Removal of Heavy Metals and Organic Compound using Hollow Fiber supported Liquid Membrane: A Review

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Abstract- The generation of liquid effluents containing organic and inorganic residues from industries present a potential hazardousness for environment and human health, being mandatory the elimination of these pollutants from the respective solutions containing them. In order to achieve this goal, several techniques are being used and among them, supported liquid membranes technologies are showing their potential for their application in the removal of metals contained in liquid effluents. Supported liquid membranes are a combination between conventional polymeric membranes and solvent extraction. Chemical and metallurgical industries are the main producers of metal-bearing liquid effluents that due to the toxic character of metals. Several drawbacks of the often known as classical removal or separation technologies reduced the grade of effectiveness in the elimination of metals, principally when the aqueous solution is complex in its composition or when the metal is presented in the liquid solution at very low concentrations. Industrial processing of chemicals almost invariably leads to streams with multiple components that must then be subjected to a train of separation or purification operations to isolate the desired product. As an alternative method to wastewater pretreatment technology, supported liquid membrane (SLM) has been paid extensive attention due to its specific characteristics. As a result, SLM has been considered as a promising technology. The future of these technologies seems to be highly exciting and promising.

Keywords - Supported liquid membrane, Alternative method, Hollow fiber, Heavy metals, Organic compound.

I. INTRODUCTION

Chemical and metallurgical industries are the main producers of metal-bearing liquid effluents that due to the toxic character of many of the metals contained in them need be treated before final discharge. Thus, industries are increasingly being forced either by the administration, regulatory, cost pressures and social pressures to reduce the amount and environmental sensitivity of the liquid waste they produce. Several drawbacks of the often known as classical removal or separation technologies reduced the grade of effectiveness in the elimination of metals, principally when the aqueous solution is complex in its composition or when the metal is presented in the liquid solution at very low concentrations[1].

Industrial processing of chemicals almost invariably leads to streams with multiple components that must then be subjected to a train of separation/purification operations to isolate the desired product. Components from fermentation broths, pharmaceutical processing streams, chemical synthesis, and metal working fluids have all been successfully purified using some form of supported liquid extraction. Extraction is also a promising technology to couple to biodegradation. The successful treatment of synthetic waste streams has been demonstrated for a wide range of pollutants. The large-scale application of bacteria-based systems has met with limited success due to the nature of industrial waste streams, which may contain high salt concentrations, exhibit extreme pH conditions, or consist of a complex mixture of organic compounds. In addition, the concentration of the target pollutant may be too

dilute to serve as an effective carbon source for the biomass. As a result, separation of organic pollutants from the waste stream using extraction-based processes may facilitate effective bio-treatment [2].

As an alternative method to wastewater pretreatment technology, supported liquid membrane (SLM) has been paid extensive attention due to its specific characteristics. First, supported liquid membrane can simultaneously carry out the extraction and stripping processes in one step. Second, the process can only use chemical energy as a driving factor, instead of transmembrane pressure or voltage. Third, because of non-equilibrium mass-transfer characteristics, solute can move from low-to-high concentration of solutions. In SLM, the membrane only acts as a barrier without significant effect on selectivity, and organic extractant which aims at target compound is imbedded in small pores of membrane and is kept in these pores by capillary forces. During the SLM process, aqueous solution flows on one side (donor side) of the membrane, the target compound migrates to the other side (acceptor side), where they are collected by organic extractants. The process takes advantage of the chemical property of the organic extractant, such as polarity and hydrophobic/hydrophilic characters. The transfer of target compound from one phase to the other is driven by a deviation from thermodynamic equilibrium, and the equilibrium state depends on the interactions between the target compound and the organic extractant. So the extraction process depends on strong chemical interactions and highly specific selectivity. The success of the SLM process mainly based on the permeation rate of the target compound and this is decided depending on the nature of the organic extractant and the extraction kinetics. As a result, SLM has been considered as a promising technology. In general, SLM is classed to flat sheet supported liquid membrane (FSSLM) and hollow fiber supported liquid membrane (HFSLM).At the present time, many attentions have been paid to HFSLM due to much high surface area in a module[3].

Advantages of HFSLM technique

- Liquid membrane phase exists in micro pores of hollow fibers, which can resist great pressure;
- As a result of the carrier agents existence, it is essentially one selective promotion transmission process, thus HFSLM has very high selectivity and efficiency;
- Relatively low consumption of energy compared to other separation processes such as distillation;
- High flux when comparing with solid membrane due to the high porosity and maximum active surface area;
- Low capital and operating costs; and
- Easy scale-up etc.

Owing to these advantages, HFSLM has been used in a wide variety of applications involving extraction and/or removal of many species such as metal, phenol, chlorophenol, aroma compounds, salbutamol and terbutaline, herbicides, pesticides, and penicillin G and so on[3].

II. TECHNIQUES OF SUPPORTED LIQUID MEMBRANE

A. Non-dispersive solvent extraction (NDSX) -

In non-dispersive solvent extraction technology with single hollow fiber module (Fig. 1), the aqueous and organic phases are contacted co- or counter currently in the module for carrying out extraction or stripping runs, either in recirculation or one through modes. In the extraction module, the feed solution flows through the tube side of the fibers, whereas the organic phase circulates through the shell side, wetting the wall of the fibers. In the stripping module, the metal-loaded organic phase flows through the shell side, whereas the stripping solution flows through the tube side. Then, the metal-free organic solution is recirculated to the first or extraction module. For the correct maintaining of the interface, the pressure of the aqueous phases is typically held 0.2-0.5 bar higher than the pressure in the organic phase. In dual function modules, the extraction and stripping of the metal are carried out simultaneously in a single hollow fiber module containing one set of fibers for extraction and another set for stripping [1].



Figure 1: schematic view of an integrated NdSX membrane process using two hollow fiber contactors. (1) Feed phase reservoir tank (2) pumps, (3) flow-meters, (4) extraction module, (5) organic phase reservoir tank, (6) stripping module, (7) strip phase reservoir tank. Operation in counter-current and recirculation of the solutions.

B. Non- dispersive solvent extraction with strip phase dispersion (NDSXSD) -

The hollow fiber strip dispersion process comprises a single module for extraction and stripping (Fig. 2).A pseudo-emulsion phase is prepared in a stirred tank, this pseudo-emulsion is formed by the organic solution and the dispersed stripping solution. Once pumped to the module for the shell side, the organic phase wets the porous wall of the fiber because of its hydrophobic nature. The feed solution is fed into the module through the tube side of the fibers. The differential pressure is always kept below the breakthrough pressure, thus in the feed phase the pressure is maintained in the 0.2-0.5 bar range higher than in the pseudo-emulsion phase. The characteristics of the pseudo-emulsion should be such that it should have clear and fast (in the order of a few minutes) phase separation when mixing in the tank is stopped (Fig. 3). Then the recovery of the metal from the stripping solution can be achieved. Recently, this technology had been implemented in a flat-sheet configuration and cell operational mode for the transport of chromium (VI) from acidic solutions using the tertiary amine Hostarex A327 as carrier and NaOH solutions as strippant [1].



Figure2: Schematic view of non-dispersive solvent extraction with strip dispersion process using a hollow fiber module. (1) Feed phase reservoir tank, (2) pumps, (3) flow meters, (4) hollow fiber module, (5) pseudo-emulsion phase reservoir tank. Operation in counter-current and recirculation of the phases.

C. Hollow fiber renewal liquid membrane (HFRLM)-

In this technology, the stirred mixture of organic phase and feed phase (or stripping phase) is pumped through the tube side of the fibers, the organic phase is uniformly dispersed in the corresponding aqueous solution and wets and fills the pores of the module (Fig. 3). The stripping phase (or the feed phase) flows through the shell side, co- or counter currently. The flows are controlled to maintain a positive pressure on the shell side, in order to prevent penetration of the organic phase into the shell side [1].



Figure 3: Schematic view of HFRLM operation with organic phase between the organic and strip solutions.

II. CARRIERS IN ORGANIC PHASES AND TRANSPORT IN HFSLM

The organic phase is formed by organic diluents, which is non-miscible in water, and dissolved the carrier which is the active substance in the metal transport process. At first, it is accepted that the organic diluents does not take part or has no influence in the transport process, but this rule is sometimes far from reality and in fact the properties of the diluents can determine the results and performance, with respect to metal transport, of a given organic solution. Normally, diluents used in membrane transport are the same as those used in liquid-liquid extraction technology, which in many cases are aromatic or aliphatic petroleum fractions. Extractants in liquid-liquid extraction terminology or carriers in membrane terminology are, of course, organic compounds. During all these years, carriers are becoming increasingly selective, allowing the specific separation of some solutes from another. The carriers employed in supported liquid membranes are nearly the same as the extractants used in liquid-liquid extraction, though due to the characteristics of supported liquid membranes technology some specific or more expensive carriers can be used for metal transport in membrane operation [1].

A. Types of transport-

a) Counter-transport:-Feed solution containing the transported metals and stripping solution counter ion. They apply in opposite direction. Counter ion concentration difference is the driving force between feed and strip phase. On this transport type cationic exchanger's extractants are observed [1].

b) Co-transport:- Feed solution containing the transported metals and stripping solution co- ion. They apply in same direction. Co-ion concentration difference is the driving force between feed and strip phase [1].

B. Steps in Transport mechanism-

- i) Solute diffusion occurs to the feed phase side diffusion layer,
- ii) Feed/Membrane interface in which chemical reaction takes place between metal species and carrier,
- iii) Complex of metal-carrier diffuses between membrane and membrane/stripping interface,
- iv) Stripping reagents chemically reacts and broken down the complex metals. In the stripping phase metals are liberated and simultaneously carrier is reform.
- v) Diffusion of the stripped metals to the bulk stripping phase,
- vi) When Transport process recycles then diffusion carried out for the reform carrier through membrane to feed/membrane interfaces [1].



C. Technical Aspects related to HFSLM-

- Due to the wetting affinity of the organic phase and hydrophobic fibers. The shear force caused by the flowing fluid in the lumen side will influence the coalescence and breakage of organic droplets during the stirred mixture flowing through the lumen side. That is, the shear force will cause the film liquid to form microdroplets on the surface of the liquid membrane layer, which will peel off from the surface of the liquid membrane layer and enter into the lumen side fluid. At the same time, the organic droplets will fill the surface of the liquid film. Then the renewal of the liquid membrane is continuous proceeding. This can enhance the mass transfer rate and greatly reduce the diffusion resistance across the aqueous boundary layer within the lumen side. The thickness of the developed liquid membrane film is thin due to the effects of shear forces caused by fluid flowing in the HFRLM process. The solute can be selectively transported across the liquid membrane from the feed phase to the stripping phase. Furthermore, the dispersed organic droplets in the lumen side fluid can automatically and continuously replenish the loss of membrane liquid caused by solubility and emulsification to prevent liquid membrane degradation. The leakage between phases is less than 0.01%. Then the HFRLM process can provide good stability [4].
- Hansen solubility parameter theory was applied to analyze and explain the different transport phenomena with different modifiers. If the Hansen solubility parameters for a solvent lie within the solubility sphere for the complex, then the complex is probably soluble in the solvent. According to the Hansen model, the distance between solvent and center of complex solubility sphere can be expressed as

$$\Delta \delta_{(S-P)} = [4(\delta_{d}S - \delta_{d}p)^{2} + (\delta_{P}S - \delta_{P}p)^{2} + (\delta_{h}S - \delta_{h}p)^{2}]^{1/2}$$

where $\Delta \delta_{(S-P)}$ = the distance between solvent and the center of complex solubility sphere; $\delta_x s$ = Hansen component parameter for solvent; $\delta_x p$ = Hansen component parameter for complex. The reason was that when the pressure difference exceeded a certain critical value, the liquid membrane phase could be pushed out of the pores. The critical displacement pressure was defined for an SLM as the minimum transmembrane pressure required displacing the liquid membrane phase out of the largest pore [5].

• In hollow fibre modules the overall mass transfer resistance for a diffusion controlled process depends on the mass transfer resistances inside the fibre, across the membrane and outside the fibre. In order to identify the limiting step of the mass transfer process, experiments were carried out maintaining the flow rate of one phase constant while varying the flow rate of the other phase.

Another limitation of the Wilson-plot method comes from the fact that it involves a two-step calculation carried out in a sequential mode: in first place the estimation of the overall mass transfer coefficient and secondly, the determination of the correlation coefficients. This procedure leads to a loss of information and possible accumulation of errors. Additionally, as the variables' inverse is represented, a distortion on the magnitude of the variables can occur [6].

On the other hand, the renewal and regeneration of the liquid membrane layer can automatically and continuously replenish the loss of membrane liquid caused by solubility and emulsification to prevent liquid membrane degradation. The flow rates of two sides are controlled to maintain a positive pressure on the shell side with respect to the lumen side to prevent the leakage between two sides when the hydrophobic fibers are used. The HFRLM process is stable and can run for long-term without any difficulty. The removal efficiency and the mass transfer flux increase with the increasing amount of organic phase in the lumen side fluid, because of the renewal effect of liquid membrane in the lumen side and the large mass transfer area arising by the direct contact between organic droplets and aqueous phase. While at the higher O/A volume ratio, the consumption of the organic phase is large, this will increase the thickness of the developed liquid membrane layer and the mass transfer resistance within the lumen side. There is a favorable O/A range from 1:10 to 1:7 for the HFRLM process under the range studied, in which the removal efficiency and the mass transfer flux are higher, and the consumption of the organic phase is smaller. As the rate of complex reaction at interfaces is faster, the mass transfer resistance resulted from complex reaction can be ignored compared to the mass transfer resistance of diffusion mobility across the aqueous phase or organic phase. The mass transfer model based on the surface renewal theory is presented by considering the renewal process of liquid membrane layer, diffusion across membrane phase and aqueous boundary layer on the shell side [7].

Sr.	References	Metals	Feed phase	Organic phase	Stripping phase	Parameters
no				with carrier		
1	[8]	Rh(III)	10^{-3} M Rh(SCN) ₆ ³⁻	0.15M Aliquat	NaSCN and	pH=5, flow rate of
				336 in	mixture of	both=0.35 ml/min,0.2M
				dodecane with	NaHSO ₃ /Na ₂ SO ₃	$HSO_3/0.8M$ SCN ⁻ .
				4% dodecanol		
2	[9]	Cu(II)	CuSO ₄ solution	LIX64N in	HCL	Feed pH=(2-6),
			$(1-10 \text{mol/m}^3)$	kerosene	$(0.4-4 \text{mol/dm}^3)$	Pressure=2-5 psig, Aqueous
				(0.1-0.4		phase flow rate=3.7 cm ³ /s,
				mol/m ³)		Organic phase
						recirculation= $3.5 \text{ cm}^3/\text{s}$.
3	[10]	Pu(IV)	Pu(IV) with	30% TBP in	0.3M HNO ₃	Flow rate =1-3ml/min, Feed
			sodium	dodecane		acidity=3M HNO ₃ ,1.09M
			nitrite(1.5×10 ⁻⁵ M)			TBP, surface area=33.91
						cm^2
4	[11]	Zr and	Zr and Hf in HCL	0.5M TONA	2M HCL	Speed=1000rpm,Contact
		Hf	(5-10M)	and 0.2M		time=5-10 min, Phase
				Aliquat 336 in		ratio=1:1,
				kerosene		Flow rate=0.8-8.8 ml/min.
5	[12]	Au(I)	Au(I) in alkaline	12%LIX79 in	0.2M NaOH	Speed=400rpm,
			cyanide(1000ppm)	n heptanes		Pressure=0.2-0.45 bar,
						pH=10.5,Feed and strip flow
						rate= 5.56 and 3.33 cm ³ /s,
						Feed:Strip =4:1, P_{Au} =5.32-
						7.53×10^{-5} cm/s, feed=1000-
						5000ppm.

Table 1: Selected published work on heavy metals separation by HFSLM

6	[13]	Cr(VI)	Cr(VI) stock solution from solid K ₂ Cr ₂ O ₇	Aliquat 336 (0.05-0.5M) in dodecane	0.5M HNO ₃ and 0.5M NaNO ₃	Feed Cr(VI)=1mg/l,pH=2,flow rate=1ml/min ⁻¹ .
7	[14]	U ion	U ion(45ppm) in	0.1M Aliquat	(0.1-0.5M)	Flow rate = 100ml/min,
			trisodium phosphate solution	336 in kerosene with 0.06M TBP	HNO ₃	Aliquqt336 =(0.02-0.14M),
8	[15]	Cu(II)	CuSO ₄ IN acetate buffer media	D ₂ EHPA in kerosene	6mol/L HCL	Tube velocity=0.001- 0.04m/s, Shell velocity=0.003-0.007m/s, pH=4.44,Feed Cu=150- 800mg/l, Organic phase=(1:9)
9	[7]	Cu(II)	CuSO ₄ solution (64.03- 91.72mg/L)	10%LIX984N in kerosene	H ₂ SO ₄ (2mol/L)	Volume ratio=(1:10to1:7) ,pH=0.5-5.5,Flow rate tube=2.7-2.9ml/min and shell=2.2-2.3 ml/min,
10	[16]	Co(II)	Co(II) in Acidic sulphate solution	DP-8R in Exxsol D100(0.16- 1.28M)	0.1M H ₂ SO ₄	pH=3-7, Co(II) in feed=0.17-1.7×10 ⁻³ M,Feed flow rate=200-400cm ³ /min, Pseudo emulsion=200 cm ³ /min,

Sr	References	Organic	Feed phase	Organic phase	Stripping	Parameters
.No		compound		with or without	phase	
				carrier		
11	[17]	Lactate	Lactate	Quaternary	1 M	Agitation=400rpm,
			solution	ammonium salt	Sodium	T=22.5-40 [°] C,
			(280 mM)	carder, Aliquat	chloride	aliquat(%)=5-50,organic phase
				336 and	solution	concentration=0-7g/L
				hydrocarbon		
				mixture as		
				diluents		
12	[6]	Phenylala	90 mM	Micellar phase	2M KCL	Feed phase (V=900 ml, flow
		nine	phenylalanine	(n-heptane		rate=73ml/min, Re=3.4,pH=9.9),
			and 0.1 M	solution 125M		Organic phase(V=900ml,flow
			KCL	in TOMAC)		rate=113 ml/min, Re=3.9),
				and $1.25\% v/v$		Stripping phase(V=300ml,flow
				1-hexanol as		rate=125.3 ml/min, Re=5.9)
				co surfactant		

Table 2: Selected published work on organic compounds separation by HFSLM

13	[18]	Lipase	(10-20mM)	PPL (20v/v%	0.1-0.2M	Flow rate feed side(0.2-5ml/min)
			equimolar	octanol in	phosphate	and strip side
			PAA and	heptane)	buffer	(0.2-4ml/min),pH=6.10-6.27 feed
			MAs or 6-		(pH=7.57-	phase, shell and tube side
			APA and		7.60)	pressure=5 and 6-9psi,
			850mM			
			ethanol			
14	[2]	p-Nitro	p-Nitro	1-octanol	Aqueous with	Feed and strip phase volume=4000
		phenol	phenol in		50mM buffer	and 500ml,flow rate=490 and
			aqueous			170ml/min, Ret=12.1
			buffer			
			solution			
15	[19]	Phenol	3000mg/L	1-decanol with	1.8M NaOH	$Re_0=0.1-0.65$, $Re_a=4-7$ and $Re_s=7$,
			phenol in	different		Va=61,Vo=0.71,Vs=0.41,
			aqueous	extractants		Va: Vo=1:1 and 2:1,
			solution	5%(v/v)		Qo=8-501/h, Qa=281/h,
						P=0.6-0.8 bar(aqueous phase)
16	[20]	Amino	Trp, Phe,	10% AOT in	0.1M Na ₂ CO ₃	Feed pH=3-4.5,flow rate organic
		acids and	Trp-Leu and	oleyl alcohol	added to the	solution=10ml/min,P=15-
		dipeptides	Phe-Leu in	(for single	organic	25kPa,feed concentration=upto
			sodium	solute)and 30%	solution (Only	4mM,
			acetate	AOT in oleyl	use in	
			Phosphoric	alcohol (for	hydrolysate	
			acid buffer,	hydrolysate	solution)	
			hydrolysate	study)		
			solution (25			
			g/l)			
17	[21]	Amino	Equimolar	D2EHPA in	HCl in	Feed and organic phase flow rate
		acids	phenylalanine	kerosene	deionized	(120-600 cm3/min)and (180-480
			and laspartic	(100-500	water(0.1-	cm3/min),strip phase(240-600
			acid in	mol/m ³)	2mol/dm ³)	cm3/s), feed pH (3-5), and
			deionized			stripping acidity (0.1-2 mol/dm3)
			water			
			(5 mol/m^3)			
18	[4]	Citric acid	0.1 mol/L	30%N235+20%	(0.11-0.2)	Shell side velocity=0.10cm/s,N235
			Citric acid	n-octanol+50%	mol/L NaOH	concentration=5%-
			solution.(300	Kerosene.	aq solution.	40%, aqueous/organic volume

			ml)	(15ml)	(150ml)	ratio=20:1,
19	[5]	Fumaric	([H+]	Trialkyl amine	(2-20%)	0.7137 mol/L N7301 in kerosene
		acid	0.022-0.631	carrier in	NaOH,	and n-octanol, volume ratio of
			mol/L)	kerosene and	(V=100ml)	kerosene/ n-octanol=7/6, Δp =7.5-
			Fumaric acid	n-octanol		10psi,pH=1-1.67,stirring
			waste water	(V=50)		speed=200-400 rpm, flow rate feed
			(V=100ml)			and strip=3.6 and 3 L/h

IV.CONCLUSION

Supported liquid membranes are the interesting field for the study as well as research for the scientists and industry peoples. The practical use of the SLM is not possible yet but the smart supported liquid membranes technologies can be used in near futures with some modification for removal of heavy metals and organic compounds from the effluent which contains heavy metals. By using the proper solvent we can improve the overall mass transfer coefficient of desired solution. The type of HFSLM with strip is generating some pollution as it is soluble in both aqueous as well as strip solution, thus some modifications can be suggested for it.

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