrane (SLM) has edge over other membrane processes with respect to its high selectivity and low energy utilization and has been a subject of a number of recent investigations for separation of metal ions from industrial liquors/waste waters/effluents, and so forth, using a variety of extractants. A clean separation of metal ions from the aqueous solution bearing more than one component can be obtained by SLM method. There is a wide scope for supported liquid membrane in separation science and technology; however, due to lack of attention of researchers, its uses have yet to find commercial applications.

Abbreviations

A :	Area of the membrane, m^2
C_0 :	Initial concentration of the complex, mol/m^3
C_f :	Concentration of the metal ion in feed, mol/m^3
C_s :	Concentration of the metal ion in strip, mol/m^3
D :	Distribution coefficient
D_f :	Distribution of metal in feed-membrane interphase.
D_s :	Distribution of metal in strip-membrane interphase
J_M :	Flux of the metal ion, $mol/m^2 \cdot s$
$[M]$:	Concentration of the metal ion, mol/m^3
K :	Mass transfer coefficient
K_{ex} :	Equilibrium constant
P :	Permeability coefficient, m/s
t :	Time, s
V :	Volume of the solution taken, m^3
α :	Separation factor
η :	Viscosity of the organic solvent.

Subscript

Org.:	Organic phase
Aq.:	Aqueous phase
1:	Major transporting metal
2:	Minor transporting metal
f :	Feed phase
s :	Strip phase
n :	Valency of the metal ion
RH/HA:	Organic extractant.

Acknowledgment

The author wishes to thank the host institute, Korea Institute Geoscience and Mineral Resources (KIGAM), Daejeon, Republic of Korea.

References

- [1] F. Fua, L. Xiea, B. Tanga, Q. Wang, and S. Jiang, "Application of a novel strategy—advanced Fenton-chemical precipitation to the treatment of strong stability chelated heavy metal containing wastewater," *Chemical Engineering Journal*, vol. 189-190, pp. 283–287, 2012.
- [2] K. P. Lee, T. C. Arnot, and D. Mattia, "A review of reverse osmosis membrane materials for desalination—development to date and future potential," *Journal of Membrane Science*, vol. 370, no. 1-2, pp. 1–22, 2011.
- [3] S. Liang, X. Guo, and Q. Tian, "Adsorption of Pb^{2+} and Zn^{2+} from aqueous solutions by sulfured orange peel," *Desalination*, vol. 275, no. 1-3, pp. 212–216, 2011.
- [4] K. H. Park, P. K. Parhi, and N. H. Kang, "Studies on removal of low content copper from the sea nodule leach liquor using the cationic resin TP 207," *Science and Technology*, vol. 47, pp. 1531–1554, 2012.
- [5] P. K. Parhi, K. H. Park, H. I. Kim, and J. T. Park, "Recovery of molybdenum from the sea nodule leach liquor by solvent extraction using Alamine 304-I," *Hydrometallurgy*, vol. 105, no. 3-4, pp. 195–200, 2011.
- [6] T. A. Kurniawan, G. Y. S. Chan, W. H. Lo, and S. Babel, "Physico-chemical treatment techniques for wastewater laden with heavy metals," *Chemical Engineering Journal*, vol. 118, no. 1-2, pp. 83–98, 2006.
- [7] S. S. Ahluwalia and D. Goyal, "Removal of heavy metals by waste tea leaves from aqueous solution," *Engineering in Life Sciences*, vol. 5, no. 2, pp. 158–162, 2005.
- [8] K. Ochromowicz and W. Apostoluk, "Modelling of carrier mediated transport of chromium(III) in the supported liquid membrane system with D2EHPA," *Separation and Purification Technology*, vol. 72, no. 1, pp. 112–117, 2010.
- [9] N. M. Kocherginsky, "Facilitated transport of alkali metal cations through supported liquid membranes with fatty acids," *ACS Symposium Series*, vol. 642, pp. 75–88, 1996.
- [10] J. Melling and D. Pearson, "Separation Processing service liquid membranes," pp. 6–53, 1985.
- [11] W. S. W. Ho and K. K. Sirkar, *Membrane Handbook*, Chapman & Hall, New York, NY, USA, 1992.
- [12] W. Zhang, C. Cui, and Z. Hao, "Transport study of Cu(II) through hollow fiber supported liquid membrane," *Chinese Journal of Chemical Engineering*, vol. 18, no. 1, pp. 48–54, 2010.

- [13] Z. Ren, W. Zhang, H. Meng, J. Liu, and S. Wang, "Extraction separation of Cu(II) and Co(II) from sulfuric solutions by hollow fiber renewal liquid membrane," *Journal of Membrane Science*, vol. 365, no. 1-2, pp. 260-268, 2010.
- [14] P. Kittisupakorn, W. Weerachaipichaskul, and P. Thitiyasook, "Modeling and simulation of copper-ion extraction with hollow fiber supported liquid membrane," *Journal of Industrial and Engineering Chemistry*, vol. 13, no. 6, pp. 903-910, 2007.
- [15] B. Swain, K. Sarangi, and R. P. Das, "Separation of cadmium and zinc by supported liquid membrane using TOPS-99 as mobile carrier," *Separation Science and Technology*, vol. 39, no. 9, pp. 2171-2188, 2004.
- [16] D. N. Mondal, K. Sarangi, F. Pettersson, P. K. Sen, H. Saxén, and N. Chakraborti, "Cu-Zn separation by supported liquid membrane analyzed through Multi-objective Genetic Algorithms," *Hydrometallurgy*, vol. 107, no. 3-4, pp. 112-123, 2011.
- [17] A. Gabelmana and S. T. Hwang, "Hollow fiber membrane contactors," *Journal of Membrane Science*, vol. 159, pp. 61-106, 1999.
- [18] B. Bansal, X. D. Chen, and M. M. Hossain, "Transport of lithium through a supported liquid membrane of LIX54 and TOPO in kerosene," *Chemical Engineering and Processing*, vol. 44, no. 12, pp. 1327-1336, 2005.
- [19] P. V. Vernekara, Y. D. Jagdalea, A. W. Patwardhana et al., "Transport of cobalt(II) through a hollow fiber supported liquid membrane containing di-(2-ethylhexyl) phosphoric acid (D2EHPA) as the carrier," *Chemical Engineering Research and Design*. In press.
- [20] P. K. Parhi, K. Sarangi, and S. Mohanty, "Extraction of Ni (II) by hollow fiber liquid membrane using response surface modeling methodology," *Minerals and Metallurgical Processing*, vol. 29, no. 4, 2012.
- [21] A. Surucu, V. Eyupoglu, and O. Tutkun, "Selective separation of cobalt and nickel by flat sheet supported liquid membrane using Alamine 300 as carrier," *Journal of Industrial and Engineering Chemistry*, vol. 18, pp. 629-634, 2012.
- [22] N. M. Kocherginsky, "Facilitated transport of Alkali metal cations through supported liquid membranes with fatty acids," *ACS Symposium Series*, vol. 642, Chemical Separations with Liquid Membranes, pp. 75-88, 1996.
- [23] R. Ruhelaa, S. Panjab, J. N. Sharma et al., "Facilitated transport of Pd (II) through a supported liquid membrane (SLM) containing *N,N,N',N'*-tetra-(2-ethylhexyl) thiodiglycolamide T(2EH)TDGA: a novel carrier," *Journal of Hazardous Materials*, vol. 229-230, pp. 66-71, 2012.
- [24] A. M. Sastre, A. Madi, and F. J. Alguacil, "Solvent extraction of $\text{Au}(\text{CN})_2^-$ and application to facilitated supported liquid membrane transport," *Hydrometallurgy*, vol. 54, no. 2, pp. 171-184, 2000.
- [25] F. Z. El Aamrani, A. Kumar, L. Beyer, A. Florido, and A. M. Sastre, "Mechanistic study of active transport of silver(I) using sulfur containing novel carriers across a liquid membrane," *Journal of Membrane Science*, vol. 152, no. 2, pp. 263-275, 1999.
- [26] S. K. Singh, S. K. Misra, S. C. Tripathi, and D. K. Singh, "Studies on permeation of uranium (VI) from phosphoric acid medium through supported liquid membrane comprising a binary mixture of PC88A and Cyanex 923 in n-dodecane as carrier," *Desalination*, vol. 250, no. 1, pp. 19-25, 2010.
- [27] L. Boyadzhiev and Z. Lazarova, "Liquid membranes (liquid pertraction)," in *Membrane Separations Technology—Principles and Applications*, R. D. Noble and S. A. Stern, Eds., pp. 283-326, Elsevier Science B. V. P., The Netherlands, 1995.
- [28] G. M. Ritcey and A. W. Ashbrook, *Solvent Extraction—Principles and Applications to Process Metallurgy. Part 1*, Elsevier Science Publishers B. V. P., The Netherlands, 1984.
- [29] N. N. Li, "Permeation through liquid surfactant membranes," *AIChE Journal*, vol. 17, pp. 459-463, 1969.
- [30] B. K. Dutta and, *Principles of Mass Transfer and Separation Processes*, Prentice-Hall, India, 2007.
- [31] K. Kondo, K. Kita, I. Koida, J. Irie, and F. Nakashio, "Extraction kinetics of copper with liquid surfactant membranes containing benzoylacetone," *Journal of Chemical Engineering of Japan*, vol. 12, no. 3, pp. 203-209, 1979.
- [32] T. Sarada, L. C. Sawyer, and M. I. Ostler, "Three dimensional structure of celgard microporous membranes," *Journal of Membrane Science*, vol. 15, no. 1, pp. 97-113, 1983.
- [33] W. Klein and W. Hoelz, "Cross flow microfiltration in chemical process," *The Chemical Engineer*, pp. 369-373, 1982.
- [34] E. Bringas, M. F. San Román, J. A. Irabien, and I. Ortiz, "An overview of the mathematical modelling of liquid membrane separation processes in hollow fibre contactors," *Journal of Chemical Technology and Biotechnology*, vol. 84, no. 11, pp. 1583-1614, 2009.
- [35] R. S. Juang and I. P. Huang, "Hollow-fiber membrane extraction of copper(II) from aqueous ethylenediaminetetraacetic acid solutions with Aliquat 336," *Industrial and Engineering Chemistry Research*, vol. 39, no. 5, pp. 1409-1415, 2000.
- [36] K. R. Chitra, A. G. Gaikwad, G. D. Surender, and A. D. Damodaran, "Studies on ion transport of some rare earth elements through solvating extractants immobilised on supported liquid membrane," *Journal of Membrane Science*, vol. 125, no. 2, pp. 257-268, 1997.
- [37] W. C. Babcock, R. W. Baker, E. D. Lachapelle, and K. L. Smith, "Coupled transport membranes III: the rate-limiting step in uranium transport with a tertiary amine," *Journal of Membrane Science*, vol. 7, no. 1, pp. 89-100, 1980.
- [38] P. K. Parhi and K. Sarangi, "Separation of copper, zinc, cobalt and nickel ions by supported liquid membrane technique using LIX 84I, TOPS-99 and Cyanex 272," *Separation and Purification Technology*, vol. 59, no. 2, pp. 169-174, 2008.
- [39] A. Alhuseini and A. Ajbar, "Mass transfer in supported liquid membranes: a rigorous model," *Mathematical and Computer Modelling*, vol. 32, no. 3-4, pp. 465-480, 2000.
- [40] P. K. Parhi and K. Sarangi, "Separation of metal ions from manganese nodule bulk sulphide leach liquor using hollow fiber membrane module," in *Proceedings of the 8th 2009 ISOPE Ocean Mining and Gas Hydrates Symposium (ISOPE OMS '09)*, pp. 180-185, September 2009.
- [41] M. Cox, "Liquid-liquid extraction and liquid membranes in the perspective of the twenty-first century," in *Solvent Extraction and Liquid Membranes—Fundamentals and Applications in New Materials*, M. Aguilar and J. L. Cortina, Eds., pp. 1-19, CRC Press, 2008.
- [42] Z. Ren, W. Zhang, Y. Liu, Y. Dai, and C. Cui, "New liquid membrane technology for simultaneous extraction and stripping of copper(II) from wastewater," *Chemical Engineering Science*, vol. 62, no. 22, pp. 6090-6101, 2007.
- [43] N. Bukhari, M. A. Chaudry, and M. Mazhar, "Cobalt(II) transport through triethanolamine-cyclohexanone supported liquid membranes," *Journal of Membrane Science*, vol. 234, no. 1-2, pp. 157-165, 2004.

- [44] J. Cao, G. Zhang, Z. Mao, Z. Fang, and C. Yang, "Precipitation of valuable metals from bioleaching solution by biogenic sulfides," *Minerals Engineering*, vol. 22, no. 3, pp. 289–295, 2009.
- [45] L. Charerntanyarak, "Heavy metals removal by chemical coagulation and precipitation," *Water Science and Technology*, vol. 39, no. 10–11, pp. 135–138, 1999.
- [46] J. E. B. Cayllahua and M. L. Torem, "Biosorptive flotation of nickel and aluminum ions from aqueous solution," *Desalination*, vol. 279, pp. 195–200, 2011.
- [47] F. Du, A. Hawari, M. Baune, and J. Thöming, "Dielectrophoretically intensified cross-flow membrane filtration," *Journal of Membrane Science*, vol. 336, no. 1–2, pp. 71–78, 2009.
- [48] H. A. Qdais and H. Moussa, "Removal of heavy metals from wastewater by membrane processes: a comparative study," *Desalination*, vol. 164, no. 2, pp. 105–110, 2004.
- [49] W. Liu and N. Canfield, "Development of thin porous metal sheet as micro-filtration membrane and inorganic membrane support," *Journal of Membrane Science*, vol. 409–410, p. 126, 2012.
- [50] M. R. I. Chowdhury and C. N. Mulligan, "Biosorption of arsenic from contaminated water by anaerobic biomass," *Journal of Hazardous Materials*, vol. 190, no. 1–3, pp. 486–492, 2011.
- [51] D. Sud, G. Mahajan, and M. P. Kaur, "Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions—a review," *Bioresource Technology*, vol. 99, no. 14, pp. 6017–6027, 2008.
- [52] W. S. Wan Ngah and M. A. K. M. Hanafiah, "Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review," *Bioresource Technology*, vol. 99, no. 10, pp. 3935–3948, 2008.
- [53] S. J. Kleinubing, E. Guibal, E. A. DaSilva, and M. G. C. DaSilva, "Copper and nickel competitive biosorption simulation from single and binary systems by *Sargassum filipendula*," *Chemical Engineering Journal*, vol. 184, pp. 16–22, 2012.
- [54] A. Hashem, A. Abou-Okeil, A. El-Shafie, and M. El-Sakhawy, "Grafting of high α -cellulose pulp extracted from sunflower stalks for removal of Hg (II) from aqueous solution," *Polymer*, vol. 45, no. 1, pp. 135–141, 2006.
- [55] S. Qaiser, A. R. Saleemi, and M. M. Ahmad, "Heavy metal uptake by agro based waste materials," *Electronic Journal of Biotechnology*, vol. 10, no. 3, pp. 409–416, 2007.
- [56] J. L. Hu, X. W. He, C. R. Wang, J. W. Li, and C. H. Zhang, "Cadmium adsorption characteristic of alkali modified sewage sludge," *Bioresource Technology*, vol. 121, pp. 25–30, 2012.
- [57] A. Demirbas, "Heavy metal adsorption onto agro-based waste materials: a review," *Journal of Hazardous Materials*, vol. 157, no. 2–3, pp. 220–229, 2008.
- [58] M. A. Hashem, "Adsorption of lead ions from aqueous solution by okra wastes," *International Journal of Physical Sciences*, vol. 2, pp. 178–184, 2007.
- [59] P. Venkateswaran, A. N. Gopalakrishnan, and K. Palanivelu, "Di(2-ethylhexyl)phosphoric acid-coconut oil supported liquid membrane for the separation of copper ions from copper plating wastewater," *Journal of Environmental Sciences*, vol. 19, no. 12, pp. 1446–1453, 2007.
- [60] J. S. Watson, *Separation Methods for Waste and Environmental Applications*, Marcel Dekker, New York, NY, USA, 1999.
- [61] A. K. Pabby and A. M. Sastre, "Developments in dispersion-free membrane-based extraction separation processes," in *Ion Exchange and Solvent Extraction*, Y. Marcus and A. K. Sengupta, Eds., pp. 331–372, Marcel Dekker, 2004.
- [62] W. Klein and W. Hoelz, "Cross flow microfiltration in chemical process," *The Chemical Engineer*, pp. 369–373, 1982.
- [63] P. Venkateswaran and K. Palanivelu, "Vegetable oil as greener liquid membrane," in *New Research on Hazardous Materials*, P. B. Warey, Ed., pp. 347–369, Nova Science Publishers, New York, NY, USA, 2007.
- [64] B. W. Reed, M. J. Semmens, and E. L. Cussler, "Membrane contactors," in *Membrane Separations Technology—Principles and applications*, R. D. Noble and S. A. Stern, Eds., pp. 467–483, Elsevier Science B. V. P., The Netherlands, 1995.
- [65] M. A. Malik, M. A. Hashim, and F. Nabi, "Ionic liquids in supported liquid membrane technology," *Chemical Engineering Journal*, vol. 171, no. 1, pp. 242–254, 2011.
- [66] A. J. B. Kemperman, D. Bargeman, T. Van Den Boomgaard, and H. Strathmann, "Stability of supported liquid membranes: state of the art," *Separation Science and Technology*, vol. 31, no. 20, pp. 2733–2762, 1996.
- [67] L. J. Lozano, C. Godínez, A. P. Ríos, F. J. H. Fernández, S. S. Segado, and F. J. Alguacil, "Recent advances in supported ionic liquid membrane technology," *Journal of Membrane Science*, vol. 376, pp. 1–14, 2011.
- [68] Z. F. Yang, A. K. Guha, and K. K. Sirkar, "Novel membrane-based synergistic metal extraction and recovery processes," *Industrial and Engineering Chemistry Research*, vol. 35, no. 4, pp. 1383–1394, 1996.
- [69] R. S. Juang and I. P. Huang, "Hollow-fiber membrane extraction of copper(II) from aqueous ethylenediaminetetraacetic acid solutions with Aliquat 336," *Industrial and Engineering Chemistry Research*, vol. 39, no. 5, pp. 1409–1415, 2000.
- [70] N. S. Rathore, J. V. Sonawane, A. Kumar et al., "Hollow fiber supported liquid membrane: a novel technique for separation and recovery of plutonium from aqueous acidic wastes," *Journal of Membrane Science*, vol. 189, no. 1, pp. 119–128, 2001.
- [71] J. N. Mathur, M. S. Murali, R. H. Iyer et al., "Extraction chromatographic separation of minor actinides from purex high-level wastes using CMPO," *Nuclear Technology*, vol. 109, no. 2, pp. 216–225, 1995.
- [72] A. Ramanujam, P. V. Achuthan, P. S. Dharmi et al., "Separation of carrier-free ^{90}Y from high level waste by supported liquid membrane using KSM-17," *Journal of Radioanalytical and Nuclear Chemistry*, vol. 247, no. 1, pp. 185–191, 2001.
- [73] Y. Q. Joaquim and M. S. Cabral, "Comparison between supported gas membrane process and supported liquid membrane process for the separation of NH_3 from aqueous media containing NH_3 and CO_2 ," *Journal of Chemical Technology and Biotechnology*, vol. 67, no. 4, pp. 323–328, 1999.
- [74] W. Zhang, C. Cui, Z. Ren, Y. Dai, and H. Meng, "Simultaneous removal and recovery of copper(II) from acidic wastewater by hollow fiber renewal liquid membrane with LIX984N as carrier," *Chemical Engineering Journal*, vol. 157, no. 1, pp. 230–237, 2010.
- [75] S. U. Rehman, G. Akhtar, and M. A. Chaudry, "Coupled transport of Tl^{3+} through triethanolamine-xylene-polypropylene supported liquid membranes," *Journal of Industrial and Engineering Chemistry*, vol. 18, pp. 492–498, 2012.
- [76] P. Kandwal, S. A. Ansari, and P. K. Mohapatra, "The transport of cesium using hollow fiber supported liquid membrane containing calix[4]arene-bis(2,3-naphtho)crown-6 as the carrier extractant—part II. Recovery from simulated high level waste and mass transfer modeling," *Journal of Membrane Science*, vol. 384, pp. 37–43, 2011.
- [77] L. Pei, L. Wang, and G. Yu, "Separation of Eu(III) with supported dispersion liquid membrane system containing

D2EHPA as carrier and HNO₃ solution as stripping solution,” *Journal of Rare Earths*, vol. 29, no. 1, pp. 7–14, 2011.

- [78] C. Moreno and M. Valiente, “Studies on the mechanism of transport of lanthanide ions through supported liquid membranes containing di-(2-ethylhexyl) phosphoric acid (D2EHPA) as a carrier,” *Journal of Membrane Science*, vol. 155, no. 1, pp. 155–162, 1999.

