



Research Paper

New Challenges and Applications of Supported Liquid Membrane Systems Based on Facilitated Transport in Liquid Phase Separations of Metallic Species

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Article info

Received 2021-08-06
Revised 2021-09-29
Accepted 2021-10-23
Available online 2021-10-23

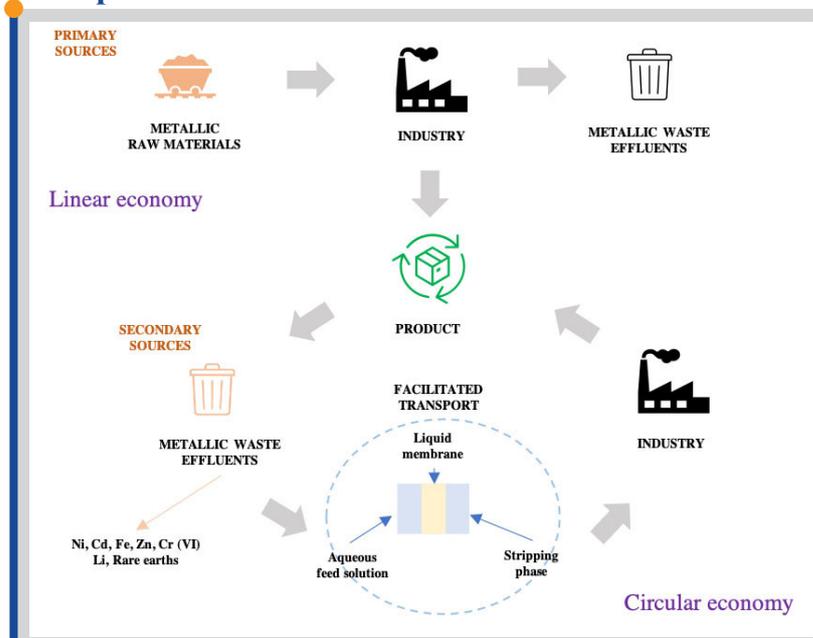
Keywords

Supported liquid membranes (SLM)
Metals
Secondary sources
Recovery
Separation
Circular economy (CE)

Highlights

- Industrial WW are a promising secondary source of metals
- Facilitated transport systems may foster CE at industrial scale
- SLM have been applied to Zn/Fe, Ni/Cd and Cr(VI) recovery
- Li and rare earth recovery still represent a challenge for SLM

Graphical abstract



Abstract

The linear economic model based on “take-make-dispose” has become unsustainable, revealing the necessity of shifting towards a circular economy (CE) approach, in which secondary raw materials play a key role in closing material cycles. In this context, industrial effluents with metallic content, are considered a potential secondary source for these elements, the lack of the availability of the appropriate technology being the main barrier when implementing circular economy principles at industrial scale. In this regard, supported liquid membrane (SLM) systems based on facilitated transport may be decisive. Thus, the objective of this research paper is to show the potential of facilitated transport systems to foster the transition to a more sustainable management of industrial metallic effluents. To accomplish that, three different applications of supported liquid membrane systems in acidic industrial effluents will be presented: a) Zn/Fe separation, b) Ni/Cd separations and c) Removal of hexavalent Cr. Additionally, the recovery and separation of two different critical raw materials, i.e. Li and rare earth elements will be discussed. Although facilitated transport systems have been successfully applied to both, Zn/Fe and Ni/Cd separation, as well as to hexavalent Cr removal, further work should be done for the successful recovery and separation of Li and rare earths with supported liquid membrane systems, especially in terms of selectivity improvement and validation with real industrial effluents.

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1. Introduction

Membrane technology allows the separation of different fluid phases while making the permeation of solutes possible [1]. Membrane processes may be: a) pressure driven, e.g. micro-, ultra- and nanofiltration or reverse osmosis, b) thermal driven like membrane distillation, c) osmotically driven,

e.g. forward osmosis (FO) and d) other types such as supported liquid membranes (SLM) [2].

Among them, SLM systems present several advantages, including the small quantity of extractant required for the process due to its continuous

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regeneration and the possibility of performing the extraction and back-extraction processes at the same time, which lead to a reduction in the initial investment and operational costs of this technique in comparison to other membrane processes [3].

It should be noted that, in SLM systems, the membrane contactor is only used as a physical interface, not presenting any selectivity for the target solute. In these systems, the recovery and/or separation of the target species is based on the facilitated transport principle, i.e. the selection of an appropriate carrier, allows the SLM technique to overcome one of the limitation of conventional membrane systems, which is the opposing relation between permeability and selectivity [4]. In addition, in contrast to other separation processes, and when suitable conditions are applied, SLM systems can be very efficient at low solute concentrations [3].

Based on the above, SLM processes have been increasingly used in the separation and concentration of pollutants or valuable compounds, such as pharmaceutical products or metals [2,5-11].

1.1. Circular economy paradigm

The linear economic model based on “take-make-dispose” has become unsustainable. The increased in raw materials demand and waste generation has led the European Union to foster circular economy as the new alternative economic model [12], which, according to the Ellen MacArthur Foundation, is based on “the principles of designing out waste and pollution, keeping products and materials in use, and regenerating natural systems” [13].

When implementing circular economy in the value chain, production, consumption, waste management and secondary raw materials should be specially considered [14], the central strategy of the European Union being to promote long-lasting products to prevent waste generation [12,15]. However, the current debate regarding the necessity of closing material cycles [15], points out that more effort should be made to recover valuable materials from secondary sources [16]. In this regard, considering that for most metals the potential recycling percentage reaches up to 75%, industrial effluents with metallic content represent a potential secondary source for these elements [14,16-17].

In this context, the availability of the appropriate technology has been identified as a key factor when implementing circular economy principles at industrial scale [18]. Therefore, the objective of this research paper is to point out the potential of SLM systems based on facilitated transport in the transition towards a more sustainable management of industrial waste effluents with metallic content [2,19-20]. For this purpose, several case studies related to the recovery and/or separation of metallic compounds (i.e. hexavalent Cr, Ni/Cd and Fe/Zn) from industrial waste effluents will be presented. Additionally, future challenges of SLM processes, such as the recovery and/or separation of rare earth and Li will be addressed.

2. Facilitated transport systems

2.1. The concept of facilitated transport

Besides considering passive diffusion, one strategy for improving the membrane permeability and/or selectivity in SLM systems consists in the use of a selective carrier [7], capable of complexing with the selected species. This is called facilitated transport. Therefore, mass transport in SLM processes typically involve several steps: a) carrier-species reaction in the feed solution-membrane interface, b) diffusion across the membrane and c) stripping [21]. In addition, if the carrier can couple the flow of two species, allowing the transport of one of them in opposition to its concentration gradient, this mechanism is called coupled transport. A common example of coupled transport would be exchange between metal cations and H⁺ ions by acidic carriers [1].

In SLM systems, flux calculation of the objective species is commonly evaluated disregarding the concentration of this species in the stripping phase [21]. Therefore, the transportation of a target element or compound through the membrane is due to the difference between its concentration in the aqueous feed and membrane phases [1]. Consequently, the driving force for mass transport, follows the Fick’s first law shown in Eq. 1.

$$J_i = -D_i \frac{dC_i}{dx} \quad (1)$$

with J_i being the diffusive mass transport flux of a specific element/compound, D_i being its diffusion coefficient, C_i being its concentration and x the diffusion direction.

Figure 1 schematically illustrates the facilitated transport concept.

Whereas simple facilitated transport occurs in permeation technologies systems and liquid-liquid abstraction of neutral species, when ionic species are present in the feed solution coupled transport takes place to keep the electroneutrality [4]. As Figure 1a shows, in simple facilitated transport the species of interest that are present in the aqueous phase (A) and the carrier (C) react, and their organic complex (AC) diffuses through the membrane and reaches the back-extraction phase, leading to the regeneration of the carrier. On the other hand, two coupled facilitated transport mechanisms may be distinguished: coupled facilitated co-transport and coupled facilitated counter-transport.

As Figure 1b illustrates, in coupled facilitated co-transport the species of interest (A), the ionic species (B) and the carrier (C) form a complex (ABC), which diffuses through the membrane, releasing both A and B species in the stripping phase. On the other hand, the coupled facilitated counter-transport mechanism is more complex. As Figure 1c shows, in this type of transport mechanism the ionic species (B₁) and the carrier (C) form an organic complex (B₁C), which reacts with the species of interest (A), leading to the formation of a different organic complex (AC) and the released of the ionic species (B₁) in the aqueous feed solution. Similarly, the regeneration of the organic complex (AC) occurs by the reaction between this complex and the ionic species (B₂) present in the stripping phase, which form the organic complex (B₂C), releasing the species of interest (A) in the mentioned phase.

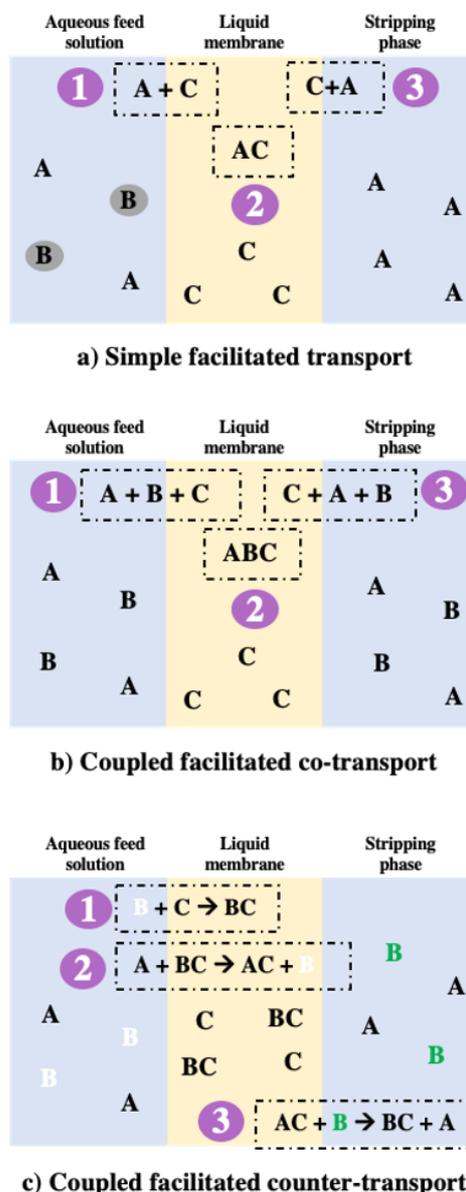


Fig. 1. Illustration of the concepts of simple and coupled facilitated transport.

2.2. The concept of facilitated transport for liquid phase separations

As it was mentioned before, the selection of the appropriate organic phase composition is key to achieve a favorable recovery rate and selectivity [2]. In this regard, carriers can be classified into cation exchangers, both carboxylic and organophosphorus acids, solvating extractants, anionic exchangers and chelating exchangers [22–34]. Among the different facilitated transport mechanisms described in detail in the previous section, the coupled facilitated co-transport mechanism is usual for both anion and solvating carriers (i.e. basic and neutral extractants, respectively), whereas cationic/acidic and ionic exchangers usually follow the coupled facilitated counter-transport mechanism [4]. Table 1 shows the full and brand name and abbreviation of several carriers used in the application of solvent extraction techniques for metal recovery and separation, as well as some examples of the extracted metals with each carrier. Noteworthy, the use of synergetic mixtures as carriers is common in the application of facilitated transport for liquid phase separations. For example, Sulaiman et al. 2018 [35] reported up to 91% and 65% of Ni extraction and recovery, respectively, by using a synergetic mixture consisting of D2EHPA and octanol and sulfuric acid as strippant. Additionally, the selection of the appropriate diluent for the organic phase also represents a key variable in facilitated transport systems. In this regard, diluents such as palm oil has high prospective as a substitute for sustainable diluent in liquid phase separations based on facilitated transport [35–36].

Facilitated transport systems have been widely applied in the recovery/separation of both anionic and cationic species [37–38]. Among the main applications of SLM systems to the recovery of anionic pollutants, two common case studies are the recovery of hexavalent Cr from acidic industrial effluents, in which the predominant hexavalent Cr species is HCrO_4^- [39–41], and the recovery of Zn from spent pickling solutions, in which Zn forms different chlorocomplexes depending on the Zn and chloride concentration and pH of the solution, being ZnCl_4^{2-} the predominant one [8,41]. On the other hand, Ni/Cd separation from concentrated solutions sourcing from the recycling process of Ni/Cd batteries is a common case study in the application of facilitated transport systems to the recovery of cationic pollutants [37].

These applications will be presented in the following subsections.

3. Case studies in metal separation and recovery from industrial wastes

3.1. Membrane contactors for industrial applications: hollow fiber contactors

Despite the advantages of SLM systems against the traditional solvent extraction processes, such as their lower energy and solvent consumption and their well phase separation, their major limitation for industrial application lies in their stability [3,42]. Instability of the membrane may be related to the inconstancy of a carrier inside pores, caused by, for example, pressure gradient, carrier solubility, pore congestion or gel formation, the re-impregnation of the membrane being proposed as one suitable method to enhance membrane stability [42].

Among the available contactors, both hollow fiber supported liquid membranes (HFSLM) and flat sheet supported liquid membranes (FSSLM) are commonly used in the literature [7,43–48]. However, HFSLM systems are preferred for industrial applications mainly due to their higher stability, easiness of application to liquid-liquid systems and higher packing density, which allows the achievement of higher transport rates with respect to

FSSLM systems [2,38,46]. In addition, FSSLM are sometimes used to optimize the conditions for the subsequent HFSLM studies [47].

In addition, hollow fiber (HF) contactors allow minimizing back-mixing effects and loss of extractant [3]. When using these contactors, one phase is retained in the pores of the membrane, where the interface between aqueous and organic streams is placed, avoiding the dispersion from one phase to another, which is also achieved by the application of a higher pressure in the aqueous stream [1] (see Figure 2). If hydrophobic fibers are used, the aqueous and organic solutions flow through the inner and shell sides of the modules, respectively, with the diluted carrier filling the membrane pores. When using hydrophilic fibers, the membrane pores are filled by the aqueous solution. The selection of which phase flows through the different channels of the module, as well as the decision of operating in co-current or counter-current flow is key due to the influence of these variables in the mass transfer coefficients and consequently in the extraction efficiency [2].

In parallel, to overcome the limitation of performing the extraction of the target element and the regeneration of the organic phase in different steps, several HFSLM configurations are usually applied. One approach is the use of two HFSLM modules. This system is named as non-dispersive solvent extraction (NDSX) [1,8]. As Figure 3 shows, in NDSX systems, the feed solution and the back-extraction phase operate in counter-current flow with respect to the organic phase in both modules, whereas the organic phase extracts the target species in the first module and is regenerated in the second. An additional approach by using only one module, would be the emulsion pertraction technique (EPT). As could be observed in Figure 4, in EPT, an emulsion, i.e. a mixture of the organic and back-extraction phases with a selected organic/aqueous volume ratio, flow with a counter-current configuration with respect to the feed solution [1,49]. In this approach, whereas the extraction of the target elements is carried out in the membrane pores, the stripping phase is mixed into the organic phase, forming droplets in which the interface between organic and stripping phase is located, and therefore where the back-extraction process occurs. The performance of EPT is usually limited when the maximum solubility of the target species in the stripping phase is reached [5].

Additional configurations, such as the hollow fiber renewal liquid membrane (HFRLM) process [50], are also found in the literature, showing several advantages with respect to other systems, mainly related to long-term stability and easiness of operation [1]. As could be observed in Figure 5, in HFRLM processes, the contactor is pre-wetted with the organic phase to fully filled the hydrophobic pores of the hollow fibers, while the feed solution and the stripping phases flow, in counter-current configuration, through the different channels of the module. Due to the hydrophobicity of the fibers, a thin organic layer coats the inner surface of the fibers. By this configuration, the organic microdroplets present in the thin organic layer will abandon the surface of the membrane and flow within the aqueous streams, being replaced by the dispersed organic microdroplets that previously abandon the surface of the membrane [1]. This mechanism allows the regeneration of the liquid membrane, which could intensify the mass transfer rate [1,50]. Additional advantages of this configuration are the possibility of working at higher aqueous/organic volume ratios with respect to the previous configurations, allowing the minimization of carrier consumption, or the higher stability of the liquid membrane, possibly due to the elimination of the instability caused by solubility related loss [50–51].

Table 1

Common carriers applied in solvent extraction techniques for metal recovery and/or separation and examples of extracted metals.

Extractant type	Compound	Name or abbreviation	Metals	Ref.	
Cation exchangers	Neodecanoic acid	Versatic 10	Ni, Co, Mn, Li	[22]	
	Carboxylic acids	Sec-octylphenoxy acetic acid	CA-12	Lanthanides	[23]
		Sec-nonylphenoxy acetic acid	CA-100	Y	[24]
		Bis-2-ethylhexyl phosphoric acid	P204, D2EHPA	Sc, Fe, Al, Mn, Zn	[25]
	Organophosphorous acids	2-Ethylhexyl phosphoric acid mono-2-ethylhexyl ester	P507	Sc, Fe, Al	[25]
		Bis-2,4,4-trimethylpentyl phosphinic acid	Cyanex 272	Mn, Zn	[26]
Bis(2,4,4-trimethylpentyl) monothio-phosphinic acid		Cyanex 302	Zn, Mn, Co	[27]	
Bis(2,4,4-trimethylpentyl) dithio-phosphinic acid		Cyanex 301	Ni	[28]	
Di-octylphenyl phosphoric acid		DOPPA	Cu, Co	[29]	
Solvating extractants	Tributylphosphate	TBP	Zn, Mn, Co	[27]	
	Neutral	Di-(1-methylheptyl) methyl phosphate	P350	Light rare earths	[30]
		Triocetylphosphine oxide	Cyanex 921 or 923, TOPO	Li	[31]
		Tetraocetyl-diglycolamide	TODGA	Eu	[32]
Anion exchangers	Basic	Primary amine mixture	N1923	V, Cr	[33]
		N,N diocetyl-octan-1-amine	N235, Alamine 336	Co, Ni	[27]
Chelating exchangers	Heptafluorodimethyloctanedione	HFDOD	Li	[31]	
	Main component: α -acetyl-m-dodecyl acetophenone	LIX 54	Zn	[34]	

AQUEOUS PHASE PRESSURE > ORGANIC PHASE PRESSURE

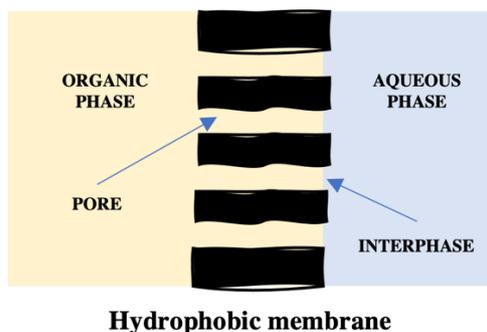


Fig. 2. Structure of a symmetric hydrophobic membrane.

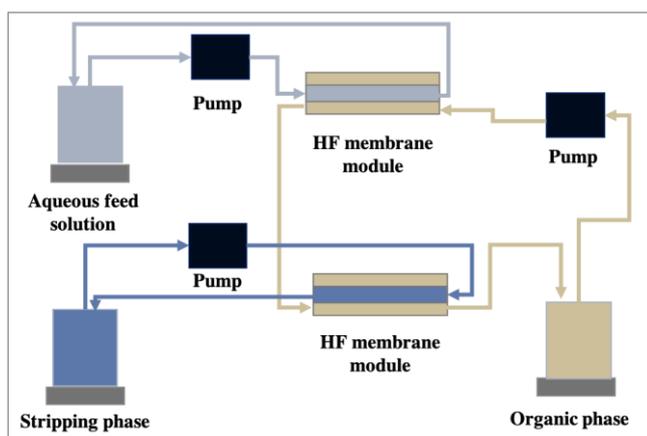


Fig. 3. Set-up for Non-dispersive solvent extraction processes (NDSX).

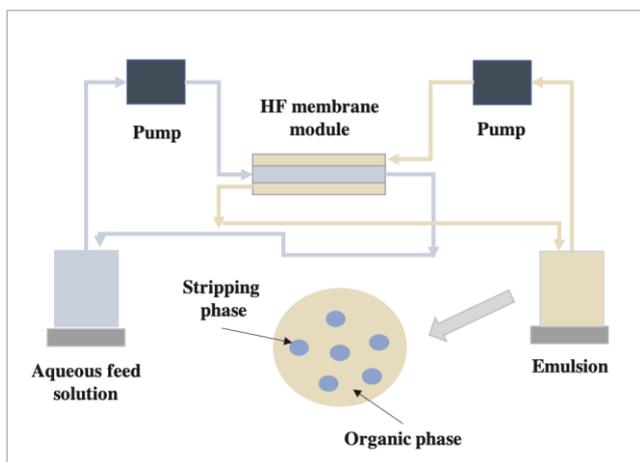


Fig. 4. Set-up for Emulsion Pertraction Technique (EPT).

Despite the several available configurations, the favorable recovery rate and selectivity coupled with its low maintenance, make NDSX systems the most interesting technology for valuable metal recovery, including rare earth elements [2,5,8]. In addition, with respect to the extraction of metals, most studies used HF modules from Liqui-Cel™. These polypropylene (PP)-based modules present around 10000 fibers per module and an area of 1,4 m² (15 cm of membrane length). In this regard, since PP membranes may present limitations in the long-term use, additional hydrophobic materials such as

polyvinylidene fluoride (PVDF), polystyrene (PS), polytetrafluoroethylene (PTFE) or even materials of greater biodegradability (i.e. styrene-butadiene-styrene, SBS) have been investigated [2]. For example, Sulaiman et al. 2019 [52] reported the SLM extraction of Ni by means of a composite membrane support consisting of PVDF and sulfonated poly (ether ether ketone) (SPEEK) using D2EHPA, 1-octanol, refined palm oil and sulfuric acid as extractant, synergist extractant, diluent and strippant, respectively.

3.2. Case study 1: Zn/Fe separations in HCl medium

Hot-dip galvanizing processes with molten Zn generate acidic effluents with high concentrations of both Fe (100-130 g/L) and Zn (20-120 g/L), therefore representing a promising secondary source for these elements [53], which would be of enormous interest for the galvanizing industry, considering Zn primary production to be the major contributor to the environmental impacts caused by this sector [19].

SLM systems have been successfully applied in Zn recovery from spent pickling solutions, acidic solutions (chloride medium, pH≈0) mainly composed of Zn and Fe and minor concentrations of other metals such as Pb, Mn, Al, Cr, Ni and Cd. For example, Samaniego et al. [53] achieved up to 92% Zn extraction and up to 84% of Zn back-extraction from spent pickling effluents by a NDSX system with a solvating extractant (tributyl phosphate, TBP) as a carrier, using kerosene as diluent, and service water as stripping agent. Also, Bringas et al. [5] achieved up to 85% of Zn extraction when using a NDSX system with TBP as carrier and service water as strippant, higher than the 46% of Zn recovery obtained with the same carrier and strippant in EPT configuration, this lower performance being caused by the solubility limitation in the back-extraction phase due to the low volume used in the EPT system in comparison to the NDSX process. Similarly, Carrera et al. [54] was able to validate the possibility of using NDSX and EPT techniques, with TBP as the selective carrier and service water as strippant, to obtain a Zn enriched stripping phase, which could be reused as electrolytic solution due to its low content of Fe, Pb, Ni, Co and Cu. Specifically, the use of the EPT technique allowed the concentration of Zn up to 600 mol/m³, when using a feed solution with a Zn content of 1200 mol/m³ [54]. Furthermore, San Román et al. [46] analyzed the performance of a hybrid membrane process combining an EPT, with an organophosphorous extractant and service water as stripping agent, for the separation of Fe and Zn (concentrations in the feed solution of 1,2 kmol/m³ and 1,6 kmol/m³, respectively) and subsequent diffusion dialysis for the recovery of the acid contained in spent pickling effluents, reaching up to 63% of Zn extraction and up to 29% of Zn back-extraction after 2 h of operation with the EPT.

In addition, Zn recovery from spent pickling acids by the NDSX approach, using the solvating carrier TBP and tap water as stripping agent, has been successfully scaled-up, achieving concentrations up to 55.7 g Zn /L and only 3.2 g Fe/L in the back-extraction phase, without transference of minor metals, therefore providing the purified zinc stripping suitable for being reused by the galvanizing industry [8]. This case study is illustrated in Figure 6a.

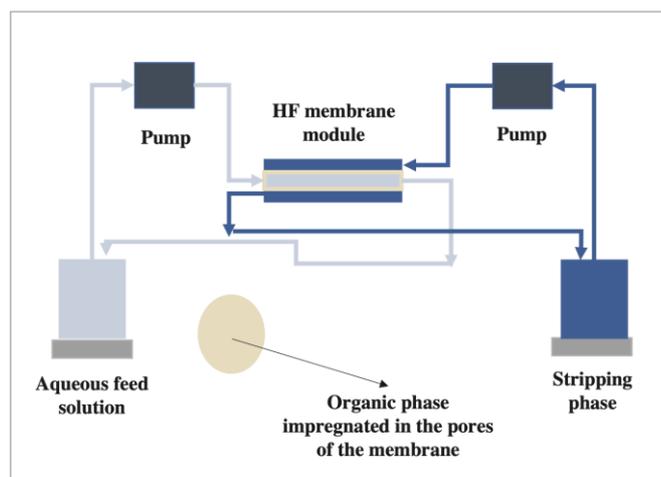


Fig. 5. Set-up for Hollow Fiber Renewal Liquid Membrane (HFRLM).

3.3. Case study 2: Ni and Cd separations in acidic medium

Spent Ni/Cd batteries constitute an interesting secondary source of these metals [22]. In this regard, Galán et al. [55] explored the viability of using a NDSX system with a synergistic organic mixture (i.e. 60% v/v D2EHPA - 10% v/v TBP, in kerosene) and H₂SO₄ as the stripping agent, for Ni/Cd separation from highly concentrated solutions (0.37 M and between 0.37-0.68 M of Cd and Ni, respectively) generated during the processing of spent Ni/Cd batteries. This case study is illustrated in Figure 6b. Under the conditions used in this study, it was possible to obtain a purity of 98.5% for Cd and 93.5% for Ni in the stripping solution and feed solution, respectively. The validation of the kinetic model of the recovery and separation of Ni/Cd from battery leachates with a NDSX technique by using the previously mentioned synergistic mixture was also reported by Ortiz et al. [37], this model including three characteristic parameters, the membrane mass-transport coefficient (K_m) and two equilibrium parameters, which represent the extraction and back-extraction reactions. Additionally, Alonso et al. [56] established the operational conditions to achieve 95% of Cd extraction by using Cyanex 302 and HCl as carrier and back-extraction agent, respectively, therefore demonstrating the viability of NDSX systems in the removal of Cd related to the phosphoric acid produced by the fertilizer industry. In this study, the regeneration of the carrier was developed by a hollow fiber ceramic module due to the acidity of the stripping phase (4 M HCl). Furthermore, Mahmoodi et al. [57] dealt with the Ni-Cd separation from an aqueous sulfate medium using a SLM system with D2EHPA and M2EHPA as carriers, H₂SO₄ as stripping solution and a PTFE film as solid support for the liquid membrane, obtaining up to 83.3% and 0.45% of extraction of Ni and Cd, respectively, when using an aqueous feed pH of 5, a strip pH of 0.5 and 40% (v/v) of the mentioned extractants.

It should be noted that, although the recovery and separation of Ni from acidic medium is presented as an example of a successful application of SLM systems, the sustainable management of metallic industrial effluents with Ni

content relies also in the substitution of petroleum-based diluents with sustainable diluents, such as, for example, palm oil [35-36].

3.4. Case study 3: Hexavalent Cr removal in acidic medium

SLM systems have been successfully applied in the recovery of hexavalent Cr from industrial effluents and polluted groundwaters. For instance, Ortiz et al. [58] were able to achieve quantitative elimination of hexavalent Cr from contaminated waters by using an EPT technique. In this study, illustrated in Figure 6c, the emulsion contained an aqueous sodium hydroxide solution as stripping agent and 10%v Alamine 336-10%v dodecanol-5%v Pluronic L31 in Isopar L, at a volume ratio of 1:4. In this regard, San Román et al. [41] applied a non-linear programming (NLP) model to EPT structure in order to minimize both the concentration of hexavalent Cr for final disposal and the necessary membrane area, while obtaining a concentrated Cr stream suitable for further reuse. The optimum structure, which considered two inlets of the emulsion phase to allow a better use of the available fiber length and an optimum residence time for the different phases, resulted in a configuration with parallel modules for the aqueous phase and a set of in-series modules for the emulsion with remarkable reduction of the necessary membrane area in comparison to conventional EPT systems. EPT systems, using Alamine 336 and NaOH, as carrier and back-extraction agent, respectively, were also validated for their application in polluted waters with low Cr concentrations (i.e. up to 15.4 mol/m³), even in presence of other anionic species (e.g. Cl⁻ and SO₄²⁻) [39-41]. Apart from EPT systems, FSSLM was also studied for the elimination of hexavalent Cr from chloride solutions [59]. In this case, both Cyanex 921 and Cyanex 923, seemed to achieve higher extractions of hexavalent Cr with respect to other neutral carriers, e.g TBP. Additionally, Onac et al. [60] demonstrated the great selectivity of a calix[4]arene diluted in dichloromethane employed as carrier in a SLM system with a polymeric membrane support, obtaining an hexavalent Cr recovery factor up to 88.1%.

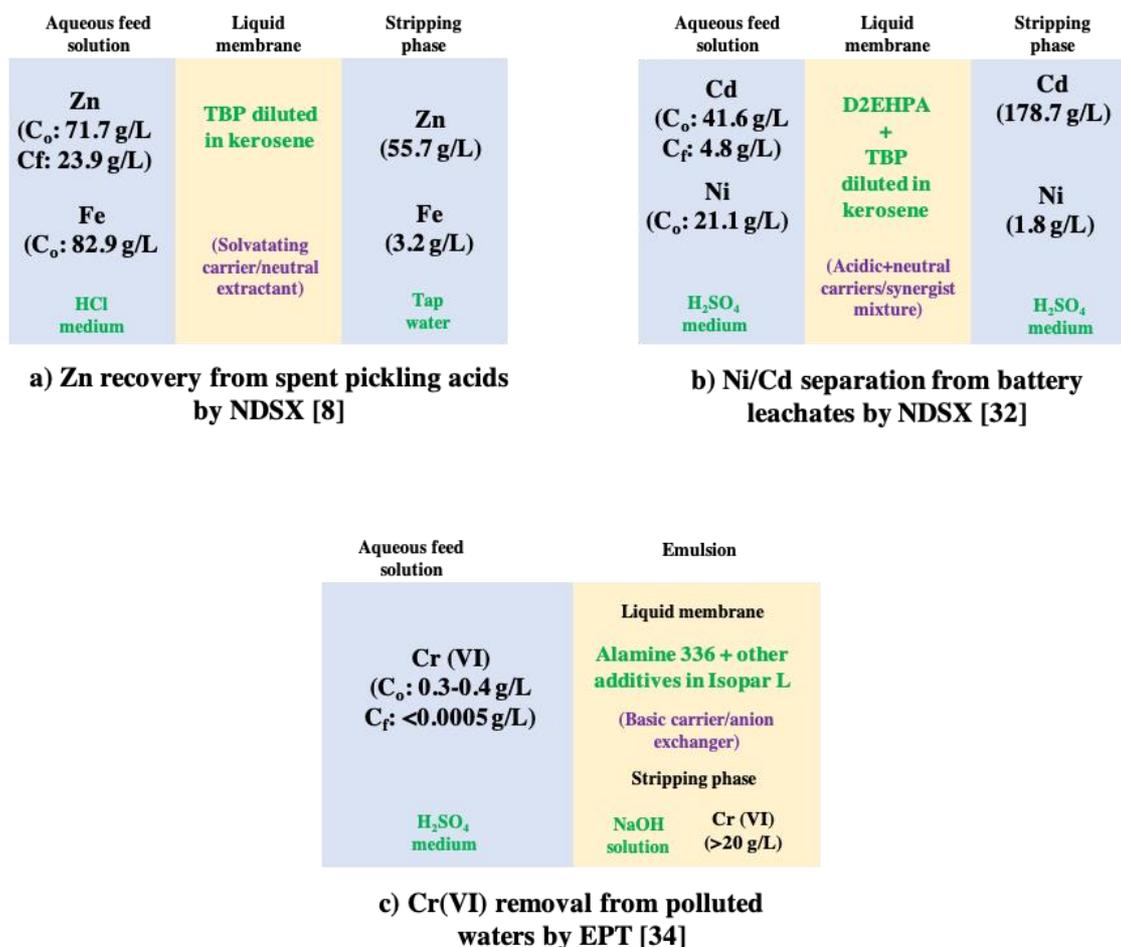


Fig. 6. Applications of SLM to the recovery and separation of metals from industrial effluents.

4. New challenges of facilitated transport liquid systems

The reinforcement of Europe's autonomy related to raw materials needs the diversification of the supply related to both primary and secondary sources, especially when considering critical raw materials for the EU. In this context, the European Commission reviewed in 2020 the list of critical raw materials [61], which is currently composed by 30 materials, including rare earth elements (REE) and Li, the latter being added to this list for the first time.

Since both, REE and Li, are of special interest due to their importance in the current ecological transition, the ongoing research related to the application of SLM systems to the recovery and or separation of these elements will be presented in the following sections and are summarized in Table 2. Noteworthy, the evaluation of these applications has been mainly performed by using synthetic solutions, therefore, the validation of these SLM systems in real industrial effluents should be addressed.

4.1. Separation of rare earth elements

REE include the group of lanthanides, Sc and Y. These elements can be classified based on physico-chemical criteria into two different groups: a) light rare earths (i.e. La, Ce, Pr, Nd and Sm) and b) heavy rare earths (i.e. Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y). Sc is usually considered individually.

Due to their magnetic, electrical, chemical and optical properties, REE are useful in multiple applications in the aerospace, defense, mobility, renewable energies or health sectors. Among the most promising secondary sources of these elements, it is possible to distinguish between secondary sources from: a) the mine industry (e.g. mine tailings, acid mine drainage, red muds, sea mining) [62-65] b) the fertilizer industry (e.g. phosphogypsum leachates) [66], c) e-waste (e.g. NdFeB permanent magnets, Ni-MH batteries, phosphors, printed circuit boards, cameras, mobile phones, hard disk drives, etc.) [67-70], d) Spent fluid catalytic cracking (FCC) catalysts [71] and e) others such as polishing powder [72].

Although multiple studies related to the application of both conventional and advanced processes (e.g. leaching, solvent extraction, ionic exchange, pyrometallurgical processes, electrochemical treatments, adsorption, extraction with ionic liquids, etc.) to REE recovery and separation can be found in the literature [73-79], only few studies deal with the implementation of SLM techniques to the recovery and separation of REE from secondary sources.

For instance, Yadav et al. [6] implemented a NDSX system with HF contactors to separate Dy from spent NdFeB permanent magnets using 0.5 M EHEHPA as a carrier and 0.3 M HNO₃ as aqueous phase (phase ratio=1:1), reaching a purity >97% in two cycles, as well as obtaining a Nd-rich solution suitable for further purification. Regarding NdFeB magnets leachates, also Asadollahzadeh et al. [80] used a SLM system to investigate the Pr-Nd extraction by a synergistic mixtures of 0.5 M TOPO and 0.5 M TBP as carriers, diluted in kerosene or in the ionic liquid [C₆MIM][NTf₂], and 1.8 M H₂SO₄ as strippant. In this study, an advantage in terms of stability was found when using the ionic liquid in the organic phase, reaching up to 90% of Nd and Pr extraction.

With respect to other REE secondary sources, Pavón et al. [7] studied a FSSLM system using Cyanex 923 or Cyanex 572-Na₂EDTA as extractants and receiving phase, for the treatment of fluorescent lamp leachates, which present Fe, Ca and P as main impurities. In this study, after the Fe removal by magnetic separation, a first leaching step (HCl or HNO₃ media when using Cyanex 572 and Cyanex 923, respectively) is applied to remove the non-ferrous impurities, mainly composed of Ca and with REE content. A quantitative Y and Eu recoveries were obtained when using 0.9 M Cyanex 923 as extractant with an aqueous feed solution pH of 1.2 and 0.05 M Na₂EDTA as receiving phase. In addition, Xu et al. [81] successfully recovered more than 95% of REE (mainly La, Ce, Pr and Nd) from a leaching solution of phosphate ores (nitric and phosphoric acid media) by a PVDF FSSLM system with 0.1 M TODGA diluted in n-octane as a carrier and deionized water as strippant.

On the other hand, Smith et al. [82] demonstrated the higher separation factors for heavy rare earths of a SLM system with 10% (v/v) DEHPA diluted in kerosene as a carrier and 5.0 M nitric acid as strippant solution, in the REE recovery from coal fly ash leachates, when compared to a liquid emulsion membrane process also with DEHPA as a carrier, but diluted in mineral oil.

Although the selective recovery of REE by SLM systems has been demonstrated in different studies [7,81-83], most of them aim to recover all the REE without further separation among them, thus the individual separation of REE by SLM systems remains a challenge. In addition, as it was previously mentioned, the use of sustainable diluents in SLM systems, such as vegetable oils, needs further investigation, due to their influence in long-term membrane stability, and because they present several advantages with respect to other solvents: low cost, availability, non-toxic and hazardous properties, etc. [84]. In this regard, Li et al. [85] dealt with rare earth extraction using functionalized ionic liquids based on common vegetable oils (i.e. peanut oil, sunflower seed oil, etc.), achieving an extraction capacity up to 0.15 mol/L and an extraction order following the reverse sequence Lu, Yb, Tm, Er, Ho, Dy, Tb, Gd, Sm, Nd, Pr, Y, Ce, La.

4.2. Recovery and separation of Li

In 2019, Li consumption increased up to 57,000 tons, i.e. 18% more with respect to the previous year, mainly due to the growth in the use of mobile devices and the development of the electric vehicle industry, the batteries representing around 71% of the total Li consumption [86-87]. In this regard, spent Li-ion batteries are considered a promising Li secondary source. Noteworthy, additional secondary sources such as brines obtained from seawater desalination, geothermal waters, or mother liquors sourcing from the Li₂CO₃ production process have also been considered.

Li batteries are mainly composed of Li, Co and Ni (g/kg: 21-33, 160-256, 0.4-14, respectively) [88-89]. The main challenge for Li recovery from spent Li batteries is Li and Co separation. In this regard, Swain et al. [90] studied the separation of Co and Li focusing on Co extraction by means of traditional solvent extraction and SLM processes. Two different SLM configurations were compared, i.e. FSSLM and HFSSLM.

Table 2
New challenges in the application of supported liquid membrane systems to metal recovery and separation.

Case study	Secondary sources	Main challenge	Ref.
1. Rare earth separation	a. Mine industry Mine tailings Acid mine drainage Red muds Sea mining	1. Selective individual separation between rare earth elements	1a: [62-65]
	b. Fertilizer industry Phosphogypsum leachates		1b: [66]
	c. E-waste NdFeB permanent magnets NiMH batteries Phosphors Others: Phones, hard disc drives, cameras, etc.		1c: [67-70]
	d. Spent fluid catalytic cracking catalysts (FCC)		1d: [71]
	e. Others Polishing powder		1e: [72]
2. Li recovery	a. Li batteries	2a. Li-Co separation	2a: [88-91]
	b. Brines	2b. Low Li concentrations in comparison to alkaline (Na, K) and alkaline earth metals (Mg, Ca)	2b: [31,92-95]

Cyanex 272 diluted in kerosene and sulfuric acid were used as carrier and stripping agent, respectively. The optimum extraction conditions for both processes were found when using an aqueous feed solution pH of 6 and a Cyanex 272 concentration of 750 mol/m³. On the other hand, a higher sulfuric acid concentration was necessary to achieve the optimum stripping conditions in the HFSLM system with respect to the FSSLM configuration (i.e. 100 and 25 mol/m³, respectively). Overall, Swain et al. [90] concluded that although the FSSLM system present the higher Li-Co separation factors, a complete separation of both metals with 99.99% purity can be achieved by the HFSLM system when applying the mentioned optimum conditions.

Also, Zante et al. [91] addressed the separation of Li from a solution with Co and Ni by using a PVDF SLM and employing a synergistic mixture of the ionic liquid ([C₄mim][NTf₂]) and TBP as carrier. In contrast to the approach implemented by Swain et al. [90], in which Li-Co separation was made by means of Co extraction, Zante et al. [91] aimed to separate Li-Co by extracting Li and keeping Co in the feed solution, achieving up to 43%, 20% and 19% of extraction for Li, Co and Ni, respectively.

On the other hand, when trying to recover Li from additional secondary sources such as brines, the main challenge lies in the low Li concentrations in comparison to other alkaline (i.e. Na and K) and alkaline earth metals (i.e. Mg, Ca). In this regard, brines obtained from desalination plants, although more enriched than seawater, may contain Li concentrations up to 0.27 mg/L, whereas Na, K, Mg and Ca are present in much higher concentrations (g/L: Na 25.2, K 0.78, Mg 2.87, Ca 0.96) [92]. In addition, both Na and Mg affects the selectivity of the Li recovery process due to their similar chemical behavior, Mg being the element with a greater impact [91]. With respect to brine and seawater, Sharma et al. [93] employed a HFSLM system with DEHPA and TBP as a synergistic mixture for Li extraction from a synthetically prepared sea bittern solution containing Li, Na and K, from which extraction efficiencies of 82%, 20%, and 28%, respectively were achieved. Additionally, Zante et al. [31] employed a PVDF SLM for Li extraction, using the β -diketone heptafluorodimethyloctanedione (HFOD) and triethylphosphine oxide (TOPO) as carriers, achieving an extraction up to 99%. The same author [91] also used the same membrane configuration, with the ionic liquid [C₄mim][NTf₂] and TBP as carriers, to study the separation between Li and Mg, achieving 71% and 36% of extraction, respectively.

For geothermal waters, Li may be present in concentrations up to 26 mg/L, whereas, as in the previous case, Na, K and Ca are present in much higher concentrations (mg/L: 682-2000, 138-300, 211, respectively) [94-95]. In this regard, Ma et al. [94] studied Li extraction by means of a FSSLM system with a spiral configuration by employing LIX54 and TOPO as carriers, achieving quantitative Li extraction and between 70-75% of Li recovery in the stripping solution (optimum conditions: aqueous feed solution pH of 12.5 and 1.0 M of sulfuric acid in the strip solution). In addition, this study found that the addition of Na or K in the feed solution decreased Li extraction, which confirmed the competitive factor between Li and these alkali metals.

Finally, although mother liquor sourcing from the Li₂CO₃ production process appears to be a promising Li secondary source, presenting concentrations up to 2.0 g/L with Na values up to 63 g/L [96-97], no studies related to the use of SLM systems for Li recovery from this source have been found in the literature.

5. Conclusions

The traditional linear economy has become unsustainable, pointing out the necessity of shifting towards a circular economy approach, in which consumption should rely on secondary sources. In this regard, industrial waste effluents with metallic content represent a promising secondary source for metals, the implementation of the appropriate technology being a key factor in the shift towards the adoption of circular economy principles at industrial scale.

Thus, this research paper aimed to point out the potential of supported liquid membrane (SLM) systems based on facilitated transport in fostering a more sustainable management of industrial waste metallic effluents. Three different applications of SLM in acidic industrial effluents have been presented: a) Zn/Fe separation, b) Ni/Cd separations and c) Removal of hexavalent Cr. In addition to this, the potential of the technology for the recovery and separation of two different critical raw materials, i.e. Li and rare earth elements (REE) has been addressed.

Although SLM systems have been successfully applied to both, Zn/Fe and Ni/Cd separations, as well as to hexavalent Cr removal, the exploitation of Li and REE from secondary sources by this technology deserves further

investigation. On the one hand, the selective separation of individual REE from a REE mixture by SLM systems remains a challenge. On the other hand, there is still a need to improve the selectivity between Li and Co, when recovering Li from spent Li-Co batteries, as well as between Li and Na and Mg, when recovering the low Li concentrations present in brines, seawater and geothermal waters. Therefore, future research in relation to SLM systems should be focused on achieving higher selectivity in Li and individual REE separations. In addition, further efforts should be done in both the substitution of petroleum-based diluents with more sustainable diluents and the validation of these systems with real industrial effluents.

Acknowledgements

Financial support from the Spanish Ministry of Science, Innovation and Universities under the projects PID2020-115409RB-I00 and RTI2018-093310-B-I00 are gratefully acknowledged.

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