Chapter2: Wastewater treatment by Bulk Liquid Membrane method

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Abstract

Liquid membrane separation is a process which is depending on rate process and chemical potential gradient. A recent development in liquid membranes is the incorporation of selective carriers within the liquid membrane phase which selectivity and efficiency via chemical reaction facilitate the transport of a specific compound across the membrane. Bulk liquid membrane (BLM) consists of a bulk aqueous feed and receiving phases separated by a bulk organic, water-immiscible liquid phase. Many more technologies that were developed and tested in the last decade have to be included in the BLM group.

Keywords: Bulk liquid membrane; Liquid membrane; Potential gradient; Carrier; Organic

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1. Introduction

Liquid membrane systems are the subject of numerous studies and they are used in separation processes in order to recover metals in hydrometallurgical processes, separation of radioactive elements, and wastewater treatment. The effective application of liquid membranes is determined by their stability (Wells, 1993). The main process that occurs in a liquid membrane system is extraction. The liquid membrane methods fulfilled for ecological treatment as well as efficient and economical leading of the process.

Liquid membranes (liquid phases), existing in either supported or unsupported form, serve as selective barriers between liquid or gas phases and have shown great potential and application in separations. Selective transport of cationic substrates by membrane carriers is of great importance in chemistry, biology, and separation sciences. Compared with conventional separation processes membrane techniques are characterized by the technical simplicity and high efficiency in separating or enriching material from gaseous or liquid mixtures. Also, these methods reduce the solvent inventory requirements.

A liquid membrane is a thin liquid layer (organic phase) which separates two homogenous liquids or gases (feed and stripping phase). The liquid membrane must be immiscible and insoluble in the external solutions (Wódzki, 1997). Transport of substances between phases is caused by a driving force, which is a concentration gradient (chemical potential). The selectivity and the rate of transport through the membrane depends on differences in the solubility and diffusion coefficients of components in the membrane and the concentration of components in the feed and stripping solutions. To improve the selectivity and influence the process capacity, the carrier is introduced into the membrane phase. The carrier has an affinity to the one of the components of the feed solution, and a complex soluble in the membrane is formed by reversible reaction.

Due to the structure and transport mechanism, three basic types of liquid membrane can be established (Kislik, 2010) as follows:

• Bulk Liquid Membrane – BLM

• Emulsion Liquid Membrane – ELM

• Supported Liquid Membrane – SLM

Among membrane technologies, the bulk liquid membrane (BLM) is one of the simple, lowest and efficient types of liquid membranes (Ma et al., 2002). Bulk liquid membrane (BLM) is one of the simple, lowest and efficient types of liquid membranes (Ma et al., 2002). In this technique similar to liquid membrane configurations, (viz ion transport across membranes) combine the extraction, diffusion, and back extraction of analytes are particularly drawing maximum attention. BLM constitute the cheapest separation techniques because of their relatively small inventory and low capital cost. In a BLM, a relatively thick layer of immiscible fluid is used to separate the donor and acceptor phase. There is no means of support for the membrane phase and it is kept apart from the external phases only by means of its immiscibility.

Many anthropogenic organic compounds are highly hydrophobic in character, that is, they possess high values of the 1-octanol/water partitioning coefficient (generally expressed as the log P). They can be present in different types of wastewaters. In such context, the two-phase partitioning bioreactors can be used for the elimination of these compounds from wastewater. They are a specific case of the BLM, where the feed and the stripping phase are one and the same, namely the treated wastewater.

2. Definition

In a BLM, a relatively thick layer of immiscible fluid is used to separate the source and receiving phase. There is no means of support for the membrane phase and it is kept apart from the external phases only by means of its immiscibility. A recent development in liquid membranes is the incorporation of selective carriers within the liquid membrane phase which selectivity and efficiency via chemical reaction facilitate the transport of a specific compound across the membrane.

3. Types and design of BLM

BLM can be designed with a wide variety of configurations which, in most cases, consists of two parts: a common part containing the M phase and a separate part where the S and R phases are either separated by a solid impermeable barrier or structurally separated without any barrier. The barrier is normally designed as a flat or cylindrical wall and placed in between the S and R phases. The former consists of the rectangular and cylindrical vessels, whereas the latter includes the H- and U-tube vessels. The experimental setup of H and U type bulk liquid membrane are shown in Fig. 1. Some of these vessels have their common parts arranged at the top and separate parts at the bottom, while some of them have the opposite arrangement depending on the density of S, M, and R phases used. Most, if not all, of these phases are stirred at an appropriate intensity to avoid mixing between them.

In general, the volume of M phase used is equal to or between those of S and R phases. For instance, Muthuraman et al. (2009) and Akin et al. (2012) used equal volumes of S, M, and R phases, that is S/M/R volume ratio of 1:1:1, in their BLM processes, while Koter et al. (2013) and Candela et al. (2013) applied S/M/R volume ratios of 4.2:2:1 and 10:2.5:1, respectively. Sometimes, the M phase with the highest volume among the phases is also used. For example, Minhas et al. (2010) applied an S/M/R volume ratio of 1:1.5:1 in their BLM processes, whereas Dadali et al. (2012) utilized an S/M/R volume ratio of 6.25:6.25:1.

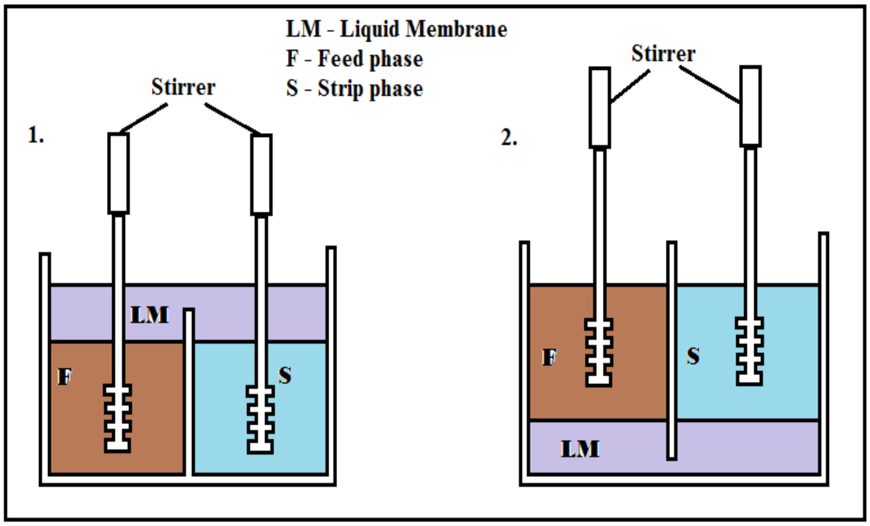

Fig. 1. Three Phase Bulk Liquid Membrane Experimental Set up 1, density of LM less than Aq. Set up 2, density of LM greater than aqueous phase

3.0. Similar types of BLM

Many more similar BLM systems are presented, such as hybrid liquid membrane (HLM), hollowfiber liquid membrane (HFCLM), (HFLM), pertraction, flowing liquid membranes (FLM), membrane-based extraction and stripping, multimembrane hybrid system (MHS), and membrane contactor systems. All these systems are based on membrane-based nondispersive (as the means for blocking the organic reagent from mixing with the aqueous feed and strip solutions) selective extraction coupled to permselective diffusion of solute-extractant complexes and selective stripping of the solute in one continuous dynamic process.The terms vary by membrane type used (hollow-fiber, flat neutral, ionexchange sheets), or by module design. Let us present some examples. The systems presented by the term membrane-based (or nondispersive) solvent extraction describe, as a rule, dynamic LM processes in which the equilibrium-based solvent extraction (forward and back) are only local processes taking place on the immiscible phases interfaces (on the surface of membrane support).

The term contactor systems present only membrane devices, mostly hollow- fiber, but not processes. The membrane in a contactor acts as a passive (not selective) barrier and as a means of bringing two immiscible fluid phases (such as gas and liquid, or an aqueous liquid and an organic liquid) in contact with each other without dispersion. The phase interface is immobilized at the membrane pore surface, with the pore volume occupied by one of the two fluid phases that are in contact. Contactor devices are used in many of the above-mentioned BLM systems (HLM, HFCLM, HFLM, FLM, pertraction, membrane-based extraction, MHS) as construction units. Sometimes, selective hydrophobic, hydrophilic, or ion-exchange membranes are used as barriers for additional selective separation in the devices similar to contactors.

Therefore, all above-mentioned bulk LM processes with water immiscible liquid membrane solutions may be unified under the term bulk organic hybrid liquid membrane (BOHLM) systems. Bulk LM processes with water-soluble carriers are defined as bulk aqueous hybrid liquid membrane (BAHLM) systems. These new technologies have the necessary transport and selectivity characteristics to have potential for commercial applications.

A great variety of carriers are used in the BOHLM transport. They may be divided into cation, anion exchangers and neutral ligands. The first group comprises the large number of organic acids and their derivatives and related proton donors.

The recently developed bulk aqueous hybrid liquid membrane (BAHLM) separation process (Kislik and Eyal, 2000) solved most of these problems. The technological concept of BAHLM transport is quite simple: an aqueous solution of a carrier, E, flows between two membrane barriers, which separate the carrier from the feed, F, and strip, R, aqueous solutions. It can be seen that the BAHLM system is similar to the BOHLM except the liquid membrane.

4.0. MEMBRANE CONTACTORS

There are two main types of hollow fiber (HF) contactors, those with parallel flow or cross-flow of phases. Cylindrical HF contactor with cross-flow of phases Contactors with flat sheet and cylindrical walls are used in MBSE or MBSS but only hollow fiber (HF) contactors in cylindrical modules in several sizes are available commercially. Flat sheet contactors are widely used in analytical chemistry (Jonsson and Mathiasson, 2001; Jonsson, 2003). There are two main types of HF contactors, those with parallel flow of phases in fibre lumen and in shell or cross flow of phases. A HF contactor with cross flow of phases is shown in Fig. 2

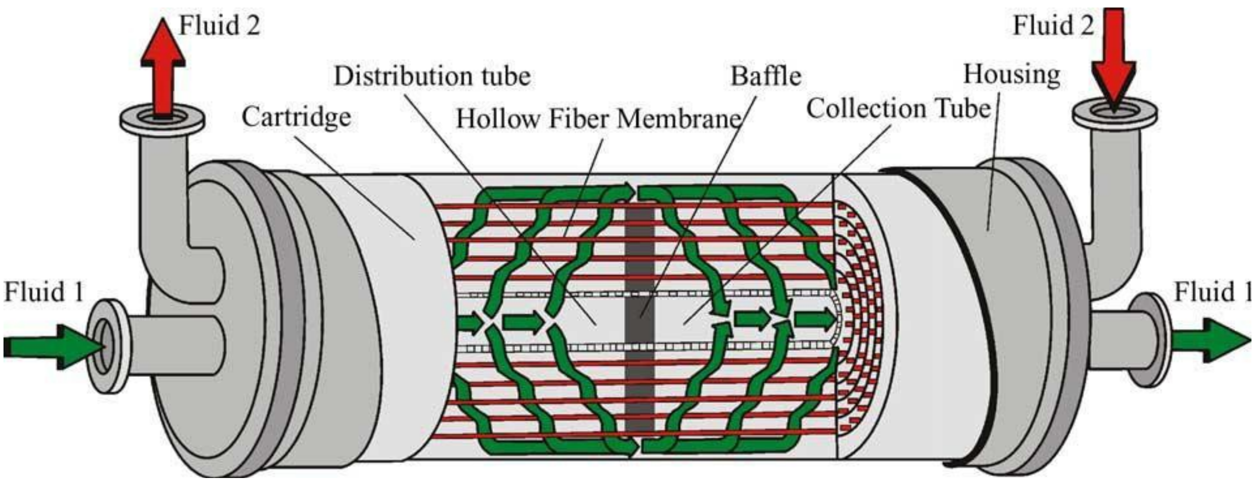

Fig. 2: Hollow fiber contactor with cross-flow of phases (Schlosser et al., 2005)

A modular HF contactor containing planar element with flowing head of fibres and cross flow of one phase can be also used as a two phase contactor (Schlosser, 1997). Reviews on two phase HF contactors are presented in papers (Schlosser, 2000; Reed, 1995; Gabelman, 1999). Mass-transfer characteristics of two phase contactors are presented in paper (Schlosser, 2005).

HF contactors have a large interfacial area per unit volume of the contactor without requirement of desperation of one phase that can be advantageous in systems sensitive to emulation. The volume ratio of phases could be varied practically without limitations. The disadvantage of HF contactors is connected with additional mass-transfer resistance introduced by porous wall(s) immobilizing L/L inter-face(s). Some problems with swelling of HF and especially of potting material of HF in solvents may occur.

5. THEORY OF BLM

Recovery and concentration of solutes, as well as separation of samples, have attracted interest of researchers, especially in connection with their recovery from fermentation broths, reaction mixtures and waste solutions. Several reviews including membrane based solvent extraction (MBSE), pertraction, The solvent can be regenerated by membrane based solvent stripping (MBSS) where the solute is re-extracted into the stripping solution (Schlosser, 2000 a&b; Schugerl, 2000; Malinowski, 2001).

The transport of metal ions and organic pollutants through liquid membranes can be subjected two modeling using two different approaches. The first very frequently used approach based on the model of Reusch and Cussler developed (1973) deals with the concentration diffusion layers and treats the interphase between the organic and aqueous phase as the platform wherein the complexation and decomplexation occur (Visser et al., 1994). Figure 5 shows the various steps involved in the transport.

Several mechanisms have been proposed to achieve transport of solute(s) through the L/L interface or through a liquid membrane. The separation mechanism could be based on differences in physical solubility of the solutes or their solubilisation into the solvent or reverse micelles or on the chemistry and rate of chemical or biochemical reactions occurring on L/L interface(s). The complexing or solubilisation agent extractant (carrier in the liquid membrane) forms by reversible reaction complex(es) or aggregate(s) with the solute, which are soluble in the solvent or membrane (Schugerl et al., 1994; Bart, 2001).

The transport from the aqueous source phase through the organic membrane into the aqueous receiving phase can be divided into various steps. There is a diffusion of solute through the diffusion boundary layer (DBL) from the feed bulk to the membrane surface with a linear concentration gradient near the membrane surface. The chemical complexation of the metal ion with the carrier at the aqueous/membrane inter phase is a fast reaction in comparison to the diffusion process resulting in equilibrium and the diffusion of metal carrier complex through DBL on the membrane side occurs. The transport of the metal carrier within the membrane toward the receiving phase is due to convection transport as a result of the continuous stirring of the membrane liquid. Then diffusion similar to that in the feed phase occurs in the receiving phase. The solute of interest is transported to the receiving phase with a simultaneous transfer of other ions of same charge from the receiving to feed phase(Figure 3)

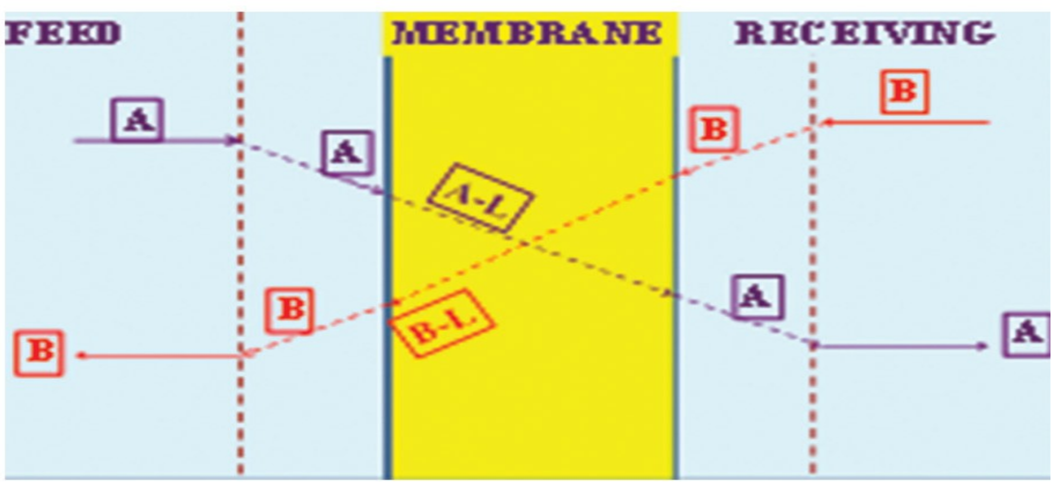

Fig. 3: Schematic representation of transport.

In the second approach (Mogutov et al., 1993) it is assumed that the carrier moves a bit out of the organic phase and the reactions occur in the portion of the aqueous phase known as "Big Carrousel." There is one more less popular approach wherein the stagnant diffusion layers on the aqueous/organic phase boundaries are not considered and the diffusion through organic layer is considered (Mogutov et al., 1993). However, this approach is justified only if stirring is efficient.

4. Applications and disadvantages of bulk liquid membrane

Applications of the BLM processes are mainly in metal separation, wastewater treatment, biotechnologies, drugs recovery-separation, organic compounds, and gas separation. In recent years, integrated hybrid systems incorporating two or more functions in one module, for example biotransformation and separation, become of great interest to researchers.

4.1. Industrial applications

To date and to the best of the author's knowledge, only one commercial application has been reported for two-phase partitioning bioreactors. It is based on the work by the research group of Prof. Andrew S. Daugulis from the Queen's University in Kingston, Canada (Daugulis, 1988).

The application of mercury is widespread in agriculture, for example, as insecticide in seed treatment, and different types of industry (Katzung, 1987). A promising method for the removal and preconcentration of mercury from wastewater has been the application of liquid membranes containing calixarenes as carriers (Alpoguz et al., 2004). A three-phase system for the extraction of Hg from industrial wastewater has been reviewed by Ersoz (2007). Models and implication of theoretical conclusions are presented.

Disadvantages

One of the disadvantages is the formation of emulsions, which can extract protein from the microbial cells, and thus leads to the rupture of cells, that is, breakdown of the bioreactor performance (Van Sonsbeek et al., 1993).

References

Wells A.F (1993) Structual Inorganic Chemistry. Wydawnictwo Naukowo Techniczne. Warszawa.

Wódzki R (1997) Liquid Membrane. Structure and mechanism of action, [in]: Narębska A. (red.): Membranes and Membrane Separation Technology. Wydawnictwo Uniwersytetu Mikołaja Kopernika, Toruń.

Kislik VS (2010) Liquid Membranes: Principles and Applications in Chemical Separations and Wastewater Treatment. Elsevier.

Ma M, He DS, Liao SH, Zeng Y, Xie QJ, Yao SZ (2002) Kinetic study of L-isoleucine transport through a liquid membrane containing di(2-ethylhexyl) phosphoric acid in kerosene. Analytica Chimica Acta 456:157.

Muthuraman G, Teng TT, Leh CP, Norli I (2009) 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: 884–890.

Akin I, Erdemir S, Yilmaz M, Ersoz M (2012) Calix[4] arene derivative bearing imidazole groups as carrier for the transport of palladium by using bulk liquid membrane. J Hazard Mater 223–224:24–30.

Koter S, Szczepan´ ski P, Mateescu M, Nechifor G, Badalau L, Koter I (2013) Modeling of the cadmium transport through a bulk liquid membrane. Sep Purif Technol 107:135–143.

Candela AM, Benatti V, Palet C (2013) 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 120:172–179.

Minhas FT, Memon S, Bhanger MI (2010) Transport of Hg(II) through bulk liquid membrane containing calyx [4]arene thioalkyl derivative as a carrier. Desalination 262:215–220.

Dalali N, Yavarizadeh H, Agrawal YK (2012) 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 18:1001–1005.

Kislik V, Eyal A (2000) Aqueous hybrid liquid membrane process for metal separation. Part I. A model for transport kinetics and its experimental verification. J Membr Sci 169:119-132.

Kislik V, Eyal A (2000) Aqueous hybrid liquid membrane process for metal separation. Part II. Selectivity of metals separation from wet-process phosphoric acid. J Membr Sci 169:133-146.

Jonsson JA, Mathiasson L (2001) Membrane extraction in analytical-chemistry, J Sep Sci 24: 495.

Jonsson JA (2003) Membrane extraction for sample preparation − a practical guide. Chromatographia 57:317.

Schlosser S (1997) Method and Equipment for Mass and Heat Transfer among Several Liquids Slovak University of Technol., Bratislava: Slovakia. p. 8.

Schlosser S (2000) Membrane based processes with immobilized interface, in: K. Bako, L. Gubicza, M. Mulder, (Eds.), Integration of Membrane Processes into Bioconversions, Kluwer Academic, p. 55.

Reed BW,. Semmens MJ, Cussler EL (1995) Membrane contactors, in: R.D. Noble and S.A. Stern (Eds.), Membrane Separation Technology. Principles and Applications, Elsevier Science, Amsterdam, p. 467.

Gabelman A, Hwang ST (1999) Hollow fiber membrane contactors, J Membr Sci 159:61.

Schlosser S, Kertesz R, Martak J (2005) Recovery and separation of organic acids by membrane-based solvent extraction and pertraction − An overview with a case study on recovery of MPCA. Sep Purif Technol 41:237.

Schlosser S (2000a) Membrane based processes with immobilized inter-face, in: Bako K, Gubicza L, Mulder M (Eds.), Integration of Membrane Processes into Bioconversions, Kluwer Academic, New York, USA.

Schlosser S (2000b) Pertraction through liquid and polymeric membranes, in: K. Bako, L. Gubicza, M. Mulder (Eds.), Integration of Membrane Processes into Bioconversions, Kluwer Academic publishers, New York.

Malinowski JJ (2001) Two-phase partitioning bioreactors in fermentation technology. Biotech Adv 19: 525.

Reusch CF, Cussler EL (1973) Selective membrane transport. AIChE J 19:736-741.

Visser HC, Reinhoudt DN, De Jong F (1994) Carrier-mediated transport through liquid membranes. Chemi Society Reviews 23:75-81.

Schlosser S, Rothova I (1994) A new type of hollow fiber pertractor With bulk liquid membrane. J Membr Sci 29:765-780.

Bart HJ (2001) Reactive Extraction. Springer, New York, USA.

Mogutov V, Kocherginsky NM (1993) Macrokinetics of facilitated transport across liquid membranes. 1. Big Carousel J Membr Sci 79:273-283.

Daugulis AJ (1988) Integrated reaction and product recovery in bioreactor systems. Biotechnol Progress 4:113.

Katzung BG (1987) Basic and Clinical Pharmacology, 3rd ed. Appleton and Lange, New York, USA 734-735.

Alpoguz HK, Memon S, Ersoz M, Yy´lmaz M (2004) Transport kinetics of Hg2þ through bulk liquid membrane using calix[4]arene ketone derivative as carrier. Sep Sci Technol 39:799-810.

Ersoz M (2007) Transport of mercury through liquid membranes containing calixarene carriers. Adv Colloid Inter Sci 134–135:96-104.

Van Sonsbeek HM, Beeftink HH, Tramper J (1993) Two-liquid-phase bioreactors. Enzyme Microbial Technol 15:722-729.