

PREPARATION AND APPLICATION OF POLYMER INCLUSION MEMBRANES (PIMs) INCLUDING ALAMINE 336 FOR THE EXTRACTION OF METALS FROM AN AQUEOUS SOLUTION

PRIPRAVA IN UPORABA MEMBRANE IZ POLIMERA (PIM) IN ALAMINA 336 ZA LOČENJE KOVIN IZ VODNIH RAZTOPIN

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Polymer inclusion membranes (PIMs) present an attractive approach for the separation of metals from an aqueous solution. The present study is about the application of Alamine 336 as an ion carrier in PIMs. The separation of copper (II), cobalt (II), nickel (II) and cadmium (II) from aqueous solutions with polymer inclusion membranes was investigated. PIMs are formed by casting a solution containing a carrier (extractant), a plasticizer and a base polymer, such as cellulose tri-acetate (CTA) or poly(vinyl chloride) (PVC), to form a thin, flexible and stable film. Several important transport parameters such as the type and amount of the plasticizer, the type of the stripping solution, the thickness of the membrane, the pH of the acid in the donor phase and the concentration of the base in the acceptor phase are discussed. The membrane was characterized to obtain information regarding its composition using AFM, FT-IR and SEM.

Keywords: polymer inclusion membranes, plasticizer, extractant, thickness of membrane

Membrane, ki vsebujejo polimere (PIM), so zanimive za ločenje kovin iz vodnih raztopin. Prikazana je študija uporabe Alamina 336 kot nosilca ionov v PIM. Preiskovano je bilo ločenje bakra (II), kobalta (II), niklja (II) in kadmija (II) iz vodnih raztopin z membrano s polimeri. PIM je bila izdelana z ulivanjem raztopine z nosilcem (ekstraktantom), z mehčalcem in osnovno iz polimera, kot je celuloza-tri-acetat (CTA) ali polivinil klorid (PVC), da je nastala tanka, gibljiva plast. Razloženih je več pomembnih transportnih parametrov, kot so delež mehčalca, vrsta raztopine za snemanje, debelina membrane, pH kisline v donorski fazi in koncentracija baze v acceptorski fazi. Izvršene so bile preiskave z AFM, FT-IR in SEM, da bi dobili podatke o sestavi membrane.

Ključne besede: membrane s polimerom, mehčalec, ekstraktant, debelina membrane

1 INTRODUCTION

The separation of metals from sulphate and chloride media has been of practical interest to the researchers. Solvent extraction is a well-established technology used for the production of metals from a relatively concentrated feed. However, industrial diluent effluents pose an important challenge as the solvent-extraction technique is not cost effective for the separation of metals from a dilute solution¹.

Recently, the supported liquid membrane (SLM) extraction has been emerging as an alternative to the conventional solvent extraction due to its advantages such as high selectivity, operational simplicity, low solvent inventory, low energy consumption, zero effluent discharge, and a combination of extraction and stripping in a single unit^{2,3}. Currently, considerable attention is focused upon polymer inclusion membranes (PIMs)⁴. Their specific advantages are an effective carrier immobilization, easy preparation, versatility, stability, good chemical resistance and better mechanical properties than in the case of SLM⁵. The large surface-area-to-volume ratio exhibited by PIMs gives them the potential to be used in

nuclear and harmful-metal waste remediation on an industrial scale. They consist of a polymer providing the mechanical strength, a carrier molecule that effectively binds and transports the ions across the membrane, and a plasticizer that provides elasticity and acts as the solvent, in which the carrier molecule can diffuse. PIMs are formed by casting a solution containing a carrier (extractant), a plasticizer and a base polymer, such as cellulose tri-acetate (CTA) or poly(vinyl chloride) (PVC), to form a thin, flexible and stable film⁶.

The choice of different constituents of the membrane is crucial to ensure its separation efficiency, so it is important to investigate the effect of different components on the extraction and transport of the target species. Among the polymers used to form a gel-like network that entraps the carrier and plasticizer/modifier, poly(vinyl chloride) (PVC) and cellulose triacetate (CTA) are most frequently encountered⁷.

Examples of such membranes are those containing only PVC and Aliquate 336 that have been used successfully for the transport of both metallic (e.g., Cd (II) and Cu (II)⁸ and non-metallic (e.g., thiocyanate)⁹ ionic species. Moreover, Konczyk et al.¹⁰ have used Aliquate 336

as a plasticizer in a PIM system containing D2EHPA as the carrier for the removal of Cr (III).

The present study focuses on the application of Alamine 336 as an ion carrier in PIMs and deals with the selective separation of Co, Cd, Ni and Cu ions from an acidic media into an NH_4SCN aqueous solution. Amines were used to extract the metal ions. The amine extraction chemistry of thiocyanate complexes was investigated by Sanuki et al.¹¹

2 EXPERIMENTAL WORK

2.1 Materials

All the reagents used were of analytical grade. Cellulose triacetate (CTA), 2-nitrophenyl pentyl ether (NPPE) and 2-nitrophenyl octyl ether (NPOE) were obtained from Fluka. Tributyl phosphate (TBP), dichloromethane, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, acetic acid, NaOH, ammonium, triethanolamine, NH_4SCN and Alamine 336 were of analytical grade (Merck) and all the stock solutions were prepared by dissolving the salts in distilled water.

2.2 Preparation of PIMs

PIMs were prepared in accordance with the casting solution. CTA (480 mg) was dissolved in 70 mL of dichloromethane at room temperature. In the following step 0.1–0.5 mL of 2-NPPE was added into the solution. After stirring, the carrier (Alamine 336 and TBP) was added and the solution was stirred for 6 h to obtain a homogenous solution. The solvent of this mixed solution was allowed to slowly evaporate in a square glass container (24 cm × 24 cm). The organic solvent was allowed to evaporate overnight at room temperature. After the evaporation of the solvent, a few drops of cold and distilled water swirled on the top of the polymer film. Afterwards, the membrane was peeled out of the container. The average thickness of the membrane was determined as 25 μm with a digital micrometer (Salu Tron Combi-D3).

2.3 PIM transport experiment

The prepared polymeric film was sandwiched between two glass cells. The transport of metal ions across the PIM from the aqueous solutions was studied by using a two-compartment permeation cell made from Pyrex glass, having flat-sheet membranes with the 12.56 cm^2 area (A), as shown schematically in **Figure 1**.

The volumes of both the aqueous feed and the strip phases were 250 mL. The feed solutions were prepared by adding cobalt, nickel, cadmium and copper salts to study the effect of the feed composition. Ammonium thiocyanate (NH_4SCN) was added into the feed mixture to increase the selectivity of cobalt against nickel. 1 M acetic acid/1 M sodium acetate buffer was used to maintain the desired feed pH. A stripping solution containing

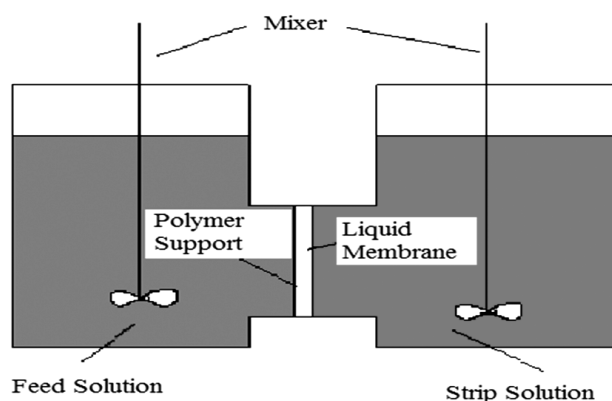


Figure 1: Schematic diagram of the experimental apparatus
Slika 1: Shema naprave za preizkuse

1 M NH_3 + 1 M TEA was selected as the stripping-phase mixture. The feed and stripping phases were mechanically stirred at the desired mixing speed of (20 ± 1) °C to avoid the concentration polarization conditions at the membrane interfaces and in the bulk of the solutions. During the PIM-transport experiments, the samples of the feed and strip phases (about 1 mL) were periodically removed for a determination of the metal concentration with ICP-OES.

3 RESULTS AND DISCUSSION

3.1 Plasticizer type and concentration

The nature of the plasticizer used to form the membrane is also a key parameter to consider. Plasticizers are organic compounds incorporating a hydrophobic alkyl backbone and one or several highly solvating polar groups. They are added to hard, stiff plastics to make them softer and more flexible. The softening action of the plasticizers, plasticization, is usually attributed to their ability to reduce the intermolecular attractive forces between the polymer chains. For this reason, it is anticipated that in PIMs the presence of these compounds may also influence the mobility of membrane components, the degree of interaction between different constituents of the membrane and the characteristics of the polymeric medium⁷. A low plasticizer concentration may cause more rigid and brittle membranes. So, it is not preferred⁴. The minimum plasticizer concentration varies widely depending on both the plasticizer and the base polymer. The influence of the plasticizer nature on the Cd^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} transport through PIMs with different plasticizers, i.e., 2-Nitrophenyl octyl ether (NPOE) and 2-nitrophenyl pentyl ether (NPPE) was tested. Copper was precipitated in the feed phase. Nickel was not transferred to the stripping solution. The cobalt and cadmium ions in the acidic feed solutions reacted with the excess NH_4SCN , whereas in the case of nickel ions, they hardly formed a thiocyanate complex^{12,13}.

The results obtained for the Cd^{2+} and Co^{2+} ion transport with different concentrations of the plasticizers

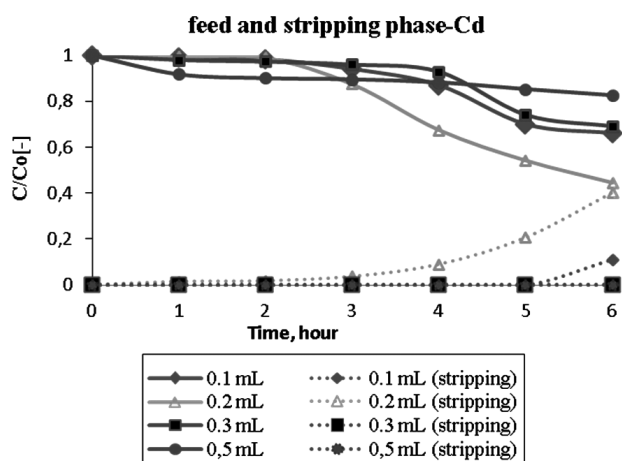


Figure 2: Effect of the NPPE concentration on the cadmium extraction (feed phase: 100 mg/L Co^{2+} , 100 mg/L Ni^{2+} , 100 mg/L Cd^{2+} , 100 mg/L Cu^{2+} ; feed stirring speed: 1200 r/min; strip-phase stirring speed: 1200 r/min; strip solution: 1 M NH_3 + 1 M TEA; complex reagent (NH_4SCN): 0.5 mol/l; temp.: 20 °C; feed solution pH: 4)

Slika 2: Vpliv koncentracije NPPE na ekstrakcijo kadmija (iz raztopine: 100 mg/L Co^{2+} , 100 mg/L Ni^{2+} , 100 mg/L Cd^{2+} , 100 mg/L Cu^{2+} ; hitrost mešanja raztopine: 1200 r/min; hitrost mešanja v fazi traku: 1200 r/min; raztopina traku: 1 M NH_3 + 1 M TEA; kompleksni reagent (NH_4SCN): 0.5 mol/l; Temp.: 20 °C; raztopina pH: 4)

in the PIMs are shown in **Figures 2 and 3**. For NPPE, this concentration can be in the range of up to 0.2 mL ($w = 27\%$) (**Figure 2**). Above this upper limit the mass transport diminishes.

The results obtained for the Cd^{2+} and Co^{2+} ion transport with different types of plasticizers in the PIMs are shown in **Figures 4 and 5**. 2-Nitrophenyl pentyl ether (NPPE) is the most frequently used plasticizer in PIMs due to its high dielectric constant that enhances the

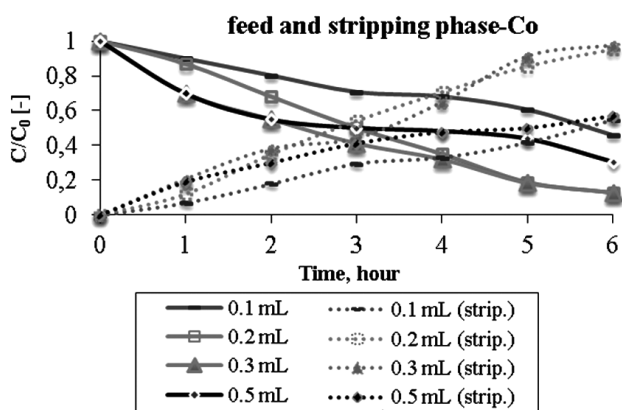


Figure 3: Effect of the NPPE concentration on the cobalt extraction (feed phase: 100 mg/L Co^{2+} , 100 mg/L Ni^{2+} , 100 mg/L Cd^{2+} , 100 mg/L Cu^{2+} ; feed stirring speed: 1200 r/min; strip-phase stirring speed: 1200 r/min; strip solution: 1 M NH_3 + 1 M TEA; complex reagent (NH_4SCN): 0.5 mol/l; temp.: 20 °C; feed solution pH: 4)

Slika 3: Vpliv koncentracije NPPE na ekstrakcijo kobalta (raztopina: 100 mg/L Co^{2+} , 100 mg/L Ni^{2+} , 100 mg/L Cd^{2+} , 100 mg/L Cu^{2+} ; hitrost mešanja raztopine: 1200 r/min; hitrost mešanja v fazi traku: 1200 r/min; raztopina traku: 1 M NH_3 + 1 M TEA; kompleksni reagent (NH_4SCN): 0.5 mol/l; temp.: 20 °C; raztopina pH: 4)

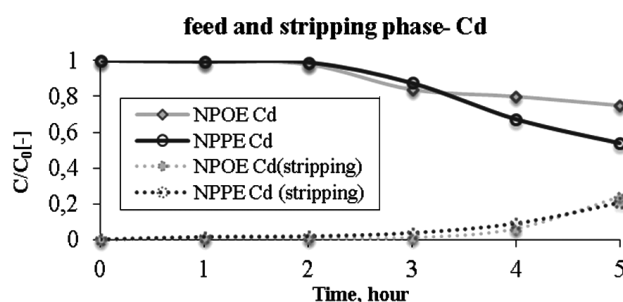


Figure 4: Effect of the plasticizer type on the cadmium transport (feed phase: 100 mg/L Co^{2+} , 100 mg/L Ni^{2+} , 100 mg/L Cd^{2+} , 100 mg/L Cu^{2+} ; feed stirring speed: 1200 r/min; strip-phase stirring speed: 1200 r/min; strip solution: 1 M NH_3 + 1 M TEA; complex reagent (NH_4SCN): 0.5 mol/l; temp.: 20 °C; feed solution pH: 4)

Slika 4: Vpliv vrste mehčalca na prenos kadmija (raztopina: 100 mg/L Co^{2+} , 100 mg/L Ni^{2+} , 100 mg/L Cd^{2+} , 100 mg/L Cu^{2+} ; hitrost mešanja raztopine: 1200 r/min; hitrost mešanja v fazi traku: 1200 r/min; raztopina traku: 1 M NH_3 + 1 M TEA; kompleksni reagent (NH_4SCN): 0.5 mol/l; Temp.: 20 °C; raztopina pH: 4)

membrane permeability. A decrease in the permeability, together with an increase in the plasticizer content, is probably related to a reduction in the viscosity of the medium⁴.

The recovery factor (RF) of the metal ions from the feed phase into the stripping phase is given by:

$$RF = \frac{C_1 - C}{C_1} \cdot 100\% \quad (1)$$

where C is the metal-ion concentration in the feed phase at some given time and C_1 is the initial metal-ion concentration in the feed phase. Recovery factors (RF) for different plasticizers are shown in **Table 1**.

Table 1: Effect of the plasticizer type on the cobalt and cadmium transport

Tabela 1: Vpliv vrste mehčalca na prenos kobalta in kadmija

Plasticizer type	RF (Co)	RF (Cd)
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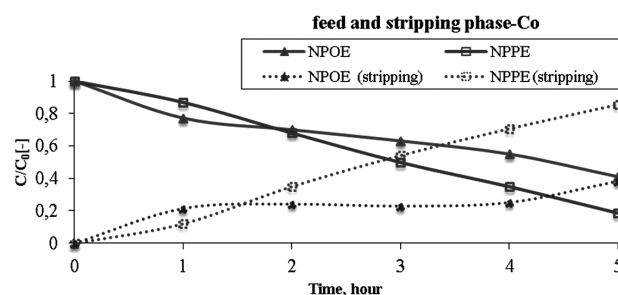


Figure 5: Effect of the plasticizer type on the cobalt transport (feed phase: 100 mg/L Co^{2+} , 100 mg/L Ni^{2+} , 100 mg/L Cd^{2+} , 100 mg/L Cu^{2+} ; feed stirring speed: 1200 r/min; strip-phase stirring speed: 1200 r/min; strip solution: 1 M NH_3 + 1 M TEA; complex reagent (NH_4SCN): 0.5 mol/l; temp.: 20 °C; feed solution pH: 4)

Slika 5: Vpliv vrste mehčalca na prenos kobalta (raztopina: 100 mg/L Co^{2+} , 100 mg/L Ni^{2+} , 100 mg/L Cd^{2+} , 100 mg/L Cu^{2+} ; hitrost mešanja raztopine: 1200 r/min; hitrost mešanja v fazi traku: 1200 r/min; raztopina traku: 1 M NH_3 + 1 M TEA; kompleksni reagent (NH_4SCN): 0.5 mol/l; temp.: 20 °C; raztopina pH: 4)

NPOE	59	25
NPPE	81	46

3.2 Effect of the stripping-solution type

In general, metallic ions extracted by amines can be stripped from the protonated amine with the removal of a proton using neutral or alkaline solutions. 1 M ammonia and 1 M triethanol amine solution mixtures were used as the reagents to strip and separate the cobalt and cadmium from the membrane phase to the aqueous phase.

3.3 Membrane characteristics

One important aspect of PIMs is the microstructure of the membrane materials, which determines the distribution of the carriers in the polymer matrix and ultimately affects the membrane transport efficiency. Consequently, a considerable research effort was devoted to clarifying this issue. While a variety of surface-characterization techniques were employed in these studies, scanning electron microscopy (SEM) and atomic force microscopy (AFM) were most frequently used. The results obtained from the SEM and AFM studies consistently indicate a remarkable influence of the polymeric composition on the membrane morphology.

The membrane was characterized to obtain information regarding its composition using AFM (**Figure 6**), SEM (**Figure 7**) and FT-IR (**Figure 8**).

The AFM technique was used to characterize the surface morphology of the prepared membranes. The AFM picture of the PIM formed with CTA + NPPE + TBP +

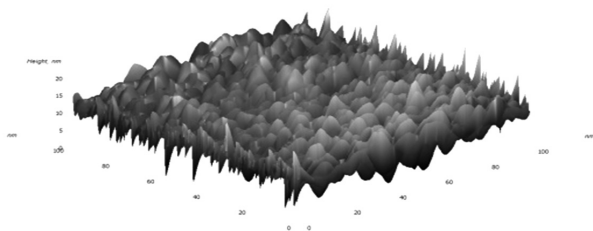


Figure 6: CTA + NPPE + Alamine 336 + TBP, AFM image
Slika 6: AFM-posnetek CTA + NPPE + Alamin 336 + TBP

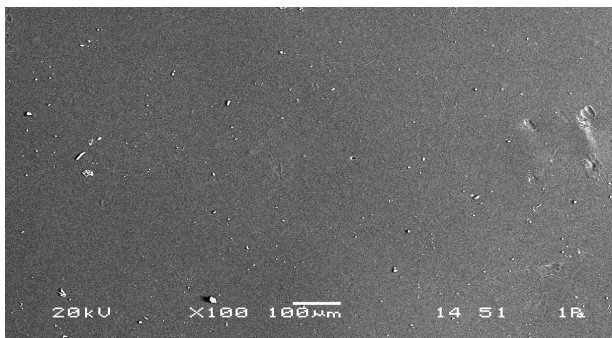


Figure 7: CTA + NPPE + Alamine 336 + TBP, SEM image
Slika 7: SEM-posnetek CTA + NPPE + Alamin 336 + TBP

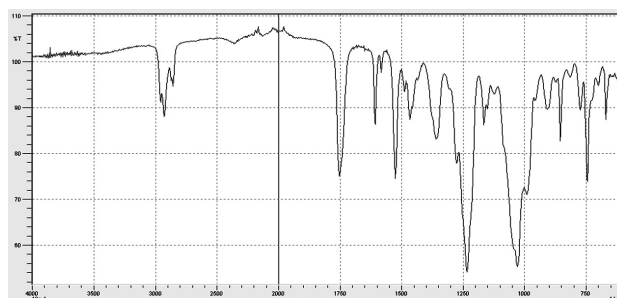


Figure 8: CTA + NPPE + Alamine 336 + TBP, FT-IR
Slika 8: FT-IR-posnetek CTA + NPPE + Alamin 336 + TBP

Alamine 336 is shown in **Figure 6**. The surface morphology of the membrane shows a rough surface. These regions may have occurred because of either a different speed of the solvent vaporization^{14, 15} or the membrane having a porous structure where the pores were filled by NPPE or NPPE + Alamine 336 + TBP^{16,17}.

Although both SEM and AFM techniques are versatile and can provide a good image of the membrane surface and, to some degree, of the membrane interior structure, to date, the studies employing these techniques have not been able to clearly elucidate the distribution of the carrier and the plasticizer within the membrane. Consequently, more advanced material-characterization techniques have been attempted.⁴

In order to investigate the absorption bands of the constituents of the membranes containing CTA + NPPE + Alamine 336 + TBP, FTIR was performed as shown in **Figure 8**. The bands at 2986 cm⁻¹ and 2936 cm⁻¹ were attributed to the stretching vibration of C-H in -CH₂ and -CH₃. The absorption at 1750 cm⁻¹ was assigned to the stretching vibration of C=O in CTA.

The fingerprint region of the spectra becomes complicated because of the P-O, C-O and C-N vibrations. These three vibrations are absorbed in the same region. For example, the peaks in the 1250 cm⁻¹ and 1100 cm⁻¹ region appear in both CTA and TBP and they overlap completely. The expected peaks in the spectra appear in almost the same region as in the case of pure components like CTA, Alamine 336 and TBP. This indicates that these four compounds do not form any new covalent interactions, but only secondary interactions like hydrogen bonding or electrostatic interactions¹⁸.

Consequently, the analysis and comparison of the obtained spectra revealed that all the membrane constituents remained as pure components inside the membrane^{17,18}. The surface of the films shows a good uniformity and the absence of cracks indicates a good regularity of the membranes as shown in **Figure 7**.

3.4 Membrane thickness

The investigated membrane thickness was 20 µm to 45 µm, shown in **Figures 9** and **10**. The best recovery factor (*RF*) was obtained with a thickness of 25 µm, with 81 % in the feed phase over 5 h as shown in **Table 2**. The

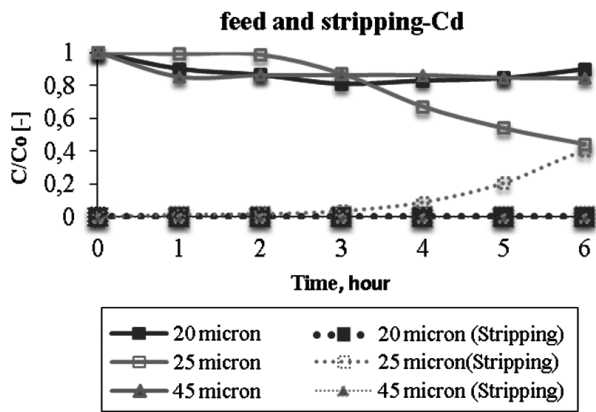


Figure 9: Effect of the membrane thickness on the cadmium transport (feed phase: 100 mg/L Co²⁺, 100 mg/L Ni²⁺, 100 mg/L Cd²⁺, 100 mg/L Cu²⁺; feed stirring speed: 1200 r/min; strip-phase stirring speed: 1200 r/min; strip solution: 1 M NH₃ + 1 M TEA; complex reagent (NH₄SCN): 0.5 mol/l; temp.: 20 °C; feed-solution pH: 4)

Slika 9: Vpliv debeline membrane na prenos kadmija (raztopina: 100 mg/L Co²⁺, 100 mg/L Ni²⁺, 100 mg/L Cd²⁺, 100 mg/L Cu²⁺; hitrost mešanja raztopine: 1200 r/min; hitrost mešanja v fazi traku: 1200 r/min; raztopina traku: 1 M NH₃ + 1 M TEA; kompleksni reagent (NH₄SCN): 0.5 mol/l; temp.: 20 °C; raztopina pH: 4)

Table 2: Effect of the membrane thickness on the cobalt and cadmium transport

Tabela 2: Vpliv debeline membrane na prenos kobalta in kadmija

Membrane thickness (µm)	RF (Co)	RF (Cd)
20	39	15
25	81	46
45	54	15

optimum membrane thickness was 25 µm. As the membrane thickness increased, the extraction would decrease.

As shown in¹⁹ thinner membranes exhibiting high permeability are formed. However, the thinnest membranes only partly allow high permeability due to a decrease in the extractant content limiting the transport efficiency.

As shown in reference²⁰ the flux decreased linearly with the membrane thickness. This is unambiguous evidence that the slow step in the transport process represents the migration through the membrane and not a decomplexation from the carrier.

4 CONCLUSIONS

With the use of Alamine 336 and TBP as the carriers, the competitive transport of metal ions shows the preferential selectivity order: Co (II) > Cd (II). The transport facilitated through the polymer inclusion membranes containing Alamine 336 and TBP was found to be an effective method for separation and recovery of cobalt (II) and cadmium (II) from aqueous solutions. Copper was precipitated in the feed phase. Nickel was not transferred to the stripping solution. The recovery factor for the cobalt ions was over 87 % over a period 6 h.

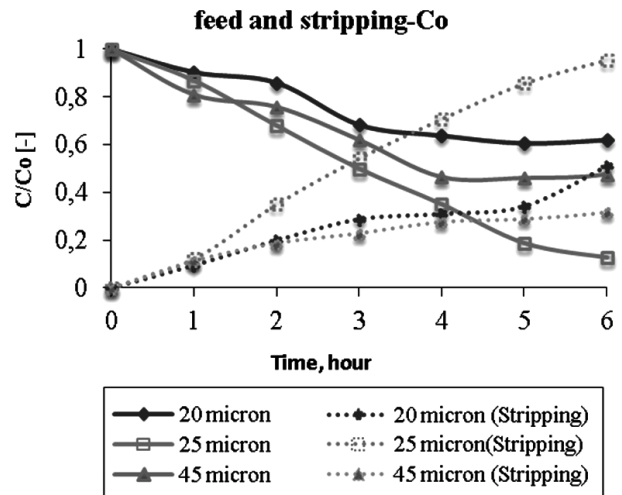


Figure 10: Effect of the membrane thickness on the cobalt transport (feed phase: 100 mg/L Co²⁺, 100 mg/L Ni²⁺, 100 mg/L Cd²⁺, 100 mg/L Cu²⁺; feed stirring speed: 1 200 r/min; strip-phase stirring speed: 1200 r/min; strip solution: 1 M NH₃ + 1 M TEA; complex reagent (NH₄SCN): 0.5 mol/l; temp.: 20 °C; feed solution pH: 4)

Slika 10: Vpliv debeline membrane na prenos kobalta (raztopina: 100 mg/L Co²⁺, 100 mg/L Ni²⁺, 100 mg/L Cd²⁺, 100 mg/L Cu²⁺; hitrost mešanja raztopine: 1 200 r/min; hitrost mešanja v fazi traku: 1 200 r/min; raztopina traku: 1 M NH₃ + 1 M TEA; kompleksni reagent (NH₄SCN): 0.5 mol/l; temp.: 20 °C; raztopina pH: 4)

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