

Received August 14, 2014; reviewed; accepted November 26, 2014

KINETICS OF CHROMIUM(III) TRANSPORT THROUGH THE DOUBLE-CARRIER SUPPORTED LIQUID MEMBRANE

Pawel RELIGA^{*}, Jakub RAJEWSKI^{**}, Paulina LOBODZIN^{***}

^{*} Department of Environmental Protection, Kazimierz Pulaski University of Technology and Humanities in Radom, Chrobrego 27, Radom, Poland, j.rajewski@ichip.pw.edu.pl

^{**} Faculty of Chemical and Process Engineering, Warsaw University of Technology, Warynskiego 1, Warsaw, Poland

^{***} Institute of Sustainable Technology – National Research Institute in Radom, Pulaskiego 6/10, Radom, Poland

Abstract: The kinetics of chromium(III) transport through a supported liquid membrane containing both a di-(2-ethylhexyl) phosphoric acid (D2EHPA) and bis-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) as an ions carrier was investigated. It was found that under a characteristic concentration of the carriers into the organic phase membrane provides much higher efficiency than the membrane containing only one of the extractants. In the studied system the optimal carrier concentration in the membrane is 0.16 mol/dm³ and 0.9 mol/dm³ for Cyanex272 and D2EHPA, respectively. Moreover, the authors indicate that only D2EHPA can act as an individual carrier in the membrane. In the case of Cyanex272 the stable structures with chromium(III) ions are formed in the membrane, which prevents effective re-extraction. Additionally, intensive stirring of an aqueous phase in another factor that has a positive influence on the transport kinetics in the double-carrier membrane. Increasing a stirring rate up to 1200 rpm shortens the process time and allows total re-extraction of chromium.

Keywords: *SLM, chromium, D2EHPA, Cyanex27, separation, membrane*

Introduction

Chromium belongs to metals commonly used in many industries, mainly in metallurgy, electroplating, tanning, paper industry, and pigment production. The partial consumption of chromium in the process (Jian-Hong et al., 2013) results in its presence in wastewaters. Due to the toxic properties of chromium, its separation from wastewater prior to its discharge to the environment is an important concern. Moreover, due to growing prices of chromium ores, the possibility to separate chromium from wastewater and recirculating it to the process is also economically

viable. Research results (Ochromowicz and Apostoluk, 2010; Religa et al., 2009) show that the process of simultaneous extraction and re-extraction (pertraction) carried out in the system with a liquid membrane (LM) may be a very effective solution with regard to the separation of metals from aqueous solutions. The reason for this is that the mass exchange in the LM system is done through facilitated transport. This type of transport is related to the presence of a carrier in the membrane – a substance which, by reversible reaction, forms chemical compound with a specific component, easily diffusible through the membrane. A popular group of substances applied as carriers/extractants of ions are alkyl derivatives of phosphoric acids (Azzoug et al., 2014). The most vital in this group are di-(2-ethylhexyl) phosphoric acid (D2EHPA) and bis-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272). The review of literature (Konczyk et al., 2010; Azzoug et al., 2014) on the transport of metal ions through the LM proves that, regardless the type of the transported ion, its effectiveness and selectivity are mostly affected by the type and concentration of the applied carrier. Unfortunately, even for optimal composition of the membrane, the LM systems are characterized by relatively low streams of transported ions, which significantly extends the process time, and adversely affects the system stability. Researchers (Darvishi et al., 2005; Iberhan and Wisniewski, 2002; Sarangi et al., 1999) examining extraction systems for the separation of metal ions from aqueous solutions, suggest an extraction with two extractants in order to increase the effectiveness of the process. They observe that a synergistic effect may be achieved with an adequate concentration ratio of extractants characterized by an increased rate of process and selectivity. Results of a few published references (Wojciechowski et al., 2008; Biswas, 2012) reveal a positive impact of the addition of the second carrier/extractants also to the liquid membrane. Similarly to extraction systems, a synergistic effect is observed for the specific ratio of carriers in the membrane. The works deal with tests on the possibility of using liquid membranes with two extractants for the separation of cobalt(II), copper(II) and nickel(II) ions. However, no results of tests on the possibility of applying immobilized liquid membranes with two extractants for the separation of chromium ions can be found in the literature. From the practical point of view, the SLM is the system with the membrane immobilized in the pores of the polymer that ensures the most effective level of separation of metal ions, including the separation of chromium(III) from aqueous solutions (Religa et al. 2009).

The aim of the work is to determine the impact of the presence of two extractants/carriers in the immobilized liquid membrane, i.e. di(2-ethylhexyl) phosphoric acid (D2EHPA) and bis-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272) on the transport kinetics of chromium(III) ions.

Experimental

Test system and process parameters

Transport experiments were carried out in a tank consisting of two cylindrical chambers (Fig. 1). The volume of both chambers was 130 cm^3 . The solutions: feed with Cr(III) concentration equal 0.002 mol/dm^3 (aqueous chromium(III) chloride solution, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) and stripping (6M HCl) were separated by SLM. The active membrane area covered 15.2 cm^2 . The initial pH of the feed phase was 5. The whole process was thermostated to ambient temperature ($T = 25 \pm 0.5 \text{ }^\circ\text{C}$). The solutions were mixed in both chambers with mechanical stirrers (IKA, OST20 digital). The study was carried out for a stirring rate of 300, 600 and 1200 rpm.

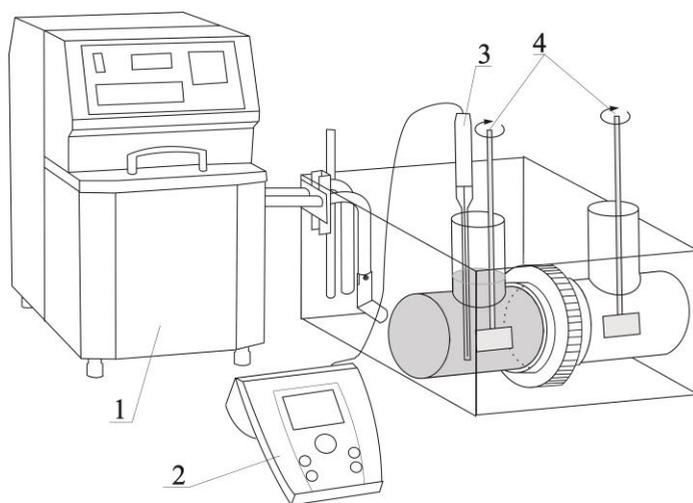


Fig. 1. Apparatus for transport experiment. 1 – circulator (thermostat) with temperature and water-level control system, 2 – pH-meter, 3 – microelectrode, 4 – stirrers

Preparation of a membrane

The immobilized liquid membrane was a PTFE porous polymer film (Sartorius) with a pore size of 0.45 mm and porosity of 64%. The membrane was soaked for 24 hours in a mixture of an organic phase consisting of kerosene (Dragon), o-xylene (Fluka) and carriers.

Di-(2-ethylhexyl) phosphoric acid (D2EHPA, Fluka) and bis-(2,4,4-trimethyl pentyl) phosphinic acid (Cyanex272, Cytec) were used as the ion carriers. The structure of the carriers shown in Fig. 2.

The Cyanex272 was selected based on the literature review (Langan and Ibana, 2002; Biswas and Singh, 2006), which concerned high activity of the Cyanex272 in the process of extraction of chromium(III). There are no works about the transport of chromium(III) through a liquid membrane with Cyanex272 as a carrier.

D2EHPA was selected on the basis of literature data (Ochromowicz and Apostoluk, 2010; Konczyk et al., 2010) and our own experience (Religa et al., 2014), that shows that D2EHPA has very good transporting properties for chromium(III) in a liquid membrane system.

The concentration of the carriers in the membrane was changed in the range of 0-1.2 M. The volume ratio of the concentrations of the other ingredients (kerosene/o-xylene) was constant and equal to 2:1.

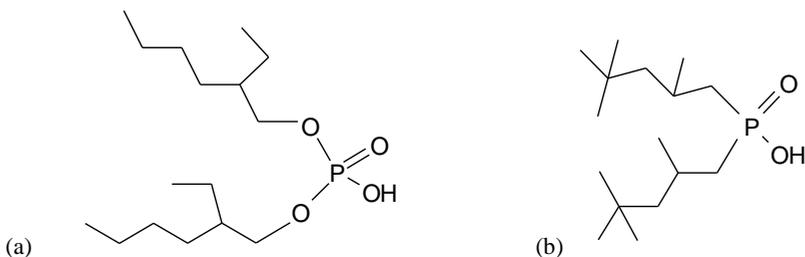


Fig. 2. The structure of the compounds used as carriers: (a) di-(2-ethylhexyl) phosphoric acid (D2EHPA), (b) bis-(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272)

Characteristics of measurement methods

To determinate chromium concentration, we regularly collected samples from the feed and the receiving phase, and then, using a Nanocolor UV/Vis NUV480 spectrophotometer and employing a 1.5-difenylokarbazyde method with the wave length $\lambda = 540$ nm, we analyzed concentration of Cr(III) ions after the mineralization of samples. Each measurement was repeated three times. The standard deviation of the measured value determined with statistical methods was ± 0.0003 . Based on the results, the flux of Cr(III) (J_0) and the penetration coefficient (k) were determined in the way described by Religa et al. (2014).

Results and discussion

SLM with Cyanex272 as a carrier

Literature data (Langan and Ibana, 2003) show that Cyanex272 is an excellent extractant of chromium(III), and that the effectiveness of the extraction process is clearly fostered by a high level of hydrolyzation of chromium(III) ions, which is ensured by pH 4.5-6.5 of the solution (Gawronski and Religa, 2007). The aim of the first stage of the tests was to investigate whether Cyanex272 can be the sole carrier of chromium(III) in the liquid membrane. To ensure good conditions of pertraction, the process was carried out at the initial pH of the feed phase equal to 5. The authors conducted experiments for various concentrations of Cyanex272 in the membrane, but they did not obtain the expected results. However, the experiments did help the authors to observe that effectiveness of the chromium(III) extraction was maintained

at the level of 20-30 %, regardless of the concentration of Cyanex272 in the membrane (Fig. 3). The process was extremely intensive in the first phase that lasted about 1 hour. In the later phase, the process came to a stop. It is also significant, that a considerable sudden decrease (from 5 to about 2) in the pH in the feed solution was observed in the first phase of pertraction. The rapid decrease in the pH determines the forms of chromium(III) to be found in the solution. They will be hydrolyzed to a slight extent at low pH. It is probably the reason for the fast decrease of the rate of extraction in the system.

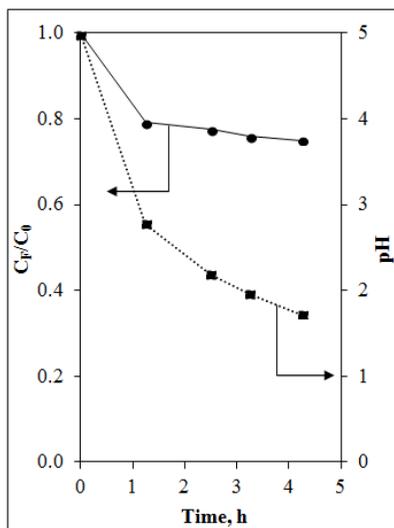


Fig. 3. Variation of chromium(III) concentration and the pH in the feed phase vs. time for SLM with 0.16 mol/dm^3 Cyanex272 as a carrier. Initial chromium(III) concentration in the feed phase $C_0 = 0.002 \text{ mol/dm}^3$; initial pH = 5. Receiving phase 6 mol/dm^3 HCl.
 C_F – actual concentration of Cr(III) in feed phase

Additionally, no presence of chromium(III) ions was reported in the receiving phase, which may suggest the formation of stable, polymeric structures between chromium(III)-Cyanex272 molecules in the membrane. The movement of these expanded structures in the membrane phase is significantly hampered. Moreover, high stability of the structure prevents effective re-extraction of chromium(III). In studies on chromium(III) extraction by Cyanex272, Lanagan and Ibana, (2003) indicate that Cyanex272 can easily create stable forms with chromium(III). In the case of the structures formed, even when 8 mol/dm^3 HNO_3 is applied, the re-extraction of chromium was partial and possible only directly after the extraction process. Therefore, the achieved results show that the ions of Cr(III) cannot be effectively transported by SLM containing only Cyanex272 as a carrier.

The double-carrier SLM

Various concentrations of Cyanex272 in the double-carrier SLM

In the next phase of the study, the authors applied, for the transport of chromium(III), a membrane with a constant concentration of D2EHPA that has proven capacity to transport chromium(III) in LM (Ochromowicz and Apostoluk, 2010; Konczyk et al., 2010), and used various concentrations of Cyanex272. The aim of the investigations was to determine the type of the effect caused by the presence of two strong extractants of chromium(III) in the membrane. According to Azzoug et al. (2014), Biswas et al. (2012), Konczyk et al. (2010) and Gawronski and Religa (2007), in the liquid membrane for a specific concentration of the transported substance the optimal concentration of a carrier can be found at which the transport of ions runs most effectively. For the initial concentration of chromium(III) ions equal to 0.002 mol/dm^3 , the most effective concentration of D2EHPA in the membrane is 0.45 mol/dm^3 (Religa et al., 2014). Therefore, the concentration of D2EHPA was adopted in further tests. The impact that the addition of various amounts of Cyanex272 has on the transport of Cr(III) ions, while maintaining constant, and optimal concentration of D2EHPA in the membrane is shown in Fig. 4. As presented, the system with a certain concentration of Cyanex272 in the membrane containing 0.45 mol/dm^3 of D2EHPA achieves significantly higher effectiveness compared to the membrane containing only D2EHPA. As to the analyzed system, this optimal concentration of Cyanex272 equals 0.16 mol/dm^3 and is almost 3 times lower than the concentration of D2EHPA. Moreover, in the case of a membrane with two carriers with concentration of 0.45 mol/dm^3 D2EHPA/ 0.16 mol/dm^3 CYANEX272 respectively, faster release of Cr(III) ions from the membrane was observed. Owing to this, the process time was shortened, and it lasted less than 3 hours for the applied conditions in the analyzed system. Therefore, for a defined ratio of concentration of carriers in the membrane, a clear synergistic effect may be observed that is reflected in the improvement of kinetic properties of the examined transport system.

Darvishi et al. (2005) who carried out the extraction of nickel(II) and cobalt(II) with a simultaneous application of D2EHPA and Cyanex272 as extractants, proved a synergistic effect, however in the case of the system they analyzed, this effect occurred with an increased content of Cyanex272 and with a simultaneous decrease in D2EHPA concentration. Therefore, the concentration proportions of carrier mixtures in the membrane have to be selected individually, depending on the type of ions transported.

Both, for lower and higher concentrations of Cyanex272 in the system, a decrease in effectiveness of pertraction compared to the membrane containing only D2EHPA, was observed. This phenomenon was accompanied by a decrease in chromium(III) concentration in the membrane, and an extension of the time needed for chromium to achieve the maximum concentration in the membrane (Fig. 5).

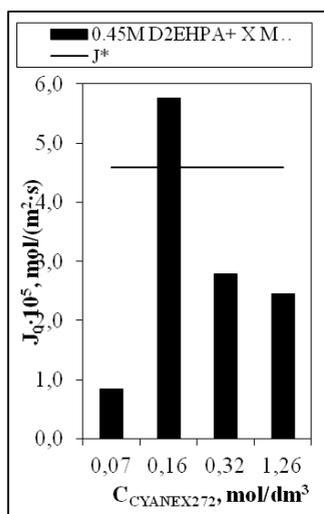


Fig. 4. Effect of addition of Cyanex272 to the membrane containing 0.45 mol/dm³ D2EHPA on Cr(III) ions flux (J_0) penetrating to the membrane. J^* - flux of chromium(III) ions penetrating the membrane containing only 0.45 mol/dm³ D2EHPA

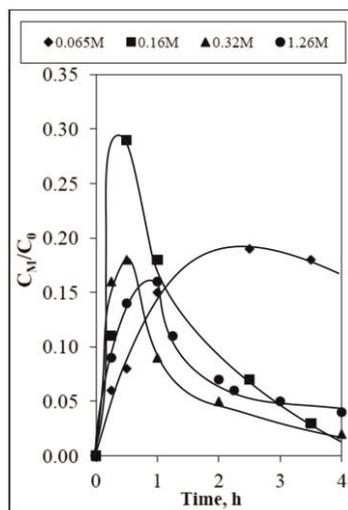


Fig. 5. Variation of chromium(III) concentration in the membrane phase containing 0.45 mol/dm³ D2EHPA and different concentrations of Cyanex272. Initial chromium(III) concentration in the feed phase $C_0 = 0.002$ mol/dm³; pH = 5. Receiving phase 6 mol/dm³ HCl

The pertraction process is a multiple stage process, therefore the course of once stage depends on the adequate accumulation of the transported substance in the previous stage. The lower the concentration and the longer the time needed for reaching it, the slower and less effective the subsequent stage, i.e. re-extraction. This explains the obtained results of experiments. The decrease in the chromium(III) concentration in the membrane and the extension of the time needed for its procurement, are probably caused by the lack of a stable transporting structure in the membrane with two carriers in concentrations different than the optimal ones. The achieved results and their analysis indicate that Cyanex272 is responsible for the stabilization of the transporting structure in the membrane.

Variable concentrations of D2EHPA in the double-carrier SLM

Based on the obtained results, the concentration of Cyanex272 of 0.16 mol/dm³, considered to be the most favorable for the speed of the process, was selected for further analyses. At this stage of the research various amounts of D2EHPA were put to the membrane at a constant concentration of Cyanex272. Upon analyzing the results (Fig. 6) the authors discovered that the presence of two carriers in the membrane in the amounts, respectively 0.9 mol/dm³ D2EHPA and 0.16 mol/dm³ Cyanex272, reduces the time of pertraction 3-fold when compared to the process carried out only with D2EHPA and by more than one hour compared to the process carried out with the membrane having 0.45 mol/dm³ D2EHPA/0.16 mol/dm³ Cyanex272. A significantly

smaller share of Cyanex272 in the membrane, compared to D2EHPA, confirms the earlier conclusion claiming that the role of Cyanex272 in the membrane is probably to join and stabilize the transporting structure formed by D2EHPA. Based on the analysis of the structure of both carriers (Fig 1), and their concentration range in the membrane, as well as the review of reports by Xu, (2009) or Kundu and Bidyut, (2013), it can be concluded that spherical aggregation of carriers molecules occurs in the membrane, combined with the formation of stable, complex micellar structures in which the polar ends of the carrier molecules together with the connected, often hydrolyzed ion of the transported substance are inside, while its non-polar elements are outside the micelles. However, the thorough analysis of chromium(III) transport mechanism requires more experiments and it will be the subject of future research.

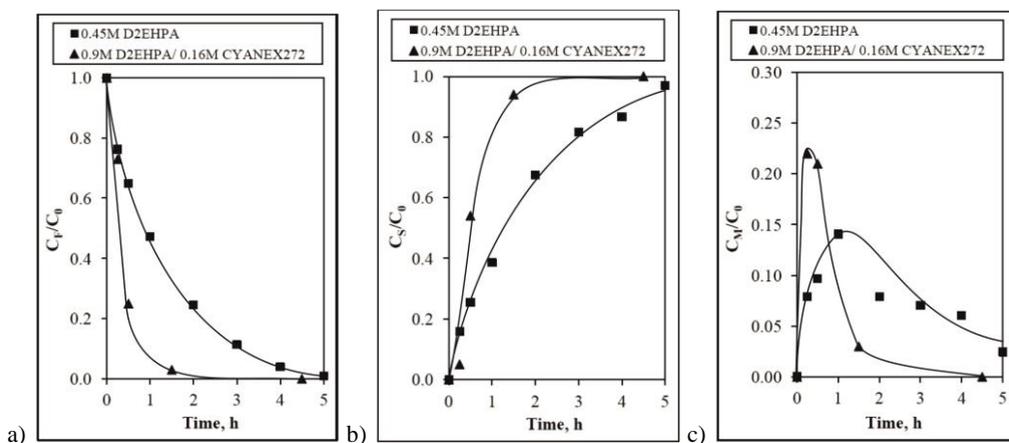


Fig. 6. Variation of chromium(III) concentration vs. time in a) feed phase, b) receiving phase and c) membrane phase, for membrane with D2EHPA and the double-carrier membrane with D2EHPA and Cyanex272 under their most effective concentration. Initial chromium(III) concentration in the feed phase $C_0 = 0.002\text{M}$; pH = 5. Receiving phase 6 M HCl

Intensity of the stirring rate of aqueous phases

It was stated that in the two-carrier membrane Cyanex272/D2EHPA the structure enabling the effective transport of chromium(III) is formed at the defined mutual ratio of the carriers. In this situation the stage limiting the rate and effectiveness of the process may be the formation of laminar layers on interphase surfaces, which slows down the stage of penetration of chromium(III) ions into and out of the membrane. A properly intensive stirring of aqueous phases may limit the thickness of these layers. Therefore, the next stage of the research was to determine the impact of the stirring rate, both of the feed phase and the receiving phase, on changes in the transport of chromium(III) ions through a liquid membrane with two carriers. The membrane with the selected optimal composition, i.e. 0.16 mol/dm^3 of Cyanex272; 0.90 mol/dm^3 of

D2EHPA was subjected to testing. The tests were carried out for the stirring rate of 300, 600 and 1200 rpm. The results are presented in Fig. 7.

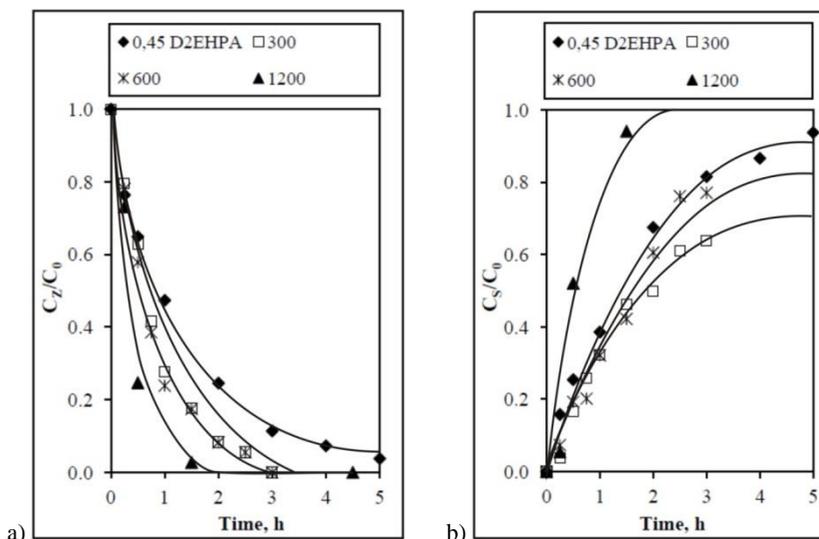


Fig. 7. Influence of the stirring rate on changes in the concentration of Cr(III) vs. time in the feed phase (a) and in the receiving phase (b) for the membrane with D2EHPA and the double-carrier membrane with 0.9M D2EHPA and 0.16M Cyanex272. Initial chromium(III) concentration in the feed phase $C_0 = 0.002\text{M}$; pH = 5. Stripping phase 6 M HCl

Increasing stirring rate up to 1200 rpm significantly improved the kinetics of the process of separation of chromium(III) ions. The time of the process was shortened, which allowed in the case of re-extraction, a complete extraction of chromium. Moreover, the thickness of the laminar boundary layers on the boundary of phases was significantly reduced as well, enabling a faster transport of chromium(III), and increased efficiency of the process.

Conclusions

Literature review helped to indicate D2EHPA and Cyanex272 as effective extractants of chromium(III), while our own experiments confirmed high efficiency of D2EHPA as a carrier of Cr(III) in the SLM system. However, for the pertraction of chromium(III) by the SLM with Cyanex272 as a carrier, there was no presence of the Cr(III) ions in the receiving phase. This result may indicate a formation of a polymeric structure in the membrane between molecules of the chromium(III) and Cyanex272, which is not able to effectively move in a membrane phase. The results indicate that the ions of Cr(III) cannot be transported through the SLM that only contains Cyanex272 as a carrier.

Transport properties of the membrane containing both the di-(2-ethylhexyl) phosphoric acid (D2EHPA) and the bis-(2,4,4-trimethylpentyl) phosphinic acid

(Cyanex272) were investigated. It was found that for certain optimum carriers ratio concentrations in the membrane, the SLM system achieves significantly higher efficiency over the membrane containing only D2EHPA as a carrier. For the investigated system, the optimal concentration of Cyanex272 is 0.16 mol/dm^3 , when the concentration of D2EHPA is 0.9 mol/dm^3 . As a result of a synergistic effect, the processing time was reduced 3-fold and took 2 hours less than the conditions set in the system investigated.

The obtained results suggest that in the double-carrier membrane there is a spherical carriers particle aggregation coupled with the formation of a stable micellar structures. Cyanex272 is responsible for stabilizing the transport structure. However, a detailed explanation of the transport mechanism of Cr(III) ions requires additional experiments. It will be the subject of a future work.

An additional factor that has a positive influence on the transport kinetics in the double-carrier membrane is intensive stirring of aqueous phases. The increase in the mixing speed to 1200 rpm improved the kinetics of separation of chromium(III) ions in the double-carrier membrane system. The process time was reduced. Moreover, in the case of re-extraction, chromium was fully recovered.

References

- AZZOUG S., AROUS O., KERDJOUJ H., 2014, *Metallic ions extraction and transport in supported liquid membrane using organo-phosphoric compounds as mobile*, J. Environ. Chem. Eng., 2, 154–162.
- BISWAS R.K., SINGHA H.P., 2006, *Purified Cyanex 272: its interfacial adsorption and extraction characteristics towards iron(III)*, Hydromet., 82, 63–74.
- BISWAS S., PATHAK, P. N., ROY S. B., 2012, *Carrier facilitated transport of uranium across supported liquid membrane using dinonyl-phenyl phosphoric acid and its mixture with neutral donors*, Desal., 290, 74–82.
- DARVISHI D., HAGHSHENAS D.F., KESHAVARZ A.E., SADRNEZHAAD S.K., HALALI M., 2005, *Synergistic effect of Cyanex 272 and Cyanex 302 on separation of cobalt and nickel by D2EHPA*, Hydromet., 77, 227–238.
- GAWRONSKI R., RELIGA P., 2007, *Transport mechanism of chromium(III) through the unmixed bulk liquid membrane containing dinonylnaphthalenesulfonic acid as a carrier*, J. Memb. Sci., 289, 187–190.
- IBERHAN L., WISNIEWSKI M., 2002, *Extraction of arsenic(III) and arsenic(V) with Cyanex 925, Cyanex 301 and their mixtures*, Hydromet., 63, 23–30.
- JIAN-HONG L., JUN L., ZHAO-PENG Y., XUE-FENG L., 2013, *Removal of chromium(III) from aqueous waste solution by predispersed solvent extraction*, Transact. Nonferr. Met. Soc. China, 23, 524–529.
- KONCZYK J., KOZLOWSKI C., WALKOWIAK W., 2010, *Removal of chromium(III) from acidic aqueous solution by polimer inclusion membranes with D2EHPA and Aliquat 336*, Desal., 263, 211–216.
- KUNDU K., BIDYUT K.P., 2013, *Physicochemical investigation of mixed surfactant reverse micelles: Water solubilization and conductometric studies*, Colloids Surf. A, 433, 154–165.
- LANAGAN M.D., IBANA D.C., 2003, *The solvent extraction and stripping of chromium with Cyanex 272*, Miner. Eng., 16, 237–245.
- OCHROMOWICZ K., APOSTOLUK W., 2010, *Modelling of carrier mediated transport of Cr(III) in the SLM system with D2EHPA*, Sep. Pur. Technol., 72, 112–117.

- RELIGA P., GAWRONSKI R., GIERYCZ P., 2009, *Kinetics of chromium(III) transport through a liquid membrane containing DNNSA as a carrier*, Int. J. Mol. Sci., 10, 964–975.
- RELIGA P., RAJEWSKI J., GIERYCZ P., ŚWIETLIK R., 2014, *Supported liquid membrane system for Cr(III) separation from Cr(III)/Cr(VI) mixtures*, J. Water Sci. Technol., 69, 2476–2481.
- SARANGI K., REDDY B.R., DAS R.P., 1999, *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*, Hydromet., 52, 253–265.
- WOJCIECHOWSKI K., KUCHARZEK M., BUFFLE M., 2008, *Mechanism of Cu(II) transport through permeation liquid membranes using azacrown ether and fatty acid as carrier*, J. Membr. Sci., 314, 152–162.
- XU Z., 2009, *Microcalorimetric study on the critical micelle concentration and thermodynamic functions of di(2-ethyl-hexyl) phosphate salts in organic solvent + sec-octyl alcohol systems at 298.15 K*, J. Chem. Eng. Data, 54, 2827–2830.