

Liquid membranes and the treatment of metal-bearing wastewaters<sup>(\*)</sup>

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**Abstract** Liquid membrane technologies are gaining a prominent role as a separation technique for the treatment of metal-contained liquid effluents. The present work describes the most important of technologies, the general mechanisms for the metal extraction and some of their applications in the separation of metals.

**Keywords** Liquid membranes. Metals. Wastewaters.

## Las membranas líquidas y el tratamiento de efluentes líquidos conteniendo metales

**Resumen** Las tecnologías de membranas líquidas están ganando importancia en el tratamiento de efluentes líquidos que contienen metales. En el presente trabajo se describen las más importantes de estas tecnologías, los mecanismos para la extracción de los metales y algunas de sus aplicaciones en la separación de metales.

**Palabras clave** Membranas líquidas. Metales. Efluentes líquidos.

## 1. INTRODUCTION

Membrane technologies are one of the most important topics in today's research and practical use, increasing their market from US\$363 million in 1987 to near US\$1.5·10<sup>9</sup> by 2002<sup>[1]</sup>. Among these technologies, liquid membrane processes have been proposed as a clean technology owing to their characteristics, i.e. high specificity, low energy utilisation, etc.<sup>[2]</sup>. Thus, the use of liquid membranes has gained a general interest in the treatment of effluents where solute concentrations are low and large volumes of solutions must be processed, and if possible, without generating any secondary waste.

The present paper reviews the most important liquid membrane technologies and their application in the treatment of metal-bearing wastewaters.

## 2. LIQUID MEMBRANES

The term liquid membranes is used to describe a process of separation which does not rely on inherent chemical characteristics of a thin, solid

(semi permeable) barrier<sup>[3]</sup>. The closest equivalent non-membrane separation process is solvent extraction<sup>[4]</sup> and consequently liquid membrane processes are referred to as liquid pertraction although other names are used i.e. carrier-mediated extraction and facilitated transport. The equivalence between liquid membranes and solvent extraction arises from the use of a multiple (two or three) phase system.

The principle of liquid membrane operation, shown in figure 1, is relatively simple; two homogeneous, miscible liquid, one the feed (donor) the other receiving (acceptor) are spatially separated by a third phase, the membrane. The membrane phase consisting of a diluent and carrier (extractant) is immiscible and practically insoluble in the donor and acceptor solutions. Separation (transport) of solute from the donor to the acceptor solutions is due to favourable conditions created at the two interfaces between the three phases. The thermodynamics at the donor/membrane interface favour extraction of solute into the membrane while simultaneously the thermodynamics at the membrane/acceptor interface favour the reverse transport, i.e. stripping.

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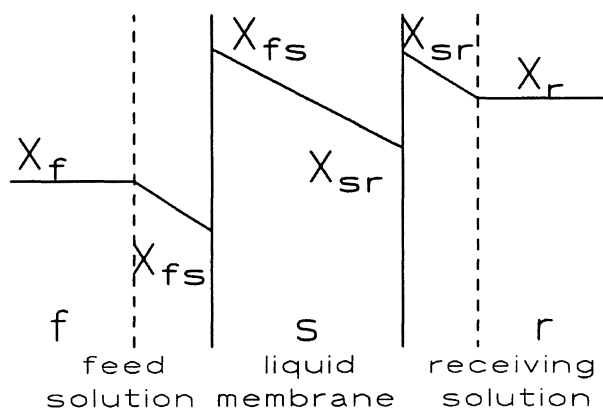


Figure 1. Liquid membrane operation scheme.

Figura 1. Esquema de operación con membranas líquidas.

The membrane phase itself in most applications is an organic liquid although aqueous based membranes can be used for separations of organic solutions. The attraction of liquid membrane for extraction processes lies in several features:

- molecular diffusion in liquids is generally several orders of magnitude faster than in solids such as polymer membranes,
- pertraction can be intensified by eddy diffusion in the mobile membrane phase,
- liquid membranes can be designed to be highly selective to specific solutes,
- a maximum driving force can be created, thus multistage processes commonly used in liquid extraction are not needed,
- the organic phase, which contains the liquid membrane carrier can be selected from a wide range of inert, insoluble, and harmless organic liquids,
- relatively small quantities of carrier are needed and therefore highly selective, relatively expensive agents can be used.

A major disadvantage of liquid membranes, in comparison to solid membranes is the greater degree of complexity in setting up the membrane phase and maintaining its stability.

## 2.1. Pertraction systems

Liquid membranes can be put into two classifications: methods with phase dispersion and methods without phase dispersion. Bulk liquid membranes (BLMs), are used for fundamental studies methods without phase dispersion, which

also include supported liquid membranes (SLMs) and liquid film pertraction (LFP). Emulsion liquid membranes (ELMs) are included in methods with phase dispersion.

In bulk liquid membranes<sup>[5 and 6]</sup>, two miscible aqueous solutions (donor and receiving) are separated via a third immiscible phase (carrier). The mass transfer from the donor to the receiving phase is carried out via the carrier. Because transport through the bulk takes place by convection, the unstirred boundary layers between the immiscible phases form the largest transport resistance.

Supported liquid membranes are based on the use of a porous solid membrane (polymer or ceramic) which supports or hold the liquid membrane phase (Fig. 2). The pore of the thin solid membrane are completely filled with the carrier and this impregnation produces, relatively stable, heterogeneous solid/liquid membranes. In some applications the liquid membrane phase may be sandwiched between two porous solid supports (contained liquid membrane). The typical supports used are thin flat-sheets or hollow fibres, manufactured from oleophilic polymers or ceramics, wettable by the membrane liquid. In application, the membranes are put in spiral wound or hollow fibre bundle modules. The attraction of liquid membranes lies in the small amount of liquid required to produce a large interfacial area, i.e. 1 m<sup>2</sup> from 10 cm<sup>2</sup> in a 20 μm thick, 50 % porous polymer.

The liquid film pertraction process (Fig. 3) has the three solutions in continuous motion: the donor and acceptor solutions flow along vertical supports alternatively arranged at small distances

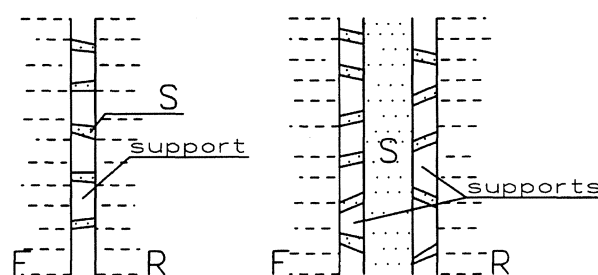
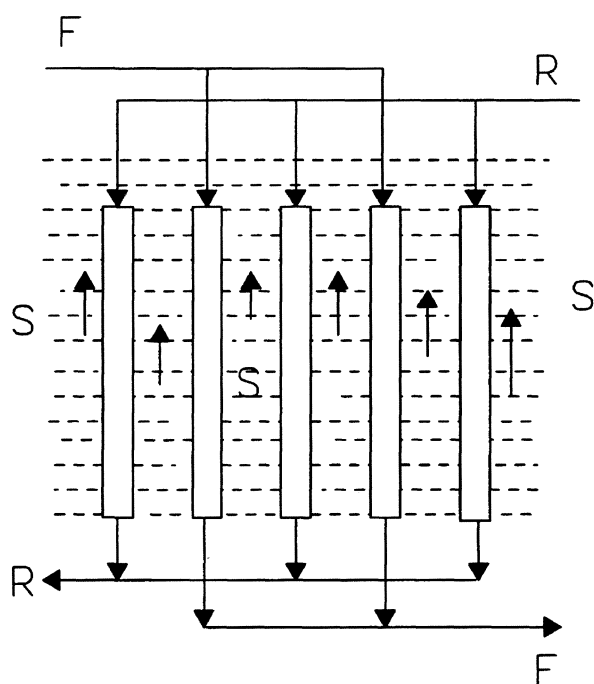


Figure 2. Supported liquid membrane process. F: feed phase. R: receiving phase. S: organic solution.

Figura 2. Proceso de membranas líquidas soportadas. F: fase de alimentación. R: fase de reextracción. S: fase orgánica.



**Figure 3.** Liquid film pertraction process. F: feed phase. R: receiving phase. S: organic solution.

*Figura 3.* Proceso de pertracción con fase líquida. F: fase de alimentación. R: fase de recepción. S: fase orgánica.

in the membrane solution. Hydrophilic membrane supports enable stable and uniform film flow of donor and acceptor solutions down the solid support.

From a practical point of view, one of the claimed advantages of liquid membrane technologies is that the extraction, stripping and regeneration operations are combined in a single stage<sup>[7 and 8]</sup>, against this, and mentioned above, the lack of membrane stability is the major drawback associated with the use of supported liquid membranes because long-lived membranes are needed in order to minimize the secondary wastes.

The instability of supported liquid membranes may be due to loss of carrier phase by its solubility in both aqueous (feed and receiving) phases, thus the carrier must be very lipophilic<sup>[9]</sup>, and to loss of the organic phase by expulsion from the pores of the membrane support. This latter loss is influenced by the characteristics of the support, the diluent of the organic phase and the aqueous solutions.

The main factor of the aqueous phases which influences the stability of the membrane phase is the osmotic pressure gradient across the membrane due to the difference in electrolyte concentrations

between both aqueous solutions. Under these conditions, water is forced to move across the membrane, from the diluted solution to the concentrated one, and thus may force the organic phase out of the support pores<sup>[10]</sup>.

The solid support must have a critical surface tension both greater than the surface tension of the organic diluent and lower than the surface tension of the aqueous phases. It must also have a pore diameter as small as possible<sup>[11]</sup>, though the best compromise within this variable may be determined experimentally.

The membrane diluent must fulfil the following requirements: low mutual solubility between organic and aqueous phases, low volatility, surface tension lower than the critical surface tension of the support, high diluent/water interfacial tension and high viscosity. It was concluded<sup>[7]</sup>, that a diluent exhibiting a high tendency to solubilize water and a low organic/water interfacial tension are the main cause of supported liquid membranes instability.

Thus, as in conventional solvent extraction technology<sup>[12-14]</sup> the diluent of the organic phase has an important function in the transport of ions through supported liquid membranes since it changes the extraction and stripping properties of the extractant.

Furthermore the diluent must ensure that<sup>[15]</sup>: the carrier is sufficiently solubilized, there is no development of a third phase between the organic and the aqueous phases (on the contrary, a modifier must be added to the organic solution); to make the supported liquid membrane stable for a long period the diluent must fulfil a number of properties (see above) allowing it to remain in the pores of the membrane.

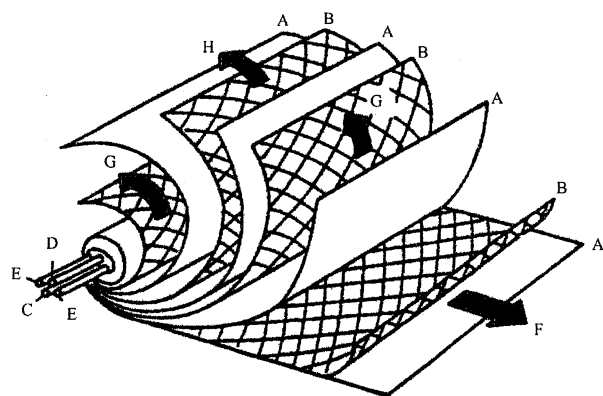
Despite the correct selection of the carrier phase (extractant and diluent) and membrane support for each particular case, various approaches have been also suggested to stabilize supported liquid membranes, i.e. gel formation in pores of the support<sup>[16 and 17]</sup>. As a medium to stabilize the membrane partially avoiding the loss of the carrier from this phase, the application of a thin polyamide layer covering the impregnated support is also described in the literature<sup>[18 and 19]</sup>.

Although flat-sheet supported liquid membranes (FSSLMs) are useful to obtain first data about the permeation of a particular metal, for industrial purposes, a planar or flat geometry is not very effective since the ratio of surface area to volume is too low. Thus, hollow fibre and spiral wound modules are used to provide high surface area to

volume ratio. The basic configuration of a hollow fibre module consists of two aqueous phases (feed and receiving) and an organic phase which contains the carrier phase confined within the membrane pores via a capillary action. The membrane serves both as a support for the organic phase and as a uniform barrier between both aqueous solutions which circulated within the inner and the outer sides of the fibre, this results in two aqueous/organic interfaces with well defined transfer areas.

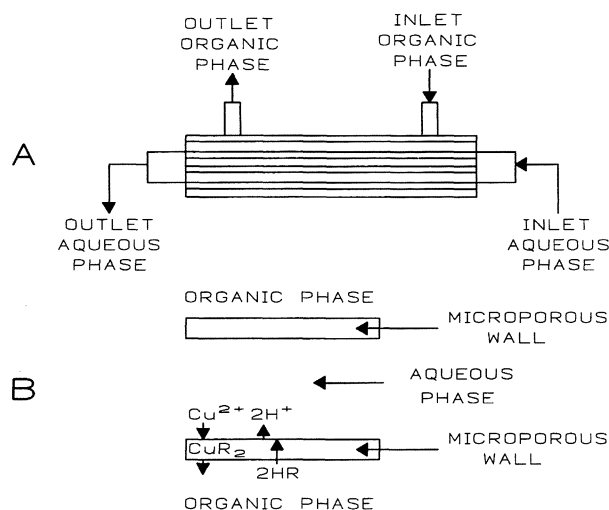
Spiral wound modules as is shown in figure 4 (though other module configurations can also be found), consist of a sandwich of flat sheet membranes and spacers wrapped around a central axle. This configuration is compact and relatively inexpensive but is prone to fouling if the feed solution is not well clarified, thus a prefiltration stage is recommended.

Though not essentially a supported liquid membrane technology, a relatively new approach to the treatment of wastewaters is the non-dispersive solvent extraction (NDSX) technology with microporous hollow fibre modules<sup>[25-27]</sup>. In this technology the hollow fibre contactors can be used in two different configurations: single function membrane modules<sup>[20 and 21]</sup> and dual function membrane modules<sup>[22 and 23]</sup>. In the single function configuration (Fig. 5), the same aqueous solution flows in all fibres in each module and two separate hollow fibre modules are needed in order



**Figure 4.** Spiral wound module. A: membrane support. B: mesh spacer. C: inlet of feed phase. D: inlet of receiving phase. E: inlet of organic phase. F: feed phase. G: organic phase. H: receiving phase.

*Figura 4. Módulo en espiral. A: membrana. B: espaciador. C: entrada de la fase de alimentación. D: entrada de la fase de reextracción. E: entrada de la fase orgánica. F: fase de alimentación. G: fase orgánica. H: fase de reextracción.*



**Figure 5.** Single function membrane module. A: actual configuration. B: mass transfer scheme.

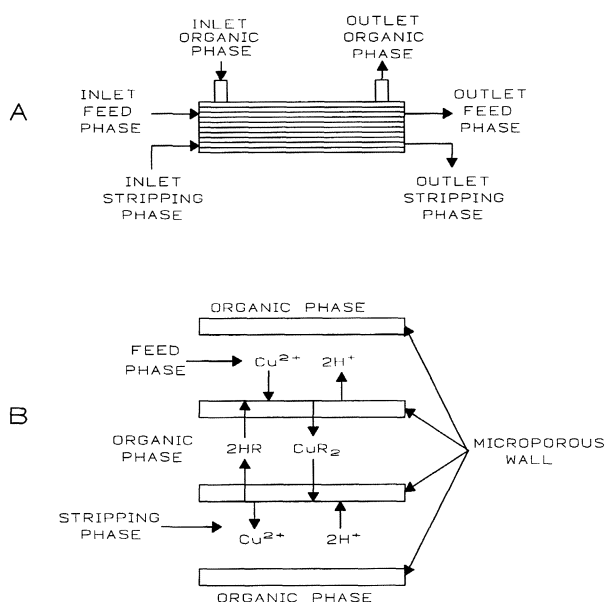
*Figura 5. Módulo de fibra hueca en función sencilla. A: configuración. B: proceso de transferencia de materia.*

to perform the extraction and stripping operations. The carrier phase is circulated between these two modules, extracting the metal from the feed aqueous phase in the extraction module and releasing it into the receiving or stripping aqueous solution in the stripping module where it can be concentrated to the desired level.

In dual function modules (Fig. 6), the extraction and stripping of the metal are carried out simultaneously in a single hollow fibre module containing one set of fibres for extraction and another set for stripping. In both configurations, the aqueous/organic interface is immobilized in the pores of the porous polymeric membrane as the phases flow on different sides of the hollow fibre. This interface can be stabilized by maintaining a higher pressure on the non-wetting liquid than that on the wetting liquid, but lower than that necessary to displace the wetting liquid<sup>[24]</sup>.

## 2.2. Emulsion liquid membranes

A second form of liquid membrane process is based on the formation of a double emulsion and are referred to as emulsion (surfactant) liquid membranes (ELMs)<sup>[28]</sup>. This is a three phase system which is stabilised by an emulsifier, which can be up to 5 % or more of the membrane liquid. The membrane liquid in the form of relatively large droplets (0.1-1 mm diameter) encapsulates the acceptor solution which in effect is a fine



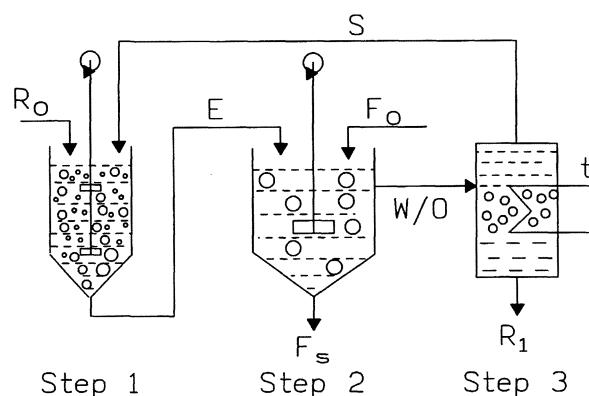
**Figure 6.** Dual function membrane module. A: actual configuration. B: mass transfer scheme.

Figura 6. Módulo de fibra hueca en función doble. A: configuración. B: proceso de transferencia de materia.

dispersion of smaller drops (1-10  $\mu\text{m}$ ). This emulsion is very stable due to the size of the drops and the high content of emulsifier or surfactant. In operation the membrane emulsion phase is then dispersed into the donor feed solution and the process of pertraction or mass transfer can take place. This process is quite rapid due to the high interfacial areas (1000-3000  $\text{m}^2$ ) produced by the emulsion droplets and the microdrops in the acceptor phase. This feature makes ELM attractive for the treatment of low concentrations of permeating species.

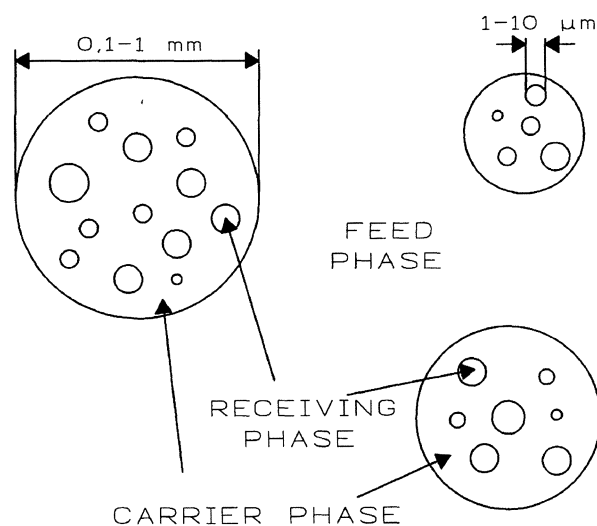
There are three essential steps in the process (Fig. 7):

- Emulsion preparation. An aqueous reception phase ( $R_0$ ) is emulsified into the organic membrane phase. The aqueous phase will be either acid or alkaline depending upon the extraction system. The organic phase will contain a surfactant to stabilise the emulsion and may contain an appropriate carrier for certain separations.
- Solute pertraction and membrane and feed separation. At this stage, the membrane emulsion (E) is contacted (dispersed) with the feed or donor solution ( $F_0$ ), as a continuous phase, for extraction to take place (Fig. 8).



**Figure 7.** Emulsion liquid membrane process.

Figura 7. Proceso con membranas líquidas emulsionadas.



**Figure 8.** Emulsion liquid membrane process. Detail in step 2.

Figura 8. Proceso con membranas líquidas emulsionadas. Detalle en la etapa 2.

Then, the emulsion membrane phase (and internal strip phase) is separated from the spent feed ( $F_s$ ).

- Emulsion break-up. The water in organic emulsion (W/O) is separated to enable recycling of the organic membrane phase ( $S$ ) and recovery of solute from the aqueous reception phase ( $R_1$ ).

In the ELM process the main problems relate to emulsion stability, poor stability incurs partial rupture of the membrane which reduces overall efficiency, high stability brings problem in the breaking-up of the aqueous-organic emulsion in

the final stages of the process in order to remove the internal phase and reformulate the emulsion. In view of the above problems associated with membrane stability alternative forms of phase dispersion without surfactants have been proposed which utilise porous polymer membranes, i.e. by using a dispersion and hollow fibre technique. In this, the aqueous reception phase is dispersed in the organic phase contained within the lumen of a porous oleophilic capillary membrane. The aqueous donor phase flows over the outer surface of the capillary membrane and mass transport takes place through the organic phase, which is also contained within the pore walls, into the dispersed aqueous reception phase.

### 3. APPLICATIONS OF LIQUID MEMBRANES IN THE TREATMENT OF METAL-BEARING WASTEWATERS

The potential applications of liquid membranes cover the separation, among others, of metals<sup>[29]</sup>.

The appropriate pertraction of these species depends on a suitable mechanism of transport, which broadly is one of two types:

- simple transport based on the use of the membrane as a physical solvent,
- facilitated transfer in which the membrane is a substrate for a selective carrier of permeate.

#### 3.1. Metals

The broad spectrum of metal extractions which have been studied with liquid membranes includes noble metals, alkaline and earth alkaline metals, rare earth and radioactive metals and heavy and toxic metals. Table I presents a number of carriers (extractants) used in these studies, whereas in table II some examples of metal extraction using liquid membranes are given.

Separation of metals is usually done by facilitated transfer sometimes referred as carrier mediated. This mechanism does not require the permeate to be soluble in the membrane liquid, as

**Table I.** A selection of carriers for liquid membranes

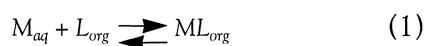
*Tabla I. Agentes de extracción empleados en procesos de membranas líquidas*

Carriers (traders)	Active substance
D2EHPA (Various)	di(2-ethyl-hexyl) phosphoric acid
DC18C6 (Various)	dicyclo-18-crown-6
DIDPA (Various)	diisodecylphosphoric acid
DTPA or D2EHDTPA (Various)	bis(2-ethylhexyl) dithiophosphoric acid
DEHPTA (Various)	di-(2-ethylhexyl) thiophosphoric acid
22DD (Various)	1,10,-didecyl diaza 18-crown-6
TBAH (Various)	tributyl aceto hydroxamic acid
TBP (Various)	tri-n-butylphosphate
TIOA (Various)	tri-iso-octylamine
TLAHC1 (Various)	trilaurylammonium chloride
TOA (Various)	tri-n-octylamine
TOPO (Various)	tri-n-octylphosphine oxide
ACORGA series (Avecia)	5-nonylsalicylaldoxime within or without modifiers (alcohols or esters)
ALAMINE 336 (Cognis)	tri-octyl amine
ALQUAT 336 (Cognis)	methyl-tri-octylammonium chloride
PRIMENE JMT (Rohm and Haas)	isomers mixture of a primary amine
AMBERLITE LA2 (Rohm and Haas)	N-lauryl-1,1,3,3,5-hexamethyl-hexyl amine
CYANEX 272 (Cytec)	bis(2,4,4-trimethylpentyl) phosphinic acid
CYANEX 471X (Cytec)	Tri-n-butylphosphine sulphide
CYANEX 302 (Cytec)	bis(2,4,4,-trimethylpentyl) monothiophosphinic acid
CYANEX 921 (Cytec)	Tri-n-octylphosphine oxide
CYANEX 923 (Cytec)	Mixture of phosphine oxides
LIX 79 (Cognis)	Guanidine derivative
LIX series, MOC series (Cognis)	Ketoximes, aldoximes and mixtures of oximes within and without modifiers (alcohols)

**Table II.** Selected metal ion extraction using liquid membranes*Tabla II.* Sistemas de extracción de metales empleando membranas líquidas

<b>Metal</b>	<b>Carrier</b>	<b>Reference</b>
Alkali metals	Crown ethers	40, 43
Li(I)	Non-cyclic polyether derivatives	28
Mg(II),Ca(II),Ba(II)	Crown ethers	28
Ag(I)	DC18C6, D2EHPA, CYANEX 471X, DTPA, thiourea derivatives	41, 65, 66
Au(I)	LIX 79, LIX 79-amines/organic phosphorous derivatives mixtures, thiourea derivatives	30, 44, 45
Pd(II)	Crown ethers, CYANEX 471X, DEHTPA, TOA, thiourea derivatives	31, 36, 70
U(VI)	TOPO, TBP, D2EHPA	53
Rare earths	D2EHPA	28
Eu(III)	D2EHPA	33
Am(III)	DIDPA	34
Pu(IV)	Crown ethers	53
Cu(II)	ACORGA series, LIX series, MOC-55TD, LIX 54	49-51, 54, 56
Cr(VI)	Amines, CYANEX 923	47, 60-62
Hg(II)	Amines, CYANEX 471X	71
Zn(II)	D2EHPA, D2EHDTPA, CYANEX 923	38, 52, 59, 67
Co(II)Ni(II)	D2EHPA, CYANEX 272, TOA, carboxylic derivative	55, 68, 69
Fe(III)	TBP, CYANEX 923	46, 48
In(III)	D2EHPA	28
W(VI)	ALIQAT 336	28
Au(III)	Phospholene derivatives, CYANEX 471X, CYANEX 923	32, 39, 78
Pt(IV)	TOA, ALIQAT 336	35, 76
Ir(IV)	TOA	37
Sr(III)	DC18C6	57
Cs(I)	Crown ethers	58
V(V)	ALIQAT 336	63
Pb(II)	22DD	64
Cd(II)	ALIQAT 336, CYANEX 923, CYANEX 302	72-75, 77

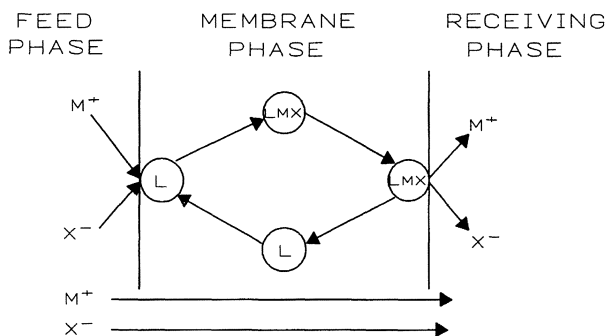
the latter contains and additive or carrier (L) which can react selectively and reversibly with the permeating species:



The carrier essentially shuttles the permeate species (M) from the donor feed to the membrane/interface where conditions are such that the equilibrium of reaction shifts to the left and the permeate is released into the receiving phase and the carrier returns to the membrane to recombine with permeate on the feed side of the membrane. This transport mechanism is called co-transport and is typical of amines and solvation extractants (Fig. 9).

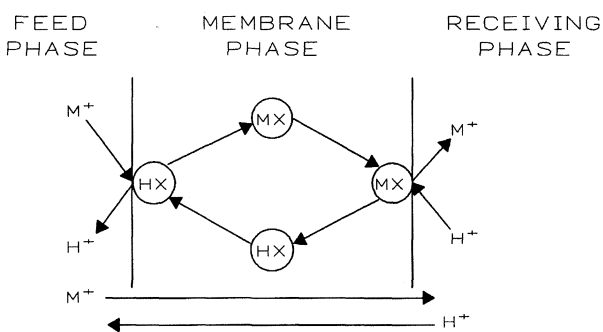
In other applications a counter-transport can be utilised in which an ion-selective carrier is used (Fig. 10). The carrier complexes with the ionic permeate ( $M^{n+}$ ) being transported which, when released into the receiving phase, is replaced by an equivalent amount of ions of a similar type stored in the reception phase. A typical example is the counter-transport of protons, in the extraction of metal ions from neutral (or slightly acidic) media with oleophilic chelating or acidic reagents. The complexation and disassociation is essentially controlled by pH differentials between donor and receptor phases.





**Figure 9.** Co-transport mechanism. M: metal. X: counter anion. L: extractant.

*Figura 9. Mecanismo de co-transporte. M: metal. X: anión. L: agente de extracción.*



**Figure 10.** Counter-transport mechanism. M: metal. HX: extractant.

*Figura 10. Mecanismo de contra-transporte. M: metal. HX: agente de extracción.*

### 3.2. Viscose fibre industry

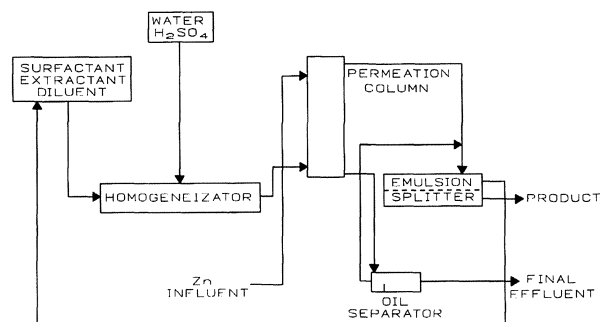
The viscose rayon industry uses zinc ions in the spinbaths to improve both the spinning process and the properties of the fibres. Further processing of the fibre requires the removal of zinc by rinsing with water which generates a waste. This wastewater should ideally be treated to recover the zinc and re-use the water. Much of this wastewater produced is quite dilute and the high volumes generated do not make ELMs generally applicable. However, certain of the wastewaters contain significant quantities of zinc to economically justify the use of emulsion liquid membranes.

To treat such a type of effluent, a plant was built in Austria in the early years of the 1980 decade (though actually is not working)<sup>[79 and 80]</sup>. The plant afforded the treatment of a wastewater (flow rate: 75 m<sup>3</sup>/h) containing 0.4-0.6 g/L zinc, with

sulphuric acid (5-8 g/L), sodium sulphate (25 g/L) and various modifiers and solids. The liquid membrane pertraction was achieved using D2EHDTPA (see Table I) as efficient metal carrier. This reagent is rarely used in conventional solvent extraction due to slow kinetics of stripping, but in ELM device, the rate is satisfactory due to the high interfacial area. D2EHDTPA is able to extract zinc at a pH of near 0.5, whereas D2EHPA cannot be used below a pH of 2. From the various surfactants experimented, ECA 4360 (a polyamine) gives the best zinc-permeation results. For the stripping phase a minimum concentration of sulphuric acid of 200 g/L is required, 250 g/L used in practice.

In figure 11, a scheme of the process is presented. The emulsion in the process is produced by pumping the organic phase and stripping phase at a pressure of 1 MPa through an homogeneizer equipped with a special nozzle.

After emulsification, the zinc solute is extracted from the wastewater in a multistage countercurrent extraction column. The stripped wastewater from this extraction is sent to an oil separator to remove any entrained organic droplets, before discharged as effluent. The emulsion membrane phase (with the solute) from this column is then split in an electrostatic coalescer to give a final product phase and the organic phase for recycle. The electrostatic coalescer is based on 2000 V, 10 kHz, AC voltage applied between two insulated electrodes. The flowrate of the membrane phase is 5 m<sup>3</sup>/h and that of the stripping phase 0.5 m<sup>3</sup>/h. The average process efficiency for treating the zinc wastewater is near 99.5 % (this mean that zinc concentration in the final effluent is around 0.001-0.003 g/L) and



**Figure 11.** Scheme for the processing of a wastewater from the fibre industry using ELMs.

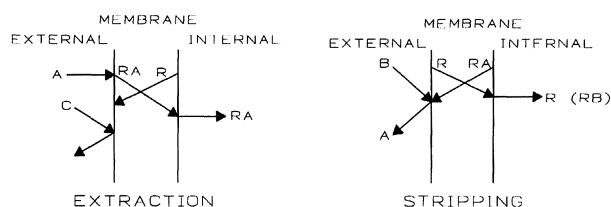
*Figura 11. Esquema del procesado de un effluente líquido, procedente de la fabricación de fibras textiles, mediante membranas líquidas emulsionadas.*



the zinc concentration in the final strip liquor is around 60 g/L. Although metal costs obviously vary, the above application point is competitive, however, the cost effectiveness is less attractive with more dilute solutions at solute concentrations below 0.1 g/L.

### 3.3. Chromium extraction using microcapsules

Microcapsules consist of particles or droplets immobilised within ultrathin membranes composed of natural or synthetic polymers with varying thickness and degree of permeability<sup>[81]</sup>. Microcapsules can be used as compact systems for use in separations, due to their large surface area, ultrathin membranes and extremely small volume. Polyurea microcapsules prepared by interfacial polycondensation are used to separate hexavalent chromium ions from aqueous solutions. The principle of separation using this technique is shown in figure 12. There are three steps in the process: preparing the microcapsules in which an extractant for the solute is encapsulated, dispersion of the microcapsules in aqueous solutions containing the solute to be separated, and following formation of a complex between the extractant and the solute, dispersion of the microcapsules into another aqueous solution containing the stripping reagent to release the solute. Various extractants can be used, but amines are favoured over, i.e. TBP. With the latter extractant, the mean diameter of the microcapsules is smaller due to lower interfacial tension at the oil/water interface. The chromium extraction rate could be enhanced by decreasing the pH in the aqueous phase, increasing the extractant concentration in the microcapsules or reducing the



**Figure 12.** Principle of separation using membrane microcapsules. A: extracted species. C: unextractable species. R: extractant. B: stripping reagent.

*Figura 12.* Separación con membranas en forma de microcápsulas. A: especie que se extrae. C: especie que no se extrae. R: agente de extracción. B: agente de reextracción.

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microcapsule diameter to increase the interfacial area and to decrease the mass transfer resistance in the microcapsule. The membrane formulations were also found to have an impact on the extraction rate. Stripping rate increased with an increase in pH, which was attributed to the increased rate of reaction between the complexes and the hydroxide in the stripping solution.

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