

EXTRACTION OF HEAVY METALS FROM WASTE WATERS BY LIQUID MEMBRANE TECHNIQUES

L. BOYADZHIEV

*Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia,
Bulgaria*

Abstract. Liquid pertraction or liquid membrane separation is a new separation method, representing a combination in time and space of two mass transfer operations: extraction and stripping. Ions or molecules are selectively transported by means of an intermediate liquid phase – a liquid membrane, which in most of the techniques proposed is a mobile, flowing film. The simultaneous interaction of three mobile liquids, separated by two interfaces, provides more efficient removal of the solutes – in the studied case – heavy metals, contained in waste waters in low concentrations. The paper is an overview of the existing pertraction techniques, revealing their advantages and shortcomings. Transport mechanisms and extraction kinetics are discussed and a series of practical applications are described.

Keywords: extraction, heavy metals, waste waters, liquid membrane technique.

AIMS AND BACKGROUND

Various methods have been proposed for removal of heavy metals from mine or industrial waste waters. Some of them are today successfully applied in practice, while others are still in the early stage of laboratory or pilot plant investigations. The latter group includes liquid membrane or pertraction methods that offer attractive advantages and cannot be overlooked by industry. Principle priority of pertraction is that it not only offers complete extraction of desired heavy metals, which are generally considered as toxic, but also provides highly concentrated, usable product solutions. Usually, when this unit operation is applied, the extraction process is highly selective, which is a supplementary advantage as compared to processes in which solid membranes are used.

Nowadays, liquid membrane separations are considered as new and perspective techniques with many applications. They are witnessing an ever increasing interest: more than 200 R&D laboratories all over the world are engaged in development of new technologically convenient and economically acceptable pertraction processes¹.

The present paper is aimed to help the reader to obtain a general idea about the state-of-the-art of this new unit operation, as well as to show how the latter can be applied for treatment of waste waters, containing heavy metals.

HOW LIQUID MEMBRANES CONCENTRATE METAL SOLUTIONS

Generally speaking pertraction is a mass-transfer process, the driving force of which is the difference between the concentrations of the transported substance in two aqueous solutions separated by a "membrane" liquid, which is insoluble the other two. According to the transport scheme, pertraction processes can be classified into two basic groups: simple and facilitated processes. The first group includes cases when the membrane liquid simply dissolves the transported species, regardless of the form they exist. In the case of facilitated pertraction processes the transported substance is insoluble in the organic membrane liquid, but it forms a soluble complex with a carrier, specially added to the membrane liquid². Therefore, often this group of transport processes is also called carrier mediated transport³.

An example of non-facilitated pertraction process is shown in Fig. 1,a. In this case the solute A, more or less soluble in the membrane phase, is transported from the feed F into the acceptor solution R, where it is transformed into another chemical species, insoluble in the membrane liquid S. The transfer of A from F into R can practically proceed until complete extraction of A from the feed F. This type of transport is called transport with a chemical reaction in acceptor R or often "up-hill" transport. The latter term means that a "pumping" of the solute is possible against its apparent concentration gradient. Thus various organic acids, or bases, even slightly soluble in the organic membrane, can be neutralised by a strong base or acid, respectively, added to strip solution and therefore extracted completely from the aqueous donor solution. It is well known that the salts obtained or their dissociates are insoluble in the organic membrane S.

The second group of transport mechanisms – the facilitated ones, are of greater practical value, since contrary to the conventional multi-

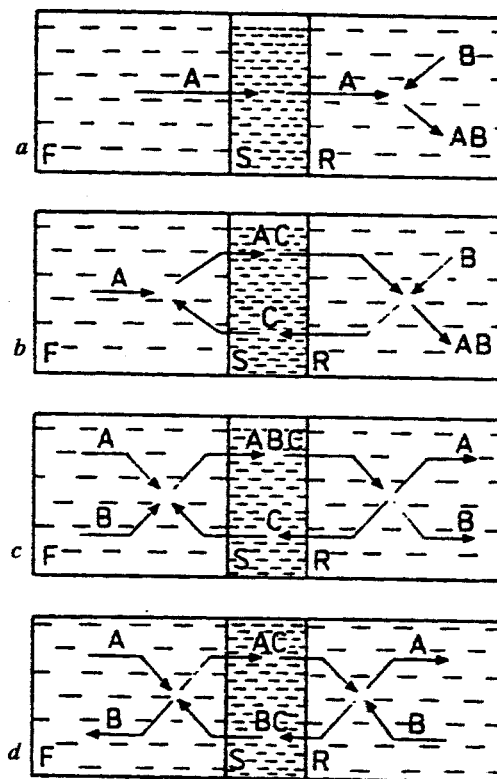
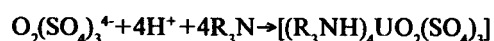


Fig. 1. Mass transfer mechanism and "pumping" effect in liquid pertraction: a) simple up-hill transport; b) facilitated up-hill transport; c) facilitated co-transport; d) facilitated counter-transport

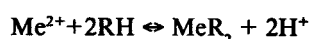
purpose solvents, the carrier added to the membrane can be with a desired, specific selectivity, which, as already mentioned, is one of the basic advantages of the liquid membrane separation as compared with other membrane processes. Fig. 1*b* shows a case, in which the facilitated transport of A is combined with the chemical reaction $A + B = AB$ in the strip solution. It is obvious that the chemical reaction with B and the selective interaction between the solute A and the carrier Cs provide practically complete removal of A from the feed. Thus, with the aid of the already existing broad spectrum of carriers, known as crown-ethers, selective extraction and concentration of various metals can be achieved, thanks to the differences in the size and the charge of their ions.

Cases of special interest are the so-called coupled transport mechanisms: the coupled co-transport and the coupled counter-transport. In the first case the solute A is transported from the feed to the strip solution together with B, since only the complex ABC is soluble in the membrane (Fig. 1*c*). For example, according to this scheme, uranyl sulphate ion, which forms a complex with the carrier – an oil-soluble amine – is transferred into the strip solution R:



In order to disintegrate the complex the pH value of the strip solution should be high enough.

Fig. 1*d* shows the second mechanism – the coupled counter-transport. Solute transfer from the feed into the strip solution is accompanied by an equivalent back transfer of the species B towards the feed. A typical case following this scheme is the ion-exchange of metal ions against hydrogen ions:



The chelate complex MeR_2 is soluble in the membrane liquid and is formed or decomposed depending on the pH value of the respective aqueous solutions.

HOW PERTRACTION PROCESSES ARE REALISED IN PRACTICE

Numerous pertraction techniques and their versions are known², but a limited number of them show a potential importance for practical applications. Some of these techniques will be considered in the following paragraphs.

Supported liquid membranes (SLM). Contrary to solid membranes, liquid membranes are more easily created, but unfortunately they are also readily destructed. Therefore, reproductive and stable separation processes using liquid membranes are difficult to achieve if no special cares are taken to stabilise them.

The most widely used supported liquid membrane technique consists in the impregnation of a porous support, made of synthetic polymer, with the membrane liquid. The stability of such system is based on the capillary forces, retaining the organic liquid in the pores of the oleophilic support. Obviously, the difference

between the pressures on the two sides of the membrane should not surpass the capillary pressure. Porous supports are flat and parallel or spirally wound sheets, but most often a bunch of hollow fibres (Fig. 2). In these configurations, SLM modules provide large contact areas, a prerequisite for their use in pilot and industrial plants. In the case of spiral wound modules the surface-to-volume ratio is in the order of $1000 \text{ m}^2/\text{m}^3$ (Ref. 4), while modules with tiny hollow fibres (Fig. 2) provide an even larger area of $10\,000 \text{ m}^2/\text{m}^3$ (Refs 5, 6).

An advantage of this liquid membrane technique, which is also their shortcoming, is the extremely low amounts of membrane liquids used. There are high risks for breakdowns and consequently for a mixing up of feed and strip liquids. This is due to the unavoidable losses of membrane liquid, by its wash-out and emulsification, or merely to the solubility in both aqueous solutions. In order to overcome these shortcomings gelation of membrane liquid is proposed, but an increase of membrane consistency reduces the diffusion fluxes across the membrane⁷.

Therefore, techniques using larger amounts of membrane liquid are less capricious and hence more promising. Such an approach has been proposed by Teramoto et al.⁸ The module of the so-called "flowing liquid membrane" comprises spirally wound porous supports and mesh spacers, which form alternatively arranged channels for the three liquids.

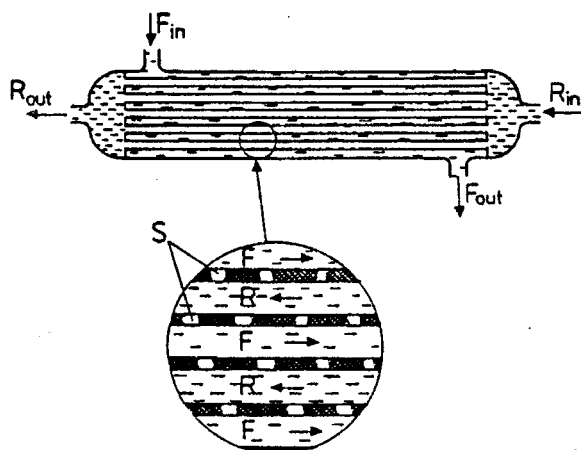


Fig. 2. Hollow fibre supported liquid membrane module. Strip solution flows in the lumen of hollow fibres, while the feed flows outside the fibre bunch in counter-current

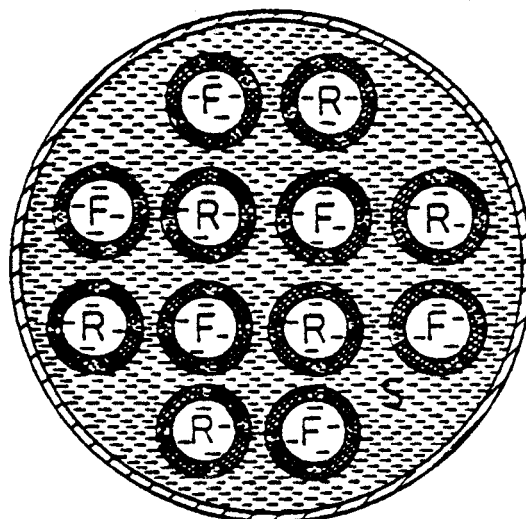


Fig. 3. Cross-section of contained liquid membrane module. Feed and strip solutions flow in the lumens of two separate fibre bundles

Sirkar et al.^{9,10} introduced the “contained” liquid membrane technique. They use two sets of porous hollow fibres, in the lumens of which feed F and strip R solutions flow, respectively. The two bunches are closely or the two aqueous solutions closely packed together inside the module tube, as shown in Fig. 3. In all SLM versions, the porous supports are used to fix the interfaces between the organic and corresponding aqueous solutions.

Bulk liquid membranes (BLM). The last SLM modification should be regarded as a transition between the supported liquid membranes and the “bulk” liquid membranes (BLM). In the latter the “membrane” is a rather thick, bulk layer occupying the space between the feed and strip solutions.

Various versions of bulk liquid-membrane techniques which could be applied not only for laboratory purposes but in larger scale are known. In the liquid film pertraction (LFP) technique^{3,11,12} the feed and the strip solutions flow down as thin liquid films on the surface of vertical solid support arranged closely next to each other (Fig. 4). The whole package is immersed in the membrane fluid which flows in counter-current mode to the falling liquids.

Another group of techniques which is similar to the described one as far as the presence of mobile liquid films of the feed and strip solutions is concerned, are the rotating film pertraction (RFP) techniques^{13,14}. The supports in this case are vertical rotating discs, partially immersed in solutions F and R. The pertractor space over the level of the solutions F and R is filled with the intermediate membrane liquid S which is stirred by the discs rotation.

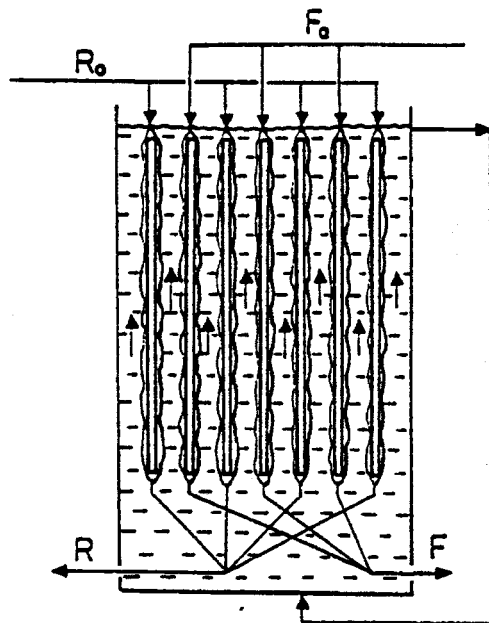


Fig. 4. Flow diagram of a falling film pertractor

The main advantage of these “flowing film” described techniques is the direct contact between flowing, non-stagnant liquids, which ensures high mass transfer fluxes and stability of the three-phase liquid systems. The results provide evidence that these methods are suitable for processes requiring long term trouble-free operation of the equipment. However, these devices have rather limited contact area – up to 300 m²/m³, which restricts their broad application.

Emulsion liquid membranes (ELM). Emulsion liquid membranes (ELM), initially proposed by N. Li¹⁵ represent three-phase liquid dispersions stabilised by surface active agents. According to

this technique, shown in Fig. 5, the strip solution R is finely emulsified into the membrane liquid S, and the obtained consistent and thick emulsion is dispersed in its turn, in the third liquid, namely the feed solution. During the second step of the process, prepared emulsion, containing enormous micro-droplets of the strip solution each 1 to 10 μm in diameter, is gently stirred in the feed solution, producing globules 1 to 2 mm in diameters. Usually, when water effluents, containing metal ions are treated, emulsion membrane liquid is mixture, containing an inert solvent, a selective carrier and an oil-soluble emulsifier for stabilisation of the water-in-oil emulsion².

Obviously, the most important feature of this pertraction technique is the very large contact area, which enhances the transport. The internal mass transfer area is in order of 10^5 - 10^6 m^2/m^3 , while the external - 1000-3000 m^2/m^3 .

The three-stage separation processes are performed both in mixer-settlers and columns. The emulsion breakage is usually carried out by means of specially designed electric coalescenes¹⁶.

The principal shortcomings of this technique originate in the emulsion instability. This instability depends strongly on the nature of the emulsifier used, the pH values of the solutions, their ionic strengths, intensity of mechanical stirring, etc. All these factors must be precisely controlled in order to reduce the negative effect of the spontaneous emulsion break during the second step of feed treatment. The spontaneous emulsion destruction decreases the process selectivity and should always be taken into consideration when evaluating the separation efficiency.

After the process is completed, in order to collect the concentrated strip liquor and to recycle the membrane liquid, the enriched emulsion has to be broken-

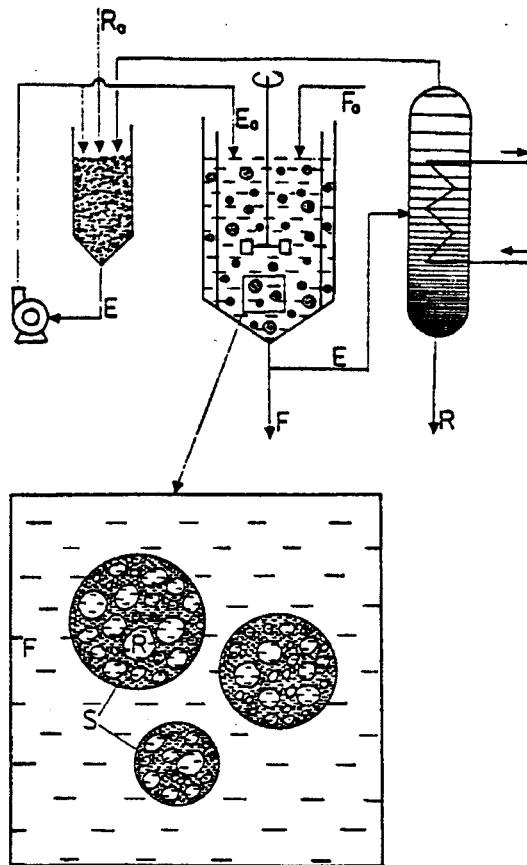


Fig. 5. Scheme of an emulsion liquid membrane process. Prepared emulsion E is dispersed and contacted with the feed F and after phase separation is broken-up by heating. The emulsion globule structure is shown in the close-up below

a difficult task, especially if strong emulsifying formulations have been used for preventing the spontaneous emulsion break. Sometimes, the presence of emulsifiers, more or less soluble in the treated effluents, leads to additional difficulties and contamination of the latter³.

APPLICATIONS FOR REMOVAL OF HEAVY METALS

Economic estimations show that liquid pertraction operations are among the cheapest separation techniques, due to their simple inventory and low running costs. Energy consumption is very low, and organic liquid losses are often negligible if the membrane formulation is properly designed^{1,2,16}.

Pertraction is especially suitable for the cases when the solute has relatively low distribution coefficient between membrane and donor liquids – the cases unacceptable in the solvent extraction. An advantage of liquid membrane separation as compared to the solid polymer membranes is the possibility to use a large variety of highly selective carriers which for the present polymer chemistry is an unattainable task.

Nowadays, due to the economical and environmental pressure, extraction and concentration of toxic or radioactive elements and various noble metals from low grade effluents becomes an issue of ever increasing importance. For the present, the industrial use of liquid membrane techniques is directed mainly toward the recovery of zinc and copper from waste waters with various compositions. The first large-scale plant for treatment of waste waters from the viscose and rayon industry was built in Austria¹⁷. Later, in addition to the Austrian industrial plant treating 100m³/h waste waters from the spin baths, containing 500 mg/l zinc, other similar plants using the ELM technique were designed in Germany and the Netherlands¹⁸. Usually zinc extraction from acid aqueous solutions is carried out with alkyl-phosphoric or alkyl-thiophosphoric acids and from alkaline solutions with extractants of LIX® series¹.

Chromates removal from waste waters discharged from electroplating and metal finishing industries is a major ecological issue since less than 0.05 mg/l chromium content in potable water is admitted. Some authors¹⁹ succeeded to extract simultaneously Cr (VI), Cr (II) and Zn (II) from cooling blow down streams applying ELM technique and using two carriers – tri-butylphosphate and Aliquat 336. Cd(II) and CN are extracted also simultaneously from electroplating bath effluents with a mixture of two extracting agents – di-2-ethylhexylphosphoric acid and an alkylphosphine oxide. The concentrate obtained can be directly re-used in the electroplating process.

Success has been achieved by the application of the ELM technique for removal of highly toxic mercury (II) from aqueous solutions.

It is well known that conventional solvent extraction is an efficient method for separation of lanthanides. In order to achieve a reasonable separation of lan-

thanides, very similar by their physico-chemical properties, it is necessary to use many consecutive stages of mixer-settlers in series. To overcome this inconvenience Nakashio et al.²⁰ created stable single stage ELM process using efficient carriers for La and Nd. Danesi et al.²¹ separated actinides and lanthanides from acidic radioactive waste waters with the aid of SLM modules, containing a large number of hollow fibres. Uranium is the major concern among the group of radioactive metals. Most of the studies in this respect have been aimed at the recovery uranium, contained in the wet process phosphoric acid. Uranium contained in ground waters²² has also been considered. Gutknecht and Schugerl et al.²³ extracted Ge (IV) from hydrochloric acid-containing fly ash solutions by applying ELM technique. Jin and Zhang²⁴ have developed a liquid-membrane technology based on ELM method for the extraction and concentration of Au and removing cyanides from alkaline waste waters discharged by the gold production industry in China.

CONCLUSIONS

It is obvious that liquid pertraction is a promising method for the extraction and concentration of numerous metals from waste waters even their concentration in the effluents is very low. The application of pertraction techniques in the case of extraction and concentration of them some heavy metals from their solutions, containing higher concentrations of them should be regarded as a very attractive.

The merits of liquid pertraction as compared to the conventional liquid-extraction are due to the simultaneous realisation of both extraction and stripping processes in a single separation device. The combination of both operations into a single step operation, and hence the combination of two very different phase equilibria, provides maximum possible driving forces in the three-phase system leading to an efficient solute extraction from very diluted solutions.

Liquid pertraction offers a possibility to use a broad spectrum of non-typical, according to the conventional solvent extraction criteria, extractant, e.g. harmless solvents showing low solute distribution coefficients or simply neutral oils doped with microamounts of very selective carriers. The choice of the most suitable pertraction technique is an issue remaining to be solved, since the membrane and acceptor solutions must be tailored according to each concrete case, moreover the information available nowadays is deficient. Obviously, studies will continue in an effort to bring this promising separation method from its cradle stage to maturity, so that it may receive a well-deserved share of the practical applications.

REFERENCES

1. L. BOYADZHIEV, Z. LAZAROVA: *Chimica Oggi*, **11** (11), 29 (1993).
2. L. BOYADZHIEV, Z. LAZAROVA: Liquid Membranes. In: *Membrane Separation Technology. Principles and Applications* (Eds R. Noble and A. Stern). Elsevier Pbl., Amsterdam, 1995, 283–352.
3. L. BOYADZHIEV: *Separ. Sci. Technol.*, **25**, 187 (1990).
4. M. TERAMOTO, H. MATSUYAMA, H. TAKAYA, S. ASANO: *Separ. Sci. Technol.*, **22**, 2175 (1987).
5. M. TANIGAKI, T. SHIODE, S. OKUMI, W. EGUCHI: *Separ. Sci. Technol.*, **23**, 1171 (1988).
6. A. B. DE HAAN, P. V. BARTELS, J. DE GRAAW: *J. Membr. Sci.*, **45**, 281 (1989).
7. A. J. B. KEMPERMANN, D. BARGEMAN, T. VAN DER BOOMGAARD, H. STRATHMANN: *Separ. Sci. Technol.*, **31**, 2733 (1996).
8. M. TERAMOTO, N. TOHNO, N. OHNISHI, H. MATSUYAMA: *Separ. Sci. Technol.*, **24**, 981 (1989).
9. A. SENGUPTA, R. BASU, R. PRASAD, K. K. SIRKAR: *Sep. Sci. Technol.*, **23**, 1735 (1988).
10. R. PRASAD, K. SIRKAR: *Sep. Sci. Technol.*, **22**, 619 (1987).
11. L. BOYADZHIEV, E. BEZENSHEK, Z. LAZAROVA: *J. Membr. Sci.*, **21**, 137 (1984).
12. B. G. FRAZER, M. D. PRIZKER, R. L. LEGGE: *Separ. Sci., Technol.*, **29**, 2097 (1994).
13. S. SCHLOSSER, E. KOSSACZKY: *J. Radioanal. Nucl. Chem.*, **101**, 115 (1986).
14. L. BOYADZHIEV, S. ALEXANDROVA: *Sep. Sci. Technol.*, **27**, 1307 (1992).
15. N. N. LI: *Ind. Eng. Chem., Proc. Des. Devel.*, **10**, 215 (1971).
16. J. DRAXLER, R. MARR: *Chem.-Ing.-Techn.*, **62**, 525 (1990).
17. J. DRAXLER, W. FURST, R. MARR: *J. Membr. Sci.*, **38**, 281 (1988).
18. R. MARR, H. J. BART, J. DRAXLER: *Chem. Eng. Process.*, **27**, 59 (1990).
19. E. J. FULLER, N. N. LI: *J. Membr. Sci.*, **18**, 251 (1984).
20. F. NAKASHIO, M. GOTO, N. YOSHI, K. KONDO: *Proceed. ICOM'90, Chicago, 1990*.
21. R. DANESI, R. CHIARIZIA, P. RICKERT, E. HORWITZ: *Solv. Extr. Ion Exch.*, **3**, 111 (1985).
22. R. CHIARIZIA, E. HORWITZ: *Solv. Extr. Ion Exch.*, **8**, 65 (1990).
23. W. GUTKNECHT, K. SCHUGERL: *Proceed. ISEC'88, Moscow, 1988*.
24. M.-F. JIN, Y. ZHANG: *Proc. ICOM'90, Chicago, 1990*.

Received 21 November 1998

Revised 25 January 2000