B. POSPIECH*,#

SEPARATION OF CADMIUM(II), COBALT(II) AND NICKEL(II) BY TRANSPORT THROUGH POLYMER INCLUSION MEMBRANES WITH PHOSPHONIUM IONIC LIQUID AS ION CARRIER

SEPARACJA JONÓW KADMU(II), KOBALTU(II) I NIKLU(II) W PROCESIE TRANSPORTU PRZEZ POLIMEROWE MEMBRANY INKLUZYJNE ZAWIERAJĄCE FOSFONIOWĄ CIECZ JONOWĄ W ROLI PRZENOŚNIKA

This paper presents study on the facilitated transport of cadmium(II), cobalt(II) and nickel(II) ions from aqueous chloride solutions through polymer inclusion membranes (PIMs) with phosphonium ionic liquid. Cyphos IL 101 (trihexyl(tetradecyl) phosphonium chloride) was used as a selective carrier for synthesis of cellulose triacetate membranes containing o-nitrophenyl pentyl ether (ONPPE) as a plasticizer. Effect of different parameters such as hydrochloric acid concentration in the source phase as well as ion carrier concentration in the polymer membrane on metal ions transport has been investigated. Cd(II) was transported preferably from hydrochloric acid solutions containing Co(II) and Ni(II) through PIM containing 18.8 wt.% CTA and 26.0 wt.% Cyphos 101 and 55.1 wt.% ONPPE into 0.5 M HNO_3 as the receiving phase. The obtained results suggest that there is a possibility of application of this membrane with Cyphos IL 101 as ion carrier for separation of Cd(II) over Co(II) and Ni(II) from hydrochloric acid solutions.

Keywords: cadmium(II), cobalt(II), nickel(II), Cyphos IL 101, polymer inclusion membrane

Przeprowadzono badania transportu jonów Cd(II), Ni(II) i Co(II) z wodnych roztworów kwasu solnego przez polimerowe membrany inkluzyjne (PIMs) zawierające fosfoniową ciecz jonową – Cyphos IL 101 (chlorek triheksylo(tetradecylo) fosfoniowy) w roli selektywnego przenośnika jonowego. Rolę polimerowej matrycy w membranie pełnił trioctan celulozy (CTA). Jako plastyfikatora użyto eteru nitrofenylopentylowego (ONPPE). W wyniku badań określono wpływ różnych czynników, takich jak stężenie kwasu solnego w fazie zasilającej, jak również stężenie przenośnika w polimerowej membranie na selektywność i efektywność transportu badanych jonów metali. Jony kadmu(II) były selektywnie transportowane z roztworów kwasu solnego zawierającego jony niklu(II) i kobaltu(II) do 0,5 M roztworu kwasu azotowego(V). Uzyskane wyniki wskazują, że istnieje możliwość zastosowania procesów transportu przez polimerowe membrany inkluzyjne z cieczą jonową w roli selektywnego przenośnika do rozdzielania jonów Cd(II) od Ni(II) i Co(II) z roztworów kwasu solnego.

1. Introduction

Cadmium, cobalt and nickel are present in solid and liquid effluents coming from steel, electronic, electroplating and metallurgical industries. The waste materials containing heavy metals are considered as hazardous materials. On the other hand, the secondary and waste materials can be an important source of many value metals which are needed for production of various materials, i.e. alloys, metal plating, batteries, catalysts, etc. It is very important to develop highly efficient, ecological and economical methods to recycle of industrial waste materials [1-5].

Recovery and recycling processes of metals, such as cadmium, cobalt and nickel from secondary materials usually are hydro/pyrometallurgical methods where materials are first leached in acidic or alkaline solution to dissolve the metals directly or after thermal treatment [6-8]. A review of the literature reveals that pyrometallurgical method consists of selective volatilization of metals at elevated temperature (around 900º C) followed by condensation to recover cadmium with > 99% purity. But most valuable metals such as nickel and cobalt are not usually recovered [9]. Hydrometallurgical methods of the secondary materials treating generate leach liquors containing cadmium and nickel as major metals. The next stage in this technology is separation of metal ions from leach liquor. This stage is very important and necessary to obtain the final product as pure metal or metal compound.

The hydrometallurgical recovery of cadmium and nickel is based on the solvent extraction processes because these metal ions are easily extractable into the organic phase with various reagents, such as: TOPS 99, Cyanex 923, Cyanex 272, Cyanex 302 and Cyanex 301 diluted in kerosene [9], D2EHPA [8], Cyanex 302 [10], Cyanex 272 and di-*n*-octyl phosphinic acid [11], Cyanex 923 [12], quaternary ammonium salt – Aliquat 336 [13], etc.

* CZESTOCHOWA UNIVERSITY OF TECHNOLOGY, DEPARTMENT OF CHEMISTRY, 19 ARMII KRAJOWEJ AV., 42-200 CZESTOCHOWA, POLAND

Corresponding author:b.pospiech@wip.pcz.pl

A survey of literature indicates that separation of Cd(II) and Ni(II) from leach liquors can be achieved either by solvent extraction as well as by liquid membrane processes. Membrane processes are economical separation technologies. Solvent extraction consumes large amounts of solvents and extractants. In the transport process of metal ions through liquid membranes, extraction and stripping processes occur at the same time and demand for organic solvents is very small [14-17]. Polymer inclusion membranes (PIMs) are type of liquid membranes. PIM contains ion carrier, which is fixed within polymeric matrix consisting of a support (cellulose triacetate, CTA or polyvinyl chloride, PVC) and plasticizer. Plasticizers have a dual role in membranes: improving membrane stability and properties such as flexibility and flux rates (diffusion) and additionally plasticizer is a solvent for the carrier [18-22]. Separation process of heavy metal ions from aqueous solutions through PIMs containing different compounds as ion carriers was subject of the many investigations [23-27]. Literature survey revealed that the transport process of Cd(II) ions through PIMs have been also reported by many researchers, employing ion carriers, such as: Aliquat 336 [28], organophosphorus acids, i.e. D2EHPA [29], etc.

Recently, ionic liquids (ILs) are frequently used for removal of metal ions from aqueous solutions. Room temperature ionic liquids (RTILs) are salts, which are liquid at room temperature. They are able to dissolve both polar and non-polar compounds and are considered as green solvents [30] because ILs have specific properties, such as: negligible vapor pressure, high thermal stability up to 300°C and non-flammability. Moreover, ionic liquids show good extractability for metal ions [31].

The main aim of the present work is to study the selective transport process of Cd(II), Co(II) and Ni(II) ions from hydrochloric solutions using PIMs based on cellulose triacetate with Cyphos IL 101 as selective ion carrier. This phosphonium ionic liquid has been not used yet as an ion carrier in PIMs for separation of Cd(II) over Co(II) and Ni(II). In the previous paper, Cyphos IL 104 (trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate) was used as the extractant/ion carrier of Cd(II) in the solvent extraction and transport processes through PIM [32]. In this investigation, several factors were studied in order to determine the optimal condition of selective transport of Cd(II) over Co(II) and Ni(II) from hydrochloric acid solutions across PIM. Among these there are the effects of hydrochloric acid concentration in the source phase and Cyphos IL 101 concentration in the polymer membrane.

2. Experimental

2.1. Reagents

Inorganic chemicals, i.e. cadmium(II) chloride (CdCl$_2$·2.5H$_2$O, purity=99%), nickel(II) chloride (NiCl$_2$·6H$_2$O, purity=99%), cobalt(II) chloride (CoCl$_2$, purity=99%), hydrochloric acid (HCl), nitric acid (HNO$_3$), were of analytical grade and were purchased from POCh (Gliwice, Poland). Aqueous solutions were prepared with deionized water.

Organic reagents, i.e. trihexyl(tetradecyl) phosphonium chloride (Cyphos® IL 101) of 95 % purity was purchased from Cytec Canada Industries Inc., cellulose triacetate (CTA), dichloromethane, toluene, *o*-nitrophenyl pentyl ether (ONPPE), were of analytical reagent grade (Aldrich) and used without further purification. The density of plasticizer, i.e. ONPPE was 1.098 gcm^{-3}.

2.2. Polymer inclusion membrane

The PIMs were prepared as described elsewhere [22-27]. The solutions of cellulose triacetate (CTA), the ion carrier (Cyphos IL 101), and the plasticizer, i.e. *o*-nitrophenyl pentyl ether (ONPPE) in dichloromethane were prepared. A portion of this solution was poured on a flat- bottom glass Petri dish which was kept on a leveled surface. The organic solvent was allowed to evaporate over a period 12 h. The resultant membrane was peeled off from the Petri dish and this membrane was washed with water and equilibrated in distillated water before use.

2.3. Transport experiments

The transport procedure has been described in previous papers [22-27]. The volumes of source and receiving phases were 100 cm^3, respectively. The effective membrane area, which was exposed to both phases was 12.56 cm^2. Both, the source and receiving aqueous phases were stirred by a magnetic stirrer. To transport of Cd(II), Co(II) and Ni(II) across PIM, a membrane module was used, to which both aqueous phases were pumped with a peristaltic pump (PP1B-05A type, Zalimp, Poland) working at a speed of 100 cm^{3}min^{-1} from tanks containing source and receiving phases, respectively. The permeation of metal ions was monitored by sampling of the source phase, which was analyzed by an atomic absorption spectrophotometer (Solaar 939, Unicam).

The kinetics of PIM transport process was described by a first-order reaction in metal ion concentration:

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

were c is the metal ion concentration (M) in the source phase at some given time, c_i is the initial metal ion concentration in the source phase, k is the rate constant (s^{-1}), and t is the time of transport (s).

To calculate the k value, a plot of $ln(c/c_i)$ versus time was prepared. The rate constant value for the duplicate transport experiment was then averaged and standard deviation was calculated. The permeability coefficient *(P)* was calculated as follows:

$$P = \frac{V}{A}k \tag{2}$$

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

The initial flux (J_i) was determined as:

$$J_i = P \cdot c_i \qquad (3)$$

The selectivity coefficient (S) was defined as the ratio of initial fluxes for M_1 and M_2 metal ions, respectively:

$$S = \frac{J_{i,M_1}}{J_{i,M_2}} \qquad (4)$$

The recovery factor (RF) of metal ions from the source phase into receiving phase was calculated as:

$$RF = \frac{c_i - c}{c_i} \cdot 100\% \qquad (5)$$

3. Results and discussion

3.1. The kinetics of Cd(II), Ni(II) and Co(II) transport

The competitive transport of Cd(II), Ni(II) and Co(II) ions across PIM with Cyphos IL 101 as the ion carrier was investigated. One of the main aim of this work was to study the transport kinetics of the studied cations across PIMs with Cyphos IL 101. The membranes used in the present work were formed by casting cellulose triacetate (CTA) from the organic solution containing Cyphos IL 101 as the ion carrier and nitrophenyl pentyl ether (ONPPE) to form a thin, stable film. In this work, ONPPE was used as plasticizer because the earlier works [23,26] showed that very good stability of the membranes obtained with this kind of plasticizer. The source phase was composed of 0.01 M Cd(II), 0.01 M Ni(II),

0.01 M Co(II) in 0.1 M HCl. The kinetics dependence of $\ln(c/c_i)$ versus time for Cd(II), Co(II) and Ni(II) transport across PIM is shown in Fig. 1 and the kinetic parameters are summarized in Table 1. Ni(II) was insignificantly transported into the receiving phase. As can be seen from Fig. 1 and Table 1, Cd(II) was transported across PIM with higher rate than Co(II) and Ni(II). The results can be attributed to the formation of anionic chlorocomplexes by Cd(II) and Co(II) in chloride solutions, while Ni(II) does not form anionic chlorocomplexes. The metal ions fluxes decrease in the order Cd(II) > Co(II) > Ni(II). The initial fluxes of Cd(II), Co(II) and Ni(II) were equal to 21.3, 2.3 and 0.009 $\mu molm^{-2}s^{-1}$, respectively. The recovery factors for Cd(II) and Co(II) after 24 hours were 90.3 % and 21.5 %, respectively.
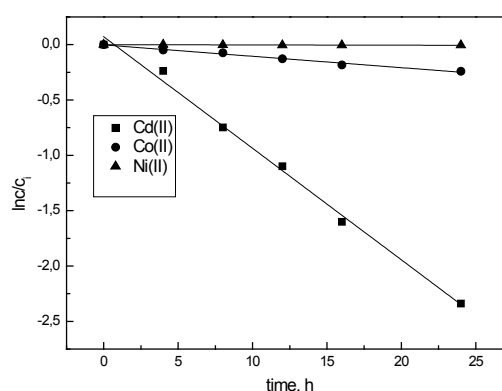

Fig. 1. Relationship of ln(c/ci) vs. time for Cd(II), Co(II) and Ni(II) transport across PIM. PIM: 0.075 g CTA, 2.7 cm³ ONPPE/1 g CTA, 1 M Cyphos 101; the source phase: 0.01 M Cd(II), 0.01 M Co(II), 0.01 M Ni(II) in 0.1 M HCl; the receiving phase: 0.5 M HNO₃

TABLE 1

The initial fluxes, rate constants, selectivity order and selectivity coefficients for competitive transport of Cd(II), Co(II) and Ni(II) across PIM with Cyphos IL 101. Conditions as in Fig.1

Metal ions	Rate constant, k, (h^{-1})	Initial flux, J_i, $(mmolm^{-2}s^{-1})$	Selectivity order and selectivity coefficient ($S_{Cd/Co}$)
Cd(II)	0.096	21.4	Cd(II)>Co(II) > Ni(II)
Co(II)	0.010	2.31	
Ni(II)	4.2·10-5	0.009	9.3 2377.7

TABLE 2

Composition of PIMs. Conditions of the transport processes as in Fig. 2

Nr	Polymer support CTA, wt. %	Plasticizer ONPPE, wt.%	Ion carrier Cyphos 101, wt. %	[Cyphos 101], M
1	21.6	63.4	15.0	0.5
2	18.8	55.1	26.0	1.0
3	14.9	43.7	41.4	2
4	12.4	36.2	51.4	3

The initial fluxes, rate constants and selectivity coefficients for competitive transport of Cd(II) and Co(II) across PIM with Cyphos IL 101.
PIM: 0.075 g CTA, 2.7 cm³ ONPPE/1 g CTA, 1 M Cyphos IL 101; the source phase: 0.01 M Cd(II), 0.01 M Co(II) in HCl; the receiving
phase: 0.5 M HNO₃

[HCl], M	Rate constant, k, (h^{-1})		Initial flux, J_i, $(mmolm^{-2}s^{-1})$		Selectivity coefficient $(S_{Cd/Co})$
	Cd(II)	Co(II)	Cd(II)	Co(II)	
0.1	0.0964	0.0104	21.3	2.3	9.3
0.5	0.0998	0.0125	22.1	2.8	7.9
1	0.1080	0.0263	23.8	5.8	4.1
2	0.1290	0.0317	28.5	7.0	4.0

3.2. Effect of CYPHOS IL 101 concentration

The significant factor determining metal ions transport across PIMs is the concentration of an ion carrier in membrane. In the next series of investigations, the effect of Cyphos IL 101 concentration in the membrane on the transport efficiency and selectivity extraction of Cd(II), Ni(II) and Co(II) from 0.1 M HCl was studied. The concentration of this phosphonium ionic salt used as the carrier varied from 0.5 M to 3 M (*on volume of plasticizer*). The composition of PIMs used in the transport process of Cd(II) is shown in Table 2. Fig. 2 shows the effect of Cyphos IL 101 concentration in PIM on the initial fluxes of Cd(II) and Co(II) from 0.1 M HCl. As can be seen, the transport of metal ions was slow at low concentration of the ion carrier. The initial flux (J_i) increases with increasing carrier concentration up to 1 M, and then decreases for higher Cyphos IL 101 concentration (Fig. 2.). This concentration of Cyphos 101 represents probably a critical value above which the initial flux of this metal ions decreases. The maximum transport of Cd(II) and Co(II) ions was obtained by using the membrane containing 1 M of Cyphos IL 101. This investigation allowed to determine the optimal concentration of Cyphos IL 101 in membrane. The resulting membrane contained 18.8 wt.% CTA and 26 wt.% Cyphos IL 101 and 55.1 wt.% ONPPE. Increase of carrier concentration in membrane phase caused decrease solubility of the ion carrier in ONPPE and decrease in permeability coefficients of the studied metal ions.

Fig. 3. Effect of HCl concentration in the source phase on the permeability coefficient; PIM: 0.075 g CTA, 2.7 cm³ ONPPE/1 g CTA, 1 M Cyphos IL 101; the source phase: 0.01 M Cd(II), 0.01 M Co(II), 0.01 M Ni(II) in HCl solutions; the receiving phase: 0.5 M HNO₃

3.3. Effect of HCl

In next series of experiments, the influence of hydrochloric acid concentration in the source phase on the transport of Cd(II), Co(II) and Ni(II) was studied. PIM containing 18.8 wt.% CTA and 26 wt.% Cyphos IL 101 and 55.1 wt.% ONPPE was used in this study. Fig. 3 shows the dependence on the permeability coefficient (P) as the function of HCl concentration. As can be seen from this figure, the permeability coefficient of Cd(II) increased with increasing of HCl concentration in the source phase from 2.13 µm/s for 0.1 M HCl to 2.85 µm/s for 2 M HCl as the source phase. As can be observed, the permeability coefficient of Co(II) increased significantly with increasing HCl concentration from 0.23 µm/s for 0.1 M HCl to 0.70 µm/s for 2 M HCl. Ni(II) was insignificantly transported into receiving phase. The percentage removal of Cd(II) and Co(II) ions from hydrochloric acid solutions across PIM with Cyphos IL 101 is shown in Fig. 4. The highest recovery factors of Cd(II) and Co(II) were obtained for 2 M HCl. Fig. 5 shows the dependence on the selectivity coefficient of Cd(II) over Co(II) as the function of HCl concentration. As can be seen from this figure, the selectivity of the transport process decreased with increasing of HCl concentration in the source phase from 9.3 for 0.1 M HCl to 4.0 for 2 M HCl as the source phase. The kinetic parameters of the transport process are summarized in Table 3. We can find in the literature [32,33]
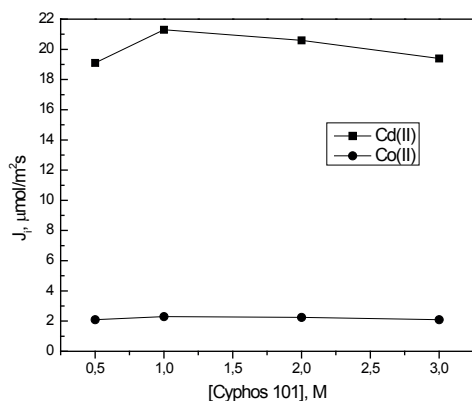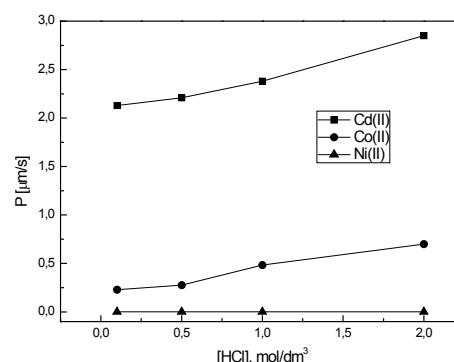

Fig. 2. The initial fluxes of Cd(II) and Co(II) vs. Cyphos IL 101 concentration in the membrane. PIM: 2.7 cm³ ONPPE/1g CTA, different concentrations of Cyphos IL 101; the source phase: 0.01 M Cd(II), 0.01 M Co(II), 0.01 M Ni(II); the receiving phase: 0.5 M HNO₃

that quaternary phosphonium salts can extract both neutral and anionic complexes according to the addition or anion exchange reactions. Extraction of Cd(II) and Co(II) by Cyphos IL 101 proceeds probably according to two different ways depending on acid and chloride concentrations in the aqueous phase [32-34]. The difference in the transport behavior of Cd(II), Co(II) and Ni(II) can be attributed to the fact that in chloride solutions only cadmium(II) and cobalt(II) form mainly stable anionic chlorocomplexes. Taken into account together the obtained results and the literature data [32-34], the following reactions can be proposed for Cd(II) and Co(II) extraction with Cyphos IL 101 from aqueous chloride solutions:

$$H^+_{(aq)} + CoCl_4^{2-}{}_{(aq)} + R_3R^{'}PCl_{(org)} \Leftrightarrow (R_3R^{'}P)HCoCl_{4(org)} + Cl^-(9)$$

$$H^+_{(aq)} + CoCl_3^-{}_{(aq)} + R_3R^{'}PCl_{(org)} \Leftrightarrow (R_3R^{'}P)HCoCl_{4(org)} \quad (10)$$

where subscripts (aq) and (org) stand for the aqueous and organic phases, respectively.

Further investigations are necessary to confirm these suggested reactions of Cd(II) and Co(II) with used phosphonium ionic liquid.

4. Conclusions

The studied PIM with Cyphos IL 101 can be recommended for the separation of Cd(II), Co(II) and Ni(II) from hydrochloric acid solutions with regard to the high values of separation coefficients. The highest initial fluxes of Cd(II) and Co(II) ions were obtained using membrane containing 18.8 wt.% CTA and 26 wt.% Cyphos IL 101 and 55.1 wt.% ONPPE. Ni(II) was insignificantly transported into the receiving phase. It was found that the initial fluxes of Cd(II) and Co(II) are the highest values for 2 M HCl as the source solution and were 28.5 $\mu molm^{-2}s^{-1}$ and 7.0 $\mu molm^{-2}s^{-1}$, respectively. However, the separation coefficients decrease with increasing HCl concentration in the source phase from 9.3 at 0.1 M HCl to 4.0 at 2 M HCl.

The transport process through PIM with Cyphos IL 101 enables removal above 90% of Cd(II) from hydrochloric acid solutions into 0.5 M HNO_3. Finally, the separation membrane system presented in this paper can be useful for the removal of Cd(II) from solutions containing Co(II) and Ni(II).
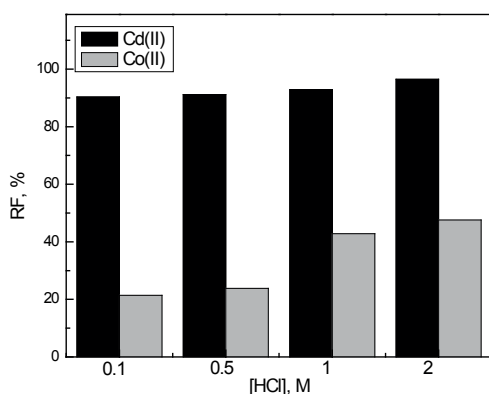

Fig. 4. Relation of the recovery factor (RF, %) of Cd(II) and Co(II) after 24 h vs. HCl concentration in the source phase. Experimental conditions as in Fig. 3
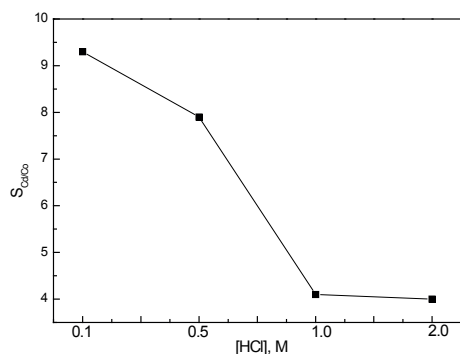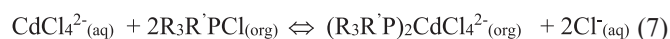
Fig. 5. The selectivity coefficient of Cd(II) over Co(II) (SCd/Co) vs. HCl concentration in the source phase. Experimental conditions as in Fig. 3

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$$CdCl_3^-{}_{(aq)} + R_3R^{'}PCl_{(org)} \Leftrightarrow R_3R^{'}PCdCl_{3(org)} + Cl^-{}_{(aq)} \quad (6)$$

$$CdCl_4^{2-}{}_{(aq)} + 2R_3R^{'}PCl_{(org)} \Leftrightarrow (R_3R^{'}P)_2CdCl_4^{2-}{}_{(org)} + 2Cl^-{}_{(aq)} \quad (7)$$

$$H^+_{(aq)} + CdCl_3^-{}_{(aq)} + R_3R^{'}PCl_{(org)} \Leftrightarrow (R_3R^{'}P)HCdCl_{4(org)} \quad (8)$$

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