



The comparison of the removal of copper(II) and zinc(II) ions from aqueous solution using 2,6-diaminopyridine in a polymer inclusion membrane and in a classic solvent extraction

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ABSTRACT

In this work, the recovery of copper(II) and zinc(II) ions from aqueous solutions using solvent extraction and polymer inclusion membranes (PIMs) was compared. 2,6-Diaminopyridine was used as an extractant in solvent extraction and as a carrier in PIMs. The characteristic parameters of these two processes were determined. The results of all the experiments were processed and, additionally, standard deviations were calculated. The percentage of extraction was dependent on the ligand concentration in the organic phase. For solvent extraction, the highest extraction percentage was 83.53% for copper(II) ions and 93.12% for zinc(II) ions. In the case of application of the PIM containing 20 wt.% of 2,6-diaminopyridine as a carrier, the highest recovery factor determined after 24 h was 72.81% for copper(II) ions and 93.65% for zinc(II) ions, respectively. The stability constants of its complexes of 2,6-diaminopyridine with copper(II) and zinc(II) ions were determined spectrophotometrically. Electrospray ionization high-resolution mass spectrometry was applied for the confirmation of the ability of 2,6-diaminopyridine to form complexes with Cu(II) and Zn(II) ions in solutions and for determination of the elemental composition of these complexes.

Keywords: 2,6-diaminopyridine; Copper(II) ions; Zinc(II) ions; Solvent extraction; Polymer inclusion membrane; Mass spectrometry

1. Introduction

2,6-Diaminopyridine is a well-known compound, widely used in the chemical industry, that is, in the production of medicinal products, cosmetics and polyamides [1]. Norris Shreve et al. [2] used 2,6-diaminopyridine for the synthesis of azo dyes (a bacteriostatic indicator of the bacterial species of *E. coli* and *Staphylococcus aureus*). Nowadays, research related to the new applicability of 2,6-diaminopyridine and its derivatives in medicine and pharmacology continues to be done. One of the examples is that the complexation properties of these compounds are used to remove toxic metal ions, such as cadmium(II)

and zinc(II) from organisms [3,4]. Because 2,6-diaminopyridine belongs to a group of compounds that are electron donors or proton acceptors [5], it can easily form complex compounds with metal ions. It has also been shown that the method of conducting coordination processes of metal ions with a 2,6-diaminopyridine can have an impact on the properties of the obtained complexes. Singh et al. [6] found that 2,6-diaminopyridine form macromolecular complexes with isatin and transition metal ions (Co(II), Ni(II), Cu(II), Cd(II)) as a result of condensation reactions. Such complexes are biologically active. 2,6-Diaminopyridine was used for the formation of type 1:1 bi- and tetranuclear cobalt(II) complexes during a reaction with polymer complexes [Co(OH)_n

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(OCCMe₃)_{2-n}]_x [7]. Asali et al. [8] reported that in the bimetallic complexes of μ -2,6-diaminopyridine [M(CO₃)₂] with chromium, molybdenum, and vanadium, metal ions were coordinated by amine groups, but not pyridine nitrogen. Rana et al. [9] have also proved that pyridine nitrogen did not participate in the formation reactions of macrocyclic complexes (2,6-diaminopyridine and acetylacetone) with trivalent metal ions. Instead, both deprotonated amine groups of 2,6-diaminopyridine were involved in the coordination of metal ions. İlhan et al. [10,11] used the complexation properties of 2,6-diaminopyridine for the synthesis of new macrocyclic Schiff bases, which are able to form complexes with metal ions such as Cu(II), Ni(II), Pb(II), Co(II) and La(III). Moreover, the 2,6-diaminopyridine has also been used for the synthesis of polymeric macrocyclic urea during the reaction with a meta-substituted aromatic amine. Böhme et al. [12] have synthesized a macrocyclic structure by the condensation of three structurally similar monomers, 1,3-phenylenediamine, and 2,6-diaminopyridine with N,N-carbonyldiimidazole. In this reaction, crown ethers were formed. They are commonly used as carriers in polymer inclusion membranes (PIMs) for the recovery of metal ions. Zhai et al. [13] modified silica-coated Fe₃O₄ nanoparticles with 2,6-diaminopyridine and used them for the selective extraction of magnetic trace amounts of copper(II) and zinc(II) in the solid phase. They found that the adsorbent can be used repeatedly and the method is cheap, fast, and environmentally friendly. 2,6-Diaminopyridine has also been used as a polymeric ion exchanger for precious metal ions recovery, for example, for gold(III) [14].

Despite many diverse applications, 2,6-diaminopyridine has not been used as a carrier in PIMs to date. In this paper, the complexation properties of 2,6-diaminopyridine were used for the recovery of copper(II) and zinc(II) ions from aqueous solutions. The classic solvent extraction and polymer inclusion membrane processes were performed, using 2,6-diaminopyridine as an extractant and a metal ions carrier, respectively. The characteristic parameters for both processes were calculated and compared.

2. Materials and methods

2.1. Reagents

All the reagents used in this work were of analytical grade purity and were used without further purification. The 2,6-diaminopyridine (shown in Fig. 1) was purchased from Sigma-Aldrich (Poznań, Poland), other compounds used in experiments, such as copper(II) nitrate, zinc(II) nitrate, nitric acid, ammonia, potassium hydroxide, chloroform and methanol have been bought from Avantor (Gliwice, Poland).

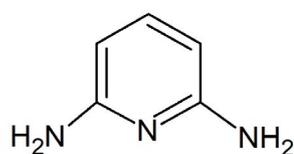


Fig. 1. The structure of 2,6-diaminopyridine.

We found in the literature that the dissociation constant of 2,6-diaminopyridine is 7.87 [15].

The concentration of the potassium nitrate solution was determined gravimetrically as potassium sulfate, whereas the concentration of the aqueous copper(II) or zinc(II) ions solutions by the atomic absorption spectrometry method. The nitric acid was standardized against anhydrous sodium carbonate. Carbonate free potassium hydroxide was prepared and standardized against a standard potassium hydrogen phthalate solution.

The pH-meter utilized in performed experiments was calibrated using commercial technical buffer solutions (Mettler Toledo, Greifensee, Switzerland) having a pH of 2.00, 4.01, 7.00, and 10.00.

2.2. Determination of the stability constant

To calculate the stability constant of the complexes of metal ions ($M = \text{Cu(II)}, \text{Zn(II)}$) with 2,6-diaminopyridine [L] it was necessary to record their absorption spectra. For this purpose, a stock aqueous solutions of copper(II) or zinc(II) ions with a concentration of 0.0012 mol/dm³ and a solution of ligand L in methanol (2.65×10^{-5} mol/dm³) were made. Then the appropriate amounts of metal ions solution and methanol solution of the 2,6-diaminopyridine were mixed to prepare samples for spectrophotometric analysis. The absorption spectra of the prepared samples were recorded on Cary 50 spectrophotometer (Varian, Melbourne, Victoria, Australia) at various $L:\text{Cu(II)}$ and $L:\text{Zn(II)}$ molar ratios, ranging from 1:0 to 1:1. The spectra were recorded in the range of the wavelength from 200 to 450 nm.

2.3. Extraction procedure

We conducted separation of copper(II) and zinc(II) ions by solvent extraction. All experiments were performed at $25^\circ\text{C} \pm 0.2^\circ\text{C}$. The aqueous phase contained 0.1 mol/dm³ of Cu(II) or Zn(II) ions, respectively and 0.2 mol/dm³ NH_{3(aq)} (pH \sim 7.8 for copper(II) ions and pH \sim 7.32 for zinc(II) ions). The organic solution contained 2,6-diaminopyridine (L) dissolved in chloroform. The chloroform solution of ligand was added to the same volume of an aqueous solution. The volume of both phases (aqueous phase and organic phase) was 4.5 cm³. The concentration of metal ions [M] ($M = \text{Cu(II)}$ or Zn(II)) in aqueous phases was constant, but the concentration of the ligand was varied in the range from 0.025 and 0.1 mol/dm³ (samples I–IV). The prepared samples were then shaken for 1 h. The equilibrium was established after approximately 15 min by the visual observation. It was checked if any changes in the phase volumes had occurred, then the phases were separated and the pH of the aqueous phase was measured. The metal ions concentration in the aqueous phases was determined by atomic absorption spectrophotometry (AAS 240FS Spectrometer, Agilent, Santa Clara, CA, USA).

2.4. Polymer inclusion membrane

2.4.1. Preparation of polymer inclusion membrane

A solution of 60 wt.% polyvinylchloride as a support, and 20 wt.% a bis(2-ethylhexyl) adipate as a plasticizer, and

20 wt.% a 2,6-diaminopyridine as an ion carrier in 10 cm³ tetrahydrofuran was prepared. The membrane was made by pouring the received solution on a glass ring. After slow evaporation of the solvent overnight, the resulting PIM was peeled off from the glass plate. Next, the PIM was immersed for 12 h in distilled water. Two samples of the PIMs were cut out from the same membrane film for duplicate transport experiments. The PIMs contained 20 wt.% of 2,6-diaminopyridine as a carrier. The membranes were homogeneous, transparent, flexible, and had good strength. The mean thickness of membranes was determined in the same way, as we described previously [16]. The average thickness of the membranes, which were used for copper(II) and zinc(II) ions transport, was 0.227 ± 0.020 mm and 0.238 ± 0.020 mm, respectively. The PIMs prepared this way were used for the removal of copper(II) and zinc(II) ions from aqueous solutions.

2.4.2. Transport studies

Transport of both metal ions was conducted in a permeation module cell in which the membrane film (having the active surface area of 2.2 cm²) was tightly clamped between two cell compartments. The feed and receiving aqueous phases (45 cm³ each) were mechanically stirred at 800 rpm. The feed phase contained a 0.1 mol/dm³ solution of copper(II) or zinc(II) ions, respectively. The pH of the feed phase was kept constant (approx. 7) using ammonia solution and controlled by pH-meter (pH meter, CX-731 Elmetron, Poland), with a combination pH electrode (ERH-126, Hydromet, Poland). The 0.005 mol/dm³ HNO₃ was used as a receiving phase. The PIMs transport experiments were carried out at $25^\circ\text{C} \pm 0.2^\circ\text{C}$. The samples of the aqueous feed and receiving phases were taken periodically and analyzed by atomic absorption spectroscopy (AAS Spectrometer, Solaar 939, Unicam) to determine the metals ions concentration.

2.4.3. Mass spectrometry

The electrospray ionization high-resolution mass spectrometry (ESI-HRMS) experiments were performed using a Q-Exactive Orbitrap mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) equipped with TriVersa Nano-Mate ESI ion source (Advion BioSciences Ltd., Ithaca, NY, USA). Samples of the separated organic phases obtained after liquid–liquid extraction described in detail above (samples IV, equal concentrations of metal ions and the ligand) were diluted (1:1) in methanol (Avantor, Gliwice, Poland). HRMS data were acquired in a positive ion mode within the *m/z* range of 50–750 at the resolution of 140,000 (*m/z* 200). Thermo Xcalibur software (ver. 4.1.31.9) was used to process obtained mass spectra.

3. Results and discussion

3.1. Determination of the stability constant

The UV spectra of the complexes of copper(II) and zinc(II) ions with 2,6-diaminopyridine are shown in Fig. 2. The obtained absorption spectra are characterized

by absorption bands in the UV region wavelengths ranging from 200 to 400 nm.

Fig. 2 shows that Cu/2,6-diaminopyridine and Zn/2,6-diaminopyridine complexes are formed in the studied systems. The isobesthetic points at 320 nm for copper(II) ions and at 315 nm for zinc(II) ions were recorded.

The stability constants were determined using an equation based on the method developed by Lis et al. [17]. The stability constants ($\log K$) were calculated using the equation:

$$\frac{1}{(\varepsilon - \varepsilon_L)} = \frac{1}{K(\varepsilon_c - \varepsilon_L)} \cdot \frac{1}{[C_{[M]}]} + \frac{1}{(\varepsilon_c - \varepsilon_L)} \quad (1)$$

where $[C_{[M]}]$ is the molar concentration of metal ions (mol/dm³), $\varepsilon = A/[L]$, A is the absorbance of the system at 336 nm ($\lambda = 1$ cm), $[L]$ is the molar concentration of the ligand (2,6-diaminopyridine), ε_L is the molar absorption coefficient of the ligand at $\lambda = 307$ (dm³/mol cm³), ε_c is the molar absorption coefficient of the complex at $\lambda = 336$ and 337 nm for Cu(II) and Zn(II) (dm³/mol cm³), respectively, K is the stability constant of the obtained complex.

The values of the stability constants ($\log K$) of Cu(II)/2,6-diaminopyridine and Zn/2,6-diaminopyridine complexes were determined based on Fig. 2. In the calculations, the 1:1 molar ratios of the complexes L : metal ions were taken. The $\log K$ was equal to 5.70 ± 0.01 and 5.93 ± 0.01 , in case of Cu(II) and Zn(II) complexes, respectively.

3.2. Solvent extraction

Based on the results of earlier studies [8,9] and ESI-HRMS experiments described later in this work it can be assumed that one of the most likely coordination structures of metal ions with 2,6-diaminopyridine molecules formed during the solvent extraction process is this, in which the metal ions to ligand ratio is 1:2 (as shown in Fig. 3). However, the results of the stability constants experiments show, that other complexes may be also formed in solution, in which the ratio of metal ions to ligand molecules is different, for example, 3:1 for L :Cu(II) and 5:1 for L :Zn(II).

One of the main parameters describing the solvent extraction is the extraction percentage ($\%E_M$) of the metal ions (Eq. (1)):

$$\%E_M = \frac{D_M}{D_M + \frac{V_{\text{aq}}}{V_{\text{org}}}} \cdot 100 \quad (2)$$

where D_M is the division ratio determined experimentally, V_{aq} is the volume of the water phase (dm³), V_{org} is the volume of the organic phase (dm³) ($V_{\text{aq}} = V_{\text{org}}$, so $V_{\text{aq}}/V_{\text{org}} = 1$).

The division ratio is the ratio of the sum of the concentrations of all the substances in the organic phase ($\Sigma[M]_{\text{org}}$) to the sum of the concentrations of all the substances in the water phase ($\Sigma[M]_{\text{aq}}$).

$$D_M = \frac{\Sigma[M]_{\text{org}}}{\Sigma[M]_{\text{aq}}} \quad (3)$$

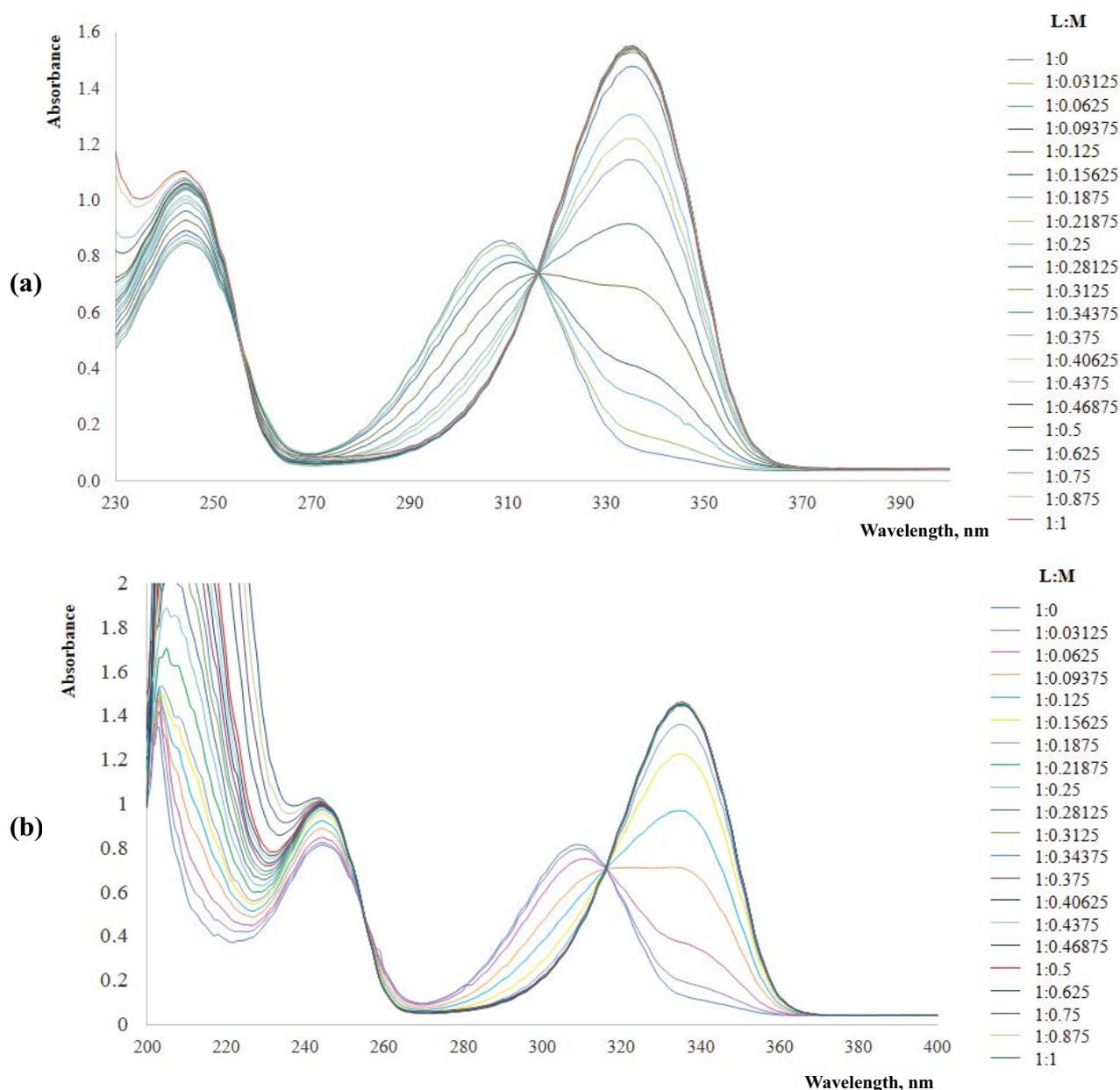


Fig. 2. The UV spectra of the complexes of copper(II) ions (a) and zinc(II) ions (b) with 2,6-diaminopyridine in various [L]:[M] molar ratios (from 1:0 to 1:1).

Obtained results were elaborated using a spreadsheet and standard deviation.

In the case where there were no phase changes in the volume after extraction, it was possible to appoint a division ratio of metals ions ($D_{\text{Cu(II)}}$ and $D_{\text{Zn(II)}}$) using Eq. (3). The division ratios of metals ions were from 0.57 to 5.07 for copper(II) and from 1.69 to 4.92 for zinc(II), depending on the ligand concentration. This allowed the authors to calculate the percentage of extraction using Eq. (2). Table 1 shows the dependence between the division ratio of metal ions ($D_{\text{Cu(II)}}$ and $D_{\text{Zn(II)}}$) and the percentage of copper(II) and zinc(II) ions extraction, and the ligand concentration in the organic phase.

The solvent extraction was performed to recovery copper(II) and zinc(II) ions using a 2,6-diaminopyridine as an extractant. Values of both parameters D and $\%E_M$ increase with an increasing concentration of 2,6-diaminopyridine in the organic phase. A higher percent of extraction was obtained for zinc(II) ions in comparison to copper(II) ions. The best percentage of extraction (83.53 % for Cu(II) and 93.12% for Zn(II)) was obtained for L:M molar ratio of 1:1.

The results indicate a high ability of 2,6-diaminopyridine to separate copper(II) and zinc(II) ions by solvent extraction. Table 2 shows a comparison of the efficiency of commonly used commercial extractants of copper(II) and zinc(II) ions recovery by solvent extraction.

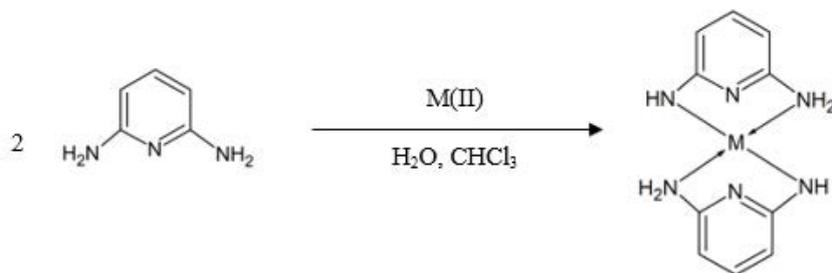


Fig. 3. Proposition of complex formation reaction by 2,6-diaminopyridine molecules with $M(\text{Cu}(\text{II})$ or $\text{Zn}(\text{II}))$ in examined solutions.

Table 1
The % of extraction of copper(II) and zinc(II) ions with 2,6-diaminopyridine as an extractant

Concentration of 2,6-diaminopyridine, (mol/dm ³)	pH	Division ratio, $D_{\text{Cu}(\text{II})}$	Extraction percentage, % $E_{\text{Cu}(\text{II})}$ (%)	pH	Division ratio, $D_{\text{Zn}(\text{II})}$	Extraction percentage, % $E_{\text{Zn}(\text{II})}$ (%)
0.025	7.70	0.57	36.32	7.26	1.69	61.84
0.05	7.77	0.73	42.25	7.71	2.02	67.00
0.075	7.92	1.66	62.45	7.08	2.04	67.13
0.1	7.82	5.07	83.53	7.26	4.92	93.12

The given values of the $D_{\text{Cu}(\text{II}),\text{Zn}(\text{II})}$ carry 0.25% tolerance and the % $E_{\text{Cu}(\text{II}),\text{Zn}(\text{II})}$ carry 0.2% tolerance.

Table 2
Comparison of extractants of copper(II) and zinc(II) ions by solvent extraction

Extractant	Highest extraction percentage		References
	Cu(II)	Zn(II)	
2,6-diaminopyridine	83.53%	93.12%	[This work]
di-(2-ethylhexyl)phosphoric acid	31.6%	88.7%	[18,24]
Mixture (1:1) of 5-dodecylsalicylaldoxime and 2-hydroxy-5-nonyl acetophenone oxime (LIX 984)	80%	90%	[19]
3-Allyl-acetylacetone	85%	–	[20]
Tri- <i>n</i> -octylamine (TOA)	46%	–	[21]
Bis(2,2,4-trimethylpentyl)phosphinic acid (Cyanex 272)	–	90%	[22]
Trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101)	–	97%	[23]

Application of 2,6-diaminopyridine as an extractant in the solvent extraction for removal of copper(II) and zinc(II) ions turned out to be a very yield. We obtained a high extraction percentage for copper(II) and zinc(II) ions. 2,6-Diaminopyridine is not more expensive than other commercial extractants used for metal ions removal in solvent extraction. In practice, a compound that can be used in a solvent extraction can also be used as a carrier in polymer inclusion membrane. All of the extractants listed in Table 2 are also used as carriers in PIMs. Therefore, in the next stage of the research work, 2,6-diaminopyridine was used in a polymer inclusion membrane for transporting the metal ions.

3.3. Transport across polymer inclusion membrane

The transport of copper(II) and zinc(II) ions across the PIMs was conducted for 24 h. Fig. 4 shows the membranes before and after transport of copper(II) and zinc(II) ions.

The transport across PIMs was described by the first-order transport rate equation kinetics in relation to the metal-ion concentration [25]:

$$\ln\left(\frac{C}{C_i}\right) = -k \cdot t \quad (4)$$

where C is the metal ions concentration in the feed phase at a given time (mol/dm³), C_i is the initial metal ions concentration in the feed phase (mol/dm³), k is the rate constants (s⁻¹), t is the time of transport (s).

The plot of $\ln(C/C_i)$ vs. time was prepared about the calculated k value. The rate constant value for the duplicate transport experiment was averaged and the standard deviation was calculated. Further parameters, for example, the permeability coefficient (P) was calculated [26] as follows:

$$P = \frac{V}{A} \cdot k \quad (5)$$

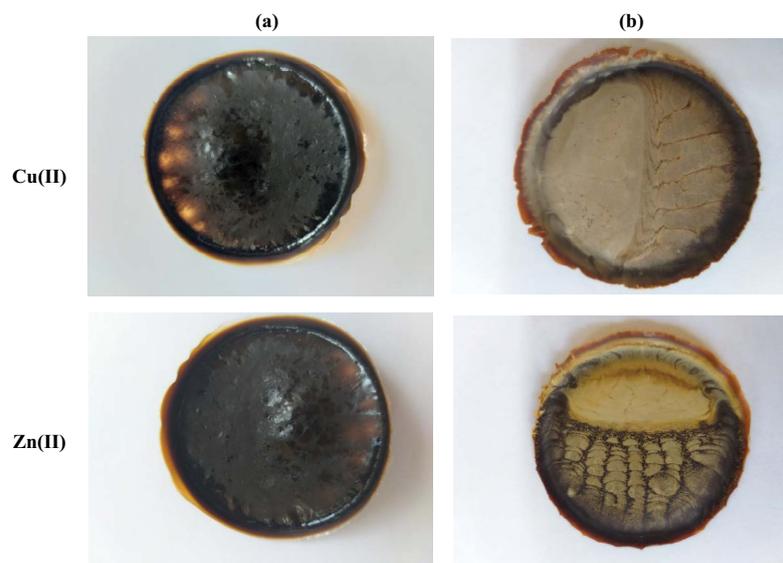


Fig. 4. PIM membranes containing 2,6-diaminopyridine as a carrier. Photographs made before transport of metal ions (a) and after transport of metal ions (b).

where V is the volume of the feed phase (dm^3) and A is the area of the effective membrane (m^2).

Therefore the initial flux (J_i) ($\text{mol}/\text{m}^2 \text{ s}$) was determined according to Eq. (6) [26]:

$$J_i = P_i \cdot C_i \quad (6)$$

The kinetics parameters of the metals(II) ions transport across PIMs from the feed phase are shown in Table 3. The initial fluxes (J_i) of all the investigated cations were decreased with the increase in over-time in the feed phase.

The transport of metal ions across the polymer inclusion membrane is based on diffusion caused by the chemical potential difference and the distribution of the substances between the membrane and the aqueous phase. During the transport processes, the metal ions are absorbed and transferred from the membrane surface to the ligand molecules inside the PIM. This process controls the rate of the sorption process [26]. The obtained results show, that increasing concentrations of Cu(II) and Zn(II) in the

membrane phases resulted in decreased concentrations of both metals ions in the aqueous solution (Fig. 5).

Parameters to quantify the amount of metal ions transported across the membrane at a given time are recovery factor (RF) [27] and accumulation factor (AF) [26], which are described as follows:

$$\text{RF} = \frac{C_0 - C}{C_0} \cdot 100\% \quad (7)$$

$$\text{AF} = \frac{C_{\text{membrane}}}{C_0} \cdot 100\% \quad (8)$$

where C_0 is the initial concentration of metal ions in the feed phase (mol/dm^3), C is the concentration of metal ions after time t in the feed phase (mol/dm^3), C_{membrane} is the concentration of metal ions in the membrane phase (mol/dm^3).

Calculated parameters (RF and AF) are presented in Table 4.

Table 3
Kinetics parameters of copper(II) and zinc(II) ions transport across PIM

Metal ions	Time (h)	Permeability coefficient, P ($\mu\text{m}/\text{s}$)	Initial flux, J_i ($\mu\text{mol}/\text{m}^2 \text{ s}$)	Metal ions	Time (h)	Permeability coefficient, P ($\mu\text{m}/\text{s}$)	Initial flux, J_i ($\mu\text{mol}/\text{m}^2 \text{ s}$)
Cu(II)	0.5	0.0192	2.54×10^{-4}	Zn(II)	0.5	0.1154	3.27×10^{-3}
	2	0.0070	9.37×10^{-5}		2	0.0246	6.98×10^{-4}
	4	0.0052	6.90×10^{-5}		4	0.0110	3.14×10^{-4}
	6	0.0046	6.05×10^{-5}		6	0.0047	1.32×10^{-4}
	8	0.0041	5.44×10^{-5}		8	0.0039	1.10×10^{-4}
	12	0.0032	4.33×10^{-5}		12	0.0010	2.99×10^{-5}
	24	0.0019	3.11×10^{-5}		24	0.0001	4.73×10^{-6}

The given values of the P carry ± 0.0001 and J_i carry $\pm 1.00 \times 10^{-6}$.

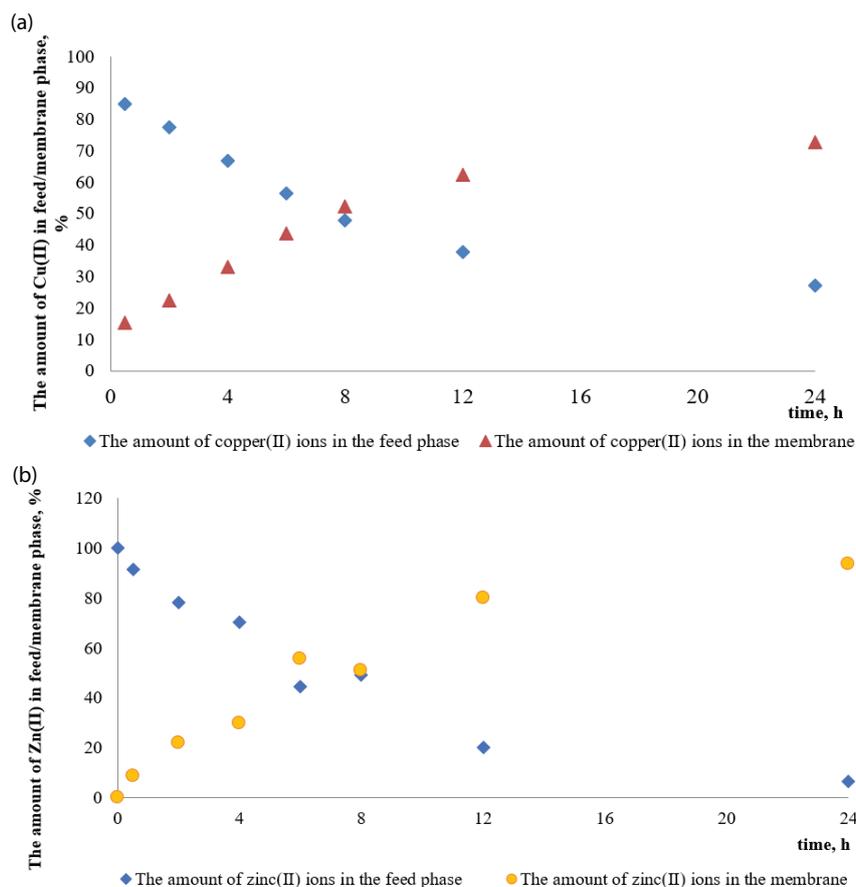


Fig. 5. Dependency graph of the amount of metal ions in the membrane phase and in the feed phase vs. time.

Table 4
Transport performance of the obtained membranes

Metal ions	Time (h)	Recovery factor, RF (%)	Accumulation factor, AF (%)	Metal ions	Time (h)	Recovery factor, RF (%)	Accumulation factor, AF (%)
Cu(II)	0.5	15.24	84.26	Zn(II)	0.5	8.53	90.16
	2	22.46	73.23		2	21.92	74.78
	4	33.10	66.5		4	29.77	68.13
	6	43.57	52.13		6	55.69	40.10
	8	52.26	43.43		8	50.73	45.97
	12	62.36	37.43		12	79.92	17.98
24	72.81	26.79	24	93.65	5.04		

The given values of the RF and AF carry $\pm 0.1\%$.

The recovery factor of metal ions transport across the polymer inclusion membrane with 2,6-diaminopyridine as a carrier was from 15.24% to 72.81% for copper(II) ions and from 8.53% to 93.65% for zinc(II) ions. The concentration of metal ions was tenfold excess than ligand concentration in the membrane. The removal of metal ions depends on the time of the transport of metal ions across the membrane. The highest recovery factor for copper(II) and zinc(II) ions was obtained after 24 h of transport across PIM, and it was 72.81% and 93.65%, respectively.

Obtained results clearly indicate, that, membranes containing 2,6-diaminopyridine as a carrier can be successfully used for the recovery of metal ions such as copper(II) and zinc(II) from aqueous solutions.

3.4. Characterization of 2,6-diaminopyridine complexes with Cu(II) and Zn(II) ions by ESI-HRMS

ESI-HRMS experiments were performed for the separated organic phases obtained after liquid–liquid extraction

of Cu^{2+} or Zn^{2+} from model solutions using 2,6-diaminopyridine L (the initial concentration of ligand L and metal ions was equal in each case). ESI-HRMS spectra of analyzed samples (shown in Figs. 6a and b) regardless of the type of metal ions present, show signals of similar intensity, corresponding to similar ions. Both spectra are dominated by signals, which can be assigned to singly charged ions of 2,6-diaminopyridine $[L + H]^+$ ($(\text{C}_5\text{H}_8\text{N}_3)^+$, $m/z_{\text{meas}} = 110.0716$, $m/z_{\text{calc}} = 110.0718$) and to ions of complexes formed by L molecules and/or its fragments, such as: $[\text{C}_5\text{H}_6\text{N}]^+$ ($m/z_{\text{meas}} = 80.0502$, $m/z_{\text{calc}} = 80.0500$), $[2L + H]^+$ ($(\text{C}_{10}\text{H}_{15}\text{N}_6)^+$, $m/z_{\text{meas}} = 219.1352$, $m/z_{\text{calc}} = 219.1358$), and $[\text{C}_{13}\text{H}_{14}\text{N}_8]^+$ ($m/z_{\text{meas}} = 282.1308$, $m/z_{\text{calc}} = 282.1341$). Formation of $[\text{C}_5\text{H}_6\text{N}]^+$ and $[\text{C}_{13}\text{H}_{14}\text{N}_8]^+$ ions was probably related to partial L molecules decomposition, for example during compound storage, in the solution or during the electrospray ionization process. Less intensive signals correspond to complexes formed by L molecules with metal ions, such as $[2L + \text{Cu}^{2+} - \text{H}]^+$ ($(\text{C}_{10}\text{H}_{13}\text{N}_6\text{Cu})^+$, $m/z_{\text{meas}} = 280.0492$, $m/z_{\text{calc}} = 280.0497$) and $[2L + \text{Zn}^{2+} - \text{H}]^+$ ($(\text{C}_{10}\text{H}_{13}\text{N}_6\text{Zn})^+$, $m/z_{\text{meas}} = 281.0572$, $m/z_{\text{calc}} = 281.0493$), respectively. It is worth emphasizing that the intensity of signals corresponding to

zinc and copper ions complexes is similar. This allows concluding that, the differences in the properties of Cu^{2+} and Zn^{2+} ions do not affect the type of complexes formed, and have no (or have very little) effect on the quantity of generated complex-ions. These findings are consistent with the liquid–liquid extraction results, where the percentage of extraction obtained for zinc and copper ions was similar (93.12% and 83.53%, respectively).

The high mass accuracy of the HRMS mass spectrometry causes that there can be no question as to the elemental composition or charge of generated complexes. The results of performed ESI-HRMS experiments clearly show that, in the analyzed solutions, 2,6-diaminopyridine forms with $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ ions complexes in which the $M:L$ ratio is 1:2 (one metal ion binds two ligand molecules). However, the solutions may also contain metals complexes with 2,6-diaminopyridine molecules of different composition, that cannot be identified by ESI-HRMS, which allows only ions analysis.

4. Conclusions

In this research work, we used a 2,6-diaminopyridine as an extractant for copper(II) and zinc(II) ions in classic solvent extraction and as a carrier in a PIMs. The results show that the highest extraction percentage in the solvent extraction for copper(II) and zinc(II) ions was 83.53% and 93.12%, respectively. The concentration of both metal ions was 0.1 mol/dm^3 , and the concentration of extractant was varied in the range from 0.025 to 0.1 mol/dm^3 .

The rate of separation of metal ions was significantly better in solvent extraction comparing to the transport of metal ions across the polymer inclusion membrane. The highest percent of extraction of metal ions was obtained after 15 min in solvent extraction while the highest recovery factor rate was achieved after 24 h. The results clearly indicate that both separation processes are very effective for the recovery of copper(II) and zinc(II) metal ions. It can also be concluded that 2,6-diaminopyridine is a better extractant in solvent extraction than transport of metal ions across PIMs. Despite obtaining in slightly worse recovery rates during transport across PIM we believe that method is better for the environment. The main parameters to the removal of copper(II) and zinc(II) ions using PIM containing 20% wt. of 2,6-diaminopyridine such as RF and AF have been determined.

The results of the performed experiments indicate that 2,6-diaminopyridine can be successfully used in both types of separation processes, that is, in the classic solvent extraction and in a relatively new technique based on the utilization of PIMs. In both cases, high copper(II) and zinc(II) ions recovery rates have been obtained. Moreover, the results of conducted ESI-HRMS experiments confirm the ability of 2,6-diaminopyridine to form complexes with Cu^{2+} and Zn^{2+} , ions in solution and provide information about the elemental composition of formed complexes.

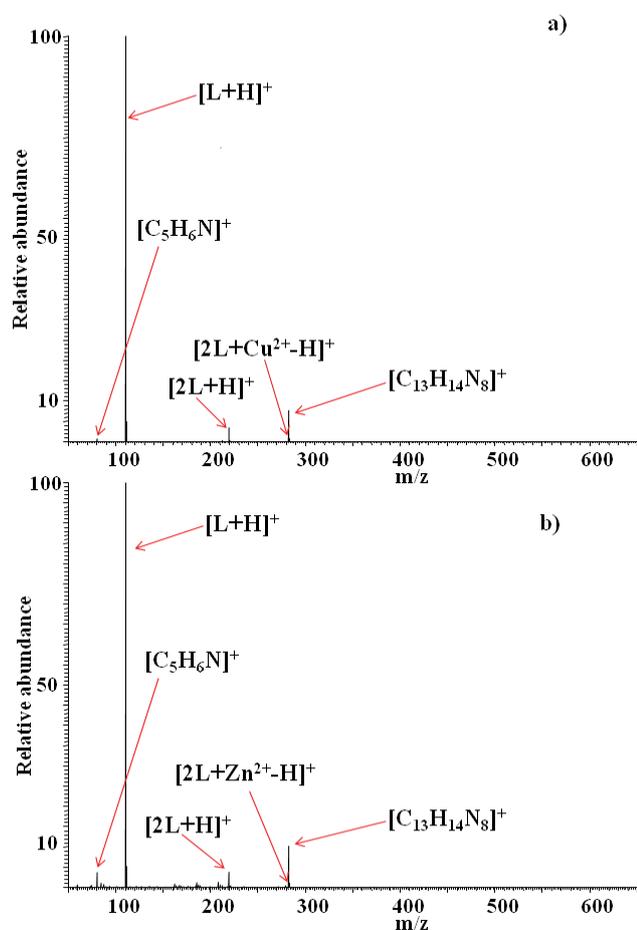


Fig. 6. ESI-HRMS spectra recorded for the samples of the separated organic phases after liquid–liquid extraction, containing 2,6-diaminopyridine (L) and metal ions (a) Cu^{2+} and (b) Zn^{2+} . Unassigned minor signals correspond to ions not relevant in this study (e.g., formed by solvent molecules).

Symbols

$C_{[M]}$	–	Molar concentration of metal ions, mol/dm^3
A	–	Absorbance

ε_L	— Molar absorption coefficient of the ligand, $\text{dm}^3/\text{mol cm}^3$
ε_c	— Molar absorption coefficient, $\text{dm}^3/\text{mol cm}^3$
K	— Stability constant
$\%E_M$	— Extraction percentage, %
D_M	— Division ratio determined experimentally
V_M	— Volume of the water phase, dm^3
V_M^{aq}	— Volume of the organic phase, dm^3
$\Sigma[M]_{\text{org}}$	— Sum of the concentrations of all the substances in the organic phase
$\Sigma[M]_{\text{aq}}$	— Sum of the concentrations of all the substances in the water phase
C	— Metal ions concentration in the feed phase at a given time, mol/dm^3
C_i	— Initial metal ions concentration in the feed phase, mol/dm^3
k	— Rate constants, s^{-1}
t	— Time of transport, s
P	— Permeability coefficient
V	— Volume of the feed phase, dm^3
A	— Area of the effective membrane, m^2
J_i	— Initial flux, $\text{mol}/\text{m}^2\text{-s}$
RF	— Recovery factor, %
AF	— Accumulation factor, %
C_0	— Initial concentration of metal ions in the feed phase, mol/dm^3
C_{membrane}	— Concentration of metal ions in the membrane phase, mol/dm^3

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