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Original Research

Advantages and Disadvantages of SLM and PIM Systems Used for Chromium(III) Separation from Aqueous Solutions

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Abstract

This study compares supported liquid membranes (SLM) and polymer inclusion membranes (PIM) used for chromium(III) separation from aqueous solutions. First, the effect of carrier concentration (di(2-ethylhexyl)phosphoric acid) in both systems was investigated. In the case of SLM membranes an optimal concentration of D2EHPA carrier for every initial Cr(III) concentration can be found. The situation is different for PIM membranes, where we can distinguish a certain range of D2EHPA carrier concentration, which guarantees a high diffusion coefficient. Then, the comparison of Cr(III) transport efficiency of SLM and PIM was studied. The SLM assures much faster Cr(III) ion transport than the PIM under the same experimental conditions, which is caused by the difference in the structure between the SLM and PIM membranes. However, the long-term stability of PIM indicated that PIM can be an alternative for traditional liquid membranes for practical implementation of chromium(III) separation from wastewaters and analytical environmental samples.

Keywords: PIM, SLM, stability, D2EHPA, chromium(III)

Introduction

Recently, resource management and environmental protection has changed the view on problems concerning recovering and recycling industrial chemical reagents. This was related to decreasing natural resources and their effective consumption. Therefore, most developed countries changed their internal regulations concerning environmental protection and established more strict norms for air, water, and soil protection. This situation also forces Poland to newly analyze its efficient resource consumption and recovery.

Special attention should be dedicated to heavy metals because of their toxic and carcinogenic properties. Moreover, they are dangerous for human life (destruction of kidneys, brain, etc.) as their components do not decompose naturally and accumulate in the food chain.

Heavy industry (chemical, paper, tannery, metallurgy, ceramic, etc.) is responsible for heavy metals pollution of the natural environment. Moreover, a sudden increase of heavy metals pollution is caused by intensification of agriculture, improper fertilizing, dust emissions, and industrial and home wastewaters, as well as increasing the number of cars whose engines emit many dangerous

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Table 1. Permissible concentrations of select metals in agricultural soils and waste released into the environment by industry [1].

Metal	Industrial wastewater (daily average concentration) [mg/L]	Agricultural soil [mg/L]
Chromium	1,0	0,15
Nickel	0,5	0,10
Copper	0,5	0,15
Cobalt	1,0	0,02
Lead	0,5	0,10
Cadmium	0,4	0,004

substances, including heavy metals. This is why the abidance of regulations and environmental norms (Table 1) concerning heavy metals concentrations in air, water (including surface waters), and soil becomes crucial.

Chromium belongs to the group of heavy metals appearing in wastewaters. It is, as the only heavy metal, widely used for production of dyes, glass, and ceramics, as well as in the tanning industry. Industrial plants that burn liquid fuels and wastes are sources of chromium in air, water, and soil.

The biological activity of chromium and its mobility in the environment is highly dependent on the form in which it appears. Especially dangerous is chromium(VI). It is characterized by high toxicity and carcinogenic activity [2]. Therefore, it is important to monitor concentrations of the different forms of chromium in the environment.

An important problem concerns the determination of very small or a trace amounts of metals in environmental and analytical samples. Preparation of the sample for analysis with the use of traditional methods includes extraction, adsorption, or ion exchange [3-5]. This means that the preparation of an analytical sample has to be carried out by a multi-stage procedure. This procedure often absorbs 60% of the time and cost of the analysis [6].

A good perspective concerning heavy metals separation (including Cr(III)) from wastewaters and diluted solutions gives liquid membranes (LM) [7, 8] – especially the system (investigated in this work) with liquid immobilized membrane SLM [9, 10]. The main advantage of such a system is its selectivity of heavy metals, which is determined by proper selection of a carrier in the form of a complex compound or ion exchanger [11]. Usually, the same compounds as in extraction processes are used as carriers of metal ions in liquid membranes. Depending on the requirements, the LM system can be used for decreasing heavy metals in wastewaters to the expected levels (Table 1), as well as for increasing the concentration and purification of samples used for environmental analysis by the use of minimal amounts of expensive solvents.

The supported liquid membranes (SLM) and polymer inclusion membranes (PIM), because of their efficiency and simplicity [12-14], seem to be the most promising for practical use. SLM, because of its properties concerning carrying transport (schematically shown in Fig. 1), assures a more effective metal separation process [10, 12]. The important feature which, despite high concentration factors and low reagent consumption, limits practical application of such processes is concerned with low stability and short lifetime of the membrane (decreasing of the solvent flux in time). The main reasons for membrane stability loosening [15, 16] are related to elusion of the carrier from the membrane phase to aqueous solutions and the formation of micro-emulsion in the membrane phase, leading to a loosening of transport properties of the membrane [17].

There are some papers that are concerned with an improvement of liquid membrane stability. Yang et al. [15] proposed re-impregnation of the support by the use of a membrane phase. Such an approach gave good results only in the first cycle of the process. In the next cycles the authors discovered much faster decreasing of the fluxes.

A different investigation strategy concerning improvement of SLM stability was proposed by Neplenbroek et al. [16]. They limited loosening of the membrane phase by gel application on the SLM membrane surface. Covering the membrane surface by a very thin PCV layer was to separate the membrane phase from aqueous phases, but it failed and the phases were partially mixed. Similar investigations were carried out by Kemperman et al. [17]. They used the surface polymerization method (IP) for the formation of hydrophilic polyamide layers on the SLM membrane surface. The external polymer layer improved the stability of SLM, but caused the membrane to become non-permeate for two- and multivalent ions.

A new polymer inclusion membrane (PIM), described recently many times in the literature [18-20], has been synthesized to limit the loose membrane phase. PIM membrane can be a good alternative for traditional liquid membranes. That is why in this paper we show both its applicability for chromium(III) ions separation from aqueous solutions and its comparison with liquid-immobilized membrane. Moreover, in this paper we analyze Cr(III) ions transport in PIM and SLM systems and compare the stability of both systems in cyclic processes.

Experimental

Our set-up described before the reactor [9, 10] consists of two cylinder chambers divided by SLM or PIM membranes. The feed phase consists of an aqueous solution of chromium(III) chloride ($CrCl_3 \cdot 6H_2O$, POCH) at concentrations equal to 0.002 M and initial pH 4. The selected chromium(III) concentration is the concentration that is observed in the effluent after the purification process using the conventional precipitation method. pH 4 of the feed phase provides a high degree of dissociation of the chromium salts. Under these conditions the dominant form of Cr^{3+} is easily extractable by the D2EHPA carrier. The receiving phase consists of an aqueous solution of sulfuric acid (96% H_2SO_4, Lach-Ner) at concentrations equal to 4 mol/dm^3. Volume of both solutions was equal to 130 cm^3.

SLM membrane was formed from polymer foil PTFE (Sartorius) with pore size of 0.45 µm, which was wet for 24 h in organic mixtures of kerosene (kerosene, Dragon), o-xylene (Fluka), and a carrier. A mixture of kerosene and o-xylene in the composition of the organic phase of the SLM provides the right transport conditions in the analyzed system. Transport studies of chromium(III) in similar LM systems were carried out inter alia, by [11, 21].

PIM membrane was formed by physical immobilization of the ion carrier with plasticizer (2-nitro phenyl-octyl ether or 2-nitro phenyl-pentyl ether, Fluka) on a polymer matrix made of triacetate of cellulose (CTA, Fluka). After evaporation of the solvent the membrane was conditioned by immersion in distilled water for 12 h.

The active membrane surface was 15.2 cm^2, and di(2-ethylhexyl) phosphoric acid (D2EHPA, Merck) (Fig. 1b) was used as a carrier. The reactor was thermostated (T=25ºC±1ºC) by use of a Circulator Julabo CF41. During the experiments the investigated solutions were mixed in both chambers by the use of mechanical stirrers (IKA Yellow Line OST 20 digital) working with a constant speed of 300 rpm.

The samples were collected both from feed and receiving phase in the defined time intervals. Measurements of Cr(III) concentration were made using a spectrophotometric method with 1,5-diphenyl-carbazyde, after previous oxidation of Cr(III) to Cr(VI) at wavelength of 540 nm (Spectrophotometer NANOCOLOR UV/VIS NUV480).

Results and Discussion

Membrane Transport Experiments; Effects of Carrier Concentration

The main part of the SLM system consists of a porous barrier (support) dividing feed and receiving phases. This barrier, saturated with an organic solution of an ion carrier (Fig. 1a), does not allow for mixing of aqueous phases. The organic phase, which stays in the membrane, allows for free movement of carrier particles and ion mobility between aqueous phases (Fig. 1b).

PIM are formed by physical immobilization of carrier ions with a plasticizer on a polymer matrix (Fig. 2a). Such a membrane form eliminates the problem of carrier elusion to aqueous phases. Carrier mobility is limited because of mutual interaction between the carrier and the plasticizer, but movement in the plasticizer carrier particles and ion transfer takes place (Fig. 2b).

Based on our own investigations [9, 10, 21] and literature data [8, 14], we can find that component transport through liquid membranes depends on initial concentrations of this substance. Moreover, for such each concentration an optimal carrier concentration in a membrane can be defined. That is why, as a first step of our investigations, we have found an optimal concentration of D2EHPA carrier in two systems: with immobilized liquid membrane and with polymer inclusion membrane for initial chromium concentration equal to 0.002M.

The obtained results are summarized in Figs. 3 and 4. They confirm that D2EHPA shows high transport ability of chromium(III) ions, and that its concentration in membranes has a huge influence on process kinetics.

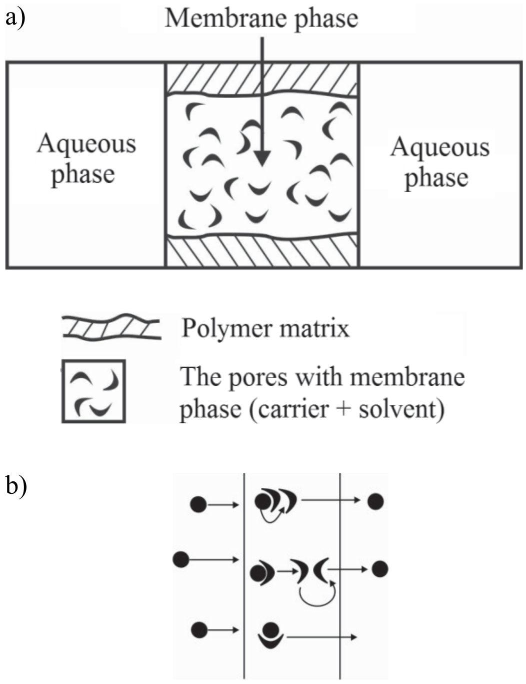

Fig. 1. Supported liquid membrane (SLM): a) simplified scheme, b) the idea of carrier transport.

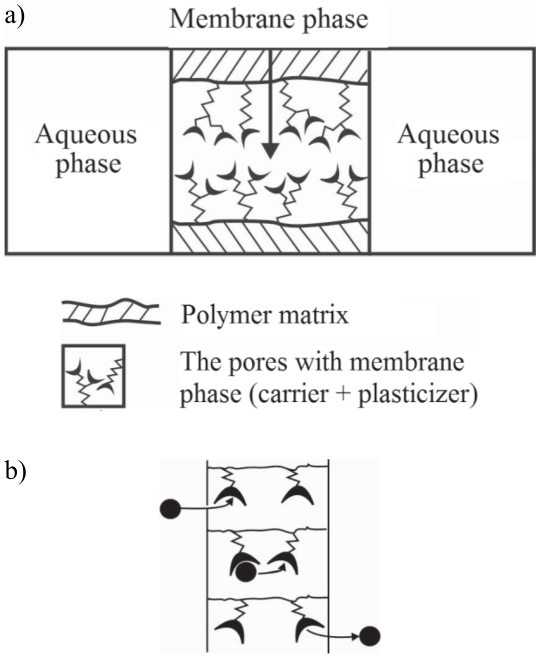

Fig. 2. Polymer inclusion membrane (PIM): a) simplified scheme, b) the idea of carrier transport.

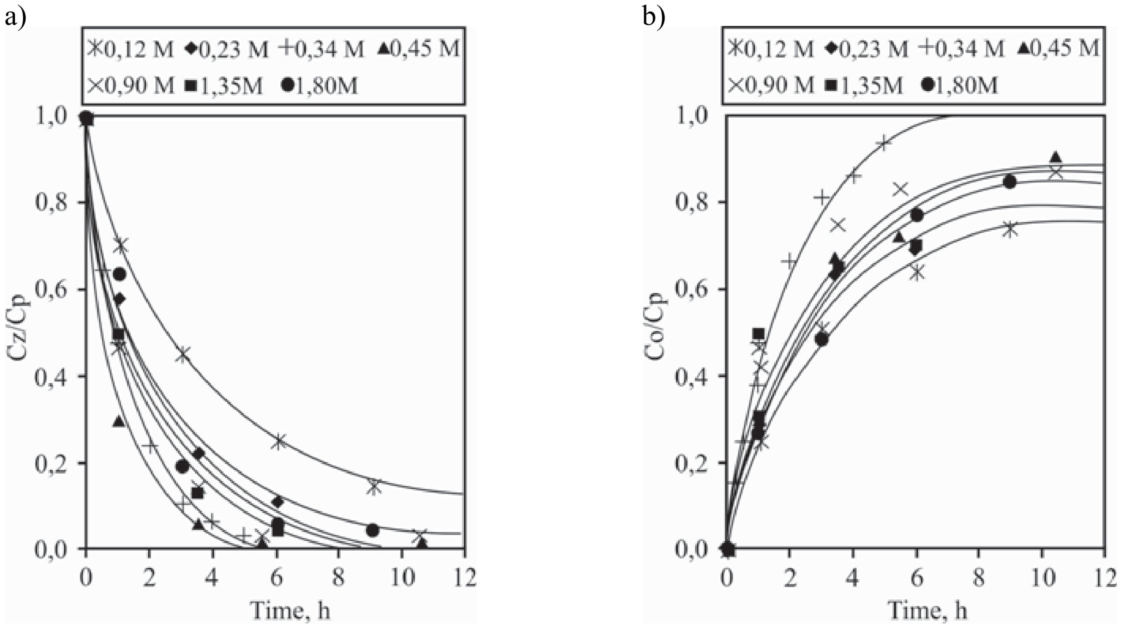

Fig. 3. Variation of chromium(III) concentration vs. time in: a) feed and b) striping phase with different concentrations of D2EHPA in SLM. Feed phase: CCr(III)=0.002 M. Cz: actual concentration of the Cr(III) ions in the feed phase; Co: actual concentration of the Cr(III) ions in the receiving phase; Cp: initial concentration of the Cr(III) ions in the feed phase.

In the case of the SLM system (Figs. 3a, b) we see that the initial concentrations of the carrier from 0.12 M to 0.23 M allow us to obtain high extraction and re-extraction levels. However, the optimal concentration, for which we get the highest efficiency, is equal to 0.34 M. Initial concentrations of the carrier higher then 0.34 M, i.e from 0.45 M to 1.8 M, cause gradual decreasing of the extraction and re-extraction processes.

According to the literature [8, 19], such a situation is caused by increasing membrane viscosity, which limits Cr(III) ion diffusion through membrane, which in turn decreases the transport rate. Fig. 5a shows the change of Cr(III) concentration in SLM membrane. The fastest membrane penetration by Cr(III) ions and re-extraction is observed for the carrier concentration equal to 0.34 M (Figs. 3b, 5a). Thus the optimal D2EHPA concentration for Cr(III) ions transport when the initial concentration of Cr(III) was equal to 0.002 M, is 0.34 M.

In the PIM membrane system (Figs. 4a, b) at the initial range of carrier concentration equal to 0.12-0.23 M, we deal

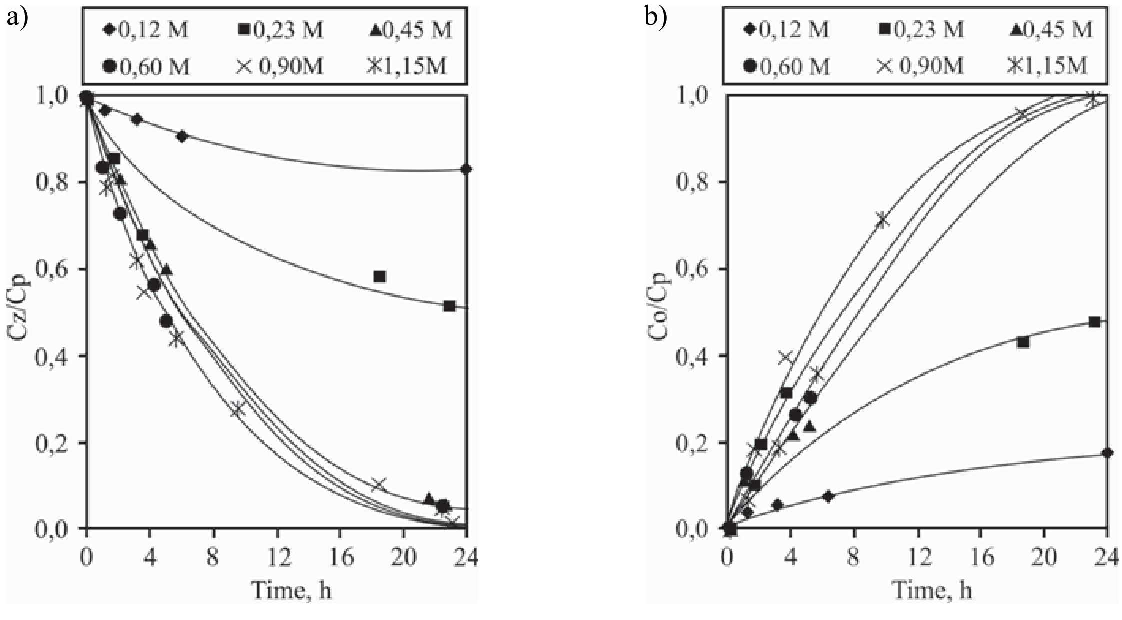

Fig. 4. Variation of chromium(III) concentration vs. time in: a) feed and b) striping phase with different concentrations of D2EHPA in PIM. Feed phase: CCr(III)=0.002M. Cz: actual concentration of the Cr(III) ions in the feed phase; Co: actual concentration of the Cr(III) ions in the receiving phase; Cp: initial concentration of the Cr(III) ions in the feed phase.

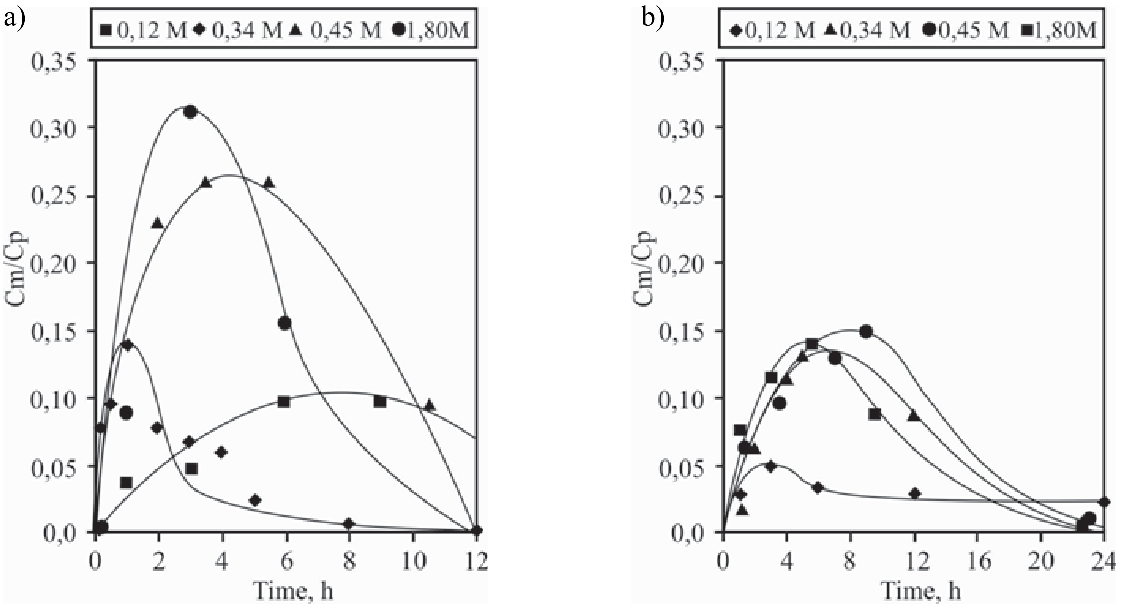

Fig. 5. Variation of chromium(III) concentration vs. time in membrane phase with different concentrations of D2EHPA in: a) SLM and b) PIM. Feed phase: CCr(III)=0. can be defined can be defined 002M. Cm: actual concentration of the Cr(III) ions in the membrane phase; Cp: initial concentration of the Cr(III) ions in the feed phase.

only with a partial extraction and re-extraction of Cr(III). Increasing the carrier concentration to 0.45-1.15 M makes the process more effective. At these concentrations both membrane penetration by Cr(III) ions and re-extraction is the fastest (Figs. 4b, 5b).

The membrane loses its properties when the D2EHPA concentration in membrane exceeds 1.15 mol/dm^3. This is caused by limitations coming from a mutual solution of carrier and plasticizer [18] (in the membrane structure where plasticizer crystals are found).

In the PIM membrane, in contrast to the SLM membrane and where an optimal concentration of carrier can be defined depending on the initial concentration of the substance, we deal with a certain range of concentrations of D2EHPA in which the process is very fast. In our investigated system this range is equal to 0.45-1.15 Similar results were obtained by Kebiche-Senhadji et al. [19] and Samuel et al. [20], who investigated metal transport through PIM membrane where the carrier consists of alkyl derivatives of phosphoric acid.

Cussler et al. [22] proved that too low a carrier concentration in the membrane prevents formation of overlooping mobility regions of carrier particles attached to the plasticizer. On the other hand, too high concentration

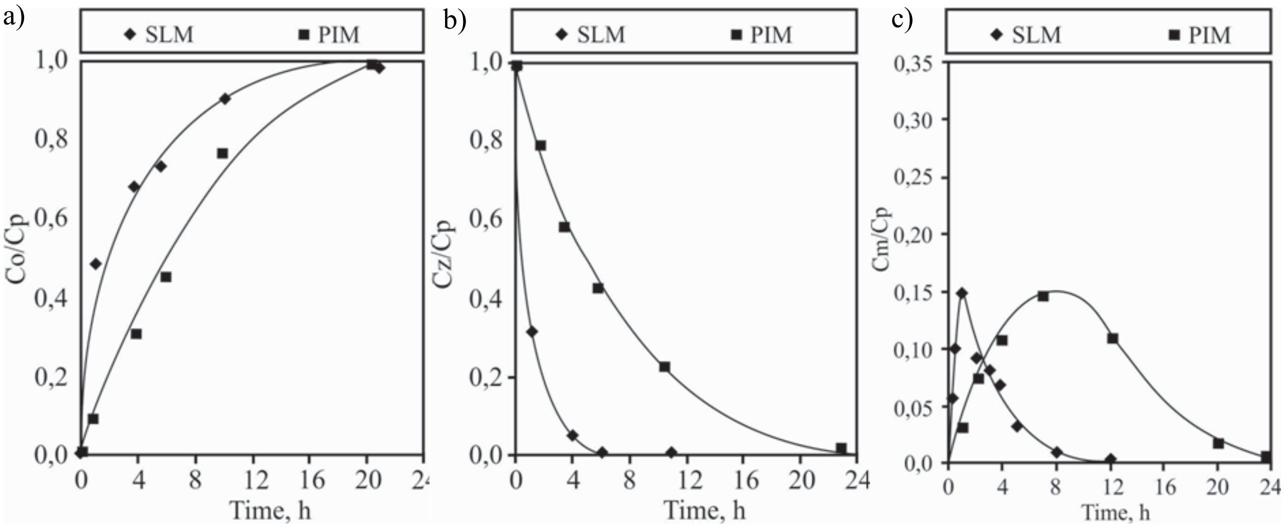

Fig. 6. Comparison of changes of the chromium (III) concentrations in the systems of the SLM and the PIM in: a) feed phase, b) striping phase, c) membrane phase for optimal concentrations of D2EHPA. The initial concentration of Cr (III) 0.002M. Cz: actual concentration of the Cr(III) ions in the feed phase; Co: actual concentration of the Cr(III) ions in the receiving phase; Cm: actual concentration of the Cr(III) ions in the membrane phase; Cp: initial concentration of the Cr(III) ions in the feed phase.

of the carrier limits the mobility of its molecules and prevents transport of Cr(III) ions. The efficient transport of Cr(III) ions is possible between these two limits.

Independently of the membrane type (SLM or PIM) on which chromium(III) was detached, proper selection of the carrier concentration for an initial Cr(III) concentration allowed for its decreasing in the feed phase or increasing in the receiving phase to the expected level determined only by time of the process. This is an important observation, which gives good prospects for the practical application of LM for Cr(III) separation from industrial wastewaters or environmental samples for analysis. However, this must be confirmed in more complex systems.

Comparison of Cr(III) Transport Efficiency of SLM and PIM

The next investigation concerned comparison of the effectiveness of Cr(III) ions transport at initial concentrations equal to 0.002 M through SLM and PIM membranes containing an optimal concentration of the D2EHPA carrier. The obtained results (Fig. 6) show the difference in process kinetics in the case of the use of SLM and PIM membranes. The immobilized liquid membrane assures much faster Cr(III) ion transport (99% of extraction after 6 h) than the PIM membrane (where the extraction process lasted 20 h).

A different character of transport kinetics is caused by the difference in the structure between the SLM and

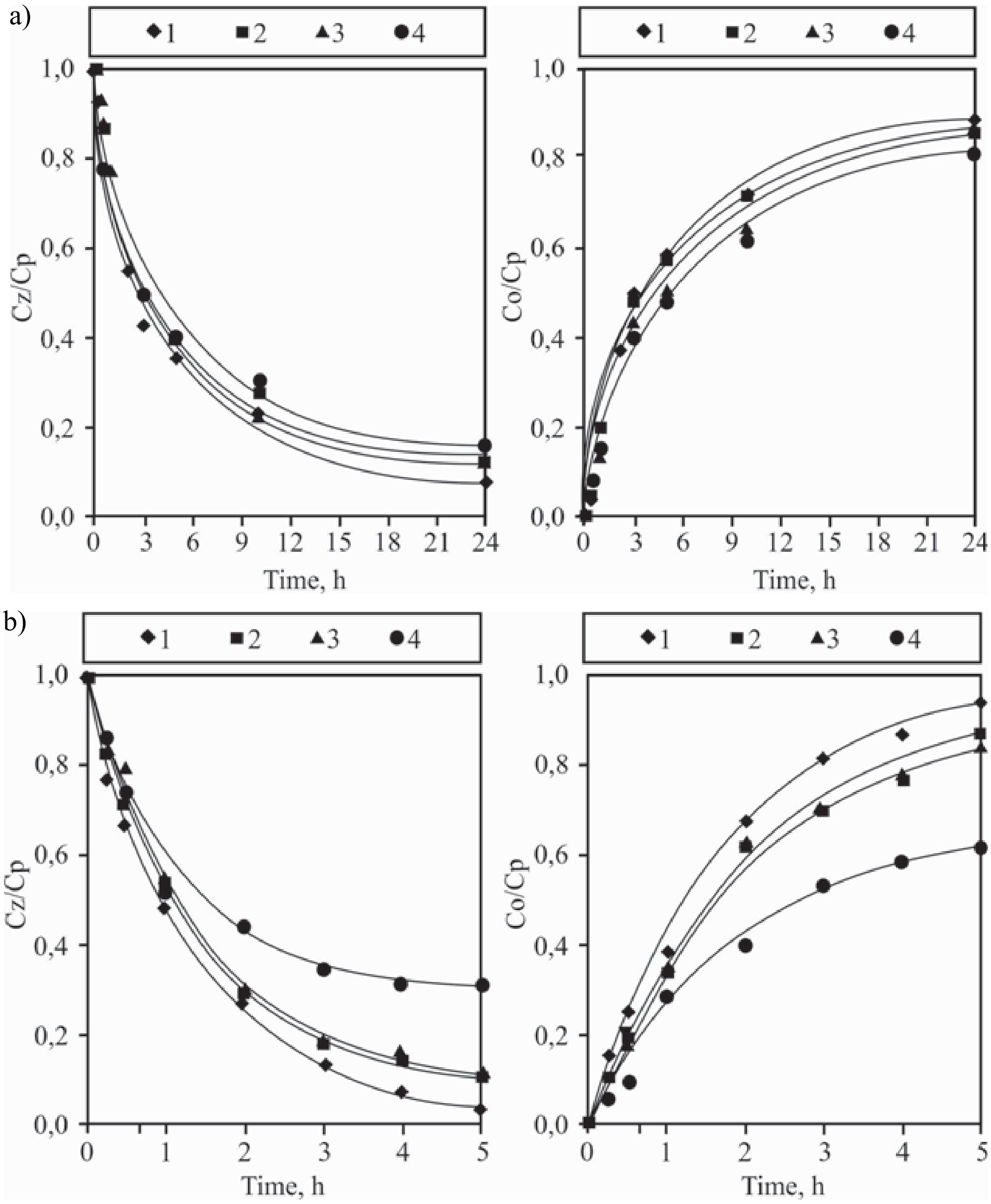

Fig. 7. Variation of chromium(III) concentration vs. time in water phases in: a) PIM and b) SLM in in repeatable (cosecutive) series of experiments. Feed phase: CCr(III)=0002M. Cz: actual concentration of the Cr(III) ions in the feed phase; Co: actual concentration of the Cr(III) ions in the receiving phase; Cp: initial concentration of the Cr(III) ions in the feed phase.

PIM membranes. The immobilized membrane is saturated with an organic liquid, which allows for free movement of carrier particles and fast membrane penetration by Cr(III) ions, as well as their fast movement between aqueous phases of the SLM membrane (Fig. 6c). Physically immobilizing the carrier with plasticizer in the polymer membrane, which protects elusion of the carrier from membrane-to-liquid phases, limits carrier mobility, which causes limitation of Cr(III) ion penetration in PIM membrane and their slower re-extraction (Fig. 6c).

Comparison of Stabilities of SLM and PIM

The stability of systems with SLM and PIM membranes, containing D2EHPA as a carrier and used for selective separation of Cr(III) ions from aqueous solutions, was investigated by the measurement of the change of Cr(III) concentrations as a function of time (during many hours), in water phases, and in repeatable (one after another) series of experiments. The experiment was carried out for the defined (before) optimal process conditions and for the fastest process of extraction and re-extraction of chromium(III): for 5 h in the case of SLM membrane and 24 h in the case of PIM membrane. The results are shown in Fig.7.

The obtained results show that the PIM membrane is stable during the long working time (Fig. 7a). Only a small decrease of process kinetics is observed in a series of experiments. This can be caused by Cr(III) ion presence in the membrane, which had not been re-extracted in the first series of the experiments. For the whole work period there is no evidence showing any negative changes in PIM membrane stability caused by the above-described reasons, which agrees with the literature data [15-18]. In the case of SLM membrane the situation is different. Already in the second and further series of experiments a permanent decrease in process speed has been observed (Fig. 7b). Such a great speed decrease can be explained by elusion of the carrier to the aqueous phase. Thus we can conclude that the PIM membrane, because of its stability, can be an alternative for traditional liquid membranes and seems to be promising for future implementation.

Conclusion

Both liquid supported and polymer inclusion membranes containing D2EHPA as a carrier allow for effective Cr(III) ion separation from aqueous solutions.

The efectiveness of Cr(III) ion transport through liquid membranes depends mainly on D2EHPA carrier concentration in the membrane. In the case of SLM membranes, for every initial chromium (III) concentration an optimal concentration of D2EHPA carrier can be found. The situation is different for PIM membrane, where we can distinguish a certain range of D2EHPA carrier concentration, which guarantees a high carrier-ion complex diffusion coefficient causing the highest speed of the process.

Independently of whether chromium separation takes place in the SLM or PIM system the Cr(III) decreasing in a feed phase (or increasing in a receiving phase to a freely defined level) is obtained and the processes are determined only by time. This is why, depending on the selected liquid membrane system, we can decrease chromium (III) concentrations in wastewaters to the level defined by the appropriate regulations as well as purify and concentrate samples used for environmental analysis, minimizing the amount of solvents and costs of the expensive components.

Physical immobilizing of the carrier with plasticizer in the polymer membrane, which protects elusion of the carrier from membrane-to-liquid phases, limits carrier mobility, which causes limitation of Cr(III) ion penetration compared to SLM membrane. The PIM membrane, which is a very complicated system, shows high stability during Cr(III) transport in cyclic and multi-hour processes. There are no changes in PIM system stability caused by general factors.

Thus we can conclude that the PIM membrane can be an alternative for traditional liquid membranes for practical implementation to chromium(III) separation from wastewaters and analytical environmental samples.

References

1. Regulation of the Minister of Environment of 24 July **2006** on the conditions to be met when sewage into the water or soil, and on substances particularly harmful to the aquatic environment.
2. FONSECA ALMEIDA M.A., BOAVENTURA R.A.R. Chromium precipitation from tanning spent liquors using industrial alkaline residues: a comparative study. Waste Manage. **17**, 201, **1997**.
3. WOJTOWICZ A., STOKLOSA A. Removal of Heavy Metal Ions on Smectite Ion-Exchange Column. Pol. J. Environ. Stud. **11** (1), 97, **2002**.
4. MUSTAFA T., MUSTAFA S. Chromium speciation in environmental samples by solid phase extraction on Chromosorb. J. Hazard. Mater. **129** (1-3), 266, **2006**.
5. MATOS G.D., DOS REIS E.B., COSTA A.C.S., FERREIRA S.L.C. Speciation of chromium in river water samples contaminated with leather effluents by flame atomic absorption spectrometry after separation/preconcentration by cloud point extraction. Microchem. J. **92**, 135, **2009**.
6. DZIARKOWSKA K., JÖNSSON J.A, WIECZOREK P.P. Single hollow fiber SLM extraction of polyamines followed by tosyl chloride derivatization and HPLC determination. Anal. Chim. Acta. **606**, 184, **2008**.
7. KAMIŃSKI W., KWAPIŃSKI W. Applicability of Liquid Membranes in Environmental Protection. Pol. J. Environ. Stud. **9**, 37, **2000**.
8. KOZLOWSKI C.A. Facilitated transport of metal ions through composite and polymer inclusion membranes. Desalination. **198** (1-3), 132, **2006**.
9. RAJEWSKI J., RELIGA P., WOJASIŃSKI M., GIERYCZ P. Selective chromium (III/VI) separation in polymer inclusion membrane system Challenge of Modern Technology. **5** (1), 14, **2014**.
10. RELIGA P., RAJEWSKI J., GIERYCZ P., ŚWIETLIK R. Supported liquid membrane system for Cr(III) separation from Cr(III)/Cr(VI) mixtures. Water Sci. Technol. **69** (12), 2476, **2014**.

11. BOUONOMENNA 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 Environ. Res. **8** (1), 69, **2006**.
12. WIJERS M.C., WESSLING M., STRATHMANN H. Removal of copper from industrial effluents with supported liquid membranes stabilized with charged toplayers. International Membrane Science and Technology Conference. **1**, **1996**.
13. SGARLATA C., ARENAA G. Heavy metal separation with polymer inclusion membranes. J. Membr. Sci. **323**, 444, **2008**.
14. KAVITHA N., PALANIVELU K. Recovery of copper(II) through polymer inclusion membrane with di (2-ethylhexyl) phosphoric acid as carrier from e-wast. J. Membr. Sci. **415**, 663, **2012**.
15. YANG X.J., FANE T. Effect of membrane preparation on the lifetime of supported liquid membranes. J. Membr. Sci. **133**, 269, **1997**.
16. NEPLENBROEK A.M., BARGEMAN D., SMOLDERS C.A. The stability of supported liquid membranes, Desalination **79** (2-3), 303, **1990**.
17. KEMPERMAN A.J.B., ROLEVINK H.H.M., BARGEMAN D. Stabilization of supported liquid membranes by interfacial polymerization top layers. J. Membr. Sci. **138**, 43, **1998**.
18. FONTAS C., TAYEB R., DHAHBI M. Polymer inclusion membranes: The concept of fixed sites membrane revised. J. Membr. Sci. **290**, 62, **2007**.
19. KEBICHE-SENHADJI O., MANSOURI L. Facilitated Cd(II) transport across CTA polymer inclusion membrane using anion (Aliquat 336) and cation (D2EHPA) metal carriers, J. Membr. Sci. **310**, 438, **2008**.
20. SAMUEL P., KUSUMOCAHYOA, KANAMORIA T. Development of polymer inclusion membranes based on cellulose triacetate: carrier-mediated transport of cerium(III). J. Membr. Sci. **244**, 251, **2004**.
21. RELIGA P., GAWROŃSKI R., GIERYCZ P. Kinetics of chromium(III) transport through a liquid membrane containing DNNSA as a carrier, Int. J. Molecular Sci., **10,** 964, **2009**.
22. CUSSLER E. L., ARIS R., BROWN A. On the limits of facilitated diffusion. J. Membr. Sci. **43**, 146, **1989**.