19. Załączniki

W rozdziale zestawiono wykaz dorobku naukowego stanowiacego podstawę niniejszej rozprawy doktorskiej zgodnie z kolejnością przedstawioną w tabelach 1 – 4 (Podrozdział 19.1) wraz z oświadczeniami Autora rozprawy oraz Współautorów artykułów naukowych (Podrozdział 19.2 i 19.3).

19.1. Kopie artykułów naukowych, rozdziałów w monografiach naukowych oraz otrzymanych patentów stanowiących cykl publikacji rozprawy doktorskiej

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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-diamopyridine; 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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$(OOCCMe_3)_{2-n}]_X$ [7]. Asali et al. [8] reported that in the bimetallic complexes of μ-2,6-diaminopyridine $[M(CO_5)]_2$ 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. Ilhan 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 Fe_3O_4 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).

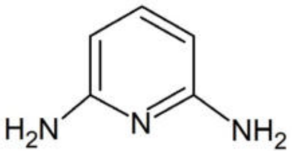

Fig. 1. The structure of 2,6-diaminopyridine.

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 = Cu(II), 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/dm^3 and a solution of ligand L in methanol (2.65×10^{-5} mol/dm^3) 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:Cu(II) and L: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°C ± 0.2°C. The aqueous phase contained 0.1 mol/dm^3 of Cu(II) or Zn(II) ions, respectively and 0.2 mol/dm^3 NH_{3aq} (pH ~ 7.8 for copper(II) ions and pH ~ 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 cm^3. The concentration of metal ions [M] (M = 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/dm^3 (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 cm^3 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 cm^2) was tightly clamped between two cell compartments. The feed and receiving aqueous phases (45 cm^3 each) were mechanically stirred at 800 rpm. The feed phase contained a 0.1 mol/dm^3 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/dm^3 HNO_3 was used as a receiving phase. The PIMs transport experiments were carried out at 25°C ± 0.2°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 NanoMate 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:

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

where $[C_{[M]}]$ is the molar concentration of metal ions (mol/dm^3), $\varepsilon = A/[L]$, A is the absorbance of the system at 336 nm (λ = 1 cm), $[L]$ is the molar concentration of the ligand (2,6-diaminopyridine), ε_L is the molar absorption coefficient of the ligand at $\lambda = 307$ ($dm^3/mol\ cm^3$), ε_c is the molar absorption coefficient of the complex at $\lambda = 336$ and 337 nm for Cu(II) and Zn(II) ($dm^3/mol\ cm^3$), 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)):

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

where D_M is the division ratio determined experimentally, V_{aq} is the volume of the water phase (dm^3), V_{org} is the volume of the organic phase (dm^3) ($V_{\text{aq}} = V_{\text{org}}$, 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 ($\Sigma[M]_{\text{aq}}$).

$$D_M=\frac{\sum\left[M\right]_{\text{org}}}{\sum\left[M\right]_{\text{aq}}} \tag{3}$$

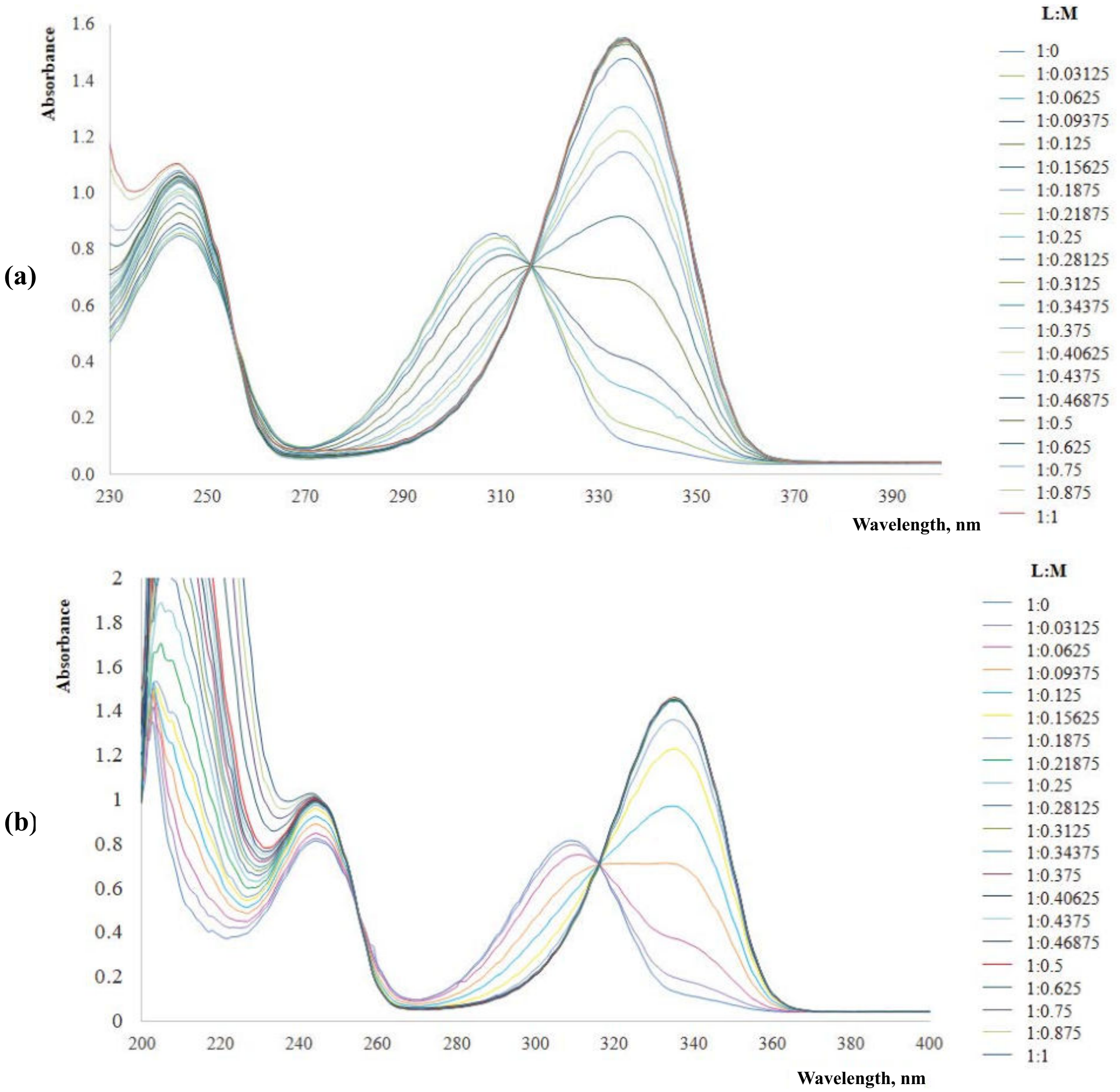

Fig. 2. The UV spectra of the complexes of copper(II) ions (a) and zinc(II) ions (b) with 2,6-diaminopyridine in various [*L*]:[*M*] molar ratios (from 1:0 to 1:1).

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 ($D_{\mathrm{Cu(II)}}$ and $D_{\mathrm{Zn(II)}}$) 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 ($D_{\mathrm{Cu(II)}}$ and $D_{\mathrm{Zn(II)}}$) 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.

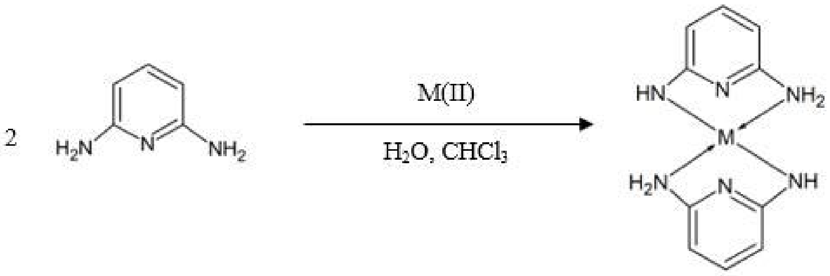

Fig. 3. Proposition of complex formation reaction by 2,6-diaminopyridine molecules with M(Cu(II) or Zn(II)) in examined solutions.

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, $D_{\text{Cu(II)}}$	Extraction percentage, $\%E_{\text{Cu(II)}}$, (%)	pH	Division ratio, $D_{\text{Zn(II)}}$	Extraction percentage, $\%E_{\text{Zn(II)}}$, (%)
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 $D_{\text{Cu(II),Zn(II)}}$ carry 0.25% tolerance and the $\%E_{\text{Cu(II),Zn(II)}}$ 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-*n*-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]:

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

where C is the metal ions concentration in the feed phase at a given time (mol/dm^3), C_i is the initial metal ions concentration in the feed phase (mol/dm^3), 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:

$$P = \frac{V}{A} \cdot k \tag{5}$$

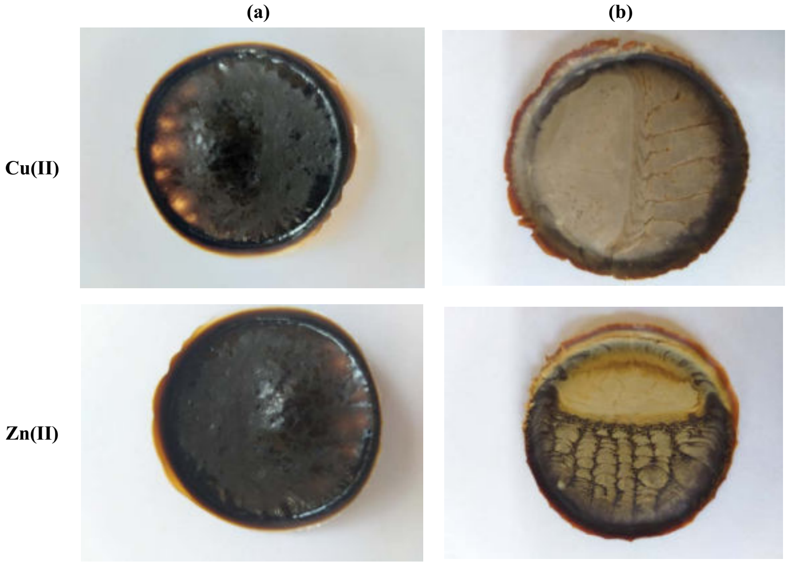

Fig. 4. PIM membranes containing 2,6-diaminopyridine as a carrier. Photographs made before transport of metal ions (a) and after transport of metal ions (b).

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) (mol/m^2 s) was determined according to Eq. (6) [26]:

$$J_i = P_i \cdot C_i \tag{6}$$

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:

$$\text{RF} = \frac{C_0 - C}{C_0} \cdot 100\% \tag{7}$$

$$\text{AF} = \frac{C_{\text{membrane}}}{C_0} \cdot 100\% \tag{8}$$

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 (μm/s)	Initial flux, J_i (μmol/m^2 s)	Metal ions	Time (h)	Permeability coefficient, P (μm/s)	Initial flux, J_i (μmol/m^2 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 $\pm 1.00 \times 10^{-6}$.

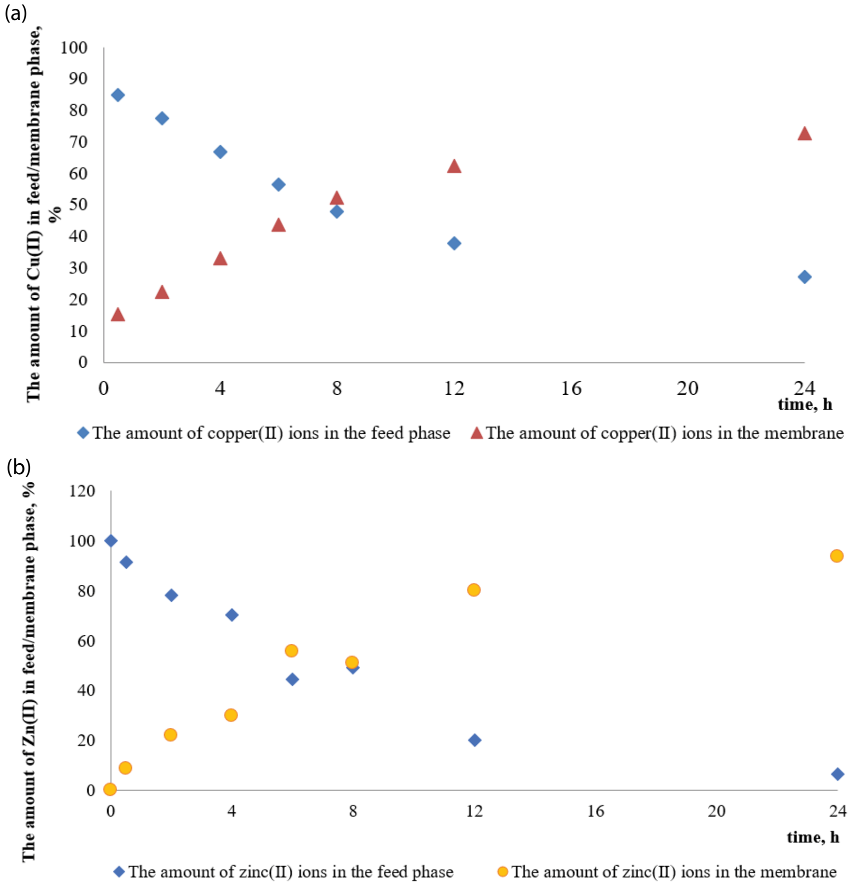

Fig. 5. Dependency graph of the amount of metal ions in the membrane phase and in the feed phase vs. time.

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 ±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 $[L + H]^+$ ($(C_5H_8N_3)^+$, $m/z_{meas} = 110.0716$, $m/z_{calc} = 110.0718$) and to ions of complexes formed by *L* molecules and/or its fragments, such as: $[C_5H_6N]^+$ ($m/z_{meas} = 80.0502$, $m/z_{calc} = 80.0500$), $[2L + H]^+$ ($(C_{10}H_{15}N_6)^+$, $m/z_{meas} = 219.1352$, $m/z_{calc} = 219.1358$), and $[C_{13}H_{14}N_8]^+$ ($m/z_{meas} = 282.1308$, $m/z_{calc} = 282.1341$). Formation of $[C_5H_6N]^+$ and $[C_{13}H_{14}N_8]^+$ 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 $[2L + Cu^{2+} – H]^+$ ($(C_{10}H_{13}N_6Cu)^+$, $m/z_{meas} = 280.0492$, $m/z_{calc} = 280.0497$) and $[2L + Zn^{2+} – H]^+$ ($(C_{10}H_{13}N_6Zn)^+$, $m/z_{meas} = 281.0572$, $m/z_{calc} = 281.0493$), 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 Cu(II) and Zn(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.

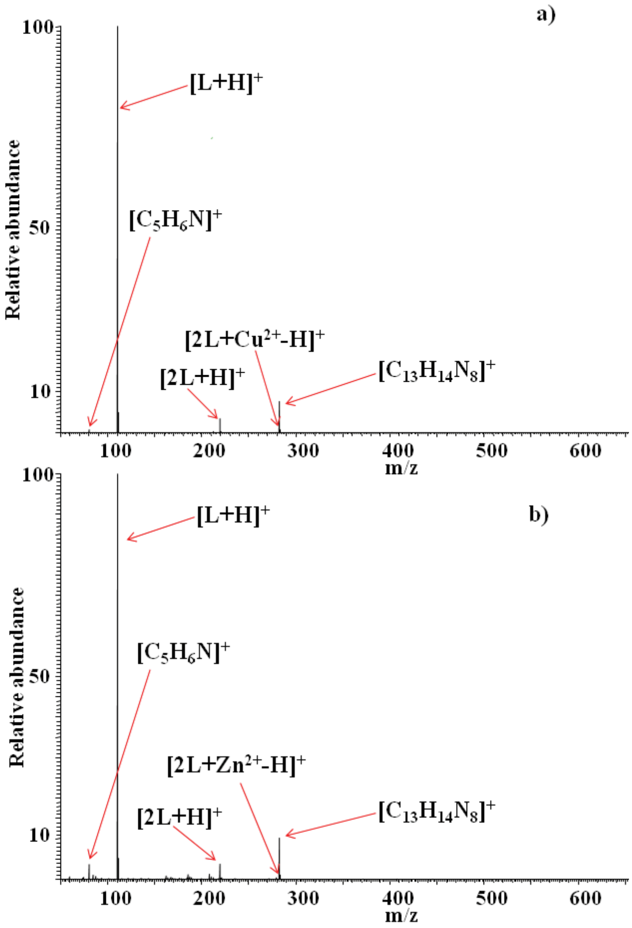

Fig. 6. ESI-HRMS spectra recorded for the samples of the separated organic phases after liquid–liquid extraction, containing 2,6-diaminopyridine (*L*) and metal ions (a) Cu^{2+} and (b) Zn^{2+}. Unassigned minor signals correspond to ions not relevant in this study (e.g., formed by solvent molecules).

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.

Symbols

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

ε_L — Molar absorption coefficient of the ligand, $dm^3/mol\ cm^3$

ε_c — Molar absorption coefficient, $dm^3/mol\ cm^3$

K — Stability constant

$\%E_M$ — Extraction percentage, %

D_M — Division ratio determined experimentally

V_{aq} — Volume of the water phase, dm^3

V_{org} — Volume of the organic phase, dm^3

$\Sigma[M]_{org}$ — Sum of the concentrations of all the substances in the organic phase

$\Sigma[M]_{aq}$ — 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, $mol/m^2{\cdot}s$

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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2,6-Bis((benzoyl-R)amino)pyridine (R = H, 4-Me, and 4-NMe_2) Derivatives for the Removal of Cu(II), Ni(II), Co(II), and Zn(II) Ions from Aqueous Solutions in Classic Solvent Extraction and a Membrane Extraction

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Abstract: In this paper, the application of new substituted 2,6-bis((benzoyl-R)amino)pyridine (R = H, 4-Me, and 4-NMe_2) derivatives for the recovery of copper(II), nickel(II), cobalt(II), and zinc(II) ions from aqueous solutions was described. The structures of the synthesized compounds were confirmed by nuclear magnetic resonance spectroscopy (NMR), electrospray ionization high-resolution mass spectrometry (ESI HRMS), and tandem mass spectrometry methods (HCD MS/MS). Three different derivatives of 2,6-bis((benzoyl-R)amino)pyridine were used as carriers in membrane processes and as extractants in classic solvent extraction. In each case, the single derivative recovery was carried out on a model solution that contained only one type of metal ions. Spectrophotometry studies were performed to determine the stability constants of the complexes formed by the synthesized species with analyzed metals ions. The results obtained indicate that the synthesized compounds form stable complexes with Cu(II), Ni(II), Co(II), and Zn(II) ions and can be used in both types of studied recovery processes. However, the effectiveness of the synthesized compounds in the recovery of metal ions depends both on the structure of compounds and properties of metals as well as on their concentration.

Keywords: 2,6-bis((benzoyl-R)amino)pyridine derivatives; metal ions Cu(II), Ni(II), Co(II), Zn(II); membranes; solvent extraction; mass spectrometry; nuclear magnetic resonance

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1. Introduction

Schiff bases, also referred to as imines, are chemical compounds containing azomethine functional group (–$R^1HC=NR^2$, where R^1, R^2—hydrogen atom, alkyl, or aryl), and are usually formed by the condensation reaction of a primary amine with an active carbonyl compound (aldehyde or ketone) [1,2]. Schiff bases are a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (C=O) is replaced by an imine (C=N) [3]. Imines have very good donor properties and can form chemically stable complex compounds with various metals [4–6] including transient metal ions [1,7], which makes them useful and widely used in coordination chemistry as organic ligands [8,9].

Many Schiff bases have been successfully used in separation processes for the recovery of metal ions (e.g., N,N′-bis(salicylidene)ethylenediamine (Salen) was applied for the removal of copper(II) ions by solvent extraction [10]) and also for the recovery of copper(II), nickel(II), and zinc(II) ions by liquid–liquid extraction and by using polymer inclusion membrane sorption/desorption and transport across the membrane [11]. Salen derivatives with different electron-accepting substituents on the aromatic ring have been utilized as extractant agents in polymeric inclusion membranes for the extraction of gold ions from aqueous solutions [12]. Other Schiff bases have also been utilized as metal ion extractants. Oshima et al. used the following imines for the selective removal of copper(II) ions: N,N′-bis(2-quinolylmethylidene)-1,2-diiminoethane (BQIE), N,N′-bis(2-pyridylmethylidene)-1,3-diimino-2,2-dimethylpropane (BPMP), and N,N′-bis(2-quinolylmethylidene)-1,3-diimino-2,2-dimethylpropane (BQMP). They found that the distance between two imine N atoms in these complexes was a factor controlling the extraction selectivity process [13]. Dede et. al. used 1-(biphenyl)-2-hydroxyimino-2-(4-chloroanilino)-1-ethanone, 1-(biphenyl)-2-hydroxyimino-2-(4-methylanilino)-1-ethanone, and 1-(biphenyl)-2-hydroxyimino-2-(N-pyrrolidino)-1-ethanone for the removal of transition metal ions such as Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Pb(II), Cd(II), and Hg(II) through a solvent extraction process [14]. Recently, Wiecka and coworkers applied pyridinium derivatives containing an imidoamide or imine moiety as novel extractants for the recovery of palladium(II) and platinum(IV) from model chloride aqueous solutions [15], while Bhargava and Uma synthesized a new Schiff base called N-(4-hydroxy-3-methoxy benzylidene)-biphenyl-4-amine) and used it for the adsorption of copper(II) ions [16]. Another compound, (E)-4-(2-hydroxyethyl imino)pentan-2-one (AcEt), was utilized during solvent extraction in the separation of thorium(IV) metal ions from chloride media [17]. Schiff bases were also applied in polymer membranes for the recovery of metal ions (e.g., Mashhadizadeh and Sheikhshoaie used a bis[5-((4-nitrophenyl)azo salicylaldehyde as a carrier in polymer inclusion membrane for the removal of mercury(II) ions [18]). Other carrier groups applicable to the removal of metal ions are calixarenes (e.g., Ulewicz and co-authors used a p-tert-butylcalix[4]arene derivative to transport Pb(II) ions across PIMs [19], whereas a calix[4]-crown-6-derivative nest carrier was used to recover Zn(II), Cd(II), and Pb(II) ions by a PIM membrane [20]). However, research on the recovery of different metal ions from aqueous solutions is not based solely on the search for new compounds (extractants and carriers); well-known compounds with relatively simple structures are increasingly being used for this purpose [21,22]. Lately, 2,6-diaminopyridine has been applied for the removal of copper(II) and zinc(II) ions from aqueous solutions in a polymer inclusion membrane and in a classic solvent extraction processes [23].

It has been reported that among the nitrogen-containing heterocycles, pyridine and its derivatives belong to a group of compounds that play an important role in biological, pharmacological, and agricultural applications [24–26]. As a tridentate ligand, 2,6-bis(imino)pyridine is often used for the synthesis of organometallic compounds [27]. Therefore, we carried out a reaction between 2,6-diaminopyridine and the appropriate benzoyl chloride derivative or ester derivative to obtain 2,6-bis(benzoylamino)pyridines substituted in the aromatic ring. 2,6-Diaminopyridine can be an electron donor or proton acceptor [26], so these derivatives can easily form complexes with metal ions. In one of the ways in which to form complexes, there is a possibility that both nitrogen atoms—from the amide groups and the pyridine ring—can be involved in the complexation, which results from the presence of two functional groups of subjected compounds [28]. However, when examining the complex-forming properties of 2,6-diaminopyridine for the separation of d-electron metal ions [26,29], it was found that only the amide group nitrogen atoms (one atom after deprotonation) are involved in the coordination of metal ions, and the pyridine nitrogen atom does not take part in this process. Based on the literature, the following structures between a metal ion and investigated compounds (Figure 1) can be proposed [30]:

Understanding the complexing properties of the newly-synthesized chemical compounds, which are A1–A3 compounds, will make it possible to use them in separation processes such as solvent extraction, sorption, membrane extraction, and transport across polymer inclusion membranes. It is worth highlighting that the currently described compounds are amides, thus are considered as more polar than Schiff bases.

In the case of all of the above-mentioned processes, the key aspect is the correct selection of carriers, which should feature the appropriate complex-forming properties. In parallel, the simple, efficient, and cheap synthesis is beneficial as well as the easy confirmation of molecular structure (NMR, HRMS). However, it should be emphasized that the effectiveness of the recovery of metal ions from aqueous solutions with the use of new non-commercial chemical compounds is also greatly influenced by the proper selection of the experimental conditions.

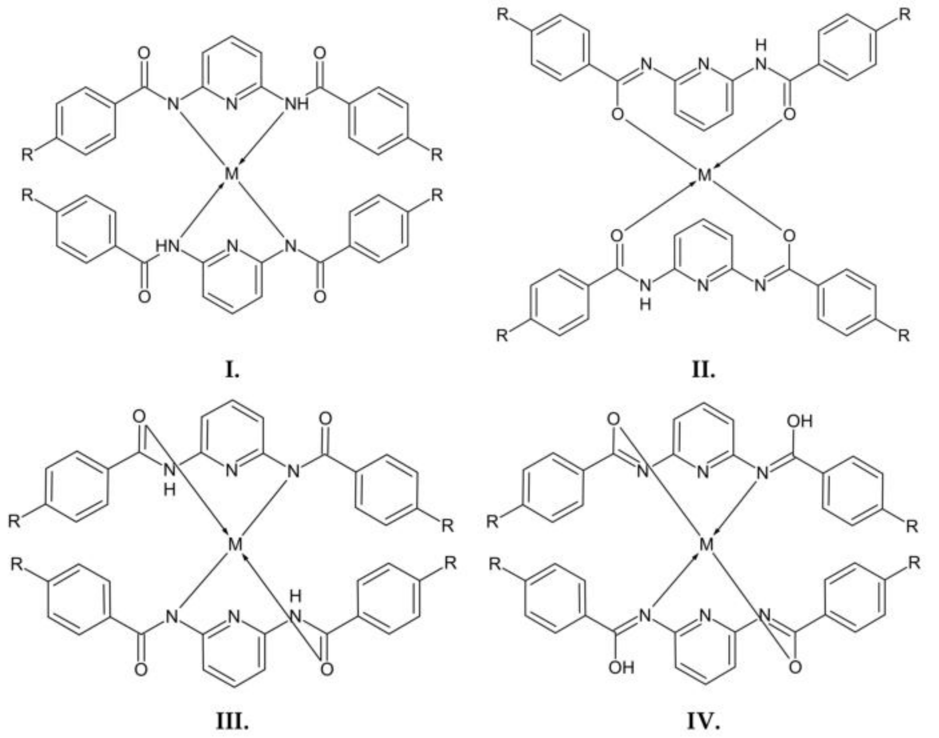


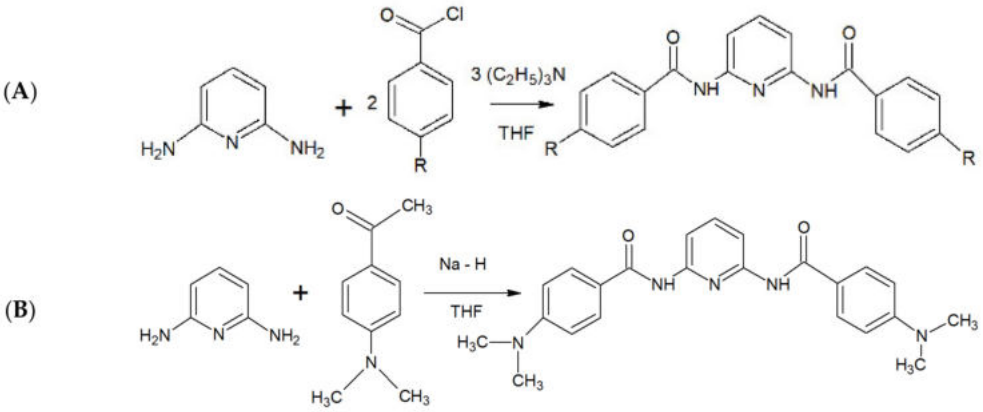
Figure 1. The proposed structures (I, II, III, and IV) of the complexes of compounds A1–A3 and metal ions (M(II)).

In this paper, the results of the application of new organic ligands A1–A3 as extractants in solvent extraction and as carriers in membrane extraction for the recovery of copper(II), nickel(II), cobalt(II), and zinc(II) ions from aqueous solutions are described.

2. Materials and Methods

2.1. Synthesis of 2,6-Bis((benzoyl-R)amino)pyridine (R = H, 4-Me, and 4-NMe$_2$) Derivatives

The investigated A1–A3 derivatives were obtained using the reactions presented in Scheme 1.



Scheme 1. The scheme of the synthesis of A1–A3 compounds during a reaction with (**A**) benzoyl chloride derivatives (R = H, 4-Me) and (**B**) ethyl 4-(dimethylamino)benzoate.

The steps of the benzoyl chloride derivative synthesis (Scheme 1A) are described below:

I. 2,6-Diaminopyridine (Sigma Aldrich, Poznan, Poland) and triethylamine (Sigma-Aldrich, Poznan, Poland) solutions were magnetically stirred in dry tetrahydrofuran (THF) (Avantor, Gliwice, Poland) (at 0 °C) and then the appropriate amount of 4-R-benzoyl chloride (solution in dry THF) was added dropwise to the mixture over a 60 min period. The 4-R-benzoyl chloride derivatives utilized included benzoyl chloride and p-toluoyl chloride (Sigma Aldrich, Poznan, Poland).
II. The mixture was stirred overnight. It was heated for 1 h, evaporated, and treated by a saturated water solution of $NaHCO_3$, and stirred for 15 min.
III. The obtained solids were re-crystallized twice from ethanol (Sigma Aldrich, Poznan, Poland).

The synthesis reaction with ethyl 4-(dimethylamino)benzoate (Scheme 1B) involved the following steps:

I. 2,6-Diaminopyridine (Sigma Aldrich, Poznan, Poland) and sodium hydride (Sigma Aldrich, Poznan, Poland) solutions were magnetically stirred under a nitrogen atmosphere for 1 h (at 25 °C).
II. The mixture was heated for 1 h and then cooled to r.t. Ethyl 4-(dimethylamino) benzoate in dry tetrahydrofuran was added dropwise to the cooled mixture over a 60 min period.
III. The mixture was heated to boiling point and stirred overnight.
IV. An NH_4Cl solution (Sigma Aldrich, Poznan, Poland) was added to the cooled mixture and was stirred to allow ammonia to evaporate.
V. The mixture was evaporated under reduced pressure and a obtained solid was crystallized from ethanol (Sigma Aldrich, Poznan, Poland).

The specific descriptions of the syntheses of all investigated compounds as well as their ^1H NMR and ^{13}C NMR spectra obtained using a Bruker Avance III 400 MHz (with a DMSO-d_6 solution in the case of all compounds synthesized) are provided in the Supplementary Materials, whereas their structures are presented in Table 1.

Table 1. The properties of the A1–A3 compounds obtained.

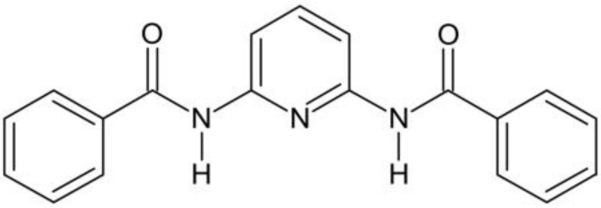
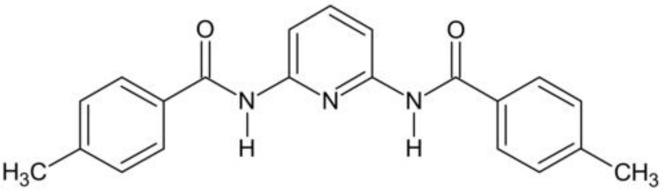
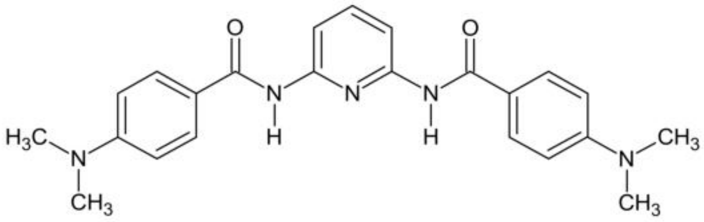
Structure of compound	
Chemical name	2,6-bis(benzoylamino)pyridine (A1)
Molecular formula	$C_{19}H_{15}N_3O_2$
Monoisotopic mass [Da]	317.1164
Structure of compound	

Table 1. *Cont.*

Chemical name	2,6-bis(4-methylbenzoylamino)pyridine (A2)
Molecular formula	$C_{21}H_{19}N_3O_2$
Monoisotopic mass [Da]	345.1478
Structure of compound	
Chemical name	2,6-bis (4-(N,N-dimethylamino)benzoylamino)pyridine (A3)
Molecular formula	$C_{23}H_{25}N_5O_2$
Monoisotopic mass [Da]	403.2008

2.2. Mass Spectrometry Experiments

A high-resolution mass spectrometry (HRMS) analysis of compounds A1–A3 was performed using a QExactive Orbitrap™ mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) equipped with a TriVersa NanoMate robotic nanoflow ESI ion source (Advion BioSciences Ltd., Ithaca, NY, USA). Samples of A1–A3 were dissolved in methanol (Avantor, Gliwice, Poland) to achieve a concentration of 1 mmol/dm^3 before being introduced into the mass spectrometer using an electrospray source. All of the HRMS data were acquired in a positive ion mode within the m/z range of 50–750 and at the resolution of 140,000 (m/z 200). Tandem mass spectrometry experiments (MS/MS) were performed using the higher-energy collisional dissociation mode (HCD) with the normalized collision energy set individually for each compound (in a range of 15–45 eV). The Thermo Xcalibur software (ver. 4.1.31.9) was used to process the obtained HRMS and MS/MS spectra.

2.3. Complexation Properties of 2,6-Bis(R-benzoyl-amino)pyridine (R = H, 4-Me, and 4-NMe$_2$) Derivatives

The absorption spectra of the complexes of metal ions and the examined compounds were recorded to calculate their stability constants. For this purpose, stock solutions of each salt of metal and methanol solutions of each 2,6-bis((benzoyl-R)amino)pyridines derivatives were made. Then, the appropriate amounts of the salt solution and the methanol solution of the examined compound were mixed to prepare samples for spectrophotometric analysis. The concentration of the ligand and metal ions in the samples was selected in such a way that the absorbance of the start solutions did not exceed one and the concentration ratios of ligand to metal in each of the next solutions were appropriate. The absorption spectra of the samples were recorded with varying molar ratios of the components (ligand:metal). The spectra were recorded in the 200–450 nm wavelength range.

2.4. Separation Procedure

2.4.1. Classic Solvent Extraction

The separation of copper(II), nickel(II), cobalt(II), and zinc(II) ions by solvent extraction was conducted. All experiments were performed at 25 ± 0.2 °C. The concentration of metal ions in the aqueous solution was obtained after the appropriate dissolution of the reference metal. The organic solution contained organic ligands A1–A3 (L), which was dissolved in chloroform. The concentration ratio of metal ions in aqueous solution to ligands in organic solution was 1:1, 1:2, and 1:5, respectively. The chloroform solution of the appropriate ligand was added to the same volume of aqueous solution. The volume of both phases (aqueous phase and organic phase) was 2500 µL. The prepared samples were then shaken for one hour. The equilibrium was established after approximately 15, 45, and 60 min by visual observation. It was then checked to see 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 ion concentration in the aqueous phases was determined by atomic absorption spectrophotometry (AAS 240FS Spectrometer, Agilent, Santa Clara, CA, USA). The parameters of classic solvent extraction with 2,6-bis((benzoyl-R)amino)pyridine (R = H, 4-Me, and 4-NMe$_2$) derivatives as extractants are shown in Table 2.

Table 2. The parameters of classic solvent extraction processes.

Metal Ions	Ligand	M:L	pH	$C_{[M]}$	$C_{[L]}$	T	μ
Cu(II)	A1 $C_{19}H_{15}N_3O_2$	1:1	10.016	0.010	0.010	20	200
		1:2	8.256	0.005	0.010	22	300
		1:5	10.424	0.002	0.010	25	400
	A2 $C_{21}H_{19}N_3O_2$	1:1	10.145	0.010	0.010	20	200
		1:2	7.985	0.005	0.010	22	300
		1:5	10.753	0.002	0.010	25	400
	A3 $C_{23}H_{25}N_5O_2$	1:1	10.160	0.010	0.010	20	200
		1:2	8.157	0.005	0.010	22	300
		1:5	10.792	0.002	0.010	25	400
Ni(II)	A1 $C_{19}H_{15}N_3O_2$	1:1	10.298	0.010	0.010	20	200
		1:2	7.845	0.005	0.010	22	300
		1:5	10.510	0.002	0.010	25	400
	A2 $C_{21}H_{19}N_3O_2$	1:1	10.043	0.010	0.010	20	200
		1:2	7.955	0.005	0.010	22	300
		1:5	10.573	0.002	0.010	25	400
	A3 $C_{23}H_{25}N_5O_2$	1:1	10.134	0.010	0.010	20	200
		1:2	8.254	0.005	0.010	22	300
		1:5	10.580	0.002	0.010	25	400
Co(II)	A1 $C_{19}H_{15}N_3O_2$	1:1	9.920	0.010	0.010	20	200
		1:2	8.5668	0.005	0.01	22	300
		1:5	10.463	0.002	0.01	25	400
	A2 $C_{21}H_{19}N_3O_2$	1:1	10.050	0.010	0.01	20	200
		1:2	7.756	0.005	0.01	22	300
		1:5	10.553	0.002	0.01	25	400
	A3 $C_{23}H_{25}N_5O_2$	1:1	10.139	0.010	0.01	20	200
		1:2	8.651	0.005	0.01	22	300
		1:5	10.645	0.002	0.01	25	400
Zn(II)	A1 $C_{19}H_{15}N_3O_2$	1:1	10.216	0.010	0.01	20	200
		1:2	8.654	0.005	0.01	22	300
		1:5	10.728	0.002	0.01	25	400
	A2 $C_{21}H_{19}N_3O_2$	1:1	10.138	0.010	0.01	20	200
		1:2	7.859	0.005	0.01	22	300
		1:5	10.716	0.002	0.01	25	400
	A3 $C_{23}H_{25}N_5O_2$	1:1	10.209	0.010	0.01	20	200
		1:2	7.6591	0.005	0.01	22	300
		1:5	10.682	0.002	0.01	25	400

where: $C_{[M]}$—the concentration of metal ions [mol/dm^3], $C_{[L]}$—the concentration of ligands A1–A3 [mol/dm^3], T—temperature [°C], μ—the mixing speed [mix./minutes].

2.4.2. The Membrane Extraction Process

The Preparation of Polymer Inclusion Membrane

A solution containing 60 wt.% of polyvinylchloride (PVC) as a support, 20 wt.% of a bis(2-ethylhexyl)adipate (ADO) as a plasticizer, and 20 wt.% of an appropriate 2,6-bis((benzoyl-R)amino)pyridine (R = H, 4-Me, and 4-NMe$_2$) derivative as an ion carrier in

10 µL tetrahydrofuran was prepared. The membrane was obtained by pouring the received solution on a glass ring. After a slow evaporation of the solvent for 12 h, the resulting polymer inclusion membrane (PIM) was peeled off from the glass plate. Through the next 12 h, PIM was immersed in distilled water. The membranes were homogeneous, transparent, flexible, and had good strength. Mean thickness of membranes was determined in the same way, as described previously [31]. The thickness of the membranes, which were used for transport of copper(II), nickel(II), cobalt(II), and zinc(II) ions, was approx. 0.25 mm.

Membrane Extraction Experiments

The circular polymer membranes were immersed in beakers containing metal ions such a copper(II), nickel(II), cobalt(II), and zinc(II). The ratio of concentrations of metal ions in aqueous solutions and appropriate ligands in organic solutions was 1:5. For each examined solution, an appropriate amount of ammonia solution was added to adjust the pH. The pH was above 8. Then, samples were taken from the aqueous phases at regular intervals over the course of 24 h of the conducted experiments. The parameters of membrane extraction processes with A1–A3 compounds as carriers are shown in Table 3.

Table 3. The parameters of the membrane extraction processes.

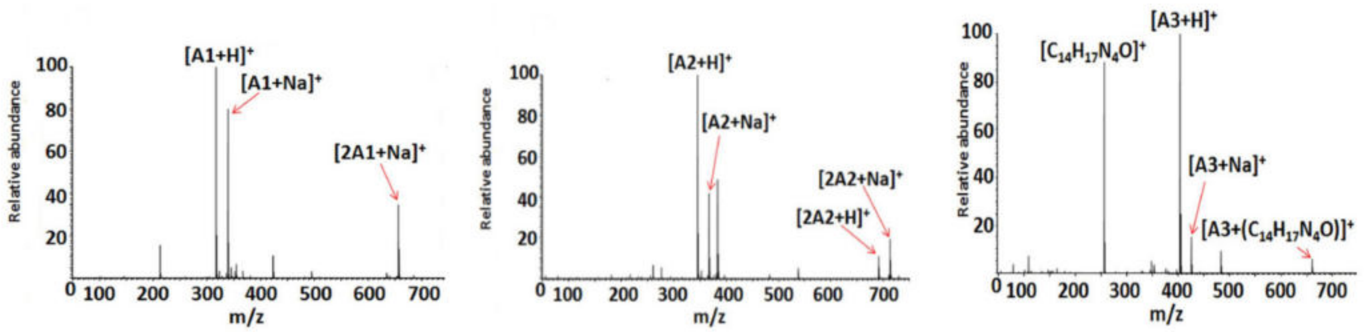
Metal Ions	Ligand	M:L	pH
Cu(II)	A1 $C_{19}H_{15}N_3O_2$	1:5	9.262
	A2 $C_{21}H_{19}N_3O_2$	1:5	9.194
	A3 $C_{23}H_{25}N_5O_2$	1:5	9.428
Ni(II)	A1 $C_{19}H_{15}N_3O_2$	1:5	10.609
	A2 $C_{21}H_{19}N_3O_2$	1:5	9.332
	A3 $C_{23}H_{25}N_5O_2$	1:5	10.895
Co(II)	A1 $C_{19}H_{15}N_3O_2$	1:5	10.654
	A2 $C_{21}H_{19}N_3O_2$	1:5	10.456
	A3 $C_{23}H_{25}N_5O_2$	1:5	9.850
Zn(II)	A1 $C_{19}H_{15}N_3O_2$	1:5	9.345
	A2 $C_{21}H_{19}N_3O_2$	1:5	10.850
	A3 $C_{23}H_{25}N_5O_2$	1:5	9.506

3. Results and discussion

3.1. Confirmation of the Structures of 2,6-Bis((benzoyl-R)amino)pyridine (R = H, 4-Me, and 4-NMe$_2$) Derivatives Using HRMS and HCD MS/MS Methods

The electrospray ionization high-resolution mass spectrometry method (ESI-HRMS) was used to confirm the molecular masses and formulas of the A1–A3 compounds analyzed, while the HCD MS/MS tandem mass spectrometry method was used to verify the compound structures. As a soft ionization technique, ESI enables most small molecules such as the ones analyzed to be transferred directly from the solvent into the mass spectrometer without a major change in their structures [32]. The HRMS method, characterized by high mass accuracy and sensitivity, enables the precise determination of the elemental composition and charge of the ions formed. The HCD MS/MS technique (called 'beam-type' CID) is based on a controlled decomposition of the selected ions of the species examined into smaller fragments, followed by an analysis of the resulting dissociation products, which provides detailed structural information [33,34].

Electrospray ionization high-resolution mass spectrometry of the samples (dissolved in methanol) containing the compounds analyzed resulted in the formation of the following singly charged ions: $[M+H]^+$, $[M+Na]^+$, and $[2M+Na]^+$, where M = A1, A2, and A3. Figure 2a–c shows the ESI HRMS spectra of compounds A1–A3, whereas Table 4 presents the ESI-HRMS data of the main ions generated under the ESI conditions. The formation of sodiated ions, typical for ESI HRMS experiments may be related to the presence of a small amount of Na^+ in the samples as a result of using certain substrates for the synthesis (i.e., $NaHCO_3$) or due to the laboratory glassware utilized [35,36].



(**a**) (**b**) (**c**)

Figure 2. Electrospray ionization (ESI) (+) HRMS mass spectra of compounds: A1 (**a**), A2 (**b**), and A3 (**c**), dissolved in methanol. The unassigned signals correspond to ions, which are not relevant in this study (i.e., complexes formed by solvent molecules, impurities).

Table 4. Electrospray ionization high-resolution mass spectrometry (ESI HRMS) data of the main ions found in the samples containing the A1–A3 compounds analyzed, dissolved in methanol.

Compound A1 ($C_{19}H_{15}N_3O_2$)		
m/z$_{meas}$	**m/z$_{calc}$**	**Assignment**
318.1233	318.1242	$[A1+H]^+$
340.1052	340.1062	$[A1+Na]^+$
657.2217	657.2226	$[2A1+Na]^+$
Compound A2 ($C_{21}H_{19}N_3O_2$)		
m/z$_{meas}$	**m/z$_{calc}$**	**Assignment**
346.1538	346.1555	$[A2+H]^+$
368.1365	368.1375	$[A2+Na]^+$
691.3022	691.3032	$[2A2+H]^+$
713.2841	713.2852	$[2A2+Na]^+$
Compound A3 ($C_{23}H_{25}N_5O_2$)		
m/z$_{meas}$	**m/z$_{calc}$**	**Assignment**
257.1393	257.1402	$[C_{14}H_{17}N_4O]^+$
404.2077	404.2086	$[A3+H]^+$
426.1896	426.1906	$[A3+Na]^+$
660.3402	660.3410	$[A3+(C_{14}H_{17}N_4O)]^+$

The results of the ESI HRMS experiments performed unequivocally confirm that the A1–A3 chemical compounds possess the correct molecular weight and elemental composition. The formation of $[C_{14}H_{17}N_4O]^+$ ions in the case of the ESI HRMS conducted using a sample containing A3 is most probably related to the decomposition of a small part of the compound molecules in the methanol solution, electrospray ionization process, or the compound storage method. Regardless of their origin, the most intensive signal on the spectrum (Figure 2c) corresponds to singly charged $[A3+H]^+$ ions, which confirms that only a small part of A3 molecules was decomposed.

The results of ESI HCD MS/MS experiments performed to confirm the structures of the A1–A3 compounds together with the relevant ESI HCD MS/MS mass spectra obtained for singly charged protonated ions of analysed molecules are presented in Table 5.

The results of the tandem mass spectrometry experiments performed indicate that the main HCD dissociation processes of all 2,6-bis((benzoyl-R)amino)pyridine (R = H, 4-Me, and 4-NMe_2) derivatives are similar, regardless of the differences in their structure. Some generated products are the result of a simple breaking of molecular bonds (i.e., $[C_7H_5O]^+$, $[C_{12}H_9N_2O]^+$ in the case of $[A1+H]^+$; $[C_8H_7O]^+$, $[C_{13}H_{11}N_2O]^+$ for $[A2+H]^+$; $[C_8H_{12}N]^+$, $[C_9H_{10}NO]^+$, and $[C_{15}H_{15}N_4O_2]^+$ in the case of $[A3+H]^+$), other fragments originate from more complex intramolecular rearrangements, which are typical for HCD MS/MS (i.e., $[C_{12}H_{11}N_2O_2]^+$ in the case of $[A1+H]^+$; $[C_{13}H_{13}N_2O_2]^+$ for $[A2+H]^+$, respectively). While a detailed analysis of the fragmentation processes was not the subject of this work, the results of the higher energy collisional dissociation experiments performed for the singly charged protonated ions of the A1–A3 compounds make it possible to confirm the structures of the species analyzed.

Table 5. Fragments observed following higher energy collisional dissociation (HCD MS/MS) of the following singly charged protonated ions: $[A1+H]^+$, $[A2+H]^+$, and $[A3+H]^+$, respectively and the relevant ESI HCD MS/MS mass spectra

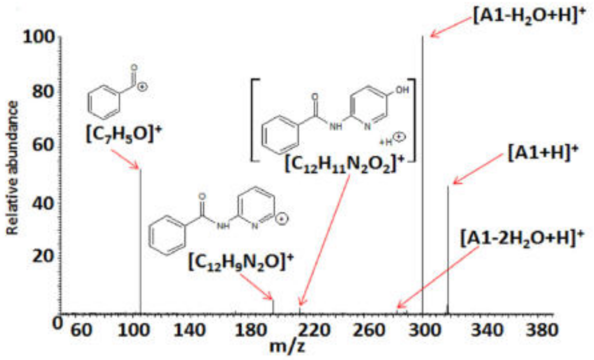
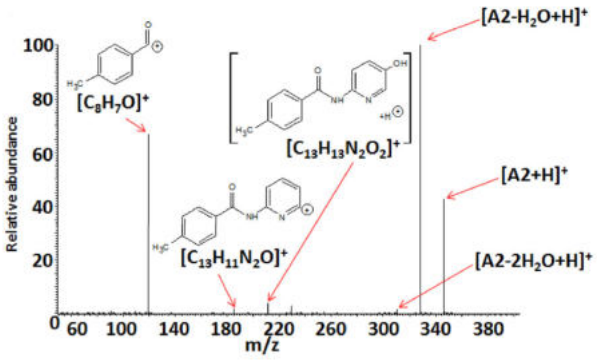
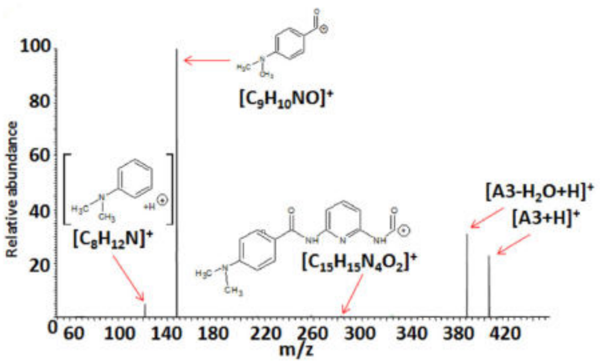
	$[A1+H]^+$		**ESI HCD MS/MS mass spectrum of $[A1+H]^+$**
m/z_{meas}	**m/z_{calc}**	**Assignment**	
318.1235	318.1242	$[A1+H]^+$, $(C_{19}H_{16}N_3O_2)$	
300.1129	300.1137	$[A1-H_2O+H]^+$, $(C_{19}H_{14}N_3O_1)$	
282.1032	282.1031	$[A1-2H_2O+H]^+$, $(C_{19}H_{12}N_3)$	
215.0815	215.0820	$[C_{12}H_{11}N_2O_2]^+$	
197.0709	197.0715	$[C_{12}H_9N_2O]^+$	
171.0553	171.0558	$[C_{10}H_7N_2O]^+$	
105.0339	105.0340	$[C_7H_5O]^+$	
95.0496	95.0497	$[C_6H_7O]^+$	
77.0392	77.0391	$[C_6H_5]^+$	
	$[A2+H]^+$		**ESI HCD MS/MS mass spectrum of $[A2+H]^+$**
m/z_{meas}	**m/z_{calc}**	**Assignment**	
346.1538	346.1555	$[A2+H]^+$, $(C_{21}H_{20}N_3O_2)$	
328.1434	328.1450	$[A2-H_2O+H]^+$, $(C_{21}H_{18}N_3O_1)$	
310.1330	310.1344	$[A2-2H_2O+H]^+$, $(C_{21}H_{16}N_3)$	
254.0917	254.0929	$[C_{14}H_{12}N_3O_2]^+$	
229.0965	229.0977	$[C_{13}H_{13}N_2O_2]^+$	
211.0860	211.0871	$[C_{13}H_{11}N_2O]^+$	
185.0704	185.0715	$[C_{11}H_9N_2O]^+$	
119.0490	119.0497	$[C_8H_7O]^+$	
109.0649	109.0653	$[C_7H_9O]^+$	
91.0545	91.0548	$[C_7H_7]^+$	

Table 5. *Cont.*

	$[A3+H]^+$		ESI HCD MS/MS mass spectrum of $[A3+H]^+$
m/z_{meas}	m/z_{calc}	Assignment	
404.2068	404.2086	$[A3+H]^+$, $(C_{23}H_{26}N_5O_2)$	
386.1963	386.1981	$[A3-H_2O+H]^+$, $(C_{23}H_{24}N_5O_1)$	
356.1463	356.1511	$[A3-H_2O-C_2H_6+H]^+$, $(C_{21}H_{18}N_5O_1)$	
283.1180	283.1195	$[C_{15}H_{15}N_4O_2]^+$	
214.0967	214.0980	$[C_{12}H_{12}N_3O]^+$	
148.0751	148.0762	$[C_9H_{10}NO]^+$	
122.0963	122.0970	$[C_8H_{12}N]^+$	
79.0547	79.0548	$[C_6H_7]^+$	

3.2. Complexation Properties of 2,6-Bis((benzoyl-R)amino)pyridine (R = H, 4-Me, and 4-NMe$_2$) Derivatives

The spectrum in the UV–VIS region is called the electronic absorption spectrum, but strictly, it is the electron-oscillation-rotation spectrum. The energy of a molecule is the sum of electron, oscillation, and rotation energies. Since the electronic transition is accompanied by transitions from a specific sequence of oscillatory and rotational sublevels to their respective combinations in the excited state, the spectrum consists of absorption bands, not single lines. In organic compounds, the absorption of radiation in the UV–VIS region leads to changes in the energy states of valence electrons, causing the transfer of an electron from one orbital to another with higher energy.

The absorption spectra of complexes of the tested compounds A1–A3 with various metal ions are shown in Figure 3. On the obtained spectra, the characteristic bands in the UV region are visible. Maxima of absorption for clear A1, A2, and A3 ligands in methanol were observed at wavelengths of 303 nm, 246 nm, and 303 nm (two maxima of absorption), and 333 nm, respectively. On each spectrum, the vanishing band of the ligand and the appearance of new ones corresponding to the complex (ligand + cation) with the isosbestic points were recorded. The shapes of the spectra for each studied compound differed because of the presence of various substituents located in the molecules of investigated derivatives A1–A3. Spectra of the A1 compound showed a hypochromic effect, while in the spectra of the A2 and A3 compounds, bathochromic shifts were visible. The bathochromic shifts are clearly shown for the A2+Cu(II) spectrum and for all spectra of the A3 compound.

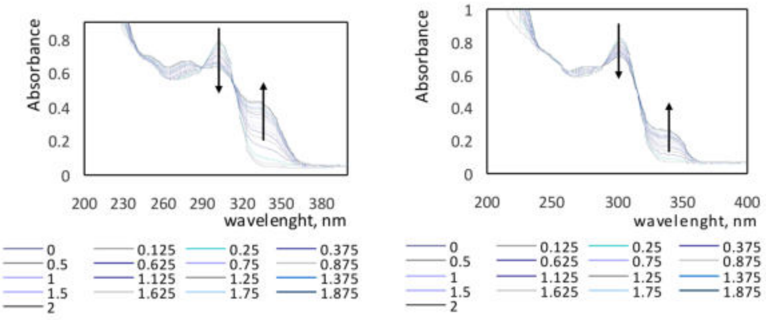
Based on the recorded absorption spectra, the stability constants (K) of the created complexes were calculated using the known method [37].

The determined values of the stability constants (log K) of complexes are shown in Table 6. The values of log K$_1$, log K$_2$ were assigned to stability constants of complexes, in which the molar ratio of ligand:metal ions was 1:1 and 1:2, respectively.

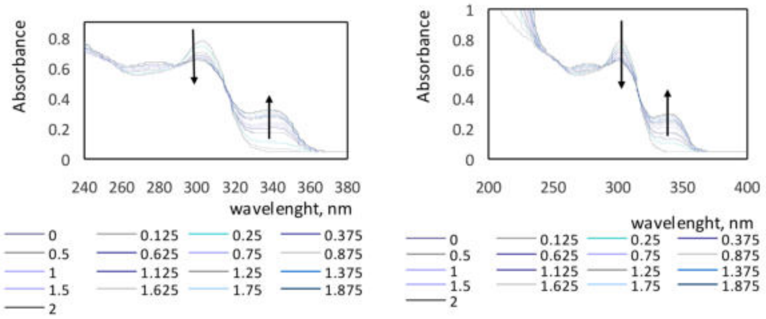
Table 6. Stability constants of the complexes of compounds A1–A3 with various metal ions.

Metal Ions	A1—$C_{19}H_{15}N_3O_2$M = 317.34 g/mol		A2—$C_{21}H_{19}N_3O_2$M = 345.39 g/mol		A3—$C_{23}H_{25}N_5O_2$M = 403.47 g/mol	
	log K$_1$	log K$_2$	log K$_1$	log K$_2$	log K$_1$	log K$_2$
Cu(II)	4.398	3.475	4.225	4.724	8.266	9.370
Ni(II)	4.544	4.515	4.500	4.605	7.695	8.131
Co(II)	4.183	4.583	5.809	6.415	4.218	5.836
Zn(II)	3.848	4.942	5.377	5.870	5.908	6.164

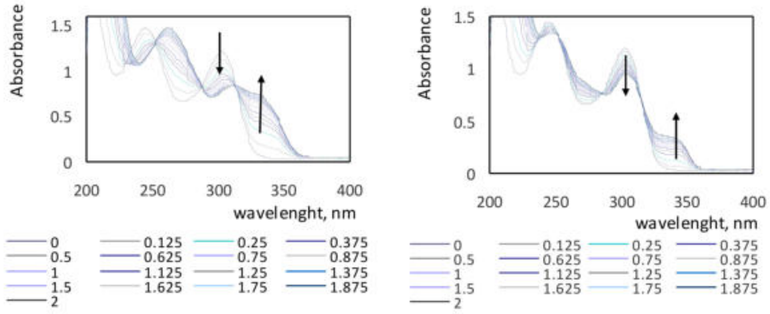
The given values of the log K carry ± 0.001.



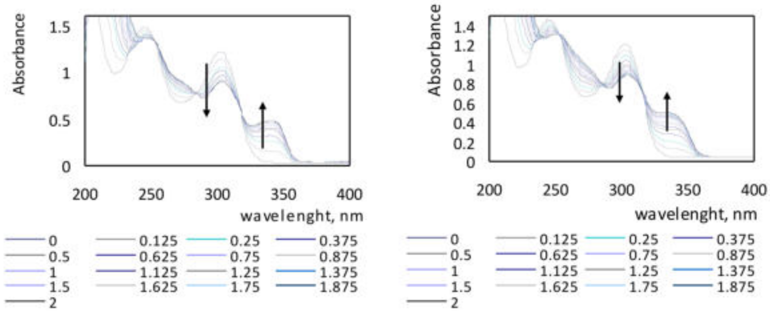
A1+Cu(II) **A1+Ni(II)**



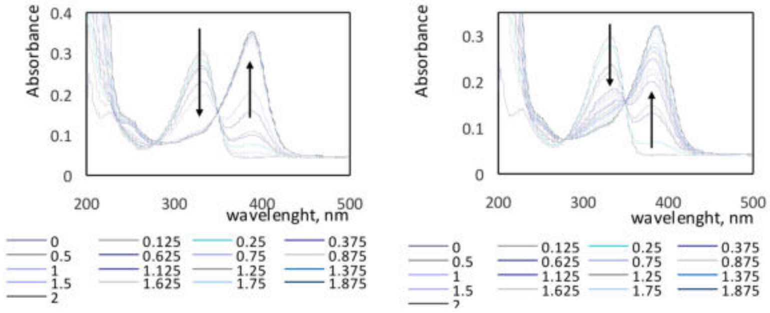
A1+Co(II) **A1+Zn(II)**



A2+Cu(II) **A2+Ni(II)**

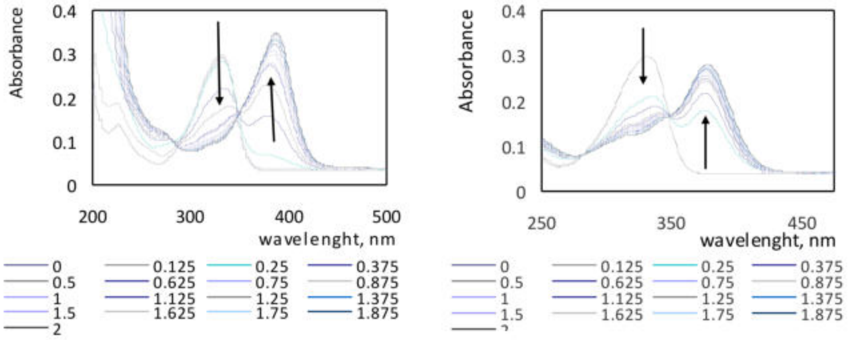


A2+Co(II) **A2+Zn(II)**



A3+Cu(II) **A3+Ni(II)**

Figure 3. *Cont.*



A3+Co(II) **A3+Zn(II)**

Figure 3. Absorption spectra of complexes of compounds A1–A3 with various metal ions in various molar ratios of ligand to metal.

The higher value of the stability constant (log K > 1.0) indicates that at equilibrium, the activity of the complex is larger than the product of activities of the metal ion and ligand (Equation (1)).

$$mL + [Me(H_2O)_m]^{n+} \rightleftarrows [MeL_n]^{n+} + mH_2O \quad (1)$$

As a result, the high value of log K indicates that the ligand binds to the metal ion more strongly than water molecules. The stability constant is then used as a measure of the thermodynamic stability of the complex. An increase in the number of ligands in the coordination sphere usually leads to a decrease in the number of water molecules to be replaced. This is why in some cases, it is found that complexes with a larger number of ligands are more stable than others because of unusual structural changes and differences in the electronic configuration of the metal ion. The complexes with a higher crystal field stabilization energy value will be stable, and the stability constant for those complexes will be high [38].

Due to their structure (i.e., the presence of deprotonated NH and C=O groups in their molecules,) the tested derivatives belong to the so-called Lewis bases. Such compounds easily react with metal ions—the so-called Lewis acids. Therefore, in aqueous solutions, complexes of the tested derivatives with selected metal ions are characterized by quite stable structures. They can be compared with the stability of complexes formed by β-diketones, whose log K_1 for complexes with metal ions such as cobalt and nickel has a value amount to 5.

The stability constants of complexes of a derivative with the $–N(CH_3)_2$ groups with the chosen metal ions were the highest. This compound created the most stable complexes, especially with copper(II) and nickel(II) ions. This may be explained by a substituent effect of the $–N(CH_3)_2$ group in the deprotonated ligand. The electron donating $–N(CH_3)_2$ moiety increased the basic character of the (O–C–N–C–N)—making it more potent to interaction with the Lewis acid.

The results suggest that the analyzed compounds may be useful in the extraction of different metal ions from aqueous solutions, and thus may be applicable as selective carriers in polymer inclusion membranes that may be used to recover metal ions.

3.3. Results of Separation Processes

3.3.1. Classic Solvent Extraction

The solvent extraction of copper(II), nickel(II), cobalt(II), and zinc(II) ions was performed with 2,6-bis((benzoyl-R)amino)pyridine (R = H, 4-Me, and 4-NMe_2) derivatives as extractants. The experiments were carried out for solutions in which the ligands and metal ions concentration ratios were 1:1, 1:2, and 1:5, respectively. The extraction percentage ($\%E_M$) of the metal ions is described by the following equation:

$$\%E_M = \frac{D_M}{D_M + \frac{V_{aq}}{V_{org}}} \cdot 100\% \tag{2}$$

where D_M is the division ratio determined experimentally; V_{aq} is the volume of the aqueous phase [dm^3]; V_{org} is the volume of the organic phase [dm^3] (V_{aq} = V_{org}, so V_{aq}/V_{org} = 1).

The division ratio (Equation (3)) is the ratio of the sum of the concentrations of all the substances in the organic phase ($\Sigma[M]_{org}$) to the sum of the concentrations of all the substances in the aqueous phase ($\Sigma[M]_{aq}$).

$$D_M = \frac{\Sigma[M]_{org}}{\Sigma[M]_{aq}} \tag{3}$$

Obtained results were elaborated using a spreadsheet and additionally, the standard deviation was calculated (Table 7).

Table 7. The division ratio of metal ions with 2,6-bis((benzoyl-R)amino)pyridine derivatives as extractants.

A1			A2			A3		
Metal Ions	**Cm [mol/dm^3]**	**D_M**	**Metal Ions**	**Cm [mol/dm^3]**	**D_M**	**Metal Ions**	**Cm [mol/dm^3]**	**D_M**
Cu(II)	0.01	0.152	Cu(II)	0.01	0.557	Cu(II)	0.01	0.141
	0.002	3.939		0.002	3.689		0.002	3.398
	0.005	0.970		0.005	1.135		0.005	0.785
Ni(II)	0.01	21.486	Ni(II)	0.01	42.765	Ni(II)	0.01	4.944
	0.002	4.953		0.002	137.861		0.002	17.993
	0.005	3.921		0.005	11.722		0.005	8.652
Co(II)	0.01	343.710	Co(II)	0.01	144.544	Co(II)	0.01	88.719
	0.002	281.621		0.002	731.722		0.002	164.552
	0.005	67.493		0.005	73.529		0.005	28.850
Zn(II)	0.01	4.327	Zn(II)	0.01	7.056	Zn(II)	0.01	4.333
	0.002	4.057		0.002	3.653		0.002	4.256
	0.005	4.035		0.005	4.461		0.005	4.274

The given values of the D_M carry ± 0.001.

The obtained division ratios (Table 7) for the analyzed metal complexes with all compounds increased in the following order: Cu(II) < Zn(II) < Ni(II) < Co(II), for the greater part of the studied extraction processes. Co(II) complexes were the best extracted, and the Cu(II) complexes were the worst extracted. In case of the process using compound A1, this sequence changes to Cu(II) < Ni(II) < Zn(II) < Co(II), for the concentration of metal ions in the solution 0.005 mol/dm^3. While for the compound A2 and the concentration of 0.002 mol/dm^3, the value of the division ratio was the highest for Zn(II) ions and the lowest for Co(II).

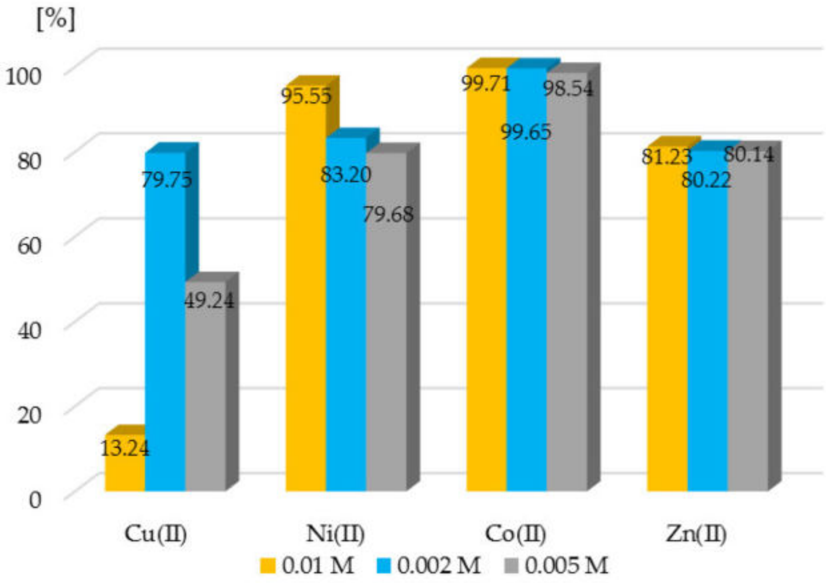
The percent of the extraction of metal ions with all of the investigated extractants is shown in the plots below.

The extraction of metal ions with extractants A1–A3 was efficient. The $\%E_M$ was more than 90% for nickel(II), cobalt(II), and zinc(II) with all A1, A2, and A3 ligands. However, those ligands were not as effective during copper ion extraction (Figure 4). The results of the conducted experiments clearly showed that the proper concentration of metal ions and appropriate ligands had a significant impact on the efficiency of the extraction processes. The conducted spectrophotometric titration (Section 3.2) confirmed the formation of complexes with various M:L ratios including compounds of the type 1:1, 1:2, and 1:5. The extraction studies were performed to take into account the mentioned molar ratios of the metal ion content in the samples to the existing concentration of the extractants. It was found that at the 1:1 molar ratio (M:L), a high recovery of metals was observed, while in most cases with a significant excess of ligand in the solution (1:5), a further slight increase in this recovery was observed.

3.3.2. Membrane Extraction Process

Shortly after the polymer membranes were immersed in a solutions containing Co(II), Ni(II), Co(II), or Zn(II) ions, respectively, the membrane extraction processes were started. Metals ions were adsorbed on the surfaces of the membranes. The ligand molecules (A1, A2, or A3) doped into the polymer membranes bound metals ions thanks to the complexation reactions.

A1



A2

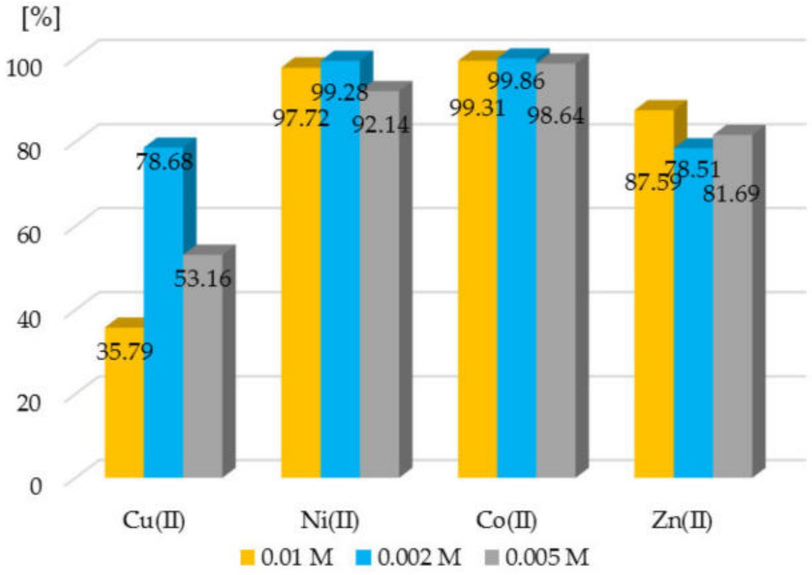


Figure 4. *Cont.*

A3

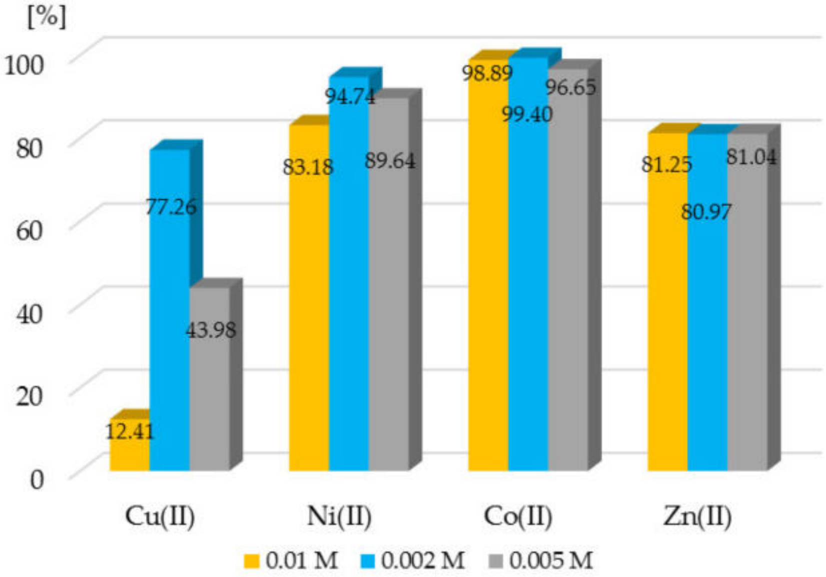


Figure 4. The dependence of the concentration of metal ions in aqueous solution on percent of extraction of metal ions with compounds A1–A3. The given values of the $\%E_M$ carry ± 0.01%.

After 24 h of membrane extraction process, the percentage of metal ion removal from the solutions (%*RF*) was also determined (Equation (4)).

$$RF = \frac{c_0 - c}{c_0} \cdot 100\% \quad (4)$$

where c_0 is the initial concentration of metal ions in the feed phase [mol/dm^3] and c is the concentration of metal ions after time t in the feed phase [mol/dm^3].

The results of the membrane extraction processes performed are presented in Figure 5. Based on these results, it can be unequivocally stated that the efficiency of the membrane processes carried out with the utilization of A1–A3 compounds as carriers was lower than in the extraction processes, in which these compounds were used as extractants. This may be caused by various factors such as, for example, inappropriate selection of the polymer or plasticizer to obtain membranes with the tested compounds. The copper(II) ions recovery was as poor in the case of the membrane process as in classical extraction, regardless of the type of A1–A3 used. As the results obtained for other analyzed ions (Ni(II), Co(II), Zn(II)) were much better (in both types of processes), it can be assumed that the individual properties of metal ions have a significant impact on the extraction and membrane processes. Additionally, for all examined metal ions, the lowest values of metal ions recovery were obtained with the application of compound A1 as a carrier.

The analysis of the metal ion sorption process onto the membranes with 20 wt.% of the investigated compounds used as a carrier was carried out using Equation (5):

$$q_t = \left(\frac{c^i - c^t}{m} \right) \cdot V \quad (5)$$

where q_t is the sorption capacity (mg/g); V is the volume of the solution (dm^3); m is the mass of the sorbent (g), and c^i and c^t are the analytical metal ion concentrations in the solution at the beginning and after an appropriate time of the sorption process (mol/dm^3), respectively.

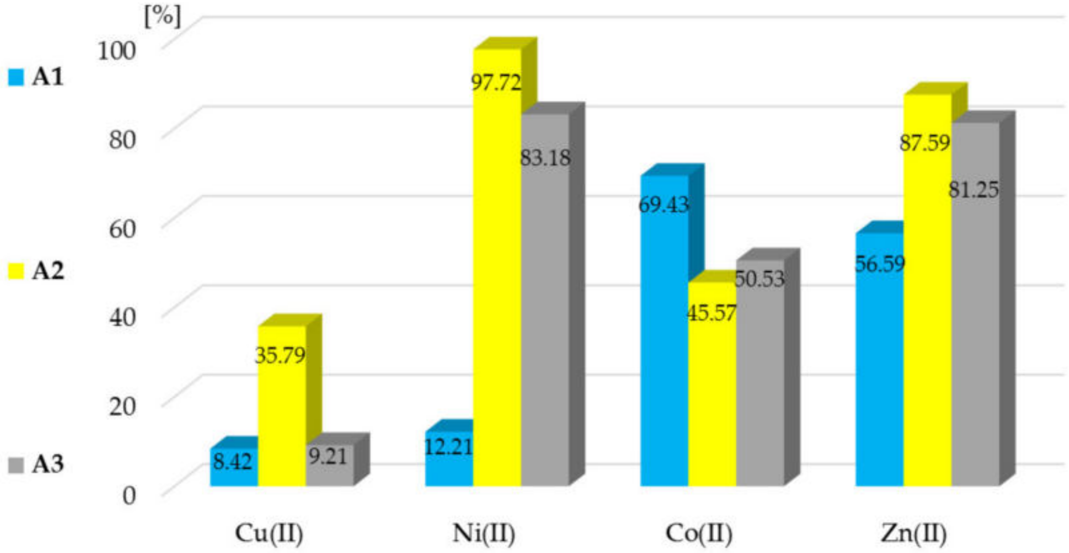


Figure 5. Recovery of metal ions in membrane extraction processes with 2,6-bis((benzoyl-R)amino)pyridine (R = H, 4-Me, and 4-NMe$_2$) derivatives as a carriers. The given values of the RF carry ± 0.01%.

The sorption capacity of the membrane with all of the ligands A1–A3 as carriers after 24 h of the sorption of investigated metal ions is presented in Table 8.

Table 8. The sorption capacity of membrane with ligands A1–A3 after 24 h of sorption.

Compound	Metal Ions	q_t
A1	Cu(II)	0.17
	Ni(II)	0.30
	Co(II)	3.42
	Zn(II)	2.44
A2	Cu(II)	0.79
	Ni(II)	0.92
	Co(II)	2.12
	Zn(II)	3.69
A3	Cu(II)	0.21
	Ni(II)	0.60
	Co(II)	2.07
	Zn(II)	3.81

The given values of the q_t carry ± 0.01 mg/g.

The highest q_t of investigated membranes was obtained for Zn(II) and Co(II) ions sorption and was equal to 3.81 mg/g and 3.42 mg/g, respectively. The lowest q_t was observed for Cu(II) ions (0.17 mg/g). The received results can be compared with other literature data (e.g., the sorption capacity of sorbent prepared from mixed local conifer sawdust (SW) and fly ash (FA) was 3.22–3.29 mg/g at 293 K [39], and the sorption capacities of novel nanosorbent (NZVI-DETA-PY) for Co(II), Cu(II), and Zn(II) ions were 2600 µmol/g, 4750 µmol/g, and 5600 µmol/g, respectively [40].

4. Conclusions

In this study, the application of a series of new 2,6-bis((benzoyl-R)amino)pyridine (R = H, 4-Me, and 4-NMe$_2$) derivatives for the removal of metal ions (copper(II), nickel(II), cobalt(II), and zinc(II)) from aqueous solutions was described.

The compounds A1–A3 were obtained in the condensation reactions of 2,6-diaminopyridine with benzoyl chloride derivatives and with ethyl 4-(dimethylamino)benzoate, respectively. NMR and electrospray ionization high-resolution mass spectrometry (ESI HRMS) and higher energy collisional dissociation tandem mass spectrometry (HCD MS/MS) methods were successfully used to confirm the structures of all synthesized ligands. Given the high mass accuracy of HRMS mass spectrometry and a relatively easy and straightforward interpretation of the simple fragmentation spectra (HCD MS/MS) of the analyzed compounds, there is no doubt about the elemental composition, charge, or structure of the ions formed.

The experiments of the complexation properties confirmed that the series of new compounds exhibited high complex-forming properties. The various molar ratio of ligand:metal was proved to form complex metal ion complexes with the investigated ligands. Application of the spectrometric method allowed us to determine the ratio of ligand to the metal in the studied complexes as well as their stability, which was quite high.

Thanks to the complex-forming properties of the compounds A1–A3, it is possible to use synthesized compounds as very efficient extractants for removing metal ions from aqueous solutions. Studied derivatives can also be used as carriers in the membrane processes. However, to increase the efficiency of membrane processes, further research is needed, where membranes containing a different polymer and/or plasticizer will be used. Since the synthesis of chemical compounds used in this study as extractants and carriers is relatively easy and cheap, and these compounds have strong complexing properties, the results of this research may prove to be a new direction in the search for simple organic ligands to remove metal ions from waste.

Supplementary Materials: The following are available online at https://www.mdpi.com/2077-0375/11/4/233/s1, Figure S1. The ^{1}H NMR (A) and ^{13}C NMR (B) spectrum of 2,6-(N,N′-dibenzoyl)-diaminopyridine (A1).; Figure S2. The ^{1}H NMR (A) and ^{13}C NMR (B) spectrum of 2,6-bis(4-methylbenzoyl)-diaminopyridine (A2).; Figure S3. The ^{1}H NMR (A) ^{13}C NMR (B) spectrum of 2,6-bis(4-dimethylbenzoylamino)pyridine (A3).

Author Contributions: Synthesis: D.B. and B.O.; NMR—B.O.; All experiments, analysis, and description of their results—D.B., M.A.K. and K.W.; Draft writing, review and editing—All authors. All authors have read and agreed to the published version of the manuscript.

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Article

The Application of 2,6-Bis(4-Methoxybenzoyl)-Diaminopyridine in Solvent Extraction and Polymer Membrane Separation for the Recovery of Au(III), Ag(I), Pd(II) and Pt(II) Ions from Aqueous Solutions

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Abstract: The work describes the results of the first application of 2,6-bis(4-methoxybenzoyl)-diaminopyridine (*L*) for the recovery of noble metal ions (Au(III), Ag(I), Pd(II), Pt(II)) from aqueous solutions using two different separation processes: dynamic (classic solvent extraction) and static (polymer membranes). The stability constants of the complexes formed by the L with noble metal ions were determined using the spectrophotometry method. The results of the performed experiments clearly show that 2,6-bis(4-methoxybenzoyl)-diaminopyridine is an excellent extractant, as the recovery was over 99% for all studied noble metal ions. The efficiency of 2,6-bis(4-methoxybenzoyl)-diaminopyridine as a carrier in polymer membranes after 24 h of sorption was lower; the percentage of metal ions removal from the solutions (%R_s) decreased in following order: Ag(I) (94.89%) > Au(III) (63.46%) > Pt(II) (38.99%) > Pd(II) (23.82%). The results of the desorption processes carried out showed that the highest percentage of recovery was observed for gold and silver ions (over 96%) after 48 h. The results presented in this study indicate the potential practical applicability of 2,6-bis(4-methoxybenzoyl)-diaminopyridine in the solvent extraction and polymer membrane separation of noble metal ions from aqueous solutions (e.g., obtained as a result of WEEE leaching or industrial wastewater).

Keywords: polymer membranes; solvent extraction; recovery of noble metal ions; 2,6-bis(4-methoxybenzoyl)-diaminopyridine; spectrophotometry

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1. Introduction

Solvent extraction (SE), a process of separating metal ions from aqueous solutions by extraction into organic solvents immiscible with water, has been used for many years to recover various metals, both common and rare [1–4]. This well-established separation method has been widely used as a tool for the recovery of precious metals from different types of industrial waste, including waste electrical and electronic equipment (WEEE) [5–7]. This type of waste contains many valuable metals, and its recovery is often more effective than extraction from decreasing ore grades; thus, the term "urban mining" has been introduced [8]. The growing interest in methods of precious metals recovery from waste is related to the various applications of these materials. They can be used as raw materials for high-technology industries (e.g., electronic materials) as well as in pharmaceutics, jewelry, catalysis, etc. Furthermore, the demand for precious metals in industrial applications has significantly increased in the last few years [9,10].

Although extraction is a relatively simple method, the long time required for analysis and the need to use organic solvents (many of which are volatile and toxic) prove to be serious limitations. Moreover, some extractants are not effective or affordable enough [8]. It has been reported by Bulgariu and Bulgariu [11] that many of the disadvantages of classical SE can be minimized by using the aqueous two-phase system in the extraction process. They investigated the extraction of gold(III) in an aqueous PEG(1500)–$(NH_4)_2SO_4$ two-phase system, using chloride ions as extracting agents. The PEG-based two-phase system they utilized was non-toxic, non-flammable and non-volatile. The obtained results showed that gold(III) was quantitatively extracted (>98%) into the PEG-rich phase in acid media. Another environmentally friendly two-phase extraction system based on polypropylene glycol 425 and sodium chloride has recently been successfully applied for the extraction of Pt(IV) and Pd(II) from diluted hydrochloric acid solutions [12]. Ecologically safe, two-phase aqueous systems have been used to extract various metal ions, not only noble ones. However, the utilization of such systems usually requires time-consuming determination of the appropriate process conditions (e.g., proper concentration of metal ions and other reagents used, temperature, pH) [13].

An alternative to the conventional method of liquid–liquid extraction is the application of membrane processes, e.g., polymer inclusion membranes (PIMs) [14], which can reduce the consumption of solvents. Other advantages of PIMs (a type of liquid membrane in which the liquid phase is held within the polymeric network, usually polyvinyl chloride (PVC) or cellulose triacetate) are their wide range of applications, high efficiency in the extraction of various metal ions, high stability and the possibility of conducting extraction and back-extraction processes [14,15]. It has been shown that the process of metal ion recovery using SE and PIMs depends on many factors, including the metal's properties, concentration, pH, matrix complexity, etc., but the vital factor in both processes is the correct selection of the chemical compounds binding the metal ions (extractants and carriers, respectively) [15,16]. Hence, many studies conducted in recent years search for new extractants/carriers that would allow for more effective recovery of precious metals from aqueous and acidic solutions (e.g., obtained as a result of leaching of WEEE waste) [17,18]. A variety of chemical compounds, both commercially available carriers (e.g., Cyphos IL 101) and non-standard ones (e.g., niacin), have been used for this purpose [19–24]. Often, the application of the same compound as the extractant in SE and as the carrier in PIMs produces different results concerning the recovery of both heavy and noble metal ions [25,26].

This paper describes the results of the application of 2,6-bis(4-methoxybenzoyl)-diaminopyridine (shown in Figure 1) for the recovery of noble metal ions such as Au(III), Ag(I), Pd(II) and Pt(II) from aqueous solutions using SE and polymer membrane processes. 2,6-Bis(4-methoxybenzoyl)-diaminopyridine can be considered a heterocyclic amide which due to its structure possesses the ability to form complexes with various metal ions. In previous work, we showed that the presence of oxygen/nitrogen atoms in the molecule of 2,6-bis(4-methoxybenzoyl)-diaminopyridine allows it to form complexes with copper(II) ions; thus, it can be successfully used for the SE recovery of Cu^{2+} (recovery percentage above 99%) [27]. Despite the ability to form complexes with metal ions, so far 2,6-bis(4-methoxybenzoyl)-diaminopyridine has not been used as an extractant in liquid–liquid extraction designed for the recovery of noble metals ions, nor as a carrier in polymer membranes.

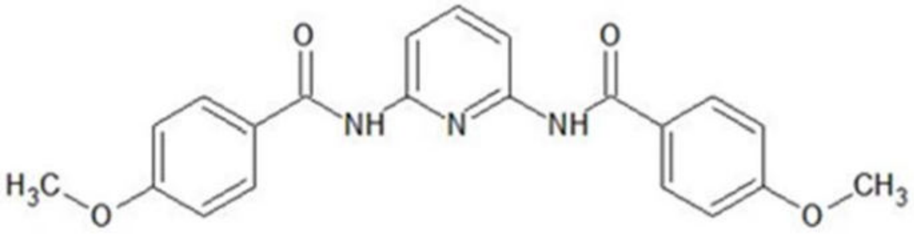

Figure 1. Structure of 2,6-bis(4-methoxybenzoyl)-diaminopyridine ($C_{21}H_{19}N_3O_4$).

2. Results and Discussion

2.1. The Stability Constants of Complexes Formed by Precious Metal Ions with 2,6-Bis(4-Methoxybenzoyl)-Diaminopyridine

For all investigated systems (ligand to chosen metal ion: Au(III), Ag(I), Pd(II) and Pt(II)) the absorption spectra were recorded in various ratios of L:M (Figure 2).

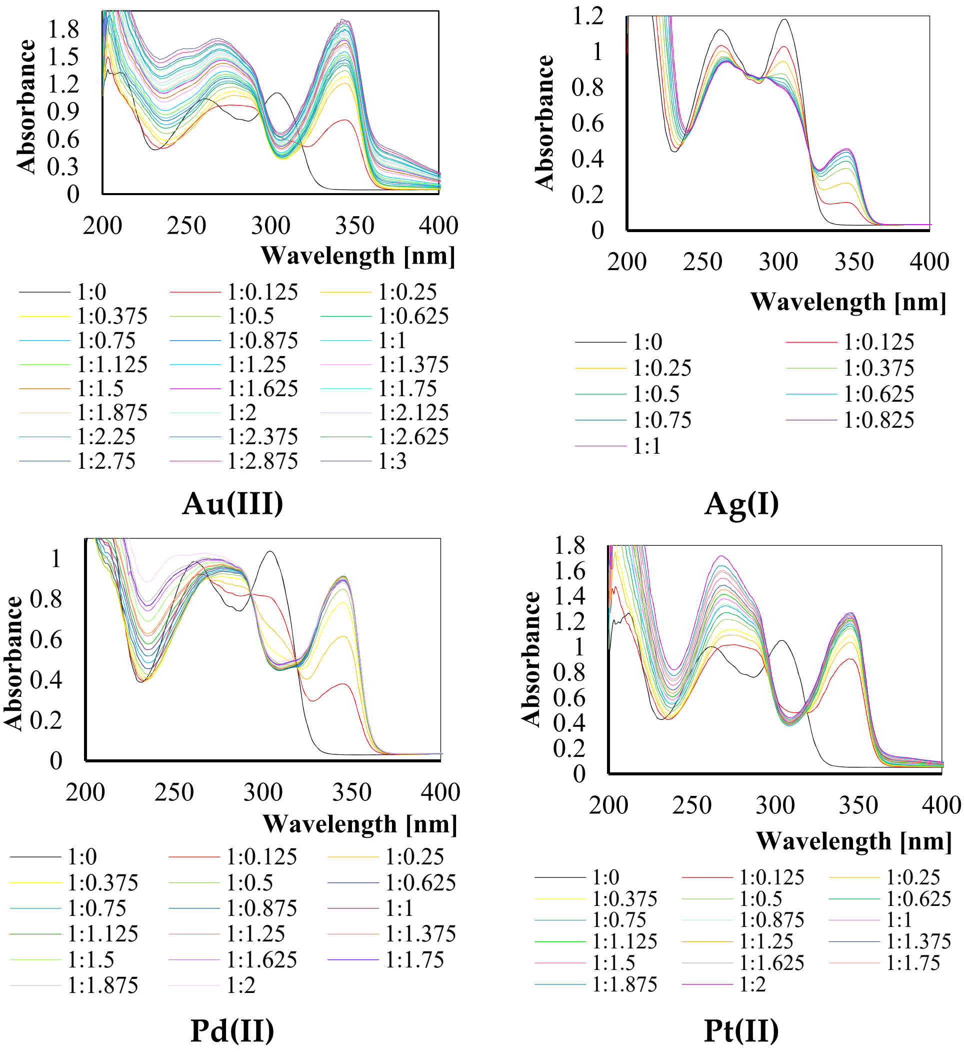

Figure 2. Absorption spectra of investigated systems of ligand to metal ions in various ratios (L:M).

The obtained absorption spectra are characterized by absorption bands together with the isosbestic points in the UV region wavelengths ranging from 200 to 400 nm. Constant changes in the shapes of recorded spectra are related to the creation of new complexes with various ratios of ligand to the metal ion. Based on the above spectra, the stability constants of complexes of 2,6-bis(4-methoxybenzoyl)-diaminopyridine with Au(III), Ag(I), Pd(II) and Pt(II) ions were calculated and are presented in Table 1.

Table 1. Stability constants of complexes of 2,6-bis(4-methoxybenzoyl)-diaminopyridine with Au(III), Ag(I), Pd(II) and Pt(II) ions in various ratios of L:M.

Metal Ion	**L—$C_{21}H_{19}N_3O_4$**		
	(L:M = 1:1)	**(L:M = 1:2)**	**(L:M = 1:3)**
	log K_1	**log K_2**	**log K_3**
Au(III)	5.540	4.851	4.607
Ag(I)	4.883	-	-
Pd(II)	4.917	5.398	-
Pt(II)	5.771	5.584	-

The given values of the log K carry ± 0.001 tolerance.

One valent, two valent and three valent metal ions created complexes of ligand to metal ion of type 1:1, 1:2 and 1:3, respectively. The most stable complexes were created by 2,6-bis(4-methoxybenzoyl)-diaminopyridine with platinum(II) ions. Only in the case of palladium(II) was its complex type 1:2 more stable than complex type 1:1, as the rest of the metal ions created exactly the most stable complexes (in which one metal ion is bound to one molecule of ligand). The values of the stability constants of complexes with two and three metal ions were lower. The values of the stability constants of complexes calculated previously with other metal ions were compared with the values obtained in this work and were equal for complex type 1:1 with Cu(II) ion 5.5 [27].

2.2. Classic Solvent Extraction

The dependence of the parameters obtained after the solvent extraction process (i.e., division ratio on the extraction percentage) is shown in Figure 3.

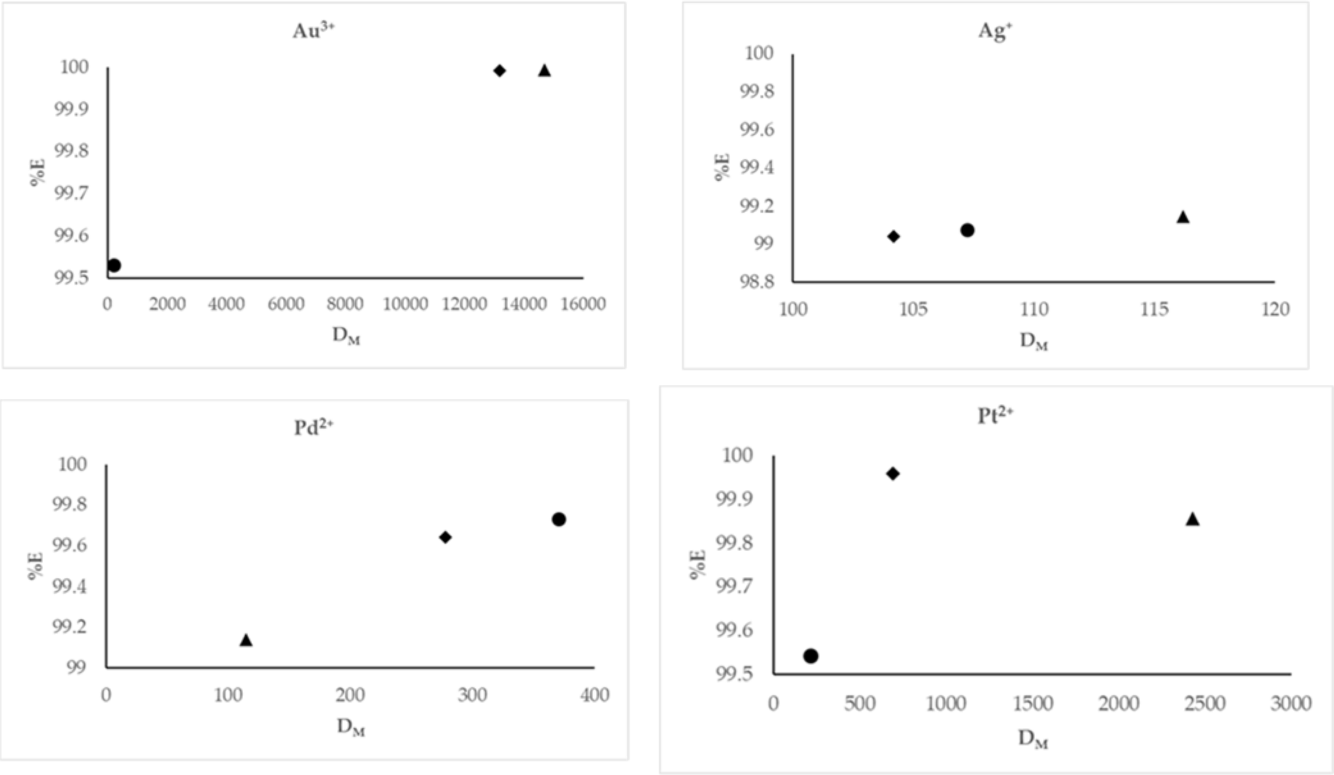

Figure 3. The dependence of the division ratio (D_M) on the extraction percentage (%E), where the ● is related to the M:L ratio 1:1, the ▲ is related to the M:L ratio 1:5, and the ◆ corresponds to the M:L ratio 1:10. The given values of %E carry ± 0.03 and D_M carry ± 0.025.

If after the extraction process the sum of the concentration of metal ions in the organic phase is higher compared to the sum of the concentration of metal ions in the aqueous phase, the division ratio (D_M) increases. The values of D_M impact the extraction percentage (%E), which is why the %E obtained for all extracted metal ions increased proportionally with increasing division ratios. The highest values of %E vs. D_M were for the ratio of M:L (metal:ligand) equaling 1:5 for gold, silver and platinum ions, while for palladium this value was the lowest.

Figure 4 shows the extraction percentages obtained for various molar ratios of analyzed noble metal ions and 2,6-bis(4-methoxybenzoyl)-diaminopyridine (*L*).

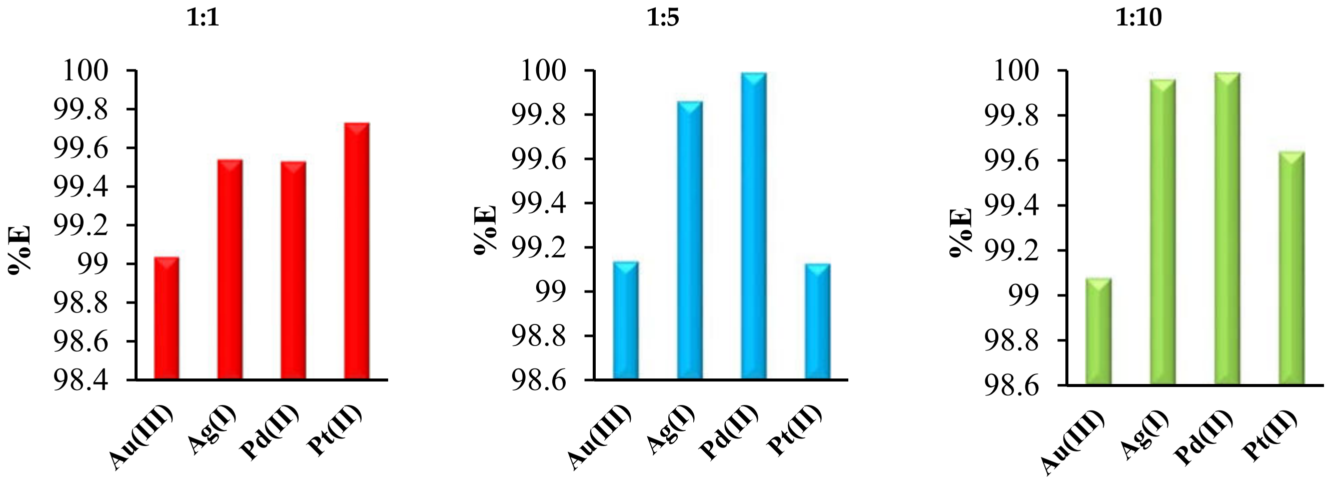

Figure 4. The extraction percentages obtained for various molar ratios of analyzed noble metal ions and 2,6-bis(4-methoxybenzoyl)-diaminopyridine (*L*, extractant).

Application of 2,6-bis(4-methoxybenzoyl)-diaminopyridine in the SE processes led to the removal of approximately 99% of all noble metal ions from the aqueous solutions. The influence of molar ratios (M:L) on the amount of metal ions removed was less significant. The best (but not much better) results for metal ions recovery were obtained when the M:L ratio was 1:10. For example, the %E of palladium ions was 99.5%, 99.9% and 99.9% when the M:L molar ratios during the extraction were 1:1, 1:5 and 1:10, respectively. The differences were very small. Based on the results of these and previous studies [27], it can be concluded that 2,6-bis(4-methoxybenzoyl)-diaminopyridine is a very effective extractant that might be used for the recovery of various metal ions, including gold, silver, platinum, palladium and copper.

2.3. Membrane Extraction and Back-Extraction Processes

The sorption and desorption of metal ions on/from polymer membranes was conducted according to the method described by Witt et al. [28].

The sorption capacities q_t were calculated according to Equation (3) for gold(III), silver(I), palladium(II) and platinum(II) for 24 h sorption processes and are presented in Table 2.

Table 2. The changes in sorption capacity of the membranes with 20 wt.% 2,6-bis(4-methoxybenzoyl)-diaminopyridine over time during sorption processes.

Metal Ions Time [h]	Au(III) q_t [mg/g]	Ag(I) q_t [mg/g]	Pd(II) q_t [mg/g]	Pt(II) q_t [mg/g]
4	0.3705	0.0326	0.0240	0.3794
6	0.3986	0.0388	0.3830	0.9588
12	0.5002	0.0923	0.4193	1.6790
24	0.9399	0.1080	0.6415	1.7516

The given values of the q_t carry ± 0.0015 tolerance.

The sorption capacity increased with the time of sorption. The highest q_t after 24 h of sorption process was observed for the membrane when the platinum ions were sorbed (q_t = 1.7516 mg/g), and the lowest was in the case of silver ions sorption (q_t = 0.1080 mg/g).

Figure 5 presents obtained results of %R_s.

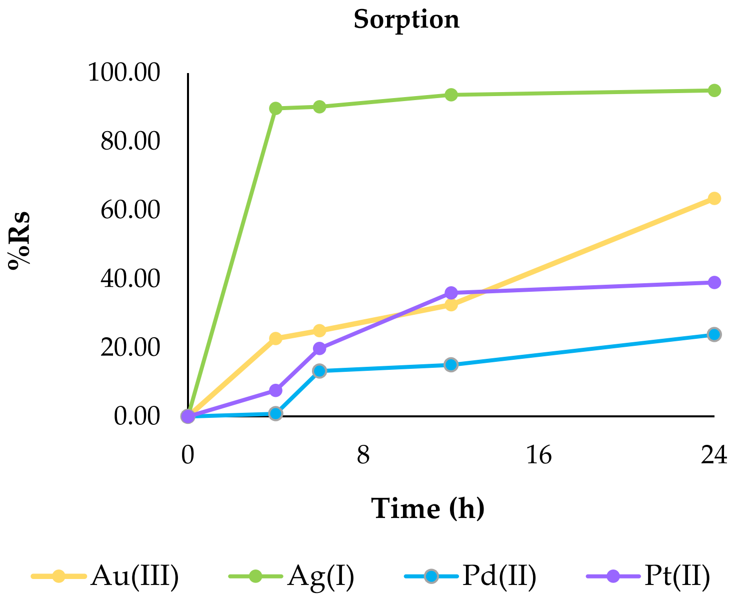

Figure 5. The percentage recovery of metals in the membrane (%R_s) after 24 h with 2,6-bis(4-methoxybenzoyl)-diaminopyridine as a carrier for gold(III), silver(I), palladium(II) and platinum(II) ions. The given values of %Rs carry ± 0.019.

The percentage of metal ion removal from the solutions (%R_s) for all metal ions increased following time, and that dependency was similar to the changes of the sorption capacity q_t parameter. The %R_s parameter for the investigated metal ions after 24 h of sorption decreased in following order: Ag(I) (94.89%) > Au(III) (63.46%) > Pt(II) (38.99%) > Pd(II) (23.82%). In the case of sorption of silver(I) ions, equilibrium was reached after 6 h. For other metal ions a longer time was needed.

In addition to sorption, the opposite process was also carried out. For desorption of Au(III), Ag(I), Pd(II) and Pt(II) ions from the surface of polymer membranes containing 2,6-bis(4-methoxybenzoyl)-diaminopyridine a solution of 5 mol/dm^3 of nitric acid was used. Figure 6 shows the percentage of metal ions desorbed as the sum of metal ions previously adsorbed on the surfaces of the membranes.

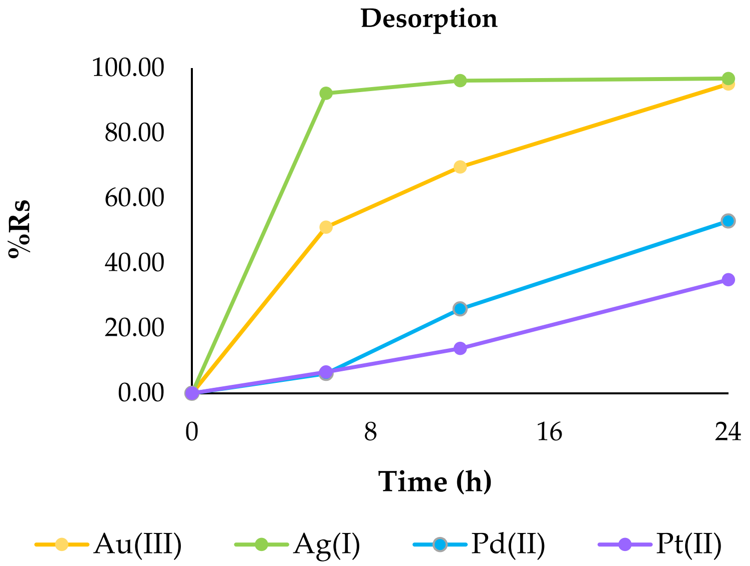

Figure 6. The sum of desorbed metal ions after 24 and 48 h. The given values of %R_{des} carry ± 0.019.

As a result of the desorption processes carried out, the metals adsorbed on the membrane surface were transferred into solutions. The metals were recovered into the concentrated solution, as its volume in relation to the solution used for sorption was three times smaller. The highest percentage recovery was observed after 48 h of desorption for silver (97.65%) and gold (96.62%) ions, whereas the lowest was for platinum (66.11%) and palladium (61.74%) ions. This confirms that by using membranes containing 2,6-bis(4-methoxybenzoyl)-diaminopyridine as a carrier it is possible not only to successfully adsorb metal, for example from wastewater, but also to transfer it to another concentrated aqueous phase and use this metal in further production processes.

Figure 7 shows the polymer membranes after the membrane extraction processes and membrane back-extraction processes.

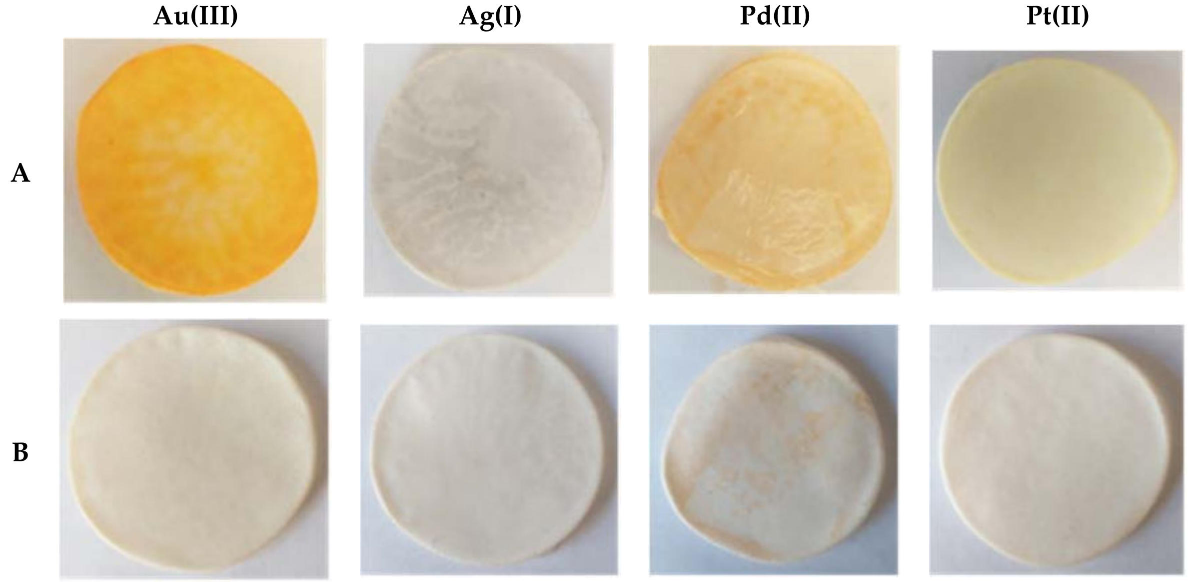

Figure 7. The polymer inclusion membranes containing 2,6-bis(4-methoxybenzoyl)-diaminopyridine after processes: membrane extraction (**A**), membrane back-extraction (**B**).

The above photos confirmed the efficiency of desorption processes, as it is clearly seen that metals adsorbed during sorption processes passed from the surfaces of the membranes (Figure 7A) into the solution of nitric acid. The surfaces of the membranes after desorption were colorless (Figure 7B).

3. Comparison of the Efficiency of Studied Processes

The results of the current research have shown that separation methods such as classic solvent extraction and membrane extraction are effective in recovering precious metals from aqueous solutions. The main aim of scientists involved in similar research is to find an effective extractant/carrier that will enable the high recovery of all precious metals. However, among the known extractants/carriers (Table 3), only 2,6-bis(4-methoxybenzoyl)-diaminopyridine enabled the effective recovery of gold, silver, palladium and platinum during the both the solvent extraction and membrane extraction processes.

Table 3. Selected metal ion extractants/carriers used in separation processes (SE, PM) for the recovery of noble metal ions.

2,6-bis(4-methoxybenzoyl)-diaminopyridine						**D$_2$EHAG**					
	Au(III)	Ag(I)	Pd(II)	Pt(II)	Ref.		Au(III)	Ag(I)	Pd(II)	Pt(II)	Ref.
SE	X	X	X	X	[This work]	SE	-	-	X	X	[29]
PM	X	X	X	X	[This work]	PM	X	-	-	-	[25]
Kelex 100						**Calix [4]pyrrole**					
	Au(III)	Ag(I)	Pd(II)	Pt(II)	Ref.		Au(III)	Ag(I)	Pd(II)	Pt(II)	Ref.
SE	-	-	X	X	[30,31]	SE	-	-	-	-	-
PM	X	-	-	-	[32]	PM	-	X	X	-	[23,33,34]
Cyphos IL 101						**Cyphos IL 102**					
	Au(III)	Ag(I)	Pd(II)	Pt(II)	Ref.		Au(III)	Ag(I)	Pd(II)	Pt(II)	Ref.
SE	X	-	X	-	[35–37]	SE	X	-	X	-	[35–37]
PM	-	-	X	-	[37]	PM	-	-	X	-	[37]
Cyphos IL 104						**Cyanex 302**					
	Au(III)	Ag(I)	Pd(II)	Pt(II)	Ref.		Au(III)	Ag(I)	Pd(II)	Pt(II)	Ref.
SE	-	-	X	-	[38]	SE	X	X	X	-	[39–42]
PM	X	-	X	-	[37,42]	PM	-	-	-	-	-

"X" indicates that the specified extractant/carrier can be used to recover the specified metal ions.

4. Materials and Methods

4.1. Materials

2,6-Bis(4-methoxybenzoyl)-diaminopyridine (*L*) (Figure 1) was synthesized following the procedure detailed in [27]. This compound is insoluble in water, but it is well soluble in organic solvents, e.g., chloroform, tetrahydrofuran, ethyl acetate or diethyl ether.

The other compounds used in the experiments, such as metal stock solutions with a concentration of 1000 mg/L (Au(III), Ag(I), Pd(II) and Pt(II)), concentrated nitric acid, ammonia, potassium hydroxide, chloroform and methanol were purchased from Avantor (Gliwice, Poland). All the reagents used in this work were of analytical grade and were used without further purification. Double-distilled water was used to dilute concentrated aqueous solutions.

The pH of aqueous solutions was measured using a SevenCompact series pH meter (Mettler Toledo, Greifensee, Switzerland), which was calibrated using commercial technical buffer solutions (Mettler Toledo, Greifensee, Switzerland) having pH values of 2.00, 4.01, 7.00 and 10.00. The metal ion concentration in the aqueous phases was determined using the atomic absorption spectroscopy method (AAS 240FS Spectrometer, Agilent, Santa Clara, CA, USA).

4.2. Determination of Stability Constants of Complexes of Au(III), Ag(I), Pd(II) or Pt(II) with 2,6-Bis(4-Methoxybenzoyl)-Diaminopyridine

Stability constants (log K) of complexes of 2,6-bis(4-methoxybenzoyl)-diaminopyridine with Au(III), Ag(I), Pd(II) and Pt(II) ions were determined according to the previously described method [27]. For this purpose, a methanol solution of L with the concentration of 3×10^{-5} mol/dm^3 and aqueous solutions of metal ions (M, each with a concentration of 100 mg/L) were prepared. When preparing solutions with different molar ratios of L:M, the appropriate higher amount of metal ion solution was added each time to a constant amount of ligand solution. The absorption spectra of obtained solutions were recorded, and stability constants of the created complexes of L with Au(III), Ag(I), Pd(II) and Pt(II) ions were calculated.

4.3. Separation Processes

The recovery of noble metal ions such as Au(III), Ag(I), Pd(II) and Pt(II) was carried out using 2,6-bis(4-methoxybenzoyl)-diaminopyridine in two different separation processes. The first process was classic solvent extraction (dynamic process), and the second was membrane extraction (static process) (Figure 8). Both processes resulted in separating metal ions from the aqueous phase.

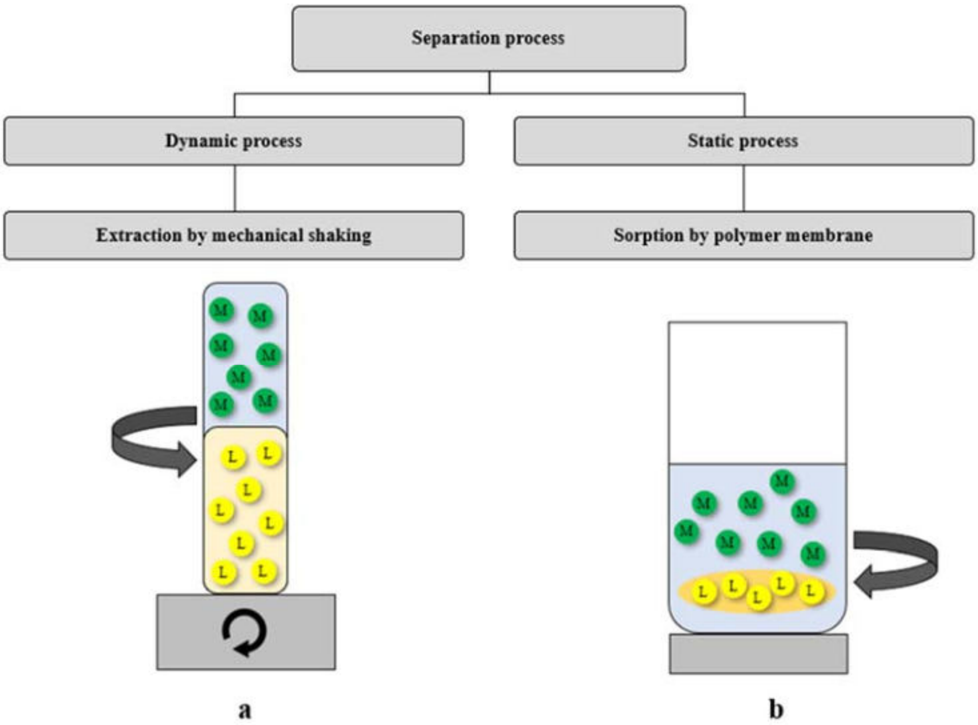

Figure 8. Scheme of the dynamic and static extraction processes, where *L*—2,6-bis(4-methoxybenzoyl)-diaminopyridine; (**a**) dissolved in the organic phase, (**b**) contained in a polymer membrane; M = Au(III), Ag(I), Pd(II) or Pt(II) ions in the aqueous phase.

For solvent extraction, 2,6-bis(4-methoxybenzoyl)-diaminopyridine (*L*) was dissolved in an organic solvent (chloroform), while in membrane extraction the ligand was immobilized in an organic polymer membrane.

4.3.1. Classic Solvent Extraction

Classic solvent extraction experiments were performed at 25 ± 0.2 °C. The proper concentration of metal ions in the aqueous solutions was obtained by dilution of stock solutions of metal ions, the concentration of which was 1000 mg/L. The limit of concentration of metal ions in different samples was from 0.0004 to 0.0016 mol/dm^3. The stock solution of the 2,6-bis(4-methoxybenzoyl)-diaminopyridine (*L*) had a concentration of 0.008 mol/dm^3 in chloroform. The chloroform solution of L was added to the same volume of the aqueous solution. The volume of both phases (aqueous phase and organic phase) was 1100 μL. The molar ratios of the concentration of metal ions in aqueous solution to the ligand in organic solution were 1:1, 1:5 and 1:10, respectively.

Prepared samples were then shaken for one hour. The equilibrium was established after approximately 30 min by visual inspection. Changes in the phase volumes were checked, the phases were then separated, and the pH and metal ion concentration of the aqueous phase were determined. Based on these measurements the parameters of solvent extraction, i.e., the extraction percentage (%E, Equation (1)) and the division ratio (D_M, Equation (2)) were calculated.

The extraction percentage is a parameter that takes into account the partition coefficient and the volume of the aqueous (V_{aq}) and organic (V_{org}) phases. The division ratio is the ratio of the sum of the concentrations of all the substances in the organic phase ($\Sigma[M]_{org}$) to the sum of the concentrations of all the substances in the aqueous phase ($\Sigma[M]_{aq}$) [43].

$$\%E = \frac{D_M}{D_{M+\frac{V_{aq}}{V_{org}}}} \times 100\% \tag{1}$$

$$D_M = \frac{\Sigma[M]_{org}}{\Sigma[M]_{aq}} \tag{2}$$

4.3.2. Membrane Extraction Processes

The Preparation of Polymer Membranes

To prepare the membranes, a solution containing 60 wt.% polyvinylchloride (PVC) as support, 20 wt.% a bis(2-ethylhexyl)adipate (ADO) as a plasticizer and 20 wt.% a 2,6-bis(4-methoxybenzoyl)-diaminopyridine as an ion carrier was prepared in 10 cm^3 of tetrahydrofuran. Next, the solutions were poured onto ANUMBRA Petri dishes. After slow evaporation of the solvent for 24 h, the resulting polymer membranes (PMs) (Figure 9) were peeled off from the Petri dishes. Through the next 12 h, PMs were immersed in distilled water. The membranes were homogeneous, transparent, flexible and had good strength. The mean thickness of the membranes was determined as described previously [44]. The thickness of the membranes used for Au(III), Ag(I), Pd(II) and Pt(II) ion extraction was approximately 0.265 cm.

Figure 9. The polymer membrane with 20 wt.% of 2,6-bis(4-methoxybenzoyl)-diaminopyridine before the membrane extraction process.

Membrane Extraction and Back Extraction Experiments

The circular polymer membranes were immersed in beakers containing one of the noble metal ions, such as Au(III), Ag(I), Pd(II) or Pt(II). The solutions of metal ions (volume 30 cm^3) used as feed phase contained 3 mg/L of metal ions (pH solution was from 1.521 to 2.121). During the static processes, the metal ions from the solutions were bound to the surfaces of the membranes (sorption process). Small samples of well-defined volumes were taken from the solutions at regular intervals for 24 h to determine the concentration of metal ions in the solutions.

Analysis of the sorption processes of metal ions on membranes with 20 wt.% of 2,6-bis(4-methoxybenzoyl)-diaminopyridine as a carrier was performed using Equation (3):

$$q_t = \left(\frac{c^i - c^t}{m}\right) \cdot V \tag{3}$$

where q_t—the sorption capacity (mg/g), V—the volume of the solution (dm^3), m—the mass of the membrane (g), and c^i and c^t—the analytical concentration of metal ions in the solution at the beginning and after a determined period of the sorption process (mol/dm^3), respectively [45].

After 24 h of sorption, the percentage of metal ion removal from the solutions ($\%R_s$) was also determined (Equation (4)).

$$\%R_s = \frac{c^0 - c^i}{c^0} \times 100\% \tag{4}$$

where: c^0 and c^i denote analytical concentrations of metal ions in the solution at the beginning and after an appropriate period of the sorption process [28].

After extraction processes, the applied polymer membranes were immersed in 10 cm^3 5 mol/dm^3 HNO_3 solutions for 24 h to desorb metal ions from the membrane surfaces. The desorption efficiency ($\%R_{des}$) was calculated using formula 5.

$$\%R_{des} = \frac{c^i}{c^a} \times 100\% \tag{5}$$

where c^a refers to the initially sorbed concentration of metals during the desorption process [28,46].

5. Conclusions

As a result of the performed separation processes, i.e., dynamic classic solvent extraction (mechanical shaking) and static membrane extraction (polymer membranes) using 2,6-bis(4-methoxybenzoyl)-diaminopyridine, it was found that this compound proved to be more efficient in SE processes. Presumably, shaking has a beneficial effect on the process of binding of noble metal ions by the studied compound (recovery of more than 99% of gold, silver, palladium and platinum ions). However, despite the high efficiency of this process, a relatively large amount of organic solvent (chloroform) was used, and the recovered metal ions remained bound to the extractant in the organic phase. Due to its sustainable chemistry, static membrane extraction appears to be the more advantageous process, despite the lower percentage recovery of metals from solutions. The recovery was the highest for silver (Ag(I) (94.89%)) and gold (Au(III) (63.46%)) ions, whereas for platinum and palladium ions it was much lower (Pt(II) (38.99%), Pd(II) (23.82%)). Moreover, the results of the performed desorption processes showed a high percentage of recovery, e.g., for gold and silver ions over 96% after 48 h. The reduction in the use of toxic solvents is important for economic and environmental reasons. The synthesis of 2,6-bis(4-methoxybenzoyl)-diaminopyridine is relatively cheap and simple. The obtained results show that 2,6-bis(4-methoxybenzoyl)-diaminopyridine may be potentially used in the future on a larger scale. One of the important areas of practical application of the tested compound may be the recovery of noble metal ions from solutions obtained as a result of WEEE leaching. The proposed methods (classic solvent extraction and polymer membrane extraction) may also be useful for the recovery of these metal ions from industrial wastewater.

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The Copper(II) Ions Solvent Extraction with a New Compound: 2,6-Bis(4-Methoxybenzoyl)-Diaminopyridine

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Abstract: A new compound 2,6-bis(4-methoxybenzoyl)-diaminopyridine (L) was used as an extractant for copper(II) ion recovery in a solvent extraction conducted at a temperature of 25 °C. The best results (99% recovery of copper(II) ions) were obtained when the aqueous phase contained 0.001 mol/dm^3 Cu(II) and 0.2 mol/dm^3 NH_3 (pH~5.8), while the organic phase was a 0.001 mol/dm^3 chloroform solution of 2,6-bis(4-methoxybenzoyl)-diaminopyridine. Spectrophotometry studies were used to determine the dissociation constant of the tested compound and determine the stability constant of the complex of subjected compound with copper(II) ions. The high-resolution mass spectrometry (HRMS) and higher energy collisional dissociation tandem mass spectrometry (HCD MS/MS) methods have been applied for the confirmation of the structure of 2,6-bis(4-methoxybenzoyl)-diaminopyridine and to determine its complexation with Cu(II) in solution.

Keywords: solvent extraction; 2,6-bis(4-methoxybenzoyl)-diaminopyridine; dissociation constant; stability constant; mass spectrometry

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1. Introduction

There are many separation processes of metal ions from water solutions. One of the most often used is the solvent extraction. Applications of liquid-liquid extraction can be found in industries such as petrochemical, pharmaceutical and hydrometallurgical. Hydrometallurgy helps concentrate metals like zinc or copper, for electrowinning as well as for separating the complex metallic system, for example, nickel/cobalt and other metal ions [1]. This method can be used for the selective separation of other metal ions: Zn(II), Cd(II), Al(III), Co(II), Ni(II) [2–6] or Cu(II) [7,8]. The copper is widely used in the industry because of its properties, therefore it can be found in electrical materials, construction, transport and industrial machines [9]. The recovery of copper(II) ions is very important for environmental protection. Copper belongs to not biodegradable metals. This metal has a tendency to accumulate in animals and humans organism, causing various diseases and disorders [10]. As a result of the application of copper in the industry its ions are present in the wastewaters and waste solutions originating from the electronic, electroplating etc. [11]. Therefore, the recovery of copper(II) ions is the subject of many studies, because copper salts are cheap and easy to obtain as well as being less dangerous than salts of other transition metals [12]. For this purpose various methods such as precipitation, coagulation, adsorption, ion exchange, membrane separation and solvent extraction are used [2].

In the extraction process, we used organic solvents and an extractant. The main success of the extraction processes is determined by the selection of an appropriate extractant [13], which from the economical point of view would be able to recovery at least 90% of metal ions from the treated water solutions. Nowadays, the common extractants for copper(II) that are available commercially are expensive. Therefore, new extractants are constantly being searched for.

In literature a lot of information can be found about aminopyridines. This group of compounds can create complexes with transitional metal ions. For example, ions like Cu(II), Zn(II), Co(II) and Cd(II) can participate in the formation of macrocyclic complexes with 2,6-diaminopyridine [14]. There are known complexes of Schiff-base macrocyclic ligands. Ilhan et al. composed a new compound of 2,6-diaminopyridine and 1,7-bis(2-formylphenyl)-1,4,7-trioxaheptane [15], and 2,6-diaminopyridine and 1,6-bis(2-formylphenyl) hexane [16] and characterized their complexes. Presented examples prove the high affinity of these compounds to metal ions. Nonetheless, there is little information about metals recovery using aminopyridines. Zhai et al. were someof the first to investigate the selective magnetic extraction of copper and zinc ions in solid phase using modified silica coated Fe_3O_4 nanoparticles with 2,6-diaminopyridine. They obtained high extraction efficiencies [17].

The results obtained in the referenced articles inspired us to attempt to use a derivative of 2,6-diaminopyridine for metal ions extraction from aqueous solutions.

In this paper for the first time a 2,6-bis(4-methoxybenzoyl)-diaminopyridine ($C_{21}H_{19}N_3O_4$) derived from 2,6-diaminopyridine was used as new extractant for copper(II) ions recovery. This work aimed to check the ability of this compound to be used in the solvent extraction process.

To achieve this aim, the structure of the obtained compound should be known and its complexation with copper(II) in solution measured. Moreover, the dissociation constant of the studied compound and constant stability of L: Cu^{2+} should be determined.

2. Materials and Methods

2.1. Synthesis and Properties of 2,6-Bis(4-Methoxybenzoyl)-Diaminopyridine

The structure of the compound 2,6-bis(4-methoxybenzoyl)-diaminopyridine (L) used in the studies is shown in Figure 1. All the substrates for the synthesis of 2,6-bis(4-methoxybenzoyl)-diaminopyridine were purchased from Sigma-Aldrich and used without further purification. The synthesis procedure consisted of the following steps: (a) to the magnetically stirred solution of 2,6-diaminopyridine (Sigma Aldrich, Poznań, Poland) and triethylamine (Sigma Aldirch, Poznań, Poland) in dry tetrahydrofuran (THF) (Avantor, Gliwice, Poland) (at 4 °C) the 4-methoxybenzoyl chloride (Sigma Aldrich, Poznań, Poland) was added (solution in dry THF) dropwise (15 min), (b) the mixture was stirred overnight, evaporated and treated with chloroform and water mixture, (c) the chloroform (Avantor, Gliwice, Poland) layer was separated, washed with water, dried with $MgSO_4$ (Avantor, Gliwice, Poland) and evaporated, and (d) the residue was recrystallized from THF/hexane. The method of the synthesis has been described in detail elsewhere [18].

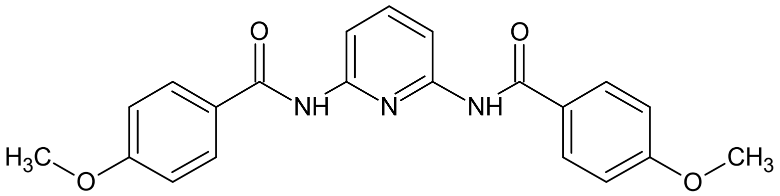
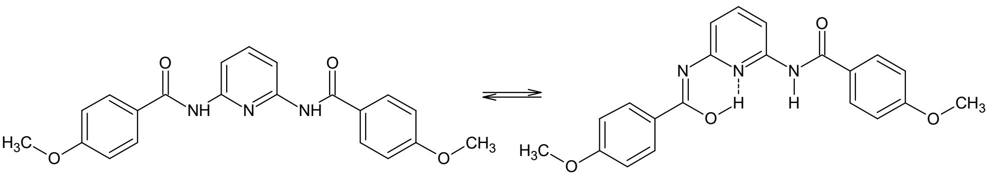


Figure 1. Structure of compound 2,6-bis(4-methoxybenzoyl)-diaminopyridine ($C_{21}H_{19}N_3O_4$).

The presence of NH group between two electron acceptors (C=O and pyridine ring) in the obtained compound (L) approaches it to the β-diketone molecule [19] in the light of its tautomerism. That is why the studied compound can probably undergoes tautomerism according to Equation (1) [20]. The obtained enol form may be stabilized by intramolecular hydrogen bonding.



(1)

2.2. Other Reagents

The copper(II) nitrates, both of analytical reagent grade (Avantor, Gliwice, Poland) were recrystallized from distilled water. The concentration of the potassium nitrate solution was determined gravimetrically as potassium sulphate, whereas the concentration of the aqueous copper ion solutions were standardized by titration using EDTA solution or by the atomic absorption spectrometry method. Nitric acid (analytical reagent grade was obtained from Avantor Company, Gliwice, Poland) was standardized against anhydrous sodium carbonate. Ammonia was obtained from Avantor, Gliwice, Poland (analytical reagent grade). Carbonate free potassium hydroxide (the titrant, Avantor, Gliwice, Poland) was prepared and standardized against a standard potassium hydrogen phthalate solution. Chloroform and methanol (analytical reagent grade, Avantor, Gliwice, Poland) were used as received. The pH-meter was calibrated using commercial technical buffer solutions (Mettler Toledo, Greifensee, Switzerland) having a pH of 2.00, 4.01, 7.00, and 10.00.

2.3. Mass Spectrometry

All mass spectrometry experiments were performed on the Q-Exactive Orbitrap mass spectrometer (Thermo Scientific, Bremen, Germany). Samples of the compound 2,6-bis(4-methoxybenzoyl)-diaminopyridine (L) and $Cu(NO_3)_2$ (Avantor, Gliwice, Poland) were dissolved in methanol (Avantor, Gliwice, Poland) and distilled water (1:1) respectively, to a concentration of 1 mmol/dm^3. Analytical solutions of L and metal salt were prepared (1:1, 1:4 and 1:10) in methanol to give a final concentration of 10 mmol/dm^3, before being introduced into the mass spectrometer using an electrospray source. Data acquisition and analysis were conducted using the Xcalibur (Thermo Xcalibur 4.1.31.9, Waltham, USA) software. All mass spectra were obtained with a resolution of 70,000 at m/z 200. HCD MS/MS experiments were performed with nitrogen gas (gas generator NiGen LCMS 40-1, Tremezzina, Italy) at a normalized collision energy of 35%.

2.4. Dissociation Constant (pK_a) of 2,6-Bis(4-Methoxybenzoyl)-Diaminopyridine

The dissociation constant (pK_a) of 2,6-bis(4-methoxybenzoyl)-diaminopyridine (L) was determined by the spectrophotometric method. Solution of (L) in methanol with a concentration of 0.0011 mol/dm^3 was prepared. Than the 11 solutions were prepared to spectrophotometric measurements in this way that to appropriate amount of the stock solution was added an appropriate amount of one of the commercial technical buffer solution (Mettler Toledo, Greifensee, Switzerland) having a pH of 2.00, 4.01, 7.00, 9.21 or 10.00. For absorption measurements a wavelength of 264 nm was used.

2.5. Determination of Cu-Ligand Stability Constant

To calculate the stability constant of the complex of copper(II) ions with ligand (2,6-bis(4-methoxybenzoyl)-diaminopyridine) it was necessary to record their absorption spectra. For this purpose, a stock solution of copper ions with a concentration of 0.0016 mol/dm^3 and solution of ligand in methanol ($2.65 \cdot 10^{-5}$ mol/dm^3) were made. Then the appropriate amounts of copper ion solution and methanol solution of the ligand were mixed to prepare samples for a spectrophotometric analysis. The absorption spectra of the prepared samples were recorded on Cary 50 spectrophotometer

(Varian, Melbourne, Victoria, Australia) with varying molar ratios of the components (L: cation). The spectra were recorded in the range of the wavelength 200 to 450 nm.

2.6. Extraction Procedure

The measurements were run at 25 °C and a fixed ionic strength maintained in the aqueous phase with 0.5 mol/dm^3 solution of potassium nitrate. The aqueous phase contained 0.001 mol/dm^3 Cu(II) ions and 0.2 mol/dm^3 NH_3 (pH~5.8), the organic phase contained 0.001 mol/dm^3 ligand in chloroform. Ammonia was used for pH adjustment during the extraction process. Copper hydroxide starts to precipitate in pH~7.5.

A 4.5 cm^3 of aqueous phase was introduced to each of the five graduated test tubes. Then a chloroform solution of (L) was added to each test tube, in this way that the volume of the organic phase was always equal to the volume of the aqueous phase but the concentration of the ligand was varied in the range from 0.0001 to 0.001 mol/dm^3 (samples I-V). The prepared samples were then shaken for one hour. The equilibrium was established after approximately 15 min. It was checked to see if any changes in the phase volumes had occurred, then the phases were separated and the pH of the aqueous phase was measured. The Cu(II) concentration in the aqueous phase was determined by atomic absorption spectrophotometry (AAS 240FS Spectrometer, Agilent, Santa Clara, CA, USA).

3. Results and Discussion

3.1. Characterization of 2,6-Bis(4-Methoxybenzoyl)-Diaminopyridine and Its Complexation with Cu(II) by Mass Spectrometry Methods

The structure of 2,6-bis(4-methoxybenzoyl)-diaminopyridine (L) and its ability to form complexes with copper(II) ions in solution was confirmed by application of the electrospray ionization high-resolution mass spectrometry (ESI HRMS) and higher energy collisional dissociation tandem mass spectrometry (HCD MS/MS) methods. ESI is a soft ionization technique, which enables most of the small molecules analyzed to be transferred directly from the solvent into the mass spectrometer without change in their structures [21]. HRMS methods, based on measurement of the mass-to-charge ratio (m/z) of the analyte ions in the gas phase were characterized by high mass accuracy and sensitivity, which were necessary for the precise determination of the elemental composition and charge of the ions formed. HCD tandem mass spectrometry method, which is variation of traditional collision induced dissociation technique (CID), enabled the controlled decomposition of selected ions of a given chemical compound into smaller fragments (as a result of inelastic collisions of ions with inert gases). Analysis of the resulting fragmentation products provided information about the structure of analyte ions [22].

Electrospray ionization of the solution containing 2,6-bis(4-methoxybenzoyl)-diaminopyridine (L) led to the formation of singly charged ions $[L+H]^+$ ($C_{21}H_{20}N_3O_4$, $m/z_{meas} = 378.1440$, $m/z_{calc} = 378.1453$) of the analyzed compound. HCD of $[L+H]^+$ ions led to the formation of a series of products, some of which were generated as a result of intramolecular rearrangements. Figure 2 shows the proposed $[L+H]^+$ ions HCD fragmentation pathways and chosen products structures. However, for some of the generated products, in addition to the structures shown in Figure 2 other ways of combining the atoms in the molecules should also be considered (for example structures differing by the location of the OH group attached to the pyridine ring in $[C_{13}H_{12}O_3N_2+H]^+$ or by the location of the charge in $[C_{13}H_{11}O_2N_2]^+$). It cannot be excluded that some of the generated products result from secondary fragmentation reactions.

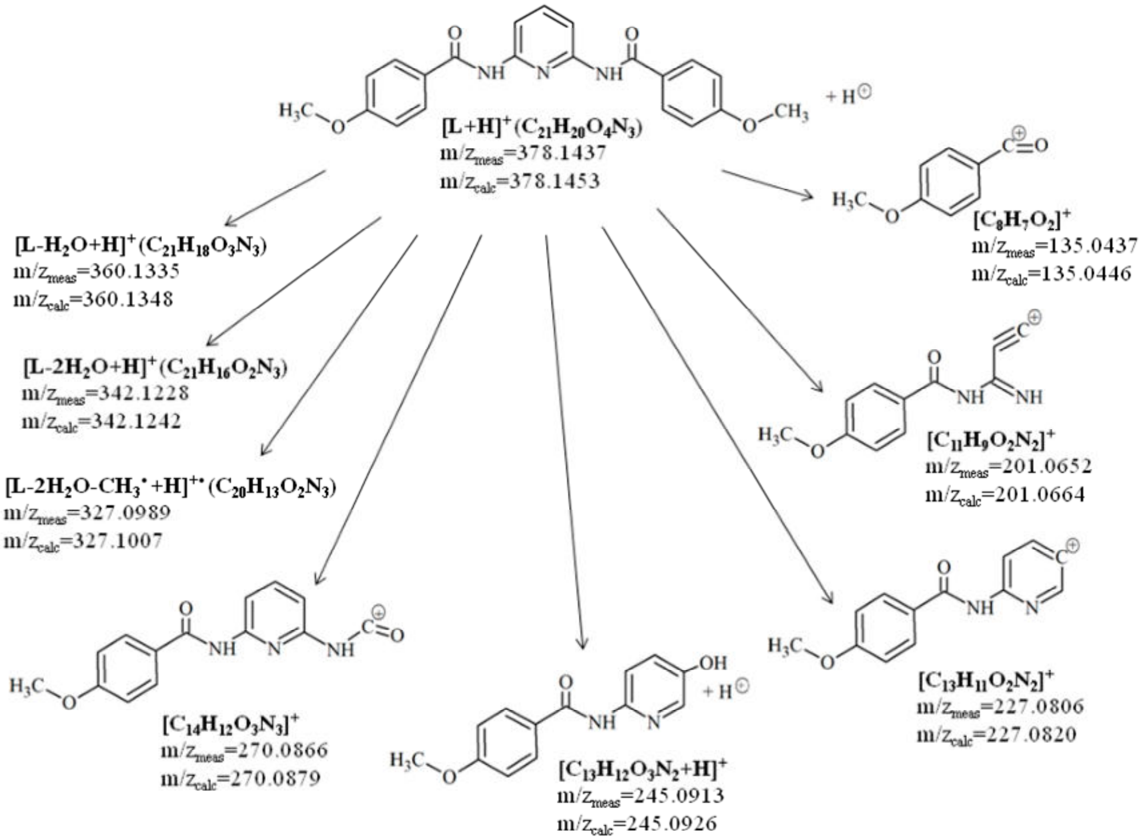


Figure 2. Proposed $[L+H]^+$ ions higher energy collisional dissociation (HCD) fragmentation pathways and products structures.

Detailed analysis of the fragmentation processes is not the subject of this work but the results of ESI HCD MS/MS experiments performed for singly charged ions $[L+H]^+$, allow for confirmation of the structure of the L compound. In comparison with conventional structure confirmation methods, (for example a combination of NMR or IR and elemental analysis), HCD provides simple mass spectra that are straightforward and easy to interpret.

Electrospray ionization of all of the examined solutions containing analytical mixtures of 2,6-bis(4-methoxybenzoyl)-diaminopyridine (L) and $Cu(NO_3)_2$ (molar ratios: 1:1, 1:4 and 1:10) led to the formation of singly charged ions: $[C_{13}H_{13}O_2N_3+H]^+$ (m/z_{meas} = 244.1075, m/z_{calc} = 244.1086), $[L+H]^+$ ($C_{21}H_{20}N_3O_4$, m/z_{meas} = 378.1441, m/z_{calc} = 378.1453), $[CuNO_3{}^+{+}L]^+$ ($C_{21}H_{19}N_4O_7Cu_1$, m/z_{meas} = 502.0533, m/z_{calc} = 502.0549), $[Cu^{2+}{+}2L{-}H]^+$ ($C_{42}H_{37}N_6O_8Cu_1$, m/z_{meas} = 816.1959, m/z_{calc} = 816.1968). Ions $[C_{13}H_{13}O_2N_3+H]^+$ were probably formed as a result of small part of L molecules decomposition in the methanol/water solution, or in electrospray ionization process, or during compound storage. Regardless of the origin of the $[C_{13}H_{13}O_2N_3+H]^+$ ions, the most intensive signals on ESI HRMS spectra corresponded to singly charged $[L+H]^+$ ions, which confirms that only a small part of L molecules had been decomposed. Moreover, HRMS spectra showed signals corresponding to complexes formed by L molecules with copper ions (i.e., $[CuNO_3{}^+{+}L]^+$, $[Cu^{2+}{+}2L{-}H]^+$), but did not show signals which could be assigned to complexes formed by $[C_{13}H_{13}O_2N_3+H]^+$ fragments with Cu(II) ions. The ESI HRMS spectrum of the analyzed methanol solution of the mixture of L with metal salt (1:4) is shown in Figure 3. Differences in the molar concentrations of the compound L and copper ions do not affect the type of ions formed but influence the intensity of the signals corresponding to generated products.

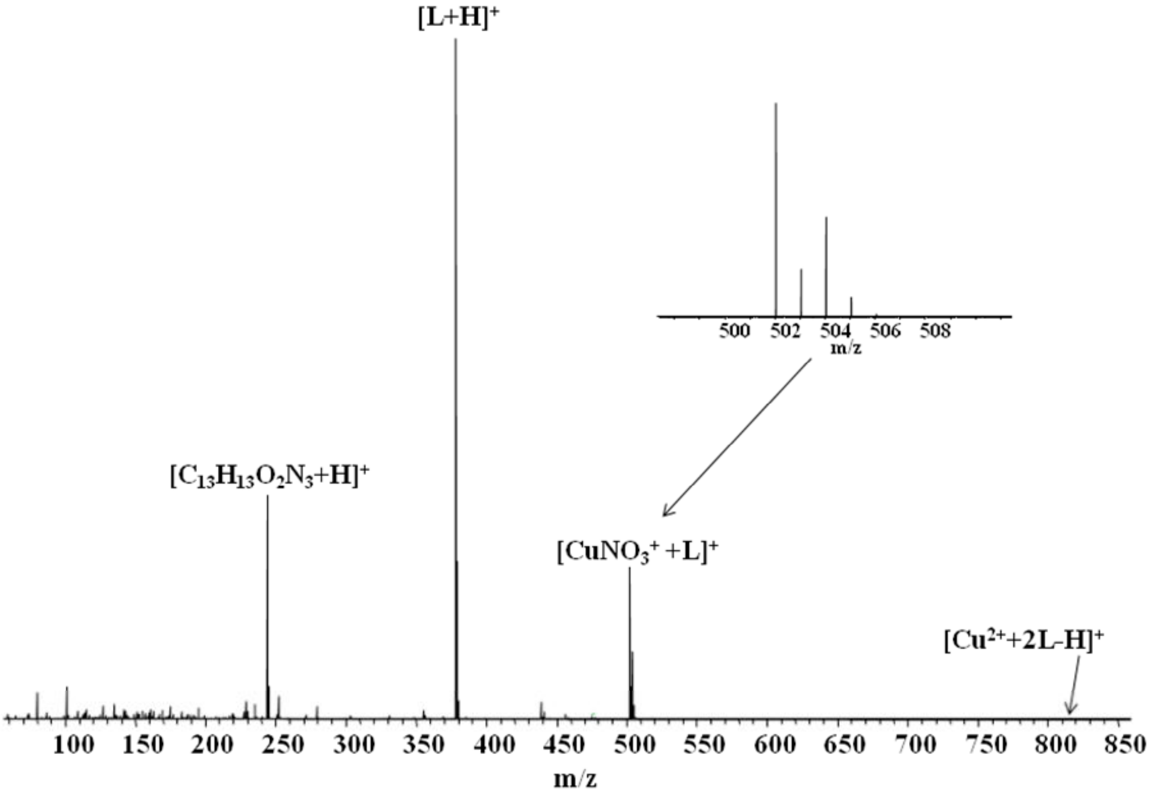
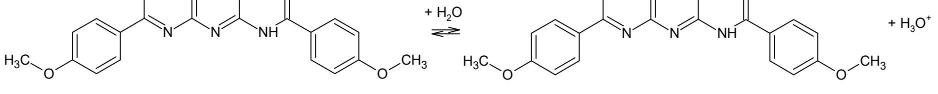


Figure 3. Electrospray ionization (ESI) (+) HRMS mass spectrum of analytical mixtures of L (2,6-bis(4-methoxybenzoyl)-diaminopyridine) and $Cu(NO_3)_2$ (molar ratios: 1:4) in methanol. The inset shows the distribution of the isotopic envelope.

Given the high mass accuracy of the HRMS mass spectrometry, there can be no question as to the elemental composition or charge of the ions formed. Based on the results of the performed HRMS experiments, it is possible to conclude that in the process of the formation of copper(II) ions complexes with 2,6-bis(4-methoxybenzoyl)-diaminopyridine can participate both the entire and the deprotonated ligand molecules. It should be emphasized that the HRMS spectrum only shows signals corresponding to ions and the HRMS method does not allow the detection of neutral complexes that can also be formed, e.g., [Cu^{2+}+2L-2H]. Nevertheless, the results of ESI HRMS experiments clearly confirm that molecules of 2,6-bis(4-methoxybenzoyl)-diaminopyridine (L) are able to form various complexes with Cu(II) ions, but they do not allow to determine all types of possible complexes.

3.2. Dissociation Constant of 2,6-Bis(4-Methoxybenzoyl)-Diaminopyridine

The spectrum of the non-ionized form of the compound is fundamentally different from that of the ionized form. The proposition of dissociation reaction for 2,6-bis(4-methoxybenzoyl)-diaminopyridine is presented by the following equation:



$$C_{21}H_{19}N_3O_4 \xrightleftharpoons{+\,H_2O} C_{21}H_{18}N_3O_4^- + H_3O^+ \quad (2)$$

The equilibrium constant pK_a of the above reaction (dissociation constant of the 2,6-bis(4-methoxybenzoyl)-diaminopyridine) is defined as follows:

$$K_a = \frac{\left[C_{21}H_{18}N_3O_4^-\right][H_3O^+]}{[C_{21}H_{19}N_3O_4]} \tag{3}$$

From here:

$$-logK_a = pK_a = pH + log\frac{[C_{21}H_{19}N_3O_4]}{[C_{21}H_{18}N_3O_4-]} \tag{4}$$

To determine the characteristic pK_a value of the test compound, the ratio of the concentration of the non-dissociated to dissociated form at the appropriate pH was determined spectrophotometrically. Using the same solution concentrations in subsequent measurements, the formulas for pK_a can be so expressed for acid:

$$pK_a = pH + log\frac{A_1 - A}{A - A_M} \tag{5}$$

where for the selected wavelength: A_1—absorbance of the completely ionized form ($C_{21}H_{18}N_3O_4^-$), A_M—absorbance of the non-ionized form ($C_{21}H_{19}N_3O_4$), A—absorbance of a mixture of both forms at a given pH.

For a more precise pKa determination, several measurements were made at different pH values and the mean value was calculated.

The absorption curve (Figure 4) of the ionized form intersects with the absorption curve of the non-ionized form in the so-called isosbestic point. At this point all the curves of the examined system intersect, regardless of the ratio value $[C_{21}H_{19}N_3O_4]/[C_{21}H_{18}N_3O_4^-]$, because the sum $[C_{21}H_{19}N_3O_4] + [C_{21}H_{18}N_3O_4^-] = C_0$ remains constant which is easy to prove.

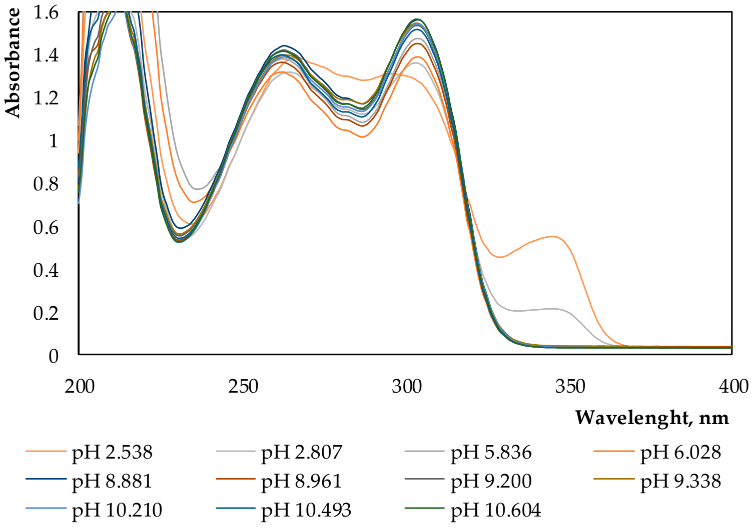


Figure 4. Acid–base balance spectra of 2,6-bis(4-methoxybenzoyl)-diaminopyridine.

The dissociation (pK_a) of investigated ligand determined using the described method was equal to 5.72. The dissociation constant was determined for further adjustment of appropriate conditions to solvent extraction (pH). The obtained value indicated that the best conditions for extraction of metal ions using 2,6-bis(4-methoxybenzoyl)-diaminopyridine were between pH from 5.72 to 7.5. Outside this range, extraction was inhibited for following reasons. First, below the pH value of 5.72 the compound exists only in non-ionized form, which is not able to bind other cations (Equation (2)). Secondly, above pH of 7.5 occurs concurrent reaction a hydrolysis of metal ions. Formation of hydroxides interferes in the process of recovery metal ions from the solution. Addition of ammonia solution during extraction process prevents creation of metal hydroxides according to reaction:

$$[Cu(H_2O)_4]^{2+} + 4NH_{3aq} \leftrightarrow [Cu(NH_3)_4]^{2+} + 4H_2O \tag{6}$$

3.3. Determination of the Stability Constant

The UV spectrum of the complex of copper(II) ions with 2,6-bis(4-methoxybenzoyl)-diaminopyridine is shown in Figure 5. The obtained spectrophotometric spectra are characterized by absorption bands in the UV region between the wavelength 250 and 380 nm.

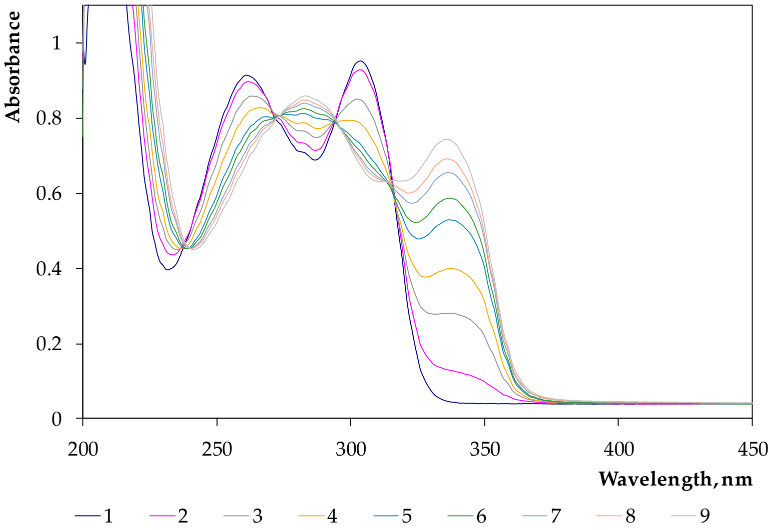


Figure 5. Absorption spectra of Cu(II) complexes with 2,6-bis(4-methoxybenzoyl)-diaminopyridine in various [L] vs. [Cu(II)] molar ratios: 1:0 (1), 1:0.125 (2), 1:0.25 (3), 1:0.375 (4), 1:0.5 (5), 1:0.625 (6), 1:0.75 (7), 1:0.875 (8), 1:1 (9).

Figure 5 shows that Cu/(2,6-bis(4-methoxybenzoyl)-diaminopyridine) complexes were formed in the studied systems. Vanishing of the bands due to ligand $C_{21}H_{19}N_3O_4$ (262 nm and 305 nm) and the appearance of new bands (287 nm and 337 nm) together with the isosbestic points at 273 nm and 297 nm were also recorded.

Based on absorption spectra the stability constant (*K*), was calculated using the Pawlicki et al. [23] method.

The stability constant was determined using Equation (7):

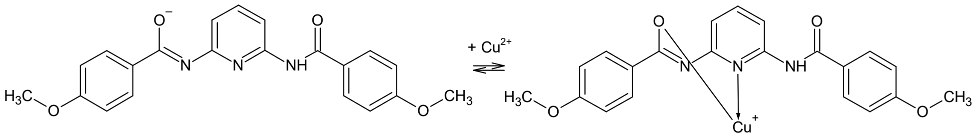
$$\frac{1}{(\varepsilon - \varepsilon_L)} = \frac{1}{K(\varepsilon_C - \varepsilon_L)} \cdot \frac{1}{[Cu(II)]} + \frac{1}{(\varepsilon_C - \varepsilon_L)} \tag{7}$$

where: $1/(\varepsilon - \varepsilon_L) = y$, $1/[Cu(II)] = x$, *Cu(II)* is the molar concentration of *Cu(II)* ions, mol/dm^3, $\varepsilon = A/L$, A is the absorbance of the system at 304 nm, *L* is the molar concentration of the ligand ($C_{21}H_{19}N_3O_4$), mol/dm^3, ε_L is the molar absorption coefficient of the ligand at 304 nm, and ε_C is the molar absorption coefficient of the complex.

The determined value of the stability constant (log *K*) of *Cu(II)*/(2,6-bis(4-methoxybenzoyl)-diaminopyridine) complex, in which molar ratio *L* vs. Cu(II) is 1:1, were equal to 5.5 ± 0.1.

3.4. Solvent Extraction

One of the possible, most likely coordination processes of coordination copper ions to investigated ligand during extraction is presented using the following Equation (8):



(8)

It is well known that Schiff bases can be created by ketones and amines [24]. The Schiff bases can create a metal complexes with transition metals [25].

In the case where there is no phase change in volume, distribution ratio of metal ion ($D_{Cu(II)}$) was defined as follows:

$$D_{Cu(II)} = \frac{C_{Cu(II)\ (org)}}{C_{Cu(II)\ (aq)}} = \frac{C^0_{Cu(II)} - C_{Cu(II)}}{C_{Cu(II)}} \tag{9}$$

where: $C^0{}_{Cu(II)}$ and $C_{Cu(II)}$ denote analytical copper ions concentrations in the aqueous phase before and after extraction, respectively.

Based on analytical calculations for each equilibrium value of pH for the aqueous phase, the distribution ratios ($D_{Cu(II)}$) were calculated using Formula (9) and subsequently extraction curves (Figure 6) were plotted for investigated ligand (log $D_{Cu(II)}$ = f(pH)).

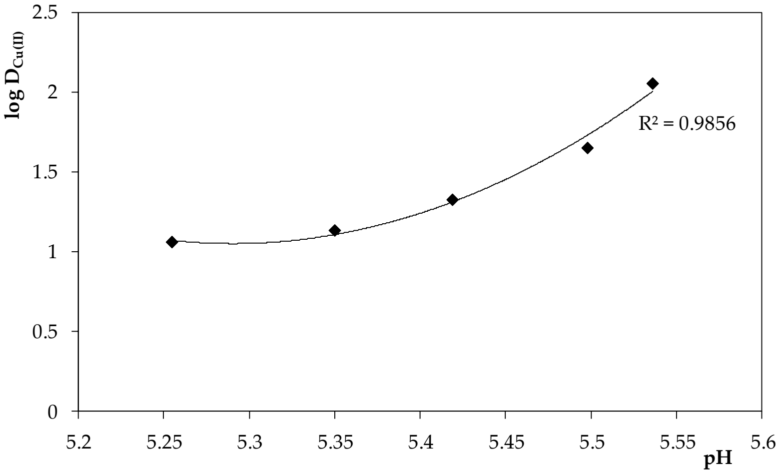


Figure 6. Relation log$D_{Cu(II)}$ = f(pH) in process of extraction Cu/(2,6-bis(4-methoxybenzoyl)-diaminopyridine) complexes.

The log $D_{Cu(II)}$ coefficient increases with ligand concentration increasing.

The percentage of copper(II) ions extraction was calculated using the following formula:

$$\%E_{Cu(II)} = \frac{D_{Cu(II)} \cdot 100\%}{D_{Cu(II)} + V_{aq}/V_{org}} \tag{10}$$

where: V_{aq} and V_{org}—volumes of aqueous and organic phases.

Table 1 shows dependence between the percentage of copper(II) ions extraction and concentration of ligand in the organic phase.

The highest percentage extraction of copper (99.13%) at pH 5.53 was obtained for 0.001 mol/dm^3 concentration of ligand in organic phase, whereas the lowest $\%E_{Cu(II)}$ was observed for 0.0001 mol/dm^3 concentration. The obtained results of solvent extraction indicated that the studied compound could be used as extractant.

Table 1. Relation between ligand concentration in organic phase and percentage of copper(II) ions extraction.

Concentration of the Ligand in Organic Phase, mol/dm^3	$\%E_{Cu(II)}$
0.00010	91.98
0.00025	93.16
0.00050	95.49
0.00075	97.83
0.00100	99.13

The given values of the $\%E_{Cu(II)}$ carry 0.7% tolerance.

4. Conclusions

Obtained in this work, results indicated that the new compound 2,6-bis(4-methoxybenzoyl)-diaminopyridine could be used as extractant in solvent extraction. During the studies, more than 99% of copper(II) ions were extracted from 0.001 mol/dm^3 Cu^{2+} water solution (pH~5.8) using chloroform phase, which contained 0.001 mol/dm^3 2,6-bis(4-methoxybenzoyl)-diaminopyridine. The electrospray ionization high-resolution mass spectrometry (ESI HRMS) and the higher energy collisional dissociation tandem mass spectrometry (HCD MS/MS) methods have been successfully used to confirm the structure of 2,6-bis(4-methoxybenzoyl)-diaminopyridine and its ability to form complexes with Cu^{2+} ions in solution. The fairly high stability of the created complexes with 2,6-bis(4-methoxybenzoyl)-diaminopyridine and Cu^{2+} ions was proved in spectrophotometry tests.

The obtained results indicate that in future 2,6-bis(4-methoxybenzoyl)-diaminopyridine can be used in other processes for metal ions recovery, for example, as an ion carrier in polymer inclusion membrane.

Author Contributions: The synthesis of 2,6-bis(4-methoxybenzoyl)-diaminopyridine was done by B.O., the solvent extraction process was conducted by D.B., K.W. determinated the dissociation constant of 2,6-bis((4-methoxybenzoyl)-diaminopyridine and stability constant of it complex with copper(II) ions, M.A.K. planned all of the HRMS and HCD MS/MS experiments and analyzed the obtained mass spectra.

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Conflicts of Interest: The authors declare no conflict of interest.

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A NEW APPLICATION OF 2–BENZOYLPYRIDINE – EFFICIENT REMOVAL OF SILVER IONS FROM ACIDIC AQUEOUS SOLUTIONS VIA ADSORPTION PROCESS ON POLYMERIC MATERIAL AND CLASSIC SOLVENT EXTRACTION

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In this article, we present the results of the first application of 2–benzoylpyridine (2–BP) as a carrier in adsorptive polymeric materials dedicated for the removal of Ag(I) and Cu(II) ions from model acidic solutions. In the first stage of the research, the classical solvent extraction, in which 2–BP was used as an extractant, allowed to determine the proper conditions for conducting adsorptive processes. The stability constants of 2–BP complexes with analyzed metal ions were determined using the spectrophotometric method. The electrospray ionization (ESI) high-resolution mass spectrometry (HRMS) method was applied for the confirmation of the ability of 2–BP molecules to form complexes with Cu^{2+} metal ions in a solution and to determine the elemental composition of generated complexes (to identify the ratio of the number of metal ions to the number of molecules of 2–BP). The obtained results indicate that both the adsorptive processes and solvent extraction strongly depend on the properties of metal ions and that the use of 2–BP as a carrier/extractant allows for efficient removal of silver(I) ions and much less effective removal of copper(II) ions. The utilization of adsorptive polymeric materials is in line with the contemporary research trends that focus on eco-friendly and cost-effective methods.

Keywords: 2–benzoylpyridine, adsorptive polymer materials, liquid–liquid extraction, silver(I) and copper(II) ions, mass spectrometry

1. INTRODUCTION

Due to the structure of the pyridine ring (the presence of electronegative nitrogen atom and its lone pair), pyridine-containing ligands are common in the field of coordination chemistry (Pal, 2018), and references therein. They are capable of forming complexes with a variety of metal ions, including transition metals (Kufelnicki et al., 2016; Farahani and Khalaj, 2021). Usually, they are monodentate ligands that have the ability to bind metals in various proportions. However, the structure of the complexes depends, apart from

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the type of ligands, on the properties of metal ions (Pal, 2018; Zolotukhin et al., 2020). The ability of 2–benzoylpyridine to form complexes (as a result of comprising N and O atoms in a molecule as donors) with different metal ions is well known and has various applications. For example, Au(III) complexes coordinated with 2–benzoylpyridine ligand were applied to discover a novel protein-directed labelling approach with propargyl ester functional groups (Lin et al., 2018). Recently, platinum 2–benzoylpyridine complexes have been used in research on cancer cell growth inhibition (Li et al., 2020). Pyridine-containing ligands can also form stable, rigid complexes with other elements, such as silicon (Peloquin and Schmedake, 2016).

The complex-forming properties of pyridine and its derivatives have been used, among others, in liquid–liquid extraction (LLE) processes, based on the transfer of the chemical compounds (e.g. metals ions) from a liquid to another liquid phase having different polarity. Typically, metal ions present in the aqueous solution are transferred to a properly selected organic phase, which contains specific pyridine derivatives. LLE processes can be carried out on both acidic (e.g. chloride) and alkaline (e.g. NH_4OH) solutions depending on the properties of the extractant and the extracted metal ions (Wojciechowska et al., 2017; Das et al., 2021; Bożejewicz et al., 2019). Extraction processes performed with utilization of different pyridine derivatives were described in the literature for many metal ions, including noble and radioactive metals (Werlinger and Rojas, 2020; Dubenskiy et al., 2020; Wang et al., 2021; Steczek et al., 2019). The process of liquid–liquid extraction is relatively easy and cheap, but its serious limitation is the need to use large amounts of chemicals, i.e. toxic solvents. An alternative to LLE is separation based on the utilization of active polymeric materials, which is considered more environmentally safe. One example of the polymeric material widely used is the polymer inclusion membrane (PIM), in which the liquid phase is held within the polymeric network of a base-polymer (Almeida et al., 2012a; Almeida et al., 2012b; Nitti et al., 2021). PIMs consisting of a polymer matrix (e.g. PVC, CTA), a plasticizer and a carrier, are characterized by high stability and selectivity and are usually inexpensive. Furthermore, their application allows both sorption and desorption processes to be performed (Carner et al., 2020). The efficiency of these two processes depends on many factors, such as composition of the material, properties of removed/recovered metal ions, experimental conditions, such as temperature, pH, and process duration (Keskin et al., 2021; Zante et al., 2022). The interest in this area is steadily growing also due to the low energy consumption, small size of the polymeric material and the potential possibilities of using them on a larger scale (Shao, 2020). In processes based on utilization of polymeric materials, the proper selection of the carrier (the component that binds the metal ions) is critical. Various compounds containing a pyridine ring in their molecules have been used in the separation process as extractants/carriers. For example, López-Guerrero et al. (2020) used pyridine–2–acetaldehyde benzoylhydrazone (2-APBH) as extractant in LLE and as a carrier for the simultaneous recovery of Cu(II), Ni(II) and Cd(II) ions from natural waters and demonstrated the applicability of the proposed polymer membrane on the real estuary and seawater samples with high salinity. Tasaki et al. (2007) used N–(6–alkylamido)–2–pyridine carboxylic acid with a pyridine moiety and a carboxylic acid as chelating ligands in LLE and PIMs processes and established that studied membranes proved to be an excellent copper(II) carrier. What is more, this PIM exhibited high selectivity for copper(II) over cadmium(II) from aqueous solution (Tasaki et al., 2007). The results of recent research based on the application of pyridine derivatives: 2,6–diaminopyridine for removal of copper(II) and zinc(II) ions (Bożejewicz et al., 2021a) and 2,6–bis((benzoyl-R)amino)pyridine (R = H, 4–Me, and 4–NMe_2) for the removal of Cu(II), Ni(II), Co(II), and Zn(II) ions (Bożejewicz et al., 2021b) from aqueous solutions clearly show that these compounds can be used in both LLE and membrane processes. Since separation methods play a vital role in many processes, e.g. in recovery of valuable metals such as silver and copper contained in waste electrical and electronic equipment (WEEE) (Tuncuk, 2019), new carriers/extractants that would allow for more effective recovery/removal are systematically sought.

This paper shows the results of the application of 2–benzoylpyridine (shown at Figure 1) as an extractant in liquid–liquid extraction and as carrier in polymeric material for the removal of Ag(I) and Cu(II) ions from acidic aqueous solutions. Due to increased concern with membrane adsorption techniques (Vo et al., 2020; Huang and Cheng, 2020; Khulbe and Matsuura, 2018) new polymer materials were used for the sorption of silver and copper ions. Despite considerable interest in the properties of 2–benzoylpyridine, this pyridine derivative has not yet been used as an extractant in liquid–liquid extraction or as a carrier in polymeric materials designed to recover/remove silver and copper ions. Our results show that the efficiency of both separation processes carried out with 2–benzoylpyridine as an extractant/carrier is particularly high in removal of silver ions.

2. EXPERIMENTAL SECTION

2.1. Materials and methods

All the reagents used in this work were of analytical grade purity and were used without further purification. The stock nitric solutions of silver(I) and copper(II) metal ions and 2–benzoylpyridine (shown in Figure 1 and described in Table 1) were purchased from Sigma Aldrich. The other compounds used in experiments, such as nitric acid, chloroform and methanol were bought from Avantor (Gliwice, Poland).

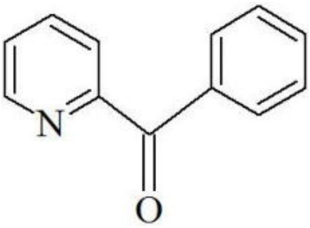


Fig. 1. The structure of 2–benzoylpyridine

Table 1. The basic parameters of 2–benzoylpyridine (Chemical Book)

Molecular formula	$C_{12}H_9NO$
Monoisotopic mass	183.0684 g/mol
Composition	C(78.67%) H(4.95%) N(7.65%) O(8.73%)
Density	1.139 ± 0.06 g/cm^3
Melting point	41–43 °C
Boiling point	317 °C
Water solubility	Insoluble

We found in the literature that the dissociation constant of 2–benzoylpyridine is 2.90 ± 0.10 (Chemical Book). The concentration of metal ions in their aqueous solutions was determined by the atomic absorption spectrometry method. Nitric acid was standardized against anhydrous sodium carbonate.

2.2. Liquid-liquid extraction experiments with 2–BP as an extractant

We separated metal ions from the aqueous solution using liquid–liquid extraction. The measurements were run at 25 °C ±0.2, at a fixed ionic strength (0.5 mol/l) maintained in the aqueous phase with KNO_3. The organic phase contained 0.1 mol/l of 2–benzoylpyridine (L, 2–BP) diluted in chloroform. The aqueous phase contained one of the metal ions: Ag(I) or Cu(II), and also nitric acid which was responsible for maintaining adequate conditions for the extraction processes. The volume of both phases (aqueous phase and organic phase) was 5000 µl. The concentration of each metal ion [M] in the aqueous solution and the basic parameters of liquid–liquid extraction are shown in Table 2. Equilibrium was established after approximately 5 minutes through visual observation. It was checked if any changes in phase volumes had occurred, then the phases were separated and the pH of the aqueous phase was measured.

Table 2. The basic parameters of liquid–liquid extraction

Metal ions in aqueous solution	Concentration of metal ions		M:L wt.	pH
	mol/l	mg/l		
Ag^+	0.009	1000.00	1:18	2.289*
Cu^{2+}	0.015			2.773*

* The pH values have a tolerance of 0.001%

The concentration of metal ions in aqueous phases was determined with the use of atomic absorption spectroscopy (AAS 240FS Spectrometer, Agilent, Santa Clara, CA, USA). The pH-meter utilized in the performed experiments was calibrated using commercial technical buffer solutions (Mettler Toledo, Greifensee, Switzerland) with a pH of 2.00, 4.01, 7.00 and 10.00.

The liquid–liquid extraction of both metal ions from aqueous nitric solutions was described using distribution ratio (D_M) and extraction efficiency (%E). Distribution ratio (Eq. (1)) is the ratio of the sum of concentrations of all the substances in the organic phase $\left(\sum [M]_{\text{org}}\right)$ to the sum of concentrations of all the substances in the water phase $\left(\sum [M]_{\text{aq}}\right)$. Extraction efficiency (%E, Eq. (2)), in turn, is the ratio of distribution ratio to the sum of distribution ratio and volume of the aqueous and organic phases, where D_M is determined experimentally, and the volume of the aqueous phase and the organic phase is equal to 1 ($V_{\text{aq}} = V_{\text{org}} = 1$). The obtained results were analyzed using a spreadsheet and standard deviation.

$$D_M = \frac{\sum [M]_{\text{org}}}{\sum [M]_{\text{aq}}} \tag{1}$$

$$\%E = \frac{D_M}{D_M + \dfrac{V_{\text{aq}}}{V_{\text{org}}}} \cdot 100\% \tag{2}$$

2.3. Sorption of Ag(I) and Cu(II) ions on polymer materials containing 2–BP as a carrier

The polymeric materials were made by pouring on a glass ring the organic solution dissolved in tetrahydrofuran containing a 60 wt.% polyvinylchloride (PVC), 20 wt.% a bis(2-ethylhexyl)adipate (ADO) and also 20 wt.% 2–benzoylpyridine. The solvent was evaporated for 24 h, and the resulting polymeric material with diameter of 4.5 cm and weight of 0.79 g was conditioned in distilled water for the next 24 h. As a result, the modified polymer materials were homogeneous, transparent, flexible, and had good strength.

The aqueous metal ion solutions (Ag(I) and Cu(II)) were prepared for sorption. In single-component metal ion solutions, the concentration of particular metal ions was 316.67 mg/l. The volume of each aqueous solution used as the feed phase was 30 ml. Small amounts of nitric acid for pH adjustment during the process were added to the metal ion solutions. The circular polymeric materials were immersed for 24 h in beakers with a prepared aqueous solution of metal ions. The contents of the beakers were stirred with a magnetic stirrer. The sorption process was carried out within 24 h. Samples from metal ions solutions were taken regularly.

The analysis of the metal ions sorption process onto the polymer materials with 20 wt.% of 2–benzoylpyridine (L) as a carrier was carried out using sorption capacity parameter (Eq. (3)):

$$q_t = \left(\frac{c^i - c^t}{m} \right) \cdot V \tag{3}$$

where q_t is the sorption capacity (mg/g); V is the volume of the solution (l); m is the mass of the sorbent (g); and c^i and c^t are the analytical metal ion concentrations in the solution at the beginning and after an appropriate time of sorption process (mg/l), respectively.

After 24 h of sorption, the percentage of metal ions removed from the solutions ($\%R_s$) was also determined (Eq. (4)) (Ipeaiyeda and Tes, 2014).

$$\%R_s = \frac{c^i - c^t}{c^t} \cdot 100\% \tag{4}$$

Furthermore, in order to determine the quantitative selectivity of the investigated sorbent (2–BP), the distribution ratio K_d (L/g) was determined (Eq. (5)) (Zhang et al., 2008):

$$K_d = \frac{\text{metal ions [mmol]}}{\text{sorbent [g]}} \cdot \frac{\text{solution [l]}}{\text{metal ions [mmol]}} \tag{5}$$

The metal ions concentration in the aqueous phases after sorption was determined with an inductively coupled plasma mass-spectrometer ICP-MS (NexION 300d PerkinElmer, Inc., Waltham, MA, USA).

2.4. Spectrophotometric examination

UV-Vis spectra of the aqueous and organic phase after extraction processes were recorded in the wavelength range of 200 nm to 400 nm. Water solution of 0.5 mol/l KNO_3 was used as reference solution while testing aqueous phases, whereas the organic phases were tested against chloroform. The spectra of the samples were recorded with spectral slits of 1 nm and with 1 nm steps using cuvettes having 1 cm path lengths.

2.5. Determination of stability constants (log K)

Stability constants ($\log K$) of complexes of 2–BP with Ag(I) and Cu(II) ions were determined based on absorption spectra and according to the previously described method (Lis et al., 2011).

2.6. Mass spectrometry experiments

High-Resolution Mass Spectrometry (HRMS) experiments were performed for samples of the separated organic phase after liquid–liquid extraction described in detail in paragraph 2.2, containing Cu(II) ions and 2–BP, diluted (1:1) in methanol. QExactive Orbitrap™mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) equipped with a TriVersa NanoMate robotic nanoflow ESI ion source (Advion BioSciences ltd., Ithaca, NY, USA) was used in all experiments. The HRMS data were acquired in a positive ion mode within the m/z range of 50–750 and at the resolution of 140,000 (m/z 200). Processing of the obtained HRMS spectra was conducted using Thermo Xcalibur software (version 4.1.31.9).

3. RESULTS

3.1. Liquid-liquid extraction

The parameters that influence the liquid–liquid extraction process are: pKa of the extractant (ligand), the concentration of both metal ions in the aqueous solution and the ligand in the organic phase, as well as temperature, pH, stirring speed and extraction time (Chimuka et al., 2010). Liquid–liquid extraction depends on the pH of the solution of metal ions ($M^{m+} = Ag^+$ and Cu^{2+}), so the equilibrium of the extraction process with 2–benzoylpyridine (HL) is as follows:

$$M^{m+}_{(aq)} + m\mathrm{HL}_{(org)} \leftrightarrow \mathrm{ML}_{m(aq)} + m\mathrm{H}^{+}_{(aq)} \tag{6}$$

Table 3 shows the values of the distribution ratios of both metal ions for the 2–benzoylpyridine concentration (0.1 mol/l).

Table 3. The distribution ratio of 2–benzoylpyridine as an extractant

Metal ions in aqueous solution	D_M
Ag^+	34.90*
Cu^{2+}	0.24*

* The D_M values have a tolerance of 0.01%

The pH value influences the ability of the molecule (pK_a) to accept protons. It is known that in the case of acidic analytes, carrying out the extraction process at a pH higher than their pK_a value usually significantly reduces the recovery/removal due to the presence of these compounds in the aqueous phase in ionized form (Zgoła-Grześkowiak, 2010). The solvent extraction process being carried out in the range of the dissociation constant value and the extraction efficiency is as follows: $Ag^+ > Cu^{2+}$ (Figure 2).

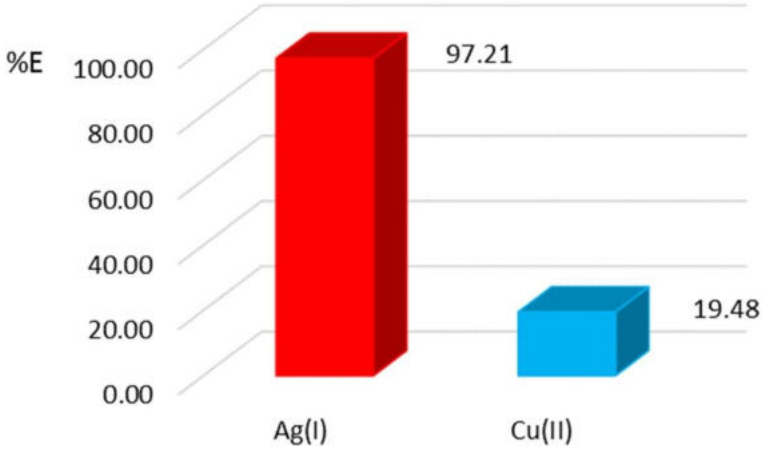


Fig. 2. Efficiency of extraction process

Summarizing, the results of extraction efficiency (%E) confirmed the selectivity of the examined extractant. Silver metal ions can be removed more efficiently from aqueous solution than copper metal ions during liquid–liquid extraction with 2–benzoylpyridine. Although 2-benzyolpyridine is a cheap and commercially available compound which shows complexing properties, it was not used so far as an extractant in liquid–liquid extraction for removal of silver metal ions from an aqueous solution.

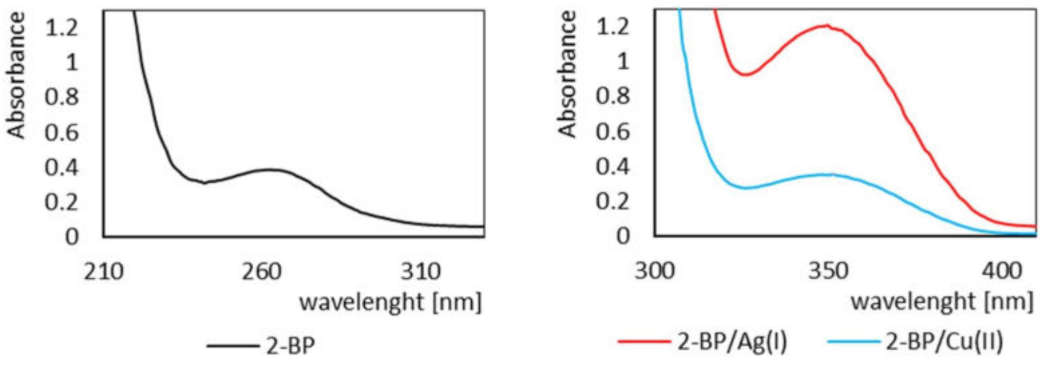
In fact, many scientists use various extractants to remove metal ions from waste/aqueous solutions. Table 4 summarizes the efficiency of selected commercial extractants commonly used for the removal of metal ions through various separation processes. Comparison of the effects of the extractants listed in Table 4 for the extraction of different metal ions with the results presented in this paper related to the utilization of 2–BP clearly show that application of 2–benzoylpyridine allows to obtain much higher values of %E in case of silver(I) ions.

Table 4. The comparison of efficiency of extractants used in various separation processes for removal of Ag(I) and Cu(II) metal ions

Separation process	Extractant	%E, %		Ref.
		Ag^+	Cu^{2+}	
Leaching	2% iodine and 3% hydrogen peroxide	99.02	–	Tuncuk (2019)
Leaching	NH_3	–	79.43	Tuncuk (2019)
Polymer inclusion membrane	Calix[4]pyrrole derivatives	92.77	–	Nowik-Zając et al. (2020)
Leaching	Aqua regia	99.0	–	Sun et al. (2017)
Extraction	Oxime	–	< 97.0	Tanha et al. (2016)
Smelting process	8–12 wt.% of spent SiC side block (SSCB)	–	98.0	Zhao et al. (2021)
Extraction	2–(1H–imidazol–2–yl)pyridine and a synergist (SDBS)	–	50.0	Pearce et al. (2019)

3.2. Spectrophotometric studies

The following figures show spectra of organic phase before (Figure 3a) and after (Figure 3b) extraction process. Figure 3a presents the spectrum of chloroform solution of pure 2–BP with maximum of absorption at 263 nm. Figure 3b presents spectra on which absorption maxima become displaced towards longer wavelengths (350 nm). These changes are caused by the complexation reaction, which takes place at the interface of aqueous and organic phase. At this moment in organic phase complexes of 2–BP (extractant) with investigated metal ions are formed. Moreover, those spectra clearly show that the concentration of created complexes is related to the value of extraction efficiency calculated in paragraph 3.1. Absorbance of spectra of 2–BP with Ag(I) ions is high, because of high concentration of these complexes in organic phase. In turn, the extractant is significantly less effective in case of separation of Cu(II) metal ions, which concentration of its complexes with 2–BP is low in organic phase.



(a) (b)

Fig. 3. The absorption spectra of organic phases: a) before extraction process, b) after extraction

3.3. Sorption of Ag(I) and Cu(II) ions on polymer materials containing 2–BP

The calculated in this paper sorption capacities (q_t) of polymer materials with 20 wt.% of 2–benzoylpyridine (L) as a carrier after 24 h of sorption processes for Ag(I) and Cu(II) ions were 276.36 mg/g and 27.06 mg/g, respectively. Especially in the case of sorption Ag(I) ions, the parameter is very high in comparison with other literature data, which describe sorption of metal ions on modified polymers, e.g. PVC. For example, Freitas et al. (2016) studied Ag^+ and Cu^{2+} binary adsorption from the aqueous solution using Verde-lodo bentonite and reported that maximum sorption capacities were 6.99 mg/g for copper(II) ions at 60 °C and 9.71 mg/g for silver(I) ions at 20 °C. In other studies, a functional polymer containing 2–mercapto–1–methylimidazole and guanylthiourea ligands from chemically modified vinylbenzylchloride/divinylbenzene copolymer (VBC/DVB) was used (Pilśniak-Rabiega and Wolska, 2020). The maximum sorption capacity of Ag(I) obtained from the Elovich model was 40.7 and 194.2 [mg Ag/g resin] for the resins I (with 2–mercapto–1–methylimidazole) and II (with guanylthiourea), respectively. Han et al. (2021) studied the adsorption of Cu(II), Cr(III), and Pb(II) ions onto polyethylene, polypropylene, and polyethylene terephthalate microplastic particles and reported that the maximum sorption capacity of Cu(II) ions was 0.51mg/g.

Further, Table 5 presents the results of the percentage of sorption of Ag(I) and Cu(II) metal ions from single-component solutions using polymer materials containing 2–benzoylpyridine.

Table 5. The percentage of sorption of Ag(I) and Cu(II) metal ions from single-component solutions using polymer materials containing 2–benzoylpyridine

Metal Ions	Ag(I)		Cu(II)	
Time [h]	$\%Rs$ [%]	q_t [mg/g]	$\%Rs$ [%]	q_t [mg/g]
4	67.03	260.2682	3.54	13.7436
6	67.94	263.7931	3.78	14.6753
12	69.55	270.0255	4.03	15.6460
24	71.18	276.3602	6.97	27.0601

The given values of $\%R_s$ and q_t carry ±0.01 and ±0.0001 tolerance

The results indicate high selectivity of the tested polymeric materials for Ag(I) ion sorption (71.18%). The obtained sorption results confirm also the results received in liquid–liquid extraction experiments. Removal of investigated ions using polymer materials with 2–benzoylpirydyne was less effective, but more environmentally friendly, as it limited the use of toxic reagents in comparison with solvent extraction.

Similar preferential selectivity order Ag(I) > Cu(II) was observed by Kołodziejska et al. (2014) for the crown ether, i.e. N–(diethylthiophosphoryl)–aza[18]crown–6 used as an ion carrier for competitive transport of Ag(I), and Cu(II). They show that N–(diethylthiophosphoryl)–aza[18]crown–6 applied as ionic extractant allows for very high removal of silver cations with good selectivity and the entire amount of Ag(I) can be removed from source aqueous phase under pH 3.0. Moreover, PIMs with immobilized calix[4]pyrrole derivative as a carrier was used for selective extraction of Ag(I) from a mixed solution of Cu(II), Pb(II), Cd(II), Ni(II), Zn(II), and Co(II) (from copper smelting wastewater) (Nowik-Zając et al., 2020).

The distribution coefficients (K_d) of polymer materials with 20 wt.% of 2–BP, as a carrier after 24 h of sorption processes for Ag(I) and Cu(II) ions were 0.1387 and 0.024, respectively.

3.4. Stability constants of 2–BP complexes with metal ions

Based on obtained electron spectra (one of the examples is Figure 4, which presents complexation reaction between 2–BP and Ag(I) ions), the stability constants of generated complexes were calculated.

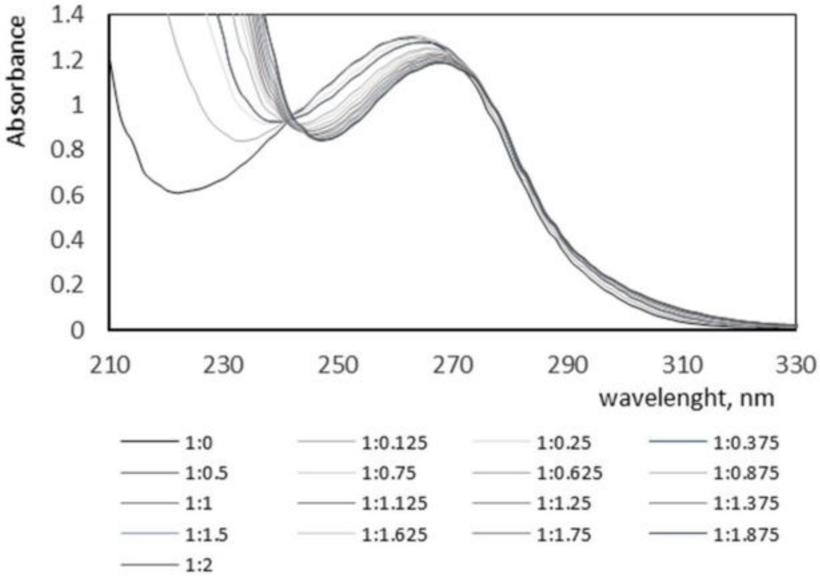


Fig. 4. Electron spectrum obtained during complexation reaction between 2–BP and Ag(I) ions

In Figure 4, the formation of Ag(I)/(2–benzoylpyridine) complexes in the studied system is shown. Vanishing of the band due to ligand 2–BP (263 nm) and the appearance of new bands (269 nm) together with the isosbestic points at 241 and 275 nm were also recorded.

Calculated stability constants of complexes of 2–BP with Ag(I) and Cu(II) metal ions in various molar ratios of metal ion to ligand (M:L) are shown in Table 6.

Table 6. Stability constants of complexes of 2–BP (L) with Ag(I) and Cu(II) metal ions in various molar ratios M:L

Metal ions M	Stability constants, log *K*			
	M:L = 1:2	M:L = 1:1	M:L = 3:2	M:L = 2:1
Ag^+	4.290	3.813	3.602	3.399
Cu^{2+}	4.301	4.287	3.824	3.653

The given values of the log *K* carry ±0.001 tolerance

The results summarized in Table 6 show that with an increasing amount of metal ions in the environment of reaction, the stability constants of the formed complexes decrease. The stability constants for complexes with both ions are similar. Both ions form the most stable complexes when the molar ratio M:L is 1:2. However, Cu(II) ions form also the same stable complexes with the molar ratio 1:1. It is most probably related to the disproportionation reaction in which copper changes its oxidation state from +II to +I.

3.5. Mass spectrometry

Electrospray ionization (ESI) high resolution mass spectrometry (HRMS) experiments were performed to determine the elemental composition of the complexes formed by 2–benzoylpyridine molecules with Cu(II) ions during extraction process, and thus to identify the ratio of Cu^{2+} to 2–BP (L) in generated complexes. The ESI (high voltage, atmospheric pressure) technique was used in experiments because it allows most small molecules to be "transferred" directly from the solution to the mass spectrometer without major changes in their structure. HRMS is characterized by high accuracy of mass measurement (more precisely mass to charge ratio (m/z) measurement) and sensitivity, which are necessary to accurately determine the elemental composition and charge of the generated ion complexes (Konermann et al., 2013; Xian et al., 2012).

ESI-HRMS spectrum recorded for the sample of the separated organic phase after liquid–liquid extraction (described in paragraph 2.2), containing 2–benzoylpyridine (L) and Cu^{2+} ions is presented in Figures 5, and the mass spectrometry data of the main compounds found in the sample are shown in Table 7. ESI HRMS spectrum is dominated by signals corresponding to 2–benzoylpyridine-related ions such as: $[L{-}H]^+$, $[L{+}H]^+$, $[C_{14}H_{14}NO_3]^+$, $[C_{13}H_{10}NO_2]^+$, $[C_{13}H_{12}NO_2]^+$, which is due to the use of an excess of ligands in performed liquid–liquid extraction experiments. The formation of a deprotonated 2–benzoylpyridine cations ($[L{-}H]^+$) in ESI(+) experiments, which typically results in generation of protonated ions ($[L{+}H]^+$), is remarkable but is not the subject of the current research. Formation of the exceptional deprotonated cations has been reported before, for example in atmospheric pressure ionization mass spectrometry of 2–(diphenylsilyl)cyclopropanecarboxylate esters (Wang et al., 2020). ESI HRMS spectrum shows a signal corresponding to doubly charged ions of complexes containing one metal atom and three 2–benzoylpyridine molecules, i.e. $[3L{+}Cu^{2+}]^{2+}$ and a signal which can be assigned to $[2L{+}Cu^+]^+$ cations, in which one copper atom is linked to two ligand (2–BP) molecules. The formation of $[3L{+}Cu^{2+}]^{2+}$ and $[2L{+}Cu^+]^+$ ions proves that in complexes with L molecules, copper ions can be present in both oxidation states (+I or +II).

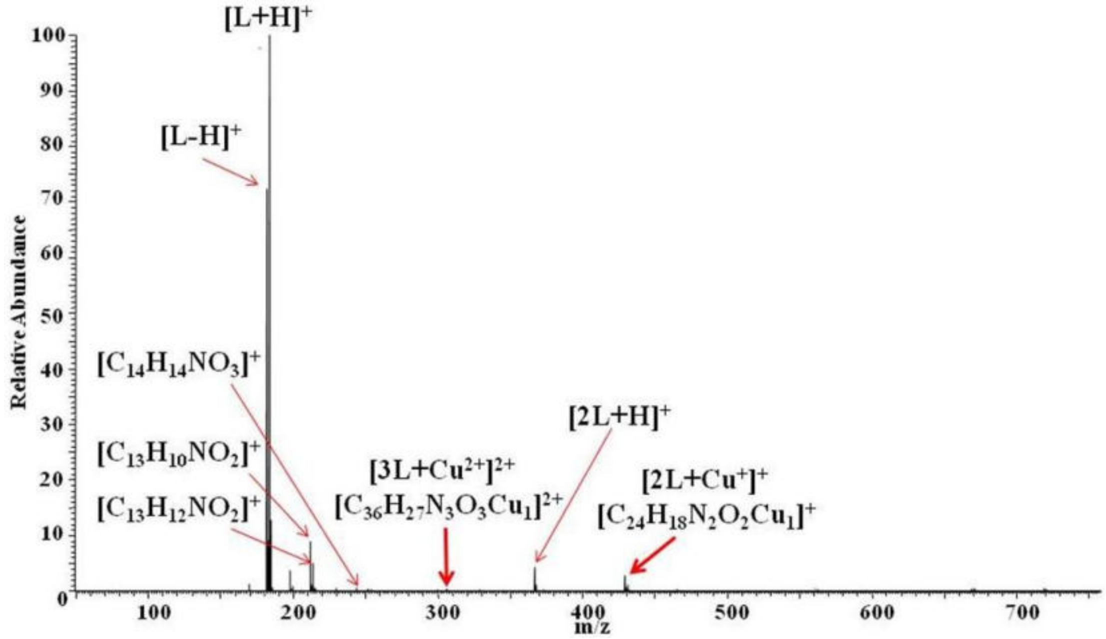


Fig. 5. ESI-HRMS spectrum recorded for the sample of the separated organic phase after liquid–liquid extraction, containing 2–benzoylpyridine (L) and Cu^{2+}ions. Unassigned minor signals correspond to ions not relevant in this study (e.g., formed by solvent molecules)

The results of the performed ESI HRMS experiments confirmed that 2–benzoylpyridine is able to form in solution complexes with copper ions in which metal ion to L ratio is 1:3 and 1:2. The obtained results do not confirm the formation of complexes in which the ratio of copper ions to 2–benzoylpyridine ligands is 1:1. However, it should be emphasized that the method (ESI HRMS) does not allow to detect neutral complexes, which may also form in the analyzed solutions.

Table 7. ESI-HRMS data of the main compounds found in the sample of the separated organic phase after liquid–liquid extraction, containing 2–benzoylpyridine (L, $C_{12}H_9NO$) and Cu^{2+} ions

2–benzoylpyridine (L)/Cu^{2+}			
m/z_{meas}	m/z_{calc}	Assignment	Mass error (ppm)
182.0598	182.0606	$[L–H]^+$, $[C_{12}H_8NO]^+$	4.39
184.0754	184.0762	$[L+H]^+$, $[C_{12}H_{10}NO]^+$	4.34
212.0705	212.0711	$[C_{13}H_{10}NO_2]^+$	2,83
214.0859	214.0868	$[(L–H)+CH_3OH]^+$ or $[(L+H)+CH_2O]^+$, $[C_{13}H_{12}NO_2]^+$	4.20
244.0966	244.0974	$[C_{14}H_{14}NO_3]^+$	3.27
306.0665	306.0674	$[3L+Cu^{2+}]^{2+}$, $[C_{36}H_{27}N_3O_3Cu_1]^{2+}$	2.94
367.1438	367.1446	$[2L+H]^+$, $[C_{24}H_{19}N_2O_2]^+$	2.17
429.0657	429.0664	$[2L+Cu^+]^+$, $[C_{24}H_{18}N_2O_2Cu_1]^+$	1.63

4. CONCLUSIONS

The obtained results of the application of 2–benzoylpyridine (2–BP) for the removal of Ag(I) and Cu(II) ions from acidic aqueous solutions by liquid–liquid extraction and adsorptive processes show that this compound is a particularly good extractant/carrier in the case of silver metal ions. The extraction efficiency for Ag(I) ions was over 97%, and the percentage of sorption of silver ions with the use of a polymer material containing 20 wt.% of 2–benzoylpyridine was 71.18%, while the corresponding values for the recovery of copper ions were much lower, i.e. 19% (LLE) and 6.97% (adsorptive process), respectively. These results indicate a high dependence of both separation processes on the properties of the removed metals ions. Based on spectrophotometric results, it can be concluded that 2–BP can form various complexes with metal ions, but the most stable are those in which the metal ion to ligand ratio is 1:2 (for Ag(I) and Cu(II) ions). The results of the ESI HRMS experiments performed for solution after extraction, containing 2–BP and Cu^{2+} show formation of doubly charged complexes (cations) in which the ratio of Me^{2+} to L is 1:3 and the generation of singly charged complexes (cations) containing one copper ion (at oxidation state +I) and two ligand molecules. The obtained results do not allow for unequivocal determination of the type of all complexes formed in solution, but indisputably show that the ligand must be present in an excess during extraction processes.

The results of the conducted research show that 2–benzoylpyridine is a much better extractant in relation to silver ions than many other commercially available chemical compounds. Besides having strong complexing properties for these ions, 2–BP is well known compound readily available and relatively cheap. The recovery of silver ions by utilization of a polymer materials containing 20 wt.% of 2–BP is slightly less efficient, but this method allows a significant reduction of the solvents used. Moreover, since the carrier is bound in the polymer matrix and is insoluble in the aqueous phase, the polymer material based process applied on a larger scale will be much more environmentally friendly than classical solvent extraction. The results of this research may show a new direction of how the properties of 2–BP used as an organic carrier can be used to remove silver metal ions from various types of waste.

SYMBOLS

c^i	analytical metal ion concentrations in the solution at the beginning time of sorption process, mg/l
c^t	analytical metal ion concentrations in the solution at the after time of sorption process, mg/l

D_M	distribution ratio
K_d	the distribution ratio, l/g
LLE	liquid-liquid extraction
m	mass of the sorbent, g
M	metal ions
V	volume of the solution, l
V_{aq}	volume of the aqueous phase, l
V_{org}	volume of the organic phase, l
q_t	sorption capacity, mg/g
$\%E$	extraction efficiency, %
$\%R_s$	the percentage of metal ion removal from the solutions, %
2–BP	2–benzoylpyridine

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Efficient Recovery of Noble Metal Ions (Pd^{2+}, Ag^{+}, Pt^{2+}, and Au^{3+}) from Aqueous Solutions Using *N,N′*-Bis(salicylidene) ethylenediamine (Salen) as an Extractant (Classic Solvent Extraction) and Carrier (Polymer Membranes)

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Abstract: This paper presents the results of the first application of *N,N′*-bis(salicylidene)ethylenediamine (salen) as an extractant in classical liquid–liquid extraction and as a carrier in membrane processes designed for the recovery of noble metal ions (Pd^{2+}, Ag^{+}, Pt^{2+}, and Au^{3+}) from aqueous solutions. In the case of the utilization of membranes, both sorption and desorption were investigated. Salen has not been used so far in the sorption processes of precious metal ions. Recovery experiments were performed on single-component solutions (containing only one type of metal ions) and polymetallic solutions (containing ions of all four metals). The stability constants of the obtained complexes were determined spectrophotometrically. In contrast, electrospray ionization high-resolution mass spectrometry (ESI-HRMS) was applied to examine the elemental composition and charge of the generated complexes of chosen noble metal ions and salen molecules. The results show the great potential of *N,N′*-bis(salicylidene)ethylenediamine as both an extractant and a carrier. In the case of single-component solutions, the extraction percentage was over 99% for all noble metal ions (molar ratio M:L of 1:1), and in the case of a polymetallic solution, it was the lowest, but over 94% for platinum ions and the highest value (over 99%) for gold ions. The percentages of sorption (%Rs) of metal ions from single-component solutions using polymer membranes containing *N,N′*-bis(salicylidene)ethylenediamine as a carrier were highest after 24 h of the process (93.23% for silver(I) ions, 74.99% for gold(III) ions, 69.11% and 66.13% for palladium(II) and platinum(II) ions, respectively), similar to the values obtained for the membrane process conducted in multi-metal solutions (92.96%, 84.26%, 80.94%, and 48.36% for Pd(II), Au(III), Ag(I), and Pt(II) ions, respectively). The percentage of desorption ($\%R_{des}$) was very high for single-component solutions (the highest, i.e., 99%, for palladium solution and the lowest, i.e., 88%, for silver solution), while for polymetallic solutions, these values were slightly lower (for Pt(II), it was the lowest at 63.25%).

Keywords: solvent extraction; polymer membranes; sorption; noble metal ions; salen; stability constant; mass spectrometry

1. Introduction

N,N′-bis(salicylidene)ethylenediamine (commonly known as salen, L) easily creates coordination compounds. It has been reported that this compound is a tetradentate chelating ligand, which can form mononuclear complexes by two covalent and two-coordinate covalent sites located in a planar array [1]. Due to the presence of two phenolic hydroxyl groups, which can lose the protons under appropriate conditions, the salen ligand can become a conjugate base (L^{2-}). Salen and its complexes are still of interest to scientists, who study the complexation reactions between salen and various metal ions [2,3]. It is known that the complex formation process depends on multiple factors including the type of solvent used. For example, Elsherif et al. [3] investigated the stoichiometry and formation constants of complexes of salen with Cu(II) in methanol, 2-propanol, acetonitrile, tetrahydrofuran, and chloroform as nonaqueous solvents at 25 °C. They reported that the stoichiometry of the investigated complexes in all solvents were the 1:1 (M:L) type, and the order of stability was as follows: chloroform~tetrahydrofuran > 2-propanol > methanol~acetonitrile. The Cu(II) ions formed the most stable complexes with salen molecules in chloroform and the least stable in methanol. Initially, complexation properties of salen were used primarily in catalysis [4]. However, over time, the uses of salen have been extended, and one of them is separation. For example, the H_2salen type bearing pendant tertiary amine groups [5] has been synthesized for the solvent extraction and membrane transport of transition metal salts for metal separation and purification processes. These ligands undergo a so-called zwitterionic transformation when binding metal salts, forming overall neutral assemblies, which can be transferred into non-polar, water-immiscible solvents. In addition, the recovery characteristics of copper and sulfate have been reported for a modified ligand, which shows copper-binding and thus facilitates copper-recovery and ligand-recycling. Similar solutions were also reported by Forgan et al. [6] and Galbraith et al. [7]. In turn, Dadfarnia et al. [8,9] developed a microcolumn for an online preconcentration of investigated metal ions with a flow injection-flame atomic absorption spectrometry (FI–AAS). Salen, in this case, was immobilized on surfactant-coated alumina. The method was applied to water samples, multivitamin tablets, and standard reference alloys. Kim et al. synthesized modified silica-salen$(NEt_2)_2$ [10] for the separation and concentration of the metal ions from an aqueous solution by solid-phase extraction. The synthesized salen(NEt_2) was chemically bonded to silica gel by a diazonium coupling reaction. The procedure of adsorption was applied to three types of water samples. The authors obtained adsorption capacities and binding constants for Cu(II), Mn(II), Pb(II), and Zn(II), and the recoveries reached more than 95%. In other studies [11], the authors used a chemically modified XAD-4-salen chelating resin for the separative concentration of Cu(II), Pb(II), and Bi(III) ions from an aqueous solution. XAD-4-salen was synthesized by the reaction of salen and Amberlite XAD-4 resin. The method has been employed to determine the investigated metal ions in samples of five kinds of river water. The adsorbed metal ions were desorbed by 10 mL of 1.0 M HNO_3, and the total recoveries of the proposed method were more than 85% in the spiked samples in which a given amount of analytes was added. The silica derivative-salen [12] formed in a series of reactions of rice husk ash, 3-(chloropropyl)triethoxysilane, potassium iodide, and ethylenediamine also showed high potential for the extraction and removal of Ni(II), Cu(II), and Co(II) ions from aqueous solutions. Furthermore, salen has found application in so-called metal–organic frameworks (MOFs) [13,14], which are dedicated to various separation processes due to their well-defined pore size and geometry. Thus, the separation of substances can be provided on mixtures of gases, vapors, and liquid phases. In this year, salen [15] and sodium tetraphenylborate (TPB) were used as extracting agents in polymeric inclusion membranes to extract gold from aqueous solutions. The fabricated membranes showed high selectivity and reactivity toward gold. The reduction of gold on the membrane surface reached more than 90%. The presence of gold was confirmed by scanning electronic microscopy. The authors proved that the addition of salen to TPB affected the size and structure of the gold nanoparticles. Campo-Cobo et al. [16] also investigated other salen-type ligands with electron-accepting substituents on the aromatic ring as extractant agents in polymeric inclusion membranes. Salen-type ligands had higher selectivity to Au(III) than to other metals (Cu(II), Pb(II), Ca(II), Al(III), Co(II), Fe(II), Fe(III), Ni(II), Mn(II), and Zn(II)). The results showed that the percentage of extracted gold depends on the type of substituent present in the ligand's aromatic ring, the pH of the working solution, and the membrane area. There was no effect of membrane thickness on the metal extraction. The time required to reach a certain extraction percentage decreased considerably as the membrane area increased.

In our previous paper [17], we also used salen as an extractant in liquid–liquid extraction, as a carrier during the transport across polymer inclusion membrane, and in sorption processes for the removal of Ni(II), Cu(II), and Zn(II) ions from aqueous solutions. The results of liquid–liquid extraction show that salen is a very effective extractant, especially for removing copper(II) ions from aqueous solutions. Still, its efficiency depends on its concentration in the system. Moreover, we proved that the separation of chosen metal ions using the investigated polymer membranes with salen was better during the sorption process (membrane extraction) than during the transport across those membranes.

In this paper, we present the novel investigation results of the recovery of chosen precious metal ions (Pd^{2+}, Ag^{+}, Pt^{2+}, and Au^{3+}) from aqueous solutions, using salen during the classical solvent extraction and sorption processes on polymer membranes. Establishing the proper conditions for membrane sorption is not easy as the process depends on various factors (for example, type and concentration of recovered metal ions, properties of base-polymer, plasticizer, and carrier used to fabricate the membrane, type of solvent used, pH, temperature, and process time). However, the polymer membranes have many advantages: they are effective, inexpensive, show high stability and versatility, and allow both the sorption and desorption processes to be carried out. Polymer-based non-fluid membranes are usually more stable because carrier ions in polymer membranes are chemically or physically bound within the membrane matrix. In addition, separation based on the utilization of polymer membranes is an environmentally safe alternative to solvent extraction by drastically reducing the use of toxic solvents. Therefore, the membrane extraction is defined as a sustainable green strategy [18–20]. The interest in the recovery of precious metals from aqueous solutions (i.e., various types of wastewater) is systematically growing due to the decline in the natural resources of these metals (ores), their intensive utilization in various industries, and the increase in the amount of waste generated (e.g., waste electronic and electrical equipment), which contain significant amounts of these metals [21]. The reuse of precious metals that originated from secondary sources is also an important part of green chemistry. In the case of known methods such as solvent extraction [22] or membrane processes dedicated to recovering precious metal ions, the key role is played by the use of a properly selected extractant/carrier that will be safe for the environment and enable sufficiently efficient recovery. The results presented in this article show the great potential of salen for the recovery of gold, silver, palladium, and platinum ions. The results of applying membrane processes are particularly promising as they are not only efficient, but are also environmentally friendly (consumption of small amounts of salen and chemical solvents), allowing for extraction and reverse extraction at low costs.

2. Materials and Methods

2.1. Reagents

All the reagents used in this work were of analytical grade purity and used without further purification. The *N,N′*-bis(salicylidene)ethylenediamine (L) was bought from Sigma-Aldrich (Poznan, Poland). The pattern metal ions (Pd^{2+}, Ag^{+}, Pt^{2+}, and Au^{3+}), nitric acid, ammonia, potassium hydroxide, chloroform, and methanol were purchased from Avantor (Gliwice, Poland).

The structure of *N,N′*-bis (salicylidene)ethylenediamine is shown in Figure 1.

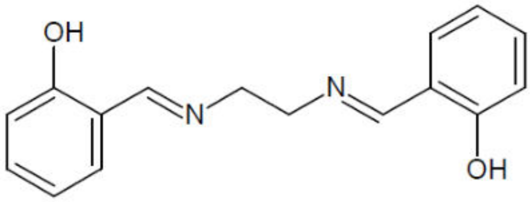


Figure 1. The structure of *N,N′*-bis(salicylidene)ethylenediamine (L, salen).

2.2. Mass Spectrometry

In all high-resolution mass spectrometry experiments, the mass spectrometer Q-Exactive Orbitrap (Thermo Fisher Scientific, Bremen, Germany) was used. This instrument was equipped with a TriVersa NanoMate robotic nanoflow ESI ion source (Advion BioSciences Ltd., Ithaca, NY, USA). Samples of the separated organic phases after liquid–liquid extraction (described in detail in Section 2.4) containing *N,N′*-bis(salicylidene)ethylenediamine and one type of the selected metal ion (Pd^{2+}, Pt^{2+}, or Au^{3+}) in a molar ratio of 5:1 were diluted (1:1) in methanol. MS data were acquired in a positive ion mode within the m/z range of 50–800 at the resolution of 140,000 (*m*/*z* 200). Obtained mass spectra were processed using Thermo Xcalibur software (ver. 4.1.31.9).

2.3. The Stability Constants

Stability constants (log K) of complexes of salen with Pd^{2+}, Ag^{+}, Pt^{2+}, and Au^{3+} ions were determined as we described in our previous paper [17]. For this purpose, a methanol solution of salen with the concentration of 5.5×10^{-5} mol/L and aqueous solutions of metal ions with the concentration of 1 g/L were prepared. Then, to prepare solutions with different molar ratios of ligand to metal ions, each time, a higher amount of metal ions solution was added according to the fixed amount of ligand solution. Finally, the absorption spectra of the obtained solutions were recorded, and stability constants of created complexes of salen with Pd^{2+}, Ag^{+}, Pt^{2+}, and Au^{3+} ions, respectively, were calculated.

2.4. Solvent Extraction

The stock aqueous solutions for Pd^{2+}, Ag^{+}, Pt^{2+}, and Au^{3+} metal ions were made by dilutions of pattern metal ion solutions in water, respectively. The organic solution contained *N,N′*-bis(salicylidene)ethylenediamine (L) dissolved in chloroform. The samples for the extraction processes were prepared so that the molar ratio of metal ions to ligand (M:L) was 1:1, 1:5, and 1:10 in single-component metal ion solutions and 1:1 and 1:4 for polymetallic solutions. Small amounts of ammonia solution were added to the metal ion solutions to avoid the creation of hydroxides during the extraction process. All experiments were carried out in graduated test tubes, and the temperature of the processes was 25 ± 0.2 °C. The volume of both phases (aqueous phase and organic phase) was 1100 µL. The parameters of the particular phases in the extraction processes are described in detail in Table 1.

Table 1. The parameters of the particular phases in the extraction process.

Type of Solution	Metal Ions	Sample	M:L	pH	C_M Metal Ion in the Aqueous Phase, [mol/L]	C_M Ligand in the Organic Phase, [mol/L]
single component solution	Pd^{2+}	1	1:1	8.997	0.009	0.009
		2	1:5	9.015	0.002	0.010
		3	1:10	9.111	0.001	0.010
	Ag^{+}	4	1:1	10.247	0.009	0.009
		5	1:5	10.354	0.002	0.010
		6	1:10	10.119	0.001	0.010
	Pt^{2+}	7	1:1	8.997	0.005	0.005
		8	1:5	9.214	0.002	0.010
		9	1:10	9.059	0.001	0.010
	Au^{3+}	10	1:1	9.132	0.005	0.005
		11	1:5	9.325	0.002	0.010
		12	1:10	9.456	0.001	0.010

Table 1. *Cont.*

Type of Solution	Metal Ions	Sample	M:L	pH	C_M Metal Ion in the Aqueous Phase, [mol/L]	C_M Ligand in the Organic Phase, [mol/L]
polymetallic solution	Pd^{2+} Ag^{+} Pt^{2+} Au^{3+}	MIX	1:1 (for the sum of all precious metal ions) 1:4 (for single metal ion)	9.285	0.00062	0.0025
	Pd^{2+} Ag^{+} Pt^{2+} Au^{3+}		1:4 (for the sum of all precious metal ions) 1:16 (for single metal ion)	9.197	0.00062	0.01

The given values of pH carry ±0.001.

Next, the prepared samples were shaken for 1 h. The equilibrium was established after approximately 15 min by visual observation. Next, it was checked for any changes in the phase volumes, then the phases were separated, and the pH of the aqueous phase was measured. Finally, the metal ion concentration in the aqueous phases was determined by an inductively coupled plasma mass-spectrometer ICP-MS (NexION 300d PerkinElmer, Inc., Waltham, MA, USA).

The extraction percentage ($\%E_M$) of metal ions was described by the equation as follows:

$$\%E_M = \frac{D_M}{D_M + \frac{V_{aq}}{V_{org}}} \cdot 100\% \tag{1}$$

where D_M is the division ratio determined experimentally; V_{aq} is the volume of the water phase [l]; V_{org} is the volume of the organic phase [l] ($V_{aq} = V_{org}$, so $V_{aq}/V_{org} = 1$).

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

$$D_M = \frac{\Sigma[M]_{org}}{\Sigma[M]_{aq}} \tag{2}$$

The results were elaborated using a spreadsheet and standard deviation.

2.5. The Preparation of Polymer Membranes

The polymer membranes (one is shown in Figure 2) were made by pouring on a glass ring the organic solution dissolved in tetrahydrofuran contained a 60 wt.% polyvinylchloride (PVC), 20 wt.% a bis(2-ethylhexyl)adipate (ADO) and also 20 wt.% *N,N′*-bis(salicylidene)ethylenediamine (salen). The solvent was evaporated for 24 h, and the resulting polymer membrane (PM) was conditioned in distilled water for the next 12 h. As a result, the membranes were homogeneous, transparent, flexible, and had good strength. The thickness of the membranes, which were used for precious metal ions such as gold(II), silver(I), palladium(II), and platinum(II) transport, was approx. 0.178 mm.

Figure 2. The polymer membrane with 20 wt.% *N,N′*-bis(salicylidene)ethylenediamine before the sorption process.

2.6. Sorption and Desorption Experiments

First, the aqueous metal ion solutions were prepared for sorption. In single-component metal ion solutions, the concentration of particular precious metal ions was 80 mg/L, whereas, in polymetallic solutions (MIX), it was 20 mg/L for single metal ions.

The volume of each aqueous solution used as the feed phase was 30 mL. Small amounts of ammonia solution for pH adjustment during the process were added to the metal ion solutions. The circular polymer membranes were immersed for 24 h in beakers with a prepared aqueous solution of metal ions. The contents of the beakers were stirred with a magnetic stirrer. The sorption process was carried out within 24 h. Samples from single-component metal ion solutions and polymetallic solutions (Nos. I–IV and MIX) were taken regularly. The polymer membrane after the sorption process was immersed in 10 mL 5 mol/L HNO_3 solution for 24 h.

The analysis of the metal ions sorption process onto the membranes with 20 wt.% of *N,N′*-bis(salicylidene)ethylenediamine (L) as a carrier was carried out using Equation (3):

$$q_t = \left(\frac{c^i - c^t}{m}\right) \cdot V \tag{3}$$

where q_t is the sorption capacity (mg/g); V is the volume of the solution (l); m is the mass of the sorbent (g); and c^i and c^t are the analytical metal ion concentrations in the solution at the beginning and after an appropriate time of sorption process (mol/L), respectively.

After 24 h of sorption, the percentage of metal ion removal from the solutions ($\%R_s$) was also determined (Equation (4)) [23].

$$\%R_s = \frac{c^i - c^t}{c^i} \cdot 100\% \tag{4}$$

While the desorption efficiency ($\%R_{des}$) was calculated using Equation (5).

$$\%R_{des} = \frac{c^t}{c^a} \cdot 100\% \tag{5}$$

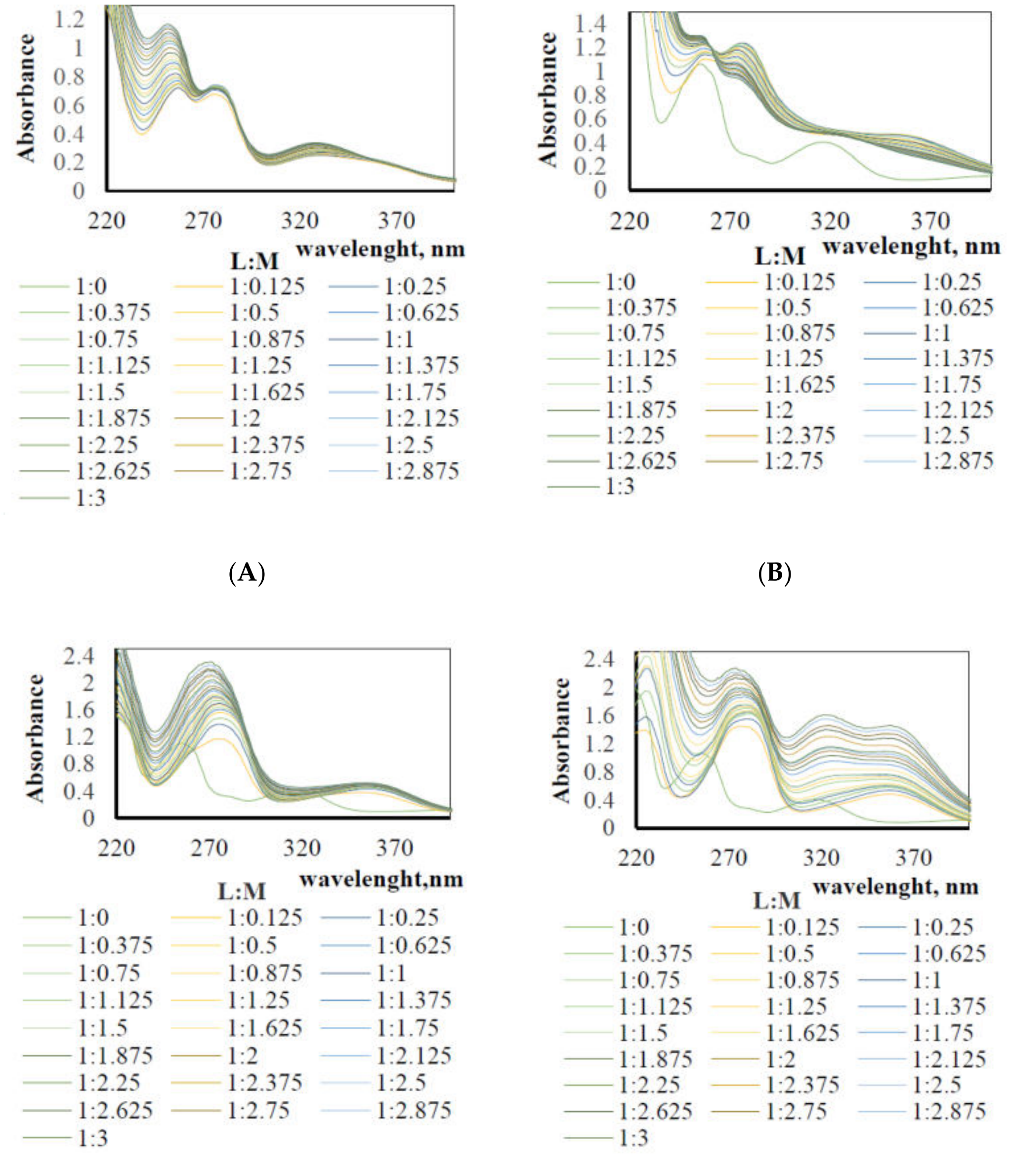
where c^a refers to the initially sorbed metal concentration during the desorption processes [23,24].

The metal ion concentration in the aqueous phases after sorption and desorption was determined with an inductively coupled plasma mass-spectrometer ICP-MS (NexION 300d PerkinElmer, Inc., Waltham, MA, USA).

3. Results

3.1. The Stability Constant

The recorded absorption spectra of the investigated systems are presented in Figure 3.



(**A**) (**B**)

(**C**) (**D**)

Figure 3. The absorption spectra of the investigated systems (complexes of salen: with (**A**). Pd^{2+}, (**B**). Ag^{+}, (**C**). Pt^{2+}, and (**D**). Au^{3+} ions, respectively.

Presented spectra show that complexation reactions between salen and the chosen metal ions occur when adding progressively higher amounts of metal ion solutions. Shapes of the spectra of systems with different L:M molar ratios changed in comparison to the spectra of clear ligand or clear metal ions. Maximum absorption of the ligand solution and Pd^{2+}, Ag^{+}, Pt^{2+}, and Au^{3+} ion solutions in the UV region were equal to 255 nm, 275 nm, 272 nm, and 275 nm, respectively. In the spectra of salen with Pd^{2+}, Ag^{+}, and Pt^{2+}, isosbestic points were also clearly visible.

Based on the above absorption spectra, the stability constants of the complexes of the chosen metal ions with salen molecules were calculated (Table 2).

Table 2. The stability constants of the complexes of salen (L) with Pd^{2+}, Ag^{+}, Pt^{2+}, and Au^{3+} ions.

L:M Complex Type	**Stability Constants**	**M**			
		Pd^{2+}	**Ag^{+}**	**Pt^{2+}**	**Au^{3+}**
		log K			
1:1	log K1	5.54	2.30	5.48	0.52
1:2	log K2	4.60	4.40	4.60	4.63
1:3	log K3	4.00	4.30	4.30	4.00

The given values of log K carry ±0.01.

The most stable complexes were formed by salen (L) with palladium (log K_1 5.54) and platinum ions (log K_1 5.48) involving one ligand molecule and one metal ion (type 1:1). Stability constants of complexes for these metal ions (L:M) decreased in the following order: type 1:1 > type 1:2 > type 1:3. One valent metal ion (Ag^{+}) formed with (L) the most stable complexes, which involved one ligand and two metal ions (type 1:2), whereas three valent metal ions such as gold usually formed complex type 1:3.

3.2. Solvent Extraction

The solvent extraction of metal ions (Pd^{2+}, Ag^{+}, Pt^{2+}, or Au^{3+}) from single-component solutions using *N,N′*-bis(salicylidene)ethylenediamine (L) was carried out in molar ratios of metal ion to ligand of 1:1, 1:5, and 1:10, respectively. In contrast, the removal of metal ions from polymetallic solutions (MIX 1 and MIX 2) was carried out in the ratios of 1:4 and 1:16. Table 3 shows the results of the extraction percentages in various M:L molar ratios.

Table 3. The results of extraction percentages in various molar ratios M (Pd^{2+}, Ag^{+}, Pt^{2+}, or Au^{3+}):L (*N,N′*-bis(salicylidene)ethylenediamine) for single-component and polymetallic solutions.

Type of Solution	**Metal Ions**	**M:L**	**The Extraction Percentage, %E_M [%]**
single component solution	Pd^{2+}	1:1	99.35
		1:5	97.39
		1:10	92.98
	Ag^{+}	1:1	99.95
		1:5	99.86
		1:10	99.83
	Pt^{2+}	1:1	99.15
		1:5	97.80
		1:10	94.98
	Au^{3+}	1:1	99.56
		1:5	97.77
		1:10	94.89
polymetallic solution (MIX)	Pd^{2+}	1:1 (for the sum of all precious metal ions) 1:4 (for single metal ion)	96.43
	Ag^{+}		95.27
	Pt^{2+}		94.62
	Au^{3+}		99.89
	Pd^{2+}	1:4 (for the sum of all precious metal ions) 1:16 (for single metal ion)	96.50
	Ag^{+}		96.46
	Pt^{2+}		94.86
	Au^{3+}		99.90

The given values of %E_M carry ±0.01.

All obtained extraction percentages had very high values, which indicates the affinity of *N,N′*-bis(salicylidene)ethylenediamine to bind metal ions from aqueous solutions. There was no visible molar ratio (M:L) dependence on extraction percentage, which confirms the high effectiveness of the compound used as an extractant, even in small concentrations. Still, on the other hand, its selectivity is low. The amount of removed metal ions from mixed solutions is similar for all investigated precious metals. The utilization of *N,N′*-

bis(salicylidene)ethylenediamine (L) in classical solvent extraction enables the removal of more than 94% of precious metal ions from the aqueous solutions.

Figure 4 presents the results of metal ion removal from single-component and polymetallic solutions, both with an identical M:L ratio of 1:1, using *N,N′*-bis(salicylidene)ethylenediamine (L) as an extractant. It was found that the effectiveness of salen as an extractant decreased when noble metal ions (Au(III), Pd(II), and Pt(II)) were removed from the polymetallic samples. However, in the case of the Ag(I) ions, almost the same extraction percentage was observed, regardless of whether these ions were present in single-component or multi-component samples.

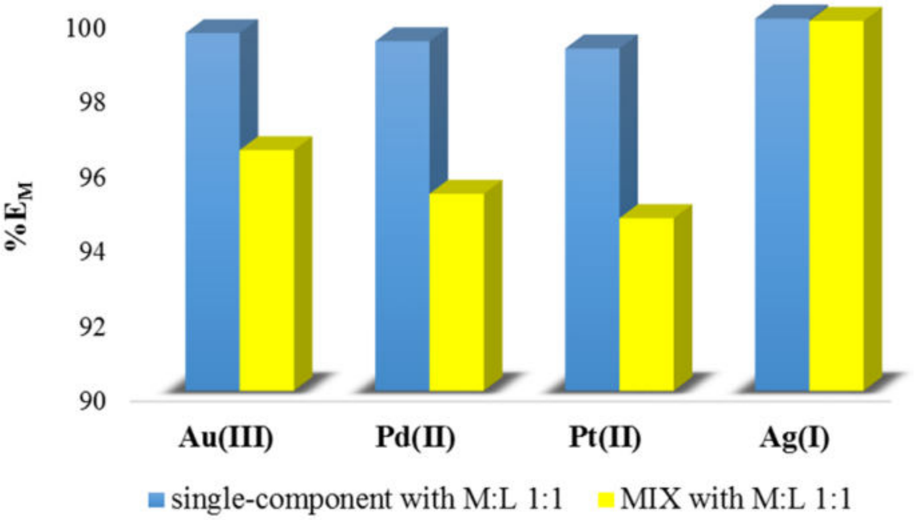


Figure 4. The comparison of metal ion removal from single-component and polymetallic solutions (both with M:L of 1:1) using *N,N′*-bis(salicylidene)ethylenediamine (L) as an extractant. The given values of $\%E_M$ carry ±0.01.

Moreover, the division ratio increased with the increase in the percentage extraction. The highest division ratio for the single-component solution was 2074.55 for Ag(I) ions (M:L molar ratio 1:1), and the lowest D_M was 13.26 for Pd(II) ions (M:L molar ratio 1:10). In the case of the polymetallic solution (MIX), the lowest D_M was for the Pt(II) ions, and the highest for Ag(I) in both M:L ratios.

3.3. Sorption and Desorption Experiments

The first process for the precious metal ion removal from the aqueous solution was sorption, and then desorption of Pd^{2+}, Ag^{+}, Pt^{2+}, and Au^{3+} ions from the surface of the membranes containing *N,N′*-bis(salicylidene)ethylenediamine (L) as an ion carrier was conducted. The figure below shows the polymer membranes after the sorption (Figure 5A) and desorption (Figure 5B) processes. The photos show massive changes on the surface of the membranes in comparison to a pure membrane (Figure 2). These were caused by the deposition of complexes of precious metal ions created together with molecules of salen contained in the structure of the membranes.

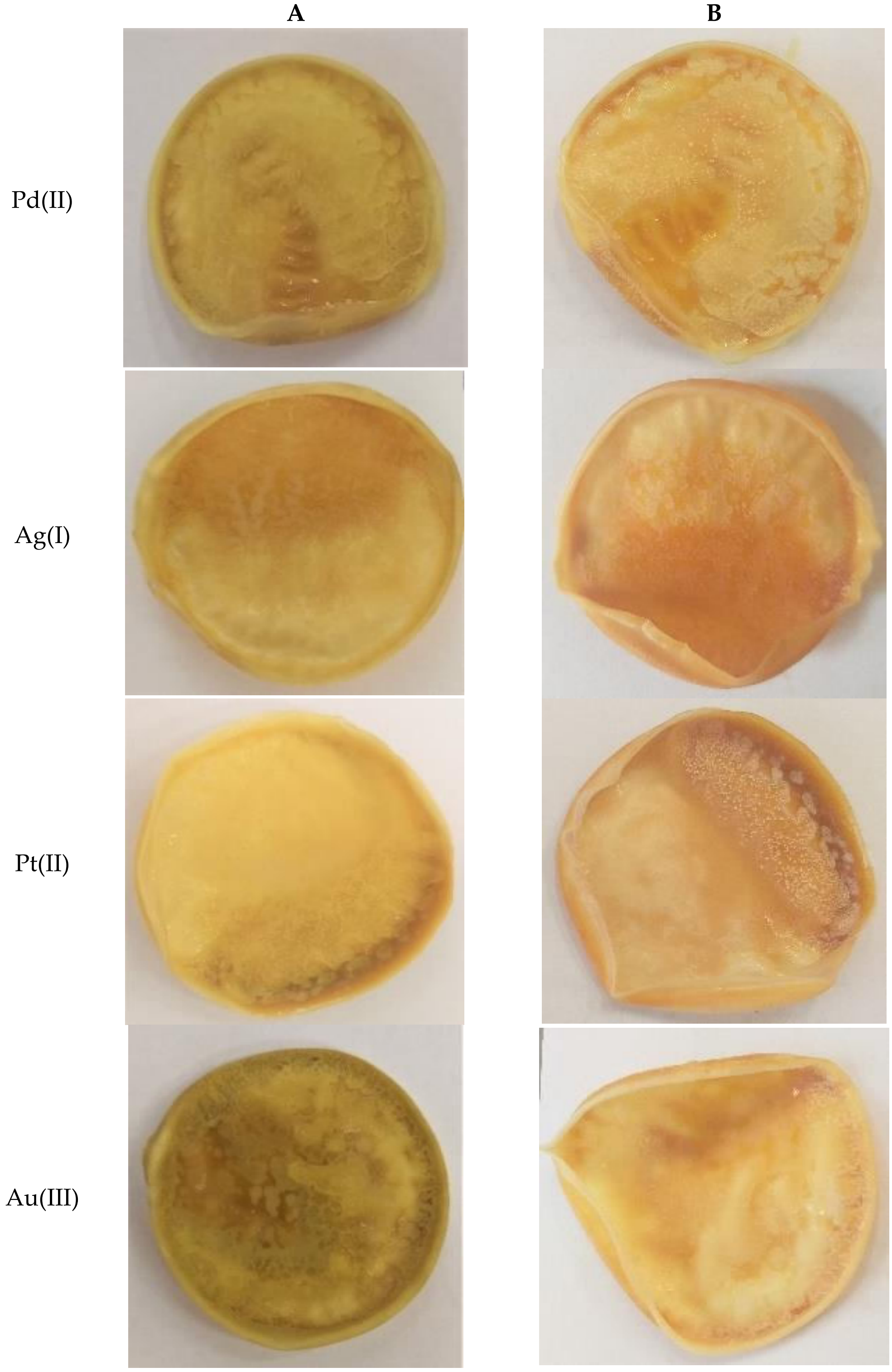


Figure 5. *Cont*.

Figure 5. The membranes containing 20 wt.% of *N,N′*-bis(salicylidene)ethylenediamine after sorption (**A**) and desorption (**B**).

As a result of the conducted experiments, the sorption capacity (q_t, mg/g) of the investigated polymer membranes was calculated, as shown in Figure 6. The q_t describes the amounts of metal ions adsorbed on the surface of the polymer membrane over a given time.

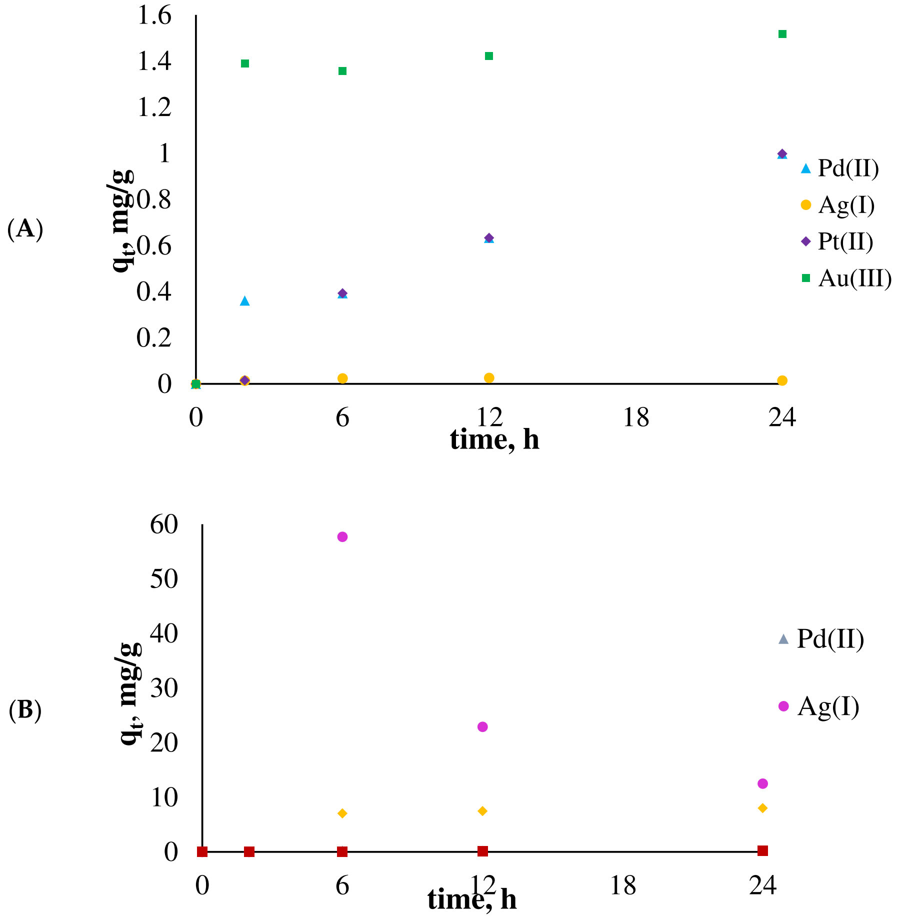


Figure 6. The changes in the sorption capacity of the polymer membranes with 20 wt.% salen as an ion carrier during sorption: (**A**) for single-component metal ions solutions, (**B**) for the polymetallic solution. The given values of q_t carry ±0.02.

In Figure 6A,B, some differences can be noticed. First of all, the values of the sorption capacities for the polymetallic solution were larger by two orders of magnitude. For the single component solutions, the sorption capacity over the whole process was the largest for Au(III) and the smallest for Ag(I) ions, respectively, whereas for the polymetallic solution, the exact opposite was observed. The qt obtained for platinum ions was similar for both solutions.

In single-component solutions, the qt decreased in the following order: Au(III) > Pt(II) > Pd(II) > Ag(I), which is the same as the order of electronegativity of the investigated metal ions: Au(III) 2.54 > Pt(II) 2.28 > Pd(II) 2.20 > Ag(I) 1.93. The greater electronegativity of the metal ion caused the greater affinity of this metal for binding to the ligand; thus, the qt of Au(III) was the largest.

On the other hand, in the polymetallic solution, the order of the values of qt was connected with the valence of investigated elements and decreased in the following order: Ag(I) > Pt(II) > Pd(II) > Au(III). Thus, the Ag(I) ions represent the greatest competition for the metal ions present in the solution because they only need one electron to return to the basic state.

Figure 7 shows the percentage of removal of noble metal ions from single-component aqueous solutions (%R_s) during the sorption process conducted after 24 h, while the efficiency of the desorption process (%R_{des}) was conducted for 48 h and is shown in Figure 8.

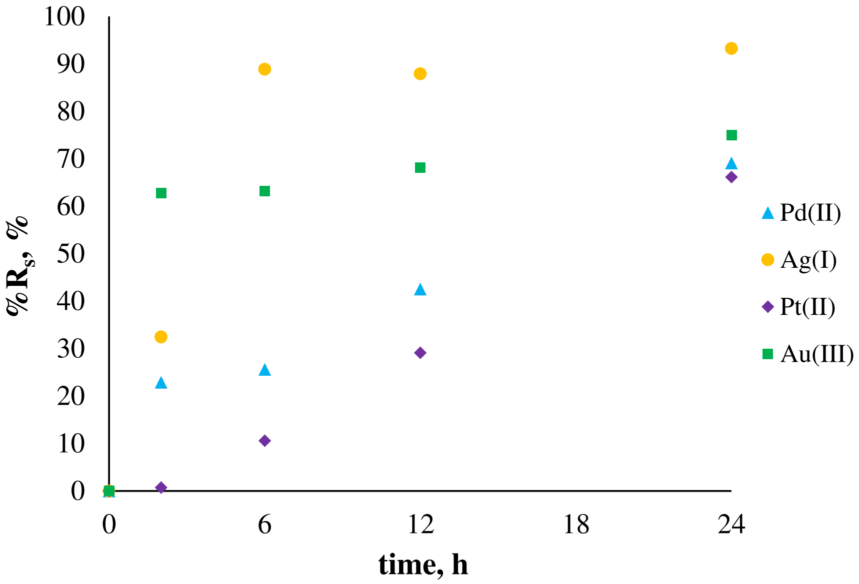


Figure 7. The percentage recovery (%R_s) of metal ions from single-component solutions using polymer membranes containing salen. The given values of %R_s carry ±0.01.

The percentage of noble metal ion removal from the single-component solutions for all metal ions increased with time. In the case of sorption of Au(III) and Ag(I) ions, equilibrium was already reached after 12 h, whereas Pt(II) and Pd(II) ions needed more time. The order of %R_s is as follows: Ag(I) > Au(III) > Pd(II) > Pt(II).

After sorption, the opposite process (i.e., desorption) was conducted. For desorption of Pd(II), Ag(I), Pt(II), and Au(III) ions from the surface of polymer membranes containing the investigated ligand (salen), the solution of 5 mol/l of nitric acid was used. Figure 8 presents the percentage of metal ion desorption as the sum of previously adsorbed metal ions on the surface of polymer membranes.

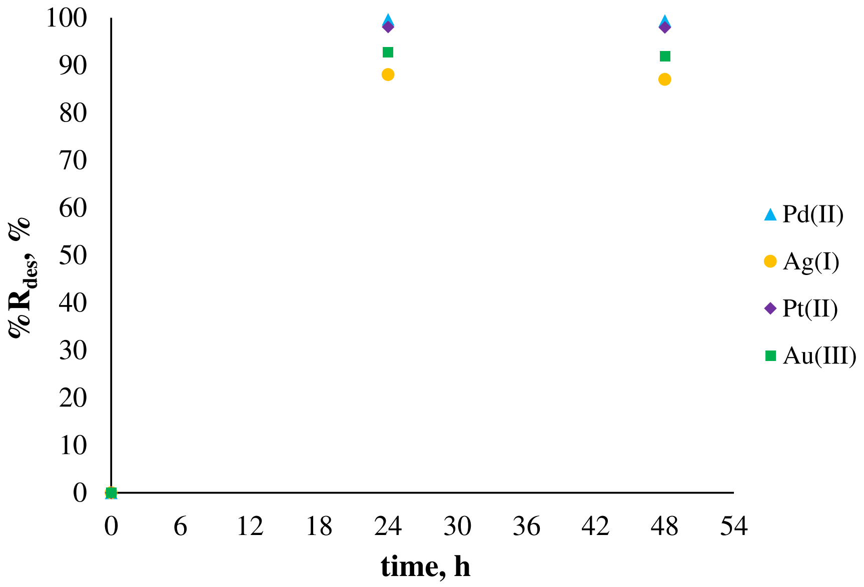


Figure 8. The sum of desorbed metal ions after 24 and 48 h from the surface of membranes previously used to absorb metal ions from single-component solutions. The given values of $\%R_{des}$ carry ±0.01.

Figure 8 shows that all previously sorbed metal ions on the surface of polymer membranes containing *N,N′*-bis(salicylidene)ethylenediamine were transferred into a solution of nitric acid. It should be noted that the volume of the solution used for desorption was three times smaller (10 mL) compared to the one used for sorption. After 24 h of desorption, almost 100% of all metal ions adsorbed. This confirms that by using investigated membranes containing salen as an ion carrier, it is possible to successfully adsorb metal ions from an aqueous solution on the surface of the membrane and recovered them to another solution.

The percentage of noble metal ion removal ($\%R_s$) from the polymetallic solution for all metal ions increased with time (Figure 9).

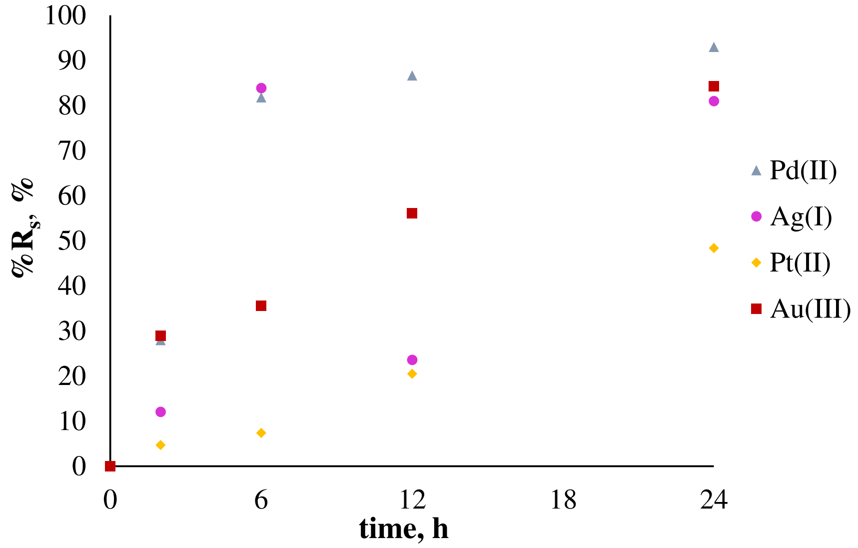


Figure 9. The percentage recovery ($\%R_s$) of metal ions from the polymetallic solution using a polymer membrane containing salen. The given values of $\%R_s$ carry ±0.01.

The percentages of noble metal ion removal after 24 h of sorption from polymetallic solution (%R_s) were 92.96%, 84.26%, 80.94%, and 48.36% for Pd(II), Au(III), Ag(I), and Pt(II) ions, respectively.

Figure 10 presents the results of desorption.

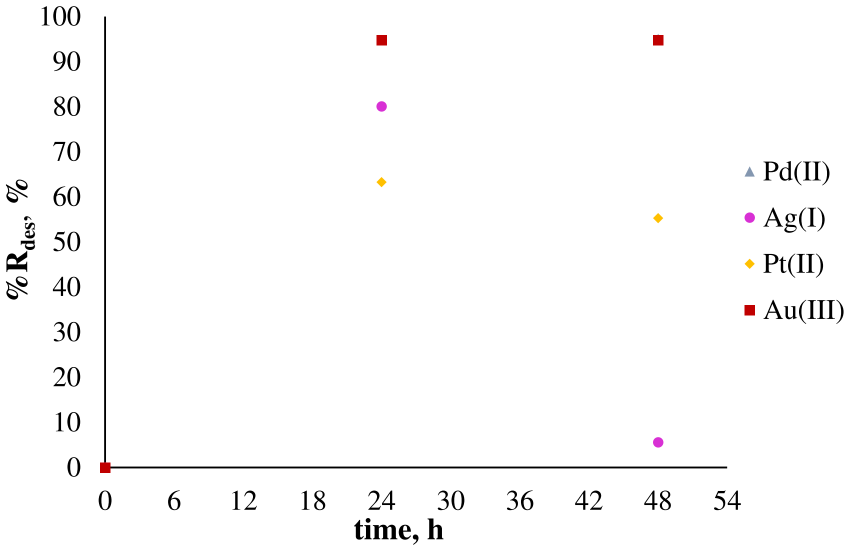


Figure 10. The sum of desorbed metal ions after 24 and 48 h from the surface of membranes previously used to absorb metal ions from a polymetallic solution. The given values of %R_{des} carry ±0.01.

The highest percentage recovery was observed after 24 h of desorption for Pd(II) (95.03%), then for Au(III) (94.75%), Ag(I) (80.06%), and Pt(II) (63.25%). Compared to desorption conducted after the adsorption of metal ions from single-component solutions, the %R_{des} was lower, and desorption was more complicated, likely because of the presence of the mixtures of salen complexes with investigated metal ions on the surface of the membranes.

As a result of the conducted experiments (Table 4), the highest percentages of noble metal ion recovery from single-component solutions were observed for Ag(I) (93.23%—sorption, 88.04%—desorption) and Au(III) (74.99%—sorption, 92.72%—desorption) ions, whereas for polymetallic solutions, the highest values were observed for Pd(II) (92.96%—sorption, 94.81%—desorption) and Au(III) (84.26%—sorption, 94.72%—desorption).

Table 4. The results of the recovery of precious metal ions (Pd^{2+}, Ag^{+}, Pt^{2+}, and Au^{3+}) from single-component and polymetallic solutions using polymer membranes containing *N,N′*-bis(salicylidene)ethylenediamine.

Type of Solution	Metal Ions	The Percentage of Sorption, %R_s [%]	The Percentage of Desorption, %R_{des} [%]
single component solution	Pd^{2+}	69.11	99.68
	Ag^{+}	93.23	88.04
	Pt^{2+}	66.13	98.07
	Au^{3+}	74.99	92.72
polymetallic solution (MIX)	Pd^{2+}	92.96	94.81
	Ag^{+}	80.94	80.06
	Pt^{2+}	48.36	63.25
	Au^{3+}	84.26	94.72

The given values of %R_s and %R_{des} carry ±0.01.

3.4. Mass Spectrometry

High-resolution mass spectrometry (HRMS) characterized by high accuracy of mass measurement (more precisely, the mass-to-charge ratio of ions, m/z) [25] was used to examine the elemental composition of complexes formed in separated organic phases obtained after liquid–liquid extraction experiments (described in detail in Section 2.4) by *N,N′*-bis(salicylidene)ethylenediamine with noble metal ions such as Au^{3+}, Pd^{2+}, and Pt^{2+}. In all experiments, ionization of molecules was performed by the utilization of the electrospray ionization method (ESI) because ESI, in the case of most small molecules/systems, allows their direct "transfer" from solution to the mass spectrometer without changing their structure [26]. ESI HRMS was previously successfully used to study the elemental composition and charge of complexes formed by salen with copper(II), zinc(II), and nickel(II) ions after the solvent extraction processes [17]. However, it is necessary to emphasize that ESI-HRMS does not allow for the detection of neutral complexes present in the solutions (which cannot be ionized under the experimental conditions) or those that may become neutral as a result of ionization (in ESI, ionization usually occurs as a result of attaching one or more protons to the molecules). ESI-HRMS spectra of the analyzed samples are shown in Figure 11 (samples containing Au^{3+}) and Figure 12 (samples containing Pd^{2+} or Pt^{2+}), while the ESI-HRMS data of the main ions found are presented in Table 5.

Table 5. ESI HRMS data of the main ions found in the samples of the separated organic phases after liquid–liquid extraction (performed for samples in which the molar ratio of metal ions to ligand (M:L) was 1:5, L-*N,N′*-bis(salicylidene)ethylenediamine) diluted (1:1) in methanol.

$Au(NO_3)_3$ and L ($C_{16}H_{16}N_2O_2$)			
m/z_{meas}	**m/z_{calc}**	**Assignment**	**Mass Error [ppm]**
122.0603	122.0606	$[C_7H_8N_1O_1]^+$	2.46
165.1023	165.1028	$[C_9H_{12}N_2O_1 + H]^+$	3.03
269.1283	269.1290	$[L + H]^+$, $(C_{16}H_{17}N_2O_2)^+$	2.60
463.0715	463.0720	$[Au^{3+} + L\text{-}2H]^+$, $(AuC_{16}H_{14}N_2O_2)^+$	1.08
$Pd(NO_3)_2$ and L($C_{16}H_{16}N_2O_2$)			
m/z_{meas}	**m/z_{calc}**	**Assignment**	**Mass Error [ppm]**
122.0604	122.0606	$[C_7H_8N_1O_1]^+$	1.64
165.1025	165.1028	$[C_9H_{12}N_2O_1 + H]^+$	1.82
269.1287	269.1290	$[L + H]^+$, $(C_{16}H_{17}N_2O_2)^+$	1.11
373.0166	373.0168	$[Pd^{2+} + L\text{-}H]^+$, $(PdC_{16}H_{15}N_2O_2)^+$	0.53
$Pt(NO_3)_2$ and L($C_{16}H_{16}N_2O_2$)			
m/z_{meas}	**m/z_{calc}**	**Assignment**	**Mass Error [ppm]**
122.0604	122.0606	$[C_7H_8N_1O_1]^+$	1.64
165.1025	165.1028	$[C_9H_{12}N_2O_1 + H]^+$	1.82
269.1288	269.1290	$[L + H]^+$, $(C_{16}H_{17}N_2O_2)^+$	0.74

The results of the ESI HRMS experiments performed for all analyzed samples showed the formation of a series of similar, singly charged ions related to the presence of salen such as protonated salen molecules $[L + H]^+$, salen fragments ions $[C_7H_8N_1O_1]^+$, and $[C_9H_{12}N_2O_1 + H]^+$. The generation of identical fragment ions of salen was also observed in the case of ESI HRMS experiments conducted for organic phases resulting from classical liquid–liquid extraction containing *N,N′*-bis(salicylidene)ethylenediamine and copper, zinc or nickel ions [17]. It is most probably related to partial L molecule decomposition (i.e., in the solution, during ESI experiments or compound storage). In the case of samples containing salen and gold(III) ions, an additional, not very intensive signal at $m/z = 463.0715$ was observed (Figure 11), which can be assigned to $[Au^{3+} + L\text{-}2H]^+$ ions. Given the high mass accuracy of the HRMS mass spectrometry, there can be no question as to the elemental composition or charge of the ions generated. The process of formation of such mononuclear complexes must be associated with the detachment of two protons from the ligand L molecules (most likely from hydroxyl oxygen atoms). In the case of samples containing palladium ions, the formation of similar mononuclear complexes with the formula $[Pd^{2+} + L\text{-}H]^+$ was also observed (Figure 12, left spectrum, minor signal at $m/z = 373.0166$), which must be accompanied by the loss of a single proton from the *N,N′*-bis(salicylidene)ethylenediamine molecules. Interestingly, no corresponding ion formation was noted in the case of samples containing platinum ions (Figure 12, right spectrum). Based on the current and previous results (experiments performed for copper, zinc, and nickel ions, where the formation of other types of salen/metal ion complexes was also observed, for example, $[M^{2+} + 2L - H]^+$, $[2M^{2+} + 2L - 3H]^+$, where M = Cu^{2+}, Zn^{2+}, Ni^{2+}) [17], it can be concluded that the properties of noble metal ions significantly affected the elemental composition of the formed species. Certainly, not only is the valence of metal ions important, as different metal ion/salen complexes were identified in the ESI HRMS experiments performed for solutions containing other divalent metal ions: copper, nickel, zinc, and palladium. It is necessary to consider the possibility of generating neutral complexes containing several noble metal ions and/or several salen ligands in the examined solutions, which the applied technique could not detect. Moreover, it is very likely considering the results of liquid–liquid extraction (very high process efficiency).

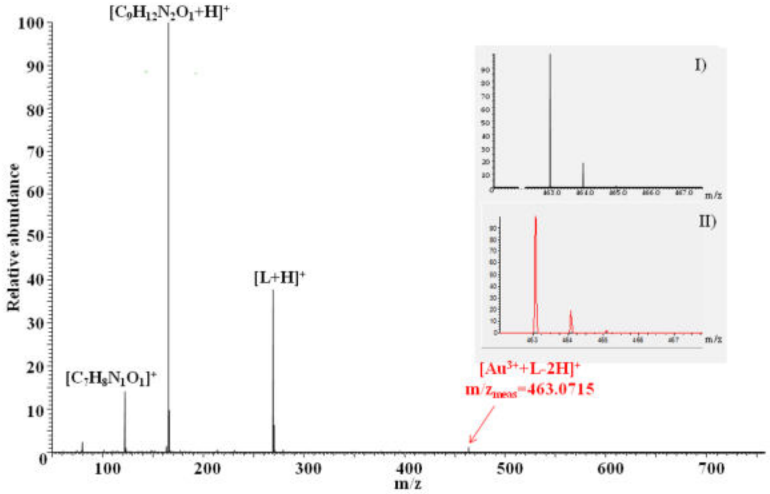


Figure 11. ESI-HRMS spectrum recorded for the sample of the separated organic phase after liquid–liquid extraction containing *N,N′*-bis(salicylidene)ethylenediamine (L) and Au^{3+} ions. Inset shows the isotopic pattern for $[Au^{3+}+L\text{-}2H]^+$ ions; (**I**) experimental, (**II**) theoretical. Unassigned minor signals correspond to ions not relevant to this study (e.g., formed by solvent molecules).

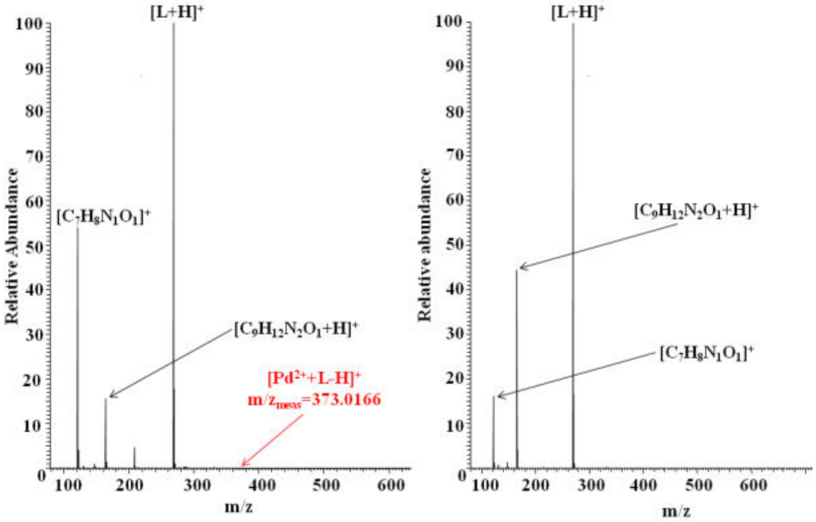


Figure 12. ESI-HRMS spectra recorded for the samples of the separated organic phases after liquid–liquid extraction containing *N,N′*-bis(salicylidene)ethylenediamine (L) and Pd^{2+} (**left**) or Pt^{2+}(**right**) ions, respectively. Unassigned minor signals correspond to ions not relevant to this study (e.g., formed by solvent molecules).

4. Summary

The results show that *N,N′*-bis(salicylidene)ethylenediamine can be used as an effective extractant/carrier in recovering noble metal ions from aqueous solutions using separation processes such as solvent or membrane extraction. For scientists involved in research on the application of the extraction and membrane processes for noble metal ion recovery, the main aim is to find an effective extractant/carrier with a high recovery rate, which is not dangerous to the environment. Table 6 compares the efficiency of selected carriers used to recover noble metal ions with the efficiency of *N,N′*-bis(salicylidene)ethylenediamine used in this study.

Table 6. Selected extractants/carriers used in the separation processes (SE, PM) for the recovery of noble metal ions.

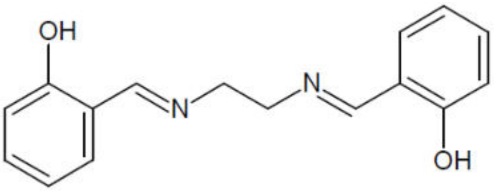
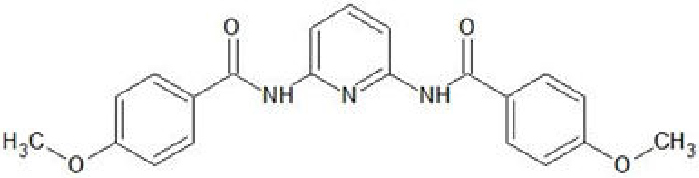
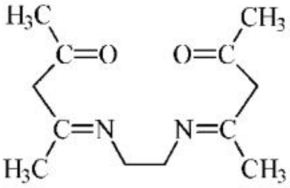
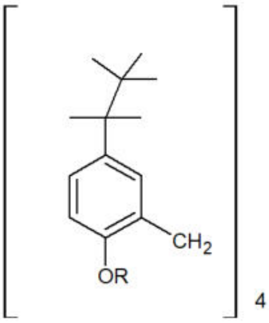
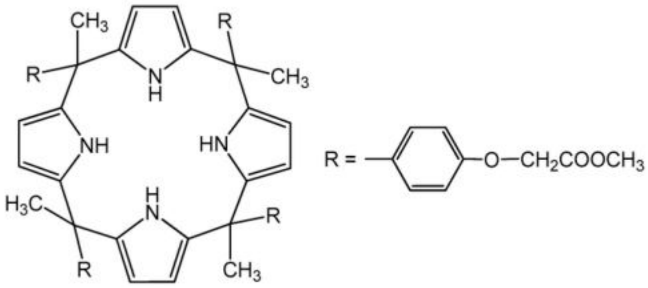
		N,N′-bis(salicylidene)ethylenediamine)			
					
[%]	Pd(II)	Ag(I)	Pt(II)	Au(III)	Ref.
$\%E_M$	92.98–99.35%	99.83–99.95%	94.98–99.15%	94.89–99.56%	[This work]
$\%R_s$	69.11%	93.23%	66.12%	74.99%	[This work]
		2,6-bis(4-methoxybenzoyl)-diaminopyridine			
					
[%]	Pd(II)	Ag(I)	Pt(II)	Au(III)	Ref.
$\%E_M$	~99%	~99%	~99%	~99%	[27]
$\%R_s$	23.82%	94.89%	38.99%	63.46%	[27]
		Ethylenodiamino-bis-acetylacetone			
					
[%]	Pd(II)	Ag(I)	Pt(II)	Au(III)	Ref.
$\%E_M$	87–93%	-	-	56–65%	[28]
$\%R_s$	-	-	-	-	-
		Calix[4]arene derivatives			
					

Table 6. *Cont.*

***N,N′*-bis(salicylidene)ethylenediamine)**

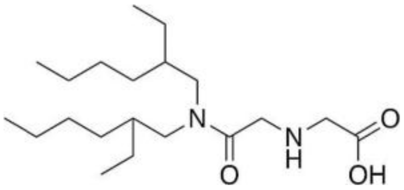
[%]	Pd(II)	Ag(I)	Pt(II)	Au(III)	Ref.
%E$_M$	70.9%	13.3%	64.4%	-	[29]
	99%	-	-	-	[30]
	95%	-	-	-	[31]
%R$_S$	-	-	-	-	-

Calix[4]pyrrole derivatives



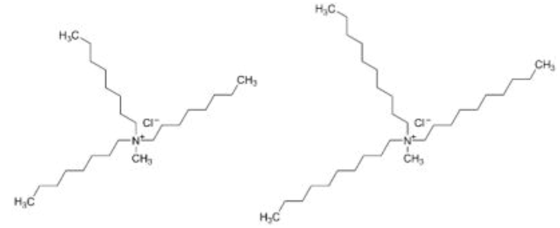
[%]	Pd(II)	Ag(I)	Pt(II)	Au(III)	Ref.
%E$_M$	-	-	-	-	-
%R$_S$	-	92.77%	-	-	[32]
	-	80.1%,	-	-	[33]

D$_2$EHAG



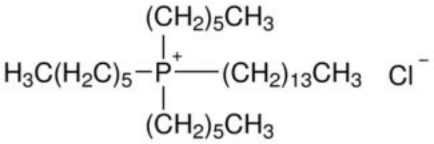
[%]	Pd(II)	Ag(I)	Pt(II)	Au(III)	Ref.
%E$_M$	-	-	-	69%	[34]
	98%	-	-	-	[35]
%R$_S$	-	-	-	96%	[34]

Aliquat 336



[%]	Pd(II)	Ag(I)	Pt(II)	Au(III)	Ref.
%E$_M$	99%	-	-	-	[36]
	99%	-	-	99%	[37]
	-	-	~100%		[38]
%R$_S$	80%	-	-	-	[39]

Cyphos IL 101



$$H_3C(H_2C)_5-\overset{(CH_2)_5CH_3}{\underset{(CH_2)_5CH_3}{P^+}}-(CH_2)_{13}CH_3 \quad Cl^-$$

[%]	Pd(II)	Ag(I)	Pt(II)	Au(III)	Ref.
%E$_M$	-	-	~100%	-	[38]
	>90%	93–95%	-	-	[40]
	99.9%	-	-	99.9%	[41]
	-	-	-	98.4%	[42]
	84–90%	-	-	-	[43]
%R$_S$	~45%	-	-	-	-

Based on the results reported by various scientists, it can be concluded that newly synthesized or commercial extractants/ion carriers can be used to recover noble metal ions (Pd, Ag, Pt, and Au). For example, calix[4]arene derivatives can be effective extractants in the recovery of palladium, silver, and platinum ions from aqueous solutions whereas calix[4]pyrrole derivatives can be used as extractants for palladium ions and as carriers for silver ions. *N*-[*N*,*N*-di(2-ethylhexyl)aminocarbonylmethyl]glycine (D2EHAG) can also be applied in solvent extraction for the recovery of palladium (98%) and gold (69%) ions, and in membrane extraction for the removal of gold ions (96%). Aliquat 336 is an effective extractant for palladium, platinum, and gold ions. Additionally, an amine derivative of β-diketone can be applied to separate palladium and gold ions by solvent extraction. Moreover, ionic liquids are commonly employed in the separation processes to remove noble metal ions from aqueous solution (e.g., Cyphos IL 101 is a good extractant of palladium, silver, platinum, and gold ion solvent extraction). Fajar et al. used a trioctyl(dodecyl) phosphonium chloride ($P_{88812}Cl$) ionic liquid as an ion carrier in polymer inclusion membrane for the removal of Pd(II) ions with an efficiency of 98% [44]. Boudessocque et al. applied ionic liquids bearing tetrahexylammonium and tetraoctylammonium cations and halide, dicyanamide, thiocyanato, and bis(trifluoromethysulfonyl)imide in the solvent extraction process for removal of Au(III) and Pt(II) ions (efficiency above 90%) [45].

Moreover, sorption is also a commonly used method for removing noble metal ions from aqueous solutions. Vojoudi et al. used modified silica-coated magnetic nanoparticles and silica gel as a sorbent to remove gold, palladium, and silver ions [46]. Tahmasebi and Yamini employed polythiophene-coated Fe_3O_4 nanoparticles as a selective adsorbent for magnetic solid-phase extraction of silver(I), gold(III), and palladium(II) [47]. Aliquat 336 can be used as an extractant to remove gold, palladium, and platinum ions by the solvent extraction process and can also be applied as sorbent-impregnated for the selective recovery of gold ions (e.g., Aliquat-336-impregnated alginate capsule (AIAC)) [48]. Huang et al. made four adsorption and desorption cycles with a trithiocyanuric-Zr based MOFs adsorbent (ZT-MOFs) for the removal of gold ions (from 94.5% to 87.5%, depending on the cycle) [49].

Despite many available extractants/ion carriers, none of the analyzed compounds were applied to recover all investigated noble metal ions (palladium, silver, platinum, and gold ions) from an aqueous solution. Moreover, *N*,*N*′-bis(salicylidene)ethylenediamine) can be used as effective active compounds for both processes (solvent and membrane extraction) for the recovery of palladium, silver, platinum, and gold ions.

5. Conclusions

The results of the application of *N*,*N*′-bis(salicylidene)ethylenediamine to recover noble metal ions (Pd^{2+}, Ag^{+}, Pt^{2+}, and Au^{3+}) from model aqueous solutions containing single metal ions or their mixture show that this compound is a very efficient extractant in solvent extraction and a carrier in membrane processes. Based on the absorption spectra of complexes of salen with silver, palladium, platinum, and gold ions, it was found that various types of complexes (different L:M ratios) can be formed in the solution. For example, the values of the stability constants were the highest for complexes of the type M:L of 1:1 in the case of palladium and platinum ions (5.54 and 5.48), whereas in the case of silver ions for M:L of 1:2 (4.40) and gold ions for M:L of 1:3 (4.00), respectively. The application of electrospray ionization high-resolution mass spectrometry allowed us to confirm that salen forms mononuclear complexes with gold and palladium ions in aqueous solutions of the type $[Au^{3+} + L\text{-}2H]^{+}$ and $[Pd^{2+} + L\text{-}H]^{+}$. However, it should be emphasized that the technique used does not allow for identifying other neutral complexes that certainly form during extraction and membrane separation. The results of the extraction experiments show the very high efficiency of salen as an extractant, both in the case of processes conducted in single-component solutions (extraction percentage reached over 99% for all noble metal ions) as well as in polymetallic solutions (the lowest extraction percentage was over 94%). The results of noble metal ion removal obtained with the polymer membranes containing

N,N′-bis(salicylidene)ethylenediamine as a carrier were slightly worse as the percentage of sorption (%R_s) of metal ions from single-component solutions was the highest for silver ions (93.23%) and the lowest for platinum ions (66.13%), whereas, for multi-metal solutions, these values were slightly lower (the highest for Pd(II) at 92.96%, and the lowest for Pt(II) at 48.36%). The critical advantage of membrane processes is the possibility of conducting desorption and, consequently, transferring noble metal ions from the surface of membranes to another solvent. The obtained percentage of desorption (%R_{des}) was very high, both for single-component solutions (the highest, i.e., 99%, for Pd(II) ions and the lowest, i.e., 88%, for Ag(I) ions) as well as for polymetallic solution (the lowest, i.e., 63.25% for Pt(II)). Another advantage of the membrane process over classic extraction is the need for much smaller amounts of chemical reagents (salen, organic solvents), which is important for economic and environmental reasons.

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membranes

Article

N,N'-Bis(salicylidene)ethylenediamine (Salen) as an Active Compound for the Recovery of Ni(II), Cu(II), and Zn(II) Ions from Aqueous Solutions

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Abstract: In this paper, three main methods of metal ion separation, i.e., liquid–liquid extraction, transport across polymer inclusion membranes (PIMs), and sorption/desorption, are described. In all of them, *N*,*N'*-bis(salicylidene)ethylenediamine (salen) was used as an active compound, i.e., as an extractant or as a carrier for the recovery of Ni(II), Cu(II), or Zn(II) ions from aqueous solutions. In each case, the recovery was performed on a model solution, which contained only a single metal ion. The obtained results were compared with the author's previous results for the separation of metal ions using β-diketones, since both β-diketones and salen form the so-called Werner-type complexes. Electrospray ionization high-resolution mass spectrometry (ESI-HRMS) was also applied to confirm the ability of the carrier to form complexes with metal ions in a solution. Moreover, spectrophotometry was used to determine the stability constant of the obtained complexes.

Keywords: *N*,*N'*-bis(salicylidene)ethylenediamine; salen; metal ions; nickel(II), copper(II), zinc(II), liquid–liquid extraction; polymer inclusion membranes; sorption

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1. Introduction

The structure of the compound molecule (ligand) has a huge influence on the process of forming its complexes as the ligand, being a chemical form directly connected with the central atom (metal ion), uses a free pair of electrons. Furthermore, this phenomenon is closely related to the possibility of using ligands as extractants or as carriers in separation processes such as liquid–liquid extraction or transport across polymer inclusion membranes, respectively. In both these processes, complex compounds of metal ions and ligands are formed. The stability of these complexes affects the efficiency of metal ion recovery from the aqueous solution. Ligands, which form very stable complexes, are successfully used as extractants in solvent extraction or precipitation processes. However, they cannot be used as carriers in PIMs, because binding between a ligand and a metal ion is so strong that the metal cannot be released to the receiving phase and, therefore, cannot be recovered.

Among many types of ligands, the most common are those that form the so-called Werner- type complexes [1]. This means that a metal ion is bound through one of three possible donor atoms of the ligand: nitrogen, oxygen, or sulfur. The ligands containing nitrogen and oxygen are imidazole [2] and trioctyl phosphine oxide (TOPO), respectively [3]. In turn, Cyanex 301 [4] and Cyanex 471X [5] have a sulfur atom in the structure. All of these are used in metal ion separation processes, e.g., in liquid–liquid extraction or transport across polymer inclusion membranes (PIMs).

Complexation reactions occur by binding one or more than one donor atoms. A ligand that has only one atom that coordinates directly to the central atom in a complex is called a monodentate [6]; in turn, a polydentate ligand (chelate) [7] is a structure that is attached to a central metal ion by bonds from two or more donor atoms.

The literature identifies many examples of polydentate ligands which form more stable complex compounds than monodentate ligands. For example, β-diketones are a group of compounds which bind cations by two oxygen atoms and form very stable chelates. LIX-54 is a well-known copper(II) extractant from the group of β-diketones [8].

N,*N*′-Bis(salicylidene)ethylenediamine (salen) is also a polydentate ligand with oxygen and nitrogen donor atoms. Its structure is shown in Figure 1.

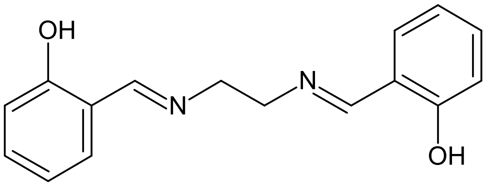

Figure 1. Structure of *N*,*N*′-bis(salicylidene)ethylenediamine (salen).

The literature states that salen easily forms complexes with various metal ions and that these complexes can have different applications. Earlier data on the complexes of salen were reported in 1966 by Gerloch et al. [9]. They described complexation reaction of ferric chloride with the Schiff base, i.e., salen in acetone solution. The obtained complex was monomeric in chloroform solution and non-conducting in nitromethane. Lewis et al. [10] reported the magnetic properties of some binuclear complexes of chromium(III) and iron(III). Furthermore, Chuguryan and Dzyubenko [11] used a spectrophotometric method for complexing neptunium with *N*,*N*′-bis(salicylidene)ethylenediamine in aqueous ethanol solutions in the range of pH = 6–10 and temperature of 25 ± 1 °C. They proved that, in the given conditions, only one mononuclear $NpO_2(salen)^-$ complex could be prepared. The determined concentration stability constant was equal to 7.5 ± 0.035. They suggested using the studied compound for spectrophotometric analysis of neptunium in aqueous alcohol solutions. Vol′pin et al. [12] in turn considered the use of chelate cobalt(II) complex [Co(*N*,*N*′-bis(salicylidene)ethylenediamine)] as an effective catalyst for NADH (nicotinamide adenine dinucleotide) oxidation in methanol at room temperature. Nielson et al. [13] described the preparation of polymeric $\{TiO(N,N'\text{-bis(salicylidene)ethylenediamine})\}_n$ from $[Ti(OCHMe_2)_2(acac)_2]$ and salen-H_2 in methanol solution. Yang et al. [14] synthesized and characterized *N*,*N*-bis(salicylidene)ethylenediamine zinc(II) iodide ($ZnLI_2$), and applied it as the electrolyte of a dye-sensitized solar cell. Huerta-Jose et al. [15] prepared and employed indium(III) complex of salen as a chemo-sensor for the recognition of HSO_4^-.

Finally, we found three papers in which salen was used for the removal of metal ions from solutions. Tadjorodi et al. [16] prepared BSEA–SBA-15 by covalently anchoring *N*,*N*′-bis(salicylidene)ethylenediamine (BSEA) on mesoporous silica (SBA-15) using a hydrothermal method. The authors suggested that BSEA–SBA-15 can be used in the future as an effective adsorbent for the removal of metal ions due to it having a porous structure and active functional groups. Dadfarnia et al. [17] synthesized silver ion-imprinted polymer, in the presence of an Ag(I)–salen complex, using 4-vinylpyridine as the functional monomer, ethylene glycol dimethacrylate as the crosslinker, and 2,2-azobis(isobutyronitrile) as the initiator. Then, the imprinted Ag(I) ions were completely removed by leaching. The polymer was employed as a selective sorbent for extraction and separation of the trace amounts of Ag(I) ions. Three years ago, Reffas et al. [18] studied the cloud point extraction for the purpose of separation of copper(II) from aqueous saline sulfate medium with salen as the chelating extractant and the polyethoxylated alcohol Tergitol 15-S-7 as the biodegradable non-ionic surfactant.

Based on the found data, due to its structure and insolubility in water, *N*,*N*′-bis(salicylidene)ethylenediamine can be used as an extractant or a carrier in both liquid–liquid extraction and transport across PIMs. That is why, in this paper, we considered the possibility of using salen in the above-mentioned processes. We also describe its use in sorption processes. The obtained complexes of salen and Ni(II), Cu(II), and Zn(II) were characterized using spectrophotometric and mass spectrometry methods.

2. Materials and Methods

2.1. Reagents

N,*N*′-Bis(salicylidene)ethylenediamine was purchased from Merck (Kenilworth, NJ, USA). Its selected properties are presented in Table 1.

Table 1. Selected properties of *N*,*N*′-bis(salicylidene)ethylenediamine (salen) [19].

Form	Crystal
Color	Yellow
Assay	98%
Melting point	127–128 °C
Boiling point	411.48 °C
Solubility in water	Insoluble
Solubility in chloroform	0.1 g/mL

The standard solutions of metal ions (Ni(II), Cu(II), and Zn(II)) were purchased from Sigma Aldrich (Poznan, Poland), while the aqueous solutions of metal ions ($Ni(NO_3)_2$, $Cu(NO_3)_2$, and $Zn(NO_3)_2$) were made from their analytical reagent grade salts (Avantor, Gliwice, Poland) in double-distilled water. The concentration of these solutions was standardized using the atomic absorption spectrometry method. The solution of analytical reagent grade nitric acid (Avantor, Gliwice, Poland) was standardized against anhydrous sodium carbonate. Ammonia was obtained from Avantor (Gliwice, Poland). Methanol, chloroform, and tetrahydrofuran (analytical reagent grade, Avantor, Gliwice, Poland) were used without further purification. Polyvinyl chloride (PVC) with an average molecular weight of 72,000 was obtained from ANWIL (Wloclawek, Poland). Bis(2-ethylhexyl)adipate (DAO) was purchased from Sigma-Aldrich (Poznan, Poland).

2.2. Stability Constants of Complexes of N,N′-Bis(salicylidene)ethylenediamine with Various Metal Ions

For calculation of stability constants of the complexes of salen with nickel(II), copper(II), and zinc(II) ions, a known spectrophotometric method was used [20]. The stock metal ions solutions were made from the appropriate standard solutions, and their concentration was equal to 0.1 g/L. The salen was dissolved in methanol, and the concentration of this stock solution was about 0.001 mol/L. Then, the spectrophotometric titration was carried out, and the absorption spectra of each prepared sample were recorded on a Cary 50 spectrophotometer (Varian, Melbourne, Victoria, Australia). The molar ratios of the components (salen with respect to Ni(II), Cu(II), or Zn(II)) were different in each sample. The spectra were recorded in the range of 200 to 500 nm.

2.3. Liquid–Liquid Extraction of Metal Ions from Model Solution Using N,N′-Bis(salicylidene)ethylenediamine

N,*N*′-Bis(salicylidene)ethylenediamine was used as an extractant during the performed liquid–liquid extraction of metal ions (Ni(II), Cu(II), or Zn(II)) from a model solution. The liquid–liquid extraction process was carried out in three variants with different salen–metal ion molar ratios (the concentration of metal ions in each case was constant):

I. 0.5:1 (3.6×10^{-5} mol of salen in organic phase with 7.2×10^{-5} mol of Ni(II), Cu(II), or Zn(II) ions in the aqueous phase);
II. 1:1 (7.2×10^{-5} mol of salen in organic phase with 7.2×10^{-5} mol of Ni(II), Cu(II), or Zn(II) ions in the aqueous phase);

III. 1.5:1 (10.8×10^{-5} mol of salen in organic phase with 7.2×10^{-5} mol of Ni(II), Cu(II), or Zn(II) ions in the aqueous phase).

All measurements were run at 25 °C, and a fixed ionic strength was maintained in the aqueous phase with 0.5 mol/L solution of potassium nitrate. The aqueous phase contained, except for various metal ions (Ni(II), Cu(II), or Zn(II)), ammonia to keep a suitable pH (12.5) during the extraction process. Chloroform was used as a solvent in the organic phase. The volume of the organic phase was always equal to the volume of the aqueous phase, which was 3.6 mL. The prepared samples were then shaken for one hour. The equilibrium was established after approximately 15 min. After checking if any changes in the phase volumes occurred, the phases were separated. The concentration of metal ions in the aqueous phase after liquid–liquid extraction was determined by atomic absorption spectrophotometry (AAS 240FS Spectrometer, Agilent, Santa Clara, CA, USA).

2.4. Polymer Inclusion Membranes with N,N′-Bis(salicylidene)ethylenediamine

2.4.1. Preparation of Polymer Inclusion Membranes (PIMs)

The membranes were obtained by the casting method as described in our earlier paper [21]. All membranes were made of three components: polyvinyl chloride (PVC; as a polymer support), DAO (as a plasticizer), and *N,N′*-bis(salicylidene)ethylenediamine (as a metal ion carrier). Two types of compositions of the membranes were created: the first type with 20 wt.% salen and the second type with 40 wt.% salen. Smaller samples of the PIMs were cut out from the same membrane film to allow repeating the experiments. Obtained membranes were homogeneous and flexible.

2.4.2. Sorption of the Metal Ions onto Polymer Inclusion Membranes

The sorption of the metal ions onto obtained polymer inclusion membranes was conducted according to the method described by Best et al. [22]. Membranes were immersed in a beaker containing 50 mL of solution, which was made in the same way as the feed phase described in Section 2.4.4. The solution was shaken using a magnetic stirrer at a speed of 50 rpm. Samples of the solution were taken at regular time intervals and diluted using nitric acid; then, the concentration of metal ion was determined using the AAS method.

2.4.3. Desorption of the Metal Ions from Polymer Inclusion Membranes

The desorption of the metal ions from the surface of PIMs was performed by rinsing the membrane after the sorption process (Section 2.4.2) with distilled water; after drying, it was immersed in 30 mL of 0.05 mol/L aqueous nitric acid. Reduced volumes of solutions were used to concentrate the initial solutions from Section 2.4.2. Further operations were the same as in Section 2.4.2.

2.4.4. Transport Studies across Polymer Inclusion Membranes

The transport experiments were carried out in a permeation module cell, which was also presented in the authors' earlier paper [21]. As a feed phase, an aqueous solution containing 0.02 mol/L of metal ions (Ni(II), Cu(II), or Zn(II)) and ammonia was used. Ammonia was added to keep a suitable pH (12.5) during the process. As a receiving phase, the 0.05 mol/L aqueous solution of nitric acid was used.

2.5. Analysis of Complexes of N,N′-Bis(salicylidene)ethylenediamine with Various Metal Ions by Mass Spectrometry

The high-resolution mass spectrometry (HRMS) experiments were performed using a Q-Exactive Orbitrap mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) equipped with a TriVersa NanoMate robotic nanoflow ESI ion source (Advion BioSciences ltd., Ithaca, NY, USA). Samples of the separated organic phases after liquid–liquid extraction described in detail in Section 2.3, in variant III, were diluted (1:1) in methanol (Avator, Gliwice, Poland). MS 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). Obtained mass spectra were processed in Thermo Xcalibur software (ver. 4.1.31.9).

3. Results and Discussion

3.1. Complexation Properties of N,N′-Bis(salicylidene)ethylenediamine

The dissociation constant of salen was found in the ChemicalBook database. Its value is equal to $pK_a = 12.59 \pm 0.50$. According to the Brønsted–Lowry theory, the value of dissociation constant K_a of the ligand determines its basicity and tendency to dissociate a proton. At this pH, the proton can be easily replaced with other cations in a complexation reaction. This means that salen can be used as an extractant or as a carrier for the removal of metal ions from strong alkalic solutions, e.g., from wastewater from concrete companies [23], electroplating companies [24], or breweries [25].

The increase in value of K_a of the ligand causes an increase in the stability constant of its complexes [26].

The stability constants of the complexes of salen with Ni(II), Cu(II), and Zn(II) ions consisted of one mole of ligand and one mole of metal ion (type 1:1). A summary is presented in Table 2.

Table 2. Values of stability constants ($\log\beta_1$) of Ni(II), Cu(II), and Zn(II) complexes with *N*,*N*′-bis(salicylidene)ethylenediamine in an aqueous methanol solution at 25 °C.

Ligand	$\log \beta_1$		
	Ni(II)	**Cu(II)**	**Zn(II)**
N,*N*′-bis(salicylidene)ethylenediamine	5.438	5.452	5.426

The given values carry ±0.001 tolerance.

The obtained $\log \beta_1$ showed similar values. Small variations can be seen. The close proximity of the studied metals in the periodic table may explain this fact. The stability of a complex correlates with the size of ionic radius of the involved metal ion [27,28]. The obtained values of stability constants were inversely proportional to the values of ionic radii of their metal ions: Ni^{2+} ($r\ Ni^{2+} = 72$ pm) < Cu^{2+} ($r\ Cu^{2+} = 69$ pm) > Zn^{2+} ($r\ Zn^{2+} = 74$ pm). The highest stability constant was obtained for the complex of salen with copper(II) ions. The values of stability constants of salen complexes with nickel(II) and zinc(II) ions were lower than those for copper(II) complexes.

A similar situation occurred in the case of β-diketone. For example, the dissociation constant of acetylacetone in a water–methanol solution is equal to 9.65 [29], and the stability constants of its complexes with nickel(II), copper(II), and zinc(II) are 4.96, 8.24, and 5.76 [29], respectively. The dissociation constant of acetylacetone is lower than the pKa of salen, but the changes in stability constants for both compounds with particular metal ions are similar, except for the zinc(II) complex.

3.2. Separation Processes

In this paper, we describe the following separation processes: liquid–liquid extraction, transport across polymer inclusion membranes, and sorption/desorption. In all of them, *N*,*N*′-bis(salicylidene)ethylenediamine was used as an active compound (extractant or carrier) for the recovery of the investigated metal ions from solution. In each process, the recovery was performed on a model solution which contained only a single metal ion (e.g., Ni(II)).

In the sections below, the parameters of all mentioned processes are quantified and discussed.

3.2.1. Liquid–Liquid Extraction

The spectra and photographs below (Figure 2) clearly show that, during the extraction, the complexes of the investigated metal ions with salen used as an extractant were formed. The complexes of nickel(II), copper(II), and zinc(II) ions with salen in chloroform solutions had specific colors of red, purple, and yellow, respectively.

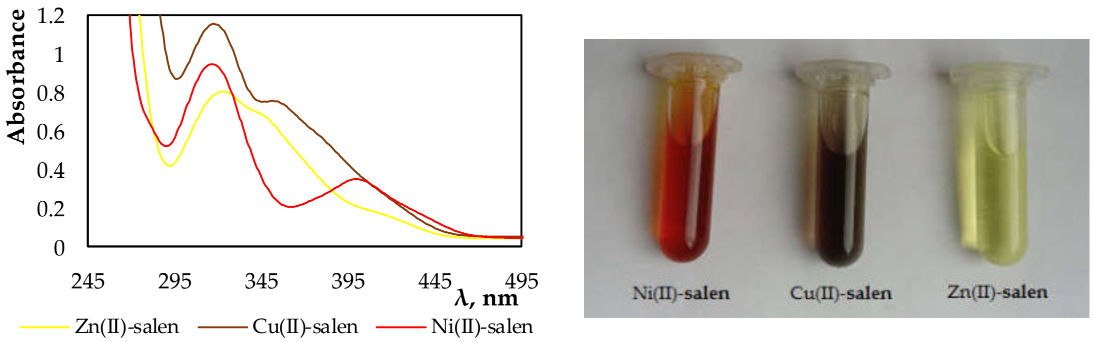

Figure 2. Absorption spectra and photography of organic phases after extraction using salen (variant III).

In order to analyze the process of extraction of metal ions from the simple model solution, further calculations were made. At the beginning, the distribution ratios (D_M) of metal ions for each investigated system were calculated using Equation (1).

$$D_M = \frac{C_{M(org)}}{C_{M(aq)}} = \frac{C_M^0 - C_M}{C_M}, \tag{1}$$

where C^0_M and C_M denote the analytical metal ion concentrations in the aqueous phase before and after attaining a partition equilibrium (mol/L), respectively.

Then, the percentage of metal ion extraction (%E) was calculated using Equation (2) for each of the investigated systems.

$$\%E = \frac{D_M \cdot 100\%}{D_M + \frac{V_{aq}}{V_{org}}}, \tag{2}$$

where V_{aq} and V_{org} are the volumes of aqueous and organic phases, respectively (V_{aq}/V_{org} = 3.6 mL/3.6 mL = 1).

Table 3 shows the values of D_M and %E, which were calculated for each of the three experiment variants with different salen–metal ion molar ratios.

Table 3. The distribution ratios (D_M) and the percentages of metal ion extraction (%E) of the investigated systems in ammonia solutions.

Variant of Experiment / salen:M	D_M			%E (%)		
	Ni(II)	**Cu(II)**	**Zn(II)**	**Ni(II)**	**Cu(II)**	**Zn(II)**
I / 0.5:1	0.40	2.04	0.72	28.54	67.14	41.89
II / 1:1	0.89	72.79	4.41	47.02	98.64	81.52
III / 1.5:1	1.56	486.00	7.12	60.98	99.79	87.68

The given values carry ±0.01 tolerance.

The received results show that the values of D_M and %E increased along with the increasing concentration of salen in the samples. The highest percentage of extraction (99.79%) was obtained for copper ions, whereas %E for zinc and nickel ions extracted in the same conditions was 87.68% and 60.98%, respectively. The obtained results proved that *N,N′*-bis(salicylidene)ethylenediamine can be successfully used as an extractant for metal ion recovery, especially for the recovery of copper(II) ions. For comparison, the values of %E obtained in our previous experiment [30], regarding the extraction of copper ions from ammonia solution using 3-allyl-acetylacetone, 3-butyl-acetylacetone, and unsubstituted acetylacetone as extractants, were lower and equal to 85%, 80%, and 72%, respectively.

3.2.2. Sorption

The analysis of the metal ion sorption process onto the membranes with 20 wt.% and 40 wt.% of salen was carried out using Equation (3).

$$q_t = \frac{C^i - C^t}{m} \cdot V \quad (3)$$

,

where q_t denotes the sorption capacity (mg/g), V is the volume of the solution (L), m is the mass of the sorbent (g), and C^i and C^t are analytical metal ion concentrations in the solution at the beginning and after an appropriate time of sorption process (mol/L), respectively.

Here, q_t describes the amount of metal ions adsorbed on the surface of the membrane over a specific period of time. Figure 3 presents plots of q_t vs. time for sorption processes of the investigated Ni(II), Cu(II), or Zn(II) ions onto the membranes containing 20 wt.% or 40 wt.% salen.

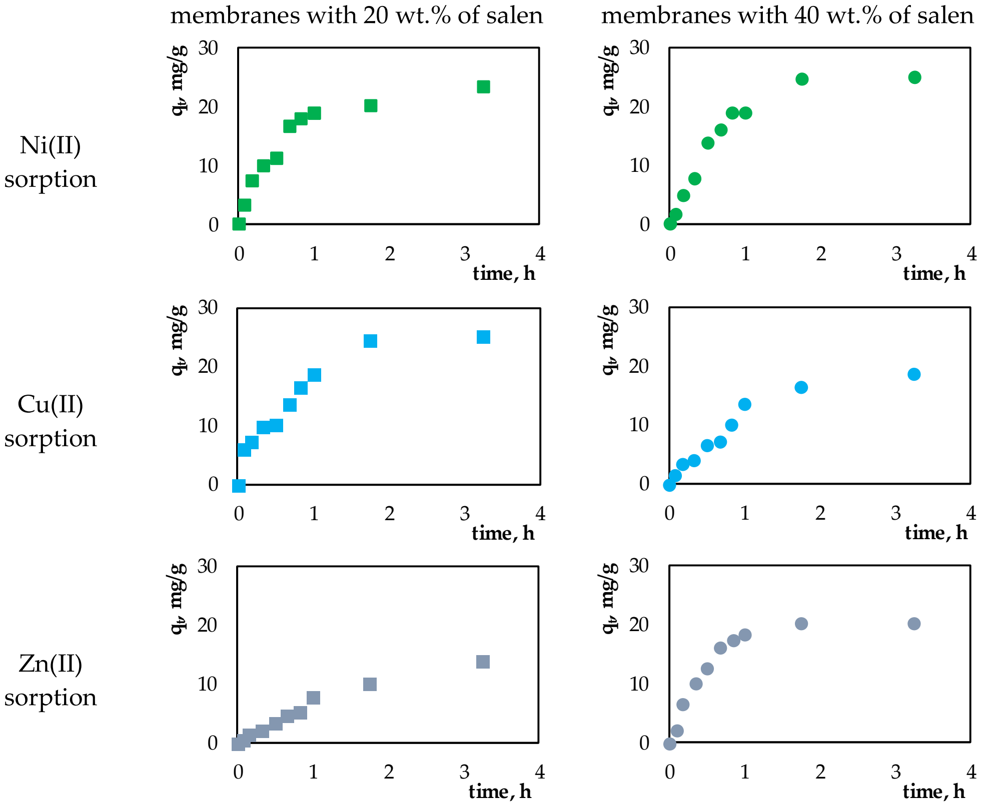

Figure 3. The changes in sorption capacity of the membranes with 20 wt.% or 40 wt.% salen during the sorption processes.

In all of investigated sorption processes, during the first hour, a rapid increase in sorption capacity was observed (q_t). This fact can be related to the large number of available active places in relation to the amount of sorbed metal ions. After that time, the adsorption of metal ions onto the surface of membranes slowed down, eventually reaching equilibrium.

After 24 h of sorption, the percentage of metal ion removal from the solutions ($\%R_s$) was also determined (Equation 4).

$$\%R_s = \frac{C^i - C^t}{C^t} \cdot 100\% \quad (4)$$

,

where C^i and C^t denote analytical metal ion concentrations in the solution at the beginning and after an appropriate time of sorption process (mol/L), respectively.

The %Rs reached the values presented in Figure 4.

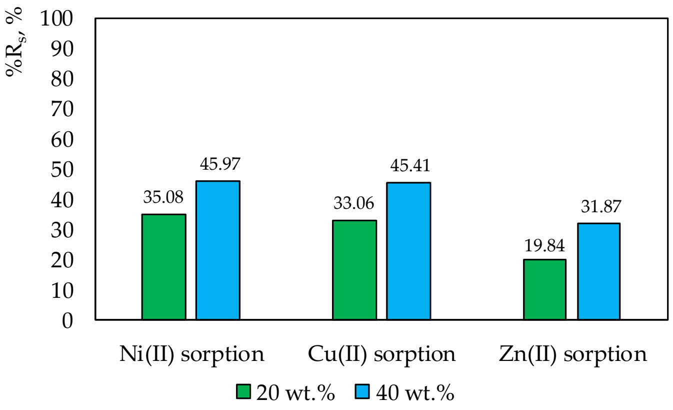

Figure 4. The percentage of metal ion removal from the solutions after 24 h of sorption processes onto membranes with 20 wt.% or 40 wt.% salen.

Figure 4 shows that the effectiveness of sorption correlated with the increasing amount of ligand in the membrane. A 20% increase in the amount of salen in the membrane increased metal ion sorption on its surface by about 10-fold. The sorption effectiveness of copper or nickel ions was almost the same on the membrane with 20 wt.% and 40 wt.% salen.

Figure 5 shows the visible result of sorption on membranes. The colors of deposits on the membranes were the same as those obtained in organic phases of the liquid–liquid extraction. This confirms the formation of complexes of the investigated metal ions with salen present in the structure of the membrane.


(A) (B) (C) (D)

Figure 5. Photography of polymer inclusion membranes (PIMs) with 40 wt.% salen: (**A**) before sorption; (**B**) after sorption from solution with Cu(II) ions; (**C**) after sorption from solution with Ni(II) ions; (**D**) after sorption from solution with Zn(II) ions.

In our previous paper [31], we considered the possibility of removing Cu(II), Zn(II), and Pb(II) ions via sorption on PVC-based composite materials with various contents of acetylacetone. The reduction in ion concentration ranged from 8% to 91%, from 10% to 85%, and from 6% to 50% for Cu(II), Zn(II), and Pb(II) ions, respectively, depending on the composite composition. The best results were obtained for the material containing 30 wt.% acetylacetone, as well as porophor, which increased the active surface of the material.

3.2.3. Desorption

The desorption of Ni(II), Cu(II), and Zn(II) ions from the surface of membranes with salen, used during the sorption processes, to the solution of nitric acid at a concentration of 0.05 mol/L was also performed. The results presented in Table 4 were calculated as a percentage of the sum of desorbed metal ions from the sum of previously adsorbed metal ions.

Table 4. The percentage of the sum of desorbed metal ions after 24-h desorption of Ni(II), Cu(II), and Zn(II) ions from the surface of membranes with salen in a 0.05 mol/L solution of nitric acid.

	Membranes with 20 wt.% Salen	**Membranes with 40 wt.% Salen**
Ni(II)	36.59	20.69
Cu(II)	39.67	74.19
Zn(II)	94.51	39.22

The given values carry ±0.01 tolerance.

Almost full desorption in nitric acid was achieved only for zinc(II) ions in the case of the membrane with 20 wt.% salen, probably because that membrane bound the smallest amount of ions during sorption. It is observed that, in the case of membranes where large amounts of metal cations were absorbed, the desorption process was complicated (the average percentage of desorption was equal to approximately 30%).

3.2.4. Transport across Polymer Inclusion Membrane

In order to describe the efficiency of metal removal from the feed phase, the recovery factor (%RF) was calculated (Equation 5).

$$\%RF = \frac{C^0 - C_r}{C^0} \cdot 100\% \quad (5)$$

,

where C^0 is the initial concentration of metal ions in the feed phase (mol/L), and C_r is the concentration of metal ions in the receiving phase after time (mol/L).

The results obtained after 24 h of metal ion transport across PIMs doped with salen in relation to various amounts of the carrier are shown in Table 5.

Table 5. Recovery factors (%RF) for the transport of investigated metal ions across polymer inclusion membranes (PIMs) with salen as a carrier.

	%RF (%)	
	Membranes with 20 wt.% Salen	**Membranes with 40 wt.% Salen**
Ni(II)	5.87	10.63
Cu(II)	3.26	9.35
Zn(II)	3.69	9.09

The given values carry ±0.01 tolerance.

The results presented in Table 5 show that the recovery of the investigated metal ions using PIMs with salen is minimal in the applied conditions.

The process of metal ion transport across a membrane is described by a linear kinetic equation (Equation (6)).

$$\ln\left(\frac{C}{C^0}\right) = -kt \quad (6)$$

,

where C^0 is the initial concentration of metal ions in the donor phase (mol/L), C_r is the concentration of metal ions in the donor phase after time t (mol/L), k is the rate constant (h^{-1}), and t is the time of transport process (h).

The following values also describe metal ion transport across PIMs:

- Initial flux (J_0):

$$J_0 = \frac{V}{A} k C^0 \quad (7)$$

,

where J_0 (μmol/m^{2}s) denotes the initial flux at $t = 0$, V is the volume of the receiving phase (m^3), and A is the interface of membrane (m^2);

- Permeability coefficient (P) [m/s]:

$$P = -\frac{V}{A}k \tag{8}$$

The results of the calculation of the above parameters are shown in Table 6.

Table 6. Permeability coefficients and initial fluxes for competitive transport of Ni(II), Cu(II), and Zn(II) ions across PIMs doped with salen.

		P 10^6 (m/s)	**J_0 10^5 (μmol/m^{2}s)**
Membranes with 20 wt.% salen	Ni(II)	6.43	12.86
	Zn(II)	4.00	7.99
	Cu(II)	3.52	7.05
Membranes with 40 wt.% salen	Ni(II)	19.17	38.33
	Zn(II)	14.53	29.07
	Cu(II)	14.33	28.65

The given values carry ±0.01 tolerance.

The obtained results show that permeability coefficients and initial fluxes for metal ion transport across the studied membranes were low (slightly higher in the case of the membrane with 40 wt.% salen). This fact explains the low values of recovery factors (%RF), which were described above. The highest recovery factors were obtained for nickel(II) ions (5.87% and 10.63% during the transport across PIMs with 20 and 40 wt.% salen, respectively), and nickel(II) ions were also transported with the highest initial fluxes by both membranes. This shows that the compositions of the received membranes were not suitable for the transport of the investigated metal ions and must be changed.

3.3. Mass Spectrometry

Electrospray ionization high-resolution mass spectrometry experiments (ESI-HRMS) were performed for the separated organic phases obtained after liquid–liquid extraction of metal ions (Cu^{2+}, Zn^{2+}, and Ni^{2+}) from model solutions, using *N*,*N*′-bis(salicylidene)ethylenediamine (this procedure was described in detail in Section 2.3, in variant III). ESI-HRMS spectra of the analyzed samples are shown in Figure 6a–c, while the ESI-HRMS data of the main compounds found are presented in Table 7.

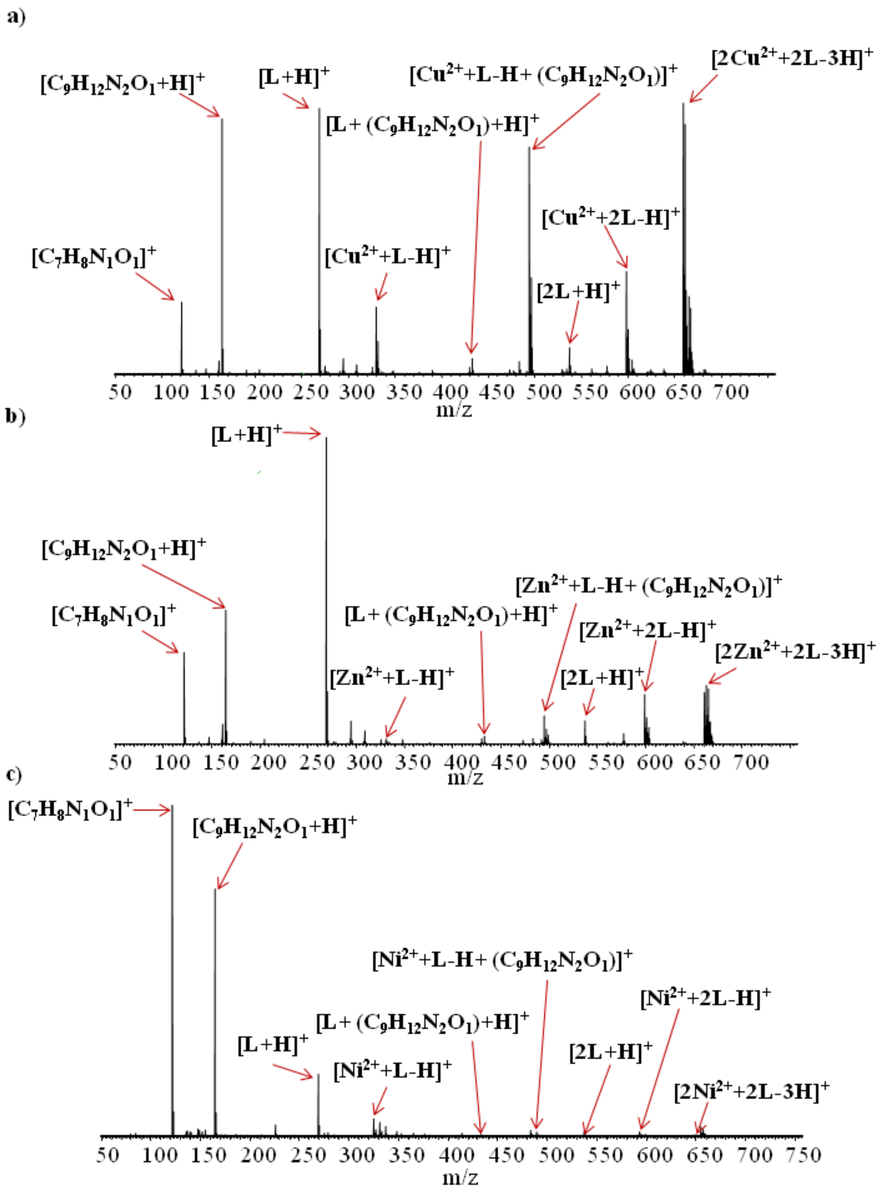

Figure 6. ESI-HRMS spectra recorded for the samples of the separated organic phases after liquid–liquid extraction, containing *N*,*N*′-bis(salicylidene)ethylenediamine (L) and metal ions (**a**) Cu^{2+}, (**b**) Zn^{2+}, and (**c**) Ni^{2+}. Unassigned minor signals correspond to ions not relevant in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

The results of ESI-HRMS experiments show that, for all of the analyzed samples in the solutions after extraction, similar complexes containing metal ions and *N*,*N*′-bis(salicylidene)ethylenediamine (L) molecule(s), were formed (i.e., $[Cu^{2+} + L - H]^+$, $[Zn^{2+} + L - H]^+$, $[Ni^{2+} + L - H]^+$, $[Cu^{2+} + 2L - H]^+$, $[Zn^{2+} + 2L - H]^+$, $[Ni^{2+} + 2L - H]^+$, $[2Cu^{2+} + 2L - 3H]^+$, $[2Zn^{2+} + 2L - 3H]^+$, $[2Ni^{2+} + 2L - 3H]^+$). However, the intensity of signals corresponding to complexes of the same type formed by different metal ions was not the same. For example, signals which can be assigned to $[2Cu^{2+} + 2L - 3H]^+$ ions were dominant (Figure 6a), and those corresponding to the $[2Zn^{2+} + 2L - 3H]^+$ were much less intense (Figure 6b), whereas the signals corresponding to $[2Ni^{2+} + 2L - 3H]^+$ (Figure 6c) ions were minor. The same reduction in intensity was observed for all signals corresponding to similar complexes differing only by metal ions. This allows for the conclusion that, although the properties of metal ions do not affect the types of complexes formed, they have a large impact on the quantity of generated complex ions.

These findings are consistent with the liquid–liquid extraction results, where the highest percentage of extraction was obtained for copper and the lowest was obtained for nickel ions.

Table 7. ESI-HRMS data of the main compounds found in the samples of the separated organic phases after liquid–liquid extraction (variant III described in Section 3.2) diluted (1:1) in methanol. L stands for *N*,*N'*-bis(salicylidene)ethylenediamine ($C_{16}H_{16}N_2O_2$).

Cu^{2+} and L		
m/z_{meas}	m/z_{calc}	**Assignment**
122.0599	122.0606	$[C_7H_8N_1O_1]^+$
165.1019	165.1028	$[C_9H_{12}N_2O_1 + H]^+$
269.1279	269.1290	$[L + H]^+$, $(C_{16}H_{17}N_2O_2)^+$
330.0414	330.0429	$[Cu^{2+} + L - H]^+$, $(CuC_{16}H_{15}N_2O_2)^+$
433.2224	433.2239	$[L + (C_9H_{12}N_2O_1) + H]^+$, $(C_{25}H_{29}N_4O_3)^+$
494.1361	494.1379	$[Cu^{2+} + L - H + (C_9H_{12}N_2O_1)]^+$, $(CuC_{25}H_{27}N_4O_3)^+$
537.2487	537.2501	$[2L + H]^+$, $(C_{32}H_{33}N_4O_4)^+$
598.1622	598.1641	$[Cu^{2+} + 2L - H]^+$ $(CuC_{32}H_{31}N_4O_4)^+$
659.0757	659.0780	$[2Cu^{2+} + 2L - 3H]^+$ $(Cu_2C_{32}H_{29}N_4O_4)^+$
Zn^{2+} and L		
m/z_{meas}	m/z_{calc}	**Assignment**
122.0600	122.0606	$[C_7H_8N_1O_1]^+$
165.1019	165.1028	$[C_9H_{12}N_2O_1 + H]^+$
269.1278	269.1290	$[L + H]^+$, $(C_{16}H_{17}N_2O_2)^+$
331.0408	331.0424	$[Zn^{2+} + L - H]^+$, $(ZnC_{16}H_{15}N_2O_2)^+$
433.2226	433.2239	$[L + (C_9H_{12}N_2O_1)+H]^+$, $(C_{25}H_{29}N_4O_3)^+$
495.1361	495.1374	$[Zn^{2+} + L - H + (C_9H_{12}N_2O_1)]^+$, $(ZnC_{25}H_{27}N_4O_3)^+$
537.2487	537.2501	$[2L + H]^+$, $(C_{32}H_{33}N_4O_4)^+$
599.1620	599.1636	$[Zn^{2+} + 2L - H]^+$ $(ZnC_{32}H_{31}N_4O_4)^+$
661.0720	661.0771	$[2Zn^{2+} + 2L - 3H]^+$ $(Zn_2C_{32}H_{29}N_4O_4)^+$
Ni^{2+} and L		
m/z_{meas}	m/z_{calc}	**Assignment**
122.0599	122.0606	$[C_7H_8N_1O_1]^+$
165.1019	165.1028	$[C_9H_{12}N_2O_1 + H]^+$
269.1276	269.1290	$[L + H]^+$, $(C_{16}H_{17}N_2O_2)^+$
325.0472	325.0486	$[Ni^{2+} + L - H]^+$, $(NiC_{16}H_{15}N_2O_2)^+$
433.2228	433.2239	$[L + (C_9H_{12}N_2O_1) + H]^+$, $(C_{25}H_{29}N_4O_3)^+$
489.1452	489.1436	$[Ni^{2+} + L - H + (C_9H_{12}N_2O_1)]^+$, $(NiC_{25}H_{27}N_4O_3)^+$
537.2483	537.2501	$[2L + H]^+$, $(C_{32}H_{33}N_4O_4)^+$
593.1677	593.1699	$[Ni^{2+} + 2L - H]^+$ $(NiC_{32}H_{31}N_4O_4)^+$
649.0877	649.0895	$[2Ni^{2+} + 2L - 3H]^+$ $(Ni_2C_{32}H_{29}N_4O_4)^+$

Electrospray ionization of all of the examined solutions also led to the formation of singly charged ions related to *N*,*N'*-bis(salicylidene)ethylenediamine, such as $[L + H]^+$, $[2L + H]^+$, $[C_7H_8N_1O_1]^+$, and $[C_9H_{12}N_2O_1 + H]^+$. Ions $[C_7H_8N_1O_1]^+$ and $[C_9H_{12}N_2O_1 + H]^+$ were probably formed as a result of partial L molecule decomposition in the solution, during electrospray ionization process or during compound storage. The ESI-HRMS spectra show that fragments of L could also form complexes with both metal ions (e.g., $[Cu^{2+} + (L - H) + (C_9H_{12}N_2O_1)]^+$, $[Zn^{2+} + (L - H) + (C_9H_{12}N_2O_1)]^+$, $[Ni^{2+} + (L - H) + (C_9H_{12}N_2O_1)]^+$) and whole L molecules (e.g., $[L + (C_9H_{12}N_2O_1) + H]^+$).

Based on the results of the performed ESI-HRMS experiments, it is possible to conclude that, in the analyzed solutions, various types of complexes of copper(II), zinc(II), and nickel(II) ions with *N*,*N'*-bis(salicylidene)ethylenediamine molecule(s) were formed. Given the high mass accuracy of the HRMS mass spectrometry, there can be no question as to the elemental composition or charge of the ions generated. However, it should be emphasized that the ESI-HRMS method does not allow the detection of neutral complexes that can also be formed in the examined solutions.

4. Conclusions

The value of the dissociation constant of *N*,*N*′-bis(salicylidene)ethylenediamine (salen) is equal to pKa = 12.59 ± 0.50, which determines the basicity of the compound and tendency to dissociate a proton. That proton can be easily replaced with other cations in a complexation reaction. The obtained stability constants of complexes of salen with Ni(II), Cu(II), and Zn(II) ions were similar since the stability correlates with the size of the ionic radius of the involved metal ion.

The results obtained in liquid–liquid extraction show that salen is a very effective extractant, especially for removing copper(II) ions from aqueous solutions, but its efficiency depends on its concentration in the system. The obtained polymer inclusion membranes with salen can be used as sorbents for the recovery of metal ions from solutions, but they cannot be successfully used as metal ion carriers in transport across those membranes. Electrospray ionization high-resolution mass spectrometry (ESI-HRMS) was successfully used to confirm the ability of *N*,*N*′-bis(salicylidene)ethylenediamine to form complexes with Cu^{2+}, Zn^{2+}, and Ni^{2+} ions in solution. The results of the performed ESI HRMS experiments provide information about the elemental composition of formed complexes.

Author Contributions: K.W. determined the stability constants of complexes of salen with various metal ions; liquid–liquid extraction, sorption/desorption, and transport across polymer inclusion membrane were conducted by D.A., M.A.K., and K.W.; M.A.K. planned all of the HRMS experiments and analyzed the obtained mass spectra; K.W. proposed the concept of publication and wrote the greater part of the paper. All authors have read and agreed to the published version of the manuscript.

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Selective transport of copper(II) ions across polymer inclusion membrane with aromatic β–diketones as carriers

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Abstract: The transport of Cu(II) ions from an equimolar mixture of Co(II), Ni(II), and Cu(II) ions as well as from solutions containing only Cu(II) ions in the feed phase through polymer inclusion membranes (PIMs) with aromatic β–diketones as carriers has been investigated. The polymer membranes consisted of polyvinylchloride (PVC) as the support, bis(2-ethylhexyl)adipate (ADO) as plasticizer, and aromatic β–diketones (benzoylacetone (**1**) and dibenzoylmethane (**2**)) as ion carriers. The transport selectivity of PIMs with **1** and **2** was: Cu(II) > Co(II) > Ni(II). The highest recovery factors of Cu(II) ions were observed for **1** (94.0%), whereas for Co(II) and Ni(II) the factors were 21.4 and 7.3%, respectively. The Cu(II)/Co(II) and Cu(II)/Ni(II) selectivity coefficients were equal to 8.9 and 33.7 (for **1**), 6.4 and 28.3 (for **2**), respectively.

Keywords: *β-diketones, polymer inclusion membrane, metal ion separation, copper(II), cobalt(II), nickel(II)*

1. Introduction

For many years, there has been an increase in the use of non-ferrous metals such as Cu, Cr, Zn, Ni, etc. (Cote, 2000), which resulted in the increase of prices of these metals. As a result, the metallurgical industry needs new sources of these metals. Such additional sources may be poor off-balance sheet ores and solid, semi-solid and liquid industrial waste (ashes, slags, dusts, sludge and sewage) (Szyczewski et al., 2009; Radzyminska-Lenarcik et al., 2015a). These metallic raw materials are usually mixtures of many metals and because of their low content, they can only be recycled using hydrometallurgical processes, e.g. extraction, ion exchange or membrane techniques. These techniques utilize differences in the formation and structure of metal complexes with appropriately selected reagents (extractants/carriers).

The polymer-based membrane concept, which has been known for over 40 years, was proposed as an alternative to conventional solvent extraction (Almeida et al., 2012). Such membranes have been termed polymer inclusion membranes (PIMs) and have shown excellent stability and versatility, in particular when compared to other liquid membrane types, e.g. supported liquid membranes (SLMs) (Bartsch and Way, 1996). The membrane processes are also characterized by a better use of the ion carrier in the organic phase (membrane) in comparison with conventional extraction systems (Wieczorek, 2007; Baczynska et al., 2013).

The PIMs are usually composed of an extractant (carrier), a base polymer (cellulose triacetate (CTA) or polyvinyl chloride (PVC)) and a plasticizer or modifier. Such membranes are highly stable during the transport of metal ions (Walkowiak et al., 2000; Nghiem et al., 2006; Sgarlata et al., 2008; Almeida et al., 2012). The carrier is essentially a complexing agent or an ion-exchanger, responsible for binding with the species of interest and transporting it across the PIM.

Actually, the application of PIMs is focused mainly on the transport of metal cations. It has been shown in many papers that this type of membranes is able to transport different metal cations with high selectivity and good efficiency. De Gyves et al. (2006) described the removal of Cu(II) ions from a

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Cu(II)-Zn(II)-Fe(III) mixture in chloride and sulfate medium across PIMs containing LIX® 84-I as the metal ion carrier.

The permeation of copper ions through PIMs containing di-(2-ethylhexyl)phosphoric acid (D_2EHPA) was investigated by Kavitha and Palanivelu (2012). High Cu(II) ion concentration in the feed phase leads to an increase in the flux values from 0.53×10^{-6} to 4.48×10^{-6} mol/m^2·s at pH 4.5. Also alkyl derivatives of imidazole: 1-heptyl-2- or 4-methylimidazole (Radzyminska-Lenarcik and Ulewicz, 2015b), 1-hexyl-2-methylimidazole (Ulewicz and Radzyminska-Lenarcik, 2012a); 1-decyl-2-methylimidazole (Ulewicz and Radzyminska-Lenarcik, 2012b), and 1-alkyl-2-methylimidazole (Radzyminska-Lenarcik and Ulewicz, 2017) were used as selective carriers for the recovery of Cu(II) ions from quaternary mixtures (Cu(II)-Zn(II)-Co(II)-Ni(II) or Cu(II)-Zn(II)-Cd(II)-Ni(II)). The best result for Cu(II) removal was obtained for the most hydrophobic alkylimidazoles (94.5%), while the selectivity ratios Cu(II)/M(II) decreased.

The hydrophobic β–cyclodextrin polymers have been used as macrocyclic ion carriers for the separation of metal ions from dilute aqueous solutions by transport across PIMs. In the case of competitive transport of Cu(II), Co(II), Ni(II) and Zn(II) ions through such PIMs, the selectivity order was: Cu(II) > Co(II) > Ni(II) > Zn(II) (Kozlowski et al., 2005).

The transport of Zn(II), Fe(II) and Fe(III) ions from chloride aqueous solutions across PIMs and supported liquid membranes (SLMs) containing one of three phosphonium ionic liquids: Cyphos IL 101, Cyphos IL 104 and Cyphos IL 167 as an ion carrier was reported (Baczyńska et al., 2016a, 2016b). The results showed that Zn(II) and Fe(III) are effectively transported through all of the investigated PIMs and SLMs, while the transport of Fe(II) is not effective. The highest values of initial flux and permeability coefficient of Zn(II) were reported for SLM containing Cyphos IL 167.

The use of 1-hexyl-4-methylimidazole as the carrier in PIMs enables the separation of 98.5% Zn(II) from a single component solution and 96.9% from a four-component solution of Zn(II)-Cd(II)-Co(II)-Ni(II) after running the process for 24 hours (Ulewicz and Radzyminska-Lenarcik, 2015).

Ulewicz et al. (2007) investigated the transport selectivity of the PIMs with five derivatives of imidazole azocrown ethers for a Pb(II)-Zn(II)-Cd(II) mixture. The transport selectivity coefficients varied in the following order: Pb(II) > Zn(II) > Cd(II). The best selectivity coefficient for Pb(II)/Cd(II) amounted to 46. Pb(II) ions present in the diluted feed solutions pH 3.0 were quantitatively removed (about 99%) in about 180–200 min. during the transport across membranes consisting of 50% D_2EHPA/50% PVC (w/w) (Gherisim et al., 2011). Aliquat 336/PVC-based PIMs enable the selective extraction of Cd(II) from chloride solutions (Xu et al., 2004; Annane et al., 2015) and can be also used to separate the Cd(II)-Cu(II) aqueous mixture (Wang and Shen, 2005; Upitis et al., 2009; Peterson and Nghiem, 2010). PIMs are also suitable for the preferential extraction of Co(II) ions from their acid solution containing Co(II)-Ni(II) because extraction of Ni(II) in the experimental conditions was not observed (Blitz-Raith et al., 2007). Moreover, there is a potential for the application of the PIMs with Cyanex 301 for Co(II) recovery from acidic leach liquor solutions from spent lithium ion batteries (Pospiech, 2013).

In most cases, the typical organic donors which form stable complexes with transition metal ions – commonly used in the extraction processes as extractants – are used as metal carriers, e.g.: crown ethers, quaternary ammonium salts, tertiary amines, pyridine derivatives, phosphoric acid derivatives, hydroxyoximes, and β-diketones (Almeida et al., 2012; Regel-Rosocka and Alguacil, 2013).

The complex-forming properties of β-diketones are used for the separation of metal ions from solutions by means of solvent extraction as well as PIMs (Miyake et al., 1990; Regel-Rosocka and Alguacil, 2013; Witt et al., 2016). LIX type extractants commercially used for the recovery of copper include 1-phenyl-3-isoheptyl-1,3-propanedione (LIX-54) (Kyuchoukov et al., 1998) or a mixture of a number of components, for instance, six isomeric 1-phenyldecane-l,3-diones (LIX 54-100) (Bermejo et al., 2000; Regel-Rosocka and Alguacil, 2013; Gotfryd and Pietek, 2013; Wejman-Gibas et al., 2017). Moreover, LIX 54 enables the separation of zinc (Alguacil and Cobo, 1998a) and nickel ions (Alguacil and Cobo, 1998b) from weakly basic media. Both, the LIX 54 and LIX 54-100 are also used as metal carriers in liquid membranes (Kyuchoukov et al., 1998).

However, a majority of commercial extractants, which were previously used as non-ferrous metal ion carriers during the transport through liquid membranes, do not have sufficient selectivity towards a number of metals. Therefore, it is necessary to find new, selective carriers, which enable the separation of metal ions from aqueous solutions.

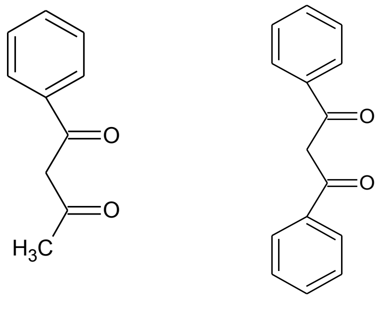
The aim of this study was to investigate the suitability of aromatic β-diketones to the selective transport of Cu(II), Co(II), and Ni(II) from model aqueous solutions using PIMs that consisted of polyvinyl chloride PVC (matrix) and bis(2-ethylhexyl)adipate ADO (plasticizer). The benzoylacetone (**1**) and dibenzoylmethane (**2**) were used as carriers. The values of three parameters: initial flux (J_0), selectivity coefficient ($S_{M(1)/M(2)}$), and recovery factor of a given metal after 60 hours (RF) were selected for the comparative analysis of the transport process.

2. Material and methods

2.1 Reagents

The inorganic chemicals, i.e. copper(II), cobalt(II) and nickel(II) nitrates, as well as tetramethylammonium hydroxide and hydrochloric acid were of analytical grade and were purchased from POCh (Gliwice, Poland). The aqueous solutions were prepared with double distilled water, the conductivity of which was 0.1 μS/m. The pH-meter was calibrated using the commercial buffer solutions (Radiometer) having a pH of 7.00±0.01 and 9.21±0.01, respectively.

The organic reagent, i.e. polyvinyl chloride (PVC) in suspension with an average molecular weight of 72000 was obtained from the Anwil company, Poland. The bis(2-ethylhexyl)adipate (ADO) and tetrahydrofuran (both of analytical grade) were purchased from POCh (Gliwice, Poland) and were used without further purification. The β-diketones (Fig. 1) were synthesized as described by Staniszewski and Urbaniak (Staniszewski and Urbaniak, 2009). Their characteristics is shown in Table 1.



1 **2**

Fig. 1. Structures of benzoylacetone (**1**) and dibenzoylmethane (**2**)

Table 1. Physicochemical parameters of carriers

Carrier	Molecular formula	Molecular mass, [g/mol]	Melting point [°C]	Boiling point [°C]	Physical state
benzoylacetone **1**	$C_{10}H_{10}O_2$	162.18	54-56	260-261	white to off-white crystalline powder
dibenzoylmethane **2**	$C_{15}H_{12}O_2$	224.25	77–79	219–221	white to yellow crystalline powder

2.2 Polymer inclusion membrane preparation

A solution of polyvinylchloride (PVC) as a support, ADO as aplasticizer and β–diketone (**1**, **2**) as an ion carrier in tetrahydrofuran was prepared. A specified portion of the solution was poured into a membrane mould which was composed of a 9.0 cm diameter glass ring fixed on a glass plate with a PVC-tetrahydrofuran glue. After a slow evaporation of the solvent overnight, the resulting polymer inclusion membrane was peeled off from the glass plate. Then the PIM was immersed for 12 hours in distilled water to make it homogeneous. In order to repeat the process in the same conditions two samples of the PIMs were cut out from the same membrane film for duplicate transport experiments. The average PIM thickness was 30-35 µm.

2.3 Transport studies

The transport experiments were carried out in a permeation module cell. The membrane film (having the surface area of 4.4 cm^2) was tightly clamped between two cell compartments. Both phases: the feed and receiving aqueous phases (45 cm^3 each) were mechanically stirred at 600 rpm. The 0.5 M HCl was used as a receiving phase. The PIMs transport experiments were carried out at 20±0.2 °C. Small samples of the aqueous receiving phase were taken periodically via a sampling port equipped with a syringe and analyzed by atomic absorption spectroscopy (AAS Spectrometer, Solaar 939, Unicam) to determine the copper(II), cobalt(II) and nickel(II) concentration. The feed phase pH (7.8) was kept constant using tetramethylammonium hydroxide and controlled by pH-meter (pH meter, CX-731 Elmetron, Poland), with a combination pH electrode (ERH-126, Hydromet, Poland).

The transport across PIMs fits the first-order kinetics in relation to the metal-ion concentration (Danesi, 1984-85), which can be described by equation 1:

$$\ln\frac{c}{c_0} = -kt \tag{1}$$

where c_0 – initial concentration of metal ions in the feed phase [M], c – concentration of metal ions in the feed phase after time t [M], k – rate constant, [h^{-1}], t – time of transport [h].

To calculate the value of k, the graph of ln(c/c_0) versus time was plotted. The rate constant values for two independent transport experiments were averaged and a standard deviation was calculated. The permeability coefficient (P, [m/s]) was calculated as follows:

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

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

The initial flux (J_0, [mol/m^2·s]) was determined as equal to:

$$J_0 = P\cdot c \tag{3}$$

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

$$S = J_{0,M1} / J_{0,M2} \tag{4}$$

To describe the efficiency of metal ions transport from the feed phase, the recovery factor (RF) was calculated:

$$RF = \frac{c_0 - c}{c_0}\cdot 100\% \tag{5}$$

3. Results and discussion

In the first series of the experiments, the authors investigated the transport of Cu(II) from nitrate aqueous solutions containing metal ions at a 0.001 M concentration through PIMs with aromatic β–diketone and ADO into 0.5 M hydrochloric acid aqueous solutions. No transport was detected after running the blank experiment for more than 60 hrs. The relationship between ln(c/c_0) and the time of Cu(II) transport across PIMs containing **1** or **2** β–diketone is shown in Fig. 2. The correlation between ln(c/c_0) and time was linear, as confirmed by the high correlation coefficient (R^2) ranging from 0.915 to 0.986.

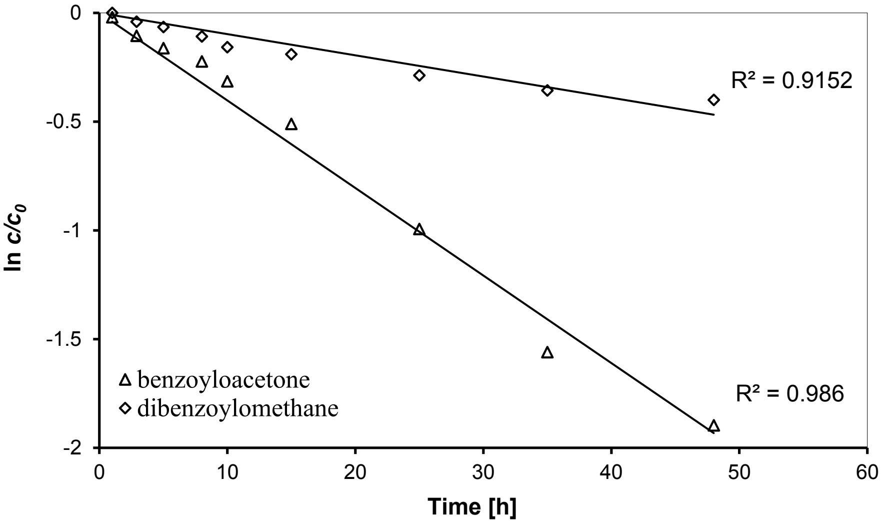


Fig. 2. Kinetics of Cu(II) ions transport across PIMs containing 0.05 M benzoylacetone (**1**) and dibenzoylmethane (**2**) from aqueous solutions. Feed phase: c_M = 1 mM, pH = 7.8, receiving phase: 0.5 M HCl, Membrane: 0.5 g PVC, 0.2 g ADO, and 60% carrier calculated on PVC

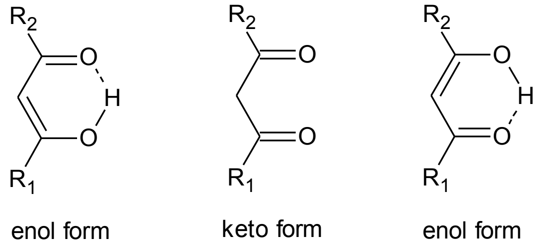
As shown in Fig. 2, the transport of Cu(II) across PIMs with β–diketone can be described by first order kinetics in relation to the metal ion concentration changes. It is in accordance with the mathematical model proposed by Danesi (Danesi, 1984-85). The kinetic parameters and recovery factor of Cu(II) are summarized in Table 2 for both carriers **1** and **2**.

Table 2. Kinetic parameters and recovery factors for competitive transport of Cu(II) across PIM with carriers **1** and **2**. Conditions as in Fig. 2

Carrier	*P* [μm/s]	*J*₀ [μmol/m²·s]	*RF* [%]
1	630.0	1.998	94
2	389.6	1.239	38

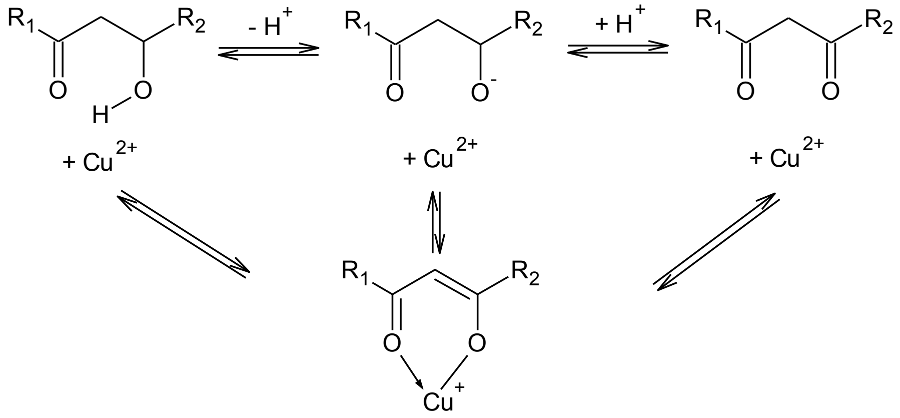
Both the permeability coefficient and the initial flux are higher for carrier **1** in comparison with **2** (Table 2). Also, the recovery factor of Cu(II) is higher (more than twice as high). Such significant differences are a result of differences in the formation and stability of the Cu(II) complexes with both of the investigated carriers.

The β-diketones exist in the enol form (Eq. 6), making them Broensted acids. Owing to their specific structure, diketones combine with cations of block d and f metals, forming highly stable 6-member chelate complexes (Eq. 7) (Lis et al., 2011). The mechanism of metal ion complexation is very complicated because according to Miyake et al. (1990) both tautomeric forms of β-diketone are reactive towards metal ions. In the case of Cu(II), the reaction mechanism was described by equation 7.



(6)

It has been noted that keto form hydrates are easily formed and are more stable in comparison with the hydrates of the corresponding enol forms (Prochaska et al., 1995). The stability constants of complexes of the studied carriers with Cu(II), Co(II) and Ni(II) ions are summarized in Table 3.



(7)

Table 3. Stability constants of complexes of benzoylacetone (**1**) and dibenzoylmethane (**2**) with selected metal ions at 30 °C

Ligand	Cu(II)	Co(II)	Ni(II)	Reference
dibenzoylmethane **2**	12.98	9.97	10.46	(van Uitert et al., 1953a)
benzoylacetone **1**	12.05	9.42	9.58	(van Uitert et al., 1953b)

The stability constants (Table 3) of the complexes with **2** are higher than those of the same metals with **1**. For both carriers, the stability constants of their metal complexes with the metal ions decrease in the following order: Cu(II) > Ni(II) > Co(II).

The increased stabilities of metal ion complexes with **2** impede the process of dissociation of the complex from PIM to the receiving phase. As a result, lower values of the kinetic parameters for carrier **2** were observed – compiled in Table 1. It seems that too high stabilities of the complexes being formed in the membrane reduce transport efficiency. Fig. 3 presents the proposed mechanism of the transport of Cu(II) across PIMs.

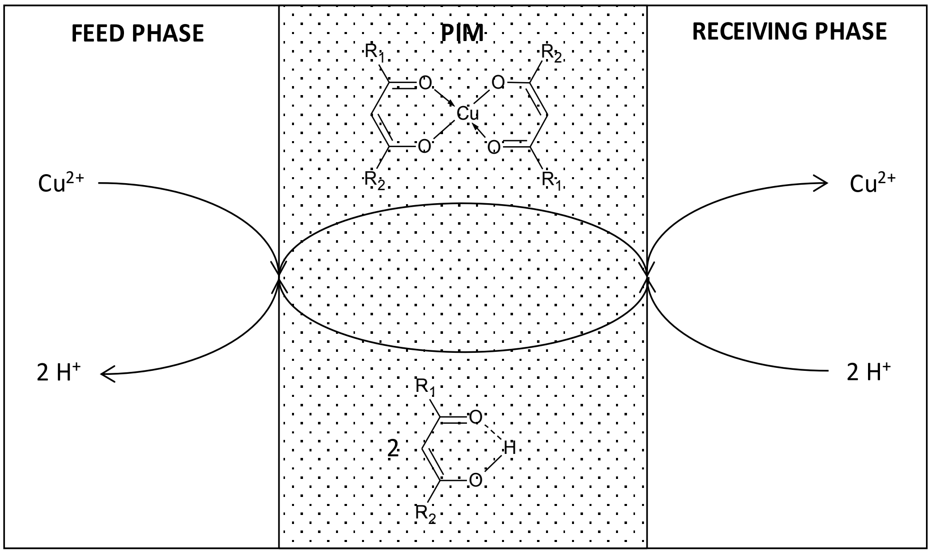


Fig. 3. Schematic transport of Cu(II) ions through the PIM doped with β-diketones

The transport of Cu(II) from an equimolar nitrate mixture of three metal ions (Cu(II)-Co(II)-Ni(II)), each at a 0.001 M concentration, across PIMs with aromatic β–diketone **1** was also investigated. The kinetic parameters and the selectivity order are summarized in Table 4.

The transport rate of Cu(II), Co(II) and Ni(II) across the studied membrane increased in the following order: Ni(II) < Co(II) < Cu(II). The stability constants of the complexes of these ions with **1** are increasing in the same order. Recovery factors for all of the investigated ions are shown in Fig. 4. The recovery factors (Fig. 4) of all ions investigated for PIMs with **1** increased with time. The highest recovery factors 94.0% (after 60 h) were obtained for Cu(II), whereas for Co(II) and Ni(II), the factors were 21.4 and 7.3%, respectively. The transport selectivity (Table 4) of the PIMs with **1** increased in the series: Cu(II) > Co(II) > Ni(II).

Table 4. Kinetic parameters, selectivity order, and selectivity coefficients for competitive transport of Cu(II), Co(II) and Ni(II) ions across PIM with carrier **1**. Conditions as in Fig. 2

Metal ions	P [μm/s]	J_0 [μmol/m^2·s]	Selectivity order, and selectivity coefficients
Cu(II)	106	0.337	Cu(II) > Co(II) > Ni(II) $S_{Cu(II)/Co(II)} = 8.9$ $S_{Cu(II)/Ni(II)} = 33.7$
Co(II)	3.8	0.038	
Ni(II)	1.1	0.010	

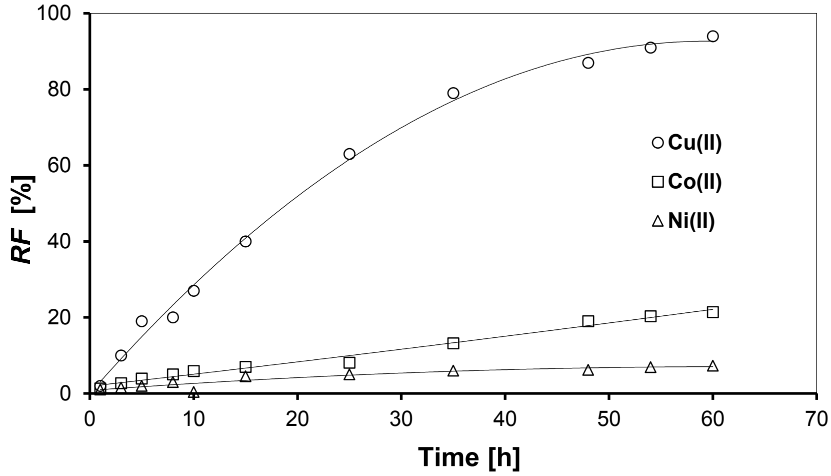


Fig. 4. Recovery of Co(II), Ni(II), and Cu(II) from feed phase from aqueous solutions in transport across PIMs with β–diketone **1**. Feed phase: c_M = 1 mM, pH = 7.8; receiving phase: 0.5 M HCl; membrane: 0.5 g PVC, 0.2 g ADO, and 60% carrier calculated on PVC

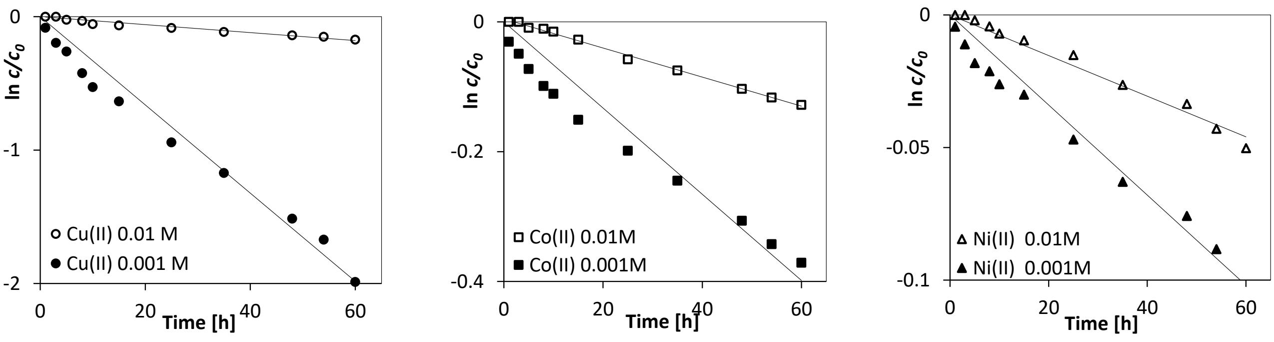


Fig. 5. Relationship of ln(c/c_0) vs. time for Cu(II), Co(II) and Ni(II) transport across PIMs with **2** from the feed phase of different metal ions concentrations; receiving phase: 0.5 M HCl, membrane: 0.5 g PVC, 0.2 g ADO, and 60% carrier **2** calculated on PVC

In order to examine the influence of the metal ions concentration in the feed phase, the transport of the metal ions from two equimolar mixtures of three ions (0.001 and 0.01 M) was performed. The relationship between ln(c/c_0) and time for Cu(II), Co(II) and Ni(II) transport across PIMs doped with carrier **2** is shown in Fig. 5, whereas the kinetic parameters (calculated for the experimental data) are summarized in Table 5.

Table 5**.** Kinetic parameters for competitive transport of metal ions across PIM with carrier **2**. Conditions - Fig. 5

Concentration of metal ions [M]	Type of metal ions	k [h^{-1}]	J_0 [μmol/m^2·s]
0.001	Cu(II)	0.0496	14.2
	Co(II)	0.0053	2.20
	Ni(II)	0.0015	0.50
0.01	Cu(II)	0.0216	0.62
	Co(II)	0.0022	0.089
	Ni(II)	0.0008	0.026

It is evident that metal ions are transported across PIMs at a higher rate from solutions of lower concentration. Also, the initial fluxes are higher for thess concentrations (Table 5). For the 0.01 M concentration, the selectivity coefficients Cu(II)/Co(II) and Cu(II)/Ni(II) are equal to 6.95 and 23.5, respectively. For the 0.001 M solutions, the same parameters are 6.43 and 28.3, respectively. For both concentrations, the transport selectivity across the PIM with **2** is ordered as: Cu(II) > Co(II) > Ni(II) (Fig. 5).

The new compounds investigated, i.e. aromatic β–diketones (benzoylacetone (**1**) and dibenzoylmethane (**2**)), can be used for recovering Cu(II) from nearly neutral solutions using PIMs. The commercial extractant LIX 54-100 containing six isomeric 1-phenyldecane-1,3-diones (Dziwinski and Szymanowski, 1996) was used for the extraction of Cu(II) from acidic waste solutions (Gotfryd and Pietek, 2013). According to these authors, the pH$_{1/2}$ corresponding to 50% of copper extraction was 2.2. Bermejo et al. (2000) investigated the membrane extraction (SLMs) of copper from ammoniacal/ammonium sulfate medium by LIX 54-100 dissolved in Iberfluid (kerosene type diluent). According to these authors, the permeability coefficients depend on pH, and at pH 8.8, 9.5, and 10.5 they were 565, 416 and 210 μm/s, respectively. The PIMs with benzoylacetone (**1**) and dibenzoylmethane (**2**) can be used for copper recovery from ammoniacal solutions obtained after leaching waste containing a small amount of copper ions.

4. Conclusions

The new PVC-based polymer inclusion membranes, with aromatic β–diketones (benzoylacetone (**1**) and dibenzoylmethane (**2**)) were prepared. Copper(II) can be effectively separated from equimolar aqueous solutions of copper, cobalt, and nickel nitrates with these PIMs.

The separation of metal ions using PIMs with benzoylacetone (**1**) was more effective than those with dibenzoylmethane (**2**). The transport selectivity of the PIMs was ordered as follows: Cu(II) > Co(II) > Ni(II). The highest recovery factors for Cu(II) were observed for benzoylacetone (94.0%), whereas for Co(II) and Ni(II), the factors were 21.4 and 7.3%, respectively. The Cu(II)/Co(II) and Cu(II)/Ni(II) selectivity coefficients of the PIMs were equal to 8.9 and 33.7 (for **1**), 6.4 and 28.3 (for **2**), respectively. The metal ions were transported across the PIMs at higher rates from solutions of lower concentrations.

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Simultaneous Recovery of Precious and Heavy Metal Ions from Waste Electrical and Electronic Equipment (WEEE) Using Polymer Films Containing Cyphos IL 101

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Abstract: In this article, the application of a polymer film containing the ionic liquid Cyphos IL 101 for the simultaneous recovery of precious and heavy metal ions ((Ni(II), Zn(II), Co(II), Cu(II), Sn(II), Pb(II), Ag(I), Pd(II), and Au(III)) from waste electrical and electronic equipment (WEEE) is described. The experiments were performed for solutions containing metal ions released from computer e-waste due to leaching carried out with concentrated nitric(V) acid and aqua regia. It was found that the applied polymer film allows for the efficient recovery of precious metals (98.9% of gold, 79.3% of silver, and 63.6% of palladium). The recovery of non-ferrous metals (Co, Ni, Cu, Zn, Sn, and Pb) was less efficient (25–40%). Moreover, the results of the performed sorption/desorption processes show that the polymer film with Cyphos IL 101 can be successfully used after regeneration to recover metals ions several times.

Keywords: electronic scrap; metal recovery; polymer films; Cyphos IL 101

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1. Introduction

The dynamic growth in the production of electrical and electronic equipment (EEE) around the world and the numerous innovations in such equipment—e.g., in terms of miniaturization and affordability—have reduced its life, consequently leading to the generation of large amounts of so-called e-waste (WEEE) [1–4]. The amount of WEEE generated varies between countries and depends mainly on economic and technological developments, consumption levels, and the availability of EEE equipment, and it is expected to increase systematically regardless of the discrepancies [5]. Electronic scrap is diverse; it includes spent products used in the production of integrated circuits, PCB, connectors, wiring, etc., as well as batteries and fluorescent lamps [6,7]. WEEE contains many different hazardous components that can be released during improper storage or processing, posing a threat to human health and the environment [8], as well as valuable precious metals, such as gold or silver, the recovery of which is desirable [7–10]. For example, conductive elements of printed circuit boards include, among others, gold, silver, tin, and zinc [11,12]. Therefore, the development of methods for reducing of the amount of electronic scrap—enabling its reuse, recycling, and various forms of recovery—is extremely important not only for the protection of the natural environment (energy saving, reduction of water and air pollution), but also for economic reasons [13–16]. The limited amounts of valuable metals in ores and the economic, political, and social problems associated with their mining also contribute to the search for new solutions/methods for the recovery of various metals from e-waste, which can be treated as their secondary source [12,17].

Methods for recovering valuable metals from e-waste, as used today, are based primarily on physical processes—in which the metal fraction is separated from non-metals using specific differences in their properties (e.g., magnetism, electrical conductivity, density, etc.)—and on chemical processes, which are utilized in pyrometallurgical, hydrometallurgical, or biotechnological techniques [18,19]. Hydrometallurgical methods are characterized by their high accuracy, predictability, simplicity of control, and possibility of planning the metal recovery processes at various scales. Therefore, they are of great interest and will probably play a key role in the management of waste electronic and electrical equipment in the future [18,20]. However, such recovery processes are usually complex, and they involve many unit operations, ranging from disassembly, grinding, and physical separation of components to leaching, which leads to the transfer of the desired substances into aqueous solutions, followed by extraction [11].

An alternative to hydrometallurgical processes is the recovery of metals through more environmentally friendly methods, such as modified polymer materials. They have been increasingly used in recent years as an alternative to classic solvent extraction in the recovery of various metal ions from e-waste [21,22]. Because the efficiency of metal recovery processes based on the application of polymer materials depends on the type and properties of the carrier (ion exchanger or compound with complexing properties), intensive research related to the possibility of using various molecules for this purpose [17,23], including commercially available chemicals, such as Cyphos IL 101, Kelex 100, Aliquat 336, and Calix[4]pyrolles [24–27], has been conducted. Campos et al. [28] tested Cyphos IL 101 for gold recovery from HCl solutions in liquid/liquid extraction systems and immobilized in a biopolymer composite matrix. They reported that gold can be easily desorbed from a loaded ionic-liquid-impregnated resin using thiourea (in HCl solutions), and the resin can be reused for at least four cycles. Vincent et al. [29] immobilized Cyphos IL 101 in capsules prepared by ionotropic gelation in calcium chloride solutions. They used resins containing various amounts of ionic liquid and found that the maximum sorption capacity was different for wet and dry resins (about 177 and 142 mg Pt g^{-1}, respectively) and depended on various factors. For example, zinc ions significantly decreased Pt sorption, which was probably due to the competition effect of chloro-anionic Zn species. Platinum can be desorbed from the loaded resin using either nitric acid (5 M) or thiourea (0.1 M in 0.1 M HCl acid solution). Regel-Rosocka et al. [30] investigated an application of phosphonium ionic liquids for removal of Pd(II) ions from aqueous chloride solutions with liquid–liquid extraction and transport across polymer inclusion membranes (PIMs). The authors obtained the highest values of the normalized initial flux for a CTA membrane containing Cyphos IL 101 and a receiving phase: mixture of 0.1 thiourea + 0.5 M HCl. Often, in the PIM separation processes described in the literature, the different metal ions were recovered in experiments based on the utilization of model solutions, of which the composition and properties can easily be changed/controlled. For example, Pospiech [31] applied PIMs containing Cyphos IL 101 and Cyphos IL 104 for the separation of Co(II) and Cu(II) ions from model chlorine ion aqueous solutions (NaCl/HCl) and reported that the selectivity coefficients for cadmium and copper ions decreased with increasing HCl concentration in the source phase. Kozłowski et al. used PIMs equipped with Calix[4]pyrrole derivative as a carrier for the separation of Ag(I) from different nitrate aqueous solutions. They found that the effective transport of silver ions depends on many factors—not only on the concentrations of the carriers and metal ions, but also on the pH and temperature of the source aqueous phase [32]. Because separation processes based on the application of PIMs and other polymer sorbents are influenced by many parameters [24,27], it is extremely important to compare the effectiveness of polymer materials with specific carriers in model and real solutions. Although such studies are carried out, they usually concern the separation of one or two metal ions [33], and many types of e-waste contain several or many different metals. Moreover, even in the case of commercial carriers with known properties, it is uncertain how effective the polymer materials containing such carriers as complexing agents will be in an environment of real composite samples.

In this paper, we present the results of the application of polymer films containing Cyphos IL 101 as a carrier for use in the simultaneous recovery of Pb(II), Ni(II), Zn(II), Co(II), Cu(II), Sn(II), Ag(I), and Au(III) ions from average computer scrap waste.

2. Materials and Methods

2.1. E-Waste

Treatment of waste electrical and electronic equipment is a complex and challenging process (Figure 1) that involves many unit operations. First, e-waste must be mechanically separated to carry out a leaching process, whereby valuable metal ions can be recovered from aqueous solutions through techniques such as solvent or membrane extraction.

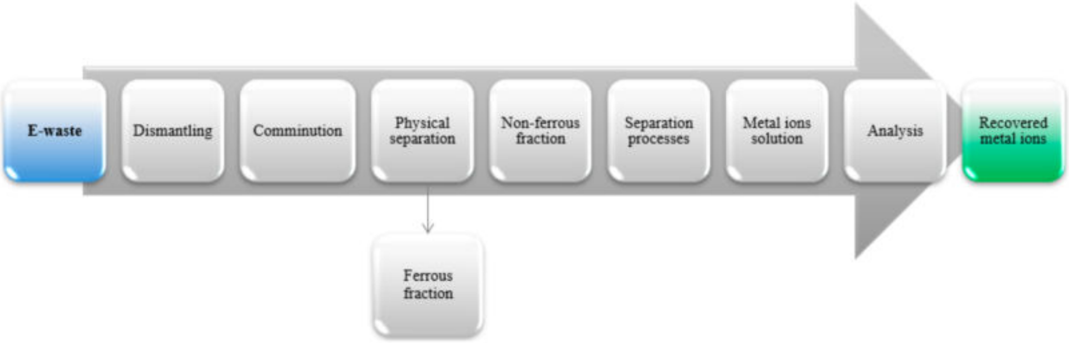


Figure 1. Stages of handling waste electrical and electronic equipment (WEEE).

The e-waste was harvested from old computers. Motherboards, compact disc drives (CDDs), and floppy disk drives (FDDs) were removed. In light of metal recovery studies, processors are the most valuable parts of computers because they contain a large amount of pure material that does not require much cleaning.

The processor pins were separated from the PCBs using a soldering torch. Graphics cards, random-access memory (RAM), and modems containing gold-plated contacts on the PCBs were separated mechanically by cutting them out. The contacts of the video graphics array (VGA) and digital visual interface (DVI) connectors were similarly separated. The computer material harvested in this way was the subject of this study (Figure 2).

Figure 2. Computer pins used in this research.

2.2. Reagents

The suspension of poly(vinyl chloride) (PVC), of an average molecular weight of 72,000, was obtained from ANWIL (Wloclawek, Poland). Tetrahydrofuran (analytical grade) was purchased from Avantor (Gliwice, Poland) and was used without further purification. The phosphonium ionic liquid Cyphos IL 101 and bis(2-ethylhexyl)adipate

(DAO) were purchased from Sigma-Aldrich (Poznan, Poland). Concentrated chloric and nitric acids were purchased from Avantor (Gliwice, Poland). The 5 M solution of nitric acid was obtained through dilution of the concentrated acid with distilled water. That solution was standardized against anhydrous sodium carbonate. The "aqua regia" solution was prepared by mixing concentrated nitric acid with concentrated chloric acid in a volume ratio of 1:3.

2.3. Preparation of Polymer Films Containing Cyphos IL 101

The polymer films (Figure 3) were prepared by pouring the received solution on a glass. The solution contained 60 wt.% poly(vinylchloride) (PVC) as a support; 20 wt.% bis(2-ethylhexyl)adipate (ADO) as a plasticizer and 20 wt.% a Cyphos IL 101 as an ion carrier were prepared in 10 cm^3 tetrahydrofuran. After slow evaporation of the solvent for 12 h, the resulting polymer film was peeled off from the glass plate and cut on a few rings with a diameter 4.4 cm. Over the next 12 h, the films were immersed in distilled water. The films were homogeneous, transparent, and flexible, and they had a good strength. The mean thickness of the films was determined and was approximately 0.25 nm.

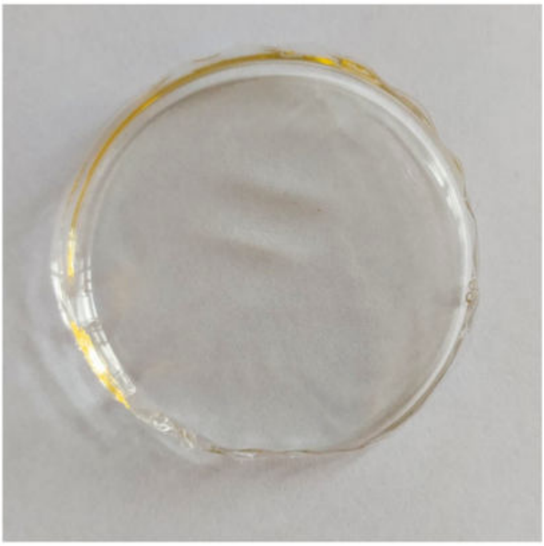


Figure 3. Prepared polymer film.

2.4. Preparation of Polymer Films Containing Cyphos IL 101

Testing of computer pins, which were harvested from e-waste after the pre-treatment described in the "E-waste" subsection (Section 2), involved the following steps (Figure 4a–c):

1. The computer pins were qualitatively analyzed for the presence of metals. This study was performed using a Panalytical XRF Minipal X-ray fluorescence spectrometer.
2. Computer pin samples (0.5 g) were flooded with 50 mL of concentrated (65%) nitric(V) acid and allowed to stand for 24 h. After some time, gold was released on the surface of the solution (Figure 4a). At the bottom, however, a certain amount of undissolved precipitate remained. The gold flakes were separated from the solution through the decantation of the solution from over the undissolved precipitate, and then this solution was centrifugated. In this way, 0.36 mg of gold was obtained.
3. The undissolved precipitate (Figure 4b) mentioned in point 2, together with the small amount of remaining solution, was separated by filtration.
4. To the filter containing precipitate mentioned in point 3, 50 mL of aqua regia was added (Figure 4c). After some time, the filter with the precipitate dissolved completely.

As a result of these operations, two solutions containing metals released from the pins were obtained: a solution of metals in nitric(V) acid (*A*) and a solution of metals in aqua regia (*B*).

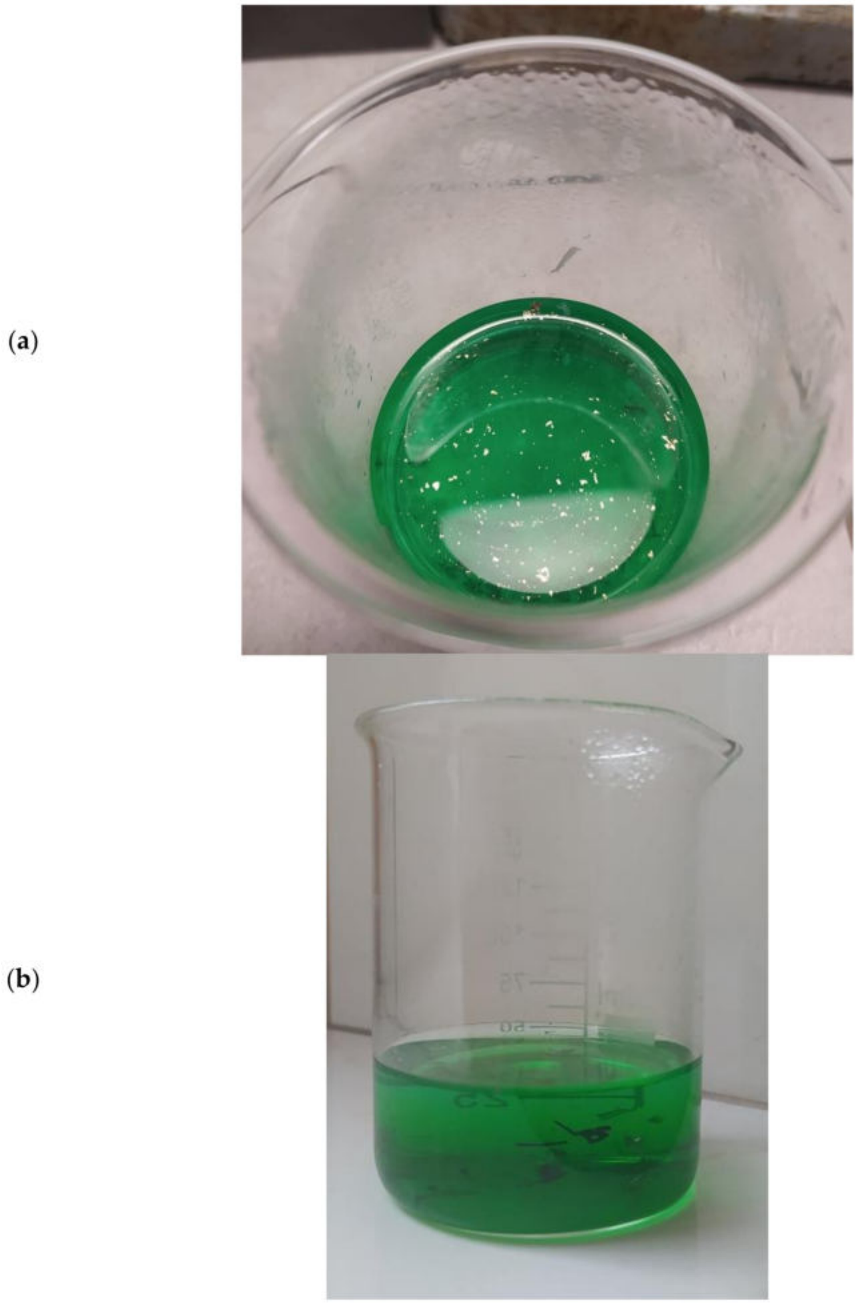


Figure 4. *Cont*.

(**c**)

Figure 4. Preparation of computer pin samples for analysis: (**a**) computer pins dissolved in nitric (V) acid—gold flakes visible on the surface; (**b**) computer pins dissolved in nitric (V) acid—visible undissolved pin residues; (**c**)—dissolving of insoluble components in nitric (V) acid residue of computer pins in aqua regia.

2.5. Recovery of Metal Ions on Polymer Films Containing Cyphos IL 101

The polymer films obtained as described in the "Preparation of polymer films containing Cyphos IL 101" subsection were used to recover metals from two solutions prepared in line with the "Leaching e-waste" subsection.

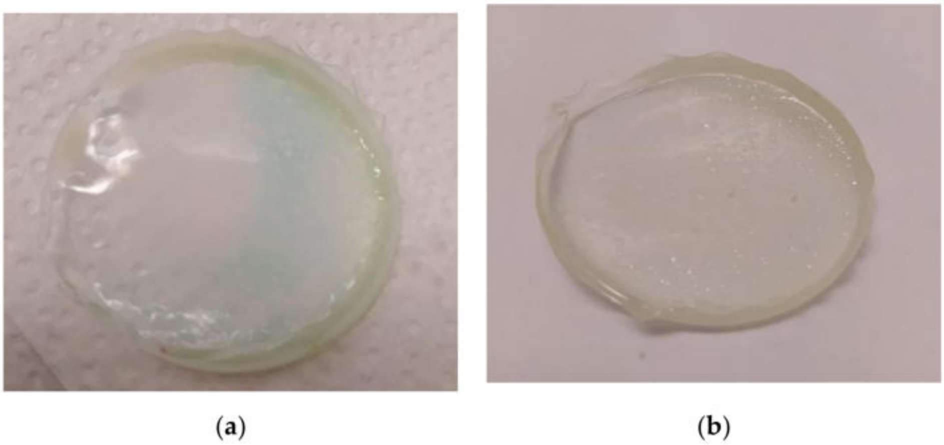
The following steps were taken next:

1. A polymer film (Figure 5) was placed in 45 mL of nitric acid(V) solution (*A*) for 24 h to bind the metal ions present in the solution on its surface. Samples of the solution were taken at set intervals.
2. At the same time, a polymer film was put into 38 mL of aqua regia solution (*B*) for 24 h to bind the metal ions present in the solution on its surface. Samples of the solution were taken at set intervals.
3. After removal from the above solutions (Figure 6a,b), the polymer films were air-dried and placed in 10 mL of 5 M nitric acid for 24 h to desorb the metal ions bound on the film surface. This step was intended to allow the films to be used in subsequent sorption and desorption cycles.

To carry out further cycles of metal sorption/desorption onto/from the polymer films, the computer pins were again dissolved, and solutions *A* and *B* were prepared (in line with the "Leaching e-waste" subsection). For each new solution, the number of metal ions present was determined. Polymer films, which were purified in 5 M nitric (V) acid, were placed in the solutions thus prepared to bind the metal ions present in the solution on their surface. Again, the solution was sampled at set intervals. A total of three consecutive cycles of sorption and desorption were carried out. The repeated cycles on the polymer films that were used several times were intended to establish the possibility of their suitability for repeated application.

The concentrations of metal ions in all probes from the sorption and desorption processes were determined with inductively coupled plasma mass spectrometry (ICP-MS, NexION 300d).

Figure 5. Polymer film immersed in nitric(V) acid solution.



(**a**) (**b**)

Figure 6. Polymer films after the first sorption process: (**a**) the membrane after removal from A solution, (**b**) the membrane after removal from B solution

3. Results and Discussion

The conductive material used in electronics is usually copper. In addition, conductive elements of nickel, silver, gold, tin, or a zinc–lead alloy are applied to the surfaces of the boards. According to the above data, it was first decided to obtain the XRF qualitative spectrum of the tested computer pins. The obtained spectrum (Figure 7a) confirmed the presence of some of these elements on the surface of the tested material, which was obtained from electro-scrap. Figure 7b is, in turn, a comparative test, i.e., it is the spectrum of an empty vessel with a special X-ray film. After approximately estimating the area of the peaks obtained in spectrum 7a, which correspond to specific elements, it can be concluded that the samples contained large amounts of copper, nickel, and zinc.

To consider the above results and high copper(II) content, the tested pins had to be dissolved in nitric(V) acid first. Copper is a semi-precious metal, which means that it does not react with non-oxidizing acids (no signs of reaction with HCl). However, Cu reacts with oxidizing acids (e.g., HNO_3).

Nitric acid and its salts are powerful oxidants—therefore, it reacts violently with metals that do not displace hydrogen (e.g., copper or silver). It also oxidizes certain non-metals, such as sulfur, carbon, and phosphorus. In addition, metals such as aluminum, chromium, and iron are passivated on contact with concentrated nitric(V) acid.

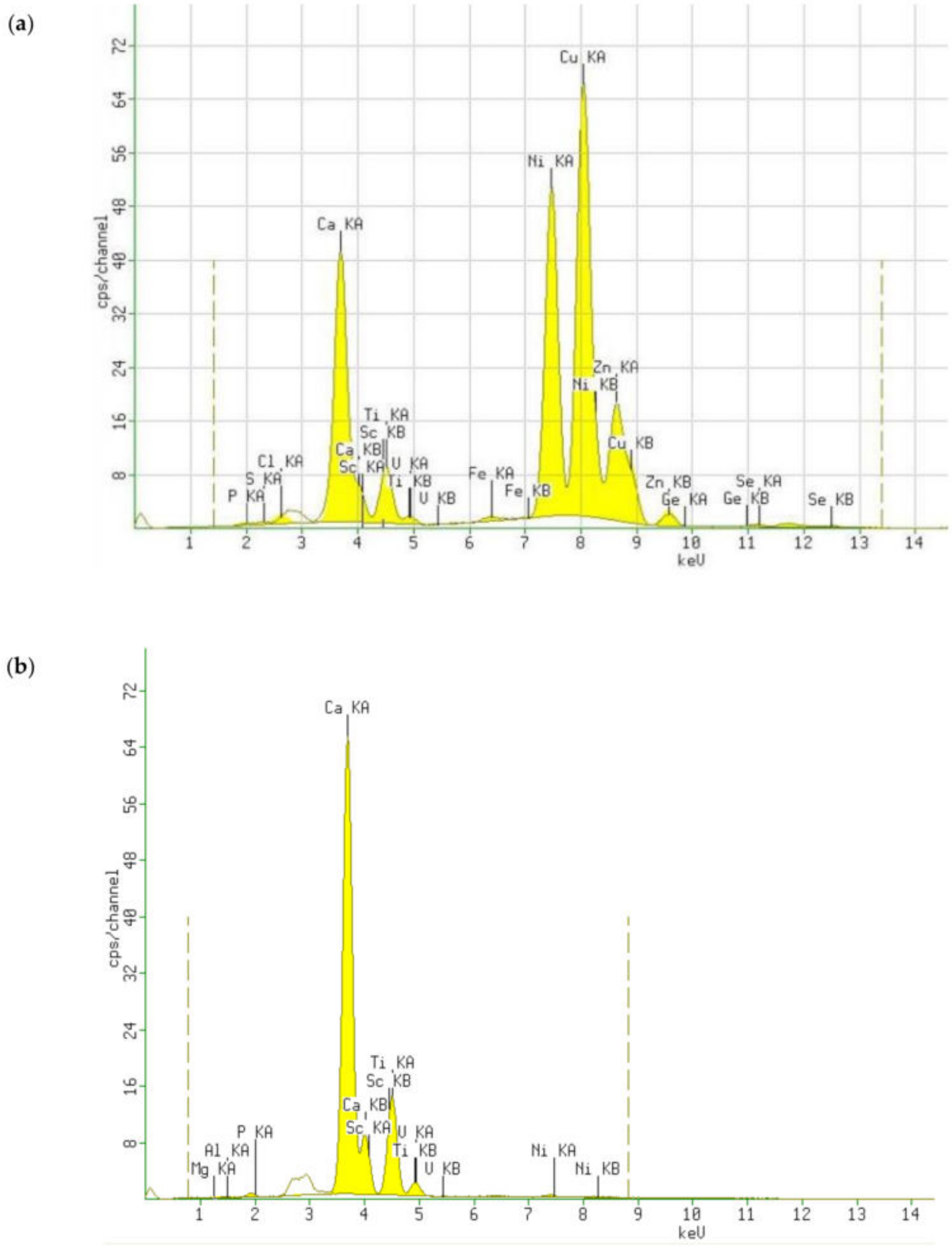


Figure 7. XRF spectra of (**a**) harvested computer pins; (**b**) blank test (X-ray film sample cell).

The course of the reaction of the selected divalent metals found in computer pins with concentrated nitric acid is as follows:

$$M^0 + 4\ HNO_{3conc.} \rightarrow M(NO_3)_2 + 2\ NO_2 + 2\ H_2O \qquad (1)$$

where M = Co, Ni, Cu, Zn, Sn, Pb.

In the case of monovalent silver, the course of the reaction is described by Equation (2).

$$Ag^0 + 2\ HNO_{3conc.} \rightarrow AgNO_3 + NO_2 + H_2O \qquad (2)$$

In the system studied here, it was observed that the nitric(V) acid dissolved the above metals, as well as the silver, leaving the remaining undissolved metals at the bottom of the vessel in the form of lumps or a brownish sludge. Gold that was not dissolved in HNO_3

accumulated on the surface of the solution in the form of flakes. The gold flakes were separated with simple centrifugation methods.

The rest of the precipitate was dissolved in another solvent. For this purpose, a mixture of nitric(V) acid and hydrochloric acid (in a 1:3 ratio), which formed the so-called aqua regia, was used. Its powerful oxidizing properties were evidenced by the fact that it dissolved all precious metals. In addition to gold, metals such as platinum, palladium, hafnium, molybdenum, and zirconium also reacted. When hot, chromium, tungsten, tantalum, rhodium, and osmium also undergo this reaction. The freshly prepared mixture was colorless but began to take on an orange–amber color after only a few minutes. This happened through the formation of nitrosyl chloride according to the equation below:

$$3\,Cl^- + NO_3 + 4\,H_3O^+ \rightarrow NOCl + 2\,Cl^0 + 6\,H_2O \tag{3}$$

The reaction of gold and palladium with aqua regia occurred in two steps, as shown in Equations (4) and (5), then (6) and (7):

$$Au^0 + 3\,NO_3{}^- + 6\,H_3O^+ \rightarrow Au^{3+} + 3\,NO_2 + 9\,H_2O \tag{4}$$

$$Au^{3+} + 4Cl^- \rightarrow [AuCl_4]^- \tag{5}$$

$$Pd^0 + 2\,NO_3{}^- + 4\,H_3O^+ \rightarrow Pd^{2+} + 2\,NO_2 + 6\,H_2O \tag{6}$$

$$Pd^{2+} + 4\,Cl^- \rightarrow [PdCl_4]^{2-} \tag{7}$$

3.1. Results of Leaching of E-Waste

After the dissolution of the computer pins in nitric(V) acid (*A*) and aqua regia (*B*), the resulting solutions were analyzed for their contents of the selected metals with the ICP-MS method. The experiments were repeated and standard deviations were calculated. Table 1 shows the results of the determination of the metal content in the freshly prepared solutions.

Table 1. Metal content found in freshly prepared solutions formed by dissolving computer pins: in nitric(V) acid (*A*) and aqua regia (*B*).

Symbol of the Sample	Co(II)	Ni(II)	Cu(II)	Zn(II)	Ag(I)	Sn(II)	Pb(II)	Au(III)	Pd(II)	Ta(V)
	(ppb)									
A.0	35.1	239,656.29	301,789.35	102,075.88	4.32	3065.40	3262.64	-	-	BLQ
B.0	22.1	-	-	-	-	15,111.88	2309.07	47.63	0.11	BLQ

BLQ—beyond the limit of quantification. The given values of the concentration carry ± 0.01 ppb.

From the data obtained, non-ferrous metals are the largest component of computer pins. Understandably, the studied material contains significantly fewer precious metals. The metal content can be ranked as follows:

$$Cu(II) > Ni(II) > Zn(II) > Sn(II) > Pb(II) > Au(III) > Co(II) > Pd(II) > Ag(I) > Ta(V).$$

3.2. Results of Recovery of Metal Ions on Polymer Films Containing Cyphos IL 101

Because previously published research results have shown that Cyphos IL 101 can be successfully used to recover gold from low metal concentrations [28] and that it works well in an acidic environment [34], we decided to use this particular ionic liquid to recover metal ions from the acidic solution obtained by leaching the computer pins with nitric acid and aqua regia. Additionally, ionic liquids also perfectly fit into the assumptions of green chemistry because they are a "green" alternative to the popular volatile, flammable, and often toxic organic solvents [35]. Their use eliminates the emission of harmful substances into the natural environment because they are characterized by a practically immeasurable vapor pressure under moderate conditions [36,37].

The mechanism of the sorption process is related to the binding of the metal ions present in the solution to the Cyphos IL 101 molecule as a result of a complexation reaction. In the first stage, in an acidic solution, the proton detaches from the Cyphos IL 101 molecule, which allows the metal ion to attach to this site and form a complex compound. The prepared polymer films were immersed in solutions A and B. From this point onwards, samples were taken from each solution at specified intervals to assess the progress of the sorption process, i.e., to determine the content of metals not yet adsorbed on the polymer surface at any given time. The experiments of the sorption processes were repeated and standard deviations were calculated (Tables 2 and 3).

Table 2. Changes in the values of metal ion concentrations in nitric(V) acid (*A*) in solution with sorption time on polymer film.

Symbol of the Sample	Time (h)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Ag(I)	Sn(II)	Pb(II)
		(ppb)						
A.1	0.50	34.92	238,563.29	296,386.02	101,145.38	2.19	2863.98	3139.67
A.2	1.50	34.94	223,442.34	290,767.62	100,853.95	1.76	2712.10	2996.41
A.3	3.00	30.83	199,932.97	257,349.24	85,830.85	1.45	2363.87	2676.53
A.4	10.00	28.31	183,021.32	232,285.68	75,987.33	1.22	2185.95	2438.11
A.5	23.00	27.91	178,906.54	220,067.10	71,645.99	1.01	2072.34	2347.74
A.6	24.00	26.72	156,570.95	206,577.27	69,413.90	0.88	1911.74	2152.41
		76.07%	**65.33%**	**68.45%**	**68.00%**	**20.37%**	**62.36%**	**65.97%**

The given values of the concentrations carry ± 0.01 ppb.

Table 3. Changes in the values of metal ion concentrations in aqua regia (*B*) in solution with sorption time on polymer film.

Symbol of the Sample	Time (h)	Co(II)	Sn(II)	Pb(II)	Au(III)	Pd(II)
		(ppb)				
B.1	0.50	1.77	14,823.34	2215.05	37.70	0.07
B.2	1.50	1.73	14,783.23	2200.64	33.95	0.07
B.3	3.00	1.72	13,281.13	1917.68	18.37	0.06
B.4	10.00	1.54	12,586.45	1734.79	7.64	0.05
B.5	23.00	1.42	11,367.46	1582.00	1.65	0.04
B.6	24.00	1.32	10,241.67	1469.91	0.54	0.04
		59.73%	**67.77%**	**63.66%**	**1.13%**	**36.36%**

The given values of the concentration carry ± 0.01 ppb.

The data in the above tables show that the best recovery occurred for the precious metals contained in the examined e-waste. In contrast, the recovery of non-ferrous metals (Co, Ni, Cu, Zn, Sn, Pb) occurred at 25–40%, as between 59 and 76% of these metals remained in the nitric(V) acid solution (*A*) and the aqua regia solution (*B*). This was most likely due to the selectivity of the metal ion binding agent found in the polymer films used, namely Cyphos IL 101.

This argument appears to be correct because when comparing the recovery of cobalt and gold, it is clear that Cyphos IL 101 performed more efficiently with the precious metal. Cobalt recovered from nitric(V) acid and aqua regia amounted only to 23 and 40%, respectively, while as much as 98.9% of the gold was recovered. The sorption process described could also be influenced by the composition of the solution that was studied. There are numerous examples in the literature of the use of Cyphos IL 101 for the recovery of various precious metal ions, e.g., palladium [38], gold [28], or platinum [29]. The authors of this publication point out that the effectiveness of this compound is closely related to the composition of the medium from which the metal recovery is carried out.

Figure 8a,b show the percentage change in metal ion concentrations during the sorption process in nitric(V) acid (*A*) and aqua regia (*B*), respectively, with the polymer film.

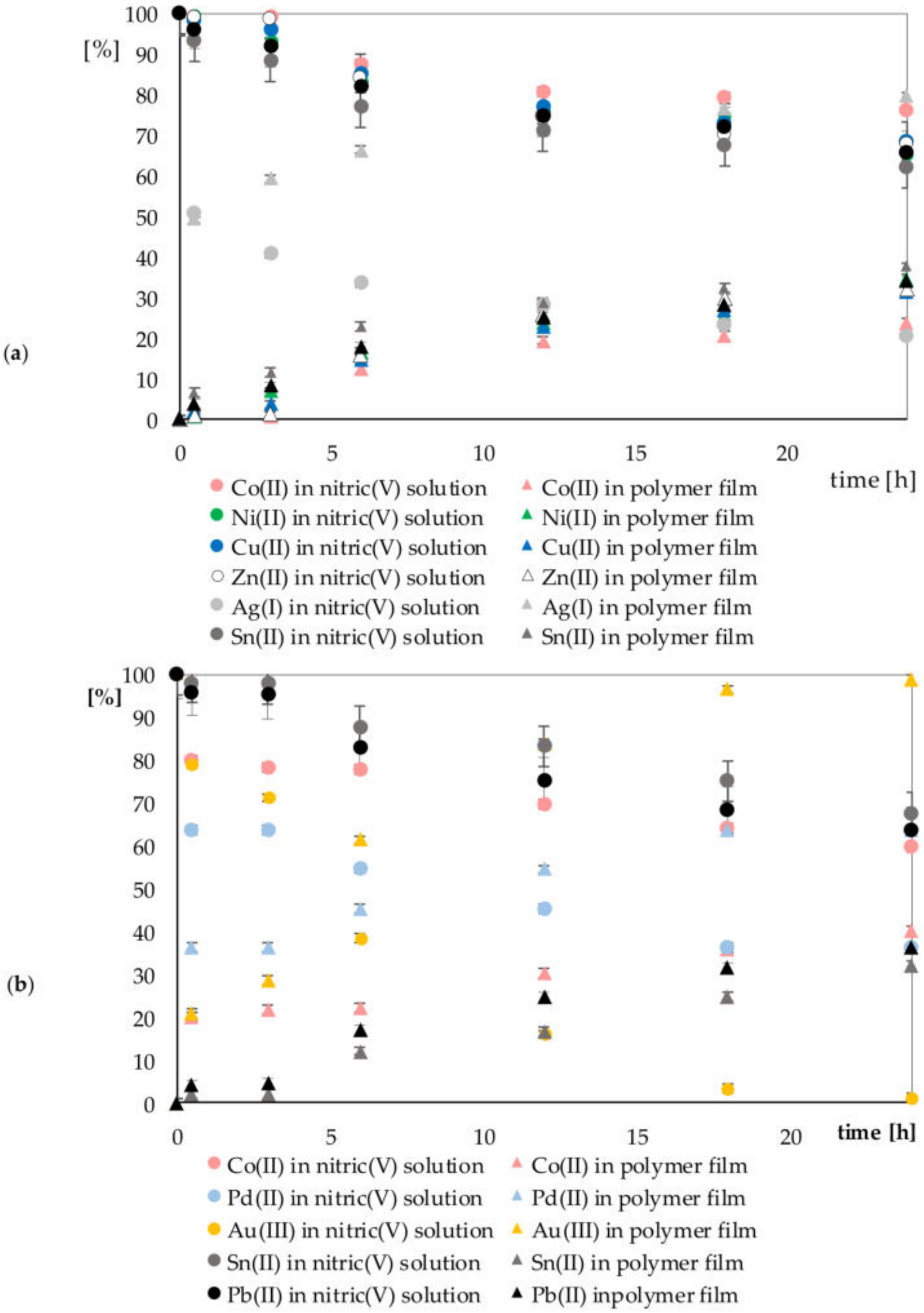


Figure 8. Percentage change in metal ion concentrations during the sorption process in (**a**) nitric(V) acid solution *A* and a polymer film containing Cyphos IL 101 immersed in it, as well as (**b**) aqua regia *B* and a polymer film containing Cyphos IL 101 immersed in it.

Only in the case of Au(III) ions can it be seen that it was possible to remove them almost completely from the solution. The amount of gold bound by the polymer films was proportional to the amount of gold lost in the solution. In the case of other metal ions, partial sorption was seen on the polymer films.

To describe the efficiency of removing metal ions from the aqueous solution using polymer films containing Cyphos IL 101, and based on the obtained results, the accumulation factor (AF) was calculated (Equation (8)). The mentioned parameter is described as follows:

$$AF = \frac{c_{membrane}}{c_0} \cdot 100\% \qquad (8)$$

where: c_0—the initial concentration of metal ions in the feed phase (mol/dm^3); $c_{membrane}$—the concentration of metal ions in the membrane phase (mol/dm^3).

From the data shown in the graphs above (Figure 9), it can be seen that the sorption process started immediately when the polymer films were dropped into the solutions. The sorption process could be quantified after only 0.5 h. For most metal ions, the accumulation factor after this time was still low, but in the case of sorption of silver, palladium, and gold ions, it was already 49.30%, 36.36%, and 20.84%, respectively. With time, all accumulation factors increased, and after 24 h, the non-precious metals did not exceed 40%. During the 24 h cycles of sorption, no decreases in accumulation factors were observed. This proved that Cyphos IL 101, which was used in the polymer films, bound the metal ions from the solution very strongly.

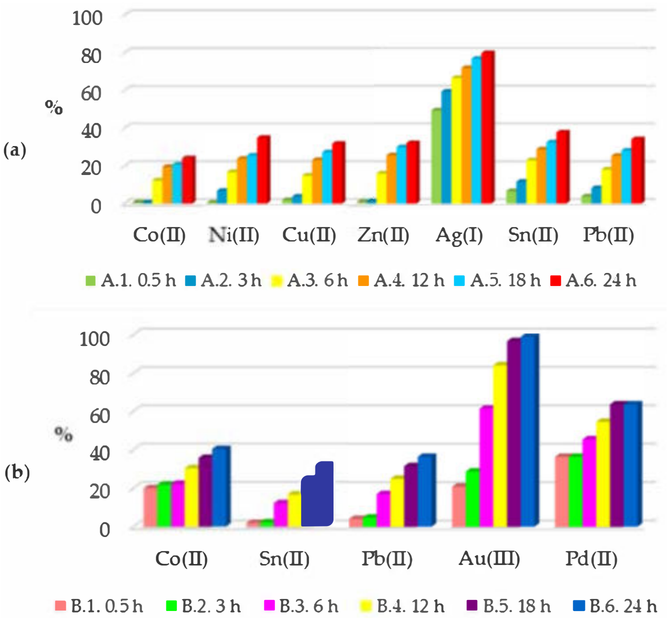


Figure 9. The accumulation factors describing the process of metal ions' sorption in (**a**) nitric(V) acid (*A*) and (**b**) aqua regia (*B*) on polymer films.

The sorption capacity of polymer films with 20 wt.% of Cyphos IL 101 was calculated using Equation (9):

$$q_t = \left(\frac{c_0 - c}{m}\right) \cdot V \tag{9}$$

where: q_t—the sorption capacity (mg/g), V—the solution volume (dm^3), c—the concentration of metal ions in the feed phase after time t (mol/dm^3), and m —the mass of the sorbent (g).

The results of the sorption capacity parameter after 24 h of sorption are presented in Table 4.

The sorption capacity is a very important parameter of all sorbents. The sorption capacity of the studied polymer films for metal ions was higher in nitric(V) acid than in aqua regia. The highest and the lowest sorption capacities was obtained for Cu(II) and Pd(II); they were 4.91 and 3.05×10^{-5} mg/g, respectively. The low values of sorption capacities for precious metal ions were caused by their small amounts in the studied WEEE. The received results can be compared with those found in the literature; e.g., the sorption capacities of materials that were obtained through impregnation of Cyphos IL101 on Florisil and Silica were 2.94 and 3.97 mg/g, respectively [39]. The sorption capacity of Amberlite XAD-7 with immobilized Cyphos IL 101 was, in turn, 71 mg/g [40], but the costs of preparing these resins were higher than those of the polymer films studied in this paper.

Table 4. The sorption capacity of the materials used.

Metal Ions	**q_t (mg/g) in *A* Solution**	**q_t (mmol/g) in *A* Solution**	**q_t (mg/g) in *B* Solution**	**q_t (mmol/g) in *B* Solution**
Co(II)	4.33×10^{-4}	7.35×10^{-7}	3.87×10^{-5}	6.57×10^{-7}
Ni(II)	4.28	7.30×10^{-2}	-	-
Cu(II)	4.91	7.72×10^{-2}	-	-
Zn(II)	1.68	2.57×10^{-2}	-	-
Ag(I)	1.77×10^{-4}	1.64×10^{-6}	-	-
Sn(II)	5.95×10^{-2}	5.01×10^{-4}	2.12×10^{-2}	1.78×10^{-3}
Pb(II)	5.72×10^{-2}	2.76×10^{-4}	3.65×10^{-2}	1.76×10^{-4}
Au(III)	-	-	2.05×10^{-3}	1.04×10^{-5}
Pd(II)	-	-	3.05×10^{-5}	2.86×10^{-8}

The given values of the qt carry ± 0.01 mg/g.

As a result of the sorption process on polymer films containing 20 wt.% of Cyphos IL 101, the following amounts of metals were recovered from 0.5 g of the computer pins studied (Table 5).

Table 5. The total amounts of metal ions recovered from computer e-waste using polymer films.

	Co(II)	**Ni(II)**	**Cu(II)**	**Zn(II)**	**Ag(I)**	**Sn(II)**	**Pb(II)**	**Au(III)**	**Pd(II)**
mg of Metal Ions/0.5 g Electro-Scrap	0.00038	3.73884	4.28454	1.46979	0.00015	0.23698	0.08185	0.00179	0.000002

The given values of the total amounts of recovered metal ions ± 0.00001 mg/g.

Based on the obtained results, it was found that using a polymer film containing 20 wt.% of Cyphos IL 101 as an ion carrier can recover copper(II) (4.28454 mg) > nickel(II) (3.73884 mg) > gold(III) (0.36179 mg) > tin(II) (0.23698 mg) and trace amounts of Pb(II) > Co(II) > Ag(I) > Pd(II) from 0.5 g e-waste. This allowed the estimation of the number of metals in a tonne of e-waste (Table 6).

Table 6. Estimated amounts of metals recovered using the method proposed in this paper per tonne of e-waste.

	Co(II)	**Ni(II)**	**Cu(II)**	**Zn(II)**	**Ag(I)**	**Sn(II)**	**Pb(II)**	**Au(III)**	**Pd(II)**
mg of Metal Ions/0.5 g Electro-Scrap	0.00076	7.47768	8.56909	2.93958	0.00031	0.47397	0.16369	0.72358 *	0.000005

* This value also includes the amount of gold obtained during the leaching of e-waste in nitric(V) acid. The given values of the total amounts of recovered metal ions ± 0.00001 mg/g.

The quantity of metals recovered with the polymer films appears to be small. However, an average Pole produces around 12 kg of e-waste per year, which amounts to almost 500,000 tonnes nationwide, which is around 77% of all waste of this type generated in the European Union. This number is so high because new sub-groups of e-waste that already exist in Western Europe are now beginning to emerge in Poland. The consequence of this phenomenon will be a continuous and dynamic increase in the amount of e-waste produced in our country. In contrast, the US produces the most electronic waste worldwide, according to a United Nations report. Western countries are also unable to recycle 100% of their e-waste, which is why they primarily transport it to African and Asian countries, as the cost of transport to these countries is twice as low as recycling on site [41].

The recovery method proposed in this paper is a good alternative for recycling valuable metals from electronic waste. Furthermore, it should be noted that this method allows for very selective recovery of precious metals because the percentage that was successfully recovered in relation to other non-ferrous metals was high (98.9% Au(III), 79.3% Ag(I), and 63.6% Pd(II)).

3.3. Evaluation of the Long-Term Suitability of Polymer Films Containing Cyphos IL101

Polymer films containing Cyphos IL 101 were regenerated after each sorption process by immersion in 5 M HNO_3 solution. The acid solution used for this process was also analyzed for the presence of the metals studied. The polymer films thus cleaned were placed again in solutions *A* and *B*, which were obtained by dissolving the computer pins in nitric(V) acid and aqua regia, respectively. The sorption and desorption processes were carried out on the same polymer films three times in 24 h cycles.

Figures 10 and 11 show the percentage distribution of the quantities of metals adsorbed on polymer films during the consecutive sorption processes or desorbed from their surface during desorption.

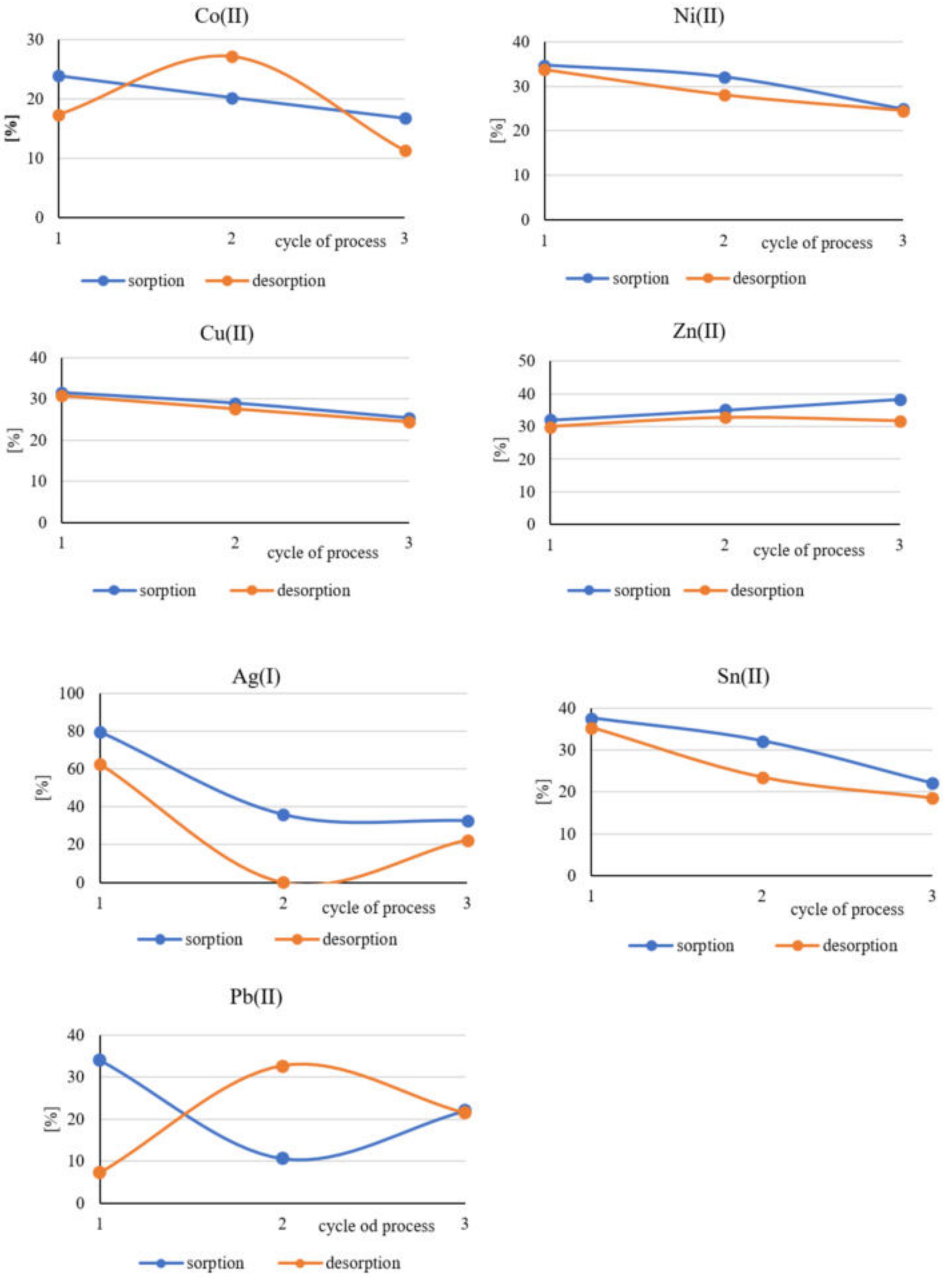


Figure 10. Percentage distribution of the quantities of metals adsorbed during the consecutive sorption processes on polymer films from the pin solution dissolved in concentrated nitric(V) acid *A* and desorbed from their surfaces during consecutive processes of desorption.

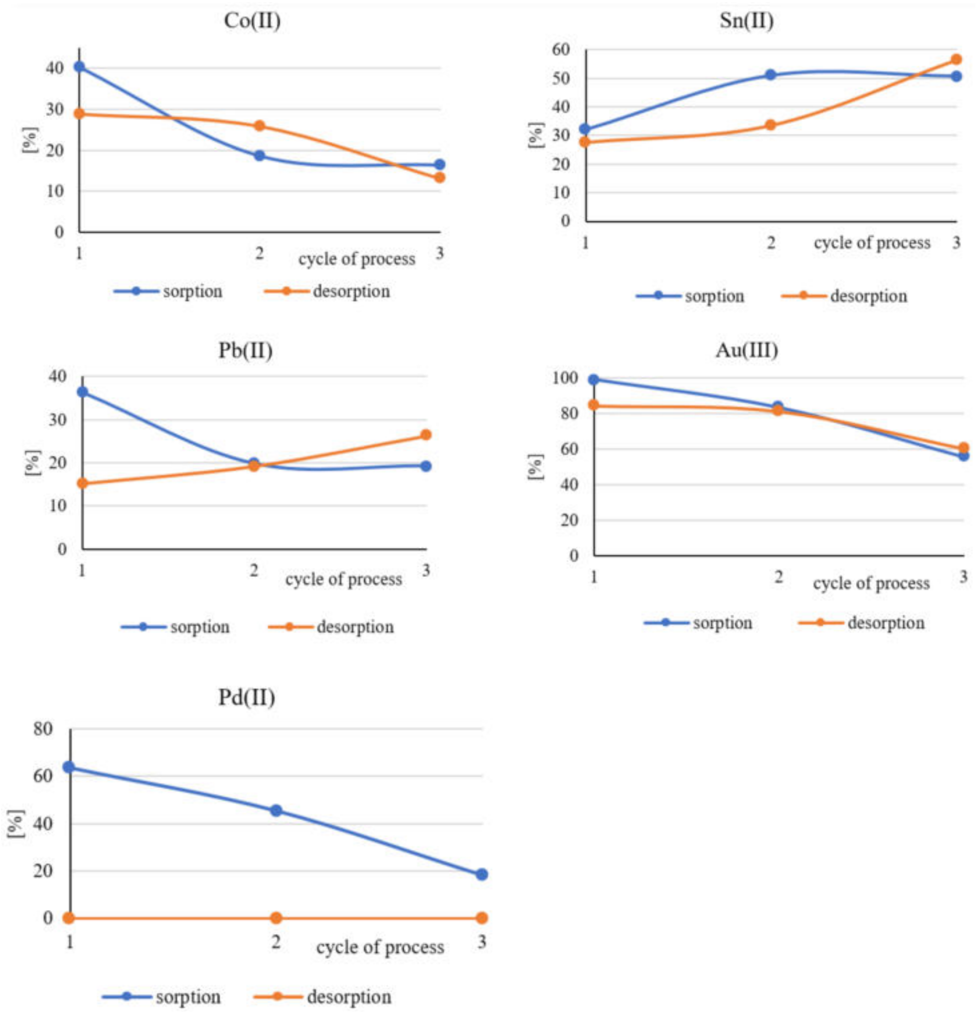


Figure 11. Percentage distribution of the quantities of metals adsorbed during the consecutive sorption processes on polymer films from the pin solution dissolved in aqua regia *B* and desorbed from their surfaces during consecutive processes of desorption.

The above graphs show that the polymer films used in this study can still bind metal ions from the solutions formed by dissolving the computer pins even after three consecutive sorption and desorption cycles. The obtained results are not unambiguous. It can be only seen that in most cases, the metal uptake by polymer films decreases with the next cycle of sorption. This may be related to the phenomenon of film clogging, which is caused by incomplete regeneration of the surface during consecutive desorption processes, during which decreasing quantities of metal ions are released into the solution. In the case of palladium, the number of desorbed ions was impossible to determine. Palladium, however, was a trace element in the material studied.

4. Summary

Although the use of polymer films does not allow the complete recovery of all of the metals present in computer pins, it indeed allows the recovery of the most precious metals. An undoubtable advantage of the materials used in this study is that they can be reused several times. The obtained films have more benefits than the other more traditional methods (e.g., electrowinning, solvent extraction, ionic exchange resin). First, the cost of obtaining polymer films is much lower than the cost of ion exchange resins because synthesis is provided by using simple and cheap substrates (commonly known polyvinyl chloride and plasticizer bis(2-ethylhexyl)adipate, and the easily accessible commercial metal ion carrier Cyphos IL 101), and special equipment is not required. Moreover, no power source is required to carry out the process of metal ion recovery. For example, the electrowinning methods need lots of power. All compounds added to polymer films are eco-friendly, so the material is safe for the natural environment and it does not cause pollution compared with solvent extraction, in which toxic solvents need to be used. Finally, the most important benefit of polymer films is that they can be easily separated from the solution after process of sorption of metal ions.

It is also important that in the described procedure of preparing e-waste samples for metals ion recovery, there is no need to use complex pre-treatments. For example, one alternative non-contaminating reagent used for gold leaching is thiourea [42], but as reported by Ippolito et al. [43], recovering gold from printed circuit boards or spent cell phones "as is" for thiourea leaching was not feasible due to the low Au grade release and recovery of only 15%. Direct leaching of thiourea onto the plate failed due to the competition between copper and gold for thiourea to form the corresponding complexes. Only the use of various pretreatment methods made it possible to dissolve the copper and increase the recovery of gold to about 80%.

The method proposed in this paper meets the requirements of a process that is carried out in the cheapest possible way and, at the same time, allows high efficiency with low energy and material inputs.

5. Conclusions

The results concerning the application of polymer films containing Cyphos IL 101 for the recovery of various metal ions ((Ni(II), Zn(II), Co(II), Cu(II), Sn(II), Pb(II), Ag(I), Pd(II), and Au(III)) from computer e-waste clearly show that the ionic liquid used allows for the effective recovery of noble metal ions. The efficiency of the recovery process was as follows: 98.9% for gold, 79.3% for silver, and 63.6% for palladium. In the case of heavy metal ion recovery, the efficiency was much lower, ranging from 25 to 40%. Moreover, the results of the experiments also demonstrate that the polymer films used in this research can still bind metal ions from solutions created by leaching computer pins even after three consecutive sorption and desorption cycles. In most cases, the metal uptake by polymer films decreases after each cycle. Due to the very high efficiency of gold ion recovery when using the ionic liquid Cyphos IL 101 and the high cost of this metal, the procedure described in this paper may be a good alternative to other less efficient, more complex, and costly recovery solutions.

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REVIEW OF RECOVERY METHODS OF WASTE FROM INDUSTRY AND POWER PLANT SERVICE

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Key words: recovery of metals, extraction methods, combustion by-products, regulations of proper energy waste usage

Summary. This review about recovery methods of waste from industry and power plant services. The following the extraction process have been described in the article, just like leaching, solvent extraction and polymer inclusion membrane. These methods can be used to recover metal transition from industry wastewater or metals contained in ores, sludges, concentrates or scrap, e.g. electronic. The Polish energy sector is still based on the combustion of conventional fuels. It is estimated that in Poland about 15 million tons of by-products are produced every year from coal combustion and about 2.5 million tons of gypsum from flue gas desulphurization. New solutions should be sought for the use of combustion by-products to minimize the wastes from the energy sector.

1. INTRODUCTION

The significant development of industry observed in recent years with one of the parties based on the development of our everyday life, and the other on the degradation of the natural environment generated by the generation of large amounts of materials by industrial plants. According Central Statistical Office in Poland was created 7 243.1 hm^3 industry waste in 2017 (Table 1).

The most wastewater re-quiring treatment discharged directly into the ground created was technology electricity, gas, steam and air conditioning supply and just ~ 0.1% was untreated. Whereas, the most untreated wastes was mining and quarrying (105.6 hm^3) and manufacturing (26.9 hm^3) [1].

Table 1

Selected information about treated and untreated industrial wastewater [source: own elaboration based ordinance of Environment 2018 r. [1]

Specification	**Discharged wastewater, hm^3**	**Wastewater requiring treatment discharged directly into the ground**	
		Treated, hm^3	**Untreated, hm^3**
Total	7243.1	775.5	105.6
Mining and Quarrying	310.5	247.3	60.5
Manufacturing	736.9	393.2	26.9
Electricity, gas, steam and air conditioning supply	6096.9	66.9	6.9

2. ENERGY PLANTS

The electricity supplied to the Power System in Poland comes from various types of power plants. Power plants are called plants where primary energy is converted into electricity.

Polish energy industry is mainly and primarily based on the functioning of the so-called conventional thermal power plants, in which non-renewable energy sources (hard coal, lignite, natural gas, etc.) are used for energy combustion. The electricity production process in a thermal power plant takes place in three stages:

- The first step: fuel is fed to the (steam) boiler and burned. This creates heat energy that changes the water into steam, which flowing in the tubes installed inside the boiler;
- The second step: in the next move, the expanding steam hits the turbine blades, thus sets in the rotating motion the device;
- The third step: then the rotating turbine shafts drives the generator (generator), finally producing electricity.

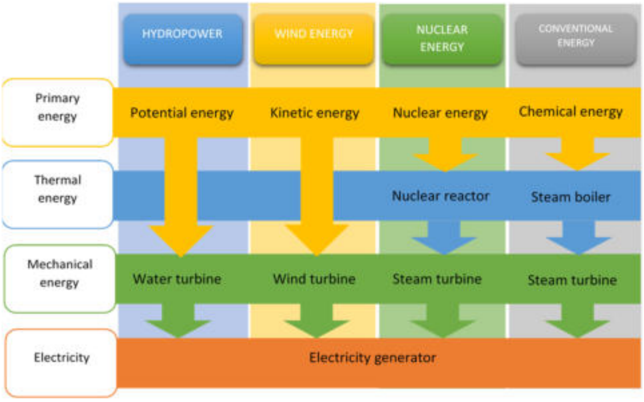

Fig. 1. Transfer of energy in selected types of power plants [2]

In a nuclear power plant it comes from the process of nuclear fission of radioactive elements, while in a thermal power plant it comes from the process of fuel combustion (Figure 1).

The alternative way to generate electricity for thermal energy based on burning coal or lignite is the production of electricity as a result of natural and repetitive processes in the environment (renewable energy). One of the main methods used in Poland to produce electricity by renewable energy sources is water. The operation of a hydroelectric power plant is relatively simple- falling water hits the turbine blades. Only in this way can the turbine be set in motion, which then drives the generator (generators) producing electricity.

The use of wind is another way to produce electricity using renewable energy sources. The operation of a wind power plant is also simple, mainly based on the operation of a generator. When the wind hits the resistance of the rotor blades, it changes the kinetic energy into mechanical work performed by the rotational movement of the rotor. Mechanical energy is transferred via a shaft and gear to the generator, finally converted to electricity.

The common element in all types of power plants discussed is the transformation of mechanical energy into electricity in generators (Figure 1).

The idea of generating electricity in conventional thermal power plants is dependence, that during the combustion of the substance a very large amount of heat is released. The heat energy conversion in a nuclear power plant is another possible way of generating electricity as a result of nuclear fission of uranium, plutonium or thorium atoms. Taking into account the production process, the stages of electricity production are analogous to those at a thermal power plant, except for the method of obtaining heat energy needed to make a steam.

The low level of implementation of renewable energy sources (RES) results from too high construction costs this type of installation and depending on the amount of electricity finally received from the prevailing weather conditions and season (constant fluctuations in energy production, except for the use of geothermal energy). At the same time, taking into account the standards imposed by the European Union, in Poland has been observed increase in the implementation of renewable energy sources in final energy pro-duction (Table 2).

Table 2

Electricity production in Poland - renewable energy is marked in blue, while thermal energy is marked in red [3]

Specification	The production in 2016	The production in 2017	Changes in production	Electrical power installed - status as at 2017
	GWh		%	MW
Total	**166 597**	**170 335**	**102,2**	43 612,0
Thermal power plants	140 378	140 259	99,9	32 233,0
- by brown coal	51 082	52 281	102,3	9 286,9
- by hard coal	80 173	79 265	98,9	20 989,5
- by gas	5 604	6 161	109,9	1 236,4
- biomass / biogas	3 519	2 552	72,5	720,2
Renewable Energy Sources power plants	26 701	30 594	560,3	12 791,9
Water power plants	2 335	2 719	116,4	2 306,0
- including pumped storage power plants	482	474	98,4	1 413,0
Wind farms	2 981	3 485	116,9	1 374,7
Industrial power plants	9 897	11 417	115,4	2 751,0
Independent power plants - renewable energy installations	11 006	12 454	113,2	4 947,2

3. ENERGY PLANTS

In order to analyze the content of chemical compounds and substances whose excessive emission to the environment could have a negative impact on society and the natural environment, this article has described the components contained in the by-products of coal combustion. Stationary sources are the main cause of air pollution emissions arising from human activities.

The latest data shows that in 2017 emissions of stationary sources fluctuated within (Figure 2):

- 73% of dust emissions;
- 50% of carbon monoxide emissions;
- 45% sulfur dioxide emissions;
- 23% nitrogen oxide emissions.

A coal is the medium used mainly as fuel to burn steam boilers in Poland, contain three components:

- organic;
- inorganic (mineral);
- water.

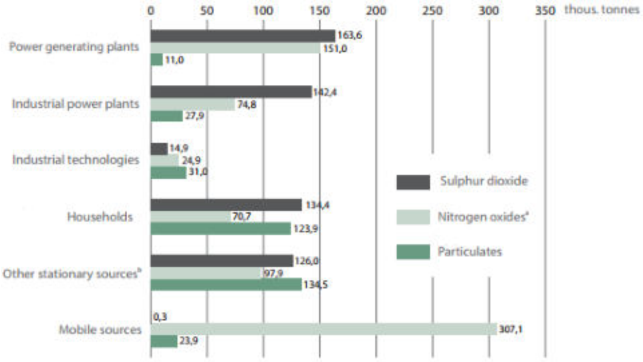

Fig. 2. Balance of main air pollutants emission in 2017 a) Expressed in NO_2, b) Local boiler plants, trade workshops agriculture and others [4]

Analyzing the carbon components reaction during the combustion process and taking apportionment by combustible substance and ballast. The ballast and the components include moisture and mineral parts from which ash is finally formed. The combustible carbon substance includes hydrocarbons, organic compounds and elements such as sulfur (S), oxygen (O) and nitrogen (N). The combustible substance also has a negligible content of some inorganic sulfides [5].

In terms of environmental protection, the processes of burning fossil fuels and coal, are the main possible sources of air and ambient contamination with solid and gaseous compounds, toxic and non-toxic combustion products. One of the side effects of coal combustion is the production of solid combustion products i.e. ash and slag, which are called combustion waste. The analyzes show that almost all exhaust components can be considered as polluting the natural environment.

The differences in the chemical composition of ashes from one power plant are small, assuming that the facility is supplied by one coal supplier, which provides a product with unchanging properties. The chemical composition of ashes in the other power plants may be different which results in burning variable fuel [6]. The physicochemical properties of ash depends on the following factors [7]:

- the type of fuel used for the combustion process;
- ash characteristics and final sulfur content in the fuel used;
- the type of sorbent used, its properties in the flue gas desulphurisation process;
- the method of combustion in the boiler and its construction;
- the oxidation state of gas desulphurization products.

Laboratories dealing with the measurement of dust-gas particles and the content of impurities in exhaust gases, distinguishes testing for the content of the following substances in fly ash and exhaust gases:

- arsenic and its compounds in fly ash;
- chlorine and its inorganic compounds in gas;
- chromium and its compounds in fly ash;
- zinc and its compounds in fly ash;
- fluorine and its inorganic compounds in gas;
- cadmium and its compounds in fly ash;
- copper and its compounds in fly ash;
- nickel and its compounds in fly ash;
- lead and its compounds in fly ash;
- total dust;
- mercury and its compounds in exhaust gases;
- mercury and its compounds in fly ash.

In addition, measurements are made for the content following compounds in the fly ash and exhaust gas: benzene, benzo (a) pyrene, benzo (b) fluoranthene, benzo (k) fluoranthene, indeno (1, 2, 3-cd) pyrene.

3.1. Types of combustion by products in Poland

The total amount of combustion by-products produced annually is estimated at around 23 million tonnes. Hard coal and lignite are the main raw materials in the energy sector. It is estimated that around 96% of the electricity production comes from its conversion [8]. With the development of the economy a cyclical increase in energy demand is observed. The one in mind coal is a strategic resource because of its very rich natural resources in Poland, technology availability, economy and process knowledge. With the increase in electricity demand, the amount and types of combustion by-products will increase analogously. The following by-products of energy combustion and flue gas cleaning installations such as [9]:

- fly ash;
- slag;
- ash-slag mixtures;
- microspheres;
- ashes from fluidized bed boilers;
- waste from flue gas desulphurisation by wet, semi-dry and dry methods have been distinguished so far.

Polish energy sector is mainly based on hard coal, which is why energy waste is one of the largest waste groups. The increasing amount of by-products of combustion is a huge problem and a challenge in environmental protection, therefore methods are sought to enable their further use. In the composition of waste resulting from the combustion of coal such as:

- non-flammable minerals remaining after burning;
- flue gas desulphurisation products;
- free calcium oxide;
- excess sorbent (limestone) and the product of secondary carbonization of calcium oxide (CaO) in the form of calcite;
- unburned coal in the form of coke breeze;
- a mineral substance that is an admixture of sorbent are distinguished.

To sum up, in connection with the operation of a coal-fired power unit, are created the following waste groups:

- wastes from energetic coal combustion (according to waste classification: non-hazardous waste);
- waste from the flue gas desulphurisation process (according to waste classification: non-hazardous waste).

3.2. Legislation relating to energy waste

Legal regulations and industry standards have a great impact on the energy waste market. These legal acts regulate the possibility of using combustion by-products (energy waste) in a specific amount and properties in a given product or product group. The following regulations refer to the flow of energy waste in Poland [10]:

- Waste Act of 14 December 2012;
- Regulation of the Minister of Environment on the waste catalogue of December 9, 2014 (RME, 2014);
- Regulation of the Minister of Environment of 10 November 2015 on the list of types of waste that natural persons or non-business entities may recover for their own needs and acceptable recovery methods;
- Regulation of the Minister of Environment of 11 May 2015 on waste recovery outside of installations and devices;
- Regulation of the Minister of the Environment of January 20, 2015 on the recovery process;
- Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC.

Other factors have conditioned the application, but also have limited the free flow of energy waste on the market with the following indicators [11]:

- the quantity and quality of production combustion by-products, which should be understood as the degree of fulfillment of the conditions contained in the standards of a given product or group of products produced based on energy waste;
- physicochemical properties of energy waste, in addition, also the level of toxicity and radioactivity of combustion by-products (e.g. granulometric composition, content of sulfur compounds, concentration of naturally radioactive elements, etc.);
- location of waste recipients relative to their producers;
- opportunities and costs of:
  - the storage of waste;
  - transport of waste to storage and recovery places;
  - transport of waste to final recipients (places of their use);
  - subjecting the waste generated to recycling;
- conditions and costs of producing the final product or group of products based on waste;
- the volume of demand for a given product or groups of products based on waste.

In addition, the properties and possibilities of using energy waste directly affect and regulate the increase in public, business and social awareness as well as the development of technology [12].

4. THE USE OF COMBUSTION BY PRODUCTS IN INDUSTRY

Because of their binding properties, fly ash is most often used in road engineering for soil stabilization, production of building materials or construction of tailing ponds. Additionally, fly ash is used in agriculture for deacidification of soils or in the municipal economy for the reaction of neutralization of acid industrial wastewater and chemical or biological neutralization of municipal wastewater. There is also the use of waste in the combustion process as a sorbent in dry flue gas desulphurisation.

Fly ash obtained in the energy sector is used for the production of lightweight ceramic aggregate, or as an admixture of cement and concrete [13]. Ceramic aggregates are used in agriculture for the production of floor panels in barns and piggeries. They are used as drainage layers and garden ballasts in gardening. Ceramic aggregates are introduced in many areas due to their vapor permeability and resistance to insects and rodents.

Waste from coal combustion can also be used as a raw material for carbon dioxide (CO_2) capture, when they have the right properties. They should have a high calcium oxide content (CaO) and free calcium oxide (CaO), because they react directly with water. The group of wastes from energy combustion that can be used to bind carbon dioxide (CO_2) includes [14]:

- fly ash from hard coal and lignite combustion in fluidized bed boilers;
- fly ash from hard coal and lignite combustion in conventional boilers;
- fly ash and solid waste mixtures from calcium flue gas desulphurisation methods;
- wastes from semi-dry flue gas desulphurisation methods.

According to the research results presented in Poland by AGH University of Science and Technology, it is possible to reduce carbon dioxide emissions (CO_2) in commercial power generation up to 117.25 Gg/year, using mineral sequestration, which allows this method to compete with others, e.g. with geological storage of carbon dioxide [14].

A slag is another by-product of combustion, that can be used in another area, which is produced around 300,000 tonnes a year in Poland [15]. Slags are used as an additive to concrete mixtures in construction, or as a component of the substrate for railway embankments. In Poland, research is ongoing on the use of ashes from biomass burning in fertilizers [16]. Combustion by-products resulting from the combustion of biomass, which is produced in uncontaminated components, usually do not contain amounts of heavy metals and other harmful substances that would exceed acceptable Polish standards, therefore they do not pose a potential threat to environmental contamination [17].

One of the most important legal documents is the REACH Regulation, which regulates the possibility of placing combustion by-products on the market [18]. This Regulation sets out capabilities related to the use of chemicals and the issuing of permits and marketing restrictions also for combustion by-products. Accurate waste management in energy combustion can become an important part of circular economy. Combustion by-products, as already mentioned, can be successfully used for cement production, soil stabilization, road foundation or the restoration of land from excavation [19-21]. Natural aggregates are under protection in Poland, but also they can be replaced by combustion by-products in Europe because of wide use of this waste in various economy sectors.

5. METAL IN INDUSTRAIL WASTES

The waste created mining and quarrying requiring treatment pose over 19% discharged directly into the ground, while the least untreated wastes discharged directly into the ground was from electricity, gas, steam and air conditioning supply (0.11%) (Table 1) [1]. In order to protect and improve the state of European inland waters and the ecosystems dependent on these waters, the European Union adopted a Water Framework Directive in 2000. The document imposes a number of guidelines that are to affect the achievement of good ecological status of waters. In addition, applicable national law and EU regulations specify the permissible levels of individual metals in industrial waste water. The average daily highest allowed value selected metals in wastewater was from 0.5 for chromium, nickel, copper and cobalt and to 2 mg/l for zinc (Table 3).

Table 3
The daily limits values selected metals in wastewater [22]

Metal	The highest allowed value
Zinc	2 mg Zn/l
Chromium	0.5 mg Cr/l
Cobalt	1 mg Co/l
Copper	0.5 mg Cu/l
Nickel	0.5 mg Ni/l

A significant amount of metals was in industrial wastewater, but you cannot forget about metals present in ores, sludges, concentrates or scrap, e.g. electronic. The main difference between them and wastewater is their physical state, and therefore the recovery method should be adapted to the material properties. In this review described commonly used the chemical methods for recovery of metals.

6. RECOVERY OF TRANSITIONS METAL FROM INDUSTRIAL WASTES

The metals present in industrial waste are most often recovered using extraction techniques. In the case of metal recovery from aqueous solutions, the traditional solvent extraction process or its alternative is used - polymer inclusion membranes. However, in the case of metal recovery from solids, e.g. sludges or post-metallurgical slag, the leaching process is used.

6.1. Recovery of metals from solid phases - leaching

Leaching is a basic unit operation during hydrometallurgical processes and it involves chemical transfer of solid-state metals into solution. Is the most difficult hydrometallurgical process, which is preceded by a series of preliminary operations. Leaching methods include percolation methods (leaching in the "In situ" deposit, leaching on an order and leaching in vats) as well as mixed leaching (suspension leaching, pressure leaching and leaching sintering). The substances used during leaching of ores, concentrates or scrap are most often inorganic acids, acidic salt solutions, alkaline hydrolyzing salts, alkalis and solutions of complexing compounds in acidic and alkaline environments. The selection of the appropriate leaching agent as well as the method and process parameters depends primarily on the chemical and mineralogical composition of the leached material. However, a good leaching agent should be selective for the separated metal, easily accessible, well soluble in water, create stable solutions and ensure obtaining the highest possible concentration. In addition, the solvent should be easy to regenerate, durable non-toxic and cheap [23-24]. Thus, the success of the process depends on the choice of the right leaching agent. In the table 4 data on the recovery of selected metal ions using various leaching agents were collated.

Table 4

Recovery of ions metal and with using leaching agent [sources: own elaboration]

Leaching agent	Parameters	Application	Percent of recovery	References
Ammonia in the presence of nitric acid	HNO_3:NH_3 1:12 pH ~ 11	Copper(II)	35.3 %	25
Oxygenated sulphuric acid acidic solution	Atmospheric leaching, Fe(II) concentration 20-30 g/dm^3 and s/l from 1:6 to 1:10	Copper(II) and zinc(II)	95% Cu 90% Zn	26
Ammonia solutions in the presence of H_2O_2	$NH_3 \cdot H_2O$ - NH_4HCO_3	Lithium(I), nickel(II), cobalt(II)	81.2% Li 96.4% Ni 96.3% Co	27

Experimental studies of scientist prove that leaching is an effective method of recovering metal ions from the steel and mining industries. Depending on the medium used and the material composition, metals such as copper, zinc, cobalt and nickel can be separated. The separation capabilities of ammonia solutions enable recovery more 90% copper, nickel and cobalt.

The effectiveness of this solvent is due to the fact that ammonia leaching of copper, nickel, zinc and cobalt sulfides with ammonia solutions and ammonium salts is based on the stability of the amminocomplexes $Me(NH_3)_n^{m+}$, that are formed during the dissolution of sulfides (n most often takes the maximum value for a given central ion) [23].

6.2. Recovery of metals from liquid phases – solvent extraction and polymer inclusion membrane

Extraction is a separation method that involves the separation of desired components of substances or chemical compounds by dissolving them in a solvent and separating them into a solution. Many extraction methods are known. One of the criteria for the division of these methods is taking into account the physical state of the tested samples, so the extraction of liquid samples and the extraction of solid samples are distinguished [28]. Solvent extraction is often the recovery technique used for the extraction of liquid samples. Solvent extraction is used to separate analytes from matrix components during pre-treatment or purification of the sample, or to concentrate analytes at very low concentrations, making them impossible to determine [29].

Solvent extraction allows the transition of the desired component from the primary to the secondary matrix. These phases must differ in polarity. In order for this process to occur, two solutions differing in polarity should be used.

To transfer metal ions in solution that are hydrophilic to the secondary (organic) phase, the hydrophobic properties need to be increased. A reaction at the interface (water phase / organic phase) then takes place and the resulting hydrophobic complex compound (ligand-metal) is transferred to the organic phase [30].

This means that in order for the metal ion recovery process to take place, an organic compound with complex-forming properties should be introduced into the system. This knowledge allows the selection of the right extractant for the separation of any metal. An example of the use of extractants is presented in the table below (Table 5).

Table 5
The parameters for recovery of metals by solvent extraction and polymer inclusion membrane [sources: own elaboration]

Solvent extraction

Extractant	Parameters	Application	Percent of recovery	References
Aliquat 336	Solution of up 63 g/l Cd or 81 g/l Zn were obtained with 97 g/l NH_3	Ammonia stripping of zinc and cadmium.	~ 99%	31
D_2EHPA	pH = 2.5, 20% and D_2EHPA (w/w)	Zinc(II)	98%	32
Cyanex 272	Sulphate solutions containing 0.01 M metal ions each and 0.1 M Na_2SO_4	Cobalt(II) and Nickel(II)	13.6-80.7% Co (pH=5.55– 6.75) 93.7% Ni (pH=3.65)	33

Polymer inclusion membrane

Ion carrier	Parameters	Application	Percent of recovery	References
D_2EHPA	1.50 M D_2EHPA, 2.50cm^3 ONPPE/1.0 g CTA, pH = 5.0	Zinc(II)	96.14%	39
D_2EHPA	Source phases 0.001 M each metals, pH = 3.0, receving chase 1.0 M HCl, 3.20 cm^3 ONPPE/1.0 g CTA, 1.0 M D2EHPA	Zinc(II), lead(II)	89.1% Zn 26.3% Pb	40
Phosphonium ionic liquid (IL) i.e., Cyphos IL : 101, 104, 167	55%CTA + 40% IL + 5% NPOE or 60% CTA + 40%IL	Zinc(II)	34 – 57% Zn (membranes without NPOE) 48-90% Zn (membranes containing 5% NPOE)	41
TOA	28.40 wt% CTA + 32.15 Wt% TOA + 39.45 Wt% ONPEE	Cobalt(II)	91.80%	42

Inclusion polymeric membranes (PIM) deserve special attention in the case of metal ion recovery. This is due to the fact that membrane processes belong to economically separation technologies, because solvent extraction consumes large amounts solvents, often toxycal. When transporting metal ions through liquid membranes, the amount of solvents used is small, and extraction and re-extraction processes occur simultaneously [34]. The membrane is a semi-permeable phase whose task is to separate two other phases, usually liquid or gas. Such a membrane acts as a passive or active barrier for mass transport. This means that if one of the components of the mixture passes through the membrane faster than the others, it can be selectively secreted from this mixture [35]. Polymer inclusion membranes besides matrix (PCV or CTA) contain a polymer and a chemical compound capable of extracting or transporting ions or chemical molecules from aqueous solutions - a carrier. Usually, PIM also contain a plasticizer, which is responsible for improving the mechanical properties of the membrane. As a result, PIMs are thin, flexible and stable films [36]. Polymer inclusion membranes classified as liquid membranes (LM) have many advantages, primarily the reduction of the use of large amounts of organic solvents, often toxic and hazardous, as well as high distribution coefficients and mass transport stream values. In addition, LM is distinguished by a relatively low operating cost and high membrane selectivity. However, it should be remembered that in addition to many advantages of liquid membranes, it is possible to wash the carrier from the membrane phase. The speed of transporting metal ions by PIM depends on many parameters, including on the type of polymer matrix, carrier concentration, amount of plasticizer and the thickness or morphology of the membrane surface [37]. The transport of metal ions depends primarily on the support used in the membrane, which is an ion exchanger or a compound with complexing properties [38], many carriers commonly used in PIM are known. Most often they are commercial extractants originally used in extraction processes. Depending on the ion carrier used, the desired metal ion can be extracted (Table 4). Due to the chemical nature of the extractants, these compounds can be divided into acidic, basic and neutral. Knowledge of the possibility by which mechanism the metal-ligand complex is formed is necessary in order to select the appropriate metal ion carrier.

There are many commercial extractants used successfully to recover transition metal ions. Table 4 shows selected commercial extractants, the recovery of transition metals is commonly used, gaining the efficiency of the process by up to approx. 90%. For zinc (II) recovery effective an extractant was D_2EHPA turned out to be, allowing 98% Zn (II) recovery. Cyanex 272 allowed the extraction of approx. 13.6-80.7% Co (II) and 93.7% Ni (II). Whereas using Aliquat 336 to ammonia stripping of zinc and cadmium in an amount approx. 99%.

The use of D_2EHPA in a polymer inclusion membrane enables the recovery of approx. 90% of zinc (II) ions. Whereas cobalt can be successfully recovered using TOA as a carrier. Scientific have proven that the composition of PIM affects the separation possibilities. As mentioned earlier, PIM usually consists of a matrix, carrier and plasticizer, and thanks to these components it retains its properties, which can be seen, for example, in the recovery of zinc ions using phosphonium ionic liquids. With the addition of 5% plasticizer, 48 to 90% of zinc (II) was obtained, while in the membrane without plasticizer the recovery percentage was 34-57%.

7. CONCLUSION

The development of the economy increases the demand for electricity, which in Poland is mainly produced in professional thermal power plants. The negative effect of producing energy is obtaining combustion by-products in various forms. New solutions and methods should be sought to enable the use and thus to minimize the level of waste storage, taking into account environmental issues.

Legal and regulatory requirements are required for the global and rational use of combustion by-products. It is also necessary to raise public awareness of the benefits from introducing combustion by-products, which will increase the promotion of new development methods. The waste discussed in the article is increasingly becoming possible to implement in various industries, but a large amount of it is still only stored and not used further in other processes.

Mainly waste from energy combustion is used in the production of cement and concrete, in land reclamation and development, or for road reconstruction. At the same time, there are many other technologies that enable the use of combustion by-products. There are methods that allow the use of waste to fill mining excavations or fertilize agricultural land. New methods are mentioned in literature and research regarding the use of combustion by-products in various spheres, however, too low demand and profitability resulting from the implementation of this waste are still observed in new areas.

In addition, industrial growth contributes to the generation of significant amounts of waste plus valuable metals. For example, galvanic protective coatings on the one hand protect metal from corrosion and on the other contribute to the formation of waste water during the production process. Waste water generated in production processes, among others the above mentioned contains metals that can be recovered and reused.

The mining and mining industry contributes to the production of a range of wastes ranging from underground wastes to processing wastes generated during processing and enrichment. In contrast, the electronics industry produces various types of cables and wires, batteries and cells, integrated circuits, capacitors, etc., which contain metals such as copper, zinc and gold. Given the limited resources of natural resources, the recovery of metals from waste is becoming a very important process that, in addition to economic reasons, improves the state of the environment. The described methods of metal recovery using extraction techniques can be successfully used to recover metals from industrial waste, and the recovered metals can be reused in production processes.

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PRZEGLĄD METOD ODZYSKIWANIA ODPADÓW Z PRZEMYSŁU I ELEKTROWNI

Słowa kluczowe: odzysk metali, metody wydobycia, uboczne produkty spalania, przepisy dotyczące właściwego wykorzystania odpadów energetycznych

Streszczenie. Niniejszy przegląd zawiera metody odzyskiwania odpadów z przemysłu i elektrowni. W artykule został opisany proces ekstrakcji, podobnie jak ługowanie, ekstrakcję rozpuszczalnikiem i membrana inkluzyjna polimeru. Metody te można stosować do odzyskiwania przemiany metali ze ścieków przemysłowych lub metali zawartych w rudach, szlamach, koncentratach lub złomie, np. elektroniczny. Polski sektor energetyczny nadal opiera się głównie na spalaniu paliw konwencjonalnych. Szacuje się, że w Polsce co roku produkowane jest około 15 milionów ton produktów ubocznych, z samego spalania węgla i około 2,5 miliona ton gipsu z odsiarczania spalin. Należy poszukiwać nowych rozwiązań dla wykorzystania produktów ubocznych spalania aby zminimalizować odpady pochodzące z sektora energetycznego.

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Recent advances in the recovery of precious metals (Au, Ag, Pd) from acidic and WEEE solutions by solvent extraction and polymer inclusion membrane processes – a mini-review

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ABSTRACT

The growing demand for precious metals, such as gold, silver and palladium, and the depletion of primary metallic resources contribute to the search for new solutions that enable the recovery of these valuable materials from waste electrical and electronic equipment (WEEE), which is now treated as their secondary source. Conventional methods based on high-temperature pyrometallurgical routes are now giving way to hydrometallurgical processes due to their greater accuracy, ease of control and the possibility of planning the metal recovery processes at various scales. Scientists are particularly interested in the precious metal recovery methods based on the utilization of solvent extraction (SE) and polymer inclusion membranes (PIMs) processes, mainly because of their high efficiency and the possibility of using various chemical compounds as extractants and carriers. The article reviews the latest achievements in the applications of SE and PIMs for the recovery of Au(III), Ag(I) and Pd(II) from acidic solutions, including those obtained as a result of leaching WEEE. The limitations and advantages of SE and PIMs processes based on the use of both commercial and non-commercial chemicals are described.

Keywords: Electronic scrap; Metals recovery; Solvent extraction; Membrane separation

1. Introduction

In recent years, there has been a rapid increase in the production of various electrical and electronic equipment (EEE), with its increased miniaturization and affordability leading to the shortening of its lifespan [1–3]. Operational problems faced by the electrical and electronic equipment repair sector also have a major impact on the decreasing lifespan of EEE [4]. This has led to the generation of significant amounts of waste electrical and electronic equipment (WEEE) [5,6]. WEEE includes but is not limited to worn-out integrated circuit (IC) manufacturing and computer industry products, printed circuit boards (PCBs), connectors, wiring, metal housings, as well as batteries and fluorescent lamps [7–10].

WEEE contains many metals, both hazardous ones that can be released in case of improper storage or processing (e.g., mercury) and may pose a threat to human health and the environment, as well as precious ones such as gold, silver and palladium, whose recovery is beneficial for economic and environmental reasons alike [11–14]. Due to the significant and systematically increasing amount of EEE waste, as well as the limited quantities of precious metals in ores and problems related to their extraction, new solutions and methods enabling proper e-waste management and fast and efficient recovery of valuable metals from such waste

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are intensively sought in recent years [15,16]. WEEE management is relatively well performed across the European Union mainly thanks to the WEEE Directive 2012/19/EU [17], which sets high targets for the Member States for the collection, recycling and recovery of valuable materials from e-waste. For many other countries outside the EU, collection, recycling and recovery rates are lower (e.g., in African countries) and WEEE legislation is constantly evolving (e.g., in India) [18,19].

Technologies for recovering valuable metals from e-waste used today are primarily based on physical processes that separate metal and non-metal fractions based on differences in their properties (e.g., magnetic, electrical conductivity, density, etc.) and chemical, such as pyrometallurgical, hydrometallurgical and biotechnological methods [16,20]. While pyrometallurgical processes in which EEE waste is subjected to high temperatures (often exceeding 1,000°C), usually in specially adapted furnaces, have been of great interest to scientists for many years, their use is systematically declining due to the high costs and the large scale of such operations (typically large amounts of WEEE are introduced into the furnaces) [10,16]. Hydrometallurgical methods involve the use of leaching agents (e.g., strong bases, acids, chlorine systems, etc.) and transfer of the desired components into a solution. Today, they are much more frequently used and modified than pyrometallurgical methods. Many researchers believe that hydrometallurgical methods will play a key role in future waste electronic and electrical equipment management processes due to their high accuracy, predictability, ease of control, and the possibility of planning the metal recovery process at different scales [21,22].

Nonetheless, the recovery of valuable metals from WEEE using hydrometallurgical methods is a complex process (Fig. 1), involving multiple unit operations ranging from disassembly, comminution, and physical separation of components to leaching, which enables the transfer of the desired substances to aqueous solutions [21,22]. The subsequent recovery of valuable metal ions from aqueous solutions is made possible by using solvent extraction (SE) processes or polymer inclusion membranes (PIMs), among others.

This paper aims to present recent developments regarding the feasibility of using SE and PIM processes to recover such precious metals as gold, silver, and palladium from acidic model solutions and solutions obtained by leaching waste electrical and electronic equipment (using

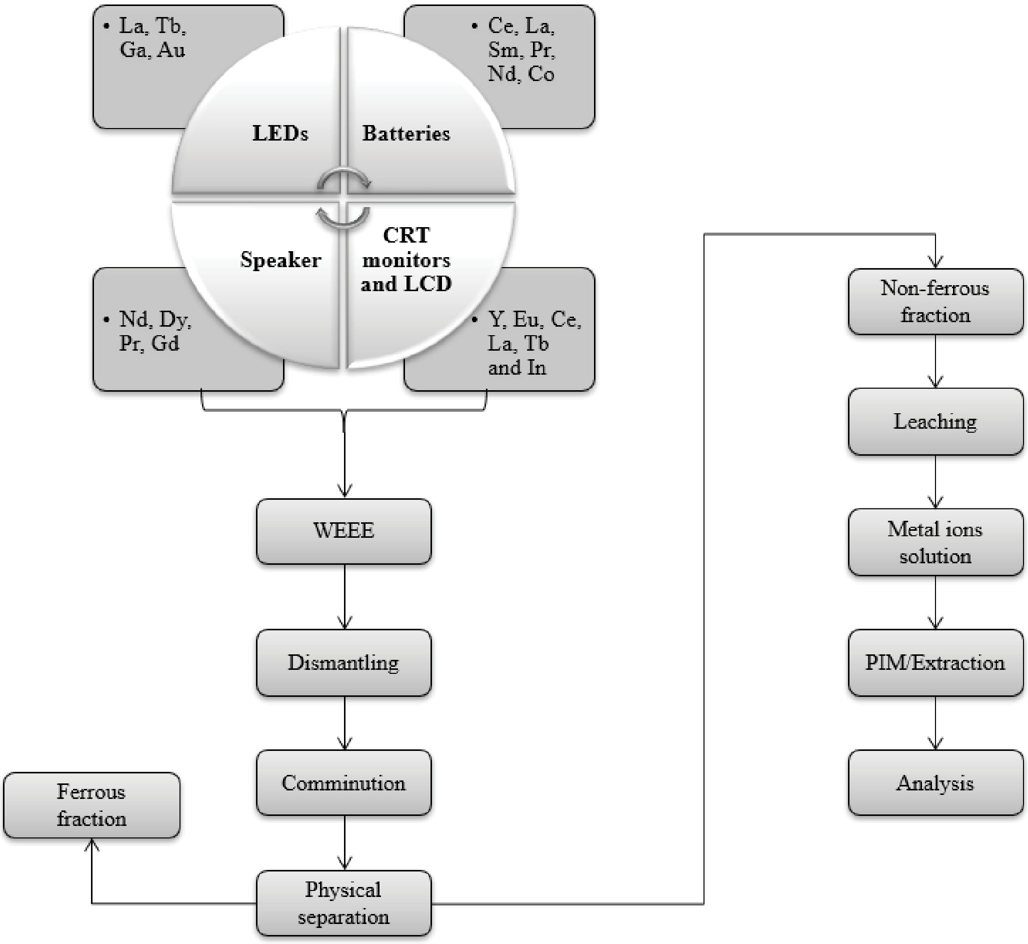


Fig. 1. Stages of WEEE proceeding for the recovery of valuable metals.
Source: own elaboration based on [21,22].

acids or their mixtures) and to discuss the limitations and challenges of implementing such solutions on a larger scale.

2. Fundamentals of solvent extraction and polymer inclusion membrane processes

2.1. Solvent extraction

Based on the samples' physical properties, extraction can be divided into liquid and solid extraction. Liquid extraction involves transferring selected components from a sample solution (feed solution) to another solution (receiving solution). In contrast, solid sample extraction involves dissolving the desired components in an appropriate solvent and then separating the solution from the insoluble matrix components [23,24].

The main parameters describing the extraction process are the partition coefficient, distribution ratio and extraction percentage [25,26].

Partition coefficient K_D [Eq. (1)], where: $[A_{\text{org}}]$ is the ratio of activities of a solute in an aqueous/organic system will remain constant and independent of the total quantity of $[A_{\text{aq}}]$.

$$K_D = \frac{\left[A_{\text{org}}\right]}{\left[A_{\text{aq}}\right]} \tag{1}$$

Since the solute exists in different forms due to such processes as ionization, protonation, complexation, or polymerization, the value of the K_D partition coefficient does not depend on the solute's total concentration. Thus, in practice, the so-called D_M distribution ratio is used, as this value is determined by the experimental conditions [Eq. (2)] [25].

$$D_M = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}} = \frac{[M]_{\text{feed}} - [M]_{\text{aq}}}{[M]_{\text{aq}}} \tag{2}$$

where $[M]_{\text{org}}$ – the concentration of metal ions in an organic phase (mol/dm^3), $[M]_{\text{aq}}$ – the concentration of metal ions in an aqueous phase (mol/dm^3), $[M]_{\text{feed}}$ – the concentration on metal ions in feed solution (mol/dm^3).

The most vital parameter in terms of process efficiency is the extraction percentage – $\%E_M$ [Eq. (3)]. It depends on the distribution ratio and the volume of the phases and is expressed as follows [26]:

$$\%E_M = \frac{D_M}{D_M + \frac{V_{\text{aq}}}{V_{\text{org}}}} \times 100\% \tag{3}$$

where V_{aq} – volume of an aqueous phase (dm^3), V_{org} – volume of an organic phase (dm^3) ($V_{\text{aq}} = V_{\text{org}} = 1$).

2.2. Polymer inclusion membrane process

Polymer inclusion membranes (PIMs) contain a polymer, carrier, and typically also a plasticizer, which are dissolved in an appropriate organic solvent; once they are poured onto a glass ring and the solvent evaporates, they form thin, stable and flexible films. The plasticizer is responsible for improving the membrane's mechanical properties. Membranes are usually conditioned in distilled water to ensure their homogeneity [27]. Numerous studies have shown that polymer inclusion membranes can serve as an alternative to traditional solvent extraction during metal ions recovery processes [28,29]. For PIM, metal ion transport depends primarily on the carrier contained in the membrane. The carrier is most often an ion exchanger or a complexing compound [30]. On the other hand, the rate of metal ion transport by PIM is a more complex process and depends on many parameters, for example, the polymer matrix type, carrier concentration, plasticizer amount, thickness and surface morphology of the membrane, as well as the composition of the feed and receiving solution [31]. The transport of metal ions by PIM occurs through the facilitated transport mechanism, which involves the ion exchange of metal ions and counterions on the membrane surface. A distinction is made between co-transport, in which both the metal ion and the counterion move in the same direction, and counter-transport, in which the metal ion moves in the opposite direction to the counterion [32] (Fig. 2). Counterions (X^-) are ions that can de-diffuse and be exchanged for another ion. The diagram below shows the mechanisms of metal ion (M^{n+}) transport across a polymer membrane.

The metal ion (M^{n+}) and the counterion (X^-) are extracted with an inert carrier (L) into an organic phase, that is, the polymer inclusion membrane, forming a complex compound (MX_nL_z) that diffuses through the PIM. This is followed by a re-extraction process during which the metal ion and counterion are transferred to the receiving phase [Eq. (4)].

$$M^{m+} + nX^- + zL \rightarrow MX_nL_z \rightarrow M^{m+} + nX^- + zL \tag{4}$$

The carrier molecule (L) released in this way diffuses back into the feed phase to extract further ions from the solution. The extraction and re-extraction processes occur in succession until the system attains chemical equilibrium.

Co-transport (A) involves the simultaneous transport of a metal ion (M^{n+}) and a counterion (X^-) across the membrane from the feed phase to the receiving phase. When an inert carrier is used, the process's driving force is the variation of the partition coefficient of the transported substance and its complex formed with the carrier at the feed phase/membrane and membrane/receiving phase interfaces. The released applied carrier molecule diffuses back toward the feed phase to extract more metal ions until a complete chemical equilibrium is attained. The facilitated transport (B) of metal ions involves the formation of a hydrophobic complex between a carrier molecule (L) and a metal ion (M^{n+}), which then diffuses through the membrane phase into the receiving phase, thereby releasing the carrier molecule (L). When acidic carriers are used, the transport of metal ions occurs according to the counter-transport mechanism (C). The counter-transport mechanism involves the transport of metal ions from the feed phase to the receiving phase across the membrane while hydrogen ion transport occurs in the opposite direction. At the feed phase/membrane interface, the metal ion forms a complex compound – ML_n with the deprotonated form

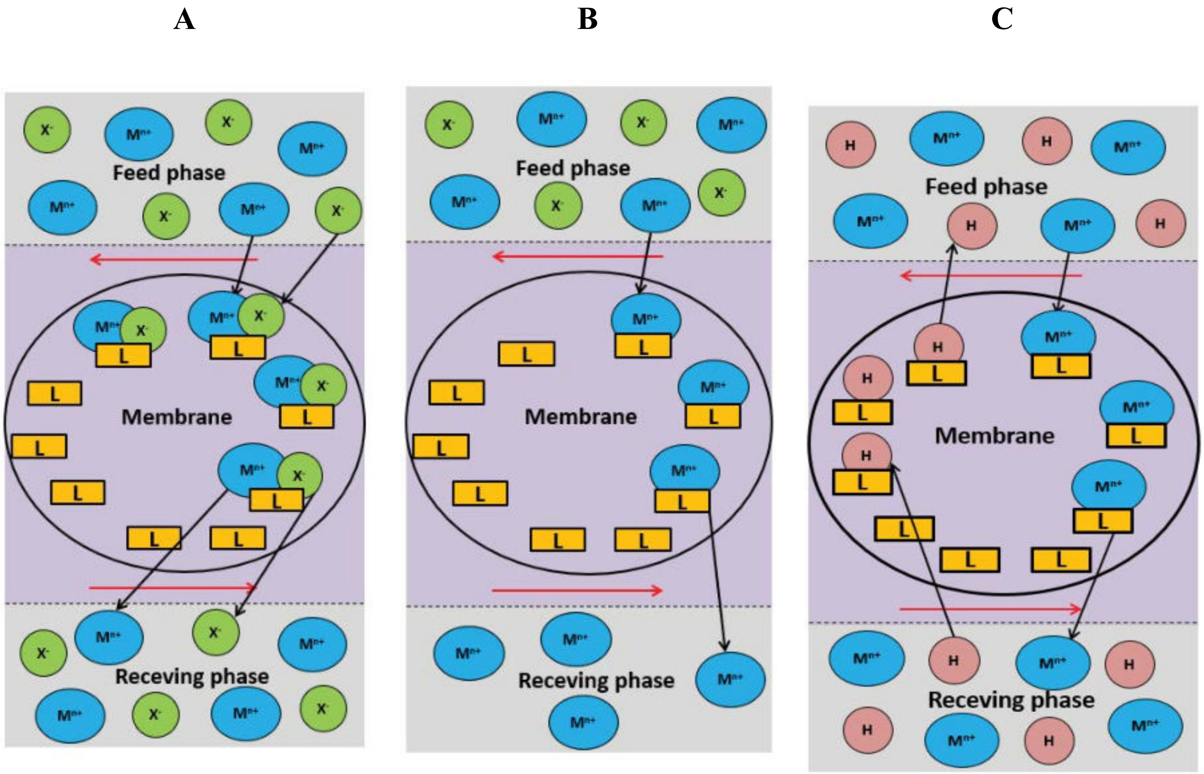


Fig. 2. Mechanisms of metal ion transport across polymer inclusion membranes, where: A – co-transport, B – facilitated transport, C – counter-transport, *L* – carrier, X^- – counterions, M^{n+} – metal ions, H – hydrogen ion.
Source: own elaboration based on [20,33–35].

of the carrier, and after the diffusion of the complex compound at the membrane/receiving phase interface, a process of re-extraction of the metal ions into the receiving phase occurs with simultaneous uptake of hydrogen ions present in this phase. The counter-transport mechanism's driving force is the difference in the values of the partition coefficients, formed by maintaining an appropriate pH gradient between the feed and receiving phases [20].

The primary parameters describing the process of transporting ions through the polymer membrane are the initial flux of metal ions – J_0, the $S_{M1/M2}$ selectivity coefficients and the percentage of metal ions separation – RF [33–35].

The initial metal ions flux J_0 is defined by Eq. (5), where P is the permeability coefficient and c_0 is the initial metal ions concentration in the feed phase (mol/dm^3).

$$J_0 = P \cdot c_0 \tag{5}$$

$$P = \left(\frac{V}{A}\right) \cdot k \tag{6}$$

where A – the effective membrane area (m^2), V – the volume of feed phase [m^3].

The reaction rate constant k (s^{-1}), takes on different values depending on the order of the reaction; for example, for a first-order reaction, it is described by Eq. (7).

$$\ln \frac{c}{c_0} = -kt \tag{7}$$

The transport of metal ions across the polymer inclusion membrane is described by the $S_{M1/M2}$ selectivity coefficients represented by Eq. (8) (where $J_{0,M1}$ and $J_{0,M2}$ represent the initial flux for $M1$ and $M2$ metal ions, respectively).

$$S_{M1/M2} = \frac{J_{0,M1}}{J_{0,M2}} \tag{8}$$

The most important parameter determining the efficiency of the process transporting metal ions across the membrane is the recovery of metal ions from the feed phase to the receiving phase Eq. (9):

$$\text{RF} = \frac{c_i - c}{c_i} \times 100\% \tag{9}$$

where c_i – initial concentration of metal ions in the feed phase (mol/dm^3), c – metal ion concentration after the period of time (mol/dm^3).

3. Recovery of gold(III) ions

Because of its value and excellent properties (non-corrosion, high electrical and thermal conductivity), gold is often recovered from WEEE [36,37]. Currently, Au is recovered from e-waste using such methods as leaching processes, as well as solvent extraction and membrane separation. Leaching processes are carried out using various solutions, such as aqua regia, which is a mixture of HCl and HNO_3 (3:1; Au(III) recovery over 99%) [38], sodium thiosulfate solutions (0.12 and 0.2 mol/dm^3, gold recovery of 70% and 75%, respectively)) [39], and 65% HNO_3 solution (recovery of ca. 82% Au(III) [40]. The solvents used in leaching processes are typically neither cheap nor environmentally inert, and as such, other methods are being developed to reduce the volumes of solvents used and limit pretreatment processes [41]. For example, gold can be easily recycled from the gold-plated layer of waste mobile phone (WMP) PCBs using a DMF-$CuCl_2$-$CaCl_2$ (DMF: dimethylformamide) system called "mild aqua regia" with no pretreatment or enrichment processes required; additionally, the reaction system can be used recurrently [42]. Wu et al. [43] utilized the process of spontaneous reduction of gold by electroactive aniline polymers during hydrometallurgical leaching (with the mixture of concentrated HCl and HNO_3) of e-waste. They reported that by coupling the metal reduction process with an increase in the intrinsic oxidation state of the polymer and the subsequent re-protonation and reduction of the intrinsically oxidized polymer to the protonated EM salt (emeraldine salt), spontaneous and sustainable gold recovery from acidic solutions can be achieved without utilizing extensive metal-extracting reagents and external energy input. Research is also being conducted to increase the selectivity of the processes of recovering precious metals from waste. Tuncuk [44] developed a method to recover Au(III), Ag(I) and Cu(II) ions from WEEE based on the use of several oxidizing agents (i.e., 2% iodine, 3% hydrogen peroxide) and a two-stage leaching process that enabled efficient and selective recovery of gold (99.98%) and silver (96.90%) ions. New methods for recovering metals from e-waste are typically designed to be eco-friendly, which often requires hybrid solutions or combinations of several different methods [45].

When recovering gold(III) ions from a solution obtained from e-waste leaching, the selection of the correct extractant and the conditions under which the extraction process is carried out are vital [46]. The used extractant must enable the selective transport of Au(III) ions from an aqueous mixture of metals into a hydrophobic (organic) phase through the coordination or supramolecular chemical recognition under properly chosen conditions [47]. Choosing the right extractant is not a simple process and the use of different compounds may lead to significantly different results even in cases where their structures are similar. For example, Doidge et al. [48] researched the recovery of gold ions from waste smartphones and the use of simple primary, secondary, and tertiary amides as reagents that selectively transport gold from aqueous to organic phases in solvent extraction experiments. They reported that while the strength of the extraction of gold from single-metal solutions is ordered 3° > 2° > 1° (where 3°, 2° and 1° stands for tertiary, secondary and primary amides, respectively), the 3° and 2° amides are ineffective at transporting gold from mixed-metal solutions due to the formation of a third phase [49]. New chemical compounds that can be used as gold extractants are constantly being sought. Oshima et al. [50] compared the extraction behaviour of Au(III) from acidic chloride media using cyclopentyl methyl ether (CPME) with processes conducted using such commercial extractants as dibutyl carbitol (DBC) and methyl isobutyl ketone (MIBK). They reported that while the extractability of CPME was relatively low compared to DBC and MIBK, CPME was advantageous in the stripping and reductive recovery of the extracted Au(III). Alzate et al. [51] used optimized quantities of ammonium persulfate to extract non-leaching gold from WEEE and reported that $[(NH_4)_2S_2O_8]$ in aqueous oxygen enriched media could be used to extract superficial gold with an efficiency exceeding 98%. Campos et al. [52] developed a two-stage method for recovering gold from HCl solutions (such solutions can be obtained during the leaching of e-waste). The first step involved liquid/liquid extraction using toluene and hexane, whereas the second step included gold recovery with the use of tetra-alkyl phosphonium chloride (Cyphos IL-101) upon immobilization in a biopolymer composite matrix. Their results indicate that the resins could be re-used for at least 4 cycles and are specially adapted for the recovery of gold from low metal concentrations.

Using polymer inclusion membranes is a common solution for recovering gold(III) ions from e-waste. The primary factor that defines PIM capabilities is the carrier and the membrane's separation properties depend on its selection. One well-known commercial carrier is the Kelex 100. Due to its chelating ability, Kelex 100 enables the recovery of not only Cd(II), Pb(II), and Ni(II) ions [53,54] but also gold(III) ions. De San Miguel et al. synthesized a polymer inclusion membrane containing 32% w/w of Kelex 100, serving as the carrier, as well as 18% w/w of CTA (matrix) and 50% w/w of NPOE (plasticizer) for the transport of gold(III) ions from concentrated chloride solutions. The researchers have demonstrated the membrane's ability to recover approximately 85% of the gold, as well as the possibility of using it for fifteen 6 h cycles without the loss of its transport capability. Studies on the recovery of gold ions from concentrated hydrochloric acid media with the use of Kelex 100 in hybrid membranes containing hydroxyl-terminated poly(dimethylsiloxane) with (3-aminopropyl) triethoxysilane were also conducted. The results have shown that this method makes it possible to recover 70% of the gold [56]. Phosphonium ionic liquids are of great interest to researchers as well. Apart from their use in traditional extraction processes (recovery of d-electron metal ions and lanthanides [57–59]), compounds such as Cyphos IL-101, 102, 104, etc. are often used in polymer inclusion membranes for the recovery of transition metal ions, for example, V(V), Zn(II), Cd(II), Co(II), and Ni(II) [26,60–62]. Phosphonium ionic liquids have also been used to separate gold ions from e-waste. Bonggotgetsakul et al. [63] used PIM containing 30% w/w of Cyphos IL-104 as a carrier, and 70% w/w of PDVF-HFP as a matrix for the recovery of gold(III) ions from a solution obtained by leaching electronic scrap with aqua regia. Based on performed experiments, they determined the stoichiometric formula of the Au(III)/Cyphos IL-104 complex, ($[P]^+[AuCl_4]^-$ $H^+[PO_2]^-$, where $[P]^+$ is the phosphonium cation and $[PO_2]^-$ is the phosphonium anion), and also concluded that the proposed PIM-based technology is an attractive alternative to conventional solvent extraction methods since it eliminates the use of diluents which are often toxic, volatile and flammable. Polymer inclusion membranes with different concentrations of Cyphos IL-104 as the membrane extractant/carrier, were also examined for their ability to extract Au(III) from hydrochloric acid solutions. It has been reported that a PIM consisting of 25% w/w of Cyphos IL-104, 5% w/w of 1-dodecanol, and 70% w/w of PVC exhibited the best performance in terms of extraction rate and the amount of Au(III) extracted (recovery of 95% Au). Nonetheless, because of the loss of 1-dodecanol from the PIM to the aqueous solutions, the membrane was suitable only for a single efficient recovery of Au(III) from e-waste hydrochloric acid solutions [64]. Another carrier used in PIMs applied in the recovery of gold ions from e-waste is dm-3N-[N,N-di(2-ethylhexyl)aminocarbonylmethyl]glycine (D_2EHAG). Kubota et al. applied the extracting organic solution and the PIM containing the synthesized D_2EHAG extractant for the selective recovery of gold from synthetic (model) and real leachates obtained from e-waste (leaching with aqua regia). They reported, that PIMs with D_2EHAG exhibited high selectivity for the gold(III) ions (recovery of 96% of the gold) over the other metal ions present in much higher concentrations in the leachates [65]. Bonggotgetsakul et al. [28] used a polymer inclusion membrane containing 20% w/w of the Aliquat 336 commercial carrier and 2-nitrophenyl acetyl ether, 1-hexanol, 1-acetanol, 1-decanol, 1-dodecanol, or 1-tetradecanol as a modifier to recover gold ions from hydrochloric acid solutions. Their results show that gold recovery depends on the type of modifiers used and that the Au(III) extraction rate increases significantly when sonification is employed, as a result of the physical effects generated during acoustic cavitation, which eliminate the aqueous stagnant diffusion layer at the membrane/solution interface. Recently, Campo-Cobo et al. [66] applied salen-type ligands with electron-accepting substituents on the aromatic ring as extractant agents in polymer inclusion membranes for the extraction of different metal ions (Cu^{2+}, Pb^{2+}, Ca^{2+}, Al^{3+}, Co^{2+}, Au^{3+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, Au^{3+}) from aqueous solutions. They reported that the examined Salen derivatives had higher selectivity to gold than to other metals and enabled the extraction of acceptable percentages of gold. The experiments were conducted in model solutions with low pH that was controlled using HNO_3, nonetheless, applying this method in the recovery of gold from real solutions obtained by e-waste leaching requires further research.

4. Recovery of silver(I) ions

Several methods have been developed for the recovery of silver(I) from waste electrical and electronic equipment, such as electrochemical processes [67] or adsorption processes [13]. However, many of these solutions have drawbacks and limitations that lead researchers to seek more effective methods. For instance, the application of cyclic voltammetry technique for gold and silver electrodeposition from synthetic solutions on graphite and copper electrode allows for removal of 97% of silver, but the metal deposits have not enough adherences on the electrode material [67]. Another solution is leaching of e-waste or a combination of leaching methods and other techniques, such as emulsion liquid membranes (ELM). In the latter case, as reported by Laki et al. [68], leaching first transfers silver from catalyst particles to an aqueous solution, and then an ELM extracts silver ions from the leaching solution in a single separation step. The use of leaching methods for the recovery of silver from WEEE, depending on the leaching reagent used and the source of the e-waste, allows the recovery of about 50%–99% of silver(I) ions [11].

Often, recovery processes are conducted using solvent extraction and membrane separation. Much of the research involves extraction processes carried out on model solutions, the results of which can be used in the future to recover silver from real WEEE after leaching. For instance, Shimojo and Goto [69] performed solvent extraction and stripping of silver ions in room-temperature ionic liquids (RTILs) containing calixarenes and reported that pyridinocalix-[4]arene showed a high extraction ability and selectivity for silver ions (90% silver recovery). Their results highlight the great potential of calixarenes as extractants in RTILs systems. Due to the high efficiency and selectivity of the process, silver ion recovery studies are increasingly being conducted using polymer inclusion membranes. For example, Nowik-Zajac et al. [70] conducted Ag(I) recovery studies from aqueous nitrate source phase using polymer inclusion membranes, which contained derivatives of calixpyrroles with methyl (KP1) and carboxyl (KP2) groups, as ion carriers, o-nitrophenyl pentyl ether (o-NPPE) as a plasticizer and cellulose triacetate (CTA) as support. Their results indicate that the competitive transport of Ag(I) from the aqueous nitrate source phase through KP1 and KP2 is an effective separation method for Ag(I) ions and allows the recovery of 98.8% of silver ions from solution. Recently polymer inclusion membranes with different concentrations of a calixpyrrole ester derivative as the membrane carriers have been studied to determine their ability to transport Ag(I) from aqueous nitrate solutions. Authors reported that the effectiveness of the transport process across the membranes depends on the concentrations of ion carriers and metal ions, the pH of the source aqueous phase, and stripping agents [71]. Radzyminska-Lenarcik et al. [72] applied polymer inclusion membranes (PIMs), which consisted of cellulose triacetate as a polymeric support, o-nitrophenyl pentyl ether as a plasticizer, and either 1-hexylimidazole (1) or 1-hexyl-2-methylimidazole (2) as an ion carrier for the separation of silver ions from model solutions and after battery leaching (silver-oxide battery). They found that Ag(I) is more easily transported through PIMs doped with (1) in the case of the model solution. In the case of the leaching solution after 24 h transport, the recovery coefficient of Ag(I) for PIM doped with (1) was 86%, and for PIM doped with (2) 47%. Examples of the use of PIMs with different carriers for the recovery of silver ions from model solutions show the high efficiency of these methods, which also exhibit high selectivity towards Ag(I) ions. In order to apply these solutions to the recovery of silver ions from real solutions obtained from WEEE leaching, further research is needed to determine the exact conditions conducive to the recovery processes or the type and amount of carriers and plasticizers.

5. Recovery of palladium(III) ions

Many different solutions have been used to date for the recovery of palladium(II) ions. Popular methods include hydrometallurgical processes based on applications of various types of ionic liquid (IL) extractants, as understanding their extraction mechanisms and influencing factors is advantageous for further development in various industries, for example, wastewater treatment [73].

Cieszyńska and Wiśniewski [74,75] carried out extraction processes of palladium(II) from chloride solutions using two ionic phosphonic liquids, Cyphos IL-101 and Cyphos IL-104 (in the presence of toluene), as extractants and showed that extraction proceeds at the interface according to the anion-exchange mechanism. The results indicate that when these compounds are used, the extraction efficiency depends both on the hydrochloric acid concentration (the increase in HCl concentration has a negative influence on the extraction) and, to a lesser extent, on the temperature (increase in temperature causes a slight decrease in the palladium(II) extraction). Depending on the extraction conditions, from 54% to 97% of palladium (II) was recovered when Cyphos IL-101 was used and from 52% to 96% of Pd(II) when Cyphos IL-104 was used. The obtained results indicate that both Cyphos IL-101 and Cyphos IL-104 are very efficient and fast extractants [74,75]. Regel-Rosocka et al. [76] carried out solvent extraction and membrane separation of palladium(II) ions from aqueous chloride solutions using three phosphonium ionic liquids: Cyphos IL-101, Cyphos IL-104 and Cyphos IL-102, which was used for the first time as a metal ion carrier. They reported that Cyphos IL-102 also efficiently extracts palladium(II) ions both with liquid-liquid extraction and PIMs. However, similarly to results obtained previously for the application of Cyphos IL-101 and Cyphos IL-104 [74,75], increasing HCl content in the feed aqueous phase caused a decrease in extraction efficiency when Cyphos IL-102 was employed. Palladium (II) recovery using Cyphos IL-102 ranged from 84% to 90%, depending on process conditions. In addition, the results obtained with extraction using the discussed ionic liquids were significantly better than those obtained with polymer inclusion membranes. Fajar et al. [77] performed separation of Pt(IV), Pd(II), and Rh(III) by sequential transport through polymer inclusion membranes containing another ionic liquid, trioctyl(dodecyl) phosphonium chloride ($P_{88812}Cl$), as a metal carrier. Their results indicate that $P_{88812}Cl$ ionic liquid is an effective carrier in PIM for the recovery of Pd(II) ions, and that generated PIM exhibited a stable performance with multiple uses (after the seventh cycle, the recovery of palladium(II) was 96%). Additionally, recovery of palladium(II) ions from hydrochloric acid solutions can be performed by application of polymer inclusion membranes containing Cyanex 471X (triisobutylphosphine sulphide) as the ion carrier. Pośpiech [78] showed that the course of the process depends on Cyanex 471X concentration in the membrane and hydrochloric acid concentration in the source phase and potassium thiocyanate (KSCN) concentration in the receiving phase. Mixed ionic liquids such as $[C_8bet]Br/[C_4mim][NTf_2]$ were also successfully used as a new extraction system to extract Pd(II) from multimetal-ion solutions. The obtained results indicated the existence of three different types of Pd(II) complexes and high palladium recovery (over 91%) after three cycles of experiments [79]. Recently Bourgeois et al. [80] have described a simple process for the recovery of palladium from printed circuit boards waste. The solution obtained by leaching waste PCBs with nitric acid was processed through solvent extraction (with a solvent based on N,N′-dimethyl-N,N′-dibutyltetradecylmalonamide (BDMA), as an extractant). They reported that the extraction yield was 99%, volume of effluents generated during the solvent extraction sequence was small and no specific metal chelator was required for palladium stripping. Jha et al. [81] stated that "PIMs are one of the most promising techniques" because they are environmentally friendly (reduction of the amount of solvents), allow for selective separation of metal ions, simultaneous extraction and re-extraction, and show long-term stability. Table 1 shows structures of selected chemical compounds used for palladium recovery in classical extraction and polymer inclusion membrane processes.

The results of the use of extraction processes and polymer inclusion membranes presented in this section indicate that these methods can be useful in the recovery of palladium found in WEEE, such as PCBs, which is important both because of the limited access to natural resources (ores) and the need to reduce the amount of e-waste generated [82].

6. Summary

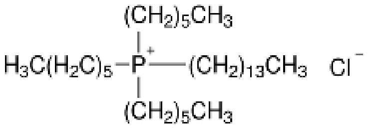
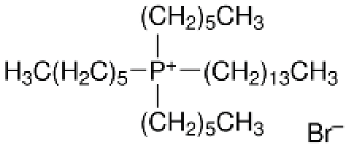
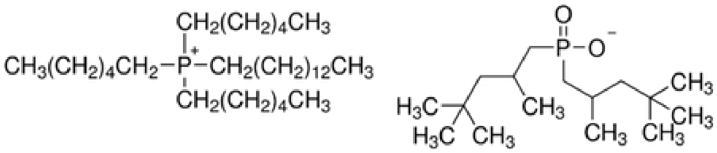
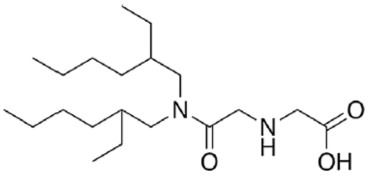
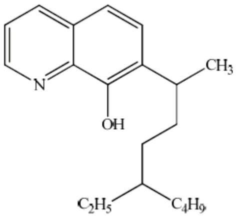
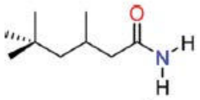
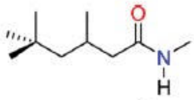
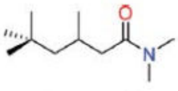
Due to the increasing development of civilization, more and more waste electrical and electronic equipment is produced, which contain among others materials made of gold, silver or palladium. Research conducted to date has proven that separation methods such as solvent extraction, and polymer inclusion membranes are effective when recovering valuable precious metals from waste. Currently, research is primarily focused on finding an effective extractant/carrier (Table 1) that will enable high recovery of precious metals from e-waste.

In summary, finding efficient extractors/carriers can significantly contribute to environmental quality by reducing landfill as well as the extraction of natural resources.

7. Conclusions

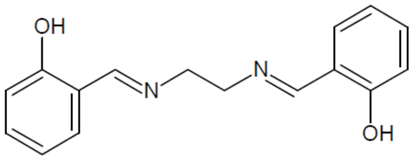
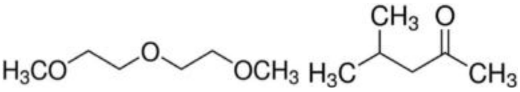
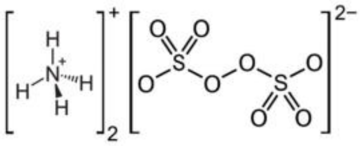
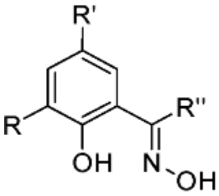
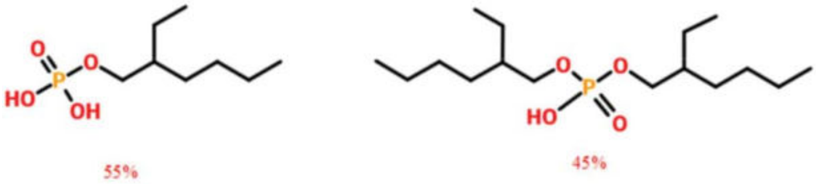
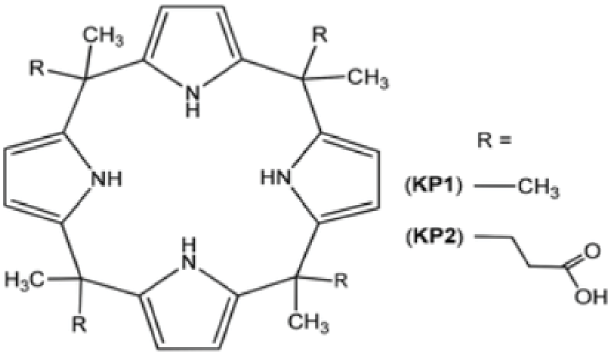
Waste electrical and electronic equipment is an important secondary source of precious metals such as gold, silver and palladium, among others, but the recovery of metals from WEEE using solvent extraction (SE) and polymer inclusion membrane (PIM) methods is a rather complex process influenced by many factors. Furthermore, before applying SE or PIMs, the WEEE leaching must first be carried out, for example, using acids or acid mixtures, resulting in acidic solutions. Therefore, the extractants used in the solvent extraction process must allow selective transport of recovered metal ions from acidic aqueous solutions containing a mixture of various metals into an organic phase. It should be emphasized that even relatively small differences in the structure of chemical compounds can significantly affect their metal ion chelating properties. Due to the variety of factors influencing the SE process, usually, the properties of a new extractant are evaluated using a less complex model solution, for example, containing only one/several metal ions, and only after determining the appropriate process conditions (e.g., pH, temperature,

Table 1
Review of extractants/ion carriers used in separation processes (SE, PIMs) for metals ions recovery

Methods of recovery of metal ions	Carrier/extractant	Metal ions
Polymer inclusion membrane	Cyphos IL-101  $H_3C(H_2C)_5-\overset{(CH_2)_5CH_3}{\underset{(CH_2)_5CH_3}{P^+}}-(CH_2)_{13}CH_3\ Cl^-$ Trihexyltetradecylphosphonium chloride	Au(III) Pd(II)
Polymer inclusion membrane	Cyphos IL-102  $H_3C(H_2C)_5-\overset{(CH_2)_5CH_3}{\underset{(CH_2)_5CH_3}{P^+}}-(CH_2)_{13}CH_3\ Br^-$ Trihexyltetradecylphosphonium bromide	Au(III) Pd(II)
Polymer inclusion membrane	Cyphos IL-104  $CH_3(CH_2)_4CH_2-\overset{CH_2(CH_2)_4CH_3}{\underset{CH_2(CH_2)_4CH_3}{P^+}}-CH_2(CH_2)_{12}CH_3$ Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate	Au(III) Pd(II)
Polymer inclusion membrane	D_2EHAG  N-[N,N-di(2-ethylhexyl)aminocarbonylmethyl]glycine	Au(III)
Polymer inclusion membrane	Kelex 100  7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline	Au(III)
Extraction	1°-, 2°- and 3°- amides  1° amide L^1  2° amide L^2  3° amide L^3	Au(III)

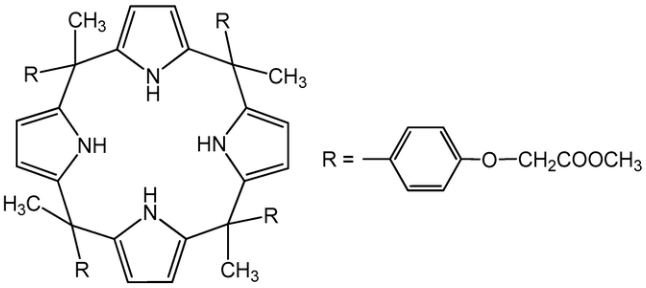
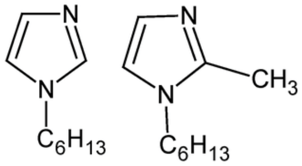
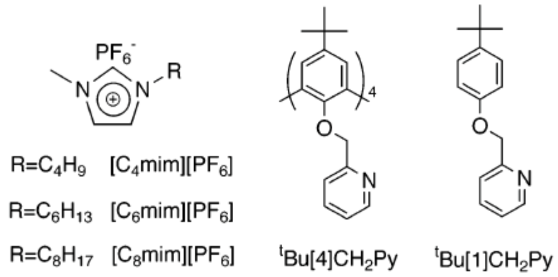
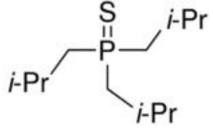
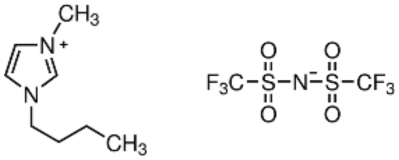
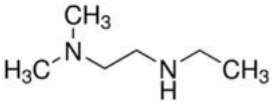
(Continued)

Table 1 Continued

Methods of recovery of metal ions	Carrier/extractant	Metal ions
Polymer inclusion membrane	Salen  N,N′-Bis(salicylidene)ethylenediamine	Au(III)
Extraction	DBC and MIBK  Dibutyl carbitol and Methyl isobutyl ketone	Au(III)
Extraction	Ammonium persulfate $(NH_4)_2S_2O_8$ 	Au(III)
Extraction	Phenolic oximes 	Au(III)
Emulsion liquid membrane	MEHPA  2-Ethylhexyl phosphoric acid ester (a mixture of 55% mono and 45% diesters)	Ag(I)
Polymer inclusion membrane	Calixpyrroles 	Ag(I)

(Continued)

Table 1 Continued

Methods of recovery of metal ions	Carrier/extractant	Metal ions
Polymer inclusion membrane	Calix[4]pyrrole 	Ag(I)
Polymer inclusion membrane	Alkylimidazole  1-Hexylimidazole and 1-Hexyl-2-methylimidazole	Ag(I)
Extraction	Calix[4]arene-bearing pyridine 	Ag(I)
Polymer inclusion membrane	Ionic liquid trioctyl(dodecyl) phosphonium chloride (P_{88812}CI)	Pd(II)
Polymer inclusion membrane	Cyanex 471X  Triisobutylphosphine sulphide	Pd(II)
Extraction	$[C_8bet]Br/[C_4mim][NTf_2]$  1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	Pd(II)
Extraction	BDMA  N,N′-Dimethyl,N,N′-dibutyltetradecylmalonamide	Pd(II)

extractant concentration and others) tests are conducted on real solutions. Choosing the right extractant is not easy, as its use should also allow for a high level of precious metal recovery (above 90%) and not pose a threat to the environment. Currently, commercial extractants such as Cyphos IL-101, Cyphos IL-102, or Cyphos IL-104, DBC, as well as non-commercial extractants such as amides, or cyclopentyl methyl ether, among others, are used in the SE processes of WEEE solutions.

The use of PIMs allows for a significant reduction in the amount of solvents used during the recovery of precious metals from WEEE compared to solvent extraction and is therefore important for environmental and economic reasons. Proper carrier selection in PIM is critical, as is extractant selection in SE. Appropriate polymer inclusion membranes should recover precious metals at high levels and show selectivity for the metals recovered. It is also important that they can be used repeatedly, with only a slight decrease in performance from cycle to cycle. This paper presents examples of the application of various PIMs for the recovery of Au, Ag and Pd from WEEE, both containing commercial carriers (e.g., Cyphos IL-101, Kelex 100), as well as new ones, not used for this purpose so far (e.g., salen and its derivatives). Currently, due to the high efficiency of the process of recovering precious metal ions from WEEE, the simplicity of performing experiments, the relatively low cost of reagents/solvents and the need to use only a small amount of them, PIMs are considered by many researchers as one of the most promising techniques that are likely to play an essential role in the recovery of precious metals on a larger scale.

Symbols

K_D – Partition coefficient
A_{org} – Ratio of activities of a solute concentration of the metal ions in the an organic phase
A_{aq} – Ratio of activities of a solute concentration of the metal ions in the an aqueous phase
$\%E_M$ – Extraction percentage, %
D_M – Division ratio determined experimentally
V_{aq} – Volume of the water phase, dm^3
V_{org} – Volume of the organic phase, dm^3
M_{org} – Concentration of metal ions in an organic phase, $\mathrm{mol/dm}^3$
M_{aq} – Concentration of metal ions in an aqueous phase, $\mathrm{mol/dm}^3$
V_{org} Volume of an organic phase, dm^3
V_{aq} – Volume of an aqueous phase, dm^3
J_0 – Initial metal ions flux, $\mathrm{mol/m}^2\ \mathrm{s}$
P – Permeability coefficient
c_0 – Initial metal ions concentration in the feed phase, $\mathrm{mol/dm}^3$
A – Effective membrane area, m^2
V – Volume of feed phase, m^3
k – Reaction rate constant, s^{-1}
RF – Recovery factor, %
c – Metal ions concentration in the feed phase at given time, $\mathrm{mol/dm}^3$
c_i – Initial metal ions concentration in the feed phase, $\mathrm{mol/dm}^3$

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membranes

Review

The Application of Polymer Inclusion Membranes for the Removal of Emerging Contaminants and Synthetic Dyes from Aqueous Solutions—A Mini Review

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Abstract: Pollution of the environment, including water resources, is currently one of the greatest challenges due to emerging new contaminants of anthropogenic origin. Of particular concern are emerging organic pollutants such as pharmaceuticals, endocrine disruptors, and pesticides, but also other industrial pollutants, for example, synthetic dyes. The growing demand for environmentally friendly and economical methods of removing emerging contaminants and synthetic dyes from wastewater resulted in increased interest in the possibility of using techniques based on the application of polymer inclusion membranes (PIMs) for this purpose. PIM-based techniques are promising methods for eliminating emerging contaminants and synthetic dyes from aqueous solutions, including wastewater, due to high efficiency, membranes versatility, ease/low cost of preparation, and high selectivity. This review describes the latest developments related to the removal of various emerging contaminants and synthetic dyes from aqueous solutions using PIMs over the past few years, with particular emphasis on research aimed at increasing the effectiveness and selectivity of PIMs, which may contribute to wider use of these methods in the future.

Keywords: emerging contaminants; pharmaceuticals; pesticides; synthetic dyes; polymer inclusion membrane; separation processes

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1. Introduction

The term "emerging contaminants" (ECs) refers to synthetic or naturally occurring chemical compounds (and microorganisms) that have not been commonly monitored in the environment, many of which have been discovered recently [1]. The group of ECs is diverse and includes a variety of chemicals, such as, for example, pharmaceuticals, hormones (animal and human), personal care products, detergents (household and industrial), perfluoroalkyl and polyfluoroalkyl substances (PFASs), pesticides, industrial chemicals, and microplastics. Substances belonging to the ECs category can be classified according to a variety of criteria, e.g., based on their structure, size, properties, or functions. In the case of the criterion of the size and structure of ECs, two main categories were distinguished: chemicals of emerging concern and particles of emerging concern, wherein the second group includes only engineered nanoparticles and microplastics [2]. The division of ECs due to their functions is not simple because such substances can be used for various purposes in different products. For example, PFASs containing aliphatic carbon backbones with the side chain hydrogens substituted by fluorines are used in consumer goods such as surfactants, firefighting foams, alkaline cleaners, carpets, non-sticky pans, room polishers, shampoos, fume resistants, photo films, semiconductors, food packaging, pesticides, denture cleaners, and masks [3]. In principle, ECs may adversely affect ecological conditions and human health; however, as they may undergo various transformations (e.g., degradation processes) when introduced into the environment, it is not easy to determine their overall impact on living organisms and research in this area is still being conducted [1,4,5]. Many reports related to the analysis of different types of environmental samples (e.g., surface water and groundwater, soil) have confirmed the increasing presence of emerging contaminants and products of their transformations [6]. The increase in the amount of these substances in the environment results from their widespread use around the world. For example, pharmaceuticals and related compounds, i.e., active pharmaceutical ingredients (APIs), are consumed in large quantities, often without a prescription, consequently getting into the water cycle [7]. APIs found in wastewater include a vast variety of substances, among others, painkillers and anti-inflammatory drugs, antibiotics, hypoglycemic drugs, anti-ulcer drugs, anti-epilepsy drugs, etc. [8], and also narcotic substances such as cocaine, barbiturates, methadone, amphetamines, opiates, heroin, etc. [9]. Various persistent and environmentally hazardous anthropogenic PFASs have been detected not only in surface waters, soils, and biosolids (by-products in the sludge treatment process) but also in human tissues and blood serum [3,10,11]. Due to PFASs potential adverse effects on human health, the United States Environmental Protection Agency has set the combined concentration of per- and polyfluoroalkyl substances in drinking water at 70 μg/L as the lifelong health advisory level [12].

Pesticides are also one of the most common groups of pollutants found in the environment because the steadily increasing use of these compounds in agricultural practices (e.g., to destroy unwanted vegetation) has resulted in the occurrence of residues of these chemicals and their metabolites in groundwater, wastewater, and soil [13]. Pesticides have been proven by many researchers as toxic substances to humans and the environment. For example, chronic exposure to herbicides causes cardiovascular problems, retinal degeneration, some muscle degeneration, and cancer in humans [14]. Due to the properties of pesticides and the diversity of compounds belonging to this group of ECs, many countries, including the EU, have set limits for individual and total pesticides in treated drinking water, respectively (e.g., the EU Drinking Water Directive) [15].

The presence of emerging contaminants (e.g., pharmaceuticals and pesticides) in the water environment is a significant problem due to their toxicity. Traditional technologies for removing these compounds from wastewater (e.g., coagulation, adsorption, advanced oxidation) have disadvantages such as, for example, excessive and toxic sludge production and high production costs. Additionally, conventional wastewater treatment plants are unable to completely remove many of ECs; therefore, new effective methods of wastewater treatment are systematically sought [16–18].

The group of chemical compounds classified as synthetic dyes is also complex, but its largest part is made up of azo dyes [19]. Synthetic dyes, due to their properties (e.g., relatively simple and inexpensive synthesis, stability, resistance to light and oxidizing agents), are widely used for dyeing different products in various industries, e.g., in the textile and paper industries, for dyeing leather and other materials. However, the widespread use of synthetic dyes is also associated with serious environmental risks, especially to aquatic ecosystems. These compounds are usually resistant to recycling and can persist in the environment for a long time, potentially posing a threat to living organisms. To remove them from aqueous solutions (e.g., from industrial wastewater), various methods are used (such as adsorption, oxidation, coagulation, precipitation, ion exchange, or methods based on the use of microorganisms) [19,20]; however, each of these methods has certain limitations, which is why new, more efficient and eco-friendly methods of removing synthetic dyes from wastewater are being sought.

In recent years, there has been increased interest in the possibility of using various types of membranes to remove ECs and synthetic dyes from wastewater. In principle, membrane-based processes are considered more environmentally friendly than many traditional methods of removing these pollutants [21,22]. One type of liquid membranes (LMs) are polymer inclusion membranes, containing a polymer matrix, carrier, and most often a plasticizer, the use of which enables simultaneous extraction and re-extraction.

Moreover, compared to other LMs, PIMs are characterized by better stability, longer lifetime, selectivity, and flexibility properties [23].

This mini-review presents an overview of the latest achievements in the use of polymer inclusion membranes for the removal of synthetic dyes and selected emerging contaminants (pharmaceuticals, endocrine-disrupting compounds, and pesticides) from aqueous solutions, with particular emphasis on the achievements of the last five years. It also contains information on the effectiveness and most important limitations in the application of the methods developed. Attention was focused on these compounds due to their systematically increasing consumption and the threat they pose to the environment.

2. Polymer Inclusion Membranes—Short Characteristics

Various contaminants can be removed from aqueous solutions using membrane techniques, e.g., with polymer inclusion membranes which have been successfully used, among others, to separate metal ions [24–26] and dyes [27–29] and different pesticides from aqueous matrices [30]. PIMs were also applied for the remediation of pharmaceuticals and endocrine-disrupting substances from water systems [16].

A membrane is a semi-permeable mass transport barrier between two phases (liquid or gaseous). It is essential that the individual components of the mixture (said mass) be separated and move at different speeds. Membrane methods are used, e.g., for gas separation and water purification, filtration, and separation. Such applications are possible thanks to the simple concept behind them, the modularity of the solution, low energy costs, ease of scaling up, and a positive impact on the environment. If membranes are viewed as semi-permeable phase separators, the traditional concept of a membrane as a polymeric film can be extended to include liquids. These membranes are called Liquid Membranes. The membrane system, in this case, consists of an organic liquid that is immiscible neither with the feeding (donor) phase nor with the receiving (acceptor) phase. The membrane is, in this case, a semi-permeable barrier between the phases, which are mostly aqueous solutions. Transport through liquid membranes includes both liquid-liquid extraction and membrane separation processes [31]. The commonly accepted transport mechanism across liquid membranes is diffusion. The components diffuse through the membrane due to the concentration gradient. The efficiency and selectivity of transport through the LM can be significantly increased by introducing a complex substance (carrier) into the liquid membrane. The carrier in the LM reacts reversibly with the substance in the donor phase to form a complex.

Solution components can be transported across the membrane in several ways. There are four possible ion transfer mechanisms:

a) Simple transport;
b) Assisted transport;
c) Coupled counter-transport;
d) Coupled transport co-transport [31].

Direct transport is one of the forms of simple transport and is defined as the phenomenon of the transfer of compounds caused by solubility in a liquid membrane. The process is continued until the substance concentrations in the feed and receiving phases are equalized. The transferred substance does not react chemically with the membrane components; it remains in the same form in both phases. Another form of simple transport occurs when the transferred substance becomes a substrate and reacts with a compound contained in the receiving phase. Then, the concentration of the substance to be removed will not reach equilibrium, and the transport will continue until the complete transition of molecules from the feeding phase takes place [31].

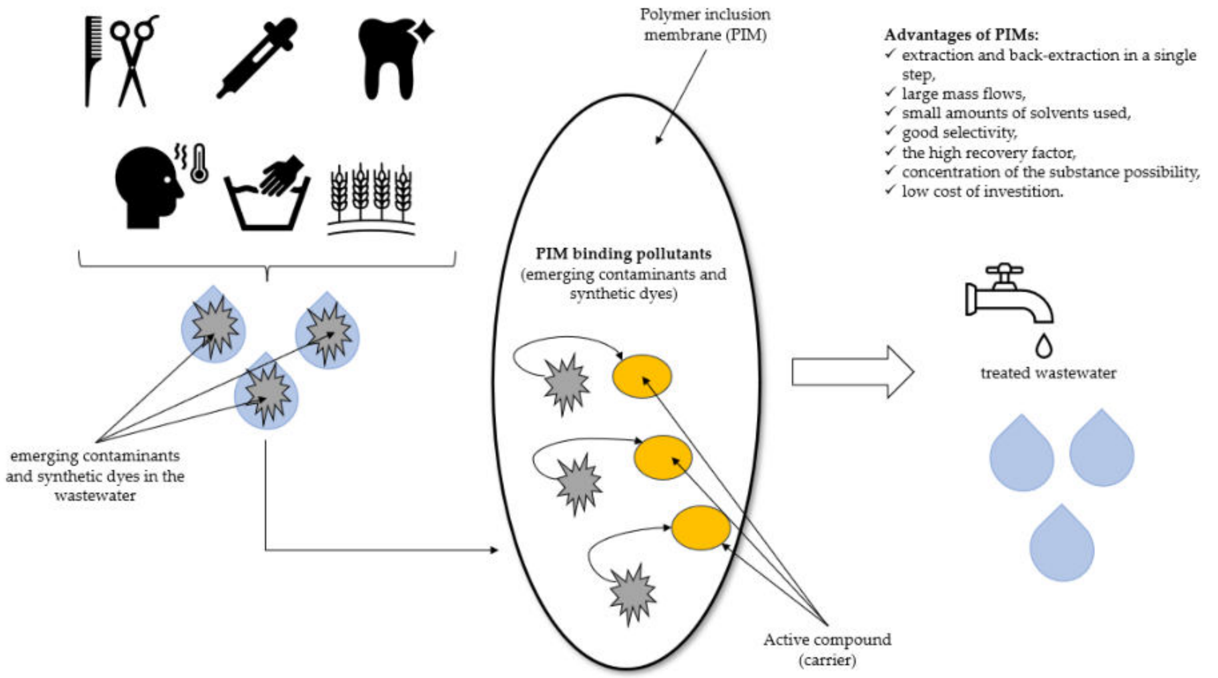
Assisted transport in liquid membranes is one of the most important applications of supramolecular chemistry. It can occur by partitioning, complexation, or diffusion reaction. The substance from the feed phase is complexed by a carrier (ionophore) contained in the membrane and released to the receiving phase. The conveyor increases the speed of transport and ensures a significant selectivity of the process. It lasts until the concentrations on both sides of the LM are equal or until the substance is completely removed from the feeding phase. Assisted and simple transport can occur simultaneously.

The synthesis and use of various chemical compounds as carriers in liquid membranes have been the subject of intensive research by scientists over the last few decades [31,32].

Counter-transport, on the other hand, is transport that takes place against the concentration gradient. It involves the transfer of substance A from the feed phase to the receiving phase by means of a carrier, with the simultaneous transfer of substance B (usually a hydrogen ion) in the opposite direction. When the concentrations of substance B are equalized, the process stops. Appropriate planning of the process, including the selection of concentrations, allows for the complete extraction of substance A from the feed phase.

In membrane co-transport, a liquid substance is co-transported with an accompanying component. The type and properties of the latter affect the parameters of the process that takes place until the concentrations are equalized. The speed of transport is regulated by the concentration of the accompanying substance. Co-transport is the most common form of transport across liquid membranes [33].

PIMs belong to the category of Supported Liquid Membranes (SLM) [33,34]. The matrix for the construction of the SLM membrane is usually made of plastics, e.g., poly(vinyl chloride), polypropylene, polyamides, modified cellulose, etc. [35]. The main problem of SLM technology is stability. This includes, e.g., the chemical stability of the carrier as well as the mechanical resistance of the porous substrate. In order to improve the stability parameters, newer and better systems are being created. For example, PIMs are created by pouring a solution obtained by mixing a polymer, an organic phase (carrier), and a so-called plasticizer. The plasticizer is added to the mixture to reduce the hardness and strength of the membrane while increasing its flexibility [31]. PIMs have many advantages, as shown in Scheme 1.



Scheme 1. The advantages of PIMs used for the removal of emerging contaminants and synthetic dyes.

3. Applications of PIMs for the Removal of Selected Emerging Contaminants

3.1. Removal of Pharmaceuticals and Endocrine-Disrupting Compounds by PIMs

Pharmaceuticals are a large group of various chemical compounds used, among others, in human health protection (e.g., anti-inflammatory drugs, antibiotics, painkillers, beta-blockers, etc.) and animal treatment (various veterinary drugs), in food preservation, and in agriculture. Their consumption is systematically growing, and it is expected that it will continue to grow due to, inter alia, the extension of the average life expectancy of people [16]. Due to the structural diversity of pharmaceuticals and the fact that they are usually found in small amounts in environmental and wastewater samples, their determination often requires the use of techniques allowing for analyte isolation and enrichment for trace analysis, which complicates the entire process and increases its costs. Removing small amounts of hazardous substances from the environment is also not easy. The processes of separation of pharmaceuticals based on the use of membranes, such as polymer inclusion membranes, not only allow the removal of even small amounts of contaminants from complex matrices with high efficiency and selectivity but also fit into the trend of the so-called "green analytical chemistry" (consumption of small amounts of chemical reagents, reduction of the use of toxic solvents, the possibility of multiple uses of membranes) [36]. Recently, PIMs have been used to remove from aqueous solutions one of the most widely utilized pharmaceuticals, ibuprofen (IBF), a non-steroidal anti-inflammatory drug, intended, inter alia, for lowering fever, pain relief and applied in the treatment of rheumatoid arthritis [8]. There is a need to develop an effective method of removing ibuprofen from the environment because it has been shown that prolonged accumulation of this compound can adversely affect the hormonal balance in the aquatic systems [8,16].

Moulahcene et al. [37] prepared novel polymer inclusion membranes containing insoluble poly(β-cyclodextrin (β-CD) polymer as a carrier, poly(vinyl chloride) as a base polymer, and dibuthylphtalate (DBP) as a plasticizer, and used them for the elimination of ibuprofen and progesterone from model aqueous samples. They found that the effectiveness of ibuprofen extraction depends on the content of β-cyclodextrin in the membrane, the agitation of analyzed samples, and reaction pH. The highest efficiency of the ibuprofen removal process (approx. 50%) was observed in an acidic environment (pH~2.0). However, based on these results, it is not possible to clearly determine the suitability of β-CD-based PIMs for removing ibuprofen from real samples because wastewater samples contain many other components that can potentially affect the membrane process. Ahmad et al. [8] reported that modification of PIMs with graphene oxide (GO) and small amounts of Aliquat 336 (methyltrioctylammonium chloride) as carrier allows for the removal of ibuprofen from model aqueous solutions. They reported that GO + Aliquat 336—doped polymer inclusion membranes made of PVC as base polymer without adding any plasticizer allow for the extraction of ibuprofen with an efficiency of ~84%, ~83%, and ~77% at a feed solution pH of 10, 6, and 2, respectively. Although obtained results indicate a high potential for ibuprofen extraction using GO-doped PIM better than those obtained with PIM containing poly(β-cyclodextrin [37]. Similar results (recoveries of analyzed pharmaceuticals in the range of 81–34%) were received by Román-Hidalgo et al. [38]. They used PIMs containing Aliquat 336 and cellulose triacetate (CTA) as base polymer, which were the support of 1-octanol liquid membranes in electromembrane extraction (EME) for the simultaneous removal of four non-steroidal anti-inflammatory drugs (such as salicylic acid (SA), ketoprofen (KET), naproxen (NAP), and ibuprofen) and four highly polar acidic drugs (such as anthranilic acid, nicotinic acid, amoxicillin, and hippuric acid). They also reported that the tested PIM can be applied for the extraction of these chemicals from real urine samples.

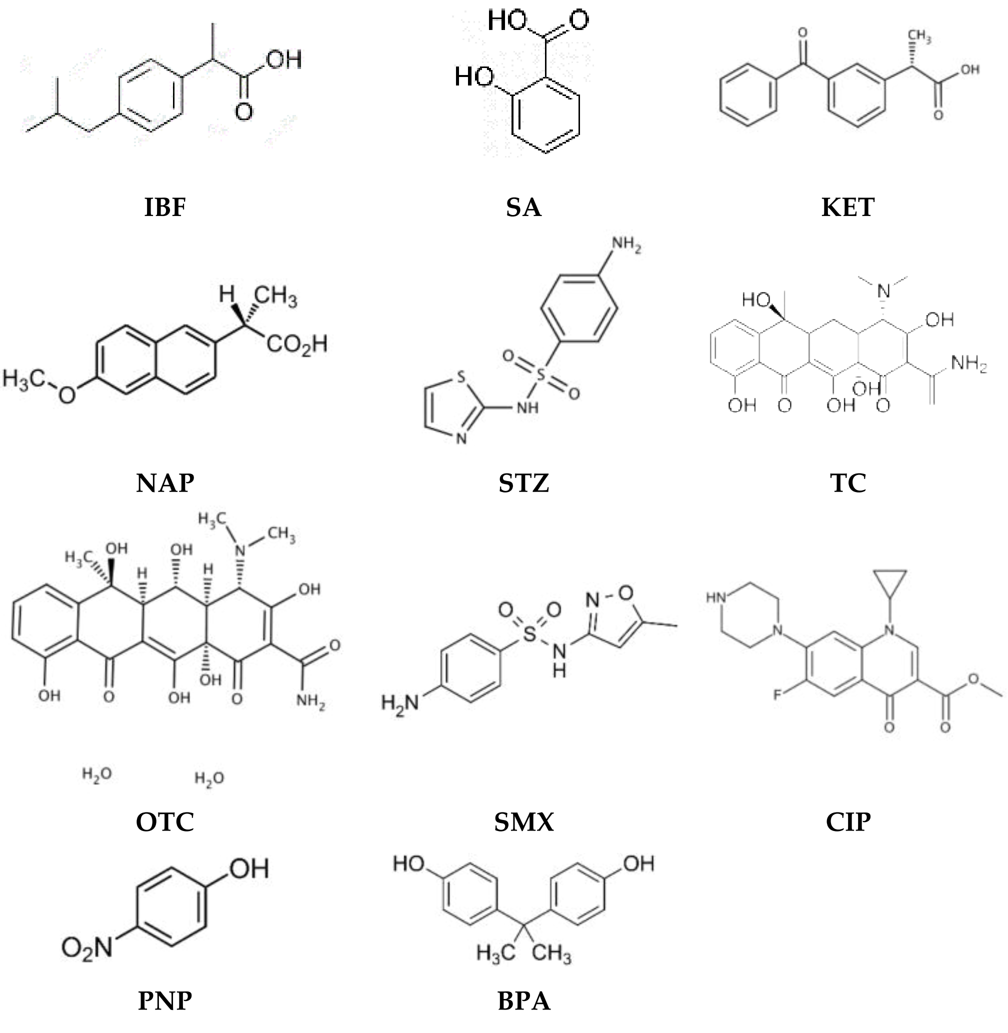
Removal of antibiotics from wastewater is also of great importance because, when introduced into the environment, they can have a toxic effect on flora and fauna, and in addition, they can potentially increase the resistance of microorganisms to antibiotics. Traditional methods of wastewater treatment do not allow the complete removal of these compounds, which is why research is systematically conducted on the possibility of using other techniques [39]. Polymer inclusion membranes have been used during the last few years for the preconcentration of antibiotics in order to allow the determination of trace amounts of these substances in environmental water samples. For example, Garcia-Rodriguez et al. [40] successfully utilized PIMs containing CTA or PVC as base polymers, Aliquat 336 as a carrier, and 2-nitrophenyloctyl ether (2-NPOE) as a plasticizer for the preconcentration of aqueous samples of sulfonamides (SAs) and tetracyclines (TCs). Garcia-Rodriguez et al. [41] also developed a passive sampler containing a polymer inclusion membrane (CTA/Aliquat 336/2-NPOE) for monitoring sulfamethoxazole (SMX) (one of the antibiotics most frequently detected in wastewater treatment plants, which can be harmful to living organisms) in water systems. They reported that the designed passive sampler minimized the influence of the flow pattern of the aquatic medium monitored, which is a significant property because the flow pattern of water cannot be controlled and possibly have an influence on the reliability of passive sampling data collection. PIMs were also used in novel methods based on a combination of various techniques. Recently, it has been reported that the hollow fiber polymer inclusion membrane liquid-phase microextraction (HF-PIM-LPME) methods, based on the use of PIMs and being a modification of the conventional HF-SLM-LPME method (Hollow Fiber Supported Liquid Membrane Liquid-Phase Microextraction), in which SLM was replaced with PIM, can be successfully used for the preconcentration of pharmaceutically active compounds in aqueous solutions. It was shown that HF-PIM-LPME is more stable compared to HF-SLM-LPME and is characterized by good selectivity for the analyzed pharmaceuticals [42]. Olasupo et al. [43] reported the efficient removal of sulfamethoxazole antibiotics from aquatic samples by utilization of an electromembrane extraction process based on polymer inclusion membranes comprised of the CTA polymer, Aliquat 336 carrier and the plasticizer dioctyl phthalate (DOP). Since sulfamethoxazole extraction using only PIM was insufficient (after 40 h of extraction at pH 9, transport efficiency was 82%), in order to improve the transport of the antibiotics across the membrane, they used electromembrane extraction and examined the impact of electric voltage on the efficiency of the extraction process. The use of a voltage of 50 V allowed for the complete removal of sulfamethoxazole from the aqueous solution (transport efficiency of 100%). Moreover, the membrane was used in 12 consecutive cycles, and only a slight decrease in extraction efficiency was observed, which confirms its stability. Formulated PIMs (CTA/Aliquat 336/DOP) were also successfully used to preconcentrate sulfamethoxazole from real environmental samples. However, it was reported that applying a voltage was essential to achieving the total recovery of this antibiotic. Olasupo et al. [43] obtained better results in comparison with results obtained by Román-Hidalgo et al. [38], who used the same PIM-EME method and the same PIM recovered 81% of analyzed pharmaceuticals.

Proper selection of all membrane components and thorough optimization of all experimental conditions enables the use of PIMs alone for the recovery of various antibiotics from aqueous solutions with satisfactory efficiency. Recently, polymer inclusion membranes with PVC and CTA base polymers and different carriers, such as bis-2-(ethylhexyl) phosphate (B2EHP) and Aliquat 336, have been applied for ciprofloxacin (CIP) removal from model aqueous solutions and real river water and wastewater samples. Ciprofloxacin has been shown to be persistent in the environment. In addition, it is present in various environmental media, which is due to the fact that this antibiotic is widely used and conventional wastewater treatment methods do not allow for its complete removal. The results of performed experiments show that at optimum conditions (proper selection of pH, receiving phase composition), the removal efficiency of 99.2% was noted using PVC/B2EHP PIM and 95% with the use of CTA/B2EHP membrane. The application of Aliquat 336 as the carrier allowed for obtaining the highest removal efficiency of 60%. The authors concluded that the formulated PIMs with B2EHP can be potentially considered a suitable alternative for the removal of CIP from the aquatic environment [44]. In turn, Olasupo et al. [45] applied PIMs containing PVC as the base polymer, B2EHP as the carrier, and DOP as the plasticizer for the removal of ciprofloxacin from the aquatic system and optimized the experimental conditions (i.e., pH of the source solution, source solution concentration, carrier concentration, the concentration of the receiving solution, and extraction time) using multivariate analysis of half-fractional factorial design. They reported that PIMs with the composition of PVC 45%: B2EHP 25%: DOP 30% allowed for almost complete removal of CIP, wherein removal efficiency strongly depended on pH (>99% at pH = 6, 90% at pH = 12, and 85% at pH = 7). The method was also successfully applied to remove ciprofloxacin from real environmental wastewater and river samples with an average percentage removal efficiency of >97%. Based on the results of the use of PVC/B2EHP/DOP PIMs for CIP removal, it can be assumed that this method may also be potentially useful in the future for the removal of other pharmaceuticals from aqueous systems.

Polymer inclusion membranes may also in the future play an important role in the removal of chemical compounds from aqueous solutions that are substrates for the synthesis of traditionally used drugs. An example of such a compound is salicylic acid, which is used in the synthesis of aspirin and glyburide (and is also a metabolite of aspirin). Additionally, it is also used as an analgesic and antipyretic drug and prevents platelet aggregation. It has been reported that salicylic acid has been detected not only in sewage but also in drinking water and is characterized by high ecological toxicity [46] and references therein. Therefore, the development of an effective method of removing this compound from complex matrices is extremely important for environmental protection. Recently, Meng et al. [47] examined the suitability of a polymer inclusion membrane containing PVC as a base polymer and *N*,*N*-bis(1-methylheptanyl)acetamide (N503) as a carrier for the separation of salicylic acid and two phenols from aqueous solutions. They analyzed the influence of carrier concentration and membrane thickness on the morphology, structure, and mass transfer stability of formulated PIMs. Their results have shown that polymer inclusion membranes had a good mass transfer capability for salicylic acid and p-nitrophenol (PNP) through a hydrogen transfer mechanism in weakly acidic environments with a properly selected receiving phase. The mass transfer of salicylic acid exhibited the characteristics of a fixed-site hopping mechanism. Moreover, at pH = 6, the phenol and p-nitrophenol coexisting with salicylic acid in the analyzed samples were selectively removed because, in such conditions, salicylic acid molecules formed intramolecular hydrogen bonds and were not transported effectively.

Efficient methods are also systematically sought to remove phenolic compounds from aqueous solutions (e.g., sewage), classified as potential endocrine-disrupting chemicals (EDCs), such as bisphenol and octylphenol. These compounds cause exogenous endocrine disruption in the neurological, reproductive, and immune systems, even in very small amounts, and are classified as highly toxic pollutants [48]. Balahouane et al. [49] used polymer inclusion membranes with calix[4]resorcin arene derivatives as the carrier, CTA as the polymer matrix, and 2-NPOE as a plasticizer to eliminate bisphenol A (BPA) from synthetic wastewater (model solutions containing bisphenol A) and to determine the process parameters that most affect its performance. They found that the efficiency of the bisphenol A removal process using PIMs was affected mainly by the concentration of membrane components, stirring rate, pH of the feed phase, and thickness of the membrane. Under optimal conditions of the membrane process, about 90% of bisphenol A was transported from the feed phase to the receiving phase, wherein PIM was an efficient tool in bisphenol A removal only when this contaminant was present in the solution in an undissociated state. The prepared membranes were also successfully used in three successive cycles of removal of this compound. All presented examples of the application of polymer inclusion membranes for the removal of various pharmaceuticals and endocrine disruptors show that with the (qualitatively and quantitatively) proper selection of membrane components and carrying out the membrane process in optimal conditions (for each pollutant removed, experimentally determined), separation based on utilization of PIMs is a promising technology for removing such organic contaminants from their aqueous solutions. As noted by Olasupo et al. [16], PIM "has a great potential for the remediation of pharmaceuticals and endocrine disruptors in the aquatic system, due to its versatility, ease/low cost of preparation and high contaminant selectivity".

Table 1 shows examples of the use of PIMs for the removal of pharmaceuticals and endocrine-disrupting compounds, such as IBF, SA, KET, NAP, sulphathiazole (STZ), TC, oxytetracyline (OTC), SMX, and also CIP, PNP, and BPA (Figure 1).



IBF **SA** **KET**

NAP **STZ** **TC**

OTC **SMX** **CIP**

PNP **BPA**

Figure 1. Structures of pharmaceuticals and endocrine-disrupting compounds removed by PIMs.

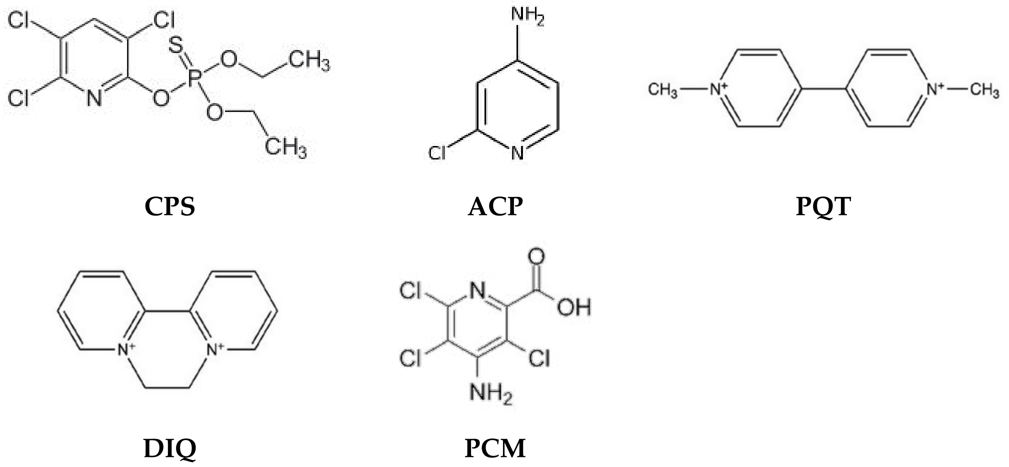
Table 1. Examples of removal of pharmaceuticals and endocrine-disrupting compounds by methods based on utilization of PIMs.

The Composition of PIM	Additional Information	Removal Efficiency	References
PVC/β-CD/DBP	Acidic environment (pH 2)	50% of IBF	[37]
PVC/Aliquat 336 + GO	Various feed solutions: at pH 10, at pH 6, and at pH 2	~84% of IBF ~83% of IBF ~77% of IBF	[8]
CTA/Aliquat 336	Posterior HPLC separation with diode array detection	34–81% SA, KET, NAP, and IBF	[38]

CTA/Aliquat 336/2-NPOE	The feed solution was at pH 9, and the stripping solution contained 1.0 M NaCl	55% of SP, 75% of STZ, and 100% of TC, and OTC	[40]
CTA/Aliquat 336/2-NPOE	Receiving solution was 2.0 M NaCl	SMX	[41]
CTA/Aliquat 336/DOP	After 40 h of extraction at pH 9	82% of SMX	[43]
PVC/B2EHP	Extraction at pH 6	99.2% of CIP	[44]
CTA/B2EHP		95% of CIP	
PVC/Aliquat 336		60% of CIP	
PVC/B2EHP/DOP	An environmental: at pH 6, At pH 12 and 7, and the environmental wastewater and river samples	90% of CIP 85% of CIP >97% of CIP	[45]
PVC/N503	The hydrogen bond mechanism at pH 6	7.54 mg/g PNP and 8.88 mg/g SA	[47]
calix[4]resorcin arene	Separation at pH 4 and stirring at 600 rpm	90% of BPA	[49]

3.2. Removal of Pesticides Using PIMs

According to the World Health Organization, pesticides are chemical compounds used to fight parasites, including insects, rodents, fungi, and weeds. A lot of pesticides released into the environment have been defined as toxic, persistent, bioaccumulative, and harmful to the health of the entire ecosystem, including humans [50]. Depending on the type of pesticide and the nature of the environmental sample, various methods are used to determine the content of these compounds, to identify them, and finally to remove pesticides (e.g., solvent extraction (SE), Solid-Phase Extraction (SPE), Solid-Phase Microextraction (SPME), High-Resolution Mass Spectrometry (HRMS), chromatography-based methods, etc.), however, all these solutions have certain limitations (e.g., SE—consumption of large amounts of toxic solvents) [50,51]. Therefore, other solutions are sought. Methods based on the use of PIMs are becoming increasingly popular because they are environmentally friendly, efficient, and selective and allow the removal of even small amounts of pesticides from aqueous solutions. Examples of removal of various pesticides, e.g., chlorpyrifos (CPS), 4-amino-2-chloropyridine (ACP), paraquat (PQT), diquat (DIQ), and picloram herbicides (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid) (PCM) (Figure 2) by methods based on the application of PIMs, are shown in Table 2.



CPS **ACP** **PQT**

DIQ **PCM**

Figure 2. Structures of pesticides removed by PIMs.

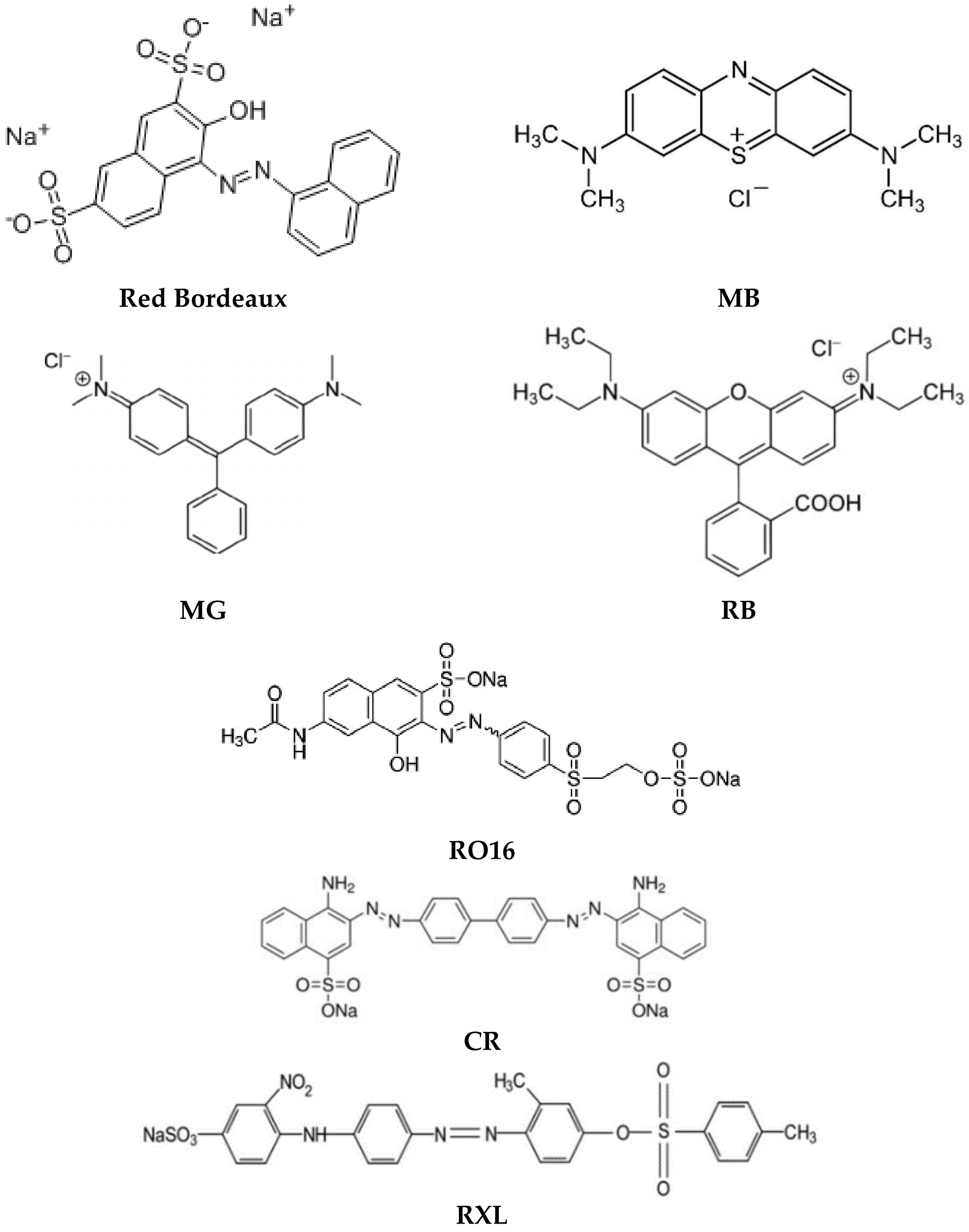
Table 2. Examples of removal of pesticides by PIMs.

The Composition of PIM	Additional Information	Removal Efficiency	References
CTA/NPOE	GC-MS prior PIM	93% of CPS	[52]
CTA/AA/2-NPOE/DDL	An initial flux of 364 (±16) × 10^{-8} mol m^{-2} s^{-1} for transport of ACP	ACP, PQT, and DIQ	[53]
CTA/Aliquat 336/2-NPOE	Receiving solution was 0.25 M NaCl	95% of PCM	[54]
	EME-HPIM	From 99.1% to 100% of cationic quaternary ammonium and anionic chlorophenoxy acetic acid herbicides	[55]

For example, Vera et al. [52] used a new extraction phase based on a polymer inclusion membrane containing cellulose triacetate (70%) and nitrophenyl octyl ether (30%) for the detection of three different pesticides: chlorpyrifos, diazinon, and cyprodinil in natural water samples. They evaluated the main factors affecting the extraction efficiency (i.e., membrane composition, stirring speed, extraction, and elution time) and reported that PIM-assisted extraction allows pesticide determination in the range of 50–1000 mg/L with good linearity and high recoveries (85% and higher, depending on pesticide). They found that CTA/NPOE PIM-assisted extraction is especially useful for the detection of chlorpyrifos in river waters (RF = 93%). Mwakalesi and Potter [53] applied polymer inclusion membranes containing anacardic acid (AA) obtained from cashew nut shells as an acidic carrier, CTA as a polymer matrix, 2-NPOE as a plasticizer and dodecanol as a modifier for the extraction of 4-amino-2-chloropyridine, paraquat and diquat. These compounds can be treated as representative target solutes of organic pesticide residues. They reported that PIM with optimal composition (i.e., 30 wt% CTA, 40 wt% NPOE, 10 wt% AA, 20 wt% dodecanol) has an extraction performance similar to polymer inclusion membrane containing commercially available synthetic bis-(2-ethylhexyl) phosphoric acid instead of AA. Additionally, AA containing PIM has also been successfully used for ACP, paraquat, and diquat removal from real environmental water samples. The developed method based on the use of PIMs with AA originating from natural sources (e.g., plants and plant waste) is part of the trend of using eco-friendly methods for the treatment of polluted waters. Another example confirming that polymer inclusion membranes with a properly selected composition in optimal conditions are excellent tools for removing pesticides from aqueous solutions are the results of research conducted by Mwakalesi and Potter [54]. They applied PIMs containing CTA polymer, NPOE plasticizer, and Aliquat 336 carrier to remove picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid), which is an herbicide used to control the growth of woody plants. Because of the poor adsorption of picloram by soils and its high leaching properties, this compound often occurs in aqueous environmental samples. Due to its adverse effect on aquatic organisms and animals, there is a need to develop safe (for living organisms) and efficient methods to remove picloram from aquatic systems. Results of performed experiments demonstrate that CTA/NPOE/Aliquat 336 PIMs with an optimized concentration of ingredients and type and concentration of stripping reagent showed good rates of flux and transport efficiency for picloram in both non-competitive and competitive transport studies. Moreover, it has been reported that this membrane can be used in a passive sampling device to recover picloram (at the maximum concentration of 500 μg/L) from a complex matrix of natural water. In principle, in the last decade, in the environmental monitoring of waters for the presence of various types of pesticides, polymer inclusion membranes have played an important role and are increasingly used for, inter alia, passive sampling, sample pretreatment, and preconcentration and also for removing these compounds from aquatic mediums [56]. There were also attempts to use polymer inclusion membranes in combination with other techniques to develop efficient methods to remove hazardous pesticides from water systems. For example, Mamat et al. [46] developed a new, more complex method for removing cationic and anionic herbicides from aqueous solutions based on the use of modified polymer inclusion membranes, namely electric-field driven extraction in which a bubbleless electrode has been integrated with electromembrane extraction across hollow polymer inclusion membranes (HPIMs). New hollow membranes based on PIMs were employed because they can be successfully used in electromembrane extraction, and, in principle, they improve extraction efficiency and reproducibility compared to traditionally used supported liquid membranes. In performed experiments, two types of HPIMs containing CTA as a polymer matrix and tris(2-ethylhexyl)phosphate as a plasticizer were used: with di-(2-ethylhexyl)phosphoric acid as an anionic carrier or Aliquat 336 as a cationic carrier. The electromembrane extraction based on the utilization of HPIMs made it possible to simultaneously determine both cationic quaternary ammonium and anionic chlorophenoxy acetic acid herbicides from river water samples with an extraction efficiency ranging from 99.1% to 100%. Based on the obtained results, the authors predict that the proposed approach may be potentially applicable in the future to remove other (both organic and inorganic) polar ions from aqueous solutions [57]. However, the use of an appropriate method based on membrane techniques to remove various pollutants, including pesticides, from the aquatic environment is not easy due to the chemical diversity of the chemical compounds removed, the complexity of the matrix in which they occur, different physicochemical properties of membranes and the wide range of parameters affecting the efficiency and selectivity of the separation processes [58].

4. Use of PIMs for Removal of Synthetic Dyes

Water pollution associated with the large-scale use of synthetic dyes, e.g., in the textile industry, is one of the most pressing environmental problems in the world. Synthetic dyes introduced into wastewater may hinder the operation of the sewage treatment plant, and introduced into the environment may be harmful to food chain species and aquatic organisms. At the same time, not only dyes can pose an environmental threat, but also products of their transformation, e.g., as a result of hydrolysis of some of these compounds, poisonous aromatic amines may be formed [59]. Due to the need to remove such contaminants from wastewater, new environmentally friendly methods with high efficiency but also low costs and easy implementation are systematically sought. The examples presented in this chapter (and in the simplified version in Table 3) clearly confirm that polymer inclusion membranes are well suited for the removal of various (both cationic and anionic) synthetic dyes from aqueous solutions, as evidenced by the high efficiency of the processes and the simplicity of membrane preparation and experimentation. Figure 3 shows the structures of acidic dyes (red Bordeaux, Yellow Erionyl (RXL), Congo Red (CR)), basic dyes (Methylene Blue (MB), Malachite Green (MG), Rhodamine B (RB)), and also reactive orange dyes (RO16).



Red Bordeaux **MB**

MG **RB**

RO16

CR

RXL

Figure 3. Structures of synthetic dyes removed by PIMs.

Table 3. Examples of removal of synthetic dyes by various PIMs.

The Composition of PIM	Additional Information	Removal Efficiency	References
CTA/Aliquat 336/2-NPOE	pH (2–9) of the aqueous solution, the concentration of extractant in the membrane (5–30 μmol/cm^2), initial dye concentration (50–250 ppm), and the stirring speed (250–400 rpm)	99% of red Bordeaux acid and RXL	[60]
CTA/EDC/2-NPOE	EDC forms inclusion complex with cationic dyes having 1:1 M ratio	~90% of MB	[29]

PVC/B2EHP/DOP	The average extraction efficiency was >98% for MG concentration of 20–80 mg/L	>98 of MG from model solution and >96% of MG for wastewater samples	[61]
PVC/B2EHP/DOP	Receiving solution was 1.0 M HNO_3, and 4 h of extraction process (with magnetic stirring). The feed solution was MG, MB, and the mixture of both dyes (all volumes are set to 100 mL)	>97% of MB and MG	[62]
PIM/APTES-CuO	APTES-modified CuO nanoparticles were integrated with PIM. The PIMs were fabricated with the diffusion-induced phase inversion technique	97% of MB	[63]
CTA/D2EHPA/2-NPOE	The feed phase was 20 mg/L MB or RB at pH 6.0. The receiving phase was 1.0 M HNO_3 or 1.0 M H_2SO_4 in the case of the MB or RB transport, respectively	93% of MB and 97% of RB	[64]
PVDF-co-HFP/B2EHP/DOP	Feed phase was 120 mL of 10 mg/L of MG, and receiving phase was 1.0 M HNO_3	97% of MG	[65]
CTA/RC8/2-NPOE	Feed solution was 100 mg/L of MB, and the receiving solution was 0.3 M HCl (pH 11)	72.55% of MB	[66]
CTA/Aliquat 336	At pH 2, with temperature and stirring speed of 30 °C and 150 rpm	87% of CR	[67]
PVDF-co-HFP/Aliquat 336	Feed solution was 10 mg/L of RO16, and receiving solution was 1.0 M HCl	99.62% of RO16	[68]
PVDF-co-HFP/Aliquat 336	Feed solution was 10 mg/L of RO16, and receiving solution was solution of HCl	99.62% of RO16	[27]

For example, Salima et al. [60] used PIMs containing CTA as the base polymer, 2-nitrophenyl octyl ether as a plasticizer, and Aliquat 336 as a carrier for removing two types of acid dyes: red Bordeaux acid and yellow Erionyl from aqueous solution. To determine the optimal conditions for conducting the membrane extraction process, they analyzed the influence of such factors as the pH of the aqueous solution, the initial concentration of dyes in the feed solution and of Aliquat 336 in the membrane, and the stirring speed. They reported the extraction of 99% of analyzed synthetic dyes under optimized experimental conditions. Minhas et al. [29] applied an ester derivative of calix[4]arene (EDC) as a carrier in polymer inclusion membranes consisting of CTA as a base polymer and 2-NPOE as a plasticizer and used the prepared membranes for extraction of cationic synthetic dyes (methylene blue, basic red, and Nile blue) from aqueous solutions. After optimization of various experimental parameters (pH of the donor and the acceptor phases, temperature, stirring speed, and concentration of membrane components and dyes in feed solutions), PIMs enabled the extraction of about 90% of dyes. Moreover, the extraction efficiency of the PIMs remained similar after ten consecutive cycles. That, as noted by the authors, "demonstrates membranes reusability potential in context of economical industrial applications". Ling and Suah [61] reported, based on the results of performed experiments, that PIMs can be applied successfully for the removal of synthetic dyes from both model and real wastewater solutions. They used polymer inclusion membranes containing PVC polymer, B2EHP extractant, and dioctyl phthalate plasticizer for the removal of malachite green dye and found that in optimal experimental conditions, the average extraction efficiency achieved was >98% for model solutions and >96% for wastewater samples. Results of experiments performed by Amin et al. [62] have also shown that polymer inclusion membranes are also suitable for the simultaneous extraction of two basic synthetic dyes, such as malachite green and methylene blue, from aqueous solutions. They used a batch reactor consisting of a polymer inclusion membrane composed of PVC as the base polymer, B2EHP as an extractant, and DOP as the plasticizer and reported that extraction efficiency was higher than 97% for the mixture of malachite green and methylene blue within 4 h of the extraction process. The results are similar to those obtained in previously described research [61] and further works [23,63–64]. Mustafa et al. [63] prepared 3-(aminopropyl)triethoxysilane (APTES) enhanced CuO nanoparticles integrated polymer inclusion membranes and used them for the removal of the methylene blue dye (model solutions) via transportation from the feed phase to the strip phase. They reported that after the optimization of experimental conditions (pH of the feed/receiving phases, stirring speed, time, the concentration of the carrier in the membrane, and concentration of the dye), a dye transportation efficiency of 97% was achieved. Studies on the development of efficient PIMs for removing synthetic dyes also refer to the possibility of using polymers other than CTA/PVC as a membrane matrix. Methylene blue and rhodamine B (cationic dyes) were also removed with comparable effect during facilitated transport on PIM (D2EHPA-PIM) [64]. The adsorption removal efficiencies under the optimal conditions reached about 93% and 97% for MB and RB, respectively. On the other hand, different extraction values were observed for MB (E% = 18.7%) and for RB (E% = 82.4%) during the process at pH 2. Desorption of both dyes from the membrane was achieved using acidic aqueous solutions, and a desorption ratio of up to 90% was obtained. The dye transport was elucidated using mass transfer analysis, where relatively high values of the initial fluxes (J_0) were found: 41.57 and 18.74 $\mu mol\cdot m^{2}\cdot s^{-1}$ for MB and RB, respectively. Soo et al. [23] used PVDF-co-HFP as the base polymer for the formulation of PIM with B2EHP as a carrier and DOP as the plasticizer and used this membrane for the extraction of cationic dye malachite green from model aqueous solutions. With optimal composition in optimal experimental conditions, the formulated PIM was able to remove more than 97% of the synthetic dye. These results may potentially influence further directions of the development of PIMs because CTA/PVC-based PIMs usually demonstrate lower performance in long extraction periods, and PVDF-co-HFP has higher stability than other base polymers. Moreover, as demonstrated by Soo et al., it has high extraction and transport efficiency for malachite green synthetic dye. Recently, Benosmane et al. [65] reported that the application of PIMs consisting of CTA polymer, 2-NPOE plasticizer, and calix[4]resorcin arene (RC8) carrier allows the efficient removal of methylene blue dye from model solution as synthetic aqueous wastewater, wherein the carrier and plasticizer content in the membrane strongly influence the properties of PIMs. Abdul-Halim et al. [66] used PIM made from cellulose triacetate and Aliquat 336 to extract Congo red from an aqueous solution. They improved some of the parameters, such as Aliquat 336 concentration, pH of extraction solution, the concentration of Congo red, the temperature of the process, and stirring speed which had an impact on the dye removal. Finally, 87% of Congo red was successfully removed after 24 h by using CTA-PIM with 50 wt.% Aliquat 336 at the optimum conditions: pH = 2, temperature 30°C, and stirring speed of 150 rpm, respectively Gunasegaran et al. [67] removed the reactive orange 16 (RO16) dye by PIM consisting of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-Co-HFP) as a base polymer, and Aliquat 336 as a carrier. The optimum extraction of RO16 dye was found in an initial dye concentration of 10 mg/L in 4 h time at pH 2 with an agitation speed of 500 rpm at room temperature using PIM with 9% carrier content. The highest percentage of removal of RO16 dye was 99.62%. Results of experiments performed by Ravi et al. [27], who applied PIMs consisting of PVDF-Co-HFP as a polymer matrix and Aliquat 336 as a carrier for the removal of the dye reactive orange 16 from aqueous solutions, confirm the suitability of this co-polymer for the development of membranes intended for the removal of synthetic dyes. In optimal experimental conditions, the extraction efficiency of reactive orange 16 was almost complete (99.62%). The presented examples of the use of PIMs containing various carriers/polymers/plasticizers for the removal of different synthetic dyes confirm the high efficiency of these methods (extraction efficiency in most cases was well over 90%) and suggest that they can potentially be used on a wider scale in the future, e.g., for the treatment of industrial wastewater from the textile industry. However, further research is needed, especially in the field of membrane stability (the possibility of their multiple uses) and in the development of techniques for their regeneration.

5. Concluding Remarks and Future Perspectives

In recent years, scientists have been particularly interested in developing effective and environmentally safe methods of removing hazardous pollutants, such as emerging contaminants and synthetic dyes, from aqueous solutions [68–72]. The environmental threat from these pollutants is primarily due to economic growth. The pharmaceutical, cosmetic, textile, and many other industries generate a large amount of often toxic wastewater, which according to European law, must be properly treated. In some cases, the toxic compounds introduced into the water ecosystem can have serious acute effects on the organisms exposed to them [73]. Emerging contaminants (e.g., pharmaceuticals and pesticides) and synthetic dyes can be removed from aqueous solutions during various separation processes such as adsorption, solvent extraction, bioremediation, etc. Table 4 presents sample information on the methods used to remove specific emerging contaminants, such as pharmaceuticals and pesticides from various aqueous mediums, and the results achieved by their applications. Comparing the results described in Table 1 with the results obtained using various PIMs to remove these contaminants from aqueous solutions (described in the text), it can be clearly stated that in many cases, polymer inclusion membranes are much more efficient (e.g., in comparison to solvent extraction, adsorption, precipitation methods). In the case of comparable performance of PIMs and other methods, the advantages of PIMs (i.e., the ease of PIMs formulation, the possibility of using various chemical compounds for this purpose, low consumption of toxic solvents, the possibility of multiple use of membranes after regeneration, relatively low costs of PIMs separation and safety for the environment) may have a key, positive impact on the decision which of the solutions are more beneficial.

Table 4. Examples of using different methods to remove selected emerging contaminants from aqueous solutions.

Method	Active Compound	Contamination	Removal Efficiency	References
Adsorption	Mixed-linker Zr-MOFs	DIC	2.04 mmol/g	[74]
Adsorption	Active carbon	TC	477.1 mg/g	[75]
Adsorption	Graphene	ATN, CB, CIP, DIC, GFZ, and IBF	>90%	[76]
Adsorption	Magnetic nanoparticles: Cu-BTC@Fe_3O_4	DIC, IBF, CIP, and OFX	IBF 13.38, DIC 12.47, CIP 12.35, OFX 11.14 mg/g	[77]
Adsorption	CDP	Pesticides	22.5%	[78]
Electro membrane extraction	HPIM 1: (CTA + TEHP + DEHPA) HPIM 2: (CTA + TEHP + Aliquat336)	Herbicides	99.1–100%	[55]
Extraction	Covalent organic frameworks (COFs)	Pesticides	>80%	[79]
Dispersive solid phase extraction	EMR-Lipid: mixture of ethyl acetate and acetonitrile	Pesticides from the oil matrix	>95%	[80]
Solvent extraction	Bio-sourced ionic liquids	Pesticides	>95%	[81]
Bioremediation	Microalgae	Parabens	Close to 100%	[82]
Co-precipitation over activated carbon	MAAC	CIP	81.97 mg/g	[83]
Adsorption	Activated carbons from argan nutshells	DIC Caffeine	126 mg/g 210 mg/g	[84]

In conclusion, this article presents examples of the application of methods based on the use of polymer inclusion membranes in the last five years to remove selected emerging contaminants and synthetic dyes from aqueous solutions (model and real wastewater samples). Separation methods based on the application of PIMs have great potential and can probably be widely used in the future for the effective removal of such pollutants because they are economical and environmentally friendly. However, the application of PIMs to remove pharmaceuticals, pesticides, and synthetic dyes from wastewater also has some limitations. In order for the membrane process to be carried out with the desired efficiency, it is necessary to determine the proper composition of the membranes (qualitative and quantitative) and the optimal conditions for the membrane process (for each type of pollutant to be removed and each type of wastewater treated). It has been shown that a variety of chemical compounds can be used to formulate PIMs, both as a polymer matrix (e.g., CTA and PVC) or pollutants carriers (e.g., D2EHPA, Aliquat 336, N503, Calix [4]resorcin arene). In addition, various modifications to PIMs can be introduced, e.g., the addition of different plasticizers and formulation of membranes containing two different carriers. Polymer inclusion membranes are also increasingly used in combination with other methods (e.g., EME). Since the membrane process is influenced by many factors (in addition to membrane composition and feed solution/wastewater composition, the composition of the receiving phase, pH, temperature, etc., play an important role), it is usually time-consuming to determine all the optimal conditions. Moreover, the efficiency of PIMs decreases after some time, so it is necessary to develop a fast and effective method for their regeneration or to change membranes frequently, which also affects the time needed to treat wastewater and the cost of the process. Solving problems related to the fouling of membranes will certainly contribute to their wider use in the future to remove various pollutants from the aquatic environment.

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Abbreviations

β-CD	Poly(β-cyclodextrin)
AA	Anacardic Acid
ACP	4-Amino-2-chloropyridine
Aliquat 336	Trioctylmethylammonium chloride
APIs	Active Pharmaceutical Ingredients
APTES	3-(Aminopropyl)triethoxysilane
ATN	Atenolol
BPA	Bisphenol A
B2EHPA or B2EHPA	Bis-2-(ethylhexyl)phosphate
4-tert-BP	4-Tert-butylphenol
CB	Carbamazepine
CDP	Cross-linked cyclodextrin polymer
CIP	Ciprofloxacin
COFs	Covalent organic frameworks
CPS	Chlorpyrifos
CR	Congo red
CTA	Cellulose Triacetate
DDL	Dodecanol
DES	Desipramine
DIC	Diclofenac
DIQ	Diquat
DOP	Dioctyl Phthalate
D2EHPA	Di(2-ethylhexyl)phosphoric acid
EDC	Calix[4]arene
ECs	Emerging Contaminants
EDCs	Endocrine-Disrupting Chemicals
EME	Electro Membrane Extraction
GC-MS	The gas chromatography and mass spectrometry detection
GFZ	Gemfibrozil
GO	Graphene Oxide
HF-PIM-LPME	Hollow Fiber Polymer Inclusion Membrane Liquid-Phase Microextraction
HPIMs	Hollow Polymer Inclusion Membranes
HF-SLM-LPME	Hollow Fiber Supported Liquid Membrane Liquid-Phase Microextraction
HRMS	High-Resolution Mass Spectrometry
KET	Ketoprofen
IBF	Ibuprofen
IMI	Imipramine
LM	Liquid Membrane
MAAC	Magnetic activated carbon
MB	Methylene Blue
MG	Malachite Green

NAP	Naproxen
NOR	Nortriptyline
N503	*N,N*-bis(1-methylheptanyl)acetamide
2-NPOE	2-Nitrophenyloctyl ether
OFX	Ofloxacin
OTC	Oxytetracycline
PCM	Picloram herbicides (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid)
PIM	Polymer Inclusion Membrane
PNP	P-nitrophenol
PFASs	Perfluoroalkyl and Polyfluoroalkyl Substances
PQT	Paraquat
PVC	Poly(vinyl chloride)
PVDF-co-HFP	Poly(vinylidene fluoride-co-hexafluoropropylene)
RB	Rhodamine B
RC8	Calix[4]resorcinarene
RO16	Reactive Orange 16 dye
RXL	Yellow Erionyl (acidic dye)
SA	Salicylic Acid
SAs	Sulfonamides
SE	Solvent Extraction
SLM	Supported Liquid Membranes
SMX	Sulfamethoxazole
SPE	Solid-Phase Extraction
SPME	Solid-Phase Microextraction
SPY	Sulfapyridine
STZ	Sulfathiazole
TCA	Tricyclic Antidepressants
TC	Tetracycline
TPB	Triphenylbenzene
TRIP	Triptycene

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ZASTOSOWANIE SPEKTROSKOPII FOURIEROWSKIEJ w PODCZERWIENI w ANALIZIE PROCESÓW SORPCYJNYCH – MINI PRZEGLĄD

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Abstrakt: Adsorpcja jest łatwą, ekonomiczną, przyjazną dla środowiska i technologią, która ma na celu oddzielenie różnych związków (jonów i cząsteczek) z jednej fazy do drugiej przy użyciu materiałów adsorpcyjnych [1]. Mechanizmy adsorpcji są zwykle niespecyficzne, dlatego można je wykorzystać do eliminacji lub zmniejszenia różnego typu zanieczyszczeń z próbek ciekłych lub gazowych. Stwierdzono, że adsorpcja jest korzystną metodą oczyszczania pod względem ekologicznym oraz ekonomicznym, o prostej konstrukcji, łatwej w użyciu i niewrażliwej na szkodliwe substancje [2]. Wiedza na temat zachodzących mechanizmów podczas procesów sorpcyjnych pozwala na dobór optymalnych parametrów procesu oraz skutecznego materiału sorpcyjnego. Jedną z metod umożliwiających optymalizację procesu sorpcji jest spektroskopia fourierowska w podczerwieni (FTIR). w pracy przedstawiono najnowsze osiągnięcia FTIR w analizie procesów sorpcyjnych, zarówno podczas analizy struktury nowych sorbentów, jak również w celu zbadania mechanizmów procesu sorpcji.

Wprowadzenie: Spektroskopia fourierowska w podczerwieni (FTIR, ang. Fourier Transform Infrared Spectroscopy) to technika analityczna polegająca na określeniu interakcji między promieniowaniem podczerwonym (IR, ang. Infrared) a analizowaną próbką (stałą, ciekłą lub gazową). FTIR mierzy zarówno częstotliwości, przy których próbka absorbuje, jak również intensywność tych absorpcji. w związku z tym, że związki wykazują charakterystyczną absorpcję/emisję w obszarze spektralnym IR można je analizować zarówno ilościowo, jak i jakościowo za pomocą spektroskopii FTIR [3]. Spektroskopia w podczerwieni jest techniką spektroskopii oscylacyjnej, która wykorzystuje zasadę, że cząsteczki mają określone dyskretne poziomy energii odpowiadające częstotliwościom, z jakimi się obracają lub wibrują [4]. w rezultacie otrzymuje się widmo, czyli wykres zależności wielkości absorpcji promieniowania od długości fali lub liczby falowej ῡ [cm^{-1}] (Tabela 1). Zatem absorpcja wynika z przejścia między stanami oscylacyjnymi i rotacyjnymi cząsteczki i występuje, gdy przejście powoduje zmianę momentu dipolowego [4,5]. Przy czym grupy funkcyjne cząsteczki odpowiadają za absorpcję promieniowania o różnych częstotliwościach, a stężenie składnika można określić na podstawie wielkości absorpcji promieniowania [3]. Podczerwień jest rodzajem promieniowania elektromagnetycznego o niższej częstotliwości niż światło widzialne w zakresie liczb falowych 12 500 – 10 cm^{-1}. Wyróżnia się podczerwień bliską (NIR, ang. Near Infrared), która zawiera się w zakresie liczb falowych od 10 000 do 4 cm^{-1} [6].

Tabela 1. Wybrane charakterystyczne liczby falowe pasm drgań wiązań występujących w związkach organicznych [7].

Zakres absorpcji, cm^{-1}	Typ drgań	Wiązanie
3760	rozciągające	O-H wody
3500-3300	rozciągające	N-H aminy
3350-3250	rozciągające	C-H aromatyczne
2970-2850	rozciągające	C-H alifatyczne
1760-1690	rozciągające	C=O (aldehydy, ketony, kwasy, estry)
1650-1550	deformacyjne	N-H
1600-1500	rozciągające	C=C

Spektroskopia FTIR może dostarczyć podstawowych informacji na temat struktury molekularnej związków organicznych i nieorganicznych np. w próbkach geologicznych podczas analizy minerałów lub skamieniałości [8] czy w analizie struktury białek [9, 10]. w analizie środowiskowej spektroskopia FTIR jest stosowana w celu określenia charakteru zanieczyszczeń oraz mechanizmu wiązania w przypadku usuwania zanieczyszczeń w procesach sorpcyjnych [3].

W niniejszym opracowaniu przedstawiono najnowsze osiągnięcia spektroskopii fourierowskiej w podczerwieni w analizie procesów sorpcyjnych, szczególnie w celu potwierdzenia struktury otrzymanego sorbentu oraz mechanizmu wiązania na jego powierzchni. Obecnie z powodzeniem wielu badaczy wykorzystuje spektroskopię FTIR w procesach sorpcyjnych w celu potwierdzenia struktury adsorbentu oraz mechanizmu wiązania z adsorbatem (Tabela 2).

Tabela 2. Wybrane zastosowanie spektroskopii FTIR w procesach sorpcyjnych.

Adsorbent	Adsorbat	Mechanizm	Struktura	Ref.
HGP-MNP	Cu(II), Ni(II), Al(III)	X	X	[11]
Fe–Al–Mn	fosforany	X	X	[12]
$La(OH)_3$	fosforany	X		[13]
β-CD-CS-EDTA	Pb(II), Cu(II), Ni(II), CIP	X		[14]
VPO_4	wielosiarczki	X		[15]
MOF	Dy^{3+}	X		[16]
Kropidlak popielaty	Cr(VI)	X		[17]
GOA	barwniki		X	[18]
hydrożelu modyfikowanego EDTA	Cu(II), Cd(II), Pb(II)		X	[19]
IFC	bitum		X	[20]

Almomani i in. zastosowali spektroskopię FTIR do analizy magnetycznych nanocząstek tlenku żelaza (MNP) na poliglicerolu (HPG) w celu usuwania metali ciężkich, takich jak nikiel, miedź i glin z wtórych ścieków przemysłowych. Dzięki analizie FTIR autorzy potwierdzili adsorpcję jonów miedzi(II), niklu(II) i glinu(III) na powierzchni HGP-MNP za pomocą grup hydroksylowych obecnych w strukturze badanego adsorbentu. Ponadto widma FTIR potwierdziły strukturę zmodyfikowanych nanocząstek HPG-MNP. Stwierdzono obecność grup: O-C-O (1099 cm^{-1}), CH_2 (2887 cm^{-1}) oraz O-H (3410 cm^{-1}) [11]. Natomiast Lü wraz z zespołem badawczym opisali zsyntetyzowany metodą utleniania i współstrącania nanostrukturalny tlenek trimetalu Fe–Al–Mn, który znalazł zastosowanie w adsorpcji fosforanów. w wyniku otrzymanych widm FTIR trimetalu Fe–Al–Mn przed i po adsorpcji fosforanów potwierdzono wiązanie fosforanów do powierzchni badanego tlenku trimetalu. Znaczące przesunięcie wartości liczb falowych wybranych pasm w widmie badanego tlenku trimetalu Fe-Al-Mn (570, 974 i 1123 cm^{-1})

potwierdziło, że tlenek trimetalu Fe-Al-Mn był raczej związkiem tlenkowym niż prostą mieszaniną. z widm FTIR wynika, że po przeprowadzonej adsorpcji prawdopodobnie utworzył się kompleks na powierzchni sfery wewnętrznej (M-O-P) między fosforanem a tlenkami. Ponadto na podstawie wzrostu pH układu stwierdzono, że powierzchniowe grupy hydroksylowe (M-O) adsorbentu mogą być wymieniane przez zaadsorbowany fosforan [12]. Zhang i in. zbadali natomiast proces adsorpcji fosforanów na adsorbencie, jakim był wodorotlenek lantanu.

W oparciu o analizę widm FTIR zaadsorbowanych fosforanów autorzy stwierdzili powstawanie w zakresie pH od 4 do 9 diprotonowanych dwukleszczowych kompleksów dwurdzeniowych lub monoprotonowanych dwukleszczowych kompleksów jednordzeniowych [13]. Spektroskopia FTIR umożliwiła również analizę mechanizmu adsorpcji jonów metali ciężkich (Pb(II) Cu(II), Ni(II)) oraz leku przeciwbakteryjnego – cyprofloksacyny (CIP) z wody za pomocą kompozytu β-CD-CS-EDTA (tj. β-cyklodekstryna-chitozan-EDTA). Widmo FTIR dla adsorpcji Ni(II) + CIP jednoznacznie wskazało zanik pasm pochodzących od drgań grup karboksylowych i przesunięcie pasm przypisanych O–H/N–H oraz jednostki glukozy β-CD, potwierdzając tym samym adsorpcję jonów Ni(II) i CIP jednocześnie poprzez kompleksowanie, oddziaływanie elektrostatyczne i tworzenie kompleksu inkluzyjnego typu „gospodarz-gość” [14]. Natomaist Jiao i in. zastosowali fosforan wanadu VPO_4, jako adsorbent wielosiarczków stosowanych w akumulatorach litowo-siarkowych. Eksperymenty sorpcyjne wykazały, że VPO_4 ma dobrą zdolność adsorpcji polisiarczków. Spektroskopia FTIR potwierdziła istnienie chemicznych oddziaływań między VPO_4 a polisiarczkami. Wibrację częstotliwości czystego VPO_4 zaobserwowano przy długości fali 648 cm^{-1} (V-O-P), 947 cm^{-1} (P-O) oraz 1103 cm^{-1} (V-O), przy czym główna pozycja piku VPO_4/Li_2S_4 była nieznacznie przesunięta ku czerwieni w porównaniu z czystym VPO_4. Częstotliwości drgań wiązania V-O-P, wiązania P-O i wiązania V-O przesunęły się odpowiednio do 642 cm^{-1}, 943 cm^{-1} i 1097 cm^{-1}. Natomiast częstotliwości drgań tych wiązań w VPO_4/Li_2S_6 były przesunięte odpowiednio do 640 cm^{-1}, 939 cm^{-1} i 1096 cm^{-1}. Powyższe wyniki jednoznacznie wskazały na wysokie powinowactwo VPO_4 do polisiarczków litu [15]. Inni badacze zastosowali spektroskopię FTIR do potwierdzenia adsorpcji jonów dysprozu za pomocą układów metaloorganicznych (MOF) modyfikowanego grupami karboksylowymi [UiO-66-$(COOH)_2$]. Na podstawie analizy widm FTIR jednoznacznie wskazano, że wolna grupa karboksylowa przyczynia się do wychwytywania jonów Dy^{3+} [16]. Metodę spektroskopii FTIR można również wykorzystać w przypadku biosorpcji jonów chromu(VI). Dhal i in. na podstawie widm FTIR udowodnili , powstawanie wiązań chemicznych pomiędzy jonami Cr(VI) a grupami karboksylanowymi, aminowymi, amidowymi i hydroksylowymi, występującymi na powierzchni ściany komórkowej grzyba (kropidlak popielaty) [17]. Ponadto za pomocą spektroskopii FTIR potwierdzono również strukturę różnych adsorbentów, np. zsyntetyzowanego aerożelu tlenku grafenu (GOA), który znalazł zastosowanie do usuwania barwników z wody [18], hydrożelu modyfikowanego EDTA stosowanego do adsorpcji jonów Cd(II), Cu(II) i Pb(II) ze ścieków przemysłowych [19], czy wewnętrznie funkcjonalizowanego węgla (IFC) pochodzącego z surowca alg w celu selektywnej adsorpcji niektórych potencjalnie niebezpiecznych emisji bitumu [20].

Wnioski: Spektroskopia fourierowska w podczerwieni znajduje coraz szersze zastosowanie w analizie środowiska, szczególnie w procesach sorpcyjnych. z najnowszych doniesień literaturowych wynika, że widma FTIR dostarczają wiedzy na temat nowych materiałów sorpcyjnych, np. HGP-MNP, GOA, IFC stosowanych do usunięcia jonów metali (Cu(II), Ni(II), Al(III)), barwników czy bitumu. Ponadto widma FTIR potwierdzają mechanizmy sorpcji z wykorzystaniem VPO_4, modyfikowanego EDTA hydrożelu, czy tlenku trimetalu Fe-Al-Mn w celu usunięcia odpowiednio wielosiarczków, jonów metali (Cu(II), Cd(II), Pb(II) i fosforanów. Podsumowując spektroskopia FTIR, jako metoda analityczna pozwala nie tylko potwierdzić strukturę nowego, zsyntezowanego materiału sorpcyjnego, ale również zinterpretować zachodzący mechanizmu wiązania zanieczyszczeń z adsorbentem w procesie sorpcji.

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A review on commonly used adsorbents using to remove metal ions from wastewater

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Abstract

The metals contained in surface and ground water come mainly from industrial effluents and domestic sewage. Currently, various techniques and processes are used to treat polluted water to remove contaminants from it, including metal ions, for this purpose processes such as extraction, ion exchange, precipitation, or sorption are used. Sorption is one of the most popular and effective methods of wastewater treatment because is a simple, efficient, and economical method. The popularity of this method is due to the availability of various synthetic as well as natural sorption materials. The main advantage of using the separation properties of various sorption materials is the decrease of amounts of metal ions, including heavy metal ions in the natural environment.

This review presents selected adsorbents (natural organic, synthetic organic/polymeric, mineral sorbents) and their modifications used for the recovery of metal ions present in sewage sludge. The basic parameters of the sorption process were also presented, which describe, among others, sorption efficiency.

Keywords: natural organic sorbent, synthetic organic/polymers, mineral sorbents, modified sorbents, removal metal ions, adsorption

1. Introduction

The main source of heavy metal ions present in sewage sludge is industrial effluents and domestic sewage. Sewage sludge is a complex mixture that consists of by-products of wastewater treatment processes of sewage from various domestic and industries sources and rainwater runoff roads through, physical, biological and/or chemical processes. Heavy metals occur in sewage sludge in the form of precipitated, dissolved, co-precipitated with metal oxides, adsorbed, or associated with biological residues. They can take the form of oxides, hydroxides, sulphides, sulphates, phosphates, silicates, organic compounds in the form of humic complexes, and compounds with complex sugars (Gawdzik, 2012; Weiner and Matthews, 2003, Obaid et al., 2018).

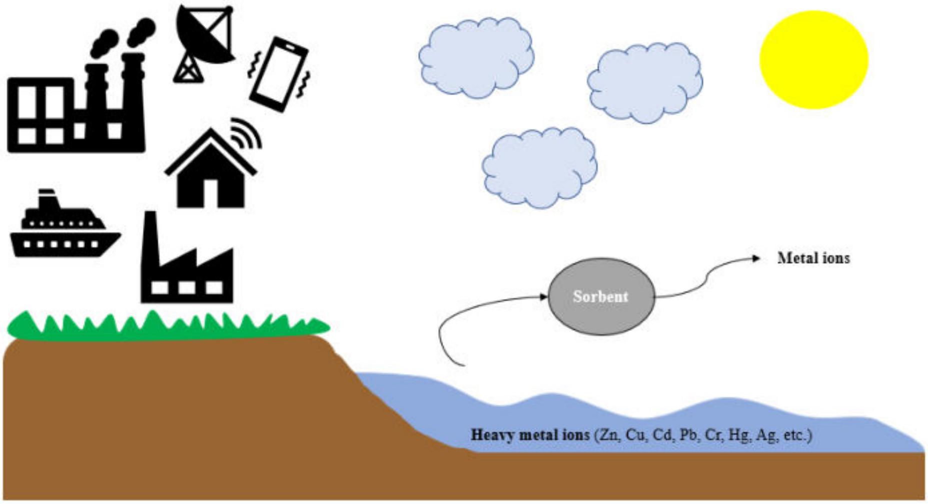

Fig. 1. The scheme of sources metal ions contained in surface and ground water and the way their recovery (own elaboration)

Methods such as chemical precipitation, ion exchange, membrane filtration, flocculation, and adsorption (Cristiani et al., 2021) have long been for the removal of metal ions from solution. One of the commonly used processes for the recovery of metal ions from wastewater is sorption. Sorption consists of the use of adsorbents, i.e. porous solids with a developed specific surface, on which the process of surface bonding of molecules from the liquid or gas phase takes place (Bandura et al., 2017). According to the definition, adsorption is the mass transport of substances from either a gas or liquid state to a solid interface as the result of physical and/or chemical interactions. During the sorption process, the molecules attach to the surface of the chemical through physical and chemical bonding (Ugwu et al., 2020). All adsorbents, both natural and synthetic, contain functional groups that allow metal ions to be adsorbed. Chemically modified adsorbents have a higher adsorption capacity than unmodified adsorbents. As the result, the modified adsorbent enhances the surface-active area of sorbent (Chakraborty et al., 2020). According to researchers, sorption is a very effective, simple and economical process for metal ion removal from wastewaters. The research works conducted so far concern the kinetics and thermodynamics of sorption, possible sorption mechanisms, and factors influencing sorption properties or modification of already existing adsorbents (Zhano et al., 2011; Ishtiag et al., 2020).

The paper presents selected adsorbents (natural, organic, synthetic, organic/polymer, mineral) used for the sorption of metal ions (e.g., Cd^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Hg^{2+}, Fe^{2+}, Cr^{3+}, Cr^{6+}, Ba^{2+}, etc.) from aqueous solutions. It also, describes the basic parameters of the sorption and desorption process.

2. Basic parameters of adsorption and desorption process

2.1. Adsorption process

It was found that the adsorption conditions are influenced by ion concentration, contact time, adsorbent content, and pH solution. The capacity sorption (q_e, mg/g) is a main parameter of the sorption process and describes the ability to bind metal ions by the adsorbent. The metal ions uptake (q_e) on the investigated adsorbent at a given time (t) is given by the following equation (Far et al., 2021):

$$q_e = \frac{V(C_0 - C_e)}{m}, \tag{1}$$

where: V is the volume of the metal ions solution [dm^3], m is the mass of adsorbent [g], and C_0 and C_e are the metal concentrations [mg/dm^3] at $t = 0$ and t, respectively.

Moreover, equation 2 describes the percentage of removal ($\%R_{ads}$) of metal ions (Ishtiag et al., 2020).

$$\%R_{ads} = \frac{C_0 - C_e}{C_0} \cdot 100, \tag{2}$$

where: C_0 and C_e are initial and equilibrium concentrations of metal ions, respectively [mol/dm^3].

Mathematical description of sorption process described below. In the mass exchange mechanism in the process of adsorption from solutions, the following steps are specified:

– diffusion or convection in solution;
– diffusion of particles from the liquid to the interface;

– mass diffusion through the interface;
– diffusion in the liquid phase inside the pores of the adsorbent;
– specific adsorption on the active centers of the adsorbent;
– diffusion in the surface layer of the adsorbent.

A dynamic equilibrium, is a defined separation of the adsorbate between the solution and the adsorbent. The amount of metal ions in the solutions adsorbed (q_e) was describe formula 1. The mechanism of the sorption process that exists between the adsorbent surface and the heavy metal ions can be described with the use of adsorption isotherms for both single and multiple component systems (Ugwu et al., 2020). During the mathematical description of the adsorption equilibrium from dilute aqueous solutions, the equations of the Freundlich (3), Langmuir (4), and Dubinin-Radushkevich (5) isotherms are commonly used (Zhao et al., 2010).

$$q_e = K_F C_e^{\frac{1}{n}}, \tag{3}$$

$$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e}, \tag{4}$$

$$q_e = q_{max} exp\left(-\left(\frac{RT\ \ln(\frac{C_e}{C_s})}{\beta E_0}\right)^2\right), \tag{5}$$

where: q_e the amount of solute adsorbed at equilibrium, C_e the equilibrium concentrations of sorbate in solution [mol/dm^3] over time [t], C_s the concentrations of sorbate in sorbent [mol/dm^3] over time [t], E_0 solid characteristic energy towards a reference compound, and others parameters or constants: β is constant of Dubinina-Radushkevicha, constant dependent on sorption energy, K_L is constant of Langumir.

2.2. Desorption process

Desorption of metal ions is based on the release of adsorbed ions from the adsorbent surface and their transfer to the receiving phase. It is the reverse of the sorption process. Desorption efficiency (%R_{des}, Eq. 6) is promoted by, among others temperature increase or reduction of the degree of dispersion (Ishatiaq et al., 2020; Ipeaiyeda and Tesi, 2014).

$$\%R_{des} = \frac{C_i}{C_a} \cdot 100, \tag{6}$$

where: C_i is a released matal concentration [mol/dm^3], C_a is an intially sorbed metal concentration [mol/dm^3].

3. Kind of adsorbents

Due to their origin, sorbents are divided into natural organic, synthetic polymeric, and mineral sorbent (Fig. 2). Natural organic sorbents include, i.a peat, sawdust, wood bark, and cellulose that forms during the production of paper. Despite their high absorbency, they are of limited use, e.g., they are not suitable for removing aggressive substances. On the other hand, synthetic polymer sorbents are characterised by high absorbency and low weight. They can be used to remove impurities formed on the water, with the so-called hydrophobic sorbents that do not absorb water. Raw materials such as wood sawdust, bark, and other wood processing wastes can be mineral sorbents. Mineral sorbents are made of natural fibees, while synthetic sorbents are artificial materials made of plastic.

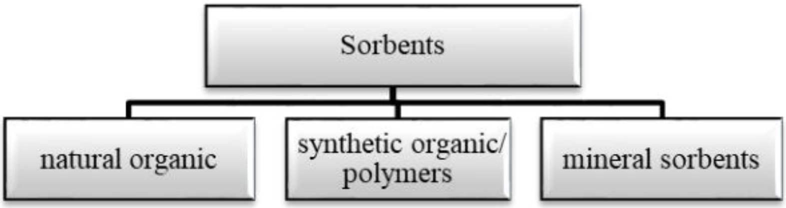

Fig. 2. Kind of adsorbents

Commonly used sorbents are mainly solid materials (granules, mats, pillows, sorption barriers, etc.). They are used to limit the horizontal and vertical migration of substances (Pijarowski and Tic, 2014).

3.1. Natural organic sorbents

Natural organic sorbents are widely used to remove metal ions by sorption process, and including, among others wood sawdust, bark, and peat (Baltinova et al., 2016), which is presented below.

3.1.1. Wood sawdust

Wood sawdust (WSD) is industrial biomass waste used as an adsorbent. WSD was obtained by wood processing units and industries that procedure furniture. This waste is cheap and eco-friendly and is commonly using to remove toxic metal ions from aqueous solutions (Varma et al., 2019).

For example, wood sawdust was used to remove copper, zinc, and cadmium from galvanic wastewater (Tan et al., 2019), e.g., Rahman et al. (2019) used maple sawdust to adsorb copper ions, obtaining maximum adsorption of 9.5 mg/g at pH = 6.0 (Rahman and Islam, 2009). Moreover, like other adsorbents, wood can be modified and used to remove metal ions from an aqueous solution. Rafatullah et al. used meranti sawdust to remove Cu(II), Cr(III), Ni(II), and Pb(II) ions from aqueous solutions with concentrations from 1–200 mg/L. The better adsorption was when the pH of the sample equals 6 for all metal ions (Rafatullah et.al., 2009). In addition Tan et. al. synthesised an innovative adsorbent based on wood flour for Pb(II) removal, assessed the experimental adsorption capacity of this adsorbent as amounting 189.9 mg/g in 180 min. Moreover, the adsorbents high selectivity of the Pb(II), Cu(II), and Zn(II) ions in mixed solution for lead ions (Tan et al., 2019). Other synthesised wood sawdust experimentation was undertaken by Guo et.al. and applied to removal Pb(II) and Cu(II) ions. The capacity sorption for Pb(II) and Cu(II) ions was 241.8 and 95.7 mg/g, respectively (Guo et al., 2020). El-Sheikh et al. (2018) prepared five adsorbents: the Cit-MOW (citric acid-coated magnetic olive wood sawdust) with the adsorption capacities (at pH = 5.6) of: 21.0, 14.4, 17.6 mg/g for Cu(II), Co(II), Zn(II), respectively, while cit-Mag (citric acid-coated magnetite) showed adsorption capacities (at pH = 5.6) of: 5.0, 1.6, 4.4 mg/g for Cu(II), Co(II), Zn(II), respectively (El-Sheikh et al., 2018).

3.1.2. Bark

The bark is a waste from wood processing, which is used as an adsorbent around an amorphous structure, irregular surface. Bark materials were composed mainly of lignin and holocellulose (Georgin et al., 2019). Bark is a cheap natural adsorbent and is commonly used to remove metal ions (Cd(II), Pb(II), Cu(II), Zn(II), Ni(II), Hg(II), Fe(II), Cr(III), Cr(VI)) (Baltinova et al., 2016; Naiya et al., 2009; Hamdaoui, 2016; da Silva Correia et al., 2018; Hashem et al., 2018; Sen et al., 2015).

For example, the bark was used to remove 94.80, 95.50, and 94.23% of Cd(II), Pb(II), and Cu(II) respectively from industrial real wastewater by Kebede et al. (2018). Akar et al. (2019) was used modified and non-modified bark to remove heavy metal ions from wastewater. The highest removal of Cr(VI) obtained 89.6% for non-modified bark and 90.7% for modified bark. The highest removal of Ni(II) was obtained 74.5 and 56.5% for non-modified and modified bark, respectively (Akar et al., 2019). Wajima obtained a modified adsorbent from cedar bark using sulfur-impregnation, and calculated the maximum adsorption capacity, of 0.30–0.74 mmol/g. The order of selectivity of the adsorbent was: Pb(II) > Fe(II) > Cu(II) > Zn(II) > Cd(II) > Ni(II) > Fe(III) (Wajima, 2017). Saeed et al. (2020) investigated the leaves (CL) and bark (CB) of cinnamomum verum to check their effectiveness in reducing the concentration of hexavalent chromium (Cr^{+6} metal ions) in the biosorption process (Saeed et al., 2020). Scientists also studied the application of green synthesis of magnetite nanoparticles from Hevea bark extract to the removal of Cd and Na ions. The highest adsorption capacity for Cd(II) and Na(I) ions was 37.03 and 3.95 mg/g, respectively (Sebastian et al., 2019).

3.1.3. Peat

The peat is a raw material of an extensive capacity, it can be a precursor for the synthesis of an adsorbent, e.g., using to the removal of metal ions from aqueous solutions. Peat is a cheap natural adsorbent, that is friendly to the environment (Men'shchikov et al., 2020).

Thus, Ringqvist et al. (2002) studied sphagnum and carex peat samples for the removal of zinc and copper ions from wastewater. The highest removal of Zn(II) and Cu(II) ions, 97–99%, 85–100%, respectively, were obtained in the effluent from the carex peat sulphide mine, and 37–77% for Zn, and 80–100% for Cu ions in the sphagnum peat sample (Ringqvist et al., 2002). Other scientists described the sorption capacity of peat for nickel(II) and lead(II) ions of 61.27 mg/g and 82.31 mg/g, respectively. The peat was an effective sorbent among natural organic sorbents, and the desorption experiments confirmed the possibility of reusing peat for the removal of harmful metal ions (Bartczak et al., 2018). Ho and Mckay studied the sorption of copper, lead, and nickel ions from an aqueous solution onto sphagnum moss peat (Ho and Mckay, 2000). Balasubramanian et. al. used Indonesian (Sumatra) peat as a metal adsorbent, with the metal ions adsorption of Pb > Cd > Zn for single- and multisolute systems. Desorption tests found that moret than 90% of Pb, Cd, and Zn can be eluted from the peat (Balasubramanian et al., 2009). In addition, peat, except for the above-mentioned metal ions, can be an effective adsorbent for removing chromium and mercury ions (Priyantha and Lim, 2016; Bulgariu et al., 2008). However, modified peat, e.g., coco-peat biomass (CPB) can be used for the removal of Pb(II), Cd(II), Cu(II), and Ni(II) ions from single and quaternary solutions. The biosorption capacity of Pb(II), Cd(II), Cu(II) and Ni(II) ions removal at pH 4 was as 0.440, 0.133, 0.335 and 0.154 mmol/g, respectively (Vijayaraghavan et al., 2016).

3.2. Synthetic organic/polymer sorbents

Porous organic polymers (POP) are of great interest, especially in wastewater treatment, due to their high porosity, flexibility, structure, and good chemical stability. Thanks to that these adsorbents can be used in the adsorption process to remove metal ions from wastewater (Huang et al., 2021).

Synthetic organic/polymeric sorbents were widely used for the recovery of various metal ions from heavy metal ions to noble metal ions. Bratskaya et al. (2016) synthesised a series of polymeric sorbents of pyridylethyl-containing derivatives of polyallylamine, polyethylenimine, and chitosan to the recovery of Au(III), Pt(IV), and Pd(II) ions. The maximum recovery of gold and palladium ions was 95% and 80%, respectively from PEC (when using 0.1 M HCl/1 M thiourea as an eluent) (Bratskaya et al., 2016). Other scientists synthesised new synthetic sorbents during co-precipitation of the PAA and linear and branched PEI and $CaCO_3$ crystallisation from supersaturated solutions for the removal of metal ions (Cu(II), Ni(II), and Co(II)) and their equimolar mixture. The results of the sorption experiments shown the sorption capacity of different ions can be correlated to the polymorph composition of the compounds (Zaharia et al., 2021). Tan et al. synthesised a mesoporous poly-melamine-formaldehyde (mPMF) polymer with a large surface area. This sorbent was characterised by good porosity and a high density of amine and triazine functional groups. Adsorption over mPMF was highly selective for lead ions commonly found in water ions (Na^+, K^+ and Ca^{2+}) (Tan et al., 2013). While Shemshadi et. al. (2012) used seven polymeric sorbents for the removal of Cd(II) from aqueous solution. The investigated adsorbents were obtained by mixing the polymers (PVP, MBAAm-N,N', and PAAm) in various ratios (Shemshadi et al., 2012). Seknal and Bicak (2001) synthesised cross-linked terpolymer beads modified by EDTA. The maximum sorption capacities for Fe^{3+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions, were equal to 1.48, 1.38, 1.72, and 1.8 mmol/g, respectively (Senkal and Bicak, 2001).

3.3. The mineral sorbents

Mineral sorbents are most often used due to the specific structure and absorption properties as well as the high efficiency of such sorbents (Pijarowski and Tic, 2014). Mineral sorbents except for modified mineral adsorbents, include zeolites, clay minerals, and silica adsorbents.

3.3.1. Zeolites

Zeolites are crystalline aluminosilicates that consist of SiO_4 and AlO_4 tetrahedra linked together to form a nanoporous, three-dimensional, cage-like structure (Mandal et al., 2020). It was, various natural zeolites have the ability to exchange different cation ions, e.g., ammonium and heavy metal ions. Moreover, modification of natural zeolites can be carried out by a few methods, for example, acid treatment, ion exchange, or surfactant functionalisation. In this way, modified zeolites were shown to have higher adsorption capacity for organic compounds and anions (Wang and Peng, 2010). Zeolites except for the removal of various metal ions from aqueous solutions are used in membrane processes, e.g., for hydrogen separation in syngas production (Coronas and Santamaria, 2004) or post-combustion CO_2 capture (Raganati et al., 2021; Xu et al., 2019). Modified zeolites are used, to e.g., the adsorption ofbBisphenol-A and propranolol hydrochloride (Rakhym et al., 2021) or for the recovery of heavy metal ions (Cr, As, Pb, Zn, Cu, Ni, Cd, Mn) present in wastewater (Shi et al., 2017).

For example, Hamed et al. studied the removal of heavy metals (such as Fe(III), Ca(II), and Mg(II)) in treated and raw water using modified zeolite. They found that when the pH was 4.5, the removal efficiency of Fe, Ca, and Mg was equal to 98.0%, 97.0%, and 94.9%, respectively (Hamed et al., 2015). Thirumavalavan et. al. synthesised mesoporous materials with commercially available β-zeolite for the adsorption of Pb(II), Cu(II), and Zn(II) ions. The capacity sorption for all synthesised compounds was approx. from 4.3 to 9.8, from 2.0 to 3.8, and from 1.2 to 2.6 mg/g for Pb(II), Cu(II), and Ni(II) ions (Thirumavalavan et al., 2011). Phuoc et. al. (2021) used NaA zeolite for Pb(II) ions adsorption studies in a fixed-bed column configuration. The sorption capacity was 118.5 mg/g with the concentration of Pb(II) ions of 100 mg/L, the adsorbent bed height of 8.1 cm, and the inflow rate of 2.5 mL/min (Phuoc et al., 2021). Borhadd et al. (2015) synthesised the adsorbent from zeolite-A to remove almost 95% of the Pb(II) and Cd(II) ions and approx. 60% of the Ni(II) ions from aqueous solution (Borhade et al., 2015). While Lu et al. (2016) investigated the adsorption of Pb^{2+} and Cu^{2+} on zeolite. The highest adsorption capacities of Pb(II) and Cu(II) ions were 135.5 and 115.5 mg/g, respectively, and for the concentration of a stock solution of metal ions was 10 g/L (Lu et al., 2016).

3.3.2. Clay minerals

Other adsorbents are clay minerals (NCM), which are among the adsorbent minerals. The NCMs are not toxic to the environment, but are inexpensive and can be used as cheap adsorbents (Alshameri et al., 2018). Clay minerals are cheap materials available all over the world and are characterised by chemical and morphological diversity (Chouikhi et al., 2019) The researchers found that the clays and their minerals (natural and modified forms) effectively remove e.g., ammonium (Alshameri et al., 2018), and various heavy metals from aqueous solution (Uddin, 2017).

Schimitt et. al. studied the influence of clay minerals (natural organic matter (NOM)) on the adsorption of various metal ions such as Al, Fe, Zn, and Pb (pH equal 5 and 7). They used kaolinite (KAO) and a smectite/illite mixture (MM) for the removal of metal ions (Schmitt et al., 2002). Gier and Johns (2000) used a series of micas and illite for the adsorption of Ba^{2+}, Pb^{2+}, Cu^{2+}, and Zn^{2+}. It was found that there is selective adsorption of Cu^{2+} ions about to Zn^{2+} and Pb^{2+} ions during the sorption of these silicates (Gier and Johns, 2000). Li et al. (2020) studied the adsorption of a number of cations (Na^{+}, K^{+}, Cs^{+}, Ca^{2+}, Pb^{2+}, Cd^{2+}, Ba^{2+} and Zn^{2+}) on the outer surface and in the montmorillonite interlayer. They investigated the role of interlayer space in determining the efficiency and the mechanism of adsorption. The stability of the adsorbed cations was found to be higher in the intermediate layer than in the outer surface, especially for M^{2+} (Li et al., 2020). Esmaeili et al. (2019) using bentonite as a sorbent for the removal of 99.9% of copper, and nickel ions, and 89.2% of zinc ions.

3.3.3. Silica adsorbents

In recent years, silica adsorbents have been increasingly used as sorbents to remove metal ions from an aqueous solution. The silica sorbents can be effectively used as adsorbents to remove various toxic metal ions (Ouyang et al., 2019; Artiushenko et al., 2020; Klapiszewski et al., 2015).

Najafi et al. (2012) used a modified silica adsorbent NH_2–SNHS (Amino-functionalised silica nano hollow sphere) for the recovery of nickel, cadmium, and lead ions. The highest adsorption capacity of Ni^{2+}, Cd^{2+}, and Pb^{2+} ions onto the investigated adsorbent was 38.982, 49.526, and 143.295 mg/g, respectively (Najafi et al., 2012). Bai et. al. (2012) was synthesised a silica-supported dithiocarbamate adsorbent (Si-DTC) as a new adsorbent for adsorption of Pb(II), Cd(II), Cu(II), and Hg(II) from aqueous solution. After the sorption experiments, the adsorption capacities were decribed, as 0.34, 0.36, 0.32, and 0.40 mmol/g for Pb(II), Cd(II), Cu(II), and Hg(II), respectively (Bai et. al., 2012). Zhao et.al. used chitosan-coated mesoporous microspheres of calcium silicate hydrate for removal of heavy metal ions of Ni^{2+}, Zn^{2+}, Cr^{3+}, Pb^{2+}, Cu^{2+} and Cd^{2+} from aqueous solution. The highest sorption capacity was 796 mg/g for lead ions and the lowest was 400 mg/g for zinc ions (Zhao et al., 2014). The next silica adsorbent is ionic liquid-modified silica gel, which was used to adsorption for Cu^{2+}, Fe^{3+}, Mn^{2+}, and Ni^{2+} ions (Qian et al., 2016). Functionalised cubic mesoporous silica, was used to removel Hg^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+} (Chatterjee and Paital, 2018). Also used was modified magnetic mesoporous silica MCM-48 to remove Pb(II), Cu(II), Cr(VI), and Cd(II) ions. The highest sorption capacity of lead, copper, chromium and cadmium ions was 127.24, 125.80, 115.60, and 114.08 mg/g, respectively (Anbia et al., 2015).

4. Summary

Research conducted to date has proved that sorption is an effective and widely used method to remove metal ions from wastewater. This paper presented various kinds of adsorbents (natural organic, synthetic organic/polymers, mineral sorbents) (Table 1) that will enable the high recovery of various metals.

5. Conclusion

Based on the results obtained by various groups of scientists, it can be concluded that natural organic sorbents such as wood sawdust and the modified wood sawdust be used for the recovery of Cr^{3+}, Pb^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, and Ni^{2+} ions, but the peat and modified peats can be effective adsorbent to remove Cr^{6+}, Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, and Ni^{2+} ions. Bark and modified bark can be used to remove Pb^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}, Pd^{2+}, Pt^{2+}, and Au^{3+} ions. Except for natural organic sorbents, mineral sorbents are used to remove various metal ions. For example the zeolites and modified zeolites be used for the removal of Cd^{2+}, Fe^{3+}, Ca^{2+}, Mn^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} ions, and the clay minerals for removal of Na+, K^{+}, Cs^{+}, Ca^{2+}, Pb^{2+}, Cd^{2+}, Ba^{2+}, Zn^{2+}, Cu^{2+}, and Ni^{2+} ions. In addition, the silica adsorbent, thanks to its properties, can be an effective adsorbent of Cr^{3+}, Cr^{6+}, Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}, and Mn^{2+} ions. The next group of the commonly used sorbents is synthetic organic/polymers sorbents, which allowed the recovery of Pb^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}, Pd^{2+}, Pt^{2+}, and Au^{3+} ions from aqueous solutions.

A review of various adsorbents for the removal of metal ions shows that the appropriate selection of the sorbent allows for the effective recovery of practically all metal ions from wastewater.

Table 1. Review of selected adsorbents used in sorption processes for metals ions recovery

Kinds of adsorbent	**Adsorbent**	**Metal ions**
Natural organic sorbents	Wood sawdust and modified wood sawdust	Cr^{3+}, Pb^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}
	Peat and modified peat	Cr^{6+}, Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}
	Bark and modified bark	Cr^{3+}, Cr^{6+}, Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Fe^{2+}, Na^{+}
Synthetic organic/polymers sorbents	Various synthetic sorbents	Pb^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}, Pd^{2+}, Pt^{2+}, Au^{3+}
Minerals sorbents	Zeolites and modified zeolites	Cd^{2+}, Fe^{3+}, Ca^{2+}, Mn^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}
	Clay minerals	Na+, K^{+}, Cs^{+}, Ca^{2+}, Pb^{2+}, Cd^{2+}, Ba^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}
	Silica adsorbents	Cr^{3+}, Cr^{6+}, Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}, Mn^{2+}

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PRZEGLĄD KOMERCYJNYCH NOŚNIKÓW STOSOWANYCH W POLIMEROWYCH MEMBRANACH INKLUZYJNYCH DO ODZYSKU JONÓW METALI NIEŻELAZNYCH

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1. WSTĘP

Metale, takie jak miedź, cynk, złoto, srebro itp., oraz ich stopy zalicza się do grupy metali nieżelaznych (kolorowych). Metale te znalazły zastosowanie w wielu dziedzinach przemysłu, począwszy od przemysłu galwanicznego aż do ciężkiego. W przemyśle ciężkim najczęściej wykorzystuje się te metale, które posiadają tzw. pamięć kształtu, czyli zdolność powrotu odkształconego elementu do pierwotnego kształtu po wielokrotnym nagrzewaniu do wysokich temperatur [8]. Metale nieżelazne wykorzystuje się również podczas osadzania powłok metali lub związków metali w celach dekoracyjnym, antykorozyjnych, czy technologicznych [22]. Istnieją też powłoki rozróżniane ze względu na mechanizm ochrony metalu. Stosuje się powłoki anodowe i katodowe. Właściwością rozróżniającą te dwa rodzaje powłok są wartości potencjału elektrochemicznego zastosowanego podłoża i powłoki.

Szerokie zastosowanie metali nieżelaznych powoduje ich nieuniknione przedostawanie się do środowiska naturalnego, a ich kumulacja stanowi zagrożenie dla zdrowia i życia zwierząt i ludzi. Konieczne jest, więc odpowiednie i zgodne z przepisami prawa unieszkodliwianie odpadów metalonośnych powstałych np. w zakładach przeróbki metali. Właściwie zaplanowane procesy utylizacji mogą okazać się opłacalne, ponieważ współcześnie możliwy staje się odzysk metali, także tych bardzo cennych. W związku z tym wielu naukowców polskich i zagranicznych prowadzi doświadczalne próby opracowania jak najbardziej prostego i ekonomicznego rozwiązania odnoszącego się do opisanych zagadnień. Jednym ze znanych sposobów odzysku metali nieżelaznych jest zastosowanie polimerowych membran inkluzyjnych (ang. *Polymer Inclusion Membrane*, PIM). Istotne stało się, aby wspomniane membrany były otrzymane z niedrogich substratów, ale także by znajdujący się w nich tzw. przenośnik jonów (ligand), który w głównej mierze odpowiada za odzysk, wykazywał duże powinowactwo do metali. Ważne jest również to, aby przenośnik selektywnie reagował jedynie z jednym ze znajdujących się w mieszaninie metali, co pozwoli na wysoko wydajnościową separację. Zastosowanie odpowiedniego związku organicznego, pełniącego rolę nośnika, umożliwia powstanie wewnątrz membrany związku kompleksowego, a później przeniesienie żądanego metalu z fazy pierwotnej do wtórnej. Polimerowe membrany inkluzyjne należą do tzw. ciekłych membran. Na przestrzeni ostatnich lat naukowcy udowodnili, iż ciekłe membrany, wykazując bardzo dobre właściwości separacyjne, są alternatywą dla tradycyjnych metod ekstrakcji jonowymiennej oraz ekstrakcji ciecz–ciecz podczas odzyskiwania jonów metali [35]. Zaletą procesów membranowych jest w tym przypadku ograniczenie dużych ilości często toksycznych rozpuszczalników. Opisane procesy membranowe można zatem z powodzeniem zastosować podczas odzysku jonów metali m.in. z odpadów przemysłowych.

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W niniejszej pracy zestawiono i scharakteryzowano powszechnie znane przenośniki jonów metali stosowane w PIM, takie jak: jonowe ciecze fosfoniowe (Cyphos IL 101, Cyphos IL 104), trioktyloaminę (TOA) oraz kwas 2(di-etyloheksylo)fosforowy (D_2EHPA). Nośniki te charakteryzują się wysoką skutecznością podczas odzysku metali nieżelaznych, m.in. cynku, miedzi, kobaltu itp.

2. POLIMEROWE MEMBRANY INKLUZYJNE

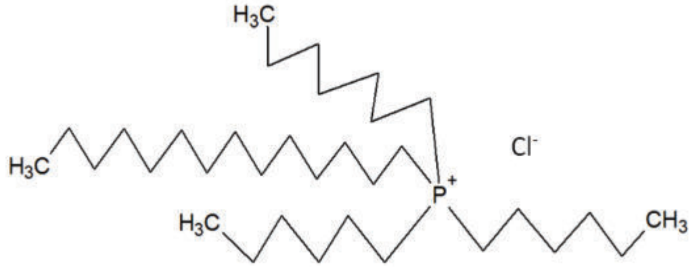
Membrana definiowana jest jako hydrofobowa organiczna ciecz, która rozdziela dwie fazy wodne: roztwór zasilający od roztworu odbierającego. Cechą charakterystyczną polimerowych membran inkluzyjnych jest jednoczesne występowanie procesu ekstrakcji oraz reekstrakcji, dzięki czemu można prowadzić proces w sposób ciągły [12]. Polimerowa membrana inkluzyjna syntetyzowana jest poprzez rozpuszczenie polimerowej matrycy (PVC lub CTA), plastyfikatora oraz odpowiedniego przenośnika jonów metali w rozpuszczalniku organicznym. Membrany te powstają na skutek wylewania roztworu zawierającego polimer oraz ciekłą fazę organiczną na szklaną płytkę. Po odparowaniu rozpuszczalnika membrana zostaje umieszczona na 12 godzin w wodzie destylowanej w celu uzyskania homogeniczności jej struktury [31]. Rolą polimeru w membranie jest zapewnienie mechanicznej wytrzymałości membrany. W amorficznym polichlorku winylu o małym stopniu krystaliczności polarne grupy funkcyjne pomiędzy wiązaniami węgiel – chlor powodują oddziaływania niespecyficznych sił dyspersyjnych, natomiast w polarnym, wysoko krystalicznym trioctanie celulozy, dzięki grupom hydroksylowym oraz acetylowym tworzą się wiązania wodorowe. Plastyfikator w polimerowej membranie inkluzyjnej odpowiada za wzrost elastyczności oraz wytrzymałości mechanicznej matrycy. Na skutek wnikania plastyfikatora pomiędzy cząsteczki polimeru następuje redukcja mocy sił międzycząsteczkowych, co powoduje wzrost odległości między cząsteczkami polimeru. Natomiast przenośnik jonów w membranie umożliwia transport jonów metalu, dzięki mechanizmowi transportu ułatwionego/przenośnikowego (ang. *Facilitated transport*), któremu często towarzyszy transport innych jonów znajdujących się w obu fazach wodnych, tj. współtransport lub przeciwtransport [10]. To od doboru przenośnika jonów metali zależy efektywność polimerowej membrany inkluzyjnej. Nośnikami w membranie są głównie organiczne ligandy rozpuszczające się w ciekłej membranie i mające silne właściwości kompleksotwórcze. Ponadto cechą pożądanego nośnika jest jego selektywność oraz możliwość odwracalnego oddziaływania z transportowanym jonem metalu. W praktyce często stosuje się komercyjne nośniki do odzysku jonów metali nieżelaznych, które można podzielić ze względu na ich charakter, tj. kwasowe, zasadowe czy chelatujące.

3. NOŚNIKI STOSOWANE W POLIMEROWYCH MEMBRANACH INKLUZYJNYCH

Na efektywność transportu jonów metalu przez PIM wpływają parametry membrany oraz szybkość mieszania fazy zasilającej i odbierającej. W przypadku składu membrany szczególne znaczenie odgrywa rodzaj oraz stężenie nośnika, jak również plastyfikator oraz matryca [1]. Dużym zainteresowaniem badaczy cieszą się komercyjne nośniki stosowane w procesach ekstrakcyjnych, m.in. Cyphos IL 101, Cyphos IL 104, TOA oraz D_2EHPA.

3.1. Charakterystyka jonowych cieczy fosfoniowych stosowanych jako nośniki w polimerowych membranach inkluzyjnych

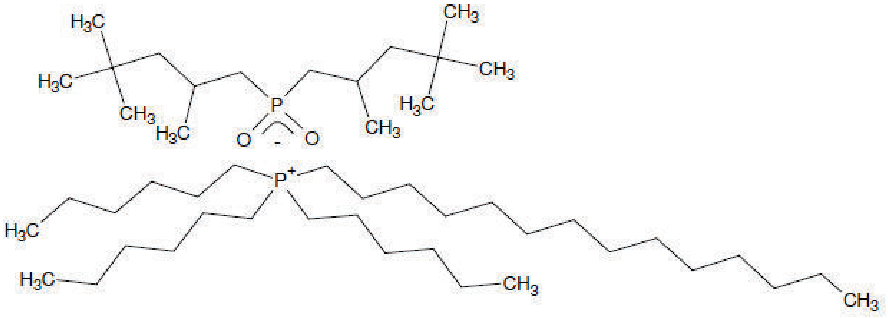
Jednym z powszechnie stosowanych nośników do odzysku jonów metali d-elektronowych w polimerowych membranach inkluzyjnych są jonowe ciecze fosfoniowe, wśród których można wyróżnić związek zawierający chlorek triheksylo(tetradecylo)fosfoniowy, o nazwie handlowej Cyphos IL 101 oraz komercyjny związek Cyphos IL 104, którym jest bis-2,4,4-(trimetylopentylo)fosfiniantriheksylu (tetradecylo)fosfiniowy. Cyphos IL 101 (rys. 1) znalazł zastosowanie w procesach ekstrakcyjnych oraz w polimerowych membranach inkluzyjnych do odzysku m.in. jonów cynku, kadmu, kobaltu, niklu, palladu, molibdenu, wanadu itp.



Rys. 1. Wzór strukturalny związku Cyphos IL 101 (opracowanie własne)

Aktualny stan wiedzy potwierdza możliwość przeprowadzenia procesu separacji jonów cynku(II) przy zastosowaniu polimerowych membran inkluzyjnych na bazie polichlorku winylu oraz Cyphos IL 101 jako nośnika jonów metalu. Kogelnig i współautorzy stwierdzili skuteczność już 30% wagowych nośnika w membranie do efektywnego odzysku cynku z 5,0 M roztworu kwasu chlorowodorowego [9]. Zbadano ponadto możliwość ekstrakcji cynku z mieszaniny zawierającej jony żelaza. Zastosowanie ekstrahenta Cyphos IL 101 powoduje wzrost współczynnika ekstrakcji w następującym kierunku Fe(II) < Zn(II) < Fe(III). Ekstrakcja cynku jest efektywniejsza niż żelaza(II), gdy oba jony zawarte są w fazie zasilającej. Badania potwierdziły, iż jony cynku(II) można selektywnie ekstrahować do fazy odbierającej z roztworów zawierających wysokie stężenie Zn(II) oraz czterokrotnie niższe stężenie Fe(II) [27]. Ekstrahent Cyphos IL 101 umożliwia również separację kadmu(II), kobaltu(II) i niklu(II) za pomocą PIM. Jak wykazała Pośpiech, membrana syntetyzowana na bazie 18,8% wagowych trioctanu celulozy (CTA), eteru o-nitrofenylopentylowego (ONPPE) w ilości 55,1% wagowych oraz 26,0% wagowych przenośnika jonów metali, jakim był Cyphos IL 101 umożliwia separację 90% jonów Cd(II) od Co(II) i Ni(II) z siarczanowych roztworów, przy zaaplikowaniu 0,5 M roztworu kwasu azotowego(V) do fazy zasilającej [24]. Kolejnym metalem, który można odzyskać z wykorzystaniem omawianego ekstrahenta, jest pallad. Według Cieszyńskiej i Wiśniewskiego Cyphos IL 101 może być wykorzystywany do odzysku palladu(II) z roztworów chlorkowych o różnym stężeniu. Zbadano, iż wzrost stężenia kwasu solnego negatywnie wpływa na proces ekstrakcji jonów palladu. Autorzy dowiedli, iż w przypadku 0,1 M roztworu HCl możliwa jest separacja 97% jonów Pd(II), natomiast w 0,3 M roztworze HCl tylko 54% [3]. Również Regel-Rosocka wraz ze współpracownikami zastosowała Cyphos IL 101 w polimerowej membranie inkluzyjnej, powstałej na bazie CTA do odzysku jonów palladu. Stwierdzono, iż najwyższe wartości znormalizowanego początkowego strumienia uzyskano, w przypadku, gdy fazą odbiorczą była mieszanina 0,1 M roztworu tiomocznika oraz 0,5 M roztworu kwasu solnego. Autorzy przeprowadzili również badania z zastosowaniem Cyphos IL 102 oraz Cyphos IL 104, jako nośnikiem. Mimo iż najwyższą wydajność ekstrakcji palladu(II) uzyskano dla membrany zawierającej Cyphos IL 101, to stwierdzono również skuteczność Cyphos IL 102 oraz Cyphos IL 104 – przy wykorzystaniu 3,0 M roztworu HCl w fazie odbiorczej [26]. Proces ekstrakcji z wykorzystaniem opisywanego związku przeprowadzili również inni badacze. W tym celu poddali badaniom jony molibdenu oraz wanadu. Wynikiem ich pracy było potwierdzenie skuteczności ekstrahenta do usuwania jonów wanadu przy użyciu 0,5 M roztworu kwasu siarkowego oraz 4-6 M roztworu kwasu siarkowego do odzysku molibdenu. Ponadto Zhu, Tulpatowicz i inni stwierdzili, iż Cyphos IL 101 jest efektywniejszym nośnikiem w porównaniu z powszechnie znanymi układami rozpuszczalników pod względem rozdziału wanadu od molibdenu oraz wanadu od żelaza(III) i glinu [34]. Yftain i inni badacze wykorzystali membranę PIM syntetyzowaną na bazie poli(winylidenofluoro-co-heksafluoropropylenu), jako matrycy w ilości 55% wagowych PVDF-HFP, 10% wagowych eteru nitrofenylooktylowego NPOE oraz 35% wagowych nośnika Cyphos IL 101. Według autorów nowo powstała membrana PIM okazała się zdolna do ekstrakcji V(V) z siarczanów przy pH 2,3 z wysoką selektywnością wobec jonów Al(III), Co(II), Cu(II), Fe(III), Mn(II) oraz Ni(II) [33].

Kolejnym nośnikiem, z grupy jonowych cieczy fosfoniowych cieszącym się dużym zainteresowaniem wśród naukowców jest komercyjny ekstrahent Cyphos IL 104 (rys. 2). Nośnik ten z powodzeniem wykorzystywany jest do separacji np. jonów cynku, kadmu, chromu czy złota itp., co potwierdzają naukowcy w przedstawionej analizie literatury tematu.



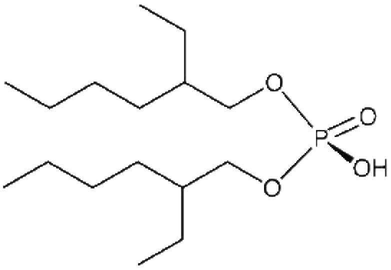
Rys. 2. Wzór związku Cyphos IL 104 (opracowanie własne)

Jak wspomniano wcześniej, jonowe ciecze fosfoniowe stosuje się w separacji jonów wielu metali. Zarówno Cyphos IL 101, jak i Cyphos IL 104 stosuje się do ekstrakcji Pd(II) z roztworów chlorkowych. Prace doświadczalne potwierdziły możliwość separacji 96% oraz 52% jonów palladu(II) podczas ekstrakcji odpowiednio z 0,1 oraz 3,0 M roztworem kwasu solnego już po 5 minutach prowadzenia procesu [3]. Skuteczność 3,0 M roztworu HCl do odzysku Pd(II) w swoich badaniach potwierdziła również Regel-Rosocka ze współpracownikami [27]. Naukowcy zbadali również możliwości ekstrakcyjne Cyphos IL 104 względem trójwartościowych lantanowców. Zbadano ekstrakcję La(III), Nd(III), Gd(III) oraz Lu(III) z następującymi nośnikami: Cyphos IL 104, Cyphos IL 101 oraz Cyanex 272. Najwyższą skuteczność ekstrakcji wykazuje Cyphos IL 104 [14]. Guo, Liu i inni zaproponowali syntezę polimerowej membrany inkluzyjnej z poli(fluorku winylidenu) (PVDF) jako matrycy oraz Cyphos IL 104 jako nośnika do odzysku jonów chromu(VI), który jest jednym z najbardziej toksycznych metali dla organizmów żywych. Wyniki ich badań potwierdziły skuteczność zastosowania nośnika w membranie. Według nich separacja jonów chromu(VI) za pomocą Cyphos IL 104 jest efektywna, a zastosowany nośnik jest 13-krotnie efektywniejszy niż powszechnie stosowany Aliquat 336 [5]. Oprócz możliwości separacji jonów chromu omawiany ekstrahent znalazł zastosowanie do odzysku złota. W tym celu Bonggotgetsakul, Cattrall i Kolev zsyntetyzowali membranę z 30% wagowych Cyphos IL 104 oraz 70% wagowych poli(fluorku winylidenu-co-heksafluoropropenu) do odzysku jonów złota(III) z chlorkowych roztworów. Do badań wykorzystano złom elektroniczny. W fazie zasilającej obecna była woda królewska, a w odbierającej – 0,5-molowy roztwór siarczanu(VI) sodu. Wykazano całkowity odzysk Au(III) do fazy odbierającej w obecności innych jonów metali przy znacznie wyższych stężeniach niż Au(III), w tym Cu(II), która była obecna w stężeniu ponad 15 000 razy wyższym od stężenia Au(III) [2]. Co więcej, Cyphos IL 104 umożliwia odzysk jonów cynku oraz kadmu, transport jonów cynku(II) i kadmu(II) z równomolowej mieszaniny z roztworów chlorkowych z mieszaniny wielojonowej. Cyphos IL 104 umożliwił separację 99% Zn(II) [17], potwierdzając tym samym wysoką selektywność nośnika wobec odzysku cynku. Natomiast Pośpiech zbadała właściwości ekstrakcyjne związku względem kadmu. Stwierdzając, iż do szybkiej i skutecznej separacji Cd(II) (ponad 99%) z wodnych chlorkowych roztworów zastosowany Cyphos IL 104 wykazuje wyższą wydajność usuwania Cd(II) w obecności kwasu azotowego niż siarkowego [23].

Reasumując, jonowe ciecze fosfoniowe, w tym Cyphos IL 101 oraz Cyphos IL 104, z powodzeniem mogą być stosowane do separacji jonów metali z roztworów oraz z ich mieszanin. Autorzy analizowanych prac naukowych, badając właściwości ekstrakcyjne Cyphos IL 101 oraz Cyphos IL 104, przeprowadzili proces tradycyjnej ekstrakcji oraz wykorzystali związek jako nośnik w polimerowej membranie inkluzyjnej.

3.2. Charakterystyka kwasu di(2-etyloheksylo)fosforowego stosowanego jako nośnik w polimerowych membranach inkluzyjnych

Tematem wielu rozważań naukowców jest również komercyjny ekstrahent, zaliczany do ekstrahentów kwaśnych: kwas di(2-etyloheksylo)fosforowy, D_2EHPA (rys. 3). Znalazł on zastosowanie m.in. podczas ekstrakcji metali nieżelaznych i ziem rzadkich oraz w procesach oczyszczania ścieków.



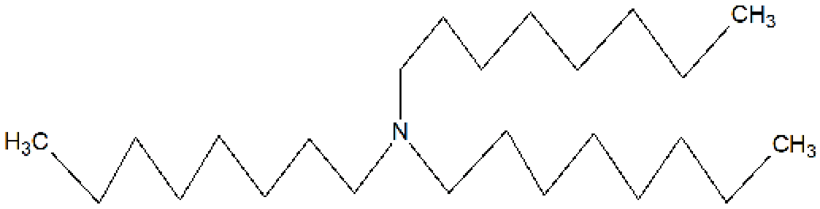
Rys. 3. Wzór strukturalny związku D_2EHPA (opracowanie własne)

Nathsarma i Devi przeprowadzili proces rozdziału jonów cynku od manganu. Proces separacji 0,01 M Zn(II) i Mn(II) z siarczanowego roztworu przeprowadzono za pomocą soli sodowych D_2EHPA, które w badanym układzie pełniły rolę nośnika jonów metalu. Stwierdzono, iż współczynnik rozdziału Zn(II) i Mn(II) zmniejszał się wraz ze wzrostem stężenia ekstrahenta z 0,03 do 0,06 M roztworu [19]. Stwierdzono ponadto, iż D_2EHPA umożliwia separację 98% Zn(II) przy pH równym 2,5. Proces ekstrakcji w tych warunkach zachodzi bardzo szybko, a równowaga zostaje osiągnięta już po 5 minutach prowadzenia procesu [21]. Oprócz tego badania nad omawianym ekstrahentem dowiodły, iż kwas D_2EHPA można stosować do rozdziału cynku z mieszaniny, tj. podczas separacji jonów Zn(II) od Cd(II) i Zn(II) od Ni(II) oraz Zn(II) od Co(II), czy Zn(II) od Cu(II) [29]. Kwas di(2-etyloheksylo)fosforowy można również zastosować do odzysku kobaltu oraz niklu z roztworów siarczanowych. Separację oraz odzysk dwuwartościowych jonów kobaltu i niklu przeprowadzono w obecności 0,1 M roztworu Na_2SO_4 za pomocą 0,03, 0,05 oraz 0,06 M roztworu soli sodowej D_2EHPA, przy pH wynoszącym 2,95. Stwierdzono, iż procentowa ekstrakcja jonów metali wzrasta wraz ze wzrostem równowagi pH w roztworze [4]. Naukowcy stwierdzili także, iż wraz ze wzrostem stężenia D_2EHPA rosną możliwości ekstrakcyjne jonów kobaltu(II) [30]. Kolejnym dwuwartościowym metalem, który można wyekstrahować z roztworu za pomocą omawianego nośnika, jest miedź. Wysoką selektywność odzysku miedzi uzyskano w obecności często spotykanych w wodach naturalnych oraz ściekach metali, takich jak: żelazo(III), glin(III), cynk(II), kadm(II), wapń(II), magnez(II) i nikiel(II) w lekko kwaśnych roztworach, w obecności kwasu solnego (pH = 2,0) [6]. W celu odzysku miedzi zsyntetyzowano polimerową membranę inkluzyjną na bazie trioctanu celulozy (CTA), który stanowił matrycę membrany, ftalanu dioktylu (DOP) – plastyfikatora oraz D_2EHPA jako nośnika jonów metalu. Kavitha i Palanivelu stwierdzili, iż optymalne warunki transportu Cu(II) to obecność w fazie zasilającej 1,0 M roztworu H_2SO_4 (pH = 4,5). Natomiast faza membranowa powinna zawierać $4,8 \cdot 10^{-2}$ mol/l nośnika [7]. Opisywany nośnik można ponadto zastosować do odzysku glinu(III) z mieszaniny zawierającej jony glinu, kobaltu i niklu stosując sole sodowe D_2EHPA w zakresie pH od 3,5 do 4,2. Badacze stwierdzili, że temperatura nie wpływa na zdolności separacyjne Al(III) badanego układu [18]. Natomiast w przypadku ekstrakcji skandu nośnik D_2EHPA pozwala na odzysk 99% jonów zawartych w roztworze, co bez wątpienia przekonuje do wykorzystania tego nośnika w praktyce [32].

Podsumowując, kwas di(2-etyloheksylo)fosforowy dzięki swoim właściwościom kompleksotwórczym znalazł zastosowanie w odzysku jonów metali przejściowych. Przytoczone w tekście wyniki badań potwierdzają efektywność D_2EHPA do selektywnej separacji jonów metali z roztworów, w tym mieszanin. Dobór odpowiednich warunków procesu umożliwi odzysk nie tylko opisywanych jonów metali, a także innych z bloku d.

3.3. Charakterystyka trioktyloaminy stosowanej jako nośnik w polimerowych membranach inkluzyjnych

Poza wymienionymi w powyższych podrozdziałach nośnikami do separacji jonów metali nieżelaznych stosuje się również nośniki zasadowe, wśród których na szczególną uwagę zasługuje trioktyloamina (TOA) (rys. 4).



Rys. 4. Wzór związku TOA (opracowanie własne)

Odzysk metali opisywanych w poprzednich rozdziałach, między innymi chromu, miedzi, cynku czy niklu, możliwy jest dzięki procesom membranowym. Polimerowa membrana inkluzyjna syntetyzowana z trioktyloaminą jako nośnikiem jonów metali znalazła zastosowanie podczas rozdziału jonów Cr(VI). Kozłowski wraz ze współpracownikami wykazał 99% skuteczność tego nośnika w odzysku jonów chromu(VI) z odpadów galwanicznych. Stwierdzono ponadto, że TOA daje wyższe współczynniki selektywności dla Cr(VI)/Cd(II) oraz Cr(VI)/Zn(II) [11]. Natomiast Kumbasar wykorzystał trioktyloaminę do odzysku kadmu(II), prowadząc proces z zastosowaniem ciekłej membrany emulsyjnej z TOA do ekstrakcji oraz zatężania Cd(II) z kwaśnych roztworów ługujących. Optymalne warunki procesu umożliwiły odzysk 98% kadmu [15].

Odnosząc się do osiągnięcia autora, można stwierdzić, iż zastosowanie TOA do separacji Cd(II) pozwoli na uzyskanie satysfakcjonującego wyniku również w przypadku innych ciekłych membran, np. PIM. Poza tym rozważania innych naukowców potwierdzają słuszność zastosowania TOA jako czynnika ekstrahującego jony miedzi(II) i kobaltu(II). Według Pośpiech i Walkowiaka transport Cu(II) i Co(II) wzrasta wraz ze wzrostem stężenia jonów chlorkowych w fazie zasilającej. Strumienie tych jonów maleją w następującej kolejności: Cu(II) > Co(II) > Ni(II). Stwierdzono również, że najwyższe strumienie Cu(II) i Co(II) obserwuje się przy 2,0 M roztworze HCl w fazie zasilającej, jednak stosunek współczynników przenikalności miedzi i kobaltu zmniejszał się wraz ze wzrostem stężenia kwasu [25]. Trioktyloamina również znalazła zastosowanie w procesie rozdziału jonów kobaltu(II) od niklu(II) w roztworach chlorkowych, o stężeniu kwasu solnego od 3,0 do 5,0 M w procesie elektrolizy galwanostatycznej [28], co jest obiecujące podczas zastosowania tego nośnika w polimerowej membranie inkluzyjnej. Zbadano proces membranowy z zastosowaniem TOA do rozdziału oraz zatężania Co(II) z 6,0 M roztworu kwasu solnego. Na transport kobaltu wpływa wiele zmiennych, w tym początkowe stężenie Co(II), szybkość mieszania, zatężenie ekstahenta itp., jednakże w optymalnych warunkach procent ekstrakcji Co(II) był wyższy niż 99% w obecności 100 mg/l Co(II) w roztworze zasilającym [16]. Kozłowski wraz ze współpracownikami zbadał możliwości separacyjne cynku i kadmu. Badania potwierdziły, że polimerowa membrana inkluzyjna zawierająca TOA jako nośnik jonów metali umożliwia efektywną separację Zn(II) oraz Cd(II) z roztworów chlorkowych. Współczynnik separacji Cd(II)/Zn(II) wzrasta wraz ze stężeniem kwasu solnego w fazie zasilającej [13].

Analiza literatury z uwagi na zdolności separacyjne trioktyloaminy oraz wykorzystanie jej w polimerowej membranie inkluzyjnej do odzysku jonów metali nieżelaznych potwierdza skuteczność oraz selektywność nośnika. Dalsze badania nad PIM mogą dostarczyć jeszcze bardziej szczegółowych informacji o zdolnościach kompleksotwórczych omawianego związku z metalami d-elektronowymi.

4. PODSUMOWANIE

W publikacji omówiono wybrane komercyjne nośniki stosowane w polimerowych membranach inkluzyjnych do odzysku jonów metali nieżelaznych. Scharakteryzowano cztery powszechnie stosowane nośniki w PIM, tj. Cyphos IL 101, Cyphos IL 104, D_2EHPA oraz TOA. Trioktyloaminę ze względu na charakter chemiczny zalicza się do nośników zasadowych, a pozostałe do kwaśnych. Aktualny stan wiedzy umożliwia odzysk jonów cynku(II) z każdym z powyższych nośników. Natomiast jony Cr(VI) można wydzielić za pomocą Cyphos IL 104 lub TOA. Co ciekawe Cyphos IL 104 umożliwia ekstrakcję lantanowców oraz złota, zaś Cyphos IL 101 molibdenu i wanadu.

Jony miedzi(II) z powodzeniem można wyekstrahować z roztworu przy użyciu D_2EHPA lub TOA jako nośnika jonów. Wyniki przedstawione przez cytowanych naukowców znacząco wpływają na rozwój omawianej dyscypliny naukowej, będąc równocześnie inspiracją do dalszych badań.

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USE OF POLYMER INCLUSION MEMBRANES FOR METALS RECOVERY

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Abstract

The growth of industrial development significantly contributes to the improvement of living comfort, however, the problem of the waste generation being a result of technological processes is still a problem of the modern world. Metal-bearing waste is among the strategic raw materials due to the possibility of their reuse, in fact natural deposits of these raw materials are protected, and it reduces the amount of waste present in landfills. Now, effective methods are being sought for the recovery of non-ferrous metals from industrial waste, using, inter alia, membrane processes (e.g. PIM). In the polymer inclusion membranes use a lot of ion carriers. Methods are being sought to understand the processes that take place inside the membrane. Detailed analysis of the resulting metal ion-carrier complex, it may be useful to use high-resolution mass spectrometry methods and tandem mass spectrometry.

Keywords

Polymer inclusion membranes (PIMs), ions carriers, high-resolution mass spectrometry, tandem mass spectrometry, recovery of metals

Introduction

Industrial waste contains, among others a lot of metals, including heavy metals. Depending on the industry, various types of pollution can be found in waste, both harmful to human and animal health, as well as useful for economic reasons. We have different types of pollution that can be found in the waste depending on the kind of industry. For example it compounds harmful substances to human and animal health and it also compounds useful substances for economic reasons. In case of metals such as zinc, copper, cadmium, nickel, gold etc. one should look for more and more effective methods of their recovery. It is really important in environmental and also economic aspects, because metal prices are oscillating in amounts of several thousand dollars, depending on the current market and political situation.

According to the document of the Central Statistical Office '*Environment Protection 2017'* in 2016 Poland generated 140 million tons of waste, including 8% of municipal waste (i.e. 12 million tons). The main source of waste generated in 2016 was mining and quarrying, who generated about 52%, while industrial processing about 21%, as well as production and supply of electricity about 16% of the total waste produced (Figure 1). Considering the last ten years, the highest volume of waste generated was the waste generated during the exploration of mining and physical and chemical processing of ores and other minerals. In 2016 it accounted for 56% of the total waste generated, and waste from thermal processes accounted for 22% [1].

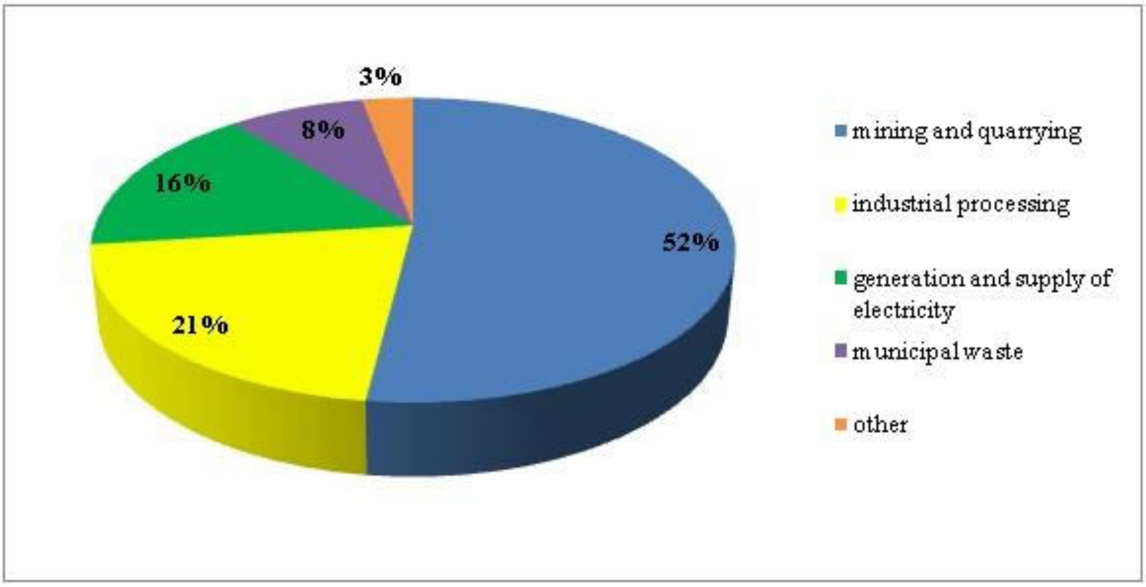

Figure 1. Percentage of waste generated in 2016 based on the study by D. Bochenek, Environmental Protection Environment 2017, October 2017
Source: own elaboration

On the basis of data available in the GUS document '*Environment 2017'*, 49% of waste was subjected to recovery, 42% was disposed of via storage, and the remaining 4% of waste was disposed of in a different way (Figure 2) [1]. The most important role in the process of waste disposal is played by the recovery process, which allows the subsequent use of raw materials. Nevertheless, the storage process is still a big problem in Poland. Storage is an ineffective process that does not bring economic and environmental benefits.

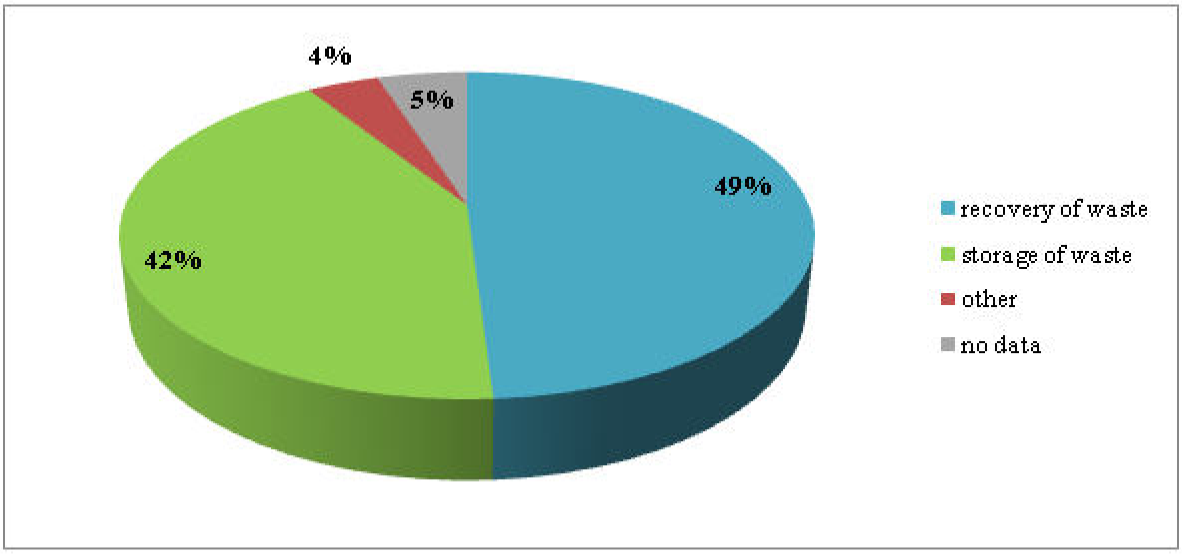

Figure 2. Percentage of waste generated in 2016 based on the study by D. Bochenek, Environmental Protection Environment 2017, October 2017
Soruce: own elaboration

Due to the large amount of waste generated, it becomes important to find an effective method of recovery of non-ferrous metals present in waste, with a view to their further use in industrial processes. The methods of metal recovery can be divided into the recovery of metals from aqueous liquid solutions and from constant precipitation. There are many known methods of the separation of metal ions from aqueous solutions. Since the end of the 20th century, membrane processes have been of increasing interest among scientists and technologists, enabling metal recovery at low concentrations. In addition, they can be used in new and already operating industrial installations. The main advantage of membrane processes is the ability to conduct separation in a continuous manner with a low energy demand and low technological costs.

In the processes of selective separation and recovery of heavy metal ions, polymer inclusion membranes (PIMs) were used. A characteristic feature of polymer inclusion membranes is the high stability during the transport of metal ions, where the carrier, which is the complexing compound, is responsible for the binding and transport of metal ions through the membrane. The polymer plays a key role in ensuring the mechanical strength of the PIM-type membrane, and its properties significantly affect the permeability and durability of the membranes [2].

Polymer inclusion membrane

The most popular, polymer inclusion membranes (PIMs) consists of an ion transporter, a polymer matrix (usually polyvinyl chloride (PVC) or cellulose triacetate (CTA)), as well as a plasticizer [2]. One method of preparation of a polymer inclusion membrane is the dissolution of appropriate amounts (e.g., % by weight) of a polymer, e.g. PVC and a suitable ion transporter. The obtained solution is then poured into a glass ring e.g. 7.5 cm in diameter, which is placed on a flat glass plate previously cleaned with acetone. The mixture is covered with a filter paper and a watch glass and it is left to stand for 24 hours to evaporate the solvent [3]. Most polymer inclusion membranes are obtained in the form of casting flat membranes. Almeida indicates the possibility of obtaining PIMs by filling a coated PIM column. This method consists in preparing a cylindrical PIM with an empty agent by passing the membrane components, which are then cast on a glass capillary tube [4]. Polymer inclusion membranes prepared in this way can be used in the separation process. Transport of metal ions through polymer inclusion membranes is possible due to the use of an appropriate ion transporter.

In the polymer inclusion membranes, the selection of an appropriate metal ion carrier is very important. In choosing a metal ion carrier, knowledge about the properties of carriers and separated metal is necessary. When selecting the ion carrier, it is important to remember that the basis for the polymer inclusion membranes is the complexation reaction. This reaction occurs due to the presence of a free electron pair on the non-ligand binding orbitals and empty orbitals present in the central atom that are able to absorb the electron pairs of these ligands [5]. In polymer inclusion membranes, metal ion transporters can be organic chemicals that are well soluble in the membrane, but do not dissolve in aqueous solutions. It is also important that the carrier used is characterized by selectivity and reversible interaction with the separated metal ion [6]. During the separation of non-ferrous metal ions, the frequently used carriers in polymeric non-ferrous membranes include D_2EHPA (di-(2-ethylhexyl) phosphoric acid), Cyanex 272 (di-(2,4,4-trimethylpentyl) phosphonic acid), β-diketone derivatives [7-9].

The D_2EHPA acid (Figure 3) in PIMs is used to separate not only zinc, but also manganese, nickel, copper, etc. Wang and co-authors for the recovery of non-ferrous metals (between zinc, magnesium) use polymer inclusion membranes containing LIX 84I ion carriers (2-hydroxy-5-nonyl acetophenone oxime) and D_2EHPA (di (2-ethylhexyl) phosphoric acid), thus proposing a PIM double membrane system for simultaneous separation and enrichment [10]. In addition, D_2EHPA acid is used as a carrier to remove selectively Fe (III) ions from acidic aqueous solutions [11].

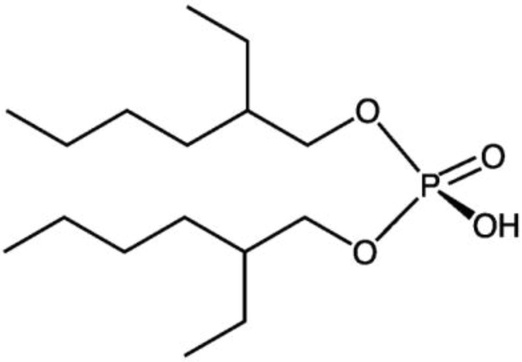

Figure 3. The chemical formula of D_2EHPA, used as an ion transporter in polymer inclusion membranes
Source: own elaboration

The next frequently used carrier in PIMs is Cyanex 272, which introduced into the CTA polymer matrix, will enable efficient transport of zinc ions. Yilmaz and co-authors have found that the Zn(II) transport by PIM is affected by variables such as the initial pH and the concentration of zinc ions of the supply phase and the concentration of the ion transporter (Cyanex 272) and the receiving phase [8]. Besides mentioned above ions metals D_2EHPA and Cyanex 272 also can use to palladium separation. According to Bonggotgetsakul, the production of the nanoparticles palladium PdNP used D_2EHPA as ions carriers, in order to maximum surface coverage polymer inclusion membrane PdNP with an average size of 38 nm [3].

And the next ions carriers are β-diketones derivatives (Figure 4), which specific construction i.e. the presence of two carbonyl groups and a methylene group per molecule, can use to transport a lot of metals including zinc, copper, cobalt or nickel. On the basis of the research carried out, Witt and co-authors found that the increase in roughness increases the porosity of the membrane. These parameters are very important in transport processes ions, because the greater the roughness, the larger the active surface of the membrane. Ions Zn(II) are transferred in supply phases to receiving phases with higher speed than ions Cu(II) and Ni(II) and depends on the type of ions carriers [12].

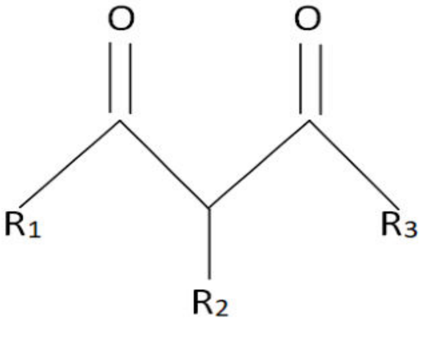

Figure 4. Chemical formula of β-diketone molecule, used as an ion transporter in polymer inclusion membranes
Source: own elaboration

Separated ammonia and calcium, lead or zinc ions from aqueous environmental solutions has been with used dinonyl naphthalenesulfonic acid (DNNS) [13]. Recovered are also the waste containing precious metals, among others from old electronic equipments, for example the mobile phones.

Kubota with co-authors points to the newly synthesized D_2EHAG extractant (N-[N,N-di-(2-ethylhexyl)aminocarbonylmethyl]glycine), which is characterized by high selectivity to Au (III) ions with respect to other metals present in solutions [14]. Nanoparticles gold can be made with polymer inclusion membranes on based polychloride vinyl and commercial ions carriers i.e. Aliquat 336. In this case through the reduction of gold(III) it is extracted into the membrane as a complex $[AuCl_4]^-$[15].

The obtained results confirm the effectiveness and rightness of using ion transporters, including such as: D_2EHPA acid, commercial Cyanex 272 or β-diketone derivative. Own research and review of specialist literature prove that polymer inclusion membranes are able to transport metal cations with very good yield and high selectivity. The PIMs studies contain mentioned above derivatives as metals ions carriers that provide the necessary information on the speed of metal transport by PIMs, process selectivity, effectiveness, etc. However, this research does not provide information of the resulting bonds between the recovered metal and the organic ion carrier. A closer understanding of the processes taking place inside the membrane may be helpful in further design of the technological process. For this purpose, mass spectrometry and tandem mass spectrometry methods can be used to determine the resulting complex between the metal and the ligand.

Mass spectrometry

Mass spectrometry (MS) is an analytical tool used to measure molecular weight and analysis of organic compounds. This method allows measurements at very low concentrations. Mass spectrometry methods can be divided into so-called soft and hard. In case of "soft" ionization, a molecular ion is formed, without fragmentation of the molecule, for example, the ESI, MALDI method. In contrast, in the "hard" ionization there is a fragmentation of the studied molecule, e.g. EI, CI. Although mass spectrometers differ from each other by ionization of molecules and separation of ions, all spectrometers operate according to one principle (Figure 5) [16].

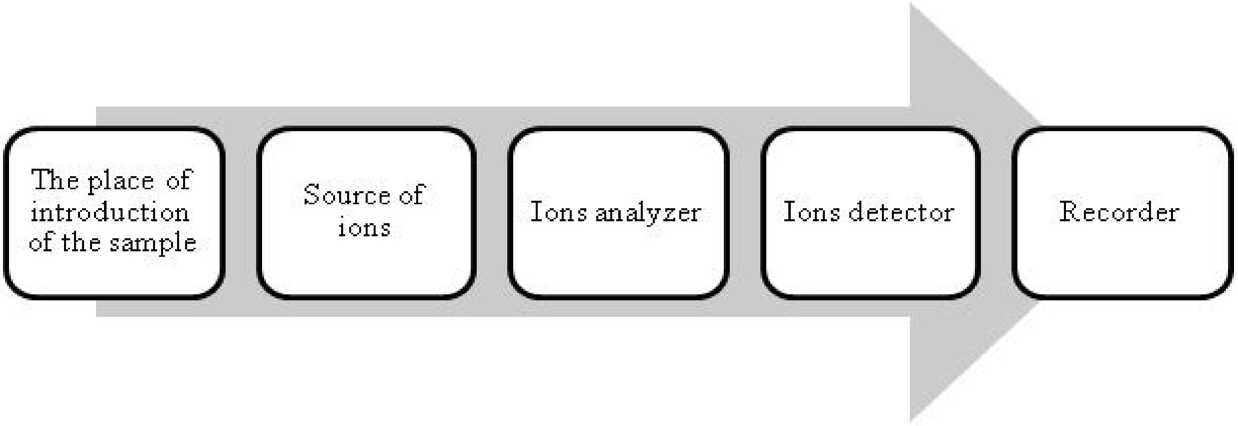

Figure 5 Block diagram of the mass spectrometer operation
Source: own elaboration

Mass spectrometry allows you to get complete information about a given compound when it is in a clean state, because the spectra of contaminated compounds are difficult to interpret. For this reason, the MS method should be accompanied by a pre-separation method. Coupled techniques play an extremely important role here. In this way, the following methods were developed: GC-MS, HPLC-MS and HPCE-MS, which combine the mass spectrometer with a gas chromatograph, high-performance liquid chromatography or high-performance capillary electrophoresis [16]. Another option is to introduce a so-called tandem mass spectrometry. This method (marked with the MS/MS symbol) consists of performing controlled ion decay of the tested compound and further analysis of the mass of the obtained fragments, i.e. the ratio of mass to ion charge m/z [17]. Tandem mass spectrometry is used to identify as well as determine the structure of simple chemical compounds, which provides information about the structure and type of fragmentation ions and how to link them. The choice of the appropriate method among the many known methods of fragmentation depends on the properties of the test compound and on the construction and parameters of the mass spectrometer [18].

The structure of macromolecular compounds is investigated by means of mass spectrometry (MS) and tandem mass spectrometry (MS/MS) methods. One of the main methods is used in the analysis of polymers is MALDI type spectrometry (laser desorption with the use of a matrix). This method provides a number of information about the chemical structure of the polymer, while allowing the identification of chains, end groups, functions and provides information about the presence of other fragments present in the structure. Thanks to the use of MALDI spectrometry during the analysis of macromolecular compounds, it is possible to examine the resulting structure or develop a further research procedure. In case of synthetic polymers analysis it's often used MALDI-TOF-MS (Matrix-Assisted Laser Desorption/Ionization-Time of Flight-Mass Spectrometry) i.e. laser desorption with the use of a matrix with measurement of ion time [19].

Since last years, an increasingly common method of ionization is the electrospray (ESI) method, which has been used in the analysis of both low molecular weight compounds and macromolecules, such as biopolymers or complex complex systems. The electrospray ionization technique is one of the mildest methods in spectrometry, because the resulting ions are characterized by a small excess of internal energy. The ESI technique has found particular application in the analysis of chiral compounds. Drabik underlines that the electrospray technique can be successfully use to analyze chiral compounds, where the relative intensity of signals of the analyzed spectrum depends on the enantiomeric composition of the analyte under study [20]. Nevertheless, experimental studies confirm that proper results are obtained only by using several spectrometry methods simultaneously.

Summary

Industrial waste is a very big problem due to environmental and economic reasons. One of metal separation method in aqueous solution is membranes processes, which is characterized as a higher efficiency process, with relatively low financial and technological costs, and the metals recovered in this way can be further used in industry. One of the membranes techniques is the polymer inclusion membranes. In the PIMs for the separation non-ferrous metals can be used among the following metal ion carriers: D_2EHPA, Cyanex 272 or β-diketones derivatives, whereas to recover precious metals (e.g. gold and palladium) commercial ion carriers i.e. Cyanex 272 or

Alquat 336 can be used. The transport and selection of the separation process using PIMs is well known and studied by many researchers, which is possible to effectively control the separation process and select the most effective metal recovery medium that we want to receive. This raises one question, if during examining the structure of the complexes created inside the membrane, will it affect even better process efficiency? For this purpose, it may be appropriate to use high-resolution mass spectrometry methods and tandem mass spectrometry. These methods are becoming more and more popular in the analysis of macromolecular compounds, in polymer chemistry or in purification processes, therefore, PIMs may be used during the study. In-depth analysis of the structures created inside the membrane between the ligand and the separated metal will allow you to learn more about the process.

Conclusion

Polymer inclusion membranes, due to the high selectivity of the process and the availability of many ion transporters, are becoming more and more popular among researchers and engineers. The researches on the PIMs confirm their effectiveness and possibility in using in industry for recovery metals in aqueous solution, and efficiency transport depends on using ion carriers. Depending on the separation conditions, many metal ion carriers are available, and so during the recovery of non-ferrous metals, D_2EHPA, Cyanex 272 and β-diketone derivatives and are proved to be effective carriers during recovery of precious metals Cyanex 272 and Aliquat 336. Analyzing the available literature data, one can conclude that the methods of high resolution mass spectrometry and tandem mass (MS/MS methods) can provide information about the structure and elemental composition of the resulting complexes, therefore the use of these methods seems to be right in order to better understand the processes occurring inside the membrane, primarily metal-ligand connections.

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CHARAKTERYSTYKA BUDOWY ORAZ PROCESÓW ZACHODZĄCYCH WEWNĄTRZ POLIMEROWYCH MEMBRAN INKLUZYJNYCH (PIM) STOSOWANYCH, JAKO PRZENOŚNIKI JONÓW METALI

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1. WSTĘP

Znaczna liczba zakładów przemysłowych odprowadza wraz ze ściekami niebezpieczne substancje chemiczne w ilościach zagrażających zdrowiu człowieka, jak również środowisku naturalnemu. W 2000 roku Unia Europejska uchwaliła Ramową Dyrektywę Wodną, aby zapobiec nieustannemu pogarszaniu się stanu wód. Celem Dyrektywy jest ochrona oraz poprawa stanu śródlądowych wód europejskich, jak również ekosystemów lądowych, które są zależne od tych wód [Kończyk 2014]. Oczyszczalnie ścieków są umiejscowione w ciągach technologicznych zakładów przemysłowych, gdzie metale ciężkie usuwa się chemicznie oraz fizykochemicznie. Zazwyczaj stosowanymi metodami oczyszczania ścieków są procesy takie jak: strącanie chemiczne, koagulacja-flokulacja, floatacja, wymiana jonowa, adsorpcja oraz biosorpcja, ekstracja rozpuszczalnikowa czy procesy membranowe, do których zalicza się ultra- oraz nanofiltrację, elektrodializę czy osmozę. Każda z wymienionych metod obciążona jest wadami technologicznymi, ekologicznymi czy ekonomicznymi [Jacukowicz-Sobala 2009, Fu Wang 2011].

W ostatnich latach rozpoczęto intensywne badania nad wykorzystaniem ciekłych membran (LM, ang. *Liquid Membranes*) do transportu jonów. Proces ten oparty jest na pertrakcji, tzn. połączeniu na jednym etapie procesu ekstrakcji i reekstrakcji. Ciekła membrana jest niemieszającą się z wodą fazą organiczną, która rozdziela dwie inne fazy ciekłe tj. fazę donorową (zasilającą) oraz fazę akceptorową (odbierającą). Zarówno faza zasilająca, jak i odbierająca zazwyczaj są roztworami wodnymi. Ze względu na budowę membran można je podzielić następująco:

- ciekłe membrany grubowarstowe (BLM, ang. *Bulk Liquid Membrane*),
- ciekłe membrany emulsyjne (ELM, ang. *Emulsion Liquid Membrane*),
- ciekłe membrany podparte (SLM, ang. *Supported Liquid Membrane*),
- polimerowe membrany inkluzyjne (PIM, ang. *Polymer Inclusion Membrane*) [Kończyk 2014].

Biorąc pod uwagę układy z ciekłymi membranami (rys. 1), w praktyce najczęściej stosuje się membrany ELM, SLM oraz PIM. Natomiast wykorzystanie układu BLM na skalę przemysłową jest niemożliwe z powodu małej powierzchni kontaktu membrany z sąsiadującymi fazami oraz grubości membrany, która wywołuje dużą retencję transportowanej substancji [Kończyk 2014].

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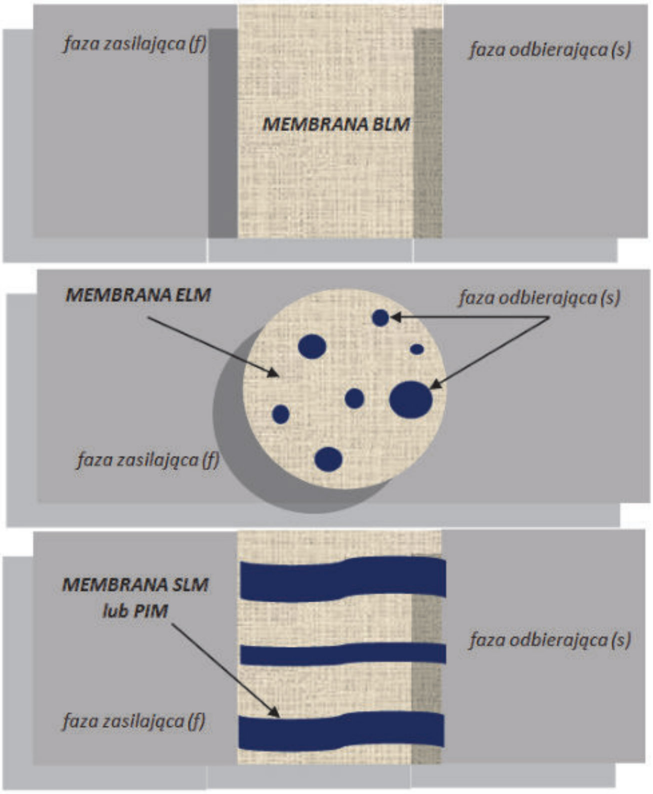

Rys. 1. Schemat układów z ciekłymi membranami [opracowanie własne]

2. BUDOWA POLIMEROWEJ MEMBRANY INKLUZYJNEJ

Polimerowe membrany inkluzyjne (PIM) znalazły zastosowanie w procesach selektywnego rozdziału, jak również odzysku jonów metali ciężkich. Zazwyczaj PIM składa się z przenośnika jonów, matrycy polimerowej oraz plastyfikatora. Cechą charakterystyczną polimerowych membran inkluzyjnych jest wysoka stabilność podczas transportu jonów metali, gdzie nośnik, którym jest związek kompleksujący odpowiada za transport oraz wiązanie jonów metalu przez membranę [O'Brayan i in. 2017]. Polimerowe membrany inkluzyjne powstają na skutek fizycznej immobilizacji przenośnika w polimerowej matrycy przez odparowanie rozpuszczalnika z roztworu składającego się z mieszaniny polimeru, plastyfikatora oraz przenośnika [Kończyk 2014]. Polimer odgrywa kluczową rolę w zapewnieniu mechanicznej wytrzymałości membrany typu PIM, a jego właściwości w znacznym stopniu wpływają na przepuszczalność i trwałość membran. Najczęściej stosuje się matryce polimerowe z polichlorku winylu PVC lub trioctanu celulozy CTA. Dzięki posiadaniu grup hydroksylowych oraz acetylowych, CTA jest polarnym polimerem zdolnym do tworzenia wiązań wodorowych. Natomiast polarne grupy C-Cl w PVC powodują działanie niespecyficznych sił dyspersyjnych, które wzmacniają oddziaływania międzycząsteczkowe. W związku z powyższym PVC jest polimerem amorficznym o małym stopniu krystaliczności, zaś CTA jest wysoce krystaliczny [Kończyk 2014]. Plastyfikator w PIM wpływa na zwiększenie elastyczności oraz wytrzymałości mechanicznej matrycy polimerowej przez wnikanie między cząsteczki polimeru oraz obniżanie mocy sił cząsteczkowych, co wpływa na powiększenie odległości między cząsteczkami polimeru. Najczęściej stosowane plastyfikatory to: eter o-nitrofenylooktylowy, eter o-nitrofenylopentylowy, adypinian dioktylu, ftalan dioktylu oraz chlorek metyltrialkiloamoniowy (Aliquat 336) [Nghiem i in. 2006, Inês i in. 2012]. Brak czynnika kompleksującego uniemożliwia transport substancji hydrofilowych, np. jonów metali, wynika to z dużej gęstości ciekłej membrany oraz występujących w niej silnych oddziaływań hydrofobowych. Wprowadzenie do fazy membranowej związku będącego przenośnikiem wywołuje transport jonów metali przez ciekłą membranę, dzięki mechanizmowi przenośnikowemu (transport wspomagany), któremu często towarzyszy transport innych, obecnych w fazach wodnych jonów. Transport jonów metali przez ciekłe membrany jest najczęściej transportem ułatwionym sprzężonym, podczas którego na powierzchni membrany oprócz jonów metalu transportowane są przeciwjony. Ze względu na kierunek transportu dzielimy go na współtransport oraz przeciwtransport. W pierwszym jon metalu oraz przeciwjon poruszają się w tym samym kierunku, a w drugim jon metalu porusza się w przeciwnym kierunku do przeciwjonu [Kozłowski i Kończyk 2014]. Przenośnikami jonów metali w PIM mogą być związki chemiczne dobrze rozpuszczalne w ciekłej membranie, nierozpuszczalne w roztworach wodnych oraz posiadające właściwości selektywnego i odwracalnego oddziaływania z przenoszonym składnikiem [Wódzki 1997]. Głównie są to ligandy organiczne stosowane w roli ekstrahentów podczas ekstrakcji rozpuszczalnikowej [Kończyk 2014]. Biorąc pod uwagę właściwości chemiczne oraz sposób oddziaływania z jonami metalu przenośniki/ekstrahenty można podzielić na kwasowe, zasadowe i obojętne (tab. 1).

Tabela 1. Oddziaływanie jonów metalu z przenośnikiem/ekstrahentem [opracowanie własne na podstawie odnośnika literaturowego [Kończyk 2014]

Rodzaj przenośnika	**Właściwości**	**Reakcja chemiczna**	
kwasowy (HL)	wymiana protonu na jon metalu M^{n+} według reakcji	$[Mn^{+}]_{w} + n[HL]_{org} \rightarrow [ML_{n}]_{org} + n[H^{+}]_{w}$	(1)
zasadowy (RN^{+})	ekstrakcja jonów metalu	$[MX_{p}^{(p-n)-}]_{w} + (p-n)[RN^{+}]_{org} \rightarrow [(p-n)RN^{+}MX_{p}^{(p-n)-}]_{org}$	(2)
obojętny (L)	tworzenie z jonami metalu obojętnego kompleksu w fazie organicznej przez zastąpienie cząsteczki wody w akwakompleksie metalu własnymi, bardziej liofilowymi cząsteczkami	$[M^{n+}]_{w} + n[X^{-}]_{w} + q[L]_{org} \rightarrow [MX_{n}L_{q}]_{org}$	(3)

3. WŁAŚCIWOŚCI PIM ORAZ CHARAKTERYSTYKA PROCESÓW ZACHODZĄCYCH W MEMBRANIE

Transport jonów metali przez polimerową membranę inkluzyjną zależy od wielu czynników i może być opisywany za pomocą parametrów takich jak: chropowatość powierzchni, współczynnik przenikalności jonów czy współczynnik dyfuzji.

Obecnie model transportu jonów metali przez polimerową membranę inkluzyjną oparty jest głównie na sześciu założeniach:

1. Reakcje zachodzące na granicy faz należą do bardzo szybkich oraz prowadzą do natychmiastowego ustalenia się stanu równowagi chemicznej.

2. Stężenie jonu metalu w fazie membranowej pomija się w stosunku do stężenia przenośnika występującego w tej fazie.
3. Stężenie związku kompleksowego metal – nośnik na granicy membrana/faza odbierająca pomija się w stosunku do jego stężenia występującego na granicy faza zasilająca/membrana.
4. Transport masy wewnątrz membrany jest wyłącznie wynikiem procesów dyfuzyjnych opisanych za pomocą I Prawa Ficka.
5. Dyfuzja występująca w wodnej warstwie na granicy faza zasilająca/membrana jest dużo szybsza niż w przypadku dyfuzji kompleksu przez membranę.
6. Faza wodna – zasilająca oraz odbierająca są idealnie mieszane [Kończyk 2014].

Charakterystykę powierzchni membran najczęściej przeprowadza się za pomocą mikroskopu sił atomowych (AFM, z ang. *Atomic Forces Microscope*), który umożliwia między innymi obliczenie chropowatości (*Rf*) [Ulewicz i in. 2010]. Jest to procent wydzielenia jonów metali z fazy zasilającej do odbierającej. Rf definiuje się jako [Radzymińska-Lenarcik i in. 2017]:

$$\mathrm{R_f} = \frac{\mathrm{c_i} - \mathrm{c}}{\mathrm{c_i}} \cdot 100\% \tag{4}$$

gdzie:

c_i – stężenie początkowe jonów metali w fazie zasilającej,
c – stężenie jonów metali w fazie zasilającej po czasie t.

Natomiast współczynnik przenikalności jonów metali przez polimerowe membrany inkluzyjne opisuje równanie [Ulewicz i in. 2010]:

$$\ln\left(\frac{c}{c_i}\right) = -\frac{A}{V} \cdot P \cdot t \tag{5}$$

gdzie:

c – stężenie jonów metali (M) w wodnej fazie zasilającej, w określonym czasie,
c_i – początkowe stężenie jonów w fazie zasilającej,
t – czas transportu [s],
V – objętość fazy źródłowej [m^3],
A – powierzchnia kontaktu membrany [m^2].

Liniowa zależność ln(c/c_i) w fazie zasilającej w funkcji czasu pozwoliła na uzyskanie współczynnika przenikalności z nachylenia linii prostej, którą otrzymuje się z danych eksperymentalnych. Początkowy strumień (J_i) określa równanie [Ulewicz i in. 2010]:

$$J_i = P \cdot c_i \tag{6}$$

Współczynnik dyfuzji D_0 [cm^2/s] kompleksu metalu w fazie organicznej można wyznaczyć przy braku oporności dyfuzyjnej w fazie wodnej/w warstwie zasobnika po przekształceniu równania (7) [Ulewicz i in. 2010].

$$c = c_i - \frac{[L]_0 \cdot A \cdot t}{n \cdot V \cdot \Delta_0} \tag{7}$$

gdzie:

$\Delta_0 = d_0/D_0$ [s/cm] – odporność transportu na dyfuzję przez membranę,
d_0 – grubość membrany [cm],
n – liczba moli nośnika w kompleksie,
$[L]_0$ – początkowe stężenie ekstrahenta w fazie organicznej (M).

4. PRZEGLĄD WYBRANYCH PRZENOŚNIKI JONÓW STOSOWANYCH W POLIMEROWYCH MEMBRANACH INKLUZYJNYCH

Transport jonów metalu przez polimerową membranę inkluzyjną jest możliwy dzięki zastosowaniu odpowiedniego przenośnika, najczęściej ligandu organicznego. Wybór odpowiedniego przenośnika zależy przede wszystkim od warunków separacji. Tabela 2 zawiera najczęściej stosowane przenośniki jonów w PIM, zestawienie sporządzone na podstawie dostępnej literatury.

Tabela 2. Charakterystyka stosowanych przenośników jonów w PIM

Nośnik	**Separowane metale**	**Literatura**
Pochodne 1-imidazolu	Zn(II), Cu(II), Cd(II), Ni(II)	[Ulewicz i Radzymińska-Lenarcik 2011]
Pochodne β-diketonów	Co (II), Ni (II), Cu (II), Zn (II)	[Radzymińska-Lenarcik i in. 2017]
Cyphos IL 101	Cd(II, Co(II), Ni(II)	[Pośpiech 2015]
TDPNO oraz TOA	Cd(II), Cr(VI), Zn(II)	[Kozłowski i in. 2002]
Kwas di(2-etyloheksylo) fosforowego (D_2EHPA)	Cr (III)Mn (II), Ni (II), Co (II), Cu (II)	[Rajewski i in. 2015] [Pośpiech i Walkowiak 2010]

Pochodne 1-alkiloimidazoli można stosować, np. do separacji jonów miedzi(II) z równomolowej mieszaniny Cu(II), Zn(II), Co(II) oraz Ni(II) w wyniku transportu przez ciekłą membranę PIM. Na podstawie badań M. Ulewicz i E. Radzymińskiej-Lenarcik stwierdziły, że wraz z wydłużeniem podstawnika w pierścieniu imidazolowym początkowy strumień jonów wzrasta, a współczynniki separacji maleją. Autorki potwierdziły, iż membrany PIM z pochodnymi 1-alkiloimidazoli jako przenośnikami jonów wykazują dużą stabilność, dzięki czemu można je wykorzystać do separacji jonów [Ulewicz i Radzymińska-Lenarcik 2011].

W przypadku użycia pochodnych β-diketonów jako nośników jonów metali polimerowych membranach inkluzyjnych badania potwierdzają zależność selektywności transportu od budowy cząsteczki przenośnika. Ponadto badania wykazały malejącą selektywność transportu w szeregu Zn(II)>Cu(II)>Co(II)>Ni(II) [Radzymińska-Lenarcik i in. 2017].

Kolejnym nośnikiem wykorzystywanym PIM jest chlorek triheksy(tetradecyl)fosfoniowny (Cyphol IL 101) stosowany do separacji jonów kadmu(II), kobaltu(II) oraz niklu(II). Badania potwierdzają skuteczność zastosowania PIM z Cyphos IL 101 do separacji tych jonów z roztworu kwasu chlorowodorowego [Pośpiech 2015].

Kozłowski C. i współautorzy na podstawie wyników badań dotyczących odzysku jonów metali cynku, kadmu oraz chromu z kwaśnych roztworów wodnych za pomocą polimerowej membrany inkluzyjnej potwierdzili skuteczność tej metody. Autorzy jako nośnika użyli N-tlenek-4-(1'-n-trececylo)pirydyny (TDPNO) oraz tri-n-oktyloaminę (TOA), dzięki czemu uzyskano odzysk jonów metali w kolejności: Zn(II)<Cd(II)<Cr(VI). Ponadto badania potwierdziły słuszność zastosowania TOA w celu efektywnego usuwania chromu(VI) ze ścieków galwanicznych tj. 99% [Kozłowski i in. 2002].

Stosuje się również polimerowe membrany inkluzyjne zawierająca D_2EHPA jako przenośnik jonów, ponieważ pozwalają one na efektywne wydzielanie jonów chromu(III) z wodnych roztworów. Wydajność transportu jonów chromu zależy przede wszystkim od stężenia przenośnika w membranie. Badania potwierdzają możliwość wykorzystania PIM m.in. do separacji jonów Cr(III) z próbek środowiskowych [Rajewski i in. 2015]. Ponadto kwas D_2EHPA można stosować jako nośnik w celu selektywnego usuwania żelaza(III) z kwaśnych roztworów wodnych zawierających roztwory Mn(II), Ni(II), Co(II) i Cu(II), gdzie współczynnik selektywności zależy od stężenia ekstrahenta w fazie organicznej [Pośpiech i Walkowiak 2010].

5. SPEKTROMETRIA MAS I TANDEMOWA SPEKTROMETRIA MAS

Proces wiązania jonów metalu z przenośnikami wewnątrz PIM można przeanalizować za pomocą metod spektrometrii mas oraz tandemowej spektrometrii mas. Metody te dają możliwość uzyskania szczegółowych informacji dotyczących struktury badanych związków.

Spektrometria mas (MS) jest narzędziem analitycznym wykorzystywanym do pomiaru masy cząsteczkowej oraz analizy związków organicznych. Jest metodą bardzo czułą umożliwiającą wykonywanie pomiarów przy bardzo niskich stężeniach analizowanych substancji.

Natomiast tandemowa spektrometria mas (oznaczana symbolem MS/MS lub MS^2) polega na przeprowadzeniu kontrolowanego rozpadu jonów badanego związku i dalszej analizie masy otrzymanych fragmentów (tj. stosunku masy do ładunku jonów m/z) [McLafferty 1983].

Początkowo tandemowa spektrometria mas była stosowana w celu identyfikacji oraz ustalenia struktury prostych związków chemicznych dostarczając informacji o budowie i rodzaju jonów fragmentacyjnych i sposobie ich powiązania. Obecnie znanych jest wiele metod fragmentacji jonów, które można stosować z wykorzystaniem tandemowego spektrometru mas. Wybór odpowiedniej metody zależy przede wszystkim od właściwości badanego związku oraz od budowy i parametrów spektrometru mas [Witt i in. 2015].

Jedną z często wykorzystywanych metod fragmentacji jest dysocjacja spowodowana zderzeniem badanego jonu z cząsteczkami gazów obojętnych (azot, argon). Na skutek zderzenia następuje wzrost energii wewnętrznej, co prowadzi do fragmentacji jonu, jest to tzw. metoda CID (ang. *Collision Induced Dissociation*) bądź CAD (*Collision Activated Dissociation*) [Witt i in. 2015]. Metoda CID może być wykorzystywana w większości spektrometrów mas ze względu na małe wymagania techniczne. Jednak w przypadku analizy złożonych cząsteczek np. białek lub peptydów zastosowanie wyłącznie metody CID nie prowadzi do uzyskania pełnych danych na temat ich budowy [Leymarie i in. 2002].

Dużym zainteresowaniem cieszy się również metoda ECD (ang. *Electron Capture Dissociation*) stosowana w przypadku analizy różnego rodzaju biomolekuł. W metodzie ECD jony analitu zderzają się z elektronami o niskiej energii, rzędu < 0,2 eV [Cooper i in. 2014]. Metoda ECD może być wykorzystywana do analizy struktury białek, budowy polimerów oraz dendrymerów.

Do jonizacji badanych substancji wykorzystuje się różne metody, z których w ostatnich latach szczególnie dużą popularnością cieszy się łagodna technika jonizacji nazywana elektrorozpylaniem (ESI, ang. *Electrospray Ionisation*) [Han i Gross 2018]. Połączenie techniki elektrorozpylania z wysokorozdzielczą oraz tandemową spektrometrią mas może być z wykorzystywane do badania budowy kompleksów utworzonych przez jony metali ze związkami organicznymi stosowanymi jako przenośniki jonów w polimerowych membranach inkluzyjnych [Witt i in. 2015]. Zrozumienie mechanizmu tworzenia takich kompleksów jest niezwykle istotne, ponieważ wiedza na temat parametrów wpływających na sposób koordynacji jonów metali z ligandami membrany jest niezbędna w badaniach mających na celu zwiększenie efektywności PIM.

6. PODSUMOWANIE

Procesy separacji oraz selektywnego wydzielania jonów metali z wodnych roztworów stanowią bardzo ważny problem technologiczny. Ze względów ekonomicznych oraz ekologicznych ważnym zadaniem stało się poszukiwanie skuteczniejszych oraz praktyczniejszych metod rozdziału [Rajewski i in. 2015].

Praca przedstawia możliwości zastosowania polimerowych membran inkluzyjnych oraz ich krótką charakterystykę. PIM skutecznie wykorzystuje się w celu zredukowania zawartości jonów metali w różnych roztworach, w tym przemysłowych.

Obecnie prowadzone badania nad PIM dotyczą głównie procesu transportu jonów przez membranę oraz efektywności i selektywności tego rozwiązania w procesie odzysku metali nieżelaznych. Procesy te są już dosyć dobrze znane, jednak ciągle prowadzi się badania mające zwiększyć efektywność PIM oraz zakres ich stosowania.

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(54) **Sposób odzyskiwania miedzi(II) z kwaśnych roztworów, zwłaszcza z roztworów odpadowych i potrawiennych**

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Opis wynalazku

Przedmiotem wynalazku jest sposób odzyskiwania miedzi(II) z kwaśnych roztworów, zwłaszcza z roztworów odpadowych i potrawiennych.

Miedź jest szeroko stosowana w przemyśle, dzięki swoim właściwościom miedź można znaleźć w materiałach elektrycznych, budownictwie, transporcie oraz w maszynach przemysłowych.

Obserwowany w ostatnich latach znaczący rozwój przemysłu z jednej strony wpływa na poprawę naszego codziennego życia, z drugiej zaś wpływa na degradację środowiska naturalnego. Zakłady przemysłowe generują dużą ilość ścieków. Według Głównego Urzędu statystycznego w 2017 roku w Polsce powstało 7 243,1 hm^3 ścieków przemysłowych. Najwięcej nieoczyszczonych ścieków wygenerowało górnictwo i wydobywanie (105,6 hm^3) oraz przetwórstwo przemysłowe (26,9 hm^3) (GUS, 2018. Ochrona Środowiska 2018, Environment 2018). Na szczególną uwagę zasługują ścieki przemysłu ciężkiego oraz przemysłu galwanicznego, ponieważ mogą zawierać m.in. miedź.

W wielu procesach przemysłowych, szczególnie w procesach galwanicznych po procesie miedziowania powstają roztwory odpadowe i potrawienne zawierające miedź(II). Szczególne problemy stwarzają kwaśne odpadowe i potrawienne roztwory zawierające miedź(II), ponieważ wymagają oczyszczania przed wprowadzeniem ich do kanalizacji komunalnej. Natomiast z uwagi na szerokie zastosowania miedzi oraz jej wartość rynkową powinno dążyć się do odzysku miedzi znajdującej się w tego rodzaju roztworach.

Z polskiego opisu patentowego nr PL 105481 znany jest sposób oddzielania miedzi z kwaśnych roztworów wodnych za pomocą ekstrakcji ciecz-ciecz, w której ekstrahentem jest rozpuszczalnik organiczny i rozpuszczony w nim hydroksy-oksym o wzorze ogólnym A-C(=NOH)-R (w którym R oznacza atom wodoru lub grupę alifatyczną, A oznacza grupę aromatyczną podstawioną grupą hydroksylową przy pierścieniowym atomie węgla w pozycji 2, przy czym pozycja 1 odnosi się do pierścieniowego atomu węgla, z którym połączona jest grupa -C(=NOH)-R).

Innym znanym sposobem odzyskiwania miedzi jest sposób opisany w polskim opisie patentowym nr PL 108918, który polega na ekstrakcji jonów miedzi(II) na drodze ekstrakcji rozpuszczalnikowej z wodnego roztworu zasilającego zawierającego miedź i żelazo, który polega na kontaktowaniu roztworu zasilającego z fazą organiczną, która zawiera kompozycje reagentową obejmującą ekstrahent hydroksyarylooksymowy. Jony miedzi przechodzą do fazy organicznej podczas ekstrakcji miedzi z wodnego roztworu zasilającego. Kontaktowanie roztworu zasilającego z fazą organiczną zachodzi w co najmniej jednym etapie ekstrakcji obejmującym mieszalnik-odstojnik i co najmniej w jednym etapie usuwania z otrzymaniem obciążonego miedzią elektrolitu, z którego jest wydzielana autolitycznie miedź. Sposób charakteryzuje się tym, że fazę organiczną zawierającą miedź przemywa się, przed usunięciem z niej miedzi, wodnym roztworem myjącym zawierającym przynajmniej część elektrolitu.

Kolejnym znanym sposobem odzyskiwania miedzi jest sposób ujawniony w międzynarodowym zgłoszeniu patentowym nr WO03054237, w którym proces ekstrakcji metali, szczególnie miedzi odbywa się poprzez kontakt kwasowego roztworu z kompozycją ekstrakcyjną rozpuszczalnika zawierającą niemieszający się z wodą rozpuszczalnik organiczny i ekstrahent, charakteryzujący się tym, że kompozycja ekstrakcyjna zawiera niemieszający się z wodą rozpuszczalnik organiczny, najlepiej o niskiej zawartości węglowodorów aromatycznych i ekstrahent stanowiący 4-acylo-(3H)-pirazol-3-on.

Z brytyjskiego opisu zgłoszeniowego nr GB2413552 znane jest zastosowanie 2-hydroksy-3-n-alkilobenzaldoksymów posiadających alkilowe łańcuchy boczne o liczbie atomów węgla w zakresie od C6 do C10, które są zsyntetyzowane z kwasów tłuszczowych. Sposób według tego wynalazku znajduje zastosowanie do odzysku miedzi ze źródeł mineralnych i odpadów.

Z artykułu naukowego autorstwa Yunhui Zhai, Qun He, Quan Han i Shu’e Duan (Microchim Acta (2012) 178:405–412) znana jest metoda selektywnej ekstrakcji miedzi(II) i cynku(II) do fazy stałej z wykorzystaniem nanocząstek o zewnętrznej powłoce modyfikowanej 2,6-diaminopirydyną. Według opisanego w tym artykule sposobie ekstrakcji, zastosowane nanocząstki wykazują właściwości magnetyczne i są mieszane z roztworem zawierającym jony Cu^{2+} i Zn^{2+} o pH równym 7. Po 5 minutach mieszania wspomaganego ultradźwiękami, prowadzi się desorpcję jonów za pomocą kwasu solnego.

Celem wynalazku jest opracowanie sposobu odzyskiwania miedzi(II) o wysokiej wydajności i selektywności z kwaśnych roztworów, zwłaszcza z roztworów odpadowych i potrawiennych.

Istotą wynalazku jest sposób charakteryzujący się tym, że pH roztworu doprowadza się do wartości 5,8 alkalizując roztwór za pomocą amoniaku albo zakwaszając roztwór za pomocą kwasu azotowego(V). Następnie do roztworu dodaje się ekstrahent będący roztworem 2,6-bis(4-metoksybenzoilo)-diaminopirydyny w chloroformie. Przy czym stosunek molowy roztworu ekstrahowanego do ekstrahentu wynosi od 1:100 do 1:1000. A tak uzyskaną mieszaninę ekstrahuje się przez 0,5–1,0 godziny, poprzez intensywne mieszanie w zakresie od 200 obr./min. do 300 obr./min., w temperaturze od 20°C do 30°C. Następnie w znany sposób oddziela się fazę wodną od fazy organicznej, a fazę organiczną zawierającą jony miedzi(II) poddaje się procesowi wydzielania tego jonu.

Korzystnie, gdy roztwór amoniaku ma stężenie od 0,15 M do 0,25 M, korzystnie, gdy roztwór amoniaku ma stężenie 0,2 M.

Korzystnie, gdy kwas azotowy(V) ma stężenie od 0,01 M do 0,05 M, korzystnie, gdy kwas azotowy(V) ma stężenie 0,02 M.

Korzystnie, gdy stosunek molowy roztworu ekstrahowanego do ekstrahentu wynosi 1:1000.

Korzystnie, gdy mieszaninę ekstrahuje się przez 1 godzinę.

Korzystnie, gdy mieszaninę miesza się intensywne z prędkością 240 obr./min.

Korzystnie, gdy mieszaninę miesza się intensywne w temperaturze 25°C.

Sposób według wynalazku pozwala na szybki i wysoce wydajny odzysk miedzi(II) z kwaśnych roztworów, zwłaszcza z roztworów odpadowych i potrawiennych za pomocą 2,6-bis(4-metoksybenzoilo)-diaminopirydyny. Dzięki sposobowi według wynalazku uzyskuje się wysoki odzysk miedzi(II), tj. stosowanie 2,6-bis(4-metoksybenzoilo)-diaminopirydyny o stężeniu równym 0,0001 M pozwala na uzyskanie 91% odzysku jonów miedzi(II), a dla stężenia równego 0,001 M odzysk tego metalu wynosi 99%. W przypadku stosowania 2,6-diaminopirydyny o stężeniu równym 0,001 M i 0,0001 M odzysk jonów miedzi(II) wynosi odpowiednio 83% i 3%, co oznacza, że 10-krotne zmniejszenie stężenia 2,6-diaminopirydyny powoduje drastyczny spadek wydajności ekstrakcji jonów miedzi(II).

Wynalazek ilustrują następujące przykłady wykonania.

Przykład I

Syntezę 2,6-bis(4-metoksybenzoilo)-diaminopirydyny przeprowadzono w następujących etapach, zgodnie z opisem przedstawionym w artykule opublikowanym w Journal of Organic Chemistry 2013. 78, 7582–7593.

Do mechanicznie mieszanego roztworu 2,6-diaminopirydyny z trietyloaminą (w stosunku molowym równym 1:3) w tetrahydrofuranie w temperaturze 4°C dodawano kroplami roztwór chlorku 4-metoksybenzoilu w tetrahydrofuranie przez 15 minut. Następnie tak otrzymany roztwór mieszano przez noc, a potem ten roztwór odparowano i przemyto mieszaniną chloroform-woda. Potem warstwa chloroformowa została przemyta wodą, a następnie wysuszona za pomocą $MgSO_4$ i pozostawiona do odparowania. Uzyskaną pozostałość rekrystalizowano z mieszaniny tetrahydrofuranu i heksanu.

Tak uzyskany związek został poddany analizie elementarnej oraz analizie strukturalnej NMR. Analiza elementarna potwierdziła procentową zawartość węgla, wodoru, azotu i tlenu (zawartość teoretyczna (%): C: 66,8, H: 5,07, N: 11,13, O: 16.96. zawartość zmierzona (%): C: 66,75, H: 5,21, N: 10.98). Analiza strukturalna NMR potwierdziła, że otrzymanym związkiem jest 2,6-bis(4-metoksybenzoilo)-diaminopirydyna. Wyniki analizy strukturalnej NMR są następujące: (1H, TMS, DMSO) 10,35 (2H, bs), 8,00 (4H, d, J=8,8Hz), 7,85 (3H, m), 7,05 (4H, d, J=8,8Hz), 3,83 (6H, s); (13C,TMS, DMSO) 165,5, 162,7, 151,1, 140,3, 130,3, 126,6, 114,2, 111,0, 55,9: (15N, NH3, DMSO 55,8, 114,4, 130,4. Wyznaczono również temperaturę topnienia uzyskanego związku i wynosiła ona 276–278°C.

W celu przeprowadzenia procesu ekstrakcji jonów miedzi(II) z roztworu za pomocą 2,6-bis(4-metoksybenzoilo)-diaminopirydyny konieczne było sporządzenie dwóch roztworów: wodnego i organicznego. Roztwór wodny sporządzono przez rozpuszczenie w wodzie soli $Cu(NO_3)_2$ oraz dodanie wody amoniakalnej, tak aby stężenia jonów miedzi(II) oraz amoniaku wynosiły odpowiednio 0,1 M i 0,2 M, a pH roztworu miało wartość 5,8. Amoniak został dodany do roztworu w celu utrzymania stałego pH podczas procesu ekstrakcji i uniknięcia strącania się wodorotlenku miedzi(II) w wyniku reakcji hydrolizy, która zachodzi przy pH powyżej 7.5. Roztwór organiczny sporządzono przez rozpuszczenie odpowiedniej ilości 2,6-bis(4-metoksybenzoilo)-diaminopirydyny w chloroformie, tak aby jej stężenie było równe 0,001 M.

Następnie do pięciu wyskalowanych probówek dodano po 4,5 cm^3 wcześniej sporządzonego roztworu wodnego uzyskując w ten sposób fazę wodną. Do tych samych probówek wprowadzono następnie różne objętości wcześniej przygotowanego roztworu organicznego oraz chloroformu tak, aby obję tość fazy organicznej równała się objętości fazy wodnej. Stężenia 2,6-bis(4-metoksybenzoilo)-diaminopirydyny w przygotowanych próbach wynosiły odpowiednio 0,00010, 0,00025, 0,0005, 0,00075, 0,00100 M. Probówki umieszczono w wytrząsarce i wytrząsano z prędkością 240 obr./min. w temperaturze 25°C przez 1 godzinę.

Następnie sprawdzono, czy zaszły jakiekolwiek zmiany objętości faz, po czym fazę wodną oddzielono od fazy organicznej. Za pomocą pehametru zmierzono pH fazy wodnej. Natomiast stężenie jonów miedzi(II) w fazie wodnej określono za pomocą atomowej spektrometrii mas.

Procentową ekstrakcję miedzi(II) obliczono, korzystając z równania 1:

$$\%E_{Cu(II)} = \frac{D_{Cu(II)} \cdot 100\%}{D_{C(II)} + \frac{V_{aq}}{V_{org}}} \qquad (1)$$

gdzie: $\%E_{Cu(II)}$ oznacza procentową ekstrakcję miedzi(II); $D_{Cu(II)}$ oznacza stosunek rozkładu jonów Cu(II) pomiędzy fazami; V_{aq} oraz V_{org}oznacza odpowiednio objętość fazy wodnej oraz organicznej.

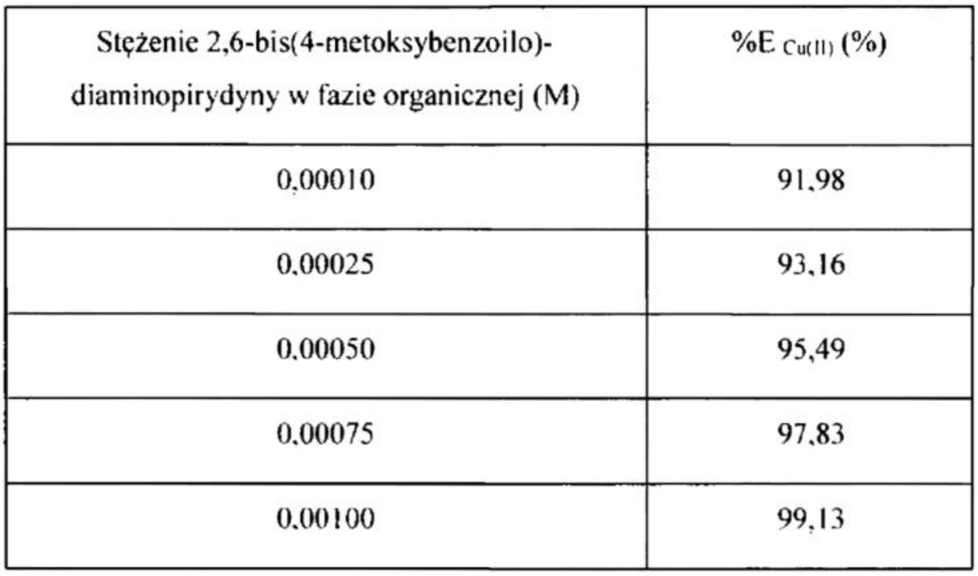
Stosunek rozkładu jonów metalu ($D_{Cu(II)}$) ujęty we równaniu (1) obliczono na podstawie równania (2):

$$D_{Cu(II)} = \frac{C_{Cu(II)(org)}}{C_{Cu(II)(aq)}} = \frac{C^0_{Cu(II)} - C_{Cu(II)}}{C_{Cu(II)(aq)}} \qquad (2)$$

gdzie: $D_{Cu(II)}$ oznacza stosunek rozkładu miedzi(II), $C^0_{Cu(II)}$ oznacza początkowe stężenie jonów miedzi(II); $C_{Cu(II)(org)}$) oznacza stężenie jonów miedzi(II) w fazie organicznej po procesie ekstrakcji; $C_{Cu(II)(aq)}$ oznacza stężenie jonów miedzi(II) w fazie wodnej po procesie ekstrakcji.

Tabela 1 przedstawia zależność pomiędzy procentowym odzyskiem jonów miedzi(II) a stężeniem 2,6-bis(4-metoksybenzoilo)-diaminopirydyny w fazie organicznej.

Tabela 1. Zależność pomiędzy stężeniem 2,6-bis(4-metoksybenzoilo)-diaminopirydyny w fazie organicznej a procentowym odzyskiem jonów miedzi(II)



Stężenie 2,6-bis(4-metoksybenzoilo)-diaminopirydyny w fazie organicznej (M)	$\%E_{Cu(II)}$ (%)
0,00010	91,98
0,00025	93,16
0,00050	95,49
0,00075	97,83
0,00100	99,13

Najwyższy procent ekstrakcji miedzi(II) wynoszący 99,13% otrzymano dla stężenia miedzi(II) w fazie organicznej równego 0,00100 M, natomiast najniższy $\%E_{Cu(II)}$ zaobserwowano dla stężenia miedzi(II) równego 0,0001 M.

Porównano procent ekstrakcji miedzi(II) z wykorzystaniem 2,6-bis(4-metoksybenzoilo)-diaminopirydyny i znanego w stanie techniki ekstrahentu – 2,6-diaminopirdyny. W tabeli 2 przedstawiono zależność pomiędzy procentowym odzyskiem jonów miedzi(II), a stężeniem 2,6-diaminopirydyny w fazie organicznej.

Tabela 2. Zależność pomiędzy stężeniem 2,6-diaminopirydyny w fazie organicznej a procentowym odzyskiem jonów miedzi(II)

Stężenie 2,6-diaminopirydyny w fazie organicznej (M)	%$E_{Cu(II)}$ (%)
0,00010	3,09
0,00025	36,32
0,0005	42,25
0,00075	62,45
0,00100	83,53

Najwyższy procent ekstrakcji miedzi (83,53%) otrzymano dla stężenia ekstrahenta 0,00100 M w fazie organicznej, natomiast najniższy %$E_{Cu(II)}$ (3,09%) zaobserwowano dla stężenia 0,00010 M. Uzyskane wyniki powyższych badań potwierdzają, że sposób wg wynalazku umożliwia wyższy odzysk jonów miedzi(II) z kwaśnych roztworów niż zastosowanie znanego w stanie techniki sposobu ekstrakcji ciecz-ciecz z wykorzystaniem 2,6-diaminopirydyny.

Przykład II

Do przeprowadzenia ekstrakcji ciecz-ciecz użyto 2,6-bis(4-metoksybenzoilo)-diaminopirydynę otrzymaną jak w przykładzie I. Do kwaśnego elektrolitu, otrzymanego po procesie miedziowania o stężeniu miedzi(II) równym 0,001 M i o pH równym 4,0 dodano amoniak o stężeniu 0,15 M alkalizując roztwór do pH równego 5,8. Przed ekstrakcją wyznaczono zawartość miedzi(II) w roztworze kwaśnego elektrolitu za pomocą absorpcyjnej spektrometrii atomowej. Następnie do roztworu dodano ekstrahent będący roztworem 2,6-bis(4-metoksybenzoilo)-diaminopirydyny w chloroformie, tak, że stosunek molowy roztworu ekstrahującego do ekstrahentu wynosi od 1:100. Mieszaninę ekstrahowano przez 30 minut intensywnego mieszania z prędkością 200 obr./min w temperaturze 20°C. Następnie oddzielono fazę wodną od organicznej w znany sposób tj. w rozdzielaczu, kolejno przeprowadzono reekstrakcję jonów miedzi(II) z fazy organicznej przy pomocy kwasu azotowego(V). Uzyskany roztwór po reekstrakcji stanowił 0,01 M roztwór miedzi(II).

Przykład III

Do przeprowadzenia ekstrakcji ciecz-ciecz użyto 2,6-bis(4-metoksybenzoilo)-diaminopirydynę otrzymaną jak w przykładzie I. Do kwaśnego roztworu odpadowego miedzi(II) o stężeniu równym 0.0025 M i o pH równym 6,0 otrzymanego po miedziowaniu metodą galwanizacji dodano kwas azotowy(V) o stężeniu 0,01 M zakwaszając ten roztwór do pH równego 5,8. Następnie do roztworu dodano ekstrahent będący roztworem 2,6-bis(4-metoksybenzoilo)-diaminopirydyny w chloroformie, tak, że stosunek molowy roztworu ekstrahującego do ekstrahentu wynosił od 1:500. Mieszaninę ekstrahowano przez 45 minut intensywnego mieszania z prędkością 240 obr./min. W temperaturze 25°C. Następnie oddzielono w znany sposób fazę wodną od fazy organicznej tj. w rozdzielaczu, kolejno przeprowadzono reekstrakcję przy użyciu kwasu azotowego(V). Uzyskany roztwór po reekstrakcji stanowił 0,01 M roztwór miedzi(II).

Przykład IV

Do przeprowadzenia ekstrakcji ciecz-ciecz użyto 2.6-bis(4-metoksybenzoilo)-diaminopirydynę otrzymaną jak w przykładzie I. Do kwaśnego roztworu potrawiennego, po trawieniu elektrolitycznym o stężeniu miedzi(II) równym 0,005 M i o pH równym 3,5 dodano amoniak o stężeniu 0,2 M alkalizując ten roztwór do pH równego 5,8. Następnie do roztworu dodano ekstrahent będący roztworem 2,6-bis(4-metoksybenzoilo)-diaminopirydyny w chloroformie, tak, że stosunek molowy roztworu ekstrahującego do ekstrahentu wynosi od 1:1000. Mieszaninę ekstrahowano przez 60 minut intensywnego mieszania z prędkością 300 obr./min w temperaturze 30°C. Następnie oddzielono w znany sposób fazę wodną od fazy organicznej tj. w rozdzielaczu, kolejno przeprowadzono reekstrakcję przy użyciu kwasu azotowego(V). Uzyskany roztwór po reekstrakcji stanowił 0,006 M roztwór miedzi(II).

Przykład V

Do przeprowadzenia ekstrakcji ciecz-ciecz użyto 2,6-bis(4-metoksybenzoilo)-diaminopirydynę otrzymaną jak w przykładzie I. Do mieszaniny kwaśnego roztworu potrawiennego i odpadowego użytych w przykładzie III i IV o stężeniu miedzi(II) równym 0,00625 M i o pH równym 5,0 dodano amoniak o stężeniu 0,25 M alkalizując ten roztwór do pH równego 5,8. Następnie do roztworu dodano ekstrahent będący roztworem 2,6-bis(4-metoksybenzoilo)-diaminopirydyny w chloroformie, tak, że stosunek molowy roztworu ekstrahującego do ekstrahentu wynosi od 1 : 1000. Mieszaninę ekstrahowano przez 60 minut intensywnego mieszania z prędkością 300 obr./min. w temperaturze 30 °C. Następnie oddzielono w znany sposób fazę wodną od fazy organicznej tj. w rozdzielaczu, kolejno przeprowadzono reekstrakcję przy użyciu kwasu azotowego(V). Uzyskany roztwór po reekstrakcji stanowił 0,0075 M roztwór miedzi(II).

Przykład VI

Do przeprowadzenia ekstrakcji ciecz-ciecz użyto 2,6-bis(4-metoksybenzoilo)-diaminopirydynę otrzymaną jak w przykładzie I. Do kwaśnego roztworu odpadowego będącego zużytymi roztworami popłucznymi między kąpielami galwanicznymi o stężeniu miedzi(II) równym 0,0075 M i o pH równym 6,0 dodano kwas azotowy(V) o stężeniu 0,02 M zakwaszając ten roztwór do pH równego 5,8. Następnie do roztworu dodano ekstrahent będący roztworem 2,6-bis(4-metoksybenzoilo)-diaminopirydyny w chloroformie, tak, że stosunek molowy roztworu ekstrahującego do ekstrahentu wynosi od 1:750. Mieszaninę ekstrahowano przez 45 minut intensywnego mieszania z prędkością 300 obr./min w temperaturze 25°C. Następnie oddzielono w znany sposób fazę wodną od fazy organicznej tj. w rozdzielaczu, kolejno przeprowadzono reekstrakcję przy użyciu kwasu azotowego(V). Uzyskany roztwór po reekstrakcji stanowił 0,011 M roztwór miedzi(II).

Przykład VI

Do przeprowadzenia ekstrakcji ciecz-ciecz użyto 2,6-bis(4-metoksybenzoilo)-diaminopirydynę otrzymaną jak w przykładzie I. Do kwaśnego roztworu odpadowego będącego zużytymi kąpielami galwanicznymi o stężeniu miedzi(II) równym 0,01 M i o pH równym 6,0 dodano kwas azotowy(V) o stężeniu 0,05 M zakwaszając ten roztwór do pH równego 5,8. Następnie do roztworu dodano ekstrahent będący roztworem 2,6-bis(4-metoksybenzoilo)-diaminopirydyny w chloroformie, tak, że stosunek molowy roztworu ekstrahującego do ekstrahentu wynosi od 1:250. Mieszaninę ekstrahowano przez 60 minut intensywnego mieszania z prędkością 240 obr./min w temperaturze 25°C. Następnie oddzielono w znany sposób fazę wodną od fazy organicznej tj. w rozdzielaczu, kolejno przeprowadzono reekstrakcję przy użyciu kwasu azotowego(V). Uzyskany roztwór po reekstrakcji stanowił 0.04 M roztwór miedzi(II).

Przykład VII

Do przeprowadzenia ekstrakcji ciecz-ciecz użyto 2,6-bis(4-metoksybenzoilo)-diaminopirydynę otrzymaną jak w przykładzie I. Do kwaśnego roztworu odpadowego po usuwaniu zgorzeliny przed procesem nakładania powłok galwanicznych o stężeniu miedzi(II) równym 0,01 M i o pH równym 6,5 dodano kwas azotowy(V) o stężeniu 0,02 M zakwaszając ten roztwór do pH równego 5,8. Następnie do roztworu dodano ekstrahent będący roztworem 2,6-bis(4-metoksybenzoilo)-diaminopirydyny w chloroformie, tak, że stosunek molowy roztworu ekstrahującego do ekstrahentu wynosi od 1:100. Mieszaninę ekstrahowano przez 60 minut intensywnego mieszania z prędkością 240 obr./min w temperaturze 25°C. Następnie oddzielono w znany sposób fazę wodną od fazy organicznej tj. w rozdzielaczu, kolejno przeprowadzono reekstrakcję przy użyciu kwasu azotowego(V). Uzyskany roztwór po reekstrakcji stanowił 0,1 M roztwór miedzi(II).

Przykład VIII

Do przeprowadzenia ekstrakcji ciecz-ciecz użyło 2,6-bis(4-metoksybenzoilo)-diaminopirydynę otrzymaną jak w przykładzie I. Do kwaśnego roztworu elektrolitu o stężeniu miedzi(II) równym 0,1 M i o pH równym 1,5 dodano amoniak, o stężeniu 0,4 M alkalizując ten roztwór do pH równego 5.8. Następnie do roztworu dodano ekstrahent będący roztworem 2,6-bis(4-metoksybenzoilo)-diaminopirydyny w chloroformie, tak, że stosunek molowy roztworu ekstrahującego do ekstrahentu wynosi od 1:100. Mieszaninę ekstrahowano przez 60 minut intensywnego mieszania z prędkością 240 obr./min w temperaturze 25°C. Następnie oddzielono w znany sposób fazę wodną od fazy organicznej tj. w rozdzielaczu, kolejno przeprowadzono reekstrakcję przy użyciu kwasu azotowego(V). Uzyskany roztwór po reekstrakcji stanowił 1 M roztwór miedzi(II).

Zastrzeżenia patentowe

1. Sposób odzyskiwania miedzi(II) z kwaśnych roztworów, zwłaszcza z roztworów odpadowych i potrawiennych, **znamienny tym**, że pH roztworu doprowadza się do wartości 5,8 alkalizując roztwór za pomocą amoniaku albo zakwaszając roztwór za pomocą kwasu azotowego(V). następnie, do roztworu dodaje się ekstrahent będący roztworem 2,6-bis(4-metoksybenzoilo)-diaminopirydyny w chloroformie, przy czym stosunek molowy roztworu ekstrahowanego do ekstrahentu wynosi od 1:100 do 1:1000, a tak uzyskaną mieszaninę ekstrahuje się przez 0,5–1,0 godziny, poprzez intensywne mieszanie w zakresie od 200 obr./min. do 300 obr./min., w temperaturze od 20°C do 30°C, następnie w znany sposób oddziela się fazę wodną od fazy organicznej, a, fazę organiczną zawierającą jony miedzi(II) poddaje się procesowi wydzielania tego jonu.
2. Sposób według zastrz. 1, **znamienny tym**, że roztwór amoniaku ma stężenie od 0,15 M do 0,25 M.
3. Sposób według zastrz. 2, **znamienny tym**, że roztwór amoniaku ma stężenie 0,2 M.
4. Sposób według zastrz. 1, **znamienny tym**, że kwas azotowy(V) ma stężenie od 0,01 M do 0,05 M.
5. Sposób według zastrz. 4, **znamienny tym**, że kwas azotowy(V) ma stężenie 0,02 M.
6. Sposób według zastrz. 1, **znamienny tym**, że stosunek molowy roztworu ekstrahowanego do ekstrahentu wynosi 1:1000.
7. Sposób według zastrz. 1, **znamienny tym**, że mieszaninę ekstrahuje się przez 1 godzinę.
8. Sposób według zastrz. 1, **znamienny tym**, że mieszaninę miesza się intensywnie z prędkością 240 obr./min.
9. Sposób według zastrz. 1, **znamienny tym**, że mieszaninę miesza się intensywnie w temperaturze 25°C.

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Sposób odzyskiwania jonów miedzi(II), niklu(II), kobaltu(II) i cynku(II) z wodnych roztworów

Opis wynalazku

Przedmiotem wynalazku jest sposób odzyskiwania jonów miedzi (II), niklu(II), kobaltu(II) i cynku(II) z wodnych roztworów znajdujący zastosowanie do oczyszczania ścieków poprodukcyjnych, ścieków przemysłowych oraz ścieków z galwanizerni (np. zużyte kąpiele galwaniczne).

W przemyśle miedź jest szeroko stosowana w przewodach miedzianych oraz między innymi do produkcji lamp elektronowych, transformatorów czy elektromagnesów. Z kolei kobalt stosuje się do produkcji elektrod akumulatorów litowo-jonowych, niklowo-kadmowych i niklowo-metalowo-wodorkowych. Natomiast nikiel powszechnie stosuje się jako powłokę galwaniczną, zwiększającą wytrzymałość i odporność na korozję pokrywanych elementów stalowych czy żeliwnych. Podczas, gdy cynk i jego stopy powszechnie stosuje się do ocynkowania płaskich elementów stalowych oraz przy produkcji mosiądzów.

Według Głównego Urzędu Statystycznego w Polsce w 2018 roku wytworzono 115 339 tys. ton odpadów przemysłowych. Odpady przemysłowe często zawierają szereg metali kolorowych, takich jak miedź, nikiel, kobalt czy cynk. Głównym źródłem odpadów przemysłowych w 2018 r. było górnictwo i wydobywanie, przetwórstwo przemysłowe oraz wytwarzanie i zaopatrywanie w energię elektryczną, gaz, parę wodną oraz gorącą wodę. Tylko 51% ogólnej ilości odpadów wytworzonych w 2018 r. poddano odzyskowi, dlatego metody odzysku metali z odpadów zasługują na szczególną uwagę (GUS, 2019. Ochrona środowiska 2019).

Z polskiego patentu nr PL/EP 1613784 znany jest sposób odzysku miedzi(II), niklu(II), kobaltu(II) i cynku(II) za pomocą kompozycji rozpuszczalnikowej zawierającej niemieszający się z wodą rozpuszczalnik organiczny, jeden lub więcej orto-hydroksyaryloaldoksymów i jeden lub więcej orto-hydroksyaryloketoksymów, i jeden lub więcej modyfikatorów równowagi wybranych spośród monoizomaślanu 2,2,4-trimetylo-1,3-pentanodiolu, monobenzoesanu 2,2,4-trimetylo-1,3-pentanodiolu, diizomaślanu 2,2,4-trimetylo-1,3-pentanodiolu, dibenzoesanu 2,2,4-trimetylo-1,3-pentanodiolu, ketonu izobutylowoheptylowego, nonanonu, 2,6,8-trimetylo-4-nonanonu, ketonu diundecylowego, 5,8-dietylododekano-6,7-dionu, tridekanolu, i nonylofenolu w ilości zapewniającej stopień modyfikacji obecnych orto-hydroksyaryloaldoksymów wynoszący od około 0,2 do 0,61.

W polskim patencie nr PL/EP 3068912 opisano sposób odzyskiwania kobaltu(II) i miedzi(II). Sposób ten składa się z siedmiu etapów. Pierwszy z nich obejmuje ługowanie w etapie ługowania materiału wyjściowego w roztworze do ługowania dla uzyskania szlamu po ługowaniu zawierającego miedź, kobalt, żelazo i glin. W drugim etapie pierwsza część miedzi jest ekstrahowana z fazy ciekłej dla uzyskania głównego strumienia miedzi i fazy ciekłej zawierającej żelazo, glin, kobalt i drugą część miedzi. Następnie zachodzi strącanie do kontaktu fazy ciekłej zawierającej żelazo, glin, kobalt i drugą część miedzi ze środkiem strącającym, zazwyczaj węglanem wapnia i/lub wodorotlenkiem wapnia, do strącania żelaza, glinu, kobaltu i drugiej części miedzi obecnych w fazie ciekłej dla uzyskania szlamu zawierającego osad. Kolejnym etapem jest poddawanie szlamu zawierającego osad drugiemu etapowi rozdzielania 10 części stałych i cieczy w celu oddzielenia osadu dla uzyskania osadu części stałych i roztworu zawierającego pozostały kobalt i pozostałą drugą część miedzi, oraz ewentualnie zawracanie oddzielonego osadu do etapu pierwszego ługowania. Potem następuje ekstrahowanie w drugim etapie ekstrakcji pozostałego kobaltu i pozostałej drugiej części miedzi z zawierającego je roztworu, gdzie roztwór ten doprowadza się do kontaktu ze środkiem ekstrakcyjnym zawierającym hydroksyoksym i kwas fosfinowy dla uzyskania roztworu wodnego i roztworu organicznego, w którym to roztworze organicznym miedź jest ekstrahowana do hydroksyoksymu i kobalt jest ekstrahowany do kwasu fosfinowego. W przedostatnim etapie usuwany jest kobalt z roztworu organicznego do roztworu elektrolitu kobaltowego. Ostatnim etapem jest usuwanie miedzi z roztworu organicznego do roztworu elektrolitu miedziowego.

Natomiast z polskiego opisu patentowego nr PL 220727 znany jest sposób selektywnej ekstrakcji jonów cynku(II) z roztworów wodnych stanowiących mieszaninę jonów cynku(II), kadmu(II), jonów chlorkowych oraz innych jonów nieorganicznych. Sposób selektywnej ekstrakcji jonów cynku(II) z roztworów wodnych stanowiących mieszaninę jonów cynku(II), kadmu(II), jonów chlorkowych oraz innych jonów nieorganicznych. Sposób charakteryzuje się tym, że ekstrakcję prowadzi za pomocą roztworów organicznych stanowiących rozcieńczalnik węglowodorowy lub mieszaninę rozcieńczalników węglowodorowych niemieszających się z wodą zawierających od 10 do 70, korzystnie 30 g/dm^3 hydrofobowych oksymów ketonów alkilowo-4-pirydylowych o wzorze 1 (fig. 1), w którym R oznacza prosty lub rozgałęziony łańcuch alkilowy zawierającą od 6 do 17 atomów węgla, oraz dodatek fosforanu tributylu w ilości od 1 do 40, korzystnie 10% objętościowych, przy czym ekstrakcję prowadzi się z roztworu zawierającego co najmniej 0,007 mol/dm^3 Cl$^-$ i nie mniej niż 1,5 mol/dm^3 wszystkich jonów nieorganicznych rozpuszczonych w roztworze wodnym, po czym otrzymane w wyniku ekstrakcji związki kompleksowe cynku(II) rozpuszczone w tym roztworze organicznym rozkłada się za pomocą wody lub wodnym roztworem kwasu mineralnego poprzez mieszanie, a następnie, po rozdzieleniu faz, roztwór wodny zawierający jony cynku(II) i pozbawiony jonów kadmu(II), poddaje się procesom wydzielania metali.

Kolejnym znanym sposobem odzysku jonów cynku(II) za pomocą hydrofobowych oksymów ketonów alkilowo-3-pirydylowych, jest sposób ujawniony w polskim patencie nr PL229733. Wynalazek wg tego patentu dotyczy sposobu selektywnej ekstrakcji jonów cynku(II) z kwaśnych roztworów chlorkowych zawierających jony cynku(II) i/lub miedzi(II) i/lub żelaza(II) i/lub żelaza(III) za pomocą hydrofobowych oksymów ketonów alkilowo-3-pirydylowych. Sposób polega na tym, że ekstrakcję prowadzi się za pomocą roztworów stanowiących rozcieńczalnik organiczny lub mieszaninę rozcieńczalników organicznych niemieszających się z wodą, zawierających od 10 do 140 g/dm^3, korzystnie roztwór 0,3 mol/dm^3 hydrofobowych oksymów ketonów alkilowo-3-pirydylowych o wzorze 2 (fig. 2), w którym R oznacza prosty lub rozgałęziony łańcuch alkilowy zawierający od 6 do 12 atomów węgla, z dodatkiem do 40% objętościowych niemieszającego się z wodą alkoholu o łańcuchu alkilowym prostym lub rozgałęzionym zawierającym od ośmiu do dwunastu atomów węgla, korzystnie dekan-1-ol i z dodatkiem fosforanu tributylu w ilości do 5% objętościowych, przy czym ekstrakcję prowadzi się z roztworu wodnego zawierającego co najmniej 1, korzystnie 4 mol/dm^3 Cl$^-$ i kwasu chlorowodorowego w ilości nie mniejszej niż stężenie molowe oksymu. Otrzymane w wyniku ekstrakcji związki kompleksowe cynku(II) rozpuszczone w tym rozcieńczalniku lub mieszaninie rozcieńczalników rozkłada się za pomocą wodnego roztworu siarczanu(VI) sodu o stężeniu nie mniejszym niż 0,1, korzystnie 0,5 mol/dm^3 poprzez mieszanie, a następnie po rozdzieleniu faz, roztwór wodny zawierający jony cynku(II) i nie zawierający jonów miedzi(II), żelaza(II), żelaza(III) poddaje się procesom wydzielania metali.

W artykule naukowym autorstwa Mądrzak-Litwa i Borowiak-Resterna (I. Mądrzak-Litwa i A. Borowiak-Resterna, „Solvent extraction of copper(II) from chloride solutions using 1,1’-dialkyl-2,2’-bibenzimidazoles as extractants”, Physicochem. Probl. Miner. Process., t. 55, nr 5, s. 1165–1178, 2019) znane jest zastosowanie 1,1’-dialkilo-2,2’-bibenzimidazolu do odzysku jonów miedzi(II) metodą ekstrakcji rozpuszczalnikowej. Stwierdzono, że procent ekstrakcji jonów miedzi(II) wzrasta wraz ze stopniem stężenia jonów metalu i chlorków.

Natomiast z artykułu naukowego autorstwa Tanha, Moftakhar, Yaftin oraz Noshiranzadeh (Z. K. Tanha, M. K. Moftakhar, M. R. Yaftian, i N. Noshiranzadeh, „Selective and Efficient Solvent Extraction of Copper(II) Ions from Chloride Solutions by Oxime Extractants”, Anal. Bioanal. Chem. Res., t. 3, nr 1, s. 53–63, 2016) wynika, że ekstrahenty: oksym 3-tert-butylo-2-hydroksy-5-metylobenzaldehydu oraz oksym 3-tert-butylo-2-hydroksy-5-metoksybenzaldehydu umożliwiają odzysk ponad 95% jonów miedzi(II) z roztworów chlorkowych.

Podczas gdy, znane jest również zastosowanie LIX 84 I, jako ekstrahenta do odzysku jonów miedzi(II), niklu(II) i cynku(II), co zostało opisane w artykule naukowym autorstwa Raddy i Priya (B. R. Reddy i D. N. Priya, „Process development for the separation of copper(II), nickel(II) and zinc(II) from sulphate solutions by solvent extraction using LIX 84 I”, Sep. Purif. Technol., nr 45, s. 163–167, 2005). Proces ekstrakcji jonów miedzi(II), niklu(II) i cynku(II) za pomocą LIX 84 I wykonano przy różnych stosunkach fazy wodnej do organicznej, uzyskując odzysk ponad 99% jonów miedzi(II), niklu(II) i cynku(II).

Z artykułu naukowego Wassink, Dreisinger i Howard (B. Wasink, D. Dreisinger, i J. Howard, „Solvent extraction separation of zinc and cadmium from nickel and cobalt using Aliquat 336, a strong base anion exchanger, in the chloride and thiocyanate forms”, Hydrometallurgy, nr 57, s. 235–252, 2000) wynika, że Aliquat 336 może być skutecznym ekstrahentem do separacji jonów cynku i kadmu od niklu. Stwierdzając, że przy użyciu 30% Aliquat 336 maksymalny transport jonów cynku wynosił 18 g/l, przy zawartości jonów kadmu wynoszącej 28 g/l.

Z kolei z artykułu naukowego Pośpiech i Walkowiak (B. Pośpiech i W. Walkowiak, „Separation of copper(II), cobalt(II) and nickel(II) from chloride solutions by polymer inclusion membranes”, Sep. Purif. Technol., nr 57, s. 461–465, 2007) wynika, że tri-oktyloamina oraz triizooktyloamina w polimerowej membranie inkluzyjnej umożliwia separację jonów miedzi(II) i kobaltu(II). Procent odzysku jonów kobaltu(II) był znacząco wyższy niż jonów miedzi(II), przy zastosowaniu obu nośników (wynosił ponad 90%).

Natomiast z artykułu naukowego Pośpiech (B. Pospiech, „Separation of cadmium(II), cobalt(II) and nickel(II) by transport through polymer inclusion membranes with phosphonium ionic liquid as ion carrier”, Arch. Metall. Mater., t. 60, nr 4, s. 2933–2938, grudz. 2015, doi: 10.1515/amm-2015-0468) wynika, że jony kobaltu(II) i niklu(II) można separować z roztworów chlorkowych za pomocą jonowych cieczy fosfoniowych. Polimerowe membrany inkluzyjne o zawartości 26 % wag. Cyphos IL 101, jako nośnika umożliwiają odzysk po 24 godzinach trwania procesu 21,5% jonów kobaltu(II).

Ponadto z artykułu Ulewicz, Kozłowskiego i Walkowiaka (M. Ulewicz, C. Kozłowski, i W. Walkowiak, „Removal of Zn(II), Cd(II) and Cu(II) ions by polymer inclusion membrane with side-armed diphosphaza-16-crown-6-ether”, Physicochem. Probl. Miner. Process., nr 38, s. 131–138, 2004) wynika, że etery koronowe w polimerowych membranach inkluzyjnych umożliwiają odzysk jonów cynku(II) i miedzi(II) z roztworów chlorkowych (0,5 M HCl). Najwyższe współczynniki odzysku dla jonów miedzi (II) i kobaltu(II) stwierdzono dla układów, gdzie fazę odbiorczą stanowił 0,1 M roztwór octanu amonu.

Celem wynalazku jest opracowanie sposobu odzysku jonów miedzi(II), niklu(II), kobaltu(II) i cynku(II) z wodnych roztworów.

Istotą wynalazku jest sposób, charakteryzujący się tym, że pH roztworu wodnego doprowadza się do wartości wyższej niż 8 alkalizując roztwór za pomocą amoniaku z wykorzystaniem ekstrakcji rozpuszczalnikowej, w której stosunek stężenia molowego ekstrahowanego jonu do stężenia molowego ekstrahentu wynosi w przedziale zawartym od 1 : 1 do 1 : 5, do ekstrahowanego roztworu dodaje się ekstrahent, którym jest 0,001 mol/dm^3 roztwór 2,6-(N,N’-dibenzoilo)-diaminopirydyny w chloroformie albo 0,001 mol/dm^3 roztwór 2,6-bis(4-metylobenzoilo)-diaminopirydyny w chloroformie albo 0,001 mol/dm^3 roztwór 2,6-bis(4-dimetyloaminobenzoilo)-diaminopirydyny w chloroformie, ekstrakcję rozpuszczalnikową prowadzi się w czasie od 15 do 60 minut poprzez intensywne mieszanie z prędkością w zakresie 200–400 obr./min, i w temperaturze w zakresie od 20°C do 25°C, następnie w znany sposób oddziela się fazę wodną od fazy organicznej, po czym fazę organiczną zawierającą jony metali poddaje się procesowi wydzielania znanym sposobem.

Korzystnie, gdy stosunek stężenia molowego ekstrahowanego jonu do stężenia molowego ekstrahentu wynosi 1 : 5.

Korzystnie, gdy ekstrakcję rozpuszczalnikową prowadzi się w czasie od 25 do 60 minut.

Korzystnie, gdy ekstrakcję rozpuszczalnikową prowadzi się poprzez intensywne mieszanie z prędkością 300 obr./min.

Korzystnie, gdy ekstrakcję rozpuszczalnikową prowadzi się poprzez intensywne mieszanie w temperaturze 25°C.

Istotą wynalazku wg drugiej odmiany jest sposób charakteryzujący się tym, że pH roztworu wodnego doprowadza się do wartości wyższej niż 8 alkalizując roztwór za pomocą amoniaku, z wykorzystaniem ekstrakcji membranowej, w której stosunek stężenia molowego ekstrahowanego jonu do stężenia molowego ekstrahentu wynosi 1 : 5, a ekstrahentem jest 2,6-(N,N’-dibenzoilo)-diaminopirydina albo 2,6-bis(4-metylobenzoilo)-diaminopirydyna albo 2,6-bis(4-dimetyloaminobenzoilo)diaminopirydyna, przy czym ekstrakcję przeprowadza się poprzez przygotowanie polimerowej membrany na drodze wylewania poprzez sporządzenie roztworu polichlorku winylu (60% wag.), plastyfikatora (20% wag.) i ekstrahentu (20% wag.) w 10 cm^3 tetrahydrofuranu, następnie roztwór jest mieszany na mieszadle magnetycznym do uzyskania jednorodnej konsystencji, po czym roztwór wylewany jest na samopoziomującą szalkę, a po całkowitym odparowaniu tetrahydrofuranu membranę odkleja się od szalki i umieszcza w wodzie destylowanej na 24 h w celu jej kondycjonowania, a tak przygotowaną membranę zalewa się wodnym roztworem z którego ekstrahowane są jony, a ekstrakcję membranową prowadzi się przez 24 godziny, następnie ekstrahowane jony wydziela się z membrany poprzez zanurzanie w roztworze kwasu azotowego(V), kwasu octowego lub kwasu siarkowego(VI), w wyniku czego otrzymuje się roztwór, który zawiera odzyskane jony.

Korzystnie, gdy plastyfikatorem jest adypianian bis(2-etyluheksylu).

Korzystnie, gdy plastyfikatorem jest ftalan di(2-etyloheksylu).

Korzystnie, gdy ekstrahowane jony wydziela się z membrany poprzez zanurzanie w roztworze kwasu azotowego(V).

Sposób według wynalazku pozwala na szybki oraz wysoce wydajny odzysk miedzi(II), niklu(II), kobaltu(II) i cynku(II) z roztworów wodnych o szerokim zakresie pH za pomocą 2,6-bis(benzoilo-R)diaminopirydyny (R=H, CH_3, $N(CH_3)_2$).

Opis figur rysunku

Fig. 1. Wzór strukturalny hydrofobowych oksymów ketonów alkilowo-4-pirydylowych, R oznacza prosty lub rozgałęziony łańcuch alkilowy zawierającą od 6 do 17 atomów węgla (wzór 1 stanowiący stan techniki).

Fig. 2. Wzór strukturalny hydrofobowych oksymów ketonów alkilowo-3-pirydylowych o wzorze 2, w którym R oznacza prosty lub rozgałęziony łańcuch alkilowy zawierający od 6 do 12 atomów węgla (wzór 2 stanowiący stan techniki).

Fig. 3. Wzór strukturalny 2,6-(N,N'-dibenzoilo)-diaminopirydyny (A1) (wzór 3).

Fig. 4. Wzór strukturalny 2,6-bis(4-metylobenzoilo)-diaminopirydyny (A2) (wzór 4).

Fig. 5. Wzór strukturalny 2,6-bis(4-dimetyloaminobenzoilo)diaminopirydyny (A3) (wzór 5).

Wynalazek zostanie bliżej przedstawiony za pomocą poniższych dwóch przykładów opisujących kolejno jego dwie odmiany.

Przykład I

Odzysk jonów miedzi(II), niklu(II), kobaltu(II) i cynku(II) z roztworów wodnych prowadzono za pomocą pochodnych 2,6-bis(benzoilo-R)diaminopirydyny (R=H, CH_3, $N(CH_3)_2$) o wzorach 3–5 (fig. 3–5). Odzysk prowadzony poprzez ekstrakcję rozpuszczalnikową.

Opis syntezy związków **A1–A3**

A1: 2,6-(N,N'-dibenzoilo)-diaminopirydyna. Roztwór chlorku benzoilu (5,326 g, 50,93 mmol, 2,0 equiv) w suchym tetrahydrofuranie (50 ml) dodano kroplami do zawiesiny 2,6-diaminopirydyny (2,065 g, 18,92 mmol, 1 equiv) w trietyloaminie (7,9 ml, 56,68 mmol, 3 equiv), które umieszone były w łaźni lodowej. Mieszaninę reakcyjną mieszano w temperaturze 20°C przez całą noc. Następnie mieszaninę ogrzewano przez 1 godzinę, następnie oddzielono warstwę organiczną, przemyto wodnym roztworem $NaHCO_3$ i rozpuszczalnik odparowano pod próżnią. Pozostały osad dwukrotnie krystalizowano z etanolu.

A2: 2,6-bis(4-metylobenzoilo)-diaminopirydyna. Roztwór chlorku p-toluilu (373 g, 37,76 mmol, 2,0 equiv) w suchym tetrahydrofuranie (50 ml) dodano kroplami do zawiesiny 2,6-diaminopirydyny (1,894 g, 17,36 mmol, 1 equiv) w trietyloaminie (7,2 ml, 51,66 mmol, 3 equiv), umieszone były w łaźni lodowej. Mieszaninę reakcyjną mieszano w temperaturze 20°C przez całą noc. Następnie mieszaninę ogrzewano przez 1 godzinę, następnie oddzielono warstwę organiczną, przemyto wodnym roztworem $NaHCO_3$ i rozpuszczalnik odparowano pod próżnią. Pozostały osad dwukrotnie krystalizowano z etanolu.

A3: 2,6-bis(4-dimetyloaminobenzoilo)diaminopirydyna. Roztwór 2,6-diaminopirydyny (2,500 g, 22,90 mmol, 1,0 equiv) w suchym tetrahydrofuranie (40 ml) mieszano w temperaturze 25°C w atmosferze azotu przez 1 godzinę z wodorkiem sodu (3,6 g 60% roztworu, 150,01 mmol, 6 equiv) . Otrzymaną zawiesinę mieszano w temperaturze wrzenia przez 1 godzinę. Po ochłodzeniu otrzymanego roztworu dodano 4-(dimetyloamino)benzoesan etylu (5,748 g, 29,74 mmol, 2 equiv) rozpuszczony w suchym THF i ponownie roztwór podgrzano. Do ostudzonego roztworu dodano roztwór chlorku amonu (8,330 g, 155,72 mmol, 1,7 equiv), w celu wygaszenia reakcji. Następnie rozpuszczalnik odparowano pod próżnią, a otrzymaną zawiesinę przesączono i dwukrotnie rekrystalizowano z etanolu.

Prowadzenie ekstrakcji rozpuszczalnikowej

Do przeprowadzenia ekstrakcji rozpuszczalnikowej stosunek stężenia molowego ekstrahowanego jonu w ekstrahowanym roztworze do stężenia molowego użytego ekstrahenta wynosił 1 : 1, 1 : 2 oraz 1 : 5. Stąd stężenie molowe Uganda (A1–A3) wynosiło 0,001 mol/dm^3 w chloroformie, a stężenie molowe metalu odpowiednio 0,010 mol/dm^3, 0,005 mol/dm^3 oraz 0,002 mol/dm^3. Roztwór doprowadzono do pH wyższego niż 8 poprzez dodanie 20 μl 25% roztworu NH_3. Tak uzyskaną mieszaninę ekstrahowano przez 15–60 minut, poprzez intensywne mieszanie w zakresie 200–400 obr./min, w temperaturze 20–25°C. W tabeli 1 przedstawiono warunki ekstrakcji dla poszczególnych metali i ligandów.

Tabela 1
Warunki ekstrakcji

Metal	Ligand	M:L	Czas ekstrakcji [min]	Prędkość mieszania [obr./min]	Temperatura ekstrakcji [°C]
Cu(II)	**A1** $C_{19}H_{15}N_3O_2$	1:1	15	200	20
		1:2	45	300	22
		1:5	60	400	25
	A2 $C_{21}H_{19}N_3O_2$	1:1	45	300	25
		1:2	60	400	20
		1:5	15	200	22
	A3 $C_{23}H_{25}N_5O_2$	1:1	60	400	20
		1:2	15	200	22
		1:5	45	300	25

Ni(II)	**A1** $C_{19}H_{15}N_3O_2$	1:1	15	200	25
		1:2	45	300	20
		1:5	60	400	22
	A2 $C_{21}H_{19}N_3O_2$	1:1	45	300	20
		1:2	60	400	22
		1:5	15	200	25
	A3 $C_{23}H_{25}N_5O_2$	1:1	60	400	25
		1:2	15	200	20
		1:5	45	300	22
Co(II)	**A1** $C_{19}H_{15}N_3O_2$	1:1	15	200	20
		1:2	45	300	22
		1:5	60	400	25
	A2 $C_{21}H_{19}N_3O_2$	1:1	45	300	25
		1:2	60	400	20
		1:5	15	200	22
	A3 $C_{23}H_{25}N_5O_2$	1:1	60	400	20
		1:2	15	200	22
		1:5	45	300	25
Zn(II)	**A1** $C_{19}H_{15}N_3O_2$	1:1	15	200	25
		1:2	45	300	20
		1:5	60	400	22
	A2 $C_{21}H_{19}N_3O_2$	1:1	45	300	20
		1:2	60	400	22
		1:5	15	200	25
	A3 $C_{23}H_{25}N_5O_2$	1:1	60	400	25
		1:2	15	200	20
		1:5	45	300	22

Za pomocą atomowej spektrometrii absorpcyjnej (ASA) określono stężenie metali w pobranych próbach po przeprowadzonym procesie ekstrakcji rozpuszczalnikowej, które przedstawiono w tabeli 2. Następnie w znany sposób oddzielono fazę wodną od fazy organicznej. Fazę organiczną zawierającą jony metali poddano procesowi wydzielania.

Tabela 2

Parametry procesów ekstrakcji rozpuszczalnikowej i procentowy odzyski jonów

Metal	Ligand	M:L	pH	Stężenie metalu [mol/dm^3]	Stężenie liganda [mol/dm^3]	% metalu związany przez ekstrahent
Cu(II)	**A1** $C_{19}H_{15}N_3O_2$	1:1	10,016	0,010	0,01	13,24
		1:2	8,256	0,005	0,01	49,25
		1:5	10,424	0,002	0,01	79,75
	A2 $C_{21}H_{19}N_3O_2$	1:1	10,145	0,010	0,01	35,79
		1:2	7,985	0,005	0,01	53,16
		1:5	10,753	0,002	0,01	78,68
	A3 $C_{23}H_{25}N_5O_2$	1:1	10,160	0,010	0,01	12,41
		1:2	8,157	0,005	0,01	43,98
		1:5	10,792	0,002	0,01	77,26
Ni(II)	**A1** $C_{19}H_{15}N_3O_2$	1:1	10,298	0,010	0,01	95,55
		1:2	7,845	0,005	0,01	79,68
		1:5	10,510	0,002	0,01	83,20
	A2	1:1	10,043	0,010	0,01	97,71

	$C_{21}H_{19}N_3O_2$	1:2	7,955	0,005	0,01	92,14
		1:5	10,573	0,002	0,01	99,28
	A3 $C_{23}H_{25}N_5O_2$	1:1	10,134	0,010	0,01	83,18
		1:2	8,254	0,005	0,01	89,64
		1:5	10,580	0,002	0,01	94,33
Co(II)	**A1** $C_{19}H_{15}N_3O_2$	1:1	9,920	0,010	0,01	99,70
		1:2	8,5668	0,005	0,01	98,54
		1:5	10,463	0,002	0,01	99,64
	A2 $C_{21}H_{19}N_3O_2$	1:1	10,050	0,010	0,01	99,31
		1:2	7,756	0,005	0,01	98,64
		1:5	10,553	0,002	0,01	99,86
	A3 $C_{23}H_{25}N_5O_2$	1:1	10,139	0,010	0,01	98,89
		1:2	8,651	0,005	0,01	96,65
		1:5	10,645	0,002	0,01	99,40
Zn(II)	**A1** $C_{19}H_{15}N_3O_2$	1:1	10,216	0,010	0,01	81,22
		1:2	8,654	0,005	0,01	80,14
		1:5	10,728	0,002	0,01	80,22
	A2 $C_{21}H_{19}N_3O_2$	1:1	10,138	0,010	0,01	87,59
		1:2	7,859	0,005	0,01	81,69
		1:5	10,716	0,002	0,01	78,51
	A3 $C_{23}H_{25}N_5O_2$	1:1	10,209	0,010	0,01	81,25
		1:2	7,6591	0,005	0,01	81,04
		1:5	10,682	0,002	0,01	80,97

Przykład II

Odzysk jonów miedzi(II), niklu(II), kobaltu(II) i cynku(II) z roztworów wodnych prowadzono za pomocą pochodnych 2,6-bis(benzoilo-R)diaminopirydyny o wzorach 2–4. Odzysk prowadzony poprzez ekstrakcję membranową.

Przygotowanie membrany

Sporządzono roztwór polichlorku winylu (60% wag.), plastyfikatora – np. adypianianu bis(2-etyluheksylu) albo ftanalu di(2-etyloheksylu) (20% wag.) i liganda – A1 albo A2, albo A3 przygotowane jak w przykładzie I (20% wag.) w 10 cm^3 tetrahydrofuranie. Roztwór mieszano na mieszadle magnetycznym do uzyskania jednorodnej konsystencji, po czym wylano na samopoziomującą szalkę ANUMBRA. Po całkowitym odparowaniu tetrahydrofuranu membranę odklejono od szalki i umieszczono w wodzie destylowanej na 24 h, w celu kondycjonowania membrany.

Prowadzenie ekstrakcji membranowej

Do każdego roztworu dodano odpowiednią ilość 25% roztworu NH_3 w celu ustalenia pH roztworu do wartości wyższej niż 8. Tak przygotowaną membranę zalano 15 cm^3 odpowiedniego wodnego roztworu miedzi(II) lub niklu(II), lub kobaltu(II), lub cynku(II). Stosunek metalu do liganda podczas ekstrakcji membranowej wynosił 1 : 5, przy czym stężenie molowe liganda wynosiło 0,05 mol/dm^3, a stężenie metalu 0,01 mol/dm^3 (tabela 3). Proces ekstrakcji prowadzono 24 godziny. Po tym czasie pobrano niewielką ilość roztworu, aby za pomocą analizy ASA stwierdzić ubytek ilości jonów metali w roztworze. Ubytek jonów z roztworu świadczy o związaniu jonów metali przez membranę.

Tabela 3

Parametry procesów ekstrakcji membranowej i procentowy odzyski jonów

Metal	Ligand	M:L	pH	%związany przez membranę
Cu(II)	**A1** $C_{19}H_{15}N_3O_2$	1:5	9,262	8,42
	A2 $C_{21}H_{19}N_3O_2$	1:5	9,194	35,79
	A3 $C_{23}H_{25}N_5O_2$	1:5	9,428	9,21

Ni(II)	**A1** $C_{19}H_{15}N_3O_2$	1:5	10,609	12,21
	A2 $C_{21}H_{19}N_3O_2$	1:5	9,332	97,71
	A3 $C_{23}H_{25}N_5O_2$	1:5	10,895	83,18
Co(II)	**A1** $C_{19}H_{15}N_3O_2$	1:5	10,654	69,43
	A2 $C_{21}H_{19}N_3O_2$	1:5	10,456	45,57
	A3 $C_{23}H_{25}N_5O_2$	1:5	9,850	50,53
Zn(II)	**A1** $C_{19}H_{15}N_3O_2$	1:5	9,345	56,60
	A2 $C_{21}H_{19}N_3O_2$	1:5	10,850	87,59
	A3 $C_{23}H_{25}N_5O_2$	1:5	9,506	81,25

Jony z membrany odzyskano za pomocą jednego z kwasów takich jak: kwas octowy, kwas siarkowy(VI) lub 5 M kwas azotowy(V). Membranę zanurzono w niewielkiej ilości takiego kwasu i uzyskano zatężony roztwór zawierający odzyskane jony metalu.

Uzyskane wyniki w przykładzie I i II potwierdziły, że sposób wg dwóch odmian niniejszego wynalazku umożliwia odzysk jonów miedzi(II), cynku(II), niklu(II) oraz kobaltu(II) z roztworów wodnych z wykorzystaniem pochodnych 2,6-bis(benzoilo-R)diaminopirydyny (R=H, CH_3, $N(CH_3)_2$).

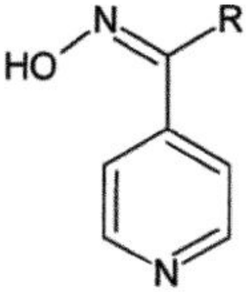
Zastrzeżenia patentowe

1. Sposób odzyskiwania jonów miedzi(II), niklu(II), kobaltu(II) i cynku(II) z wodnych roztworów, **znamienny tym**, że pH roztworu wodnego doprowadza się do wartości wyższej niż 8 alkalizując roztwór za pomocą amoniaku z wykorzystaniem ekstrakcji rozpuszczalnikowej, w której stosunek stężenia molowego ekstrahowanego jonu do stężenia molowego ekstrahentu wynosi w przedziale zawartym od 1 : 1 do 1 : 5, do ekstrahowanego roztworu dodaje się ekstrahent, którym jest 0,001 mol/dm^3 roztwór 2,6-(N,N'-dibenzoilo)-diaminopirydyny w chloroformie albo 0,001 mol/dm^3 roztwór 2,6-bis(4-metylobenzoilo)-diaminopirydyny w chloroformie albo 0,001 mol/dm^3 roztwór 2,6-bis(4-dimetyloaminobenzoilo)diaminopirydyny w chloroformie, ekstrakcję rozpuszczalnikową prowadzi się w czasie od 15 do 60 minut poprzez intensywne mieszanie z prędkością w zakresie 200–400 obr./min, i w temperaturze w zakresie od 20°C do 25°C, następnie w znany sposób oddziela się fazę wodną od fazy organicznej, po czym fazę organiczną zawierającą jony metali poddaje się procesowi wydzielania znanym sposobem.
2. Sposób odzyskiwania jonów według zastrz. 1, **znamienny tym**, że stosunek stężenia molowego ekstrahowanego jonu do stężenia molowego ekstrahentu wynosi 1 : 5.
3. Sposób odzyskiwania jonów według zastrz. 1, **znamienny tym**, że ekstrakcję rozpuszczalnikową prowadzi się w czasie od 25 do 60 minut.
4. Sposób odzyskiwania jonów według zastrz. 1, **znamienny tym**, że ekstrakcję rozpuszczalnikową prowadzi się poprzez intensywne mieszanie z prędkością 300 obr./min.
5. Sposób odzyskiwania jonów według zastrz. 1, **znamienny tym**, że ekstrakcję rozpuszczalnikową prowadzi się poprzez intensywne mieszanie w temperaturze 25°C.
6. Sposób odzyskiwania jonów miedzi(II), niklu(II), kobaltu(II) i cynku(II) z wodnych roztworów, **znamienny tym**, że pH roztworu wodnego doprowadza się do wartości wyższej niż 8 alkalizując roztwór za pomocą amoniaku, z wykorzystaniem ekstrakcji membranowej, w której stosunek stężenia molowego ekstrahowanego jonu do stężenia molowego ekstrahentu wynosi 1 : 5, a ekstrahentem jest 2,6-(N,N'-dibenzoilo)-diaminopirydina albo 2,6-bis(4-metylobenzoilo)-diaminopirydyna albo 2,6-bis(4-dimetyloaminobenzoilo)diaminopirydyna, przy czym ekstrakcję

przeprowadza się poprzez przygotowanie polimerowej membrany na drodze wylewania poprzez sporządzenie roztworu polichlorku winylu (60% wag.), plastyfikatora (20% wag.) i ekstrahentu (20% wag.) w 10 cm^3 tetrahydrofuranu, następnie roztwór jest mieszany na mieszadle magnetycznym do uzyskania jednorodnej konsystencji, po czym roztwór wylewany jest na samopoziomującą szalkę, a po całkowitym odparowaniu tetrahydrofuranu membranę odkleja się od szalki i umieszcza w wodzie destylowanej na 24 h w celu jej kondycjonowania, a tak przygotowaną membranę zalewa się wodnym roztworem, z którego ekstrahowane są jony, a ekstrakcję membranową prowadzi się przez 24 godziny, następnie ekstrahowane jony wydziela się z membrany poprzez zanurzanie w roztworze kwasu azotowego(V), kwasu octowego lub kwasu siarkowego(VI), w wyniku czego otrzymuje się roztwór, który zawiera odzyskane jony.

7. Sposób odzyskiwania jonów według zastrz. 6, **znamienny tym**, że plastyfikatorem jest adypianian bis(2-etyluheksylu).
8. Sposób odzyskiwania jonów według zastrz. 6, **znamienny tym**, że plastyfikatorem jest ftalan di(2-etyloheksylu).
9. Sposób odzyskiwani a jonów według zastrz. 6, **znamienny tym**, że ekstrahowane jony wydziela się z membrany poprzez zanurzanie w roztworze kwasu azotowego(V).

Rysunki

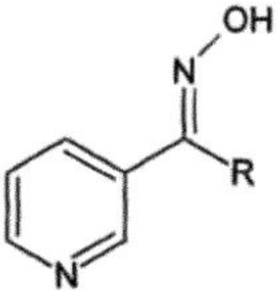


R – prosty lub rozgałęziony łańcuch alkilowy zawierającą od 6 do 17 atomów węgla

wzór 1

(stan techniki)

Fig. 1

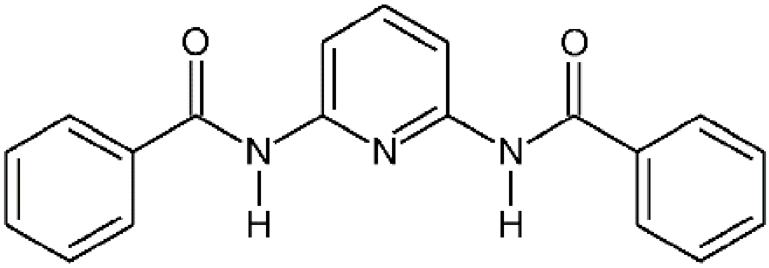


R – prosty lub rozgałęziony łańcuch alkilowy zawierający od 6 do 12 atomów węgla

wzór 2

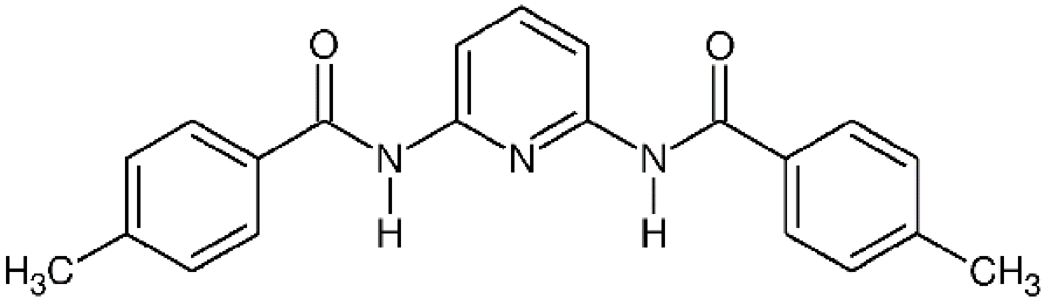
(stan techniki)

Fig. 2



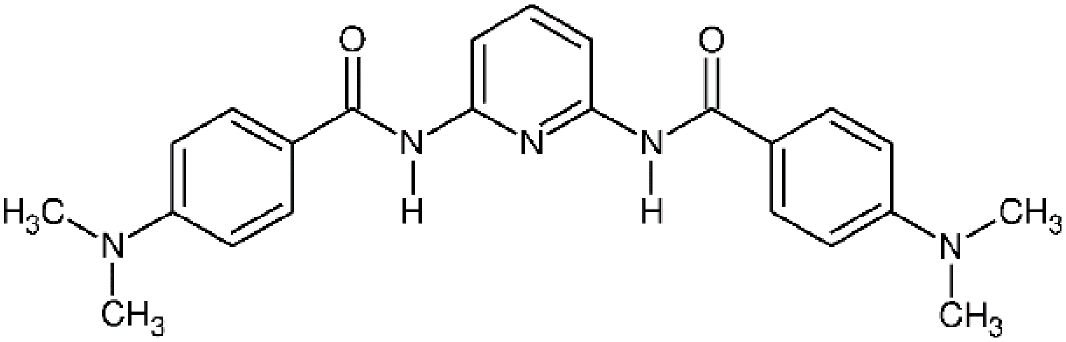
(A1)
wzór 3

Fig. 3



(A2)
wzór 4

Fig. 4



(A3)

wzór 5

Fig. 5