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The application of polymer inclusive membranes for removal of heavy metal ions from waste solutions

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ABSTRACT

Purpose: The aim of the conducted studies was to determine the possibility of selective separation and precipitation of metal ions from polimetalic solution containing nickel(II), cobalt(II), cadmium(II) and zinc(II) cations using polymer inclusive membranes. 1-decylimidazole was used in membrane as a carrier of ions. The influence of chloride anions concentration on the process has also been investigated.
Design/methodology/approach: Polymer inclusive membranes (PIM) containing cellulose acetate as a matrix, orto-nitrophenyl octyl ether (ONPOE) as a plasticizer and 1-decylimidazole as a carrier were used in investigations. The membrane processes were carried out in a membrane module for 24 hours.
Findings: The results obtained point out a significant influence of chloride anions concentration on separation process of certain metal ions. It was observed that zinc(II) ions are isolated most effectively from the solution containing 2M of chloride anions. About 88% of Zn(II), 5.5% of Co(II), 6.5% of Cd(II) and below 1% of Ni(II) were separated from such a solution.
Research limitations/implications: The obtained results show that it is possibility of the selective extraction of heavy metal ions from polymetallic chloride solutions in membrane processes. The aqueous solution containing 2M of chloride ions was used in the investigation.
Practical implications: The results show that Zn(II) can be effectively recovered from solutions containing Co(II), Cd(II) and Ni(II). This process would allow the utilization of waste solutions containing the heavy metal ions. The results of the study presented in the paper can be used in the utilization process of the spent batteries and accumulators.
Originality/value: The innovative issue shown in this paper concerns the usage of 1-decylimidazole in selective separation of nickel(II), cobalt(II), cadmium(II) and zinc(II) ions in membrane process using PIM.
Keywords: Ions separation; Polymer inclusive membranes; 1-decylimidazole; Nickel(II) cobalt(II), zinc(II), cadmium(II) ions

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1. Introduction

The metallurgical industry produces various waste products containing heavy metals. These wastes are usually solid in form of various dusts and cinders. In some cases liquid or semi-liquid wastes can also come into being in the form of mud, solutions from miscellaneous scrubbers or postelectrolytic solutions and mud. The other source of waste products in the form of solutions are mine waters drained off to the surface.

Solid waste products can contain various amounts of such metals as lead, zinc, cadmium, chromium or arsenic, but also iron, manganese, nickel, cobalt and copper. In case of mine waters their composition depends on the mine, the type of ore mined there and the geological conditions [1,3]. Moreover, mine waters can contain some amounts of radioactive elements, especially radium isotopes [2].

Considering the occurrence of heavy metals, these wastes are very hazardous to environment. At the same time though, they can be a valuable resource. For these reasons it is not only necessary, but also profitable to prepare the waste products recycling technology.

When it comes to the process of production and recovery of metals such as nickel, cobalt, zinc, cadmium and others, more and more stress is being put on the hydrometallurgical processes, involving a solvent extraction, ion exchange and a process of transport through liquid membranes. The necessity of mining and processing poorer and poorer ores, necessity of full exploitation of secondary materials, and also numerous threats connected with application of pyrometallurgical methods (i.e. air pollution, greenhouse effect) have the large influence on increasing common usage of these methods.

Lately, polymer inclusive membranes (PIM) are gaining more and more popularity. PIM possess better mechanical properties and chemical resistance than support liquid membranes. The addition of plasticizer to the polymer membrane helps in blending the carrier with a polymer matrix and causes an increase of membranes elasticity.

The typical and well-known metal extractants, such as phosphoorganic acids [4-7], trioctylamine [8] and some rarely used as carriers compounds such as crown ethers [9] were adapted as metal carriers.

Lately, alkyl derivatives of imidazoles are gaining more and more interest of scientists [10-12]. These compounds have two atoms of nitrogen in a particle. One of them can form coordinate bonds using a free electron pair, creating complexes with neutral nonorganic metal complexes, i.e. metal chlorides in form of MCl_2. Taking into account the nature of complexes created with 1-alkylimidazoles and metal ions, it is right to expect that the chloride anions concentration will have a significant influence on the selectivity of separation process including PIM.

The aim of this study is to investigate the possibility of application of metal ions separation process of polimetalic solutions containing nickel(II), cobalt(II), zinc(II) and cadmium(II) with the usage of polymer inclusive membranes. 1-decylimidazole was used as a carrier. The influence of chloride anions concentrations on the selectivity of separation process of particular metal cations was also examined thoroughly.

2. Experimental

2.1. Materials and work methodology

The 1-decylimidazoles obtained in reaction of imidazole with appropriate bromoalkane were used [13].

To synthesize polymer inclusive membranes (PIM) the following solutions were used: 1.25 g of cellulose triacetate (CTA) in 100 cm^3 of dichloromethane, 10% v/v plasticizer solution (*orto*-nitrophenyl octyl ether - ONPOE, Fluka) in dichloromethane and 0.1 M solution of ions carrier in dichloromethane. The CTA solution was mixed with a plasticizer and carrier mixture and then spilled on the glass ring of 4 cm diameter fixed on a flat glass plate. The membrane was created through the evaporation of the solvent over 12 hours and afterwards wetted using distilled water for next 12 hours. The membrane contained 8.0 dm^3 of ONPOE per 1.0 g of CTA and 1.0 M of 1-decylimidazole in reference to plasticizer. The molar concentration of the carrier was counted up for the volume of plasticizer.

The metal ions transport through polymer inclusive membranes (PIM) was investigated in a glass measurement vessel (Fig. 1). The vessel was composed of two cells, 50 cm^3 each, divided by the membrane of 4.9 cm^2 surface. The experiment was carried out for 12 hours.

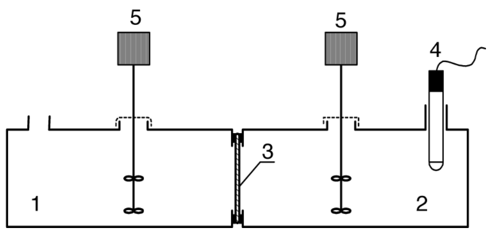

Fig. 1. The experimental apparatus for metal ions transport through PIM. 1 - receiving phase, 2 - feeding phase, 3 - membrane, 4 - pH electrode, 5 - stirrers

The feeding phase was made up of solutions of cobalt(II), nickel(II), zinc(II) and cadmium(II) of concentrations equal to: cobalt, nickel and zinc - 0.01 M, cadmium - 0.005 M. In order to obtain solutions containing 1, 2, 3 moles of chloride anions the addition of appropriate amount of sodium chloride was used.

The receiving phase was made up of demineralized water. Both solutions were mixed with frequency of 600 rpm. During the process the 0.2 ml samples of feeding and receiving phases were collected. After dilution the samples were analyzed using atomic absorption spectrometry (AAS spectrometer, Solar 939, Unicam) in order to determine the amount content of the solutions.

2.2. Modelling

Conducting studies in an initial stage of transport, it can be assumed that the rate of metal transport is directly proportional to the difference of metal ions concentrations in feeding and receiving phases. Under such an assumption the concentration of metal ions in a feeding phase can be described using first order kinetic equation. The constant in this equation takes into account all occurring during the transport processes.

Under this assumption acquired results allow to calculate the rate of metal ions transport coefficient (k, 1/s) from the dependence:

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

where: c, mol/m^3 - concentration of metal ions in a time t, c_i, mol/m^3 - initial concentration of metal ions.

Analyzing the investigated process of metal ions transport the following values have been taken into consideration:

- initial stream, J_i, mol/(m^{2}s):

$$J_i = \frac{V}{A} k c_i \tag{2}$$

where V, m^3 - volume of feeding phase, A, m^2- surface of membrane; and

- permeability coefficient, P, m/s:

$$P = \frac{V}{A} k \tag{3}$$

Additionally, to quantitatively describe the separation process through PIM the selectivity coefficients, defined as follows, have been calculated:

$$S_{M_I/M_{II}} = \frac{J_{M_I}}{J_{M_{II}}} \tag{4}$$

Table 1.
Parameters characterizing the transport and separation of nickel(II), cobalt(II), zinc(II) and cadmium(II) ions from chloride solutions. Matrix - cellulose acetate, carrier - 1-decylimidazole, plasticizer - ONPOE. Chloride anions concentration 1 M

	Metal ion			
	Co(II)	Ni(II)	Cd(II)	Zn(II)
k, s^{-1}	1.26E-4	7.72E-5	1.62E-4	1.20E-3
P, m/s	1.30E-6	7.87E-7	1.65E-6	1.23E-5
J_i, mol/(m^{2}s)	1.40E-5	7.58E-6	9.37E-6	1.14E-4
%R	5.5	<1.0	6.5	71

Table 2.
Parameters characterizing the transport and separation of nickel(II), cobalt(II), zinc(II) and cadmium(II) ions from chloride solutions. Matrix - cellulose acetate, carrier - 1-decylimidazole, plasticizer - ONPOE. Chloride anions concentration 2 M

	Metal ion			
	Co(II)	Ni(II)	Cd(II)	Zn(II)
k, s^{-1}	1.89E-4	7.15E-5	1.47E-4	1.16E-3
P, m/s	1.93E-6	7.30E-7	1.50E-6	1.19E-5
J_i, mol/(m^{2}s)	1.93E-5	7.35E-6	8.54E-6	9.90E-5
%R	14.5	2	6	88

Table 3.
Parameters characterizing the transport and separation of nickel(II), cobalt(II), zinc(II) and cadmium(II) ions from chloride solutions. Matrix - cellulose acetate, carrier - 1-decylimidazole, plasticizer - ONPOE. Chloride anions concentration 3 M

	Metal ion			
	Co(II)	Ni(II)	Cd(II)	Zn(II)
k, s^{-1}	5.01E-5	7.50E-6	5.02E-5	8.45E-4
P, m/s	5.11E-7	7.65E-8	5.12E-7	8.62E-6
J_i, mol/(m^{2}s)	5.32E-6	7.58E-7	2.82E-6	8.44E-5
%R	2.5	<1	5.5	65

Table 4.
Dependence of chloride anions concentration in feeding phase on separation coefficient of nickel(II), cobalt(II), zinc(II) and cadmium(II) ions. Matrix - cellulose acetate, carrier - 1-decylimidazole, plasticizer - ONPOE

	Chloride concentration		
	1M	2M	3M
Co/Ni	1.84	2.62	7.01
Co/Cd	1.49	2.26	1.88
Cd/Ni	1.24	1.16	3.72
Zn/Co	8.14	4.61	15.9
Zn/Ni	15.0	12.1	111
Zn/Cd	12.2	10.4	29.9

In order to describe the efficiency of metal ions separation process the recovery coefficient have also been calculated from the equation:

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

3. Results

The results of nickel(II), cobalt(II), zinc(II) and cadmium(II) transport through polymer inclusive membranes containing 1-decylimidazole as a carrier acquired show the large influence of chloride anions concentration on the rate of transport, the amount of metal ions transferred through the membrane and their separation (Figs. 2-4, Tables 1-4).

The analysis of results obtained for the particular metal ions points that the most privileged is the transport of zinc(II) ions. In this case all kinetic parameters are at least one order of magnitude higher than for cobalt(II) and cadmium(II) ions and two orders of magnitude higher than for nickel(II) ions. In the case of cobalt(II) and cadmium(II) ions kinetic parameters are comparable. The transport of nickel(II) ions is characterized by the worse kinetic parameters. In case of nickel(II) these parameters are one order of magnitude lower than cobalt(II) and cadmium(II).

The influence of chloride anions concentration on the transport of particular metal ions through PIM is not identical for all of the studied metal ions. Thus, in case of cadmium(II) and zinc(II) ions the increase in chloride anions concentration in feeding phase causes an insignificant drop in values of determined kinetic parameters. When it comes to cobalt(II) ions the values of kinetic parameters increases with the rise in chloride anions concentration from 1 to 2 M and drops afterwards. In case of nickel(II) the change in chloride anions concentration does not influence the kinetics of transport.

In the same way is affected the coefficient of metal ions recovery. Thus, the increase of chloride anions concentration causes drop of this parameter in case of zinc(II) and cadmium(II), the increase in case of cobalt(II) ions and insignificant influence is noted in case of nickel(II) ions.

The recovery coefficient shows also the possibility of selective separation of zinc(II) from polimetalic solution containing all of the studied metal cations. Depending on the chloride anions concentration 71, 88 and 65% of zinc(II) ions can be isolated for 1, 2 and 3 M of chloride anions concentration respectively. The least recovery was observed for nickel(II) ions - it does not exceed 2%. In case of cadmium(II) ions the recovery coefficient is on the level of 6.5 to 5.5%. For cobalt(II) this coefficient increases from initial value of 5.5 to 14.5 in order to drop afterwards to 2.5% for chloride anions concentration 1, 2 and 3 M respectively.

The changes in separation coefficients calculated for the pairs of particular metal cations are also noteworthy. The separation coefficient for zinc(II) ions in comparison with other metal ions is the largest. However, what is specific, its value goes through minimum for 2 M of chloride anions. The separation coefficients for nickel(II), cobalt(II) and cadmium(II) are several times lower then for zinc(II) ions. The comparison of values of these coefficients for these three metals shows that the lowest values are obtained for nickel(II) ions, while the coefficients for cobalt(II) and cadmium(II) ions are comparable.

a)

b)

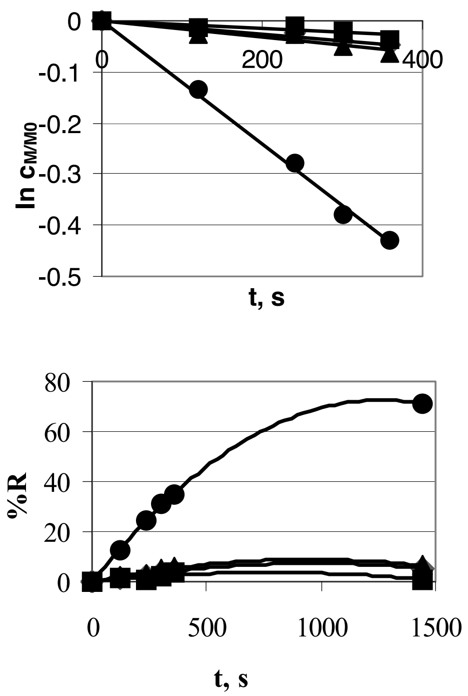

Fig. 2. Co(II), Ni(II), Zn(II), Cd(II) ions transport through PIM. Matrix - cellulose acetate, carrier - 1-decylimidazole, plasticizer - ONPOE. Chloride anions concentration 1 M. ◆ - Co(II), ■ - Ni(II), ▲ - Cd(II), ● - Zn(II). A) The change of concentration in time; b) The change of recovery coefficient

4. Conclusions

The experimental results of nickel(II), cobalt(II), cadmium(II) and zinc(II) ions transport through PIM obtained prove the possibility of application of the process to selective separation and, afterwards, precipitation of ions of these metals from polimetalic solutions. The parameters determined based on experimental results, such as rate of transport through PIM, recovery coefficient and separation coefficient prove that the ions being easiest to extract from the studied solutions are zinc(II) ions. In this case adjusting the concentration of chloride anions enables to extract 80-90% of these ions. The rest of the metal ions could be separated using successive membrane module. In that case cobalt(II) and cadmium(II) ions will permeate through the membrane, leaving nickel(II) ions in a feeding phase. For cobalt(II) and cadmium(II) respective parameters have comparable values. For nickel(II) however the calculated parameters have the lowest values, which suggests assumption that this ion will stay in feeding phase in second membrane module.

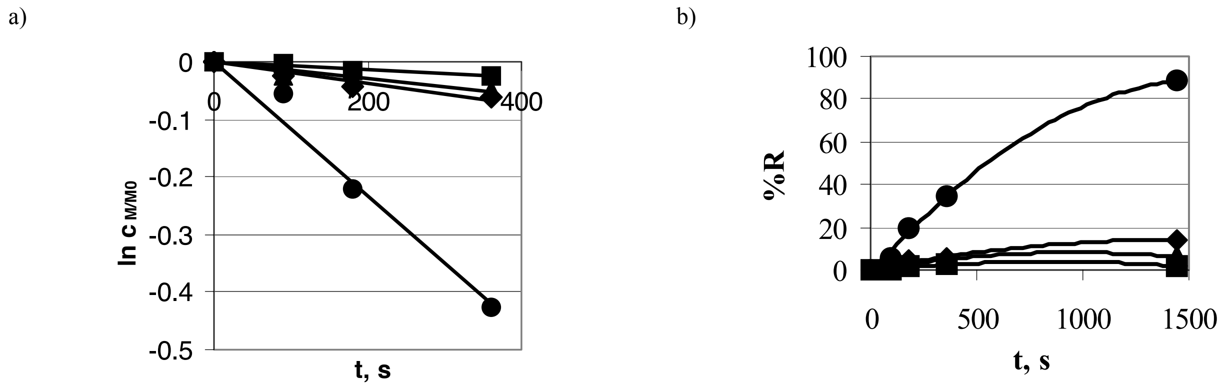

Fig. 3. Co(II), Ni(II), Zn(II), Cd(II) ions transport through PIM. Matrix - cellulose acetate, carrier - 1-decylimidazole, plasticizer - ONPOE. Chloride anions concentration 2 M. ◆ - Co(II), ■ - Ni(II), ▲ - Cd(II), ● - Zn(II). A) The change of concentration in time; b) The change of recovery coefficient

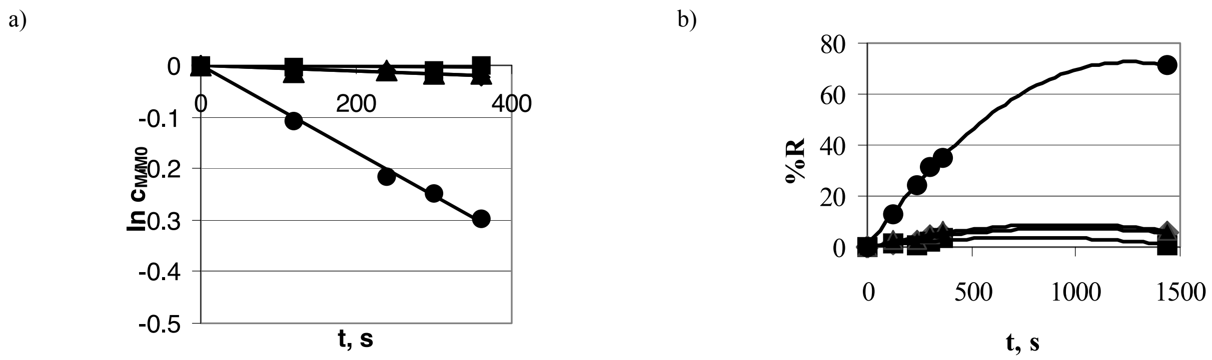

Fig. 4. Co(II), Ni(II), Zn(II), Cd(II) ions transport through PIM. Matrix - cellulose acetate, carrier - 1-decylimidazole, plasticizer - ONPOE. Chloride anions concentration 3 M. ◆ - Co(II), ■ - Ni(II), ▲ - Cd(II), ● - Zn(II). A) The change of concentration in time; b) The change of recovery coefficient

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