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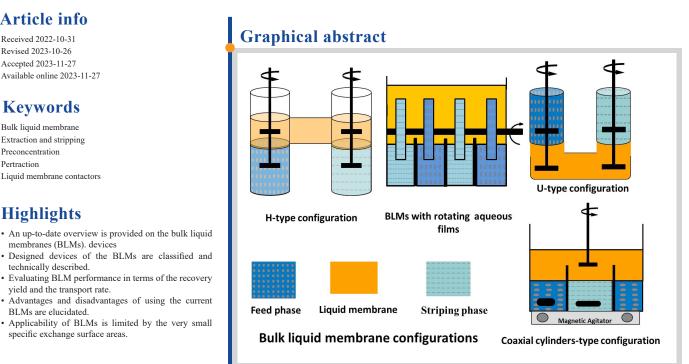
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Review Paper

Bulk Liquid Membrane Configurations: Technical Aspects, Applications and Evaluations

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Abstract

Contents

Bulk liquid membranes (BLMs) are so far an important research subject in the field of separation processes of target components from a chemical mixture. Both flexibility of the BLM configurations as separation tools along with using very expensive selective extractants as carriers without the risk of being wasted during processing render superior separation ability. The current paper aims to provide useful, up-to-date information about the common types of BLM devices. An attempt has been made to classify most of the tested BLM configurations with a sufficient description of the relevant technical aspects. Moreover, the different applications of BLM configurations are thoroughly discussed and evaluated describing advantages and drawbacks. Non-dispersive BLMs are only useful for laboratory-scale separation purposes as a preparation step of diluted analytical samples to separate and enrich the analyte. They can also serve as available and easy experimental methods in the laboratory to investigate the transport and extraction properties of new extraction systems. Based on the literature, the emulsion BLMs are likely to be more suitable for use in larger-scale applications on the pilot or plant level due to their larger contact surfaces and faster mass transfer.

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Membrane

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1. Introduction

Liquid membrane methods have progressively been developed after the publication of the first patent in 1968 on the separation of a mixture of hydrocarbons into their component parts by selective permeation through a liquid membrane [1]. In the last two decades, continuously growing attention in studying the separation of various solutes by liquid membrane techniques was observed in different areas such as analytical chemistry, the environment, chemical engineering, and biology [2-5].

Bulk (thick layer) liquid membranes are commonly categorized into three types [6-9]: BLMs with free liquid/liquid interfaces including both layered BLMs and BLMs in film contactors. The second type is BLM with one immobilized interface between the two contacted liquids (L/L); which is called BLM with emulsion (dispersion). The third type is BLM with two immobilized L/L interfaces (three-phase hollow fiber contactors). Practically, both the easy fabrication of laboratory-scale devices and the operational simplicity led the researchers to use BLMs as a separating tool to extract and transport target species. If a selective extractant that separates an element of interest from other impurities is added into the organic phase, BLM will become more selective and efficient for the transport of that element. This combination has enabled the application of BLMs as a new method of separation and enrichment for various solutes such as metal ions [10-13], organic compounds [14-19], bioactive compounds [20-23], precious metals [24-26], radioactive elements [27-33], and toxic species from wastewaters [34,35].

To the best of the author's knowledge, no review paper has yet sufficiently addressed the construction, configuration, and technical aspects of the BLM device [8,36-39]. In this paper, an attempt was made to characterize the most common types of laboratory-scale BLM devices including classification, configuration, and technical aspects. Moreover, the uses of the BLMs in various separation applications are thoroughly evaluated and discussed.

2. Principle of Bulk Liquid Membranes

2.1. Definition of BLM as a separating tool

A bulk liquid membrane is an immiscible liquid layer located between two other liquid phases [40]. This layer has transporting properties varied toward mixture components which are contained in the adjacent liquid phases. If one component of a mixture moves through the membrane faster than another mixture component, a separation can be accomplished. Thus, the BLM is a solute-transporting phase from one adjacent liquid phase (source or feed phase) to another adjacent liquid phase (receiving or stripping phase). It is noteworthy that this technique is called "layered bulk liquid membrane" by some authors [41], but the most common term is bulk liquid membrane.

The process of liquid membrane extraction is analogous to the unit operation of solvent extraction. While the extraction step is identical for both processes, the stripping step of the liquid membrane occurs simultaneously with the extraction, instead of the need for another contacting unit [42]. The simultaneity of extraction and stripping operations will increase the matter transfer during the extraction process itself due to the reduction of the extracted matter in the membrane phase by the stripping step.

2.2. Transport principle

In the simplest cases, the composition of the liquid membrane can be a water-immiscible organic phase, which dissolves solute species to different extents as a function of both the properties of the solutes and liquid phases. The solute, the most soluble is separated by a liquid membrane and then diffuses across the membrane (Fig. 1) due to an imposed concentration gradient between adjacent phases [43].

In more complex cases, a reactive extractant that has binding properties towards some elements of interest is added to a liquid membrane (diluent) to enhance the separation of this element through the membrane (Fig. 2). This extractant is called a carrier, and the process is known as facilitated or carrier-mediated liquid membrane separation. It is noticed that terms such as carrier-assisted transport or carrier-enhanced transport were also encountered in the literature [37,43-45].

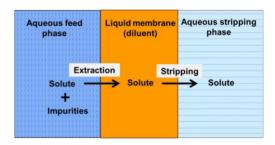


Fig. 1. Schematic representation of solute transport across BLM: simple transport [11].

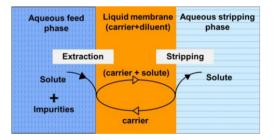


Fig. 2. Schematic representation of solute transport across BLM: facilitated transport [11].

The amount of transported solute across the simple and facilitating liquid membranes is determined as a result of the effects of a group of physical and chemical factors of three liquid phases within the BLM. These factors include the concentration gradient of the target solute, the effect of the counter-ions and co-ions present in the feed phase, the pH of the medium, the type and concentration of the carrier, the type of the diluent, the composition of the stripping phase, concentrations of all the involved reactants, temperature and the viscosity of each liquid phase. On the other hand, the way of design of the BLM devices plays also an important role in accelerating the transport processes of the solute under the effects of several factors such as configuration type, volume ratios of the phases, stirring mode, and the contact surfaces available for transport. It is known that the mass transfer increases with increasing biphasic contact interfaces and the speed of stirring [3,39,46]. But at extremely high stirring speeds the contact interfaces between liquids could be deformed and drops of the stripping phase may be transferred mechanically to the feed phase [34].

3. Configurations of bulk liquid membrane devices

There are some important considerations to be taken into account when configuring a BLM, as follows: (i) The device configuration must ensure the stability of phases; i.e., preventing any dispersion or emulsion between each of the two aqueous phases with the organic phase. (ii) The position of the LM phase whether in the up or down parts in the device compartments is determined according to the membrane density compared with two other liquid phases. (iii) The choice of stirring mode (mechanical agitators, magnetic stirring, or pumping) for each of the three liquid phases must be appropriate with the geometric configuration of device compartments and ensure the stability of phases. (iv) The contact surfaces must be made as large as possible to accelerate the overall transport rate. (v) The device must enable easy sampling from each phase.

3.1. Coaxial cylinders-type configurations

The coaxial cylinder-type configurations are shown in (Fig. 3). This type is used for the first time by Schulman, therefore this type is called "Schulman Bridge" in some publications [47,48]. According to the density of the liquid membrane, there are two configurations of coaxial cylinders-type devices.

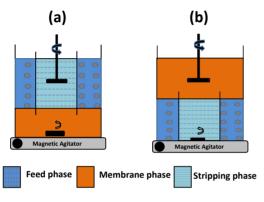


Fig. 3. Schemes of coaxial cylinders-type BLM devices [47].

3.1.1. Liquid membrane is heavier than water

In this case, the LM is positioned under the two other aqueous phases, and the BLM device consists of two cylindrical concentric glass vessels as shown in (Fig. 3, a). The outer cylindrical glass vessel which has a longer inside diameter and an open end only at the top, holds the inner glass cylinder, which is opened at both ends. The inner cylinder was suspended vertically a few centimeters above the bottom of the outer glass cell so that it divides the inside of the formed cell into three spaces; two compartments at the upper part, separated by the inner cylinder wall, and a clearance the bottom of the glass cell. The stripping phase is placed in the inner compartment while the feed phase is in the outer compartment. Thus, the liquid membrane lies below two other liquid phases and bridging them.

In this type of configuration, homogeneity in each phase can be achieved by mechanical stirrers [49,50]. In some research works [4, 51, 52], only the bottom organic layer was magnetically stirred by a Teflon-coated magnetic stir bar. Other researchers used both magnetic and mechanical stirring to homogenize organic and aqueous phases [10]. For instance, Alpaydin [4] used a BLM containing p-tert-butylcalix[4]arene 3-diethylamino propyl diamide derivative as an extractant for removal of toxic metal Cr(VI) ions from a model contaminated solution containing potassium dichromate. He reported that 96.65% of Cr(VI) ions were transferred to the acceptor solution after 10 h of contact time.

3.1.2. Liquid membrane is lighter than water

In this case, the membrane phase will overlay at the top of the two other aqueous phases and bridge them [35,53-56]. The inner cylinder is suspended above the bottom of the outer cylinder (Fig. 3, b). The feed and the stripping phases can be located commonly in the outer and inner cylindrical parts of the vessel, respectively. The aqueous phases can be stirred by two Teflon-coated magnetic stir bars. The organic phase was agitated with a mechanical stirrer. Tight tubes could also be connected to the bottom cylinders in order to facilitate the solution sampling [55].

Based on coaxial cylinder configuration, Altin and coworkers [54] have studied sodium ions transport from aqueous solutions using a liquid membrane containing dibenzo18-crown-6 as a carrier dissolved in toluene. The sodium ions have transported with a good yield (~90%) but too slowly during 24 hours.

3.2. Plate-inside-cylinder configurations

Instead of using an inner concentric cylinder in the outer vessel, a thin glass plate can be used as a separating barrier for dividing the cell inside into two compartments reserved for aqueous phases (Fig. 4) [14, 57, 58] This thin glass plate can be fixed on the inner wall of the cylinder with the help of an adhesive for glass. Depending on the density of the liquid membrane, the open path may be at the top or bottom of the device.

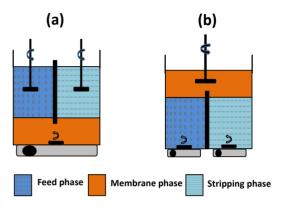


Fig. 4. Schemes of plate-inside-cylinder BLM devices [59].

3.2.1. Liquid membrane is heavier than water

The glass plate is fixed so that a clearance of a few millimeters is kept at the bottom of the outer vessel for the LM phase (Fig. 4-a). The aqueous feed and stripping phases are then transferred into their respective compartments and bridged by the LM.

Ng [60] used a plate-inside-cylinder configuration for the study of the technical feasibility of three different hydrophobic ionic liquids when applied as BLM for phenol removal. This work showed that even though a high ionic liquid membrane viscosity is higher by approximately two orders of magnitude than that of dichloromethane and kerosene, the ionic liquid membrane gives high phenol extraction and stripping efficiencies of 96.21% and 98.10%, respectively after 6 hours. This result means that the BLM technique enables the investment of ionic liquids for separation purposes and even offers a better choice of organic membrane solvents.

3.2.2. Liquid membrane is lighter than water

The separating plate must be placed at the bottom of the outer vessel as shown in (Fig. 4-b) [61-63]. The liquid membrane layered the two aqueous phases in the upper opened path. Das and others [61] conducted kinetic experiments of U(VI) transport using a plate-within-cylinder BLM configuration. The authors investigated the transport of U(VI) by the extractant di-(2-ethylhexyl) phosphoric acid (D2EHPA) dissolved in light paraffin. The U(VI) concentrations were decreased in the feed phase and increased in the recovery phase. It was observed the variations of U(VI) concentrations in the organic phase take a plateau form after a certain time of the start of the transport process because the rate of extraction is higher than the rate of stripping. The transport rate was too slow because the biphasic contact surfaces were small in the manufactured laboratory-scaled BLM.

3.3. U-shaped BLM configurations

The U-shaped configuration is used when the LM is heavier than the two other phases [64,65]. This configuration can be obtained by using a U-shaped tube (Fig. 5). LM was located at the bottom of the U-tube cell, while the feed and strip phases were placed in the vertical half compartments. The feed and stripping solutions can be connected with respective external tanks by making orifices on each compartment and with the help of mini-pumps which enable renewal phases in each half cell [66,67].

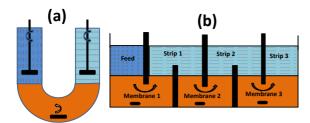


Fig. 5. Schemes of U-shaped BLM devices [64,65].

Krieg [68] made a U-tube multiple membrane cell consisting of three aqueous membranes and three strip phases in series, as illustrated in (Fig. 5-b). b-cyclodextrin was used as a chiral mobile carrier dissolved in water for the chiral enrichment of racemic chlorthalidone which is diluted in the ethylacetate feed phase. The organic strip phases were ethyl acetate solutions with saturated water. The obtained results showed that the BLM technique enabled to enrichment of the target solute racemic chlorthalidone, although the distribution coefficient was small (0.04). Moreover, the selectivity for the multiple BLM was higher than that for the single BLM. These results showed further features over other separation conventional methods, which are based on biphasic equilibriums during liquid-liquid extraction.

3.4. H-type and Y-inverse-type configurations

When the LM is the lightest phase, a H-shaped configuration (Fig. 6-a) can be used [69-71]. The feed and stripping solutions are each filled in the two lower vertical arms so that their solution levels are well under a horizontal bridge containing membrane liquid. The systems were mechanically agitated with stirrers.

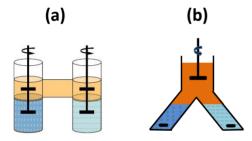
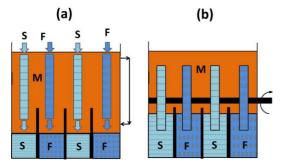


Fig. 6. H-type (a) and Y-inverse-type (b) configurations [71-73].

This configuration is used for the removal of chromium (VI) from aqueous acidic solution with tri-n-butyl phosphate (TBP) dissolved in hexane to a stripping solution of NaOH [74]. The results showed the majority of chromium (VI) was transported by TBP within 5 hours, noting that the organic membrane wasn't stirred.

Few researchers [72,73] applied a Y-inverse-type configuration (Fig. 6-b) for the transport of metal ions across the liquid membrane being the lighter phase. Ma and his coworkers [73] used this configuration in the study of the coupled transport of Eu(III) ions by the carrier mono(2-ethylhexyl)2-ethylhexyl phosphonate (P507) in kerosene. It is observed that the transport rates of Eu(III) ions were very low in the feed, membrane, and stripping phases.



3.5. BLM in film contactors

BLMs with creeping (Fig. 7- a) and rotating (Fig. 7- b) aqueous films were invented [75-77]. In these apparatuses, all three phases are in motion. Boyadziev's laboratory [75-77] developed creeping film BLM contactors with feed F and stripping S solution films creeping down hydrophilic vertical plates made of foamed porous viscose (80 % porosity) with organic solvent layered or flowing between them.

In the BLMs with rotating discs [78,79], the vertical hydrophilic discs are immersed with their lower part in compartments which are alternately filled with the stripping solution and the feed (Fig. 7- b). The remaining part of the discs, on which films of water phases are formed due to rotation, is immersed in the membrane phase. The surfaces of the discs should be hydrophilic to ensure the formation of adhering aqueous films. Mass transfer from the feed films to the stripping solution films through the bulk membrane occurs. This configuration was studied in the separation of phenol [80], tylosin [81], atropine [82], and metals [83-85]. In most cases, the discs are alternately positioned on a horizontal shaft (Fig. 7- b). Rotating disc contactors with two parallel shafts one with the feed discs and the other with stripping solution discs were also tested [83,86,87].

3.6. BLM with emulsion in hollow fibers

Some researchers [88] have developed a BLM with emulsion in hollow fibers where only one immobilized interface was made between the feed and membrane phases (Fig. 8). While the emulsion (dispersion) of the stripping solution took place in the membrane phase and carried out without the use of any surfactant. The emulsified BLM was circulating in the shell side of the microporous hollow fiber (HF) contactor, while the feed phase was flowing in the lumen of HFs. Mass transfer of solute from the feed to stripping solution droplets occurred through organic solvent in the same equipment. The dispersed BLM phase fills the pores of hollow fibers and is a continuous phase of emulsion. In this way, compared to other BLM configurations with two immobilized interfaces, one microporous wall resistance is avoided leading to an increase in the mass transfer.

Separation of chromium [89] and zinc [90] by pertraction through BLM with emulsion in HF modules was studied on a pilot plant and industrial scale. Also, the separation of Stransuim was studied in a laboratory-scaled HF module [91]. It is worth noting that the term supported LM used in these papers is not the case, thus the continuous organic phase of emulsion is true BLM.

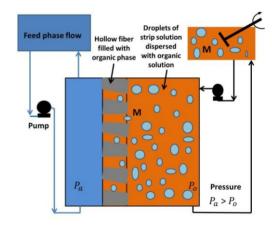


Fig. 8. Schematic diagram of the supported liquid membranes with strip dispersion [88].

4. Evaluation of the uses and applications of BLM devices

For the last three decades, the use of BLM techniques in the separation of diverse species has been the focus of hundreds of research works. (Fig. 9) shows the number of research publications focusing mainly on the use of BLMs in separation processes from 1993 until mid-2023. Research work has grown in the last two decades. Examining the titles and contents of these publications indicates that the efforts of the researchers have focused on separating the solutes of interest utilizing BLMs more than on developing the technique itself.

Fig. 7. BLMs with creeping (a) and rotating (b) aqueous films [75-77].

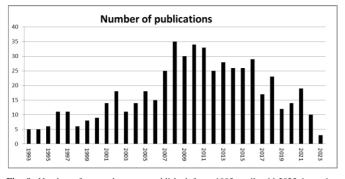


Fig. 9. Number of research papers published from 1993 until mid-2023 in various journals specialized in separation processes. The criterion followed here for paper counting is that the phrase "liquid bulk membrane" should be explicitly mentioned in the paper titles or the research content of the paper is focused on BLMs.

Based on published research work, BLM techniques are evaluated from several aspects, as follows:

4.1. From the design point of view

Most laboratory-scale BLM devices were easy to construct without requiring a lot of moving parts. The BLM devices have different options in the construction and this flexibility allows selecting the suitable configuration that matches better with the requirements of each chemical system. In particular, working with liquid phases of close or different densities and/or the operation with wider ranges of the phase volume ratios. Moreover, the BLM devices do not need large working areas, and they enable the intensification of process units within small spaces. In addition, the possibility of linking several BLM cells in series to enrich more target solutes in the final stripping phase is available [68].

Nevertheless, laboratory-scale designs of BLMs are not yet feasible to be scaled up to larger devices for industrial use. This is because of the long slowness of the kinetics of the mass transfer [24,36,59] caused by the small contact surface area available between liquid phases in the case of non-dispersive BLM configuration. On the contrary, the emulsion BLM allows to significantly accelerate the mass transfer. Therefore, it is beneficial to continue developing the BLM emulsion to enable its use on an industrial scale in the future.

4.2. From the operational point of view

The BLM devices made in the laboratory are simple to operate and enable easy control of the operation conditions to improve transport efficiency. There are different ways of homogenizing the phases (mixing by flowing pump, agitation by magnetic or mechanic stirrers) while keeping the stability of non-dispersive liquid phases. There is no problem of emulsion or formation of new unwanted phases as it may take place with conventional separation techniques either in the extraction columns or the mixer-settlers. Additionally, there is a unique feature of the BLM technique; it is to construct a carrier-mediated BLM that transports a specific solute against its concentration gradient between the feed and stripping phases. Such a membrane can move a single solute from a region of low solute concentration into a region of high solute concentration. The role of BLM becomes like a pump flowing a target solute. For further information, the reader is referred to the related research literature [92, 93].

4.3. From the economic point of view

The liquid membrane technology is featured by the combination of the extraction and stripping steps in one single step. This makes the organic membranes act as only short-term mediators and increases the membrane capacity of charging by solute and consequently increases recovery yields without the need to use larger quantities of expensive carriers [59]. On the other hand, the combination of extraction and stripping steps reduces equipment sizes. There is no need for lots of pumps or settlers, which is considered economically advantageous. Furthermore, since the contact surfaces are stable and definite, this will greatly reduce the occurrence of organic phase entrapment by other aqueous phases and then there will be no quantitative losses in carriers and solvents. For these reasons, very expensive, highly selective, tailor-made carriers can also be used economically in the BLM technique in comparison with conventional separation techniques such as liquid-liquid extraction.

4.4. From an application point of view

By surveying the different applications of BLM devices in the published research papers, two purposes can be clearly distinguished. The first is a research purpose by using the BLM device as an experimental tool for studying the transport and extractive properties. The second is an analytical purpose by using a BLM device as a preparation method for analyte samples.

4.4.1. Studying and understanding the transport and separation properties

The research works carried out in the last decades on the separation and the transport of solutes by various extractants using BLM permitted the acquisition of important information on the extraction and transport properties of these extractants. In fact, because of their easy construction, and strictly determined contact surface area, BLMs are used for the evaluation of the extraction properties of novel synthetic extractants. In addition, BLMs are very helpful tools in understanding the main factors influencing the transport of solutes complexed by extractants and the kinetic behavior such as driving force and coefficients of diffusion and transfer. It is known that over the past 30 years, dozens of new macrocyclic chemical compounds have been synthesized by chemists, and these new compounds have been used as extractant carriers towards dissolved solutes across liquid membranes in order to evaluate their extractability and transport properties. Thus, various synthetic carriers and their derivatives such as calixarenes, crown ethers, cyclodextrins, and organophosphorus compounds have been investigated as carriers for the transport through the liquid membrane of different metal ions [4,94].

4.4.2. BLMs for preparation of analyte samples

A good number of researchers have proposed the use of BLM techniques as new methods for preparing analyst samples for the quantitative determination of target solute, which is usually present in trace levels with other interfering impurities [95-97]. Usually, sample preparation serves to transfer selectively as much of the analyte as possible from the sample phase to the acceptor phase. The well-known separation and preconcentration methods are liquid-liquid extraction, solid phase extraction, ionic exchange, and selective precipitation [98]. The BLM containing a selective extractant can transport the target analyte molecules from the sample phase to the strip phase. In some literature, this separation process across the liquid membrane is called pertraction (permeation-extraction). The BLM techniques can provide several clear advantages over other conventional separation methods, especially with regard to selectivity, enrichment factor, and automation potential.

The pertraction across BLM is applied on natural water and other environmental matrices for the quantitative determination of heavy metals which are typically present in microgram per liter or nanogram per liter range [99,100]. Table (1) resumes the applications of pertraction of heavy metals. In those mentioned works, BLM is used to prepare metallic element samples as an off-line preparation step before the subsequent analytical instrument except for vanadium. For the latter, the BLM device was linked in-line with the analytical instrument. It follows that the BLM technique has more potential to be automated with analytical instruments than other traditional preconcentration methods [101]. In fact, the advantages of the non-dispersed BLM method, which does not need a phase separation step and gives very clean extracts in the strip phase make the automation of BLM with analytical instruments possible. Moreover, the BLM technique offers a high selectivity and a high degree of concentration enrichment.

However, there are some disadvantages to using the BLM as a method for sample preparations. One disadvantage that follows from the characteristics of the BLM techniques is that they are only applicable to certain analyte classes at a time and that it is often necessary to perform a number of optimization experiments, before the real application to practical problems. Another more fundamental disadvantage is related to time consumption. It is probably true that extraction with BLM is inherently slower than using liquid-liquid extraction. These disadvantages have to be balanced with the higher selectivity and permitting the analysis of the trace elements in extremely diluted solutions.

Table 1

Uses of BLMs for separation and preconcentration of heavy metals

Metal ions/Sample nature/References	Analytical instrument ⁽¹⁾	Recovery yield (RY, %) and preconcentration factor $(F)^{\left(2\right)}$	BLM used ⁽³⁾
Ni/natural and sea waters/[102, 103]	ICP-MS	F=18 RY=100.54±0.94%	Pyridine-2-acetaldehyde benzoyl hydrazone dissolved
Ni/natural and sea waters/[102, 103]	AAS	$RY = 98 \pm 5$ F= 20.83	2-Hydroxybenzaldehyde N-ethylthiosemi-carbazone (2- HBET)
Cd/natural and sea waters/ [35, 99]	AAS	RY=99 F=1.66	Di-(2-ethylhexyl) phosphoric acid (DEHPA)
Cd natural and sea waters/ [35, 99]	FAAS	RY=101.0±2.7% F=17.9	2-acetylpyridine benzoyl hydrazone
Cu/natural and sea waters/ [104, 105]	FAAS	RY= 76.21% F=4.30.	Di-(2-ethylhexyl)phosphoric acid (DEHPA)
Cu natural and sea waters [104, 105]	FAAS	RY=100% F=18 0.24 µg l−1 of Cu.	Pyridine-2-acetaldehyde benzoyl hydrazone (2-APBH)
Pb/real samples at environmental concentration levels/ [96]	ICP-MS	RF= 93.8% F=4.2	DEHPA
Pb/environmental water samples with salinity levels ($\geq 10 \text{ g.L}^{-1}$)/[106]	AAS	$RY=83.7\pm2.5\%$ F=20.45 $DL=0.391 \ \mu g.L^{-1}$	2-hydroxybenzaldehyde-N-ethyl thiosemicarbazone
V/real saline seawater samples/[107]	Uv-vis	$\begin{array}{c} RY = 100\% \\ DL = 4.7 \ \mu g.L^{-1} \\ QL^{-(2)} = 15.8 \ \mu g.L^{-1} \end{array}$	Aliquat 336

(1)- AAS: atomic absorption spectroscopy, ICP-MS: inductively coupled plasma-mass spectrometry, FAAS: flame atomic absorption spectroscopy, Uv-vis: Spectrophotometer

(2)- F preconcentration factor, RY: recovery yield, DL: detection limit, QL: quantification limit

(3)- The configuration used was the two concentric cylindrical cells.

Table 2

A summary of the information about the advantages and limitations of different BLM devices.

Configurations and References	Advantages	Limitations
Coaxial cylinders-type [4,49,50]	-Easy construction in labs -Multiple design options -Possible for laboratory applications	-Some difficulties in operations. -Specific exchange area ^(a) is very low -Slow transport process -No feasible industrial applications
Plate-inside-cylinder [14, 57-59]	 Easier to construct at laboratory-scale Multiple design options Possible for laboratory applications 	-Fewer operational difficulties. -Specific exchange area is very low. -Slow transport process -No feasible industrial applications
U-shaped and Y-inverse-type [65-67,72,73]	-Easier to construct -Easy to operate -Possibility to link several cells -Possible for laboratory applications	-Adapted only to LMs higher than water -Specific exchange area is very low -Much slow transport process -No feasible industrial applications
H-type [70,71,74]	-Easy to construct and operate -Possible for laboratory applications	-Adapted to LMs lighter than water -Specific exchange area is very low - Much slow transport rates -No feasible industrial applications
BLM in film contactor	-Specific exchange area is larger -Possible for laboratory applications	-Complicated to construct and operate -Faster transport rates
Emulsion BLM in HF	-Rapid transport rates -Specific exchange area is much larger -Volume ratio of phases can be varied in a wide interval -More applicable for large-scale applications	-Dispersion of the stripping solution can introduce a problem in some systems sensitive to emulsion

(a) Ratios of the available surface areas between contacted phases per their total volumes

5. Conclusion remakes and perspectives

Table 2 compares briefly the advantages, disadvantages, and limitations of the current BLM configurations. The following points were concluded:

- The easiness of the construction and the simplicity of operation of BLM devices led many researchers in the last three decades to use them as suitable tools to study the separation capabilities for new extraction systems. In particular, determining selectivities of new synthetic carriers and studying their transport properties, as well as seeking the optimal chemical and operational conditions for giving the higher mass transfer within them.

- The effectiveness of the performance of laboratory-manufactured BLM devices during the separation processes can be assessed by discussing both the resultant recovery yields and transfer rates. Generally, it is obvious that the optimization of the chemical composition of the three liquid phases of BLM improves both the selectivity and the yield of the separation, while the establishment of appropriate hydrodynamic conditions in each liquid phase accelerates the transport rate of the target solute within it.

- The BLM techniques combined with highly selective extractants have potential power as an efficient method for sample preparation to meet both industrial development needs and environmental requirements. These impose the necessity of determining low trace element concentrations of the order of a few parts per million, or even per billion, for certain pollutants. BLMs can also provide advantages over other conventional separation methods, especially with regard to selectivity and enrichment factors. Moreover, BLMs could be automated with analytical instruments.

- The emulsion BLM devices have both larger contact surfaces between phases and higher mass transfer efficiencies. These may enhance the ability to use them for industrial applications and promote research works to find applications for emulsion BLMs on larger scales.

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CRedit authorship contribution statement

Z. Albaraka: Conceptualization; Data curation; Formal analysis; Writing – original draft; Writing – review & editing.

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Declaration of Competing Interest

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

6. References

- Li NN. Separating hydrocarbons with liquid membranes. United States patent (3410794) 1968. http://www.google.com/patents/US3410794.
- [2] Chaturabul S., Srirachat W., Wannachod T., Ramakul P., Pancharoen U., Kheawhom S. Separation of mercury(II) from petroleum produced water via hollow fiber supported liquid membrane and mass transfer modeling. Chem.Eng.J.(Amsterdam, Neth.), 265 (2015) 34-46. https://doi.org/10.1016/j.cej.2014.12.034.
- [3] Minhas F.T., Memon S., Bhanger M.I. Transport of Hg(II) through bulk liquid membrane containing calix[4]arene thioalkyl derivative as a carrier. Desalination, 262 (2010) 215-220. https://doi.org/10.1016/j.desal.2010.06.014.
- [4] Alpaydin S., Ahmat O.s., Bozkurt S., Sirit A. Kinetic study on removal of toxic metal Cr(VI) through a bulk liquid membrane containing p-tertbutylcalix[4]arene derivative. Desalination, 275 (2011) 166-171. https://doi.org/10.1016/j.desal.2011.02.048.
- [5] Hernndez-Pellanona A., Gallart Tauler L.E., Ibanez R., Ortiz I., San-Roman M.F. New Challenges and Applications of Supported Liquid Membrane Systems Based on Facilitated Transport in Liquid Phase Separations of Metallic Species. J.Membr.Sci.Res., 8 (2022) 1-10. https://doi.org/10.22079/jmsr.2021.535315.1484.
- [6] Kislik VS. Liquid membranes: principles and applications in chemical separations and wastewater treatment, 1st Ed., Amsterdam, Elsevier B.V., 2010. https://doi.org/10.1016/C2009-0-18491-X.
- [7] Vilt M.E., Ho W.S.W., Li N.N. Liquid Membranes, In: Drioli E., Giorno L. (Eds.), Comprehensive Membrane Science and Engineering, Oxford: Elsevier, 2010, 79-107. https://doi.org/10.1016/B978-0-08-093250-7.00033-5.
- [8] Eljaddi T., Laurent L., Miloudi H. Review on Mechanism of Facilitated Transport on Liquid Membranes. J.Membr.Sci.Res., 3 (2017) 199-208. https://doi.org/10.22079/jmsr.2017.50137.1110.
- [9] Amini M., Rahbar-Kelishami A., Alipour M., Vahidi O. Supported Liquid Membrane in Metal Ion Separation: An Overview. J.Membr.Sci.Res., 4 (2018) 121-135. https://doi.org/10.22079/jmsr.2017.63968.1138.
- [10] Dalali N., Yavarizadeh H., Agrawal Y.K. Separation of zinc and cadmium from nickel and cobalt by facilitated transport through bulk liquid membrane using trioctyl methyl ammonium chloride as carrier. J.Ind.Eng.Chem.(Amsterdam, Neth.), 18 (2012) 1001-1005. https://doi.org/10.1016/j.jiec.2011.11.151.
- [11] Albaraka Z. Carrier-mediated liquid membrane systems for lead (II) ion separations. Chemical Papers (2019). https://doi.org/10.1007/s11696-019-00868-w.
- [12] Albaraka Z. Use of D2EHPA-Mediated Liquid Membranes for Heavy Metal Ions Separation: A Review. Rev.Roum.Chim, 64 (2019) 113-124. https://doi.org/10.33224/rrch.2019.64.2.01.
- [13] Albaraka Z. The study of transfer mechanisms during the extraction by hollow fiber membrane of alkaline salts by macrocyclic systems. (Ph.D. Thesis supervised by Prof. Michel Burgard). Strasbourg University, (2010) 1-183. https://www.theses.fr/2010STRA6012
- [14] Chakrabarty K., Krishna K.V., Saha P., Ghoshal A.K. Extraction and recovery of lignosulfonate from its aqueous solution using bulk liquid membrane. J.Membr.Sci., 330 (2009) 135-144. https://doi.org/10.1016/j.memsci.2008.12.069.
- [15] Cichy W., Schlosser S., Szymanowski J. Extraction and pertraction of phenol through bulk liquid membranes. J.Chem.Technol.Biotechnol., 80 (2005) 189-197. http://dx.doi.org/10.1002/jctb.1178.
- [16] Zidi C., Tayeb R., Dhahbi M. Extraction of phenol from aqueous solutions by means of supported liquid membrane (MLS) containing tri-n-octyl

phosphine oxide (TOPO). J.Hazard.Mater., 194 (2011) 62-68. https://doi.org/10.1016/j.jhazmat.2011.07.071.

- [17] Hayyan A., Abed K.M., Hizaddin H.F., Yusoff W.M., Ng Y.S., Junaidi M.U.M., Saleh J., Aljohani A.S.M., Alhumaydhi F.A., Abdulmonem W.A., Alkandari K.H., Alajmi F.D., Aldeehani A.K., Basirun W.J., Abidin M.I.I.Z. Application of natural deep eutectic solvents in bulk liquid membrane system for removal of free glycerol from crude fatty acid methyl ester. Colloids Surf., A, 650 (2022) 129449. https://doi.org/10.1016/j.colsurfa.2022.129449.
- [18] Baylan N., Turk F.N., Cehreli S. Use of Cyclopentyl Methyl Ether (CPME) as Green Membrane for Acetic Acid Removal by Facilitated Bulk Liquid Membrane: A Transport and Kinetic Study. Can.J.Chem.Eng., n/a (2022). https://doi.org/10.1002/cjce.24711.
- [19] Chasib K.F., Mohsen A.J., Jisha K.J., Gardas R.L. Extraction of phenolic pollutants from industrial wastewater using a bulk ionic liquid membrane technique. Environ.Technol., 43 (2022) 1038-1049. https://doi.org/10.1080/09593330.2020.1813209.
- [20] Ersoz M., Vural U.S., Okdan A., Pehlivan E., Yildiz S. Transport studies of amino acids through a liquid membrane system containing carboxylated poly (styrene) carrier. Journal of Membrane Science, 104 (1995) 263-269. https://doi.org/10.1016/0376-7388(95)00036-C.
- [21] Ma M., Chen B., Luo X., Tan H., He D., Xie Q., Yao S. Study on the transport selectivity and kinetics of amino acids through di(2-ethylhexyl) phosphoric acid-kerosene bulk liquid membrane. J.Membr.Sci., 234 (2004) 101-109. https://doi.org/10.1016/j.memsci.2004.01.014.
- [22] Ma M., He D., Liao S., Zeng Y., Xie Q., Yao S. Kinetic study of lisoleucine transport through a liquid membrane containing di(2ethylhexyl) phosphoric acid in kerosene. Anal.Chim.Acta, 456 (2002) 157-165. https://doi.org/10.1016/S0003-2670(02)00003-X.
- [23] Halim S.F.A., Morad N., Shahadat M., Chang S.H. Palm kernel fatty acid distillate-based bulk liquid membrane for Cu(II) separation: Design and its operating parameters. J.water Process.Eng., 47 (2022) 102646. https://doi.org/10.1016/j.jwpe.2022.102646.
- [24] Akin I., Erdemir S., Yilmaz M., Ersoz M. Calix[4]arene derivative bearing imidazole groups as carrier for the transport of palladium by using bulk liquid membrane. J.Hazard.Mater., 223-224 (2012) 24-30. https://doi.org/10.1016/j.jhazmat.2012.03.043.
- [25] Alizadeh N., Salimi S., Jabbari A. Transport study of palladium through a bulk liquid membrane using hexadecylpyridinium as carrier. Sep.Purif.Technol., 28 (2002) 173-180. https://doi.org/10.1016/S1383-5866(02)00003-5.
- [26] Berhe H.G., Bourne S.A., Bredenkamp M.W., Esterhuysen C., Habtu M.M., Koch K.R., Luckay R.C. High and selective Ag(I) bulk liquid membrane transport with N,N-diethyl-N'-camphanyl thiourea and structure of the complex. Inorg.Chem.Commun., 9 (2006) 99-102. https://doi.org/10.1016/j.inoche.2005.10.008.
- [27] Candela A.M., Benatti V., Palet C. Pre-concentration of Uranium (VI) using bulk liquid and supported liquid membrane systems optimized containing bis(2-ethylhexyl) phosphoric acid as carrier in low concentrations. Sep.Purif.Technol., 120 (2013) 172-179. https://doi.org/10.1016/j.seppur.2013.09.047.
- [28] Kocherginsky N.M., Zhang Y.K., Stucki J.W. D2EHPA based strontium removal from strongly alkaline nuclear waste. Desalination, 144 (2002) 267-272. https://doi.org/10.1016/S0011-9164(02)00326-0.
- [29] Ramkumar J., Nayak S.K., Maiti B. Transport of uranyl ion across a bulk liquid membrane using calixarene and synergistic agents as carriers. J.Membr.Sci., 196 (2002) 203-210. https://doi.org/10.1016/S0376-7388(01)00591-9.
- [30] Rana D., Matsuura T., Kassim M.A., Ismail A.F. Radioactive decontamination of water by membrane processes - A review. Desalination, 321 (2013) 77-92. https://doi.org/10.1016/j.desal.2012.11.007.
- [31] Yaftian M.R., Zamani A.A., Rostamnia S. Thorium (IV) ion-selective transport through a bulk liquid membrane containing 2thenoyltrifluoroacetone as extractant-carrier. Sep.Purif.Technol., 49 (2006) 71-75. https://doi.org/10.1016/j.seppur.2005.08.009.
- [32] Yazdani Ahmad Abadi N., Kheradmand Saadi M., Charkhi A., Ammari Allahyari S. Intensification of tellurium separation through the multistage bulk liquid membrane technique from nitric acid leaching liquor of Copper anode slime. J.Iran.Chem.Soc., 19 (2022) 413-421. https://doi.org/10.1007/s13738-021-02311-y.
- [33] Milani S.A., Zahakifar F., Faryadi M. Membrane assisted transport of thorium (IV) across bulk liquid membrane containing DEHPA as ion carrier: kinetic, mechanism and thermodynamic studies. Radiochim.Acta, 110 (2022) 841-852. https://doi.org/10.1515/ract-2021-1143.
- [34] Aydiner C., Kobya M., Demirbas E. Cyanide ions transport from aqueous solutions by using quaternary ammonium salts through bulk liquid

membranes. Desalination, 180 (2005) 139-150. https://doi.org/10.1016/j.desal.2005.01.003.

- [35] Irigoyen L., Moreno C., Mendiguchia C., Garcia-Vargas M. Application of liquid membranes to sample preconcentration for the spectrometric determination of cadmium in seawater. J.Membr.Sci., 274 (2006) 169-172. https://doi.org/10.1016/j.memsci.2005.08.008.
- [36] Ferraz H.C., Duarte L.T., Di Luccio M., Alves T.L.M., Habert A.C., Borges C.P. Recent achievements in facilitated transport membranes for separation processes. Braz.J.Chem.Eng., 24 (2007) 101-118. https://doi.org/10.1590/S0104-66322007000100010.
- [37] Sastre A.M., Kumar A., Shukla J.P., Singh R.K. Improved Techniques in Liquid Membrane Separations: An Overview. Sep.Purif.Rev., 27 (1998) 213-298. http://dx.doi.org/10.1080/03602549809351641.
- [38] Boyadzhiev L., Alexandrova S. Recovery of copper from ammoniacal solutions by rotating film pertraction. Hydrometallurgy, 35 (1994) 109-121. https://doi.org/10.1016/0304-386X(94)90022-1.
- [39] Nezhadali A., Mohammadi R., Mojarrab M. An overview on pollutants removal from aqueous solutions via bulk liquid membranes (BLMs): Parameters that influence the effectiveness, selectivity and transport kinetic. J.Environ.Chem.Eng., 7 (2019) 103339. https://doi.org/10.1016/j.jece.2019.103339.
- [40] Coulson J.M., Richardson J.F. Membrane Separation Processes, Coulson and Richardson's Chemical Engineering, Vol. 2, Butterworth-Heinemann, 2002, 868-900.
- [41] Schlosser S, Forgova-Hovancikova E. Pertraction of zinc through a bulk liquid membrane. Proc. 6th Conf. Separation of Ionic Solutes, Piestany, Slovak Chemical Society of Slovak Academy of Sciences, (1995), p. 26-28, Bratislava (Slovakia).
- [42] Charcosset C. 7 Other membrane processes, In: Charcosset C. (Ed.), Membrane Processes in Biotechnologies and Pharmaceutics, Amsterdam: Elsevier, 2012, 253-293. http://www.sciencedirect.com/science/article/pii/B9780444563347000071
- [43] Kislik V.S. Chapter 1 Introduction, General Description, Definitions, and Classification. Overview, In: Kislik V.S. (Ed.), Liquid membranes: principles and applications in chemical separations and wastewater treatment, Amsterdam: Elsevier, 2010, 1-15. https://doi.org/10.1016/B978-0-444-53218-3.00001-5.
- [44] Tomar J., Awasthy A., Sharma U. Synthetic ionophores for the separation of Li+, Na+, K+, Ca2+, Mg2+ metal ions using liquid membrane technology. Desalination, 232 (2008) 102-109. https://doi.org/10.1016/j.desal.2008.01.008.
- [45] Singh S.K., Asfari Z., Trebouet D. Recent Advances in the Extraction of Target Metal Ions with Liquid Membrane Processes Incorporating Macrocycle Carriers. Sep.Purif.Rev., 42 (2012) 28-86. https://doi.org/10.1080/15422119.2012.681744.
- [46] Ersoz M. Transport of mercury through liquid membranes containing calixarene carriers. Adv.Colloid Interface Sci., 134-135 (2007) 96-104. https://doi.org/10.1016/j.cis.2007.04.007.
- [47] Fakhari A.R., Khorrami A.R., Shamsipur M. Selective uphill Zn2+ transport via a bulk liquid membrane using an azacrown ether carrier. Sep.Purif.Technol., 50 (2006) 77-81. https://doi.org/10.1016/j.seppur.2005.11.011.
- [48] Rosano H.L., Breindel K., Schulman J.H., Eydt A.J. Mechanism of ionic exchange with carrier molecules through non-aqueous liquid membranes. J.Colloid Interface Sci, 22 (1966) 58-67. https://doi.org/10.1016/0021-9797(66)90067-1.
- [49] Nezhadali A. Selective transport of Ag (I) ion across a bulk liquid and polymer membranes incorporated with di-N-benzylated O3N2 donor macrocycles. Chin.Chem.Lett., 21 (2010) 1111-1114. https://doi.org/10.1016/j.cclet.2010.04.028.
- [50] Nezhadali A., Rabani N. Competitive bulk liquid membrane transport of Co(II), Ni(II), Zn(II), Cd(II), Ag(I), Cu(II) and Mn(II), cations using 2,2dithio(bis)benzothiazole as carrier. Chin.Chem.Lett., 22 (2011) 88-92. https://doi.org/10.1016/j.cclet.2010.06.018.
- [51] Candela A.M., Coello J., Palet C. Doehlert experimental design as a tool to study liquid-liquid systems for the recovery of Uranium (VI) traces. Sep.Purif.Technol., 118 (2013) 399-405. https://doi.org/10.1016/j.seppur.2013.07.017.
- [52] Jafari S., Yaftian M.R., Parinejad M. Facilitated transport of cadmium as anionic iodo-complexes through bulk liquid membrane containing hexadecyltrimethylammonium bromide. Sep.Purif.Technol., 70 (2009) 118-122. https://doi.org/10.1016/j.seppur.2009.09.003.
- [53] Mendiguchia C., Moreno C., Garcia-Vargas M. Separation of heavy metals in seawater by liquid membranes: preconcentration of copper. Sep.Sci.Technol., 37 (2002) 2337-2351. https://doi.org/10.1081/SS-120003516.

- [54] Altin S., Demircioglu N., Peker I., Altin A. Effects of acceptor phase and donor phase properties on sodium ions transport from aqueous solutions using liquid membrane systems. Colloids Surf., A, 306 (2007) 14-21. https://doi.org/10.1016/j.colsurfa.2007.01.042.
- [55] Koter S., Szczepanski P., Mateescu M., Nechifor G., Badalau L., Koter I. Modeling of the cadmium transport through a bulk liquid membrane. Sep.Purif.Technol., 107 (2013) 135-143. https://doi.org/10.1016/j.seppur.2013.01.032.
- [56] Strzelbicki J., Charewicz W.A. Effect of some operating variables on cobalt(II) transport across a bulk liquid membrane. Hydrometallurgy, 13 (1984) 89-102. https://doi.org/10.1016/0304-386X(84)90019-7.
- [57] Kogelnig D., Stojanovic A., Jirsa F., Korner W., Krachler R., Keppler B.K. Transport and separation of iron(III) from nickel(II) with the ionic liquid trihexyl(tetradecyl)phosphonium chloride. Sep.Purif.Technol., 72 (2010) 56-60. https://doi.org/10.1016/j.seppur.2009.12.028.
- [58] Teramoto M., Matsuyama H., Nakai K., Uesaka T., Ohnishi N. Facilitated uphill transport of eicosapentaenoic acid ethyl ester through bulk and supported liquid membranes containing silver nitrate as carrier: a new type of uphill transport. J.Membr.Sci., 91 (1994) 209-213. https://doi.org/10.1016/0376-7388(94)00063-8.
- [59] Nabieyan B., Kargari A., Kaghazchi T., Mahmoudian A., Soleimani M. Bench-scale pertraction of iodine using a bulk liquid membrane system. Desalination, 214 (2007) 167-176. https://doi.org/10.1016/j.desal.2006.08.018.
- [60] Ng Y.S., Jayakumar N.S., Hashim M.A. Behavior of hydrophobic ionic liquids as liquid membranes on phenol removal: Experimental study and optimization. Desalination, 278 (2011) 250-258. https://doi.org/10.1016/j.desal.2011.05.047.
- [61] Das D., Juvekar V.A., Rupawate V.H., Ramprasad K., Bhattacharya R. Effect of the nature of organophosphorus acid moiety on co-extraction of U(VI) and mineral acid from aqueous solutions using D2EHPA, PC88A and Cyanex 272. Hydrometallurgy, 152 (2015) 129-138. https://doi.org/10.1016/j.hydromet.2014.12.018.
- [62] Chang S.H., Teng T.T., Norli I. Cu(II) transport through soybean oilbased bulk liquid membrane: Kinetic study. Chem.Eng.J., 173 (2011) 352-360. https://doi.org/10.1016/j.cej.2011.07.062.
- [63] Gawronski R., Religa P. Transport mechanism of chromium(III) through the unmixed bulk liquid membrane containing dinonylnaphthalenesulfonic acid as a carrier. J.Membr.Sci., 289 (2007) 187-190. https://doi.org/10.1016/j.memsci.2006.11.053.
- [64] Chakraborty M., Bart H.-J. Highly selective and efficient transport of toluene in bulk ionic liquid membranes containing Ag+ as carrier. Fuel Process.Technol., 88 (2007) 43-49. https://doi.org/10.1016/j.fuproc.2006.08.004.
- [65] Kokufuta E., Nobusawa M. Uphill transport of phosphate ion through an oxomolybdenum(v)-tetraphenylporphyrin-complex-containing bulk liquid membrane: effect of halogen ions on phosphate ion flux. J.Membr.Sci., 48 (1990) 141-154. https://doi.org/10.1016/0376-7388(90)85002-3.
- [66] Singh R., Mehta R., Kumar V. Simultaneous removal of copper, nickel and zinc metal ions using bulk liquid membrane system. Desalination, 272 (2011) 170-173. https://doi.org/10.1016/j.desal.2011.01.009.
- [67] Yoshida S., Hayano S. Kinetics of partition between aqueous solutions of salts and bulk liquid membranes containing neutral carriers. J.Membr.Sci., 11 (1982) 157-168. https://doi.org/10.1016/S0376-7388(00)81398-8.
- [68] Krieg H.M., Lotter J., Keizer K., Breytenbach J.C. Enrichment of chlorthalidone enantiomers by an aqueous bulk liquid membrane containing beta-cyclodextrin. J.Membr.Sci., 167 (2000) 33-45. https://doi.org/10.1016/S0376-7388(99)00274-4.
- [69] Leon G., Guzman M.A. Facilitated transport of copper through bulk liquid membranes containing different carriers: compared kinetic study. Desalination, 223 (2008) 330-336. https://doi.org/10.1016/j.desal.2007.01.216.
- [70] Kontrec J., Kralj D., Brecevc L. Cadmium removal from calcium sulphate suspension by liquid membrane extraction during recrystallization of calcium sulphate anhydrite. Colloids Surf., A, 223 (2003) 239-249. https://doi.org/10.1016/S0927-7757(03)00148-1.
- [71] Leon G., los Santos R., Guzman M.A. Reduction of sodium and chloride ion content in aqueous solutions by bulk liquid membranes: a kinetic approach. Desalination, 168 (2004) 271-275. https://doi.org/10.1016/j.desal.2004.07.008.
- [72] He D., Ma M. Effect of paraffin and surfactant on coupled transport of cadmium(II) ions through liquid membranes. Hydrometallurgy, 56 (2000) 157-170. https://doi.org/10.1016/S0304-386X(00)00069-4.
- [73] Ma M., He D., Wang Q., Xie Q. Kinetics of europium(III) transport through a liquid membrane containing HEH(EHP) in kerosene. Talanta, 55 (2001) 1109-1117. https://doi.org/10.1016/S0039-9140(01)00525-2.

- [74] Muthuraman G., Teng T.T., Leh C.P., Norli I. Use of bulk liquid membrane for the removal of chromium (VI) from aqueous acidic solution with tri-n-butyl phosphate as a carrier. Desalination, 249 (2009) 884-890. https://doi.org/10.1016/j.desal.2009.09.008.
- [75] Boyadzhiev L., Lazarova Z. Study on creeping film pertraction. Recovery of copper from diluted aqueous solutions. Chem.Eng.Sci., 42 (1987) 1131-1135. https://doi.org/10.1016/0009-2509(87)80062-3.
- [76] MEIFANG J.I.M., LAZROVA Z., Boyadzhiev L. Study of copper extraction by liquid film pertraction. Water treatment, 6 (1991) 219-226
- [77] Boyadzhiev L., Bezenshek E., Lazarova Z. Removal of phenol from waste water by double emulsion membranes and creeping film pertraction. J.Membr.Sci., 21 (1984) 137-144. https://doi.org/10.1016/S0376-7388(00)81550-1.
- [78] Schlosser I., Kossaczky E. Pertraction through liquid membranes. J.Radioanal.Nucl.Chem., 101 (1986) 115-125. http://dx.doi.org/10.1007/BF02039397.
- [79] Bobok D, Schlosser J, Kossacsky E. Method of Separation of Solutions and Related Equipment for Realisation of this Method. Slovak patent (235362) 1984.
- [80] Boyadzhiev L., Alexandrova S. Dephenolation of Phenol-Containing Waters by Rotating Film Pertraction. Sep.Sci.Technol., 27 (1992) 1307-1317. https://doi.org/10.1080/01496399208019427.
- [81] Boyadzhiev L., Kirilova N. Extraction of tylosin from its aqueous solutions by Rotating Film-pertraction. Bioprocess Engineering, 22 (2000) 373-378. https://doi.org/10.1007/s004490050746.
- [82] Dimitrov K., Metcheva D., Boyadzhiev L. Integrated processes of extraction and liquid membrane isolation of atropine from Atropa belladonna roots. Sep.Purif.Technol., 46 (2005) 41-45. https://doi.org/10.1016/j.seppur.2005.04.008.
- [83] Alexandrova S., Dimitrov K., Saboni A., Boyadzhiev L. Selective recovery of silver from dilute polymetal solutions by rotating film pertraction. Sep.Purif.Technol., 22-23 (2001) 567-570. https://doi.org/10.1016/S1383-5866(00)00139-8.
- [84] Dimitrov K., Alexandrova S., Saboni A., Debray E., Boyadzhiev L. Recovery of zinc from chloride media by batch pertraction in a rotating film contactor. J.Membr.Sci., 207 (2002) 119-127
- [85] Raszkowska-Kaczor A., Adamczak P., Wodzki R. Hybrid rotating pertractor for Zn(II) recovery and separation. Desalination, 257 (2010) 66-72. https://doi.org/10.1016/j.desal.2010.03.004.
- [86] Boyadzhiev L., Dimitrov K. Recovery of silver from nitrate solution by means of rotating film pertraction. J.Membr.Sci., 86 (1994) 137-143. https://doi.org/10.1016/0376-7388(93)E0135-7.
- [87] Dimitrov K., Alexandrova S., Boyadzhiev L., Ruellan S., Burgard M. Recovery of copper from solutions by rotating film pertraction. Sep.Purif.Technol., 12 (1997) 165-173. https://doi.org/10.1016/S1383-5866(97)00046-4.
- [88] Schulz G. Separation techniques with supported liquid membranes. Desalination, 68 (1988) 191-202. https://doi.org/10.1016/0011-9164(88)80054-7.
- [89] Ho W.S.W., Poddar T.K. New membrane technology for removal and recovery of chromium from waste waters. Environ.Prog., 20 (2001) 44-52. https://doi.org/10.1002/ep.670200115.
- [90] Klaassen R., Jansen A.E. The membrane contactor: Environmental applications and possibilities. Environ.Prog., 20 (2001) 37-43. https://doi.org/10.1002/ep.670200114.
- [91] Ho W.S.W., Wang B. Strontium Removal by New Alkyl Phenylphosphonic Acids in Supported Liquid Membranes with Strip Dispersion. Ind.Eng.Chem.Res., 41 (2002) 381-388. https://doi.org/10.1021/ie0101339.
- [92] Caracciolo F., Cussler E.L., Evans D.F. Membranes with common ion pumping. AIChE J., 21 (1975) 160-167. http://dx.doi.org/10.1002/aic.690210121.
- [93] Cussler E.L. Membranes which pump. AIChE J., 17 (1971) 1300-1303. http://dx.doi.org/10.1002/aic.690170607.
- [94] Zahedi M.M., Mohamad Ghasemi S. Separation study of Mg+2 from seawater and RO brine through a facilitated bulk liquid membrane transport using 18-Crown-6. J.Water Reuse Desalin., 7 (2016) 468-475. https://doi.org/10.2166/wrd.2016.103.
- [95] Jonsson J.A., Mathiasson L. Liquid membrane extraction in analytical sample preparation: I. Principles. TrAC, Trends Anal.Chem., 18 (1999) 318-325. https://doi.org/10.1016/S0165-9936(99)00102-8.
- [96] Benomar M., Mendiguchia C., Garcia-Vargas M., Moreno C. A Liquid Membrane-Based Green Method for the Separation and Determination of Lead in Saline Waters. Spectrosc.Lett., 44 (2011) 83-87. https://doi.org/10.1080/00387011003649662.
- [97] Chimuka L., Cukrowska E., Jonsson J.A. Why liquid membrane extraction is an attractive alternative in sample preparation. Pure

Appl.Chem., 76 (2004) 707-722. https://doi.org/10.1351/pac200476040707.

- [98] Barri T., Jonsson J.A. Advances and developments in membrane extraction for gas chromatography: Techniques and applications. J.Chromatogr.A, 1186 (2008) 16-38. https://doi.org/10.1016/j.chroma.2008.02.002.
- [99] Granado-Castro M.D., Galindo-Riano M.D., Garcia-Vargas M. Separation and preconcentration of cadmium ions in natural water using a liquid membrane system with 2-acetylpyridine benzoylhydrazone as carrier by flame atomic absorption spectrometry. Spectrochim.Acta, Part B, 59 (2004) 577-583. https://doi.org/10.1016/j.sab.2004.01.006.
- [100] Safavi A., Shams E. Selective transport of silver ions through bulk liquid membrane using Victoria blue as carrier. Talanta, 48 (1999) 1167-1172. https://doi.org/10.1016/S0039-9140(98)00344-0.
- [101] Jonsson J.A., Mathiasson L. Membrane-based techniques for sample enrichment. J.Chromatogr.A, 902 (2000) 205-225. https://doi.org/10.1016/S0021-9673(00)00922-5.
- [102] Dominguez-Lledo F.C., Galindo-Riano M.D., Diaz-Lopez I.C., Garcia-Vargas M., Granado-Castro M.D. Applicability of a liquid membrane in enrichment and determination of nickel traces from natural waters. Anal.Bioanal.Chem., 389 (2007) 653-659. https://doi.org/10.1007/s00216-007-1472-z.
- [103] Aouarram A., Galindo-Riano M.D., Garcia-Vargas M., Stitou M., El Yousfi F. A permeation liquid membrane system for determination of nickel in seawater. Talanta, 71 (2007) 165-170. https://doi.org/10.1016/j.talanta.2006.03.038.
- [104] Mendiguchia C., Moreno C., Garcia-Vargas M. Determination of copper in seawater based on a liquid membrane preconcentration system. Anal.Chim.Acta, 460 (2002) 35-40. https://doi.org/10.1016/S0003-2670(02)00144-7.
- [105] Granado-Castro M.D., Galindo-Riano M., Vargas M. Model experiments to test the use of a liquid membrane for separation and preconcentration of copper from natural water. Anal.Chim.Acta, 506 (2004) 81-86. https://doi.org/10.1016/j.aca.2003.11.004.
- [106] Casanueva M., Galindo R., Granado C. Coupled Transport of Pb(II) Ions Through a Bulk Liquid Membrane as a Preconcentration Method for Saline Natural Waters. Current Anal.Chem., 14 (2018) 135-144. https://doi.org/10.2174/1573412913666170705095341.
- [107] Pinto J.J., Garcia-Vargas M., Moreno C. A bulk liquid membrane-flow injection (BLM-FIA) coupled system for the preconcentration and determination of vanadium in saline waters. Talanta, 103 (2013) 161-165. https://doi.org/10.1016/j.talanta.2012.10.026.