

**Paulina ŁOBODZIN<sup>1,2</sup>, Paweł RELIGA<sup>2</sup>, Jakub RAJEWSKI<sup>3</sup>**

<sup>1</sup> Institute for Sustainable Technologies, Radom

<sup>2</sup> Kazimierz Pulaski University of Technology and Humanities, Radom

<sup>3</sup> Warsaw University of Technology, Warszawa

paulina.lobodzin@itee.radom.pl, j.rajewski@ichip.wp.edu.pl

## **TRANSPORT OF Cr(III) THROUGH A SUPPORTED LIQUID MEMBRANE**

### **Key words**

Liquid membrane, SLM, carriers transport, chromium, D2EHPA, DNNSA.

### **Summary**

In this study, facilitated transport of Cr(III) ions through supported liquid membrane (SLM) was investigated. As a carrier di-nonylonaphthalenesulfonic acid (DNNSA) and di(2-ethylhexyl) phosphoric acid (D2EHPA) were used. Additionally, the effect of carrier concentration in the membrane on ion transport was observed and the optimum concentration of carriers was determined. The most effective transport of Cr(III) ions across SLM consisting of 15% D2EHPA and 25% DNNSA was found. The facilitated transport of chromium in the SLM system depended on the type of carrier, its concentration, and the pH value of the aqueous solutions.

### **Introduction**

Heavy metals are one of the most troublesome environmental pollutants. They are widely used in many industries such as iron and steel, energy, mining

and transport, so the reduction of heavy metals from wastewater compounds is relatively difficult to achieve [1].

The present limitation of pollutant concentration has caused that the conventional methods of water purification and treatment of toxic metal ions (the precipitation, the ion exchange, electrochemical processes) have become inadequate and too expensive. Researchers are still searching for new and effective separation methods. In recent years, a remarkable increase in the applications of liquid membranes especially supported liquid membrane (SLM) for metal ion separation processes has been found [2, 3]. This interest is due to the advantages of these processes, such as a low requirement of organic solvents compared to the extraction processes, and a high mass flux and good selectivity. Those advantages result from the possibility of using various organic solvents and doping carriers in the SLM.

Chromium, one of the heavy metals, is considered a main contaminant in the environment. The presence of chromium in wastewater is caused by incomplete consumption of Cr in production processes. Traditional methods of wastewater treatment and chromium recovery from aqueous solutions have been used in cases of high concentrations [4, 6]. They do not render complete removal of chromium, and the small amounts of metal ions are still present in refined solutions. Complete removal of chromium might be obtained by liquid membranes. The selectivity of liquid membranes allows the separation of different mixtures of metals ions or its forms [2]. Developments in material science have enabled the production of a wide range of membranes with different transport properties. At the end of the 1960s, for the first time, Li [7] proposed the concept of liquid membranes. He used a liquid membrane to separate hydrocarbons. 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 [8].

The main process that occurs in a liquid membrane system is extraction. 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 [9]. 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, four basic types of liquid membrane can be established [3] as follows:

- *Bulk Liquid Membrane* – BLM
- *Emulsion Liquid Membrane* – ELM
- *Polymer Inclusion Membrane* – PIM
- *Supported Liquid Membrane* – SLM

The processes of chromium separation in a SLM has a practical application [2–4]. The supported liquid membrane is a microporous polymeric support soaked with the solution of a specific carrier in organic diluent. A general scheme of the SLM is presented in Figure 1. Thanks to the immobilization of the carrier, the volume of the organic phase is reduced in comparison to the volume of external solutions.

The microporous filter (support) should be stable in an organic medium and with invariable porosity as a function of the time. In general, transport of chromium also depends on the thickness and morphology of the polymeric membrane used as a support. The support must be resistant to the harsh environment of the process and must retain its properties during long-term operation [3, 9, 10].

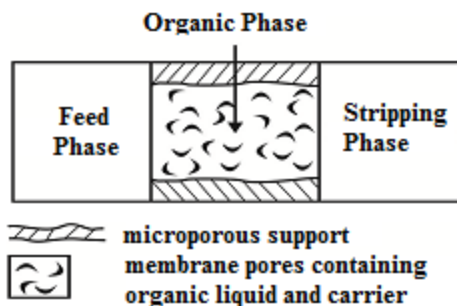


Fig. 1. Scheme of supported liquid membrane

## 1. Case Studies

Removal of heavy metals, including chromium, from wastewater due to economic and environmental protection, toxicology, and health reasons, is required. An important role in the recovery of Cr(III) is played by liquid membranes due to the good selectivity and capacity of pure chromium from diluent solutions.

Lanagan et al. [11] investigated Cyanex272 used as a extractant of Cr(III) ions, and found that Cyanex272 caused the feed solutions to be completely

stripped of chromium. Cr(III) could be completely stripped from the loaded organic phase using mineral acids at relatively short contact times, but only if stripping is carried out immediately after extraction. Kongolo et al. [12] studied the possibility of cobalt and zinc recovery from copper sulphate solutions by solvent extraction. D2EHPA was used in the experiments as a carrier. Extraction processes ran quickly but needed a large volume of extractant. This drawback is not present in the case of liquid membranes. Cr(III) ions were transported across SLMs with DNNSA in work of Molinari et al. [13]. It was found that the proper ratio of o-xylene and kerosene allows stable work of the membrane, and that an additive in the membrane (DNNSA) provides good conditions.

Transport of Cr(III) by D2EHPA through PIM and SLM was compared by Ali Tor et al. [14]. It was observed that, although SLM had low stability and a short lifetime, this type of membrane gave higher experimental flux than those of PIM.

SLM with DNNSA and D2EHPA is a selective barrier separating Cr(III) and Cr(VI) ions. Both D2EHPA and DNNSA have no complex properties of anions. Thanks to these properties, separation of anionic forms of chromium(VI) and cationic forms of chromium (III) are possible [15].

A significant advantage of the ion transport in a SLM is a combination of extraction and reextraction processes which occur simultaneously in the same system. Therefore, they are used for the selective separation of ions, especially when their concentration in wastewater is relatively low and the usage of other techniques are inadequate. Moreover, it is also known that the introduction of a carrier into the membrane can improve the efficiency of the process. Hence, in this work, the influence of parameters such as the type and the concentration of the carrier on the Cr(III) ion transport was studied.

## 2. Experimental

Transport experiments were carried out in a tank consisting of two cylindrical chambers divided by the SLM (Fig. 2). The feed solutions were prepared by mixing aqueous chromium(III) chloride solution ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , POCH) at a concentration of  $0.1 \text{ g/dm}^3$  Cr(III). The initial pH of the feed phase was equal to 4. The receiving phase consist as an aqueous sulphuric acid solution (96%  $\text{H}_2\text{SO}_4$ , Lach-Ner) at concentration of  $4 \text{ mol/dm}^3$ . The volume of both solutions was equal to  $130 \text{ cm}^3$ . The whole process was thermostatted to ambient temperature ( $T=25^\circ\text{C}\pm 1^\circ\text{C}$ ). The solutions were mixed in both chambers by mechanical stirrers (300 rpm).

D2EHPA (Aldrich) and DNNSA (Merc) which have shown good properties in respect to the Cr(III) ion extraction were used as a carriers [3, 8, 16]. In order to monitor changes in the chromium content in the feed and receiving phases,

the samples were collected from both phases and their analysis was determined with a spectrophotometer UV/VIS using a 1.5-diphenylcarbazide method with a wavelength of 540 nm.

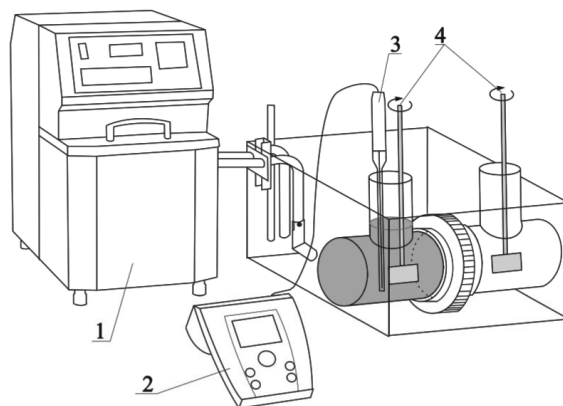


Fig. 2. Schematic diagram of apparatus for transport experiment. 1 – circulator (thermostat) with temperature and water-level control system, 2 – pH-meter, 3 – microelectrode, 4 – stirrers

The SLM membrane was formed from polymer filter PTFE (Sartorius) with a pore size of  $0.45 \mu\text{m}$ , which was soaked for 24 h in organic mixtures of kerosene (lighting kerosene, Dragon), *o*-xylene (Fluka) and a carrier. The ratio of kerosene to the *o*-xylene was 1:2 v/v. The active membrane surface was equal to  $15.2 \text{ cm}^2$ .

### 3. Result and discussion

According to the published data about Cr(III) transport through a SLM [17–20], a determined carrier concentration in SLM for the highest flux can be found for a defined initial concentration of a carried substance [18–19]. Therefore, at the beginning, the most efficiency concentrations of the investigated carriers (D2EHPA and DNNSA) have been defined for an initial chromium(III) concentration equal to  $0.1 \text{ g/dm}^3$ . The results obtained from Figures 3 and 4 shows that both D2EHPA and DNNSA can be used for Cr(III) ion transport across the SLM. The highest rate of chromium transport was obtained with 15% of D2EHPA and 25% of DNNSA in the membrane phase. It was noted that the transport of Cr(III) with DNNSA was slower than with D2EHPA (Fig. 4). The molecular size and ring structure of DNNSA (Fig. 5) might be responsible for such behaviour. The observation is consistent with results obtained by M.G. Buonomenna et al. [21], which explained that the complex of Cr(III) – DNNSA has a rather significant size and it has affected the chromium transport efficiency.

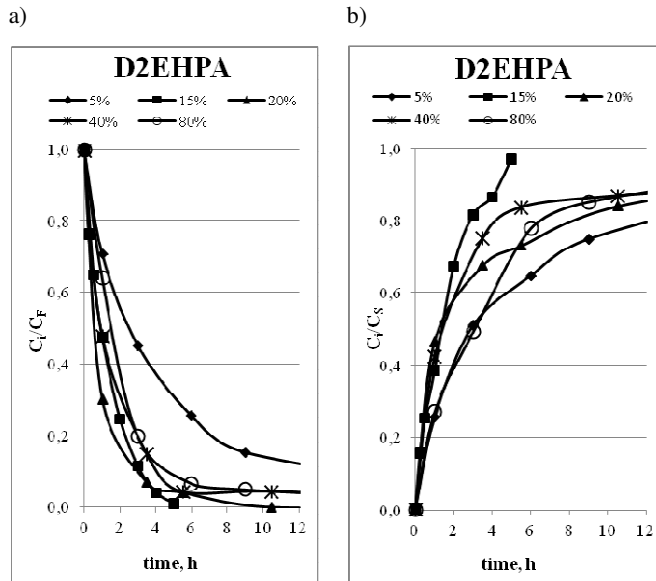


Fig. 3. Variation of chromium(III) concentration vs. time in feed (a) and stripping phase – 4M  $H_2SO_4$  (b) with different concentrate of D2EHPA in membrane. Feed phase:  $C_{Cr(III)} = 0.1 \text{ g/dm}^3$ ,  $pH = 4$ .  $C_i$  – initial concentration of Cr(III) in feed;  $C_F$  – concentration of Cr(III) in feed at time;  $C_S$  – concentration of Cr(III) in stripping phase at time

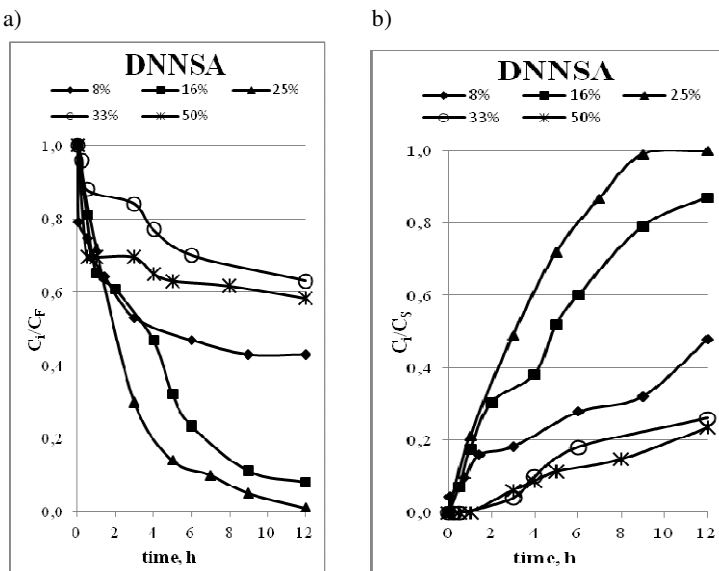


Fig. 4. Variation of chromium(III) concentration vs. time in feed (a) and stripping phase – 4M  $H_2SO_4$  (b) with different concentrate of DNNSA in membrane. Feed phase:  $C_{Cr(III)} = 0.1 \text{ g/dm}^3$ ,  $pH = 4$

It was also observed that an increase in the carrier concentration leads to a significant increase in the flux. The increase of flux is observed only to the optimum concentration of the carrier, but exceeding the optimum concentration decreases flux. It might be caused by the viscosity of the membrane phase, which changes with the growth of carrier concentration. According to Koekemoer et al. [22], the viscosity is one of the main factors that determine the diffusion of the metal species across the liquid membrane.

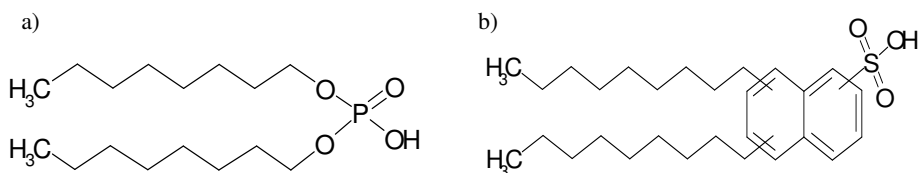


Fig. 5. Chemical structure of carriers used in investigations: a) D2EHPA, b) DNNSA

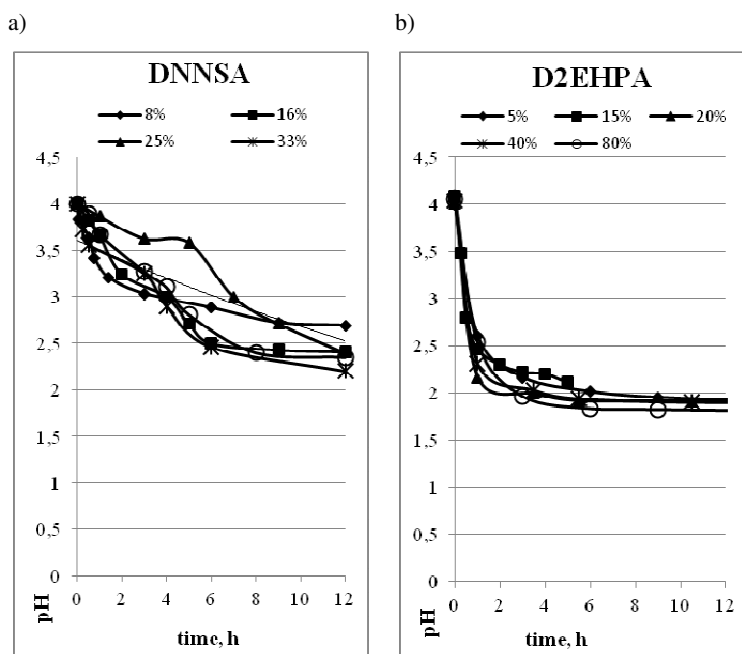


Fig. 6. Effect of feed phase pH on Cr(III) transport through SLM: a) DNNSA, b) D2EHPA

In the liquid membrane system, the transport is coupled, and the counterions are the  $H^+$  ions [23]. According to this fact, the pH of separated solutions changes during the process. These changes inflict the shift in the hydration of transported metal ions. It is well known that chromium(III) may exist in

different ionic (pH-dependent) forms. In more acidic solutions ( $\text{pH} \leq 3$ ), chromium occurs mainly in the form of  $\text{Cr}^{3+}$ , while at  $\text{pH} 3.8\text{--}6.3$ , chromium exist as  $\text{Cr}(\text{OH})^{2+}$ . When the  $\text{pH} 6.3\text{--}11.5$ , chromium exist as  $\text{Cr}(\text{OH})_3$ , and at  $\text{pH} > 11.5$ , chromium exist as  $\text{Cr}(\text{OH})_4^-$  [24]. Consequently, the ion transport has been slowed down or even stopped. Studying of the effect of feed  $\text{pH}$  during the transport of chromium (III) by the SLM, it can be seen that, with DNNSA,  $\text{pH}$  values changed gradually over the time. In case of D2EHPA, during the first hour of the process, the  $\text{pH}$  value decreases. In the next stage of the process, these values are not significantly changed (Fig. 6).

## 6. Conclusions

According to the published data and our own studies, the effectiveness of the removal and separation of heavy metals from aqueous solutions by liquid membranes is confirmed. Both, D2EHPA and DNNSA has been confirmed for Cr(III) ion transport. A significant influence on the transport of ions through the membrane is the carrier concentration in the organic phase. Additionally, the ion transport rate is dependent on the  $\text{pH}$  value of the feed phase. Decreasing the  $\text{pH}$  value causes a reduction of the hydrolysis degree of Cr(III). A supported liquid membrane allowed the removal of Cr(III) from  $0.1 \text{ g/dm}^3$  aqueous solution to the level of  $2\text{--}5 \text{ mg/dm}^3$ . The determined concentrations of D2EHPA and DNNSA in the membrane phase for the highest flux are established as 15% and 25%, respectively.

## References

1. Gambus F., Gorlach E.: Origin and harmfulness of heavy metals. *Aura*, 2011, 6, 11–13.
2. Kamiński W., Kwapiński W.: Applicability of Liquid Membranes in Environmental Protection. *Polish Journal of Environmental Studies*, 2000, 1, 9–37.
3. Kislik V.S.: *Liquid Membranes: Principles and Applications in Chemical Separations and Wastewater Treatment*. Elsevier, 2010.
4. Bartsch R.A., Way J.D.: *Chemical separations with liquid membranes*. American Chemical Society, 1996, 642.
5. Hintermeyer B.H., Lacour N.A.: Separation of the chromium (III) present in a tanning wastewater by means of precipitation, reverse osmosis and adsorption. *Latin American Applied Research*, 2008, 38, 63–71.
6. Samaratunga S., Nishimoto J., Masaaki Tabata: Separation of Cr(VI) from Cr(III) in  $\text{CaCl}_2$  aqueous salt medium using hydrocarbon (as toluene, n-hexane, n-heptane or n-octane) mixed solvents of ter-butanol. *Hydrometallurgy* 2007, 89, 207–216.



7. Li N.N.: Separating Hydrocarbons with Liquid Membranes. US, Patent 1968, 3,410, 794.
8. Wells A.F.: Structural Inorganic Chemistry. Wydawnictwo Naukowo Techniczne, Warszawa 1993.
9. Wódzki R.: Liquid Membrane. Structure and mechanism of action, [in]: Narębska A. (red.): Membranes and Membrane Separation Technology. Wydawnictwo Uniwersytetu Mikołaja Kopernika, Toruń 1997.
10. Kołtuniewicz A.: Membrane processes in clean technologies, [in]: Szwaśc M. (red.): Membranes and membrane techniques. From an idea to the industry. Polymen Ltd, Warszawa 2009.
11. Lanagan M.D., Ibane D.C.: The solvent extraction and stripping of chromium with Cyanex 272. Minerals Engineering, 2003, 16, 237–245.
12. Kongolo K., Mwema M.D., Banza A.N., Gock E.: Cobalt and zinc recovery from copper sulphate solution by solvent extraction. Minerals Engineering 2003,16, 1371–1374.
13. Molinari R., Drioli E, Pantano G.: Stability and effect of diluents in supported liquid membrane for Cr(III), Cr(VI) and Cd(II) recovery. Separation Science and Technology, 1989, 24, 1015–1032.
14. Ali Tor a,\* , Gulsin Arslanb, Harun Muslub, Ahmet Celiktab, Yunus Cengeloglub, Mustafa Ersoz: Facilitated transport of Cr(III) through polymer inclusion membrane with di(2-ethylhexyl)phosphoric acid (DEHPA). Journal of Membrane Science, 2009, 329, 169–174.
15. Religa P., Rajewski J., Świetlik R., Łobodzin P.: Selective chromium III/VI separation in supported liquid membrane system. Inżynieria i Aparatura Chemiczna, 2011, 50, 5, 96–97.
16. Kotas J., Stasicka Z.: Chromium occurrence in the environment and methods of its speciation. Environmental Pollution, 2000, 107, 263–283
17. Darvishi D., Haghshenas D.F., Keshavarz Alamdari E.T., Sadrnezhad S.K., Halali M.: Synergistic effect of Cyanex 272 and Cyanex 302 on separation of cobalt and nickel by D2EHPA. Hydrometallurgy, 2005, 77, 227–238.
18. Muhammad Idiris Saleh, Fazlul Bari Md., Bahrudin Saad: Solvent extraction of lanthanum(III) from acidic nitrate-acetate medium by Cyanex 272 in toluene. Hydrometallurgy, 2002, 63, 75–84.
19. Sarangi K., Reddy B.R., Das R.P.: Extraction studies of Cobalt(II) and Nickel(II) from chloride solutions using Na-Cyanex 272. Separation of Co(II)/Ni(II) by the sodium salts of D2EHPA, PC88A and Cyanex 272 and their mixtures. Hydrometallurgy, 1999, 52, 253–265.
20. Religa P., Rajewski J., Gierycz P.: Facilitated transport of Cr(III) and Fe(III) ions through a polymer inclusion membrane. Monografie Komitetu Inżynierii Środowiska, 2010, 66, 169–174.

21. Buonomenna M.G., Oranges T., Molinari R., Drioli E.: Chromium (III) removal by supported liquid membranes: a comparison among D2HEPA, DNNSA, and a novel extractant as carriers. *Water Environment Research*, 2006, 78, 69–75.
22. Koekemoer L.R., Badenhorst M.J.G., Everson R.C.: Determination of viscosity and density of di-(2-ethylhexyl) phosphoric acid + aliphatic kerosene. *Journal of Chemical and Engineering Data*, 2005, 50, 587–590.
23. Szpakowska M., Nagy O`B.: Membrane material effect on copper coupled transport through liquid membrane. *Journal of Membrane Science*. 1991, 57, 23–30.
24. Badura L.: Chromium in the environment and its impact on living organisms, [in:] Kabata-Pendias A., Chromium, nickel and aluminum in the environment – environmental problems and methodological. *Zeszyty Naukowe Komitetu Naukowego PAN Człowiek i środowisko*, 1993, 5, 89–93.

## **Transport Cr(III) przez immobilizowaną membranę ciekłą**

### **Słowa kluczowe**

Membrana ciekła, immobilizowana membrana ciekła SLM, transport przenośnikowy, chrom, D2EHPA, DNNSA.

### **Streszczenie**

W pracy zbadano transport przenośnikowy jonów Cr(III) w układzie z immobilizowaną membraną ciekłą (SLM). Jako przenośników jonów użyto kwasu di(2-etyloheksylo) fosforowego (D2EHPA) oraz kwasu dinonylnaftaleno fosforowego (DNNSA). Zbadano wpływ stężenia przenośnika na kinetykę transportu jonów Cr(III). Określono optymalne stężenia dla przenośników, przy którym transport zachodził najefektywniej. Dla D2EHPA wynosiło ono 15%, natomiast dla DNNSA 25%. Stwierdzono, że transport jonów Cr(III) przez SLM jest zależny przede wszystkim od rodzaju i stężenia przenośnika w membranie. Na wydajność procesu ma również wpływ pH.