





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 Cu²⁺ 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-NMe₂) 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).

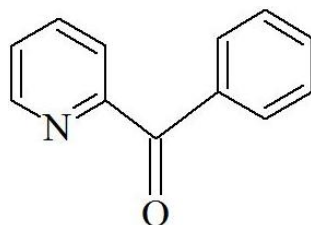


Fig. 1. The structure of 2-benzoylpyridine

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

Molecular formula	C ₁₂ H ₉ NO
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 KNO₃. 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 ($\sum [M]_{\text{org}}$) to the sum of concentrations of all the substances in the water phase ($\sum [M]_{\text{aq}}$). 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.

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

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

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)):

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

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).

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

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):

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

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 OrbitrapTM 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:

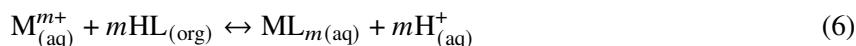


Table 3 shows the values of the distribution ratios of both metal ions for the 2–benzoylpyridine concentration (0.1 mol/l).

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-Grzeskowiak, 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).

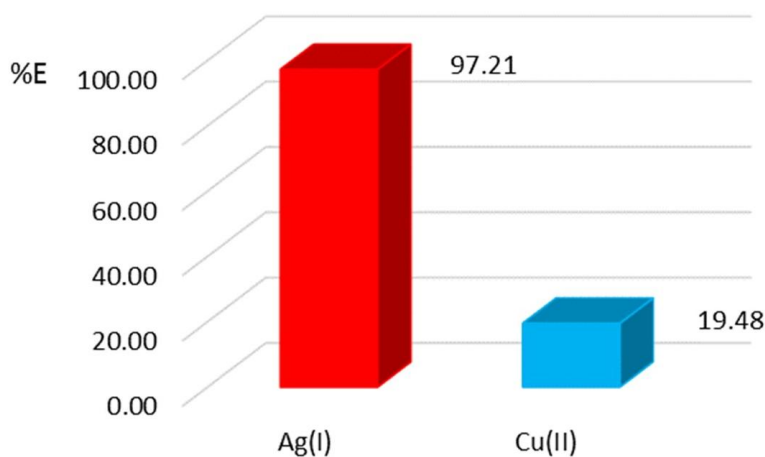


Fig. 2. Efficiency of extraction process

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–benzoylpyridine 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-Zajac 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.

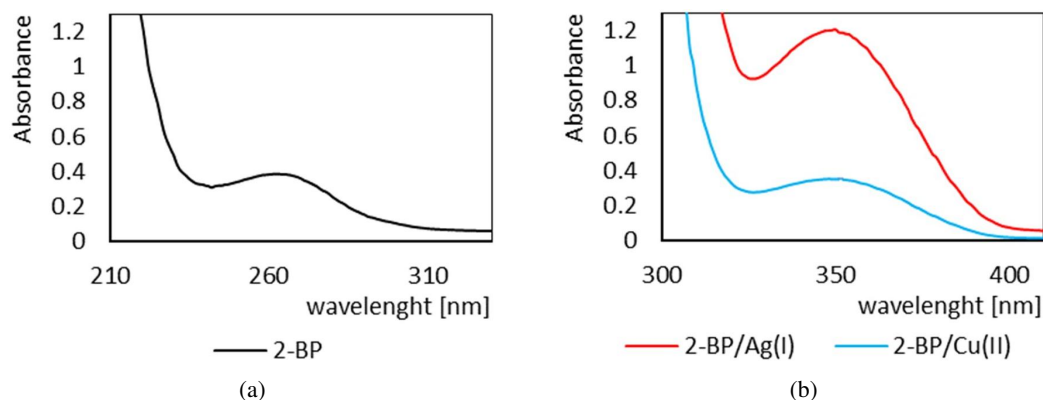


Fig. 3. The absorption spectra of organic phases: a) before extraction process, b) after extraction

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 Cu²⁺ 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 (Piłśniak-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 [%]	Time [h]	%Rs [%]
		q_t [mg/g]		q_t [mg/g]
	4	260.2682	4	13.7436
	6	263.7931	6	14.6753
	12	270.0255	12	15.6460
	24	276.3602	24	27.0601

The given values of %Rs, 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-benzoylpyridine 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-Zajac 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.

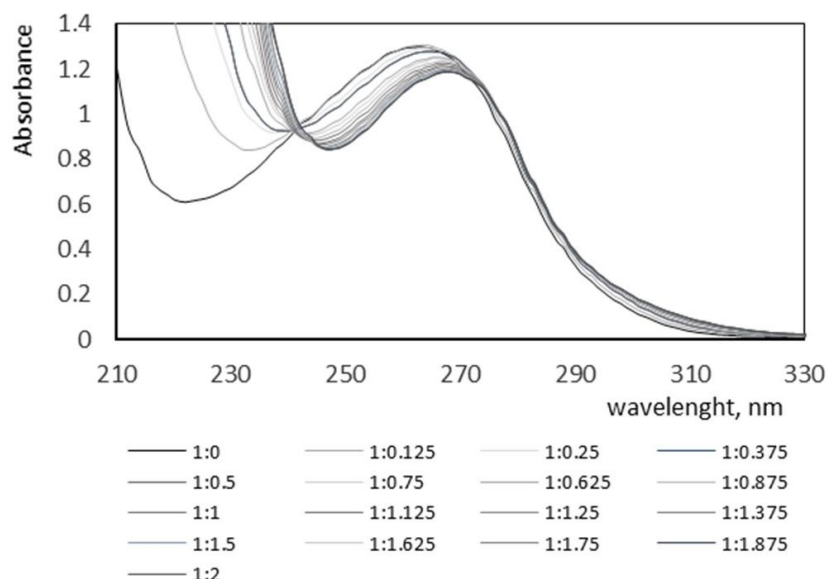


Fig. 4. Electron spectrum obtained during complexation reaction between 2-BP and Ag(I) ions

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 <i>K</i>			
	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 (Koner mann 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: $[\text{L}-\text{H}]^+$, $[\text{L}+\text{H}]^+$, $[\text{C}_{14}\text{H}_{14}\text{NO}_3]^+$, $[\text{C}_{13}\text{H}_{10}\text{NO}_2]^+$, $[\text{C}_{13}\text{H}_{12}\text{NO}_2]^+$, 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 ($[\text{L}-\text{H}]^+$) in ESI(+) experiments, which typically results in generation of protonated ions ($[\text{L}+\text{H}]^+$), 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. $[\text{3L}+\text{Cu}^{2+}]^{2+}$ and a signal which can be assigned to $[\text{2L}+\text{Cu}^+]^+$ cations, in which one copper atom is linked to two ligand (2–BP) molecules. The formation of $[\text{3L}+\text{Cu}^{2+}]^{2+}$ and $[\text{2L}+\text{Cu}^+]^+$ ions proves that in complexes with L molecules, copper ions can be present in both oxidation states (+I or +II).

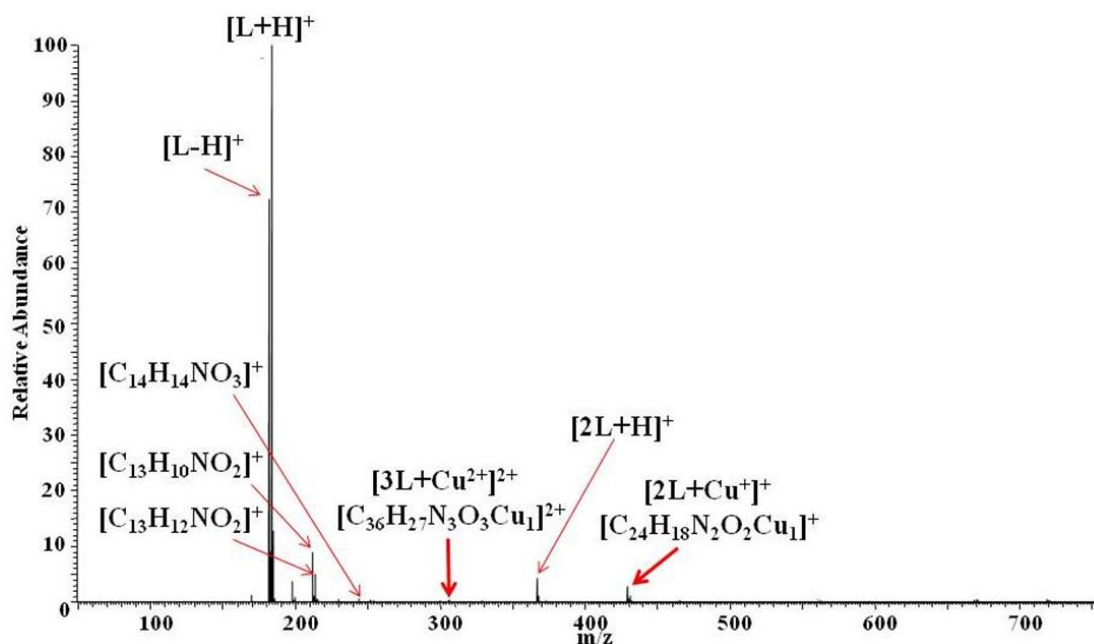


Fig. 5. ESI-HRMS spectrum recorded for the sample of the separated organic phase after liquid–liquid extraction, containing 2–benzoylpyridine (L) and Cu^{2+} ions. Unassigned minor signals correspond to ions not relevant in this study (e.g., formed by solvent molecules)

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, C₁₂H₉NO) and Cu²⁺ ions

2-benzoylpyridine (L)/Cu ²⁺			
<i>m/z</i> _{meas}	<i>m/z</i> _{calc}	Assignment	Mass error (ppm)
182.0598	182.0606	[L–H] ⁺ , [C ₁₂ H ₈ NO] ⁺	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 ₃ OH] ⁺ or [(L+H)+CH ₂ O] ⁺ , [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 ₃ O ₃ Cu ₁] ²⁺	2.94
367.1438	367.1446	[2L+H] ⁺ , [C ₂₄ H ₁₉ N ₂ O ₂] ⁺	2.17
429.0657	429.0664	[2L+Cu ⁺] ⁺ , [C ₂₄ H ₁₈ N ₂ O ₂ Cu 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 Cu²⁺ show formation of doubly charged complexes (cations) in which the ratio of Me²⁺ 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

- cⁱ* 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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