

Liquid membrane Technology for precious metals recovery from industrial waste

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Abstract

A basic principle of the liquid membrane technology is reviewed by highlighting some interesting features of the system over other processes especially for metal separation and recovery from industrial wastes. Some of commercial liquid membrane extraction processes of precious metals are presented as examples of potential applications of the system. The advantages and drawbacks of the liquid membrane technology and the future research direction are also included.

Keywords : liquid membrane; metal recovery; industrial waste.

1. Introduction

In the near future, the exhaustion of heavy metals from industry will become a more serious problem all over the world. In order to overcome the problem towards creating favorable environment, recovering the valuable metals from industrial waste effluents offers a good alternative approach. This is important in order to save precious raw materials and to protection the environment from heavy metal contamination.

There are many methods, which have been established commercially to recover precious metals from industrial waste such as solvent extraction, precipitation, ion exchange, electrolysis, cementation, and membrane separation (Figure 1). Current technology shows that the electrochemical of metal recovery is promising technique, but it has low plate efficiency due to waste streams are often dilute in metals. As a result, solvent extraction of metals has been extensively used in hydrometallurgical process, however because of metal salts usually is not soluble in organic solvents, the process requires the introduction of an extractant that will combine with the metal ion to form an organic soluble species. However, the capital outlay for such equipment can be expensive, large volumes of organic extractants are required and the performance is often limited by hydrodynamic constraints such as flooding and entrainment. There is also the potential for cross-contamination of the aqueous stream with the organic solution and it is not suitable for dilute metal concentration of wastes in term of cost and equipments.

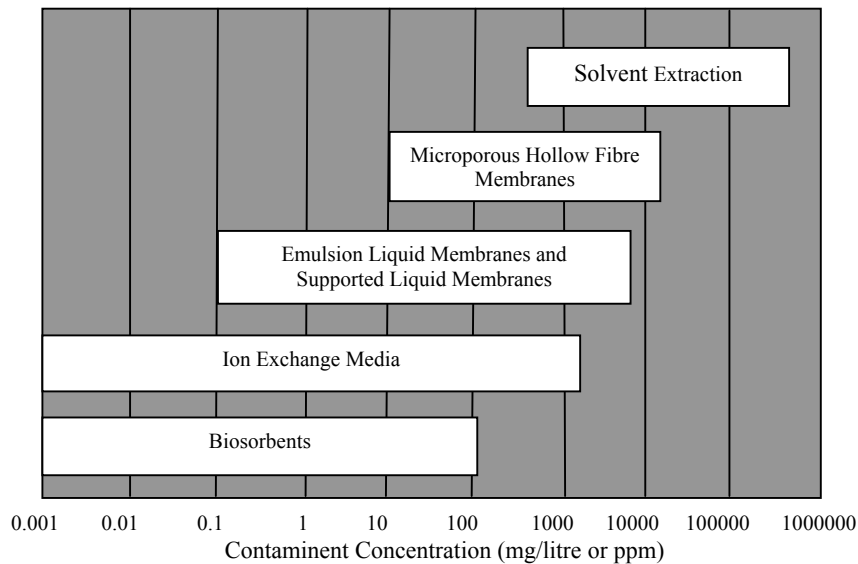


Figure 1: Solute Concentration Ranges for Separation Technologies ^[1]

One of promising techniques to overcome those problems is liquid membrane process, which provides a potentially powerful technique for metal separation and recovery. Compared to conventional membrane processes, liquid membrane extraction processes have certainly some attractive features like simple operation, high efficiency, extraction and stripping in one stage, larger interfacial area and scope of continuous operation. It could also be tailored to make so that their separation properties could be adjusted according to specific task especially in liquid membrane formulation. The technology is particularly attractive when involving very dilute solutions since the treating ratio between receiving phase and source phase can be drastically reduced. Due to these reasons, the separation of metals using liquid membrane has been subjected to extensive study by many researchers as reported in many publications ^[2,3,4,5,6].

2. Basic principles

The basic principle of the liquid membrane process lies basically on solute partitioning between three liquid phases; feed, membrane and receiving phases, which can be fashioned either as supported or emulsion (unsupported) liquid membrane (Figure 2). In supported liquid membrane, the liquid film is immobilized within the pores of porous membrane. The porous membrane serves only as framework or supporting layer for the liquid film. Such membrane can be easily be prepared by impregnating a hydrophobic porous membrane with a suitable organic solvent. On the other hand, the emulsion liquid membrane process has three phases dispersion system, which is also known as double emulsion system. This system consists of organic solution (membrane phase), stripping solution (internal phase) and dispersed phase (external phase), which is the feed or effluent to be treated.

In emulsion liquid membrane process, after the extraction step, the emulsion must be demulsified into two immiscible phases, which is accomplished by heating, application of electric field, or centrifugation. The liquid membrane phase containing the surfactant and carrier (extractant) could be recycled to the emulsion preparation step while the internal phase of the emulsion containing the concentrated solute would undergo further purification in the recovery process or treatment and disposal in the purification process.

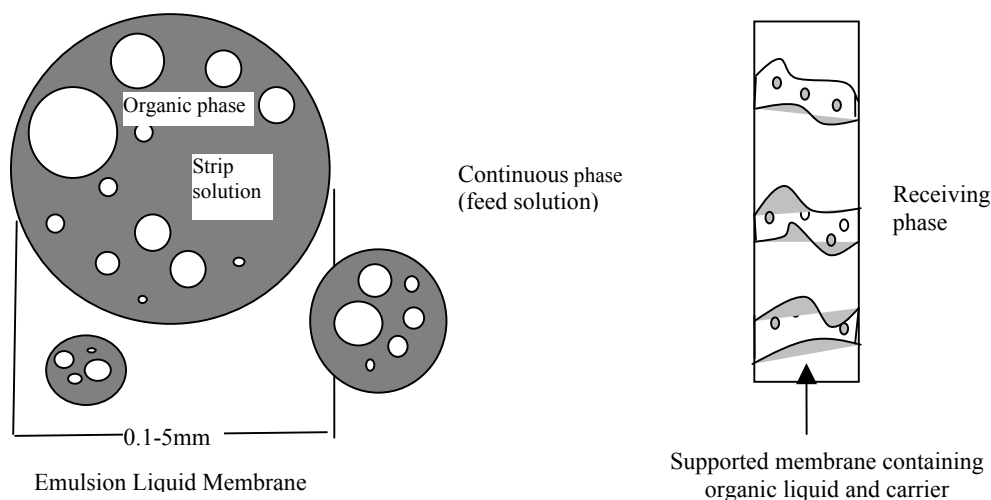


Figure 2: A Schematic Diagram of Liquid Membrane of Configurations.

3. Liquid membrane transport mechanisms

There are three types of mass transfer mechanism in liquid membrane process namely selective permeation, chemical reaction inside emulsion droplets and chemical reaction in membrane phase (Figure 3). In term of metal extraction chemistry, it is basically identical to that found in solvent extraction but the overall process is governed by kinetics rather than equilibrium parameters. However, little information concerning the liquid membrane transport of precious metals have been reported, since many transport systems have encountered different problems, for instances, slow extraction kinetics in stripping and deposition of metal species. For the recovery and enrichment process of metal ions, the third mechanism should apply, which is the carrier species may be incorporated into the organic solvent in the membrane phase and gives rise to facilitate transport ^[6,7,8,9,10,11]. According to this mechanism, the carrier molecule could selectively and reversibly react with the solute. The reversible reaction provides a means of enhancing the solute flux and improving the selectivity at the same time. This mechanism also called carrier-facilitated transport, the diffusing species are carried across the membrane phase by a carrier/extractant compound. Reaction of the diffusing species and the carrier compound takes place both at the external interface, between external and

membrane phases, and the internal interface, between the membrane and internal phases, which mean that the free carrier could diffuse back into bulk membrane phase.

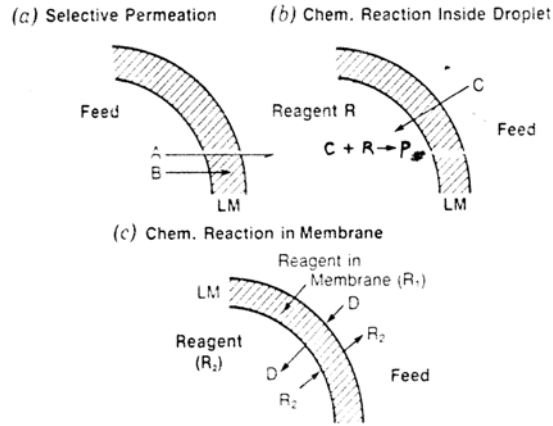


Figure 3: Transport Mechanism in Liquid Membranes ^[12]

4. Liquid membrane extraction process

In recent years liquid membrane extraction process has gained considerable interest in hydrometallurgical recovery of metal ions as well as removal of toxic metals from wastewater generated by various metallurgical industries. Some review papers on liquid membrane extraction process have appeared in the literature ^[13,14,15,16,17].

The important part in liquid membrane process is liquid membrane formulation, which includes the selection of carrier, strip agent, surfactant and diluents. The choice of those components and its formulation often decides the success of the process. The carrier must be very selective to the target metal ions in both external and internal aqueous phases while strip agent and type of surfactant must be properly chosen in minimizing the co-transport of water during extraction process. Various types of surfactants have been tested, only a few are suitable like Span 80 and ECA 4360. There are no special requirements on the choice of the diluents except it should provide high extractant solubility, high boiling point, low solubility in feed and stripping phases, non-toxic and cheap. Table 1 shows some previous studies on metal extraction using conventional solvent extraction and liquid membrane extraction processes, which clearly indicate that the variety of the system has been used for different metals and feed solutions.

Several commercial applications of emulsion liquid membrane process are currently in operation such as zinc removal from wastewater from the viscous fiber plant at Lenzing, AG, Austria, having capacity of 75m³/ hours and it can removed zinc from about 200 to 0.3 ppm with an extraction efficiency of greater than 99.5%. To date, there are three more industrial plants installed on various scales for zinc recovery, which are

700m³/hour capacity plant at Glanzstoff, AG, Austria, 200m³/ hour capacity plant at CFK Schwarza,

Table 1
Extractant Used in Metals Extraction Using Conventional Solvent Extraction (CSE), Emulsion Liquid Membrane (ELM) and Supported Liquid Membrane (SLM) Processes.

Type of Extractant	Metal Ions	Feed Solution	Method	Surfactant	Stripping Solution	Diluent	References
GROUP 1 Cyanex 272	Cu	CuSO ₄	ELM	ECA 5025 DNP-8	6 N H ₂ SO ₄	Tetradecane	[18]
	Ni	NiNO ₃	ELM	ECA 5025 DNP-8	6 N H ₂ SO ₄	Tetradecane	[18]
	Zn	ZnSO ₄	ELM	ECA 5025 DNP-8	6 N H ₂ SO ₄	Tetradecane	[18]
			SLM ^a		4.5 M HNO ₃ HCl	Kerosene	[19]
			SLM ^a		H ₂ SO ₄	Dodecane	[20]
Cyanex 302	Ag	AgNO ₃ Pure	CSE SLM ^a			Xylene/Hexane n-Dodecane	[21] [22]
	Ag	AgNO ₃ AgNO ₃	CSE CSE		HCl	Kerosene Xylene/Hexane	[23] [21]
	Cd	Pure Cd	SLM ^b			Kerosene	[24]
Cyanex 301	Ag	AgNO ₃ AgNO ₃	CSE CSE	Not mention	HCl	Kerosene Xylene, Hexane	[23] [22]
D2EHPA	Ni	NiCl ₂ NiSO ₄	ELM SLM ^a SLM ^a	Span 80 Span 80	HNO ₃ 5-6 M HNO ₃ 1.6-2.2 M	Kerosene Kerosene n-Dodecane	[25] [26] [27]
	Te	TeCl ₄	ELM		HNO ₃	Kerosene	[28]
	Sr	SrCl ₂	ELM	Span 80	HNO ₃	Kerosene	[29]
			SLM ^a	Span 80	HCl	Kerosene	[30]
	Ag	AgNO ₃	ELM	Span 80	HNO ₃	Toluene	[31]
		AgNO ₃	ELM	Not mention	H ₂ SO ₄	Kerosene	[32]
	Pb	Pb(NO ₃) ₂	ELM	ECA5025	HCl	Toluene	[31]
	An		ELM	DNP-8	H ₂ SO ₄	Kerosene	[33]
	Zn	ZnCl ₂ ZnSO ₄	ELM ELM	ECA5025 DNP-8	H ₂ SO ₄	Kerosene Tetradecane	[34] [18]
		Cu	CuSO ₄	ELM		HCl H ₂ SO ₄	Tetradecane
DEHPA	Co	CoSO ₄	SLM ^a	Not mention Span80, ECA 4360	H ₂ SO ₄ HNO ₃	Kerosene Kerosene	[26] [25]
	Cd	CdCl ₂	ELM				
	Zn	ZnSO ₄	ELM	Span 80 Flat sheet	HNO ₃	n-Dodecane	[35]
PC-88A	Cd	Pure Rare earth	ELM SLM ^a	PX 100 Span 80	H ₂ SO ₄	Paraffin oil n-Dodecane	[36] [37]
	Co	CoSO ₄	ELM	PX 100 Span 80	H ₂ SO ₄	n-Heptane	[38]
	Ni	NiSO ₄	ELM	Span 80	H ₂ SO ₄ water	n-Heptane	[38]
DEHMTPA	Zn	ZnCl ₂ Rare earth Rare earth	ELM SLM ^a SLM ^b		HNO ₃ H ₂ SO ₄	n-Heptane Kerosene n-Heptane	[39] [9] [40]
	Zn	ZnSO ₄	ELM	Span 80, ECA 4360	Thiourea	n-Dodecane	[35]

Table 1
Continued

Type of Extractant	Metal Ions	Feed Solution	Method	Surfactant	Stripping Solution	Diluent	References	
MSP-8	Pd	Simulated waste	ELM	ECA4360 Span 80	H ₂ SO ₄ H ₂ SO ₄	n-Heptane	[41]	
LIX 65N	Ag	Ag nitrate	CSE	ECA 5025 DNP-8	H ₂ SO ₄	Kerosene	[23]	
	Cu	Cu salt	ELM			n-Heptane	[3]	
LIX 984	Cu	Cu salt	ELM	ECA 5025 DNP-8	H ₂ SO ₄	Kerosene	[2]	
		CuSO ₄	ELM			Tetradecane	[18]	
LIX 860	Ni	Ni(NO ₃) ₂	SLMa ELM	ECA5025 DNP-8	H ₂ SO ₄ H ₂ SO ₄	Kerosene Tetradecane	[42] [18]	
	Zn	ZnSO ₄	ELM	ECA5025 DNP-8	H ₂ SO ₄	Tetradecane	[18]	
	Cu	CuSO ₄	ELM	ECA5025 DNP-8	H ₂ SO ₄	Tetradecane	[18]	
	Ni	Ni (NO ₃) ₂	ELM	ECA5025, DNP-8	H ₂ SO ₄	Tetradecane	[18]	
LIX 64N	Zn	ZnSO ₄	ELM	ECA5025 DNP-8	H ₂ SO ₄	Tetradecane	[18]	
	Cu	Cu salt	ELM	Span 80	H ₂ SO ₄	Kerosene	[2]	
	Zn	ZnCl ₂	ELM	Not mention	HCl	Kerosene	[25]	
LIX 63 Acorga P17 Acorga P50	Cd	CdCl ₂	ELM	Not mention	HCl	Kerosene	[25]	
	Ni	NiCl ₂	ELM	Not mention	HCl	Kerosene	[25]	
	Cu	Cu salt	ELM	Span 80	0.25-2.5MH ₂ SO ₄	Kerosene	[2]	
	Cu	Cu salt	ELM	Span 80	2.3 M H ₂ SO ₄	Kerosene	[2]	
AcorgaM5640 KELEX 100	Cu	Cu salt	ELM	Span 80	2.3 M H ₂ SO ₄	Kerosene	[2]	
	Cu	Cu salt	ELM	Span 80	2.3 M H ₂ SO ₄	Kerosene	[2]	
	Cu	Cu (NO ₃) ₂	SLM CSE	Span 80	1-2 M H ₂ SO ₄ 2 M H ₂ SO ₄	n-Octane Kerosene	[43] [44]	
SME 529 LIX 84	Cu	Cu salt	SLM ELM	Span 80	0.5-2 M H ₂ SO ₄ 2.3 M H ₂ SO ₄	n-Octane Kerosene	[45] [2]	
	Cu	Cu salt	ELM	Span 80	2.3 M H ₂ SO ₄	Kerosene	[2]	
LIX 84	Cu	Cu salt	SLM ^a	Span 80	H ₂ SO ₄ H ₂ SO ₄	Kerosene	[27]	
	Cu	Cu salt	SLM ^b				[46]	
GROUP 2 PrimeneJMT	Ag	Ag salt	ELM ^b	Not mention	H ₂ SO ₄	Tetradecane	[47]	
Tridecyl-amine	Cr	CrSO ₄	CSE				Kerosene	[48]
	Au	Gold cynide	CSE				Xylene	[49]
Amberlite	Cr	CrSO ₄	SLM ^a	NaOH	NaOH	n-Dodecane	[50]	
	Co	CoSO ₄	SLM ^a			n-Dodecane	[50]	
Alamine336	Ni	Ni salt	SLMa	Distilled water Distilled water Distilled water	Distilled water Distilled water Distilled water	Kerosene	[51]	
	Cu	Cu salt	SLMa			Kerosene	[51]	
	Cd	Cd salt	SLMa			Kerosene	[51]	
	Cr	Cr(III)&(VI)	SLM ^a			o-Xylene, Kerosene	[52]	
TOA	Hg	HgCl ₂	ELM	Span 80	NaOH	Toluene	[53]	
	Cr	Cr salt	SLM ^b			NaOH	Xylene	[54]
	Fe	Fe salt	SLM ^b			NaOH	Xylene	[55]
Adogen 364	Co	CoSO ₄	SLM ^a	Span 80	NH ₄ OH NH ₄ OH	n-Dodecane	[56]	
	Pt	Pure	SLM ^a			n-Dodecane	[56]	
	Cd	Pure Cd	SLM ^a			Kerosene	[57]	
			ELM			Dimethyl- Benzene	[58]	
Aliquat 336	V	NH ₄ VO ₃	SLM ^b	Monesan	Ammonia nitrate NaOH	Dodecane	[59]	
	Mo	Na-Mo salt	ELM			Kerosene, Heptane,	[60]	

Table 1
Continued

Type of extractant	Metal ions	Feed Solution	Method	Emulsifier	Stripping Solution	Diluent	References
Aliquat 336	Cr	Cr ion	SLM ^a	Span 80	NaOH	Xylene, Dodecane	[61]
		Cr ion	ELM			Kerosene	
Aliquat 336	Cr U	Granite ore	Cr(IV)	Span 80	NaOH	Kerosene	[11]
			Cr(IV)			SLM ^a	LiCl
GROUP 3 MIBK TBP	Cr U	AgNO ₃	SLM ^b	Span 80	NaCl	Kerosene	[62]
			SLM			Na ₂ CO ₃	Kerosene
TOPO	Pt Rare earth	Cr(IV)	ELM	Span 80	/(NH ₄) ₂ CO ₃	Kerosene	[64]
			SLM ^a				
Cyanex 923	Cr Au	Au cyanide	CSE	Span 80	HCl	n-Dodecane	[65]
			SLM ^a			HNO ₃	Kerosene
Cyanex 921 Cyanex 471X	Au Ag	Ag(NO ₃) ₂	SLM ^a	Span 80	HCl	Kerosene	[67]
			CSE			NH ₄ CO ₃	Kerosene
Crown ether H18C6	Ag Ag	AgNO ₃	SLM ^a	Span 80	HCl	Dodecane	[69]
			CSE			NaCl/HCl	Toluene
D16C4 Bis(benzothiac rownether)	Ag Ag	AgNO ₃	SLM ^a	Span 80	HCl	Kerosene	[67]
			CSE			n-Dodecane	[71]
Cyclic- tetrathioether	Ag	AgNO ₃	CSE	Span 80	HCl	Xylene	[72]
			CSE			Xylene	[44]
Calixarene Calix[4]arene	Pb Ag	Pb(NO ₃) ₂ Silver salt	CSE	Span 80	0.4 M HCl	Xylene	[73]
			CSE			HCl	Toluene
Ketonic	Rare earth Ag	Lanthanide Chloride	ELM	2C ₁₈ Δ ⁹ GE	H ₂ SO ₄	Toluene	[74]
			CSE			HCl	Benzene, Hexane
Carboxyl	Pd Rare earth	Pd(NO ₃) ₂ Lanthanide Chloride	CSE	2C ₁₈ Δ ⁹ GE	H ₂ SO ₄	Chloroform	[75]
			ELM			Na ₂ S ₂ O ₃	Chloroform
p-tert-butyl calixarenes	Na K	NaOH KOH	ELM	2C ₁₈ Δ ⁹ GE	H ₂ SO ₄	Chloroform	[77]
			ELM			H ₂ SO ₄	Chloroform
p-tert- octylcalix[n] arene (1,4,6)	Rare earth	Lanthanide Chloride	ELM	2C ₁₈ Δ ⁹ GE	H ₂ SO ₄	Chloroform	[79]
			ELM			Acid	
p-tert- octylcalix[n] arene (1,4,6)	Rare earth	Lanthanide Chloride	ELM	2C ₁₈ Δ ⁹ GE	H ₂ SO ₄	Chloroform	[81]
			ELM			Acid	
p-tert- octylcalix[n] arene (1,4,6)	Rare earth	Lanthanide Chloride	ELM	2C ₁₈ Δ ⁹ GE	H ₂ SO ₄	Chloroform	[83]
			ELM			CH ₂ Cl ₂	[82]
p-tert- octylcalix[n] arene (1,4,6)	Rare earth	Lanthanide Chloride	ELM	2C ₁₈ Δ ⁹ GE	H ₂ SO ₄	Toluene	[83]
			ELM			H ₂ SO ₄	Chloroform
p-tert- octylcalix[n] arene (1,4,6)	Rare earth	Lanthanide Chloride	ELM	2C ₁₈ Δ ⁹ GE	H ₂ SO ₄	Chloroform	[84]
			ELM			H ₂ SO ₄	Toluene
p-tert- octylcalix[n] arene (1,4,6)	Rare earth	Lanthanide Chloride	ELM	2C ₁₈ Δ ⁹ GE	H ₂ SO ₄	CH ₂ Cl ₂ +CCl ₄	[86]
			ELM			DI water	CH ₂ Cl ₂ +CCl ₄
p-tert- octylcalix[n] arene (1,4,6)	Rare earth	Lanthanide Chloride	ELM	2C ₁₈ Δ ⁹ GE	H ₂ SO ₄	Toluene	[85]
			ELM			DI water	CH ₂ Cl ₂ +CCl ₄
p-tert- octylcalix[n] arene (1,4,6)	Rare earth	Lanthanide Chloride	ELM	2C ₁₈ Δ ⁹ GE	H ₂ SO ₄	Toluene	[85]
			ELM			DI water	CH ₂ Cl ₂ +CCl ₄
p-tert- octylcalix[n] arene (1,4,6)	Rare earth	Lanthanide Chloride	ELM	2C ₁₈ Δ ⁹ GE	H ₂ SO ₄	Toluene	[85]
			ELM			DI water	CH ₂ Cl ₂ +CCl ₄

Note: a – Flat sheet
b – Hollow fiber
Group 1 Ion Compound Formation Extractant
Group 2 Ion Association Extractant
Group 3 Solvating Extractant

Germany, and 200m³/hour capacity plant at AKZO Ede, Netherlands^[86]. Figure 4 shows an example of liquid membrane extraction process flow diagram.

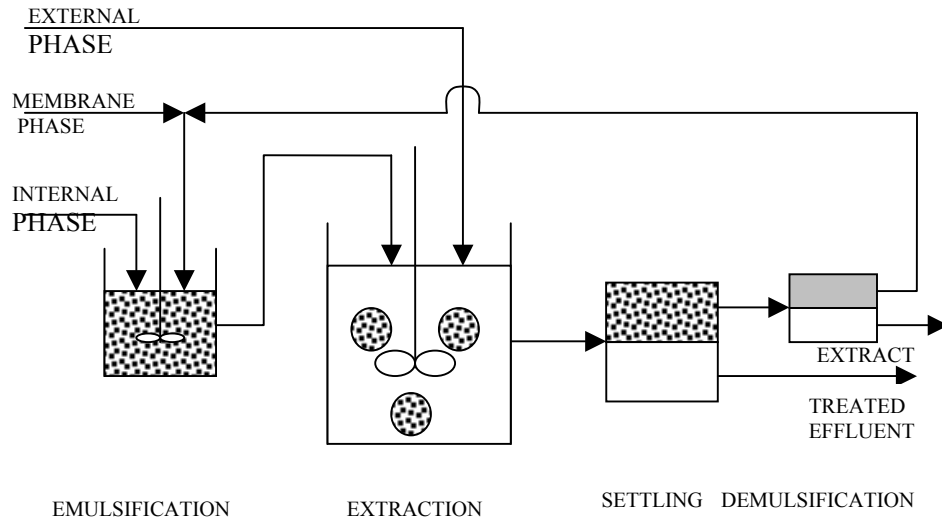


Figure 4: A Schematic Diagram of Emulsion Liquid Membrane Extraction Process

5. Future prospects

Liquid membrane separation technology has been regarded as an emerging technology and extensively examined for potential application in many fields such as metal recovery, gas separation, organic compound removal, pollutant removal and bioseparation. The difficulties in the application of this process did not consist in sophisticated equipment or installation but they consisted in the adequate choice of reagent to allow the selective extraction of solute in requested quantity. Therefore, in emulsion liquid membrane extraction process, the issues of limited their commercial potential application are emulsion stability and the membrane breakage. As a result, current research has been directed in minimizing membrane leakage or rupture through the use of bifunctional surfactants, which act as both emulsifier and extractant^[87] and added some additives to impact elasticity of membrane^[88]. On the other hand, the two primary problems associated with the use of immobilized liquid membrane are solvent and carrier loss. Solvent loss occurs because of evaporation, dissolution or large pressure differences forcing solvent out of the pore support structure while carrier loss due to irreversible side reactions or solvent condensation on one side of the membrane. To overcome the problems, ion exchange membranes and the used of hydrophilic coating layer at the side of organic phase have recently been study by many researchers.

6. Summary

The liquid membrane extraction process has more attractive due to its high selectivity and could be used for dilute metal system than conventional solvent extraction process. However, the extraction efficiency of the solutes or metals and the achievement of optimal system performance for the success of the process depends more on liquid membrane formulation especially on carrier selection to obtain high selectivity and capacity, and the capability in selecting the proper operating conditions of the whole extraction process.

Acknowledgement

The authors would like to acknowledge the financial support from the Ministry of Science, Technology and Environment, Malaysia (IRPA Grant No. 74032) and the University Technology Malaysia for the scholarship awarded to Norasikin Othman to make this study possible.

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