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Membrane-based extraction with strip/organic dispersion methodologies for metals removal and recovery from wastewaters

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ABSTRACT

The generation of liquid effluents containing organic and inorganic residues from industries presented 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. Several configurations are used: flat-sheet supported liquid membranes, spiral wounds and hollow fiber modules. In order to improve their effectiveness, smart operations have been developed: pseudo-emulsion membrane based strip dispersion (PEMSD), pseudo-emulsion based hollow fiber strip dispersion (PEHFSD), hollow fiber renewal liquid membrane (HFRLM) and double strip dispersion hybrid liquid membrane (SDHLM). This paper overviewed some of these smart supported liquid membranes technologies and their applications to the treatment of metal-bearing liquid effluents.

Keywords: Wastewaters; Supported liquid membranes; Strip/organic dispersion methodologies; Removal; Metals; Toxicity; Carriers

1. Introduction

Stricter product quality requirements, environmental legislation, energy efficiency demands and the need to reduce costs are some of the reasons why new and advanced separations technologies are needed in order to treat in a more efficient manner metal-containing liquid effluents or wastewaters produced in industrial plants or even during attempts to remediate soils, contaminated with such metals. Moreover, it may be considered that such streams are produced in relatively high volumes, are diluted in the metals that they contained, and in many cases they are complex in their nature, that is, they may contained metals with different toxicity and/or value.

Thus, three types of technologies are currently considered for such a task: liquid–liquid extraction, adsorption-biosorption-ion exchange processes and liquid membranes. Considering the latter, there are two basic types of liquid membrane technologies: unsupported and supported liquid membranes, the former including bulk liquid membranes and emulsion liquid membranes.

The facilitated transport of metals through supported liquid membranes has long been pursued by the scientific and industrial community. In supported liquid

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membranes technology, the organic solution, containing the carrier, filled the micropores of the solid support, whereas the feed solution and the strip solution are contained or flow from both sides of the support. The main drawback of this technology is its apparent lack of stability under long-term operation.

Due to the exposed above a more stable supported liquid membrane technology is needed and description of recent developments of the technology under the generic name of membrane-based extraction with strip/organic dispersion methodologies is the goal of this work.

Four methodologies are considered: pseudo-emulsion membrane based strip dispersion (PEMSD), pseudo-emulsion based hollow fiber strip dispersion (PEHFSD), hollow fiber renewal liquid membrane (HFRLM) and double strip dispersion hybrid liquid membrane (SDHLM).

In the first case, a permeation cell is the device used for studying the transport of metals from a feed solution to a strip solution *via* a solid support filled with an organic solution, this organic solution formed a pseudo-emulsion phase with the dispersed strip solution. In the second case, the same concept is considered, but the device used is a hollow fiber module, the feed solution flows through one side of the fibers, generally the tube side, and the pseudo-emulsion phase formed by the organic and the dispersed strip solution flows through the other side, generally the shell side, of the fibers. In the third methodology into consideration, and due to the hydrophobic nature of the fibers and the wetting affinity of these fibers by the organic solution, a thin liquid membrane film is formed in the tube side of the fibers. The organic solution is dispersed in either the feed or the strip solutions, and the pseudo-emulsion flows through the tube side of the fibers. The fourth of the dispersion membrane technologies considered is based also in the use of a simple permeation cell, but against PEMSD technology, two different organic-strip solutions formed two pseudo-emulsion phases allowing for the separation of two metals accordingly with their respective affinities with the two different pseudo-emulsion phases. In the four methodologies, the pseudo-emulsion phase is an emulsion that is formed temporarily between the organic and the selected aqueous solution and it should have clear and fast phase separation when mixing of the solutions stopped.

The application of such methodologies in metal (Cu, Zn, Cd, Cr, Au, etc.) separation is considered.

2. The toxicity of metals

Some metals are essential for human life and others are highly toxic, in the middle, there a number of metals which depending upon the dosage to humans can be considered as beneficial or harmful to human live. In this section, we described some of the peculiarities of such behaviour with respect to metals, that, until date had been removed and recovered from aqueous solutions using membrane-based strip/organic dispersion methodologies.

Zinc is a trace element, essential for life. Zinc occurs in hundreds of enzymes and in thousands of protein domains. This metal is essential for growth and development. At the cellular level, it is critically involved in proliferation, differentiation, and apoptosis immunity, intermediary metabolism, DNA metabolism and repair, reproduction, vision, taste, and cognition/behaviour zinc is essential for neurogenesis, synaptogenesis, neuronal growth, and neurotransmission [1]. An initial common event in the action of all toxic metals seems to be the generation of oxidative stress. Zinc can retard oxidative mechanisms induced by other metals such as copper and iron, by modulating reactive oxygen species (ROS), maintaining an adequate level of metallothioneins (MTs), and reducing copper and iron through competitive mechanisms. Nevertheless, different concentrations of zinc can block or accelerate the apoptotic processes [2].

Apoptosis, also known as programmed cell death is a highly regulated and crucial process found in all multicellular organisms. It is not only implicated in regulatory mechanisms of cells, but has been attributed to a number of diseases, that is inflammation, malignancy. A variety of toxins can induce apoptosis. Carcinogenic transition metals, promote apoptosis along with DNA base modifications, strand breaks and rearrangements [3].

High concentrations of zinc up to 2500 mg l^{-1} with an estimated dose of 325–650 mg, have been linked to poisoning of individuals, causing nausea, abdominal cramping, vomiting, tenesmus, and diarrhea with or without bleeding. Excess zinc during embryogenesis can be teratogenic or lethal, but zinc is apparently neither a mutagen nor a carcinogen [1].

In human populations, cigarette smoke is by far the largest source of cadmium exposure; curiously, cadmium is bioconcentrated in the tobacco plant. For nonsmokers in the general population, cadmium-contaminated food is a major source to this element exposure: fish, shellfish, organ meat (especially liver and kidney), and grains and cereal products [4].

Cadmium is classified as a human carcinogen (group I) on the basis of sufficient evidence for carcinogenicity in both humans and experimental animals [5]. The underlying mechanism appears to be related to Cd-induced oxidative stress with DNA damage that is mediated in part by anti-oxidative cellular defence systems, such as glutathione [6]. As a result, these alterations are manifested in almost all the organs affected by cadmium such as liver, kidney, testes, lungs and bones. It also increases the risk of peripheral arterial disease [7]. The kidney is the critical organ. For chronic dietary exposure, the kidneys constitute the target organ. Cadmium-induced renal damage is characterized by proximal tubular reabsorptive dysfunction [8].

Cadmium can also cause bone damage, either via a direct effect on bone tissue or indirectly as a result of renal dysfunction. After prolonged and/or high exposure the tubular injury may progress to glomerular damage with decreased glomerular filtration rate, and eventually to renal failure. For smokers this proportion is considerably higher. [8].

Chromium, in the form of Cr(III), is a trace element, essential material for humans and animals, and plays an important role as a glucose-tolerance factor (GTF) in insulin, lipin, and protein metabolism although in excess can cause allergic skin reactions and cancer [9]. On the other hand, Cr(VI) is very toxic for humans and living organisms being carcinogenic and mutagenic to living organisms. Hexavalent chromium is a potent teratogen, however, trivalent chromium has not been found to be teratogenic. Cr(VI) can diffuse through cell membranes after absorption and has been classified as an A1 carcinogen [3]. Cr(VI) enters the body by inhalation, ingestion, or absorption through the skin. Occupational exposure to Cr(VI) is a well-established cause of skin damage such as skin ulcers and irritant contact dermatitis, and delayed hypersensitivity reactions. Also, Cr(VI) has allergenic potential cause skin eczema and atopic dermatitis. Recently, it has been reported that Cr(VI) induce dermal toxicity [10].

Cr(VI) is reduced by cellular reductants to its lower oxidation states, pentavalent chromium (Cr(V)) and tetravalent chromium (Cr(IV)). These intermediate states of chromium are reactive to produce ROS which are known to cause oxidative damages such as DNA strand breaks, base modification and lipid peroxidation [10].

In humans copper is a trace element, and is necessary for the development of connective tissue, nerve coverings, and bone. Copper also participates in both iron and energy metabolism. Copper acts as a reductant in several that reduce molecular oxygen (i.e., superoxide dismutase, cytochrome oxidase, etc.). It is transported in the organism by the protein ceruloplasmin [11]. The recommended intake of copper for adults is 0.9 mg d^{-1} with an upper limit of 10 mg d^{-1}. A healthy human contains about 110 mg of copper with about 9 mg present in the brain [12]. Excessive dietary zinc can cause copper deficiency [11]. If the balance between the uptake and efflux of copper ions does not function correctly, copper can become cytotoxic and contribute to the development of several pathologies such as cancer, diseases of the nervous system, and aging [2].

Copper ions are prone to participate in the formation of ROS. Cu(II) is reduced in the presence of ascorbic acid and (γ-glutamylcysteinylglycine) (GSH) to Cu(I), which catalyzes the formation of OH^- through the decomposition of H_2O_2 via Fenton reactions leading finally to lipid peroxidation. Copper is also capable of inducing DNA strand breaks and oxidation of bases via ROS. Cu-induced apoptosis has been demonstrated to involve the generation of ROS [13]. In addition to the generation of ROS, copper may manifest its toxicity by displacing other metal cofactors from their natural ligands [2].

Iron is an essential trace element [14]. Iron is essential for cellular proliferation and for maintaining cell viability. It represents an irreplaceable component of some key enzymes, such as those in the mitochondrial respiratory chain, in addition to ribonucleotide reductase [2]. The total body iron content in normal human adults is about 40–50 mg kg^{-1} body weight. About 80% of the total iron content is found in haemoglobin in circulating red blood cells and in myoglobin in the muscle; the remaining 20% is distributed between storage proteins, ferritin and haemosiderin, a small amount in various iron containing enzymes, and about 3–4 mg circulates in the plasma bound to transferrin [15].

As mentioned above, a common event in the action of all toxic metals seems to be the generation of oxidative stress. Iron can directly catalyze generation of hydroxyl radicals from hydrogen peroxide (Fenton reaction) and other ROS, whereas the redox-inactive metals, can diminish the ROS-scavenging capacity in cells, but may also stimulate the generation of ROS indirectly by displacing iron and copper from metallothionein (MT) and other metal-containing cellular proteins, which then can accelerate production of ROS via the Fenton reaction. Iron can then become cytotoxic and contribute to the development of apoptosis [2]. Iron accumulation introduces progressive damage in liver, heart, and in the endocrine system if a chelating therapy is not introduced. Iron is deposited in parenchymal tissues and in reticuloendothelial cells [15].

Elemental gold has been employed as medicinal agents throughout the history of civilization. In modern medicine, gold therapy (chrysotherapy) of various salts and derivatives of Au(I) has been widely used, mostly for the treatment of rheumatoid arthritis. A number of Au(III) compounds have been assessed as potential anticancer agents. Gold, especially gold nanoparticles (AuNPs) has become an important biomedical tool for scientists in cancer research due to several advantages of AuNPs [16]. Recently, it has been demonstrated that AuNPs possess an enormous potential to improve the efficacy of cancer treatment. Several groups have demonstrated the noncytotoxic behavior of AuNPs. They concluded that Au(0) nanoparticles were not cytotoxic, reduced the production of reactive oxygen and nitrite species, and did not elicit secretion of proinflammatory cytokines tumour necrosis factor alpha (TNF-α) and interleukin 1-β (IL1-β), making them suitable candidates for nanomedicine. AuNPs have exceptional stability against oxidation and therefore will play a significant role in the advancement of clinically useful diagnostic [17]. On the other hand, other researches have concluded that gold compounds are nephrotoxic, produce neurological complications and several biochemical effects. Au(III) has been also reported to cause oxidization of proteins such as insulin and ribonuclease [16].

Thulium is the least abundant of the lanthanides, and can be employed as a medicament, in lasers or in portable equipments of X-rays. A ^{170}Tm-based radiopharmaceutical for bone pain palliation could offer significant advantages over other employed commonly, such as ^{89}SrCl$_2$. Naturally occurring thulium is composed of one stable isotope, ^{169}Tm (100% natural abundance), but ^{170}Tm is produced by thermal neutron bombardment on natural Tm$_2$O$_3$ target. ^{170}Tm-ethylenediaminetetramethylene phosphonic acid (^{170}Tm-EDTMP) showed selective skeletal uptake with insignificant retention in any of the vital organ/tissue and rapid urinary excretion, and shows promising features and warrants further investigation for development as a cost-effective bone pain palliative with higher potential for global distribution [18].

Dysprosium is a rare earth element with and it is never found in nature as a free element, though it is found in various minerals, such as xenotime. Dysprosium is used, in conjunction with vanadium and other elements, in making laser materials, in making control rods in nuclear reactors and in data storage devices. Dysprosium was tested on primary cells and cell lines and it has been demonstrated that is well tolerated [19]. This rare earth exhibits antimicrobial effects at a concentration of 300 μM [20]. Parallel to Gd(III), Dy(III) is also used as contrast medium for Magnetic Resonance Imaging (MRI) [21].

The harmful effects or uranium and other actinides on humans are well known, and their ingesta concluded in various severe illnesses.

3. Description of strip/organic dispersion methodologies

To overcome some of the drawbacks related with the operational method of supported liquid membranes in either their configuration, flat-sheet, hollow fiber and spiral wound, a technology is required which incorporates all the benefits of the supported liquid membranes and the advantages of high efficient emulsion liquid membranes. This result in the development of dispersion membrane-based methodologies, which are described below.

Pseudo-emulsion based membrane strip dispersion (PEMSD) operation is a direct development of flat-sheet supported liquid membrane methodology. PEMSD is performed in a simple permeation cell consisting in two chambers which are separated by a solid membrane support (Fig. 1). One side of the cell contained the feed solution with the metal to be removed from it, whereas the other side contained the system formed by an organic solution and a strip solution. A proper agitation device makes that these two phases are mixing and the strip solution is dispersed into the continuous organic solution, both formed the so-called pseudo-emulsion phase. Due to the hydrophobic nature of the solid support, the organic solution immediately filled the pores of the membrane, and the transport process begins. Once this process is finished, and the agitation is stopped, the pseudo-emulsion phase breaks off and two clear phases are immediately separated: the organic solution and the strip solution now containing the metal. From the latter, the metal must be recovered by the most convenient method.

PEHFSD processing comprises a unique membrane module for extraction and stripping operations, one stirred tank for aqueous feed phase homogenization and one stirred tank for preparation and homogenization of the pseudo-emulsion phase formed by the organic and stripping solutions. These two phases, fed and pseudo-emulsion, are pumping to the module by suitable pumps, where the organic solution wets and fills the microporous wall of the fibers because of their hydrophobic nature. The interface between the aqueous feed and the organic solution was maintained at the pore by applying a higher pressure, normally 0.2 bar, to the feed

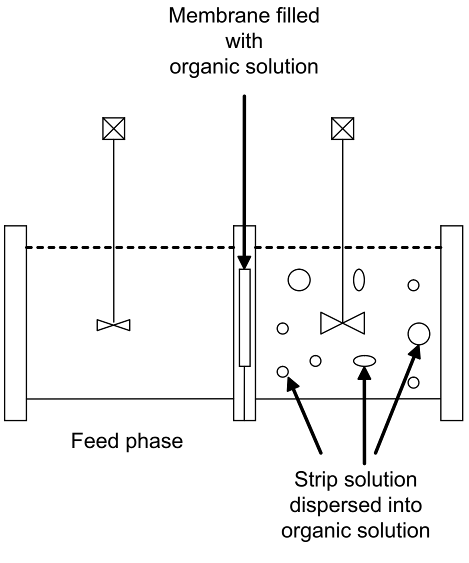

Fig. 1. Schematic view of PEMSD operation.

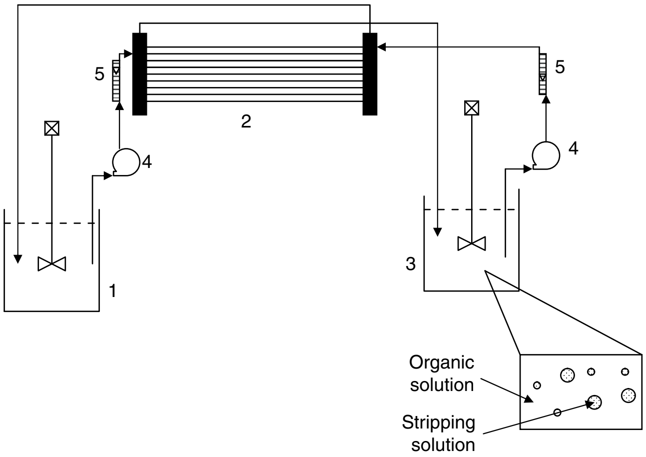

Fig. 2. Schematic view of PEHFSD operation. 1: Feed phase reservoir tank. 2: Hollow fiber module. 3: Pseudo-emulsion phase reservoir tank. 4: Pumps. 5: Flowmeters.

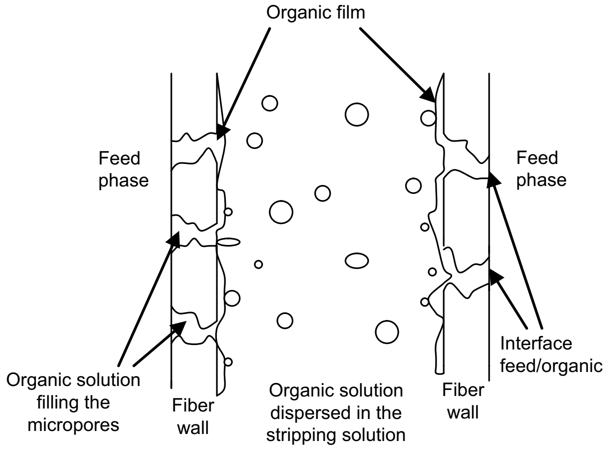

Fig. 3. HFRLM operation concept.

phase than to the pseudo-emulsion phase, but always this differential pressure was kept below the breakthrough pressure. The view of PEHFSD operation using a single contactor and in recirculation mode is shown in Fig. 2. Normally the aqueous feed phase passed through the tube side and the pseudo-emulsion through the shell side of the fibers either in co or counter-current modes. The characteristics of the pseudo-emulsion should be such that it should have clear and fast phase separation when mixing in the tank is stopped: pseudo-emulsion breaks down and the organic and strip solutions separate, ideally after <2–3 min, then the recovery of the separated and concentrated metal can be accomplished from the stripped solution.

HFRLM processing resembles in many ways PEHFSD technology. Also a single membrane module is used for extraction and stripping, and mixing tanks are needed for the pseudo-emulsion preparation and as reservoir tank and for the aqueous solutions not mixed with the organic solution. Here, the stirred mixture of the organic and aqueous feed solutions (or stripping solution) at a high aqueous/organic volume ratio is pumped through the tube side of the fibers, then, the organic droplets of the dispersed organic solution wet and fill the pores of the fibers. The stripping phase (or aqueous feed phase) flows through the shell side of the fibers. A detail of the operation is shown in Fig. 3. The pressure of the two phases are controlled to maintain a positive pressure on the shell side with respect to the tube side, in order to prevent loss of the organic solution into the shell side and allowing the stabilization of the interface between the respective aqueous and organic solutions at the membrane micropores. In this technology, and due to the hydrophobic nature of the fibers, a thin organic film is built-up in the tube side. The shear force due to the flow of the phase in the tube side results in the coalescence and breaking of the organic drops during the flow of the pseudo-emulsion through the tube side of the fibers. Thus, the shear force forced to the formation of drops from the liquid membrane layer, which separated form the layer; at the same time, the organic drops coalesced and form the liquid film. This result in the renewal of the liquid membrane. As in the PEHFSD technology, once the operation is finished, the pseudo-emulsion phase must be immediately separated in two clear solutions and the final recovery of the separated metal can be accomplished from the stripped solution.

SDHLM processing (Fig. 4) is operating on the basis of the different affinities that two metals have for two

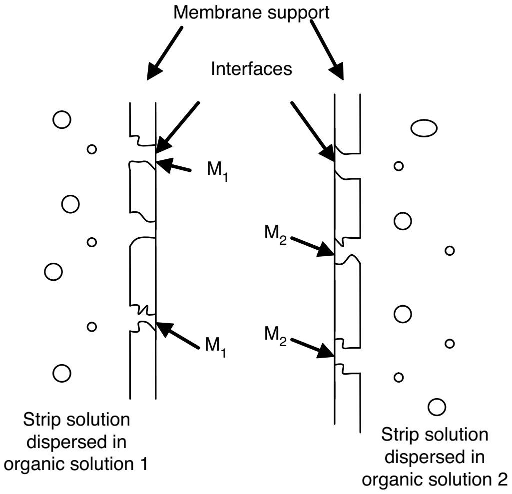

Fig. 4. Schematic view of DSHLM operation.

different extractants or carriers, and thus, they are stripped by the use of two different strippants. In this technology, a three chamber permeation cell may be used, the middle chamber is occupied by the feed solution containing the metals (M_1 and M_2) to be separated, the two-sides chambers contained the respective carriers and strip solutions from which the metals are first transported and then stripped. As in all the techniques described above, the organic solution filled the micropores of the solid supports, and agitation is needed in order to maintain homogeneity in the feed solution and providing mixing for the formation of the pseudo-emulsion phases, finally, the metals must be recovered from the strip solution by the most convenient procedure.

4. Carriers, diluents and modifiers

Extractants used in commercial liquid–liquid extraction operation may be necessarily produced on a large scale basis, and they may not to have the purity of analytical grade reagents. However, due to the operational characteristics of membrane technologies, extractants used in the latter may be of a greater purity and thus of an increase cost.

In liquid membranes technologies, the carrier, or strictly speaking the carrier phase, is mostly the same that those that one can find in liquid–liquid extraction practice and known as organic phase. Thus, the carrier phase is normally composed of a (or mixed) organic extractant, a diluent and sometimes a modifier, another organic compound, to avoid third phase formation mainly in the stripping operation.

The general requirements of organic extractants suitable for their practical use are that they have the next (or as much as possible) characteristics:

i. be relatively inexpensive, but exceptions are considered,
ii. be non-flammable (high flash-point), non-volatile, and (better) non-toxic,
iii. be non-soluble in aqueous solutions (feed and striping),
iv. be very stable under continuous use.

Organic extractants are divided in three main groups, according with the chemical mechanism involved in the extraction of metals:

i. cationic or acidic extractants,
ii. anionic or basic extractants,
iii. neutral or solvation extractants.

Cationic extractants extracted metals via a cationic exchange reaction between hydrogens of the organic molecule and the corresponding metal cation:

$$M^{n+}_{aq} + nHR_{org} \Leftrightarrow R_nM_{org} + nH^{+}_{aq} \quad (1)$$

A special case of acidic extractants are acidic/chelating reagents. These extractants extracted metals by a common cationic exchange reaction but at the same time they contained donor groups capable of forming bidentate complexes with metal ions.

With acidic extractants, metal stripping is performed by the use of a highly acidic aqueous solution which shifts the above equilibrium to the left.

Anionic extractants extracted metal-anionic complexes via an anionic exchange reaction between an anion of the organic molecule and the metal-anionic complex:

$$MX^{n-}_{y_{aq}} + nR_3NH^{+}CL^{-}_{org} \Leftrightarrow \left(R_3NH^{+}\right)_n MX^{n-}_{y_{org}} + nCl^{-}_{aq} \quad (2)$$

In order to extract the metal complex, the amine needed first to be converted to the appropriate amine salt to provide the anion to exchange with the metal species:

$$R_3N_{org} + H^{+}_{aq} + Cl^{-}_{aq} \Leftrightarrow R_3NH^{+}Cl^{-}_{org} \quad (3)$$

That is, the amine extracts a mineral acid to form the amine salt in the organic phase. In this case, metal stripping is carrying out by changing the condition in which the metal-anionic complex is stable.

Neutral extractants extracted metals by the solvation of neutral inorganic molecules by electron–donor atoms contained in the organic compound. Against the two above cases, here is very difficult to generalize a global extraction reaction, whereas some of the extracted species stoichiometries are $UO_2(NO_3)_2 \cdot 2L$, $H_2CdCl_4 \cdot L$, etc., where L represented the respective extractant. Metal stripping is achieved by several ways: changing the oxidation state of the metal, varying the ionic strength of the aqueous solution, etc.

Considering them a separate class of extractants, are ionic liquids. Ionic liquids are liquids that are composed entirely of ions, thus, they are similar to the ionic melts that it is produced by heating metallic salts, that is, NaCl, to high temperatures. Ionic liquids that are suitable for separation processes are in fact, ionic media resulting from combinations of organic cations and various anions that may be liquid at temperatures below 100°C, with properties such as high thermal stability, non-flammable products, negligible vapour-pressure, etc. Common formulation of these class of extractants rely on pyridinium or imidazollium cations, whereas common anion moieties are based in $[PF_6]^-$ (hexafluorophosphate), $[BF_4]^-$ (tetrafluoroborate), $[NO_3]^-$ (nitrate ion), $[SO_4]^{2-}$ (sulphate ion), $[Cl]^-$ (chloride ion), $[OTf]^-$ (trifluoromethylsulfonate), etc.

However, until date, very little use had been done of these ionic liquids to extract metals by the use of the dispersion membranes technologies considering in this chapter. In fact, there are only two: Cyphos IL101 (a quaterrnary ammonium phosphonium salt) and the quaternary ammonium salt derived from the reaction of sulphuric acid with the primary amine Primene JMT, and formulated as $[PJMTH^+]_2[SO_4]^{2-}$, however, quaternary ammonium salts and the product obtained by the reaction of the tertiary amine Hostarex A327 and hydrochloric acid, can be also considered as ionic liquids.

Table 1 summarized carriers commonly used in dispersion membrane technologies, for separation of metals from liquid effluents, grouped into the classes given above.

As it has been said, the diluent also is a part of the organic phase or carrier phase. The term diluent refers to the organic liquid in which the extractant (and the modifier) are dissolved to form the carrier phase, and normally, the diluent is the major component of this carrier phase. The general requirements of a diluent are basically the same that those of the extractants summarized above and the reasons of using such a diluent in the make-up of a given carrier solution may be stated as:

i. to provide a concentration of the extractant to suit a particular operational requirement, thus reducing the extractant inventory in the process,
ii. decreasing the viscosity of the extractant, and thus, reducing the possibilities of formation of stable emulsion in the respective reservoir tank.

At first instance, diluents may be an inert part of the organic phase, but in the practice there are many examples which demonstrated the influence that these diluents have on the transport of metals. Then, the choice of a proper diluent for a particular process cannot be predicted easily and it is better done after experimental work has been carried out on the system.

The formation of a third phase or two organic phases after phase separation is generally avoid by the addition of an organic compound, named modifier, to the organic solution. This third phase is an organic phase with a density intermediate between the organic solution and the aqueous phase, and results from the various equilibria and solubility problems associated with a given system. In any case, the formation of a third phase simply invalidated the system for practical use, and its presence may be overcome by changing the diluent (normally aliphatics to aromatics), or by adding the modifier to the organic solution.

Though a priori there is no any preference to use any organic compound in this role, in practice, the most common used modifiers are alcohols and TBP (tri-*n*-butyl phosphate). On the other hand, the amount of modifier to be added to the organic solution is better

Table 1
Selected carriers used in dispersion membrane technologies

Type	Active substance	Trade name
Acid	di(2-ethylhexyl) phosphoric acid	D2EHPA, DP-8R
Acid	bis(2,4,4-trimethylpenthyl) phosphinic acid	Cyanex 272
Acid	2-ethylhexyl phosphonic acid-mono-2-ethylhexyl ester	PC-88A
Acid	1-phenyl-3-methyl-4-benzoyl-pyrazolone -5	PMBP
Acid	mono(2-ethylhexyl) 2-ethylhexyl phosphonate	HEH(EHP)
Acid/chelating	2-hydroxy-5-nonylbenzaldehyde oxime	Acorga M5640
Acid/chelating	2-hydroxy-5-dodecylbenzaldehyde oxime/ 2-hydroxy-5-nonylacetophenone oxime	LIX 984 N
Basic	tri-*n*-octyl amine	TOA, Alamine 336
Basic	tri-*n*-octyl/tri-*n*-decyl amine	Hostarex A327
Basic	tri-*n*-octylmethyl ammonium chloride	TOMACl
Solvation	tri-*n*-butyl phosphate	TBP
Solvation	tri-*n*-octylphosphine oxide	TOPO
Solvation	mixture of phosphine oxides	Cyanex 923
Ionic liquid	(trihexyl-tetradecyl) phosphonium chloride	Cyphos IL101
Ionic liquid	terc-alkyl(C_{18}–C_{22})hydrogen ammonium sulphate	$(PJMTH^+)_2(SO_4^{2-})$
Ion pair	*N*,*N*′-bis(2-ethylhexyl) guanidine	LIX 79

experimentally determined, whereas the properties of such compounds may be the same that those described by the extractants or carriers.

5. Types of transport in membrane technologies

In order to explain the transport of a given metal o metal species across the membrane, two concepts may be defined: coupled transport and facilitated transport.

In coupled transport, the transport of the target metal species is coupled to the transport of another species which acts as the driving force for the transport of the metallic one, whereas in facilitated transport, the carrier reacts with the target species facilitating the transport of this across the membrane. Most commonly the transport of the target species is against its concentration gradient. Thus, in the membrane technologies considered in this chapter, the above two concepts joined and the transport of the metals is related to a facilitated coupled transport.

Again, two new concepts may be defined: facilitated coupled co-transport and facilitated coupled counter-transport, which are normally associated with the type of extractant presented in the organic solution.

For basic and solvation extractants, metals are transported across the membrane through a facilitated coupled co-transport mechanism (Fig. 5). The target species M^- and the counter-ion C^+ react with the carrier L, to form the neutral species MCL that diffuses across the membrane support and the organic solution to the stripping environment where due to the different chemical conditions, the species M^- and C^+ are released to the strip solution and the carrier is regenerated. Thus, both M^- and C^+ diffuse in the same direction.

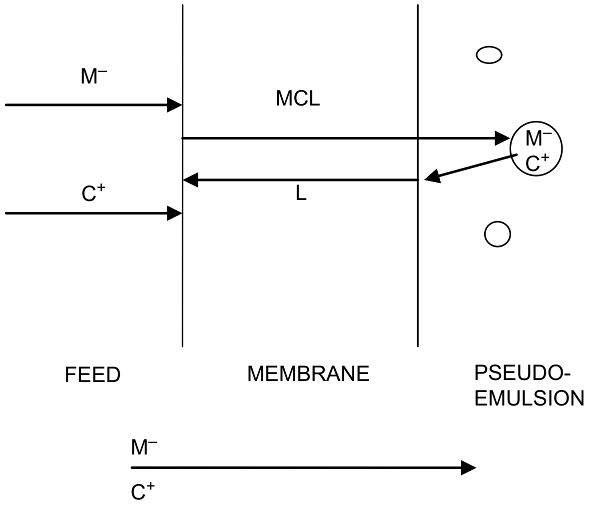

Fig. 5. Co-transport mechanism. L = solvation extractant.

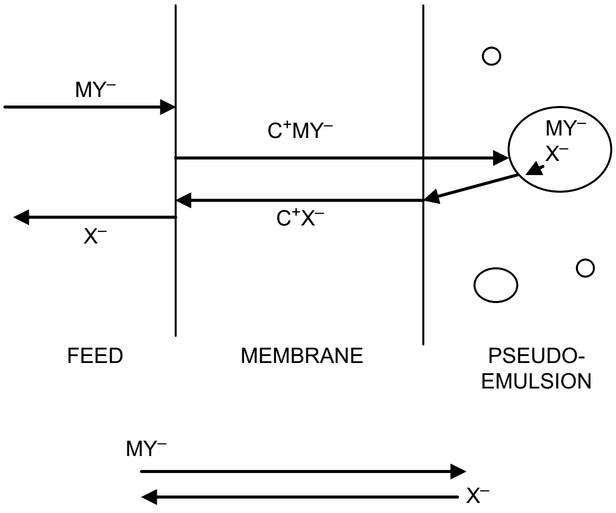

Fig. 6. Counter-transport mechanism. C^+X^-: quaternary organic salt.

In the case of acidic, acidic/chelating and quaternary organic salts extractants, the facilitated coupled counter-transport mechanism (Fig. 6) is the one that represented the behaviour of such carriers. Here, the metal target species MY^- reacts with the carrier C^+X^- to form the organic C^+MY^- species, releasing the counter X^- ion to the feed phase, at the same time the new organic species diffuses through the membrane to the strip solution interface where the carrier is regenerated and the metal is released into the strip solution. MY^- and X^- diffuse in opposite directions across the membrane.

6. Modelling dispersion membrane technologies

Various approaches to the mathematical modeling of liquid membrane separation processes in hollow fiber contactors are considered [22]. Besides the simplified model described elsewhere for flat-sheet configuration [23], in hollow fiber modules two different approaches are commonly considered to relate the interfacial concentrations:

i. diffusional-kinetic regime, in which the chemical reaction of the extraction process is considered to be fast and, thus, the equilibrium is reached instantaneously. The mass transport resistances only influenced the global rate of the transport process,
ii. mixed-kinetic regime, in this approach the chemical reaction of the extraction process is not fast and thus, the global rate of the process depends either of the reaction kinetics and the mass transport.

In case (i), the overall mass transfer coefficient is related to the individual mass transfer resistances by:

$$\frac{1}{K} = \frac{1}{k_i} + \frac{r_i}{r_{lm} K_m} + \frac{r_i}{r_o k_o} \tag{4}$$

where k_i, and k_o are the interfacial coefficients corresponding to the inner and outer aqueous boundary layers; K_m is the overall membrane mass transfer coefficient or membrane permeability; r_i, r_o and r_{lm} are the hollow fiber inner, outer and log mean radius, respectively. The membrane permeability is related to the distribution coefficient (D) of the extraction process for a given system, thus:

$$K_m = D \cdot k_m \tag{5}$$

where k_m is the membrane mass transfer coefficient.

On the other hand and when the reaction is instantaneous on the stripping side, the contribution of the outer aqueous solution, third term in the right hand side of Eq. (4), can be removed from this equation.

In case (ii), the derived equation which related the overall mass transfer coefficient or the overall mass transfer resistance with the individual mass transfer resistances is given by:

$$\frac{1}{K} = \frac{1}{k_f} + \frac{1}{k_i} + \frac{d_i}{d_{lm} k_m D} + \frac{d_i}{d_o k_s D_2} \tag{6}$$

where d_i, d_o and d_{lm} are the hollow fiber inner, outer and log mean diameters, respectively; D_2 is the distribution coefficient of the stripping process. The first term on the right-hand side of Eq. (6) represents the resistance due to the chemical reaction, the second term indicates the mass transfer resistance in the feed phase, the third term denotes the membrane resistance, and the fourth term is the resistance due to the organic solution.

Generally, the distribution coefficient appears in the membrane resistance, because the organic solution wets the hydrophobic membrane support but water does not.

7. Applications of strip/organic dispersion methodologies

PEMSD processing was used to investigate the transport of Zn^{2+} as a function of several variables such as fluxes, membrane composition and pH of the source solution [24]. The carrier solution investigated was D2EHPA dissolved in kerosene, whereas the strip solution was of sulphuric acid. The transport of zinc(II) ions was coupled to the counter-transport of protons from the strip to the feed solution. The optimum value of pH in the feed phase for separation of Zn^{2+} and Cu^{2+} is 2.0–2.5, with recoveries in the strip phase of 75% and 17% for zinc(II) and copper(II), respectively, after 6 h operation. In this system, metal permeation coefficients increased with the increase of the circulating feed solution flux.

Also based on zinc(II) transport, it was investigate the recovery of this element from hot-dip galvanizing effluents [25]. These effluents come from a number of stages such as washing, pickling and galvanizing steps, and besides zinc, they may contain a number of elements such as iron, manganese, chromium, etc., the pH value of such effluents are in the 0 range. The technology used to investigate zinc transport was PEHFSD, using undiluted TBP as carrier phase and service water as stripping solution. It was concluded that the mass transport was dominated by the resistance in the fiber and in the organic phase boundary layer and that it is feasible the reuse of the zinc-bearing strip solution to the process. Moreover, it is proposed that the extraction and strip reactions responded to the next equilibrium:

$$ZnCl_{2aq} + 2HCl_{aq} + 4TBP_{org} \Leftrightarrow ZnCl_2 \cdot 2HCl \cdot 4TBP_{org} \tag{7}$$

Extraction is carrying out shifting the equilibrium to the right and stripping to the left. In the above equation, aq and org subscripts refereed to the respective aqueous and organic solutions.

The separation of Zn^{2+} and Fe^{3+} from Cr(III) spent passivation baths used in the galvanic industry had been investigated by the use of PEHFSD technique and Cyanex 272 (phosphinic acid) as ionophore [26]. The investigation was carried out on real solutions of pH in the 2.1 range. However, zinc(II) extraction kinetics increases when the pH of the solution increases from 2.1 to 3.0, furthermore, the ratio among initial Zn(II) and Cr(III) mass-transfer rates reveals that the selective Zn^{2+}/Cr^{3+} separation is maximized at pH 2.5. Also, it is observed that with respect to zinc transport, the higher the carrier concentration is, the faster the extraction kinetics are. Sulphuric acid solutions are the strippant of choice for the system.

The transport of Cd(II) from hydrochloric acid media was investigated with PEMSD technique [27]. In this study, tri-*n*-octylamine/secondary alcohol/kerosene was the organic solution, whereas CH_3COONH_4 solution was the strippant. In this system, the use of the alcohol as modifier is probably due to avoid third phase formation. Maximum metal flux was reached at 0.1 M HCl concentration in the feed phase, also the metal flux increases continuously as the carrier concentration increases from 0.1 mol l^{-1} to 0.4 mol l^{-1}. Investigations carried out on binary solutions showed that the transport of Cd(II) is more efficient than that of Zn(II). The technology is compared against conventional supported liquid membrane and emulsion liquid membrane technologies. It is concluded that PEMSD has several advantages over the other two membranes procedures including increased membrane stability, improved flux, improved recovery of target species concentration, no usage of high active surfactant and demulsification device, and finally, but not the least important, reduced costs.

Cadmium(II) and CN^- ions transport was investigate by the use of PEMSD methodology with a double carrier (trialkyl-phosphine oxide and D2EHPA) membrane phase, alkaline stripping solution and weak acidic feed phase [28]. The feed solution simulated an electroplating rinse wastewater. Cyanide(I) ions are transported more faster from the feed phase to the strip solution than cadmium(II) when the organic solution only contains the phosphine oxide, it is necessary to add D2EHPA to the organic solution in order to reach the same transport rate for both solutes. The alkaline strip solution containing the concentrated $Cd(CN)_4^{2-}$ species could be again used in the electroplating process. The analysis of mass transfer resistances indicates that the mass transfer resistance due to the membrane phase diffusion is dominant in the overall mass transfer process.

Cadmium(II) transport was also investigated using the phosphine oxide Cyanex 923 dissolved in an aromatic diluent and the PEMSD technique from HCl feed solutions [29], whereas the stripping solutions was water. A model that describes the transport process is derived, consisting of diffusion through the feed aqueous diffusion layer, a fast interfacial chemical reaction and diffusion across the membrane. In this investigation it was shown that cadmium(II) is transported preferably to copper(II) and chromium(VI) but not to iron(III) and zinc(II). On the other hand, permeation coefficients values for Cyanex 923 are similar than these obtained with a quaternary ammonium salt (Aliquat 336) and a tertiary amine (Hostarex A327) and far greater than in the case of secondary (Amberlite LA2) and primary (Primene 81R) amines and a phosphoric ester (TBP). Table 2 showed the experimental P values obtained from this investigation using various carrier phases.

Table 2
Transport of Cd(II) (0.05 g l^{-1}) from 5 M HCl feed solution using various carriers

Carrier (20% v/v in Solvesso 100)	$P \times 10^3$, cm s^{-1}
Cyanex 923	3.0
Aliquat 336	3.0
Amberlite LA2	1.3
Tri-*n*-butyl phosphate	0.97
Primene 81R	0.09
Hostarex A327	2.8

The transport of this toxic element was also described using the same Cyanex 923 extractant and the PEHFSD technology [30]. Results concluded that it is possible to use this technology for separation/recovery of Cd(II) from neutral and/or acidic chloride medium and water as stripping agent. However, metal removal from the feed solution improved when the acidity of this solution increased from 0 to 1 M HCl (20% to >90% after 100 min operation, respectively).

The recovery of chromate anions from polluted ground waters by means of PEHFSD that used the tertiary amine Alamine 336 as selective extractant and NaOH as stripping solution was investigated [31]. Results showed that, in relation with the extraction process, the pseudo-steady state of the system is reached quickly, and the inlet chromium concentration of 0.5 g l^{-1} is reduced to 7.8×10^{-4} g l^{-1} at the module outlet in one pass across the module, being the residence time of <1 min. Chromium(VI) can be concentrated in the alkaline strip solution by a concentrating factor of 18,700.

Chromium(VI) is recovered from HCl solutions using the PEMSD technology [32]. In this case, the tertiary amine Hostarex A327 dissolved in cumene is used as carrier solution, whereas NaOH solutions formed the strippant. Though not described as such in the paper, probably the extractant for chromium(VI) was the ionic liquid $R_3NH^+Cl^-$ first formed by reaction of the amine with the hydrochloric acid which is present in the feed solution. Chromium(VI) is transported selectively to the presence of other metals, Mn(VII), Fe(III), Ni(II), Cu(II) and Zn(II), if present in the feed phase.

Though chromium(III) is not as toxic as chromium(VI), the possibility of chromium(III) oxidation to chromium(VI) is a potential hazard which claims the removal of Cr(III) from effluents a primary target. Thus, the transport of this element using PEHFSD technology was also investigated [33]. In this investigation, tryoctylmethylammonium chloride (TOMACl) dissolved in *n*-decane was used as carrier solution, which also contained *n*-decanol as modifier to prevent third phase formation in the organic solution, since the strip solution was of 0.5 M sulphuric acid. It is worth to note here, that in this investigation the carrier used is an ionic liquid, though in the paper it was not described as such. The process is feasible for the separation of chromium(III) from alkaline solutions and further concentration of the element in the acidic strip solution. It is also concluded, that the rate-controlling step for metal transport is membrane diffusion.

Back to chromium(VI), three more investigations used dispersion membrane technologies were developed in order to remove this pollutant from aqueous solutions.

HFRLM operation was used to investigate the transport of Cr(VI) from acidic dilute solution and

TBP diluted in kerosene as mobile carrier [34]. In this investigation, the organic solution was dispersed into the NaOH stripping solution. The pseudo-emulsion phase flows through the tube side of the fibers. More than 99.9% of chromium(VI) is removed from the feed phase, whereas the concentration factor in the stripping solution is larger than 25. A resistance-in-series model for mass transfer process was derived in which the overall mass transfer coefficient (K) is a function of three individual mass transfer coefficients, thus, K is expressed as:

$$\frac{1}{K}=\frac{1}{k_\mathrm{i}}+\frac{1}{mk_\mathrm{m}}+\frac{1}{mm_2k_\mathrm{s}} \tag{8}$$

where k_i, k_m and k_s are the individual mass transfer coefficients of the feed, membrane and stripping phases, respectively; m and m_2 are the respective metal distribution coefficients for extraction and stripping. The model gives good prediction over a wide range of experimental conditions.

Cyanex 923 as carrier and PEHFSD technique were used to investigate the transport of Cr(VI) from HCl (0.5–1.5 M) solutions and using hydrazine sulphate solutions as strippants. Conclusions derived from this investigation indicated that the removal of Cr(VI) is effective when this membrane technology is coupled to the use of carrier solutions of Cyanex 923 in kerosene, whereas hydrazine sulphate solutions can be used as effective strippants and thus reducing Cr(VI) to the less toxic form Cr(III) and that Cr(VI) is separated from Fe(II), Cu(II), Ni(II) and Zn(II) in HCl solutions [35]. In this system, resistance due to the membrane is dominant under the experimental conditions used in the investigation.

A novel carrier such as CYPHOS IL101 (quaternary phosphonium chloride) was used to study the transport of Cr(VI) also from hydrochloric acid solutions [36]. As it is described above, CYPHOS IL101 is an ionic liquid, being its performance in the carrier phase role first-time studied by means of the pseudo-emulsion membrane strip dispersion technology. Under given experimental conditions of initial Cr(VI) and HCl concentrations in the feed phase of 0.01 g l^{-1} and 0.01 M, respectively, and carrier concentration of 10% v/v CYPHOS IL101 in cumene, metal removal from the feed solution exceeding 95% is regularly achieved, whereas recoveries in the 60% range are found in the strip alkaline solution. From experimental data, it can be inferred that the rate-controlling step is due to the feed phase at low metal and HCl concentrations in the feed phase, resistance due to the membrane is predominant at higher Cr(VI) and HCl concentrations in the feed phase and at all (1–10% v/v) carrier concentrations.

Rare earths processing is become more interesting due to the use that these elements have and will have in 21st century technologies. Dispersion membrane technologies are using in the efficient and low-cost removal of these valuable metals. The transport of thulium(III) using PEMSD technique and a dispersed solution of HCl in an organic solution containing PC-88A (2-ethyl hexyl phosphonic acid-mono-2-ethyl hexyl ester) as carrier phase was investigated [37]. Optimum feed solution pH value for metal transport is around 5.1 and two kinetic equations were derived to describe the transport of Tm(III) across the membrane. The transport is related to a counter-transport mechanism in which the difference in proton concentrations between the near neutral feed solution and the highly acidic strip solution is the driving force for thulium transport.

Dysprosium(III) is another rare earth which transport has been investigated using the same membrane technology, carrier and strip solution than these described above for thulium [38]. Basically, the results derived from this investigation are the same than those derived for Tm(III). For the kinetic equations derived for both elements:

$$P=\frac{1}{A+B\left[\mathrm{H}^+\right]^3} \tag{9}$$

$$P=\frac{1}{C+D\left[\mathrm{HR}\right]^{-3}} \tag{10}$$

the values of the coefficients A, B, C and D are summarized in Table 3. In Eq. (9), the permeation coefficient P is expressed as a function of the proton concentration in the feed phase, whereas in Eq. (10), P is a function of the initial carrier concentration in the organic solution.

The pseudo-emulsion phase formed by the mixture of Acorga M5640 (oxime derivative) and DP-8R (organophosphoric acid) extractants and 1 M sulphuric acid was evaluated to investigate the transport of Ni(II) in PEHFSD technology [39]. From the various experimental variables studied, it is concluded that maximum nickel permeation is achieved at moderate acidic (4.0–5.0) pH values in the feed phase. A limiting value of

Table 3
Values of the coefficients in Eqs. (9) and (10) for Tm(III) and Dy(III) transport

Element	*A*	*B*	*C*	*D*
Tm(III)	3.1565×10^4	4.098×10^{14}	3.16×10^4	1.518
Dy(III)	3.1946×10^4	4.834×10^{16}	3.19×10^4	1.510

5.7×10^{-4} cm s^{-1} for permeability is found, being the transport process controlled by the diffusion in the feed film, though membrane diffusion becomes dominant at low feed pH and low carrier concentrations in the organic solution. The system is far to be highly selective for this metal in the presence of Co(II), Fe(III) and Cr(III) in the feed solution.

By the reaction of the primary amine Primene JMT dissolved in *n*-decane and sulphuric acid as stripping solution, the ionic liquid $(PJMTH^+)_2(SO_4^{2-})$ was formed in situ in the pseudo-emulsion phase, and this ionic liquid was used as mobile carrier to investigate the transport of iron(III) using PEHFSD technology [40]. The organic solution also contained *n*-decanol to prevent the formation of the undesiderable third phase. Results indicated that iron(III) is removed efficiently from acidic feed solutions and that the interfacial mass transfer resistances due to extraction and stripping reactions are dominant in the transport process. The technology was proved against other membrane operation modes, and the results shown in Table 4 indicated that iron(III) transport is better in the case of PEHFSD technology.

Since iron regularly appeared in many hydrometallurgical processes and liquid effluents, that is, pickling liquors and rinse waters, dispersion membrane technologies may be a serious challenge to consider in the elimination of this element from the corresponding solution, though it is apparent that the membrane community, until now, has not shown a wide interest in applying them in this role.

HFRLM technology was used to investigate the transport of copper(II) using acidic and chelating extractants. In the case of acidic extractants, D2EHPA was the selected reagent and the influence of several variables on copper extraction were investigated using dispersion of the organic solution into the feed [41] or the stripping [42] solution. Modelization of mass transfer was also derived from both operational modes. Using this same metal-carrier system, it was compared the performance of HFRLM and hollow fiber supported liquid membrane configurations [43]. The former technology being more stable than the latter, moreover, HFRLM process had a higher overall mass transfer coefficient than that of the supported liquid membrane configuration ($K = 8 \times 10^{-6}$ m s^{-1} against 6×10^{-6} m s^{-1}), this is explain in terms that the renewal effect of the liquid membrane layer reduces the mass transfer resistance of the tube side.

Table 4
Iron(III) transport using different hollow fiber operation modes

Membrane technology	K, cm s^{-1}
Pseudo-emulsion hollow fiber with strip dispersion	1.2×10^{-4}
Hollow fiber renewal liquid membrane	7.5×10^{-5}
Hollow fiber supported liquid membrane	8.6×10^{-5}

Copper(II) can be successfully transported into a HCl stripping solution from a feed phase of pH 3–4 by PEMSD technology containing PMBP (1-phenyl-3-methyl-4-benzoyl-pyrazolone-5) dissolved in xylene [44]. It is concluded that the use of this technology has various advantages over supported liquid membrane and emulsion liquid membrane techniques, due to increased of membrane stability, improved flux, improved recovery of target species concentration, no use of high active surfactant and demulsification device and reduced costs. Copper(II) transport is related to a facilitated coupled counter-transport mechanism.

LIX 984N chelating reagent was the selected extractant to investigate the transport of copper(II) from feed solutions of pH greater than 3 to a strip solution of near 2 M sulphuric acid [45]. In this investigation, the stirred mixture of dispersed organic solution and stripping solution at low organic/strip volume ratio was pumped through the tube side of the fibers, consequently the feed solution flows through the shell side of the membrane fibers. The transport of copper from the feed to the organic and then to the strip solution is represented by the next reaction:

$$Cu^{2+}_{aq} + 2HR_{org} \Leftrightarrow R_2Cu_{org} + 2H^{+}_{aq} \quad (11)$$

by shifting the equilibrium to the right copper is transported from the feed to the organic solution and when the equilibrium is shifted to the left copper is stripped and the carrier is regenerated. Here, the driving force for metal transport is the difference in acidity between the feed (low) and the strip (high) solutions. A mathematical model to model metal transport is also derived, showing the model a good agreement with experimental data.

The transport of copper(II) from binary [46] and tertiary [47] feed solutions was also described in the literature. In the case of a binary solution of Cu(II) and Co(II), LIX 984N was first used to remove copper from the feed solution at a pH value of around 2.5, then Cyanex 272 (phosphinic acid) was used as carrier to remove Co^{2+} from the copper-free feed solution, but adjusting the pH value to around 7.5. In both cases, the organic solution was dispersed into the strip solution of 2 M sulphuric acid for copper or 0.5 M sulphuric acid for cobalt. A mathematical model for the transport of both metals through the fibers was developed by consideration of the influence of the renewal process of liquid membrane, the diffusion across the membrane phase and the diffusion across feed aqueous boundary layer flowing through the shell side.

SDHLM operation was used to investigate the transport of copper, zinc and cobalt from a sulphate feed solution of pH 2. In the case of copper, the carrier was Acorga M5640 (2-hydroxy-5-nonylbenzaldehyde oxime), whereas in the case of zinc, HEH(EHP) (mono(2-ethylhexyl) 2-ethylhexyl phosphonate was the selected extractant. With respect to the dispersed strip solutions, of the one used for copper was of 3 M HCl and the corresponding to zinc was of 2 M sulphuric acid. Typical experimental data showed that copper and zinc are extracted in percentages around 97% and 92%, respectively, whereas recoveries in the strip solutions were around 90% for zinc and slightly higher for copper. In the case of copper, the mass transfer resistance is controlled by the diffusion in the aqueous boundary layer and the diffusion in the membrane phase, in the case of zinc, resistance is controlled by the diffusion in the membrane phase. Obviously, cobalt(II) remained unextracted in the feed solution.

The transport of gold(I) from alkaline cyanide solutions had been also investigated using PEHFSD technique [48,49]. As organic solution, LIX 79 (*N*,*N*-bis (2-ethylhexyl) guanidine) dissolved in *n*-heptane was used, whereas NaOH solutions were employed as strippant for gold. The transport of gold(I) from feed solutions of pH around 10.5 is related to an ion pair mechanism:

$$H^+_{aq} + Au(CN)^-_{2_{aq}} + R_{org} \Leftrightarrow HAu(CN)_{2R_{org}} \qquad (12)$$

where R represented to the extractant molecule. In terms of membrane technologies, the transport of the precious metal is associated to a co-transport mechanism. A model for the transport of gold(I)-cyanide complex in the hollow fiber device, when operating in the recycling mode, had been developed for this system. This model consists in four equations describing:

i. the change in the precious metal concentration in the feed and stripping solutions when both are flowing in the contactor, and
ii. the change in gold(I) concentration in the feed and stripping (pseudo-emulsion) reservoir tanks, in which the aqueous solutions are continuously recirculated and perfectly mixed.

On the other hand, gold(I) cyanide complex is transported preferably at alkaline pH values to other metal-cyanide complexes which are normally associated with gold in many raw materials. Thus, gold(I) cyanide is selectively transported to $Zn(CN)_4^{2-}$, $Ag(CN)_2^-$, $Ni(CN)_4^{2-}$, $Fe(CN)_4^{6-}$ and $Cu(CN)_4^{3-}$ complexes, the separation factor gold/metal varies between 61 and 96 for the pairs Au/Zn and Au/Ag, respectively.

Plutonium reconversion in reprocessing plants generated oxalate supernatant during plutonium precipitation by oxalic acid as plutonium oxalate. Recently, it was investigated the transport of U(VI) using PEHFSD technique [50]. The pseudo-emulsion phase consist in a continuous phase of TBP dissolved in *n*-paraffin hydrocarbon and a dispersed solution of 0.01 M nitric acid, whereas the feed solution containing uranium at various nitric acid concentrations. It was found that optimum uranium transport was achieved at 4 M HNO_3 concentration in the feed phase (82% transport after 90 min). It was also investigated the feasibility of direct recovery of UO_2^{2+} from the treated or untreated oxalate supernatant, the term treated supernatant means that the oxalate ions are destroyed by treatment of the solution with $KMnO_4$/H_2O_2. Results showed that the permeation coefficient for treated solution is 51.1×10^{-3} cm s^{-1} and 45.4×10^{-3} cm s^{-1} for the untreated supernatant, this difference being attributable to the interference of oxalate ions in the transport process. The plutonium present in the waste oxalate solution was also transported but stripping from the organic solution it was not possible by the 0.01 M nitric acid solution.

Solvation extractants were used in the recovery of actinides from process effluents [51]. Plutonium (IV) transport from 4 M nitric acid solution was carried out using TBP dissolved in normal paraffin hydrocarbon and PEHFSD technique. The transport proceeds through formation of the $Pu(NO_3)_4 \cdot 2TBP$ neutral complex in the organic solution, whereas stripping is possible using 0.1 M $NH_2OH \cdot HCl$ in 0.3 M nitric acid as strippant.

Americium(III) was extracted using the same technology but using tri-octylphosphine oxide (TOPO) as carrier, again the diluent for the extractant was normal paraffin hydrocarbon. Various experimental variables were investigated, and from a feed acidity of 0.3 M nitric acid, the maximum permeation for the actinide was achieved at 6% w/v carrier in the diluent and 5 M nitric acid as stripping solution, whereas the optimum performance of the system was attained with an organic to aqueous ratio of 0.5.

8. Conclusions

The four dispersion membrane technologies described in this chapter can be considered the most efficient membrane based techniques of separation. They works by the principle of the difference of chemical energy as the driving factor of the process coupled with the chemical reaction of the metal species with the corresponding carrier which facilitates the metal transport from dilute to concentrated solutions. Thus, enrichment and selective separation of targeted species are feasible in one single operation.

Probably, the most relevant features of the various membrane technologies under consideration are:

i. to maintain a constant supply of the organic solution in the micropores of the membrane support, which ensures stable and continuous operation,
ii. the direct and intimate contact of the organic and stripping solutions in the pseudo-emulsion reservoir tank and along the circuit, which provided and additional area for carrying out the stripping operation,
iii. the recovery of the metal of interest is not complicated since the pseudo-emulsion phase breaks-off quickly, typically in a few minutes, separating the organic and stripping solutions in two well defined solutions,
iv. since the operation mode allows to the selective separation and concentration of the metal of interest, the recovery of it becomes facilitated from the stripped solution, and if not and since the volume of this stripped solution is much lesser than that of the feed phase, it is more easy and probably cheaper its storage in the corresponding security dumps.

Though in recent years a number of investigations had been done using these technologies, more research is needed in order to better understand flows in the contactors, improving the materials of construction of the contactors which offered a better range of compatibilities with respect to organic and inorganic compounds, investigation of the dispersion methodologies using multi-elemental solutions and the best, with real solutions from the industry, all the above leading to more reliable scaling-up procedures.

It can be expected that dispersion membrane methodologies will find a lot of practical and, hopefully, industrial applications in the near future. Moreover, if the process will be conducted in a proper manner it could be clearly considered as a Green Chemistry process.

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Symbols

M^{n+}	—	Total analytical metal concentration in the aqueous solution
HR_{org}	—	Cationic extractant in the organic phase
R_nM_{org}	—	Species formed in the organic phase in a cationic exchange reaction
n	—	Stoichiometric number
aq subscript	—	Aqueous solution
org subscript	—	Organic solution
R	—	Alkyl chain
MX^{n-}	—	Metal-anionic complexes in the aqueous solution
$R_3NH^+Cl^-$	—	Anionic extractants—amine salt
$(R_3NH^+)_nMX^{n-}_y$	—	Species formed in the organic phase in an anionic exchange reaction
L	—	Solvation extractant in the organic phase
M^-	—	Target species for transport
C^+	—	Counter-ion
MCL	—	Neutral species formed in the organic phase using a solvation carrier
MY^-	—	Metal target species for transport
C^+X^-	—	Quaternary organic salt extractant in the organic phase
C^+MY	—	Organic species formed in the organic phase using a basic carrier
X^-	—	Counter ion
K	—	Overall mass transfer coefficient
k_i	—	Interfacial coefficient corresponding to the inner aqueous boundary layers
k_o	—	Interfacial coefficient corresponding to the outer aqueous boundary layers
K_m	—	Overall membrane mass transfer coefficient or membrane permeability
r_i	—	Hollow fiber inner radius
r_o	—	Hollow fiber outer radius
r_{lm}	—	Log mean radius
D	—	Distribution coefficient of the extraction process
k_m	—	Membrane mass transfer coefficient
d_i	—	Hollow fiber inner diameter
d_o	—	Hollow fiber outer diameter
d_{lm}	—	Log mean diameter
D_2	—	Distribution coefficient of the stripping process
k_f	—	Interfacial coefficient corresponding to the chemical reaction
k_s	—	Individual mass transfer coefficient of the stripping phases
M	—	Metal distribution coefficients for extraction

m_2 — Metal distribution coefficients for stripping
P — Permeation coefficient
A, B, C and D — Coefficients for Eqs. (9) and (10)

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