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SELECTIVE REMOVAL OF TRANSITION METAL IONS IN TRANSPORT THROUGH POLYMER INCLUSION MEMBRANES WITH ORGANOPHOSPHORUS ACIDS

Separation of transition metal ions from aqueous chloride solutions by transport through polymer inclusion membrane (PIM) process is presented. The competitive transport of equimolar mixtures of Zn(II) and Cd(II) as well as Zn(II), Cu(II), Co(II), Cd(II), and Ni(II) was investigated. The selective transport of metal ions from aqueous chloride source phase through PIM-containing cellulose triacetate (support), *o*-nitrophenyl pentyl ether (plasticizer) and organophosphorus acidic compounds, i.e. di(2-ethylhexyl)phosphoric acid (D2EHPA), di(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), di(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) and bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302) as ion carriers, is shown. The influence of extractant nature on the selectivity and efficiency of cation transport has been examined. Zn(II) can be effectively removed from dilute aqueous chloride solutions containing equimolar mixture of Zn(II) and Cd(II) ions in transport through PIMs with di(2,4,4-trimethylpentyl)phosphinic acids, bis(2,4,4-trimethylpentyl)monothiophosphinic acid or di(2-ethylhexyl)phosphoric acid as the ionic carriers into 1.0 M HCl as the receiving phase. The per cent removal of Zn(II) and Cd(II) ions increases with an increase in pH, but more efficient separation of Zn(II) than Cd(II) ions decreases with pH increase in the source phase. Zn(II) can be also effectively removed from dilute aqueous chloride solutions containing equimolar mixture of Zn(II), Cd(II), Cu(II), Co(II) and Ni(II) ions by its transport through PIMs with D2EHPA, Cyanex 272 and Cyanex 302. All ions investigated are effectively removed with di(2,4,4-trimethylpentyl)dithio-phosphinic acids (Cyanex 301) as the ionic carrier into 1.0 M HCl as the receiving phase. The per cent removal of all metal ions investigated increases with an increase in pH of solution in the source phase. The initial transport fluxes of all metal ions through PIM with Cyanex 272 increase with an increase in an initial chloride acid concentration in the receiving phase.

Keywords: *polymer inclusion membrane, organophosphorus acids, zinc(II), cadmium(II), cobalt(II), nickel(II), copper(II)*

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1. INTRODUCTION

Selective removal of metal ions from industrial and waste solutions is frequently required in hydrometallurgical processing. In recent years, liquid membranes are commonly used for separation of metal ions from aqueous solutions [1], [2]. The use of liquid membranes containing ion carriers offers an alternative to solvent extraction in selective removal of metal ions from source aqueous phase and their concentration. In this case, the concentration of metal ionic species is above $1 \cdot 10^{-4}$ M.

A variety of liquid membrane types is represented, among others, by bulk (BLM), emulsion (ELM), supported (SLM), and polymer inclusion membranes (PIM) [3], [4]. The PIMs are formed by casting cellulose triacetate (CTA) from an organic solution to form a thin film. The casting solution also contains an ion exchange carrier and a membrane plasticizer.

Solvent extraction using organophosphorus compounds such as di(2-ethylhexyl)phosphoric acid (D2EHPA), di(2,4,4-trimethylpentyl)-phosphinic acid (Cyanex 272), di(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) and bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302) has been widely used for selective recovery of heavy metal from acidic solutions in hydrometallurgical process. According to SOLE and HISKEY [5] the solvent extraction order for Cyanex 272 is as follows: Fe(III) < Zn(II) < Cu(II) < Co(II) < Ni(II); Cyanex 302: Cu(II) < Fe(III) < Zn(II) < Co(II) < Ni(II) and Cyanex 301: Cu(II) < Zn(II) < Fe(III) < Co(II) \approx Ni(II). BINGHUA et al. [6] have established the following solvent extraction order for D2EHPA: Fe(III) > Zn(II) > Mn(II) > Cd(II) > Cu(II) > Mg(II) > Co(II) > Ni(II).

A liquid membrane containing specific ion carriers can be an alternative to the solvent extraction allowing selective separation of metal ions from aqueous solutions and their concentration. The separation of Co(II) and Ni(II) by supported and hybrid liquid membranes with D2EHPA, Cyanex 272, Cyanex 301, and Cyanex 302 was presented by WALKOWIAK et al. [7], [8]. The Co(II) and Ni(II) ions fluxes are increased in the following order of ion carriers: Cyanex 272 < Cyanex 302 < D2EHPA < Cyanex 301. Zinc(II) ions were effectively transported through the multimembrane hybrid system with D2EHPA [9] and through the supported liquid membrane with D2EHPA [10]. It was found that the ion carrier concentration has no effect on the transport of zinc ions, while temperature, pH of feed phase, flow rate of feed and stripping phases and the stripping concentration are important parameters of the transport. ULEWICZ et al. [12], [13] studied selective removal of zinc from chloride aqueous solutions and its transport across polymer inclusion membranes with D2EHPA [11], [12] and Cyanex 272 [13]. Cadmium (II) ions were also effectively transported through polymer inclusion membrane (PIM) with Cyanex 923 [14]. Optimal experimental conditions were obtained after 3 h using membrane containing 30% v/v Cyanex 923 dissolved in xylene and soaked in microporous Durapore GVHP support.

Now we present the results of competitive transport of zinc(II) and cadmium(II) ions

through polymer inclusion membranes as well as the results of transport of transition metal ions from equimolar mixture of all metal ions investigated, i.e. Zn(II), Cu(II), Co(II), Ni(II) and Cd(II) ions from dilute aqueous solutions ($c_{Me} = 0.01$ M). In both types of solutions, the same metal ion carriers, i.e. di(2-ethylhexyl)phosphoric acid (D2EHPA), di(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), di(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) and bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302), were used. The selectivity of metal ions' separation with organophosphorus acidic compounds as a function of pH of aqueous solution and an initial concentration of hydrochloric acid in the receiving phase is shown.

2. EXPERIMENTAL

Initial aqueous solutions were prepared with redistilled water, hydrogen chloride and the following salts: CdCl₂, ZnCl₂, CuCl₂, CoCl₂, NiCl₂ (all from POCh, Gliwice, reagents of analytical grade). The organic chemicals, i.e. cellulose triacetate (Fluka), *o*-nitrophenyl pentyl ether (Fluka), and dichloromethane (POCh), were also of analytical reagent grade. The organophosphorus acidic compounds (Fluka) were: di(2-ethylhexyl)phosphoric acid (D2EHPA), di(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), di(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301), and bis(2,4,4-trimethylpentyl)monothiophosphinic acid, (Cyanex 302). The values of pK_a were: 2.75 (D2EHPA), 6.37 (Cyanex 272), 2.61 (Cyanex 301), 5.63 (Cyanex 302).

The solutions of cellulose triacetate (CTA) (as the support), organophosphorus acidic compounds (as the ion carrier), and *o*-nitrophenyl pentyl ether (ONPPE) (as the plasticizer) in dichloromethane were prepared. A portion of this organic solution was poured into a membrane mould made of a glass ring attached to a glass plate covered with cellulose triacetate-dichloromethane glue. Dichloromethane as an organic solvent was allowed to evaporate slowly overnight and the resultant polymer inclusion membrane was separated from the glass plate by immersing it in water. The membrane was stored in water. The concentration of organophosphorus acidic compounds in membrane was 1.0 M in terms of plasticizer; 2.50 cm³ of ONPPE / 1.0 g of CTA. Thickness of membranes was 35 μm. Freshly synthesized membranes were used in each experiment.

Transport experiments were conducted in a permeation cell in which the membrane film (of the surface area of 4.9 cm²) was tightly clamped between two cell compartments. Both solutions, i.e. the source and receiving aqueous phases (45 cm³ each), were mechanically stirred at 600 rpm. The receiving phase was 0.01–1.0 M aqueous solution of hydrochloric acid. The source phases were aqueous solutions containing Zn(II) and Cd(II) ions and the solution containing Zn(II), Cu(II), Co(II), Cd(II) and Ni(II) ions. The concentration of each ion in the solutions was 0.01 M.

The PIM transport experiments were carried out at the temperature of 20 ± 0.2 °C.

Small samples (0.1 cm³ each) of the aqueous receiving phase were removed periodically via a sampling port with a syringe and analyzed to determine zinc, copper, nickel, cobalt and cadmium concentrations by atomic absorption spectroscopy method. The acidity of source aqueous phase was controlled by pH-meter (pH meter, CX-731 Elmetron, with combined pH electrode, ERH-126, Hydromet, Poland) and kept constant by adding periodically to each sample a small amount of 1.0 M aqueous solution of NaOH.

The kinetics of metal ion transport through PIM was described by the first-order equation:

$$\ln\left(\frac{c}{c_i}\right) = -kt, \quad (1)$$

where c is the metal ion concentration (M) in the source phase at some given time, c_i is the initial concentration of metal ions in the source phase, k is the rate constant (s⁻¹), and t is the time of transport (s).

In order to calculate k , the plots representing $\ln(c/c_i)$ versus transport time were drawn. The rate constant value for the duplicate transport experiment was averaged and standard deviation calculated. The initial flux (J_i) is defined by:

$$J_i = \frac{V}{A} \cdot k \cdot c_i, \quad (2)$$

where V is the volume of the aqueous source phase, and A is the effective area of the membrane.

The selectivity coefficient (S) was defined by the ratio of the initial fluxes of $M1$ and $M2$ metal ions, respectively:

$$S = J_{i,M1} / J_{i,M2}. \quad (3)$$

The per cent removal (R) in PIM transport of metal ions from the source phase into receiving phase was calculated as follows:

$$R = \frac{c_i - c}{c_i} \cdot 100\%. \quad (4)$$

3. RESULTS AND DISCUSSION

The paper deals with a competitive transport of metal ions through polymer inclusion membranes containing 1.0 M organophosphorus acidic compounds as an ion carrier, i.e. di(2-ethylhexyl)phosphoric acid (D2EHPA), di(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), di(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301),

and bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302). During this transport the ions are transferred from aqueous source phase ($c_{Me} = 0.01$ M) to receiving aqueous phase. The kinetic parameters and selectivity orders of Zn(II) and Cd(II) ions transported through PIM are shown in figure 1. The initial fluxes of Zn(II) and Cd(II) cations increase with an increase in pH of the feed phase. Comparison of the ion fluxes through PIM shows that Zn(II) cations are transported much faster than Cd(II) ions with Cyanex 272 and D2EHPA as ion carriers. When Cyanex 301 is a carrier, the difference in the values of fluxes is not great. On the other hand, if Cyanex 302 is used as ion carrier, Cd(II) cations are transported faster than Zn(II) cations. The values of selectivity coefficients of Zn(II)/Cd(II) for D2EHPA, Cyanex 272 and Cyanex 301 decrease with an increase in pH values. Also the values of selectivity coefficients of Cd(II)/Zn(II) for Cyanex 302 decrease with an increase in pH values. The values of selectivity coefficients of Zn(II)/Cd(II) for transport with D2EHPA at pH 2.0, 3.0, 4.0 and 5.0 were 10.7, 6.0, 5.4, and 5.0, respectively, whereas for the transport with Cyanex 301 they were 2.4, 1.3, 1.2, 1.1, respectively. The values of selectivity coefficients of Zn(II)/Cd(II) for transport with Cyanex 272 at pH 3.0, 4.0 and 5.0 were 11.5, 8.4, and 7.9, respectively. The values of selectivity coefficients of Cd(II)/Zn(II) for transport with Cyanex 302 were 2.4, 1.8, 1.7 and 1.6 at pH 2.0, 3.0, 4.0, and 5.0, respectively.

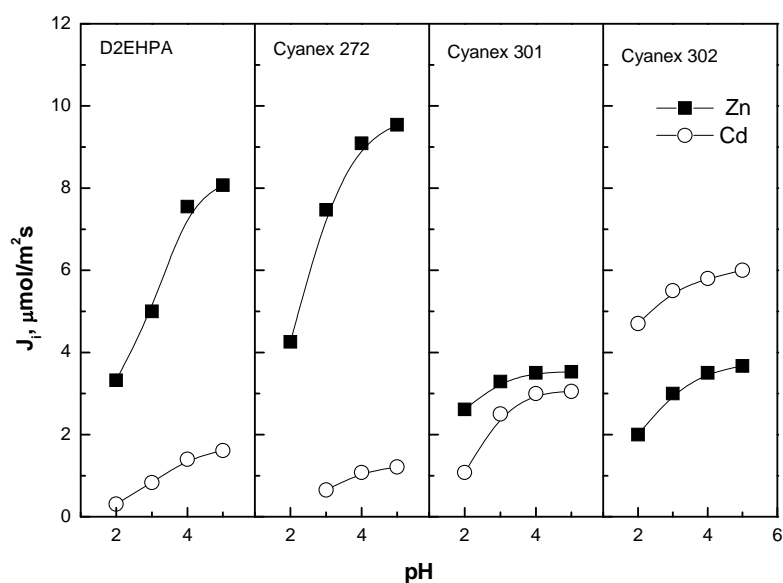


Fig. 1. Initial fluxes of Zn(II) and Cd(II) ions through polymer inclusion membranes vs. pH of the feed phase. Source phase: $c_{Me} = 0.01$ M, receiving phase: 1.0 M HCl. Membrane: 2.50 cm^3 ONPPE / 1.0 g CTA, 1.0 M carriers

The removal of metal ions after 24 hours of membrane transport is shown in fig-

ure 2. According to this figure, removal of zinc(II) with Cyanex 272 and D2EHPA is more efficient compared with that of cadmium(II), whereas removal of Zn(II) is comparable to that of Cd(II), provided that Cyanex 301 is used. With Cyanex 302 removal of Cd(II) is more efficient in comparison with that of Zn(II) ions. The best, i.e. 91.4%, removal of zinc(II) with D2EHPA occurs at pH 5.0.

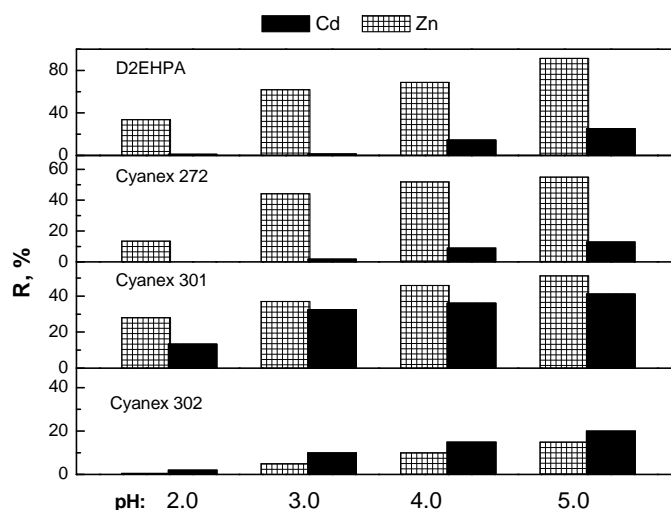


Fig. 2. Removal of Zn(II) and Cd(II) ions from chloride aqueous solutions in transport through PIM after 24 hours. Conditions as in figure 1

In the next series of experiments, the transport of Zn(II), Cd(II), Cu(II), Co(II) and Ni(II) ions was studied. The kinetic parameter and selectivity order for the ions transported through PIM from aqueous source phase containing equimolar mixture of all metals is given in the table. As can be seen, the values of initial fluxes of Cu(II), Co(II) and Ni(II) ions increase in the following order of organophosphorus acidic compounds: Cyanex 272 < D2EHPA < Cyanex 301, whereas the values of initial fluxes of Zn(II) and Cd(II) ions decrease. The identical order was obtained for extraction process with Cyanex 301 [5]. These results for Cyanex 301 testify to very poor selectivity of PIM transport, whereas selectivity for Cyanex 272 is good. The per cent removal of metal ions after 24 hours of experiment is shown in figure 3. According to this figure, the per cent removal of zinc(II) by Cyanex 272 or D2EHPA is much higher compared to that of copper(II), cadmium(II), cobalt(II) and nickel(II) ions. But the per cent removal of Cu(II) by Cyanex 301 is slightly higher than that of zinc(II), cadmium(II), cobalt(II) and nickel(II) ions.

Table

The values of initial fluxes and selectivity orders for competitive transport of metal ions through PIM at pH = 5.0

Carrier	Metal ions	Initial flux, J_0 ($\mu\text{mol}/\text{m}^2\text{s}$)	Selectivity order and selectivity ratios
Cyanex 301	Cu(II)	3.68	Cu(II) \geq Zn(II) \geq Cd(II) > Co(II) > Ni(II) 1.0 1.2 1.4 1.5
	Zn(II)	3.53	
	Cd(II)	3.05	
	Co(II)	2.70	
	Ni(II)	2.44	
D2EHPA	Zn(II)	7.91	Zn(II) > Cu(II) > Co(II) > Cd(II) > Ni(II) 3.7 5.4 6.8 8.3
	Cu(II)	2.12	
	Co(II)	1.46	
	Ni(II)	0.95	
	Cd(II)	1.17	
Cyanex 272	Zn(II)	9.16	Zn(II) > Cu(II) > Cd(II) > Co(II) > Ni(II) 6.1 9.4 11.7 76.3
	Cu(II)	1.49	
	Cd(II)	0.97	
	Co(II)	0.78	
	Ni(II)	0.12	

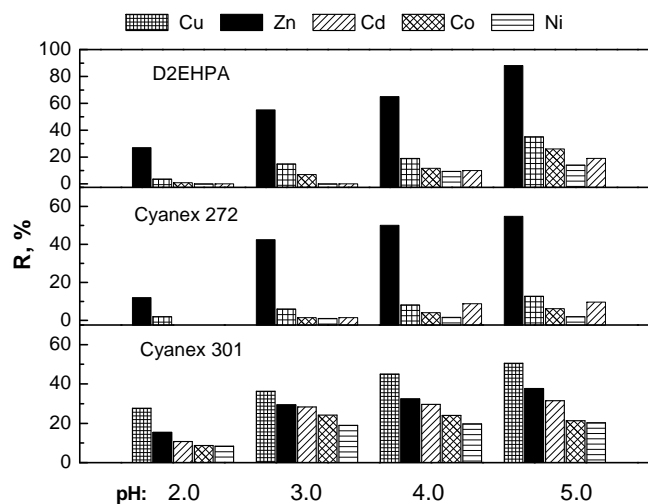


Fig. 3. Removal of metal ions from chloride aqueous solutions in PIM transport at different pH after 24 hours. Source phase: $c_{\text{Me}} = 0.01 \text{ M}$, receiving phase: 1.0 M HCl . Membrane: $2.50 \text{ cm}^3 \text{ ONPPE} / 1.0 \text{ g CTA}, 1.0 \text{ M carriers}$

The influence of an initial hydrochloric acid concentration in the receiving phase on the transport of initial fluxes through PIM by Cyanex 272 is shown in figure 4. The

initial flux of zinc(II) ions is much greater in comparison with the fluxes of other metal ions. The initial fluxes of all ions investigated increase with an increase of hydrochloric acid concentration in the receiving phase.

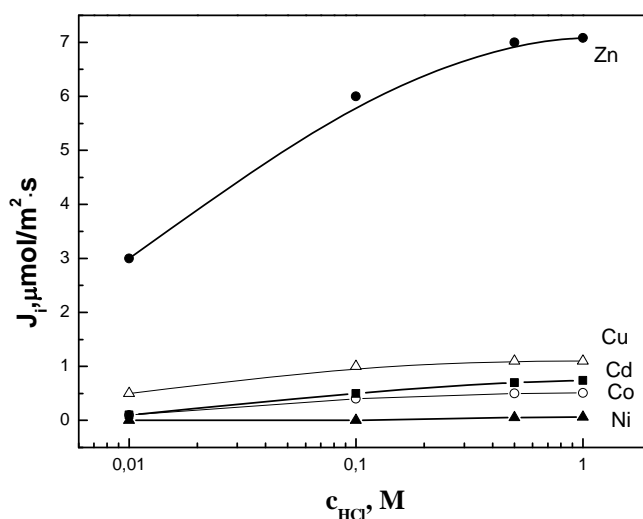


Fig. 4. Influence of an initial hydrochloric acid concentration in the receiving phase on the transport of initial fluxes through PIM with Cyanex 272.

Source phase: $c_{\text{Me}} = 0.01 \text{ M}$, $\text{pH} = 4.0$; membrane: $2.50 \text{ cm}^3 \text{ ONPPE} / 1.0 \text{ g CTA}$, 1.0 M Cyanex 272

For the feed phase with Cyanex 272 the selectivity order was as follows: $\text{Zn(II)} > \text{Cu(II)} > \text{Cd(II)} > \text{Co(II)} > \text{Ni(II)}$.

4. CONCLUSION

Zinc(II) ions can be effectively separated from aqueous chloride solutions containing cadmium(II) ions due to the transport of the former through polymer inclusion membrane with di(2-ethylhexyl)phosphoric acid (D2EHPA) or Cyanex 272 as the ion carrier. However, Cyanex 302 used as ion carrier allowed much faster transport of Cd(II) cations than that of Zn(II) ions from solutions containing both ions. The values of selectivity coefficients of Zn(II)/Cd(II) for D2EHPA, Cyanex 272, Cyanex 301 and of Cd(II)/Zn(II) for Cyanex 302 decrease with an increase in pH values. The best selectivity coefficients for Zn(II) ions compared to Cd(II) ions were obtained at pH 2.0 and 3.0.

Zinc(II) ions can be also effectively separated from aqueous chloride solutions containing another metal ions, i.e. cadmium(II), copper(II), cobalt(II) and nickel(II),

due to the transport through polymer inclusion membrane with di(2-ethylhexyl) phosphoric acid (D2EHPA) or Cyanex 272 as the ion carrier. The highest selectivity coefficients for Zn(II)/Cu(II), Zn(II)/Cd(II), Zn(II)/Co(II), Zn(II)/Ni(II) were equal to 6.1, 9.4, 11.7 and 76.3, respectively, for polymer inclusion membrane with Cyanex 272. In the transport with Cyanex 272, an initial flux of zinc(II) is much higher than that of other metal ions. The initial fluxes of all ions investigated increase with an increase in hydrochloric acid concentration in the receiving phase.

REFERENCES

- [1] SASTRE A.M., KUMAR A., SHUKLA J.P., SINGH R.K., *Improved Techniques in Liquid Membrane Separations: An Overview*, Separation and Purification Methods, 1998, 27, 213–298.
- [2] WODZKI R., SIONKOWSKI G., *Hybrid: polymer-liquid-polymer membrane system for removal of heavy metal ions from waste waters*, [in:] Howell J.A., Noworyta A. (Eds.), *Towards Hybrid Membrane and Biotechnology Solutions for Polish Environmental Problems*, Wrocław Technical University Press, Wrocław, 1995, 235–239.
- [3] BARTSCH R.A., WAY J. (Eds.), *Chemical Separation with Liquid Membranes*, ACS Symposium Series 642, Amer. Chem. Soc., 1996, Washington, DC.
- [4] SUGIURA M., KIKKAWA M., URITA S., *Sep. Sci. Technol.*, 1987, 22, 2263–2271.
- [5] SOLE K.C., HISKEY J.B., *Solvent extraction characteristic of thiosubstituted organophosphinic acid extractants*, Hydrometallurgy, 1992, 30, 345–365.
- [6] BINGHUA Y., NAGAOSA M., SATAKE A., NOMURA K., HORITA K., *Solvent Ext. Ion Exch.*, 1996, 14, 849–870.
- [7] WALKOWIAK W., GĘGA J., *Transition metal cation separation by organophosphorous compounds in liquid membrane processes*, [in:] *Chemical separations with liquid membranes*, Bartsch R.A. (Ed.), Kluwer Academic Pub., 1996, Washington.
- [8] GĘGA J., WALKOWIAK W., GAJDA B., *Separation of Co(II) and Ni(II) ions by supported and hybrid liquid membranes*, *Sep. Purification Technol.*, 2001, 22–23, 551–558.
- [9] WODZKI R., SIONKOWSKI G., POZNIAK G., *Sep. Sci. Technol.*, 1999, 34, 627–649.
- [10] ATA O.N., BESE A.V., DÖNMEZ B., ÇAKICI A., *Effect of parameters on the transport of zinc ion through supported liquid membrane*, *Chemical Engineering and Processing*, 2004, 43, 895–903.
- [11] ULEWICZ M., WALKOWIAK W., *Separation of zinc(II) and cadmium(II) ions from sulfate solutions by ion flotation and transport through liquid membranes*, *Physicochemical Problems of Mineral Processing*, 2003, 37, 77–86.
- [12] ULEWICZ M., WALKOWIAK W., GĘGA J., POŚPIECH B., *Zinc(II) selective removal from other transition metal ions by solvent extraction and transport through polymer inclusion membranes with D2EHPA*, *Ars Separatoria Acta*, 2003, 2, 47–55.
- [13] ULEWICZ M., GĘGA J., WALKOWIAK W., *Selektywne wydzielanie jonów Zn(II) w procesie transportu przez polimerowe membrany inkluzyjne zawierające Cyanex 272*, *Monografie Komitetu Inżynierii Środowiska PAN*, 2004, 22, 305–312.
- [14] ALGUACIL F.J., NAVARRO P., *Permeation of cadmium through a supported liquid membrane impregnated with Cyanex 923*, *Hydrometallurgy*, 2001, 61, 137–142.