Solvent extraction of copper(II) from chloride solutions using 1,1′-dialkyl-2,2′-bibenzimidazoles as extractants

Iwona Mądrzak-Litwa, Aleksandra Borowiak-Resterna

Poznan University of Technology, Institute of Chemical Technology and Engineering, ul. Berdychowo 4, 60-965 Poznań, Poland

Corresponding author: aleksandra.borowiak-resterna@put.poznan.pl (Aleksandra Borowiak-Resterna)

Abstract: The solvent extraction ability of 1,1′-dialkyl-2,2′-bibenzimidazoles (L) for the recovery of copper(II) ions from aqueous chloride solutions has been investigated. It was found that 1,1′-didecyl-2,2′-bibenzimidazole is a useful extractant for the separation of copper(II) ions from both weakly and strongly acidic solutions. Copper(II) can be effectively stripped of organic solutions by a water or ammonia solution in a one-stage process. In low acidity media ($pH_{feed} > 1$), the extraction percentage of Cu(II) increases with an increase in metal ions and chloride concentrations. Copper(II) ions are extracted as binuclear complexes $(CuCl_2)_2L_2$ (L = extractant). The constructed McCabe−Thiele diagram shows that the reduction of copper(II) ions concentration from 25 to approximately 5 g/dm³ in an aqueous feed is possible in two extraction stages. When $[HCl]_{feed} \geq 1$ M, $(LH^+)_2(CuCl_4^{2-})L$ complex is formed. From the strongly acidic solutions ([HCl] = [LiCl] = 4 M), almost 100% of copper(II) ions can be removed by 1,1′-didecyl-2,2′-bibenzimidazole. Benzyl alcohol, used as an organic phase modifier, enables the selective extraction of copper(II) over zinc(II) ions from a weakly acidic chloride solution.

Keywords: copper, solvent extraction, metal removal, chloride solution, 2,2′-bibenzimidazole

1. Introduction

Copper is a valuable metal used in many industries. Electrical conductivity, thermal conductivity and corrosion resistance of copper allow the use of copper in electrical and electronic products, construction of buildings, in industrial machinery and equipment (Schlesinger et al., 2011). The result of a widespread use of the metal in industry is the presence of copper in wastewater and waste solutions originating, inter alia, from the electronic (Regel-Rosocka, 2018), electroplating (Reis and Ismael, 2018) or mineral extraction industries (Wieszczycka, 2018). Although copper is not poisonous in its metallic state, copper ions are toxic to humans and to the natural environment (Lossin, 2002; Ashish et al., 2013). Thus, the removal and recovery of copper ions from wastewater and waste solutions have a significant role.

Hydrometallurgical methods (20% of primary copper production) allow the recovery of copper both from primary and from secondary raw materials (Schlesinger et al., 2011). There is an economic and environmental need to recover valuable metals from secondary raw materials. Over 33% of copper in use comes from recyclable materials (Wieczorek and Kwaśniewska, 2018). The long lifetime of copper products (e.g., more than 30 years for copper wire) and a huge increase in copper mining are the reason for the low percentage of recycled copper (Lossin, 2002).

Apart from such hydrometallurgical operations as flotation (Feng et al., 2018; Feng et al., 2019), or leaching (McDonald and Muir, 2007; Park et al., 2006), solvent extraction is one of the most important methods for the separation of metal ions from multi-component solutions obtained in hydrometallurgy. The advantages of solvent extraction are the ability to treat large amounts of waste solutions and selective metal recovery. This method, combined with electrowinning, makes it possible to obtain pure cathodic metals. The extractants used in solvent extraction must meet a number of requirements

(Schlesinger et al., 2011) and, therefore, synthesizing the ideal extractant is a very difficult task. For the given extraction conditions, an extractant is selected which will best fulfill its task in such conditions. Hydroxyoximes are the best-known group of copper extractants. Currently, the most commonly used commercial extractants are LIX 84-I (Hu and Wiencek, 2000; Sengupta et al., 2007; Panigrahi et al., 2009), LIX 622 and LIX 622N (Owusu, 1999; Sastre and Alguacil, 2001; Ocio and Elizalde, 2006; Rúa et al., 2006; Panigrahi et al., 2009), LIX 984N (Aminian and Bazin, 2000; Asghari et al., 2009; Sridhar et al., 2009). In addition to hydroxyoximes, extractants with other functional groups, such as pyridinecarboxylic acid derivatives, e.g., ACORGA CLX50 (Dalton et al., 1988; Dalton et al., 1991), 8-hydroxyquinoline derivatives, e.g., KELEX 100 (Kyuchoukov and Kounev, 1994; Bogacki et al., 2000), β-diketones, e.g. LIX 54 (Alguacil and Alonso, 1999; Ismael et al., 2004), derivatives of thiophosphinic acid, e.g., Cyanex 302 (Sole and Hiskey, 1995; El-Hefny and Daoud, 2007) have been proposed for the recovery of copper(II) in the hydrometallurgical industry.

In scientific literature, numerous examples of copper recovery from wastewater, waste solutions and solid waste are described. Alguacil and Regel-Rosocka (2018) used flue dusts from flash, reverberatory and converter furnaces for the recovery of copper. Their method includes ammonium-based leaching, liquid-liquid extraction with LIX 860, LIX 84 or LIX 54, and electrowinning. Shah et al. (2017) recovered copper and zinc from spent chloride brass pickle liquors using LIX 84I-C as an extractant for copper and D2EHPA for zinc. Also, Kul and Oskay (2015) used the solvent extraction method for the recovery of copper, iron, zinc, chromium, and nickel from electroplating wastewater using the extractants Aliquat 336, LIX 984N-C, DEHPA, and Cyanex 272. Taking into account the influence of the acidity of an aqueous solution on the extraction degree of various metals, it was possible to separate the metal ions present in the aqueous feed. Waste electrical and electronic equipment (WEEE) is another source of copper and other valuable metals (Regel-Rosocka, 2018). The separation of copper from waste-printed circuit boards leach solution using solvent extraction with Acorga M5640 as extractant was presented by Wang et al. (2019).

The solutions obtained after the leaching of waste have various compositions and, therefore, researchers are constantly looking for new extractants for the selective separation of metals, e.g., copper and zinc. The use of hydroxyoxime extractants is not viable in chloride systems, most often obtained in hydrometallurgical processes. The solvating extractants, for example pyridine derivatives: esters (Dalton et al., 1982; Dalton et al., 1988; Dalton et al., 1991; Cote et al., 1994), amides (Borowiak-Resterna, 1999; Borowiak-Resterna and Lenarcik, 2004), ketoximes (Klonowska-Wieszczycka et al., 2009; Wojciechowska et al., 2017), or alkylimidazoles (Radzyminska-Lenarcik and Witt, 2018), are more desirable. Therefore, these authors carried out extraction studies using 2,2'-bibenzimidazole derivatives as solvating extractants for copper(II) in chloride media.

The compound 2,2'-bibenzimidazole has been known for more than a century (Hübner, 1881). Owing to the presence of four nitrogen atoms in it, different types of 2,2'-bibenzimidazole complexes with metal ions are formed (Galán-Mascarós and Dunbar, 2003; Mo et al., 2009; Lin et al., 2010). The substitution of hydrophobic groups into the 2,2'-bibenzimidazole molecule improves the solubility of 2,2'-bibenzimidazole derivatives in organic solvents. Various 1,1'-derivatives of 2,2'-bibenzimidazole are used for dye-sensitized solar cells (Huang et al., 2010), selective recognition and rapid detection of Fe(III) by fluorescence quenching in aqueous media (Wei et al., 2013). Moreover, these derivatives show antiviral activity (Dai et al., 2009). Zeneca Specialties has developed a commercial extractant ACORGA ZNX 50 which is selective to zinc over iron, lead, cadmium, and antimony ions (Dalton et al., 1992; Dalton and Burgess, 1993). The main active component of the extractant is dimethyl-1,1'-bis(tridecyloxycarbonyl)-2,2'-bibenzimidazole (Dziwiński et al., 2000). However, there is no information in scientific literature about the properties of 1,1'-dialkyl-2,2'-bibenzimidazoles with long alkyl carbon chains. The synthesis of dialkyl derivatives of 2,2'-bibenzimidazole is simpler than the synthesis of 1,1'-bis(alcoxycarbonyl)-2,2'-bibenzimidazoles. These compounds can be obtained in the simple coupling of 1-alkylbenzimidazoles in the presence of copper(II) acetate with a good yield (Mądrzak-Litwa and Borowiak-Resterna, 2018). It is much easier to obtain high-purity dialkyl derivatives of 2,2'-bibenzimidazole by using the coupling reaction than by the direct alkylation of 2,2'-bibenzimidazole (Mądrzak-Litwa et al., 2016). Studies carried out by present authors indicate that the obtained new 1,1'-

dialkyl-2,2'-bibenzimidazoles are good extractants for zinc(II) in weakly and strongly acidic, chloride systems (Mądrzak-Litwa and Borowiak-Resterna, 2018).

This paper presents the results of detailed studies on the extraction of copper(II) from chloride solutions by 1,1'-dialkyl-2,2'-bibenzimidazoles. The conducted studies show that 1,1'-didecyl-2,2'-bibenzimidazole can be used for the efficient recovery of copper(II) ions from concentrated chloride solutions and that the separation of copper(II) from zinc(II) in these conditions is possible when benzyl alcohol is used as an organic phase modifier. Our research work shows that hydrophobic 1,1'-dialkyl-2,2'-bibenzimidazoles can be applied as the extractants of copper(II) ions from liquid industrial waste and secondary materials, e.g., from brass wastes where copper and zinc are main components.

2. Materials and methods

2.1. Reagents

Aqueous solutions were prepared from analytical grade: ammonia (25%), copper nitrate (trihydrate), hydrochloric acid (36%), sodium nitrate, sodium chloride, and nitric acid (65%) (POCH, Poland), copper(II) chloride (dihydrate), lithium chloride (monohydrate), and magnesium nitrate (hexahydrate) (Chempur, Poland), lithium nitrate (anhydrous) (Acros Organics, Belgium), zinc chloride (anhydrous) (Fluka, Switzerland). Deionized water was used as diluent. Decan-1-ol, 2-ethylhexan-1-ol, 4-methylpentan-2-one (Sigma Aldrich, Germany), toluene and benzyl alcohol (POCH, Poland) of analytical grade were used to compose the organic phase.

2.2. Synthesis of extractants

Three model 1,1'-dialkyl-1H,1'H-2,2'-bibenzo[d]imidazoles were synthesized and used in these studies. In the description of the experimental studies, the simplified name of the extractants - 1,1'-dialkyl-2,2'-bibenzimidazoles, is used. The 1,1'-dialkyl-2,2'-bibenzimidazoles were obtained in a three-step synthesis (Scheme. 1; R = C$_{10}$H$_{21}$ – diC10; R = C$_8$H$_{17}$ – diC8; R = C$_6$H$_{13}$ – diC6). In the first step, simple compounds o-phenylenediamine and formic acid were used to obtain benzimidazole. Then, benzimidazole was reacted with sodium hydroxide in DMF and then with an appropriate alkyl halide giving 1-alkyl-1H-benzimidazole (simplified name: 1-alkylbenzimidazole). Finally, 1-alkylbenzimidazoles were used in coupling reactions. The structure and purity of the synthesized 1,1'-dialkyl-2,2'-bibenzimidazoles were proved by the high-resolution mass spectra and the ^{1}H NMR and ^{13}C NMR spectra. The characteristics of 1,1'-dialkyl-2,2'-bibenzimidazoles have been described in the previous paper by the same authors (Mądrzak-Litwa and Borowiak-Resterna, 2018).
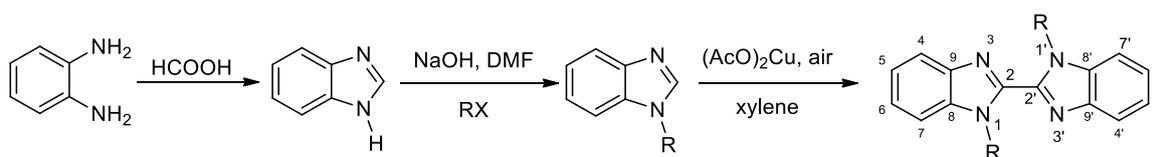
Scheme. 1. Synthesis route of 1,1'-dialkyl-2,2'-bibenzimidazoles

2.3. Extraction procedure

Copper(II) extraction and stripping were carried out at 293-296 K. Equal volumes of aqueous and organic phases (toluene-benzyl alcohol = 3:2 v/v in weakly acidic media and toluene in strongly acidic media) were shaken in a glass test tube for 15 minutes (using Bio-mix BWR 04), while the time required for attaining the extraction and stripping equilibrium did not exceed 5 minutes. The phases were separated. The copper(II) concentration was determined in the aqueous phases by atomic absorption spectrometry (AAS) using a Z8200 Polarised Zeeman apparatus (Hitachi). Measurements of pH were made using the 713 pH meter (Metrohm).

The extraction of copper(II) from chloride solutions with 1,1'-dialkyl-2,2'-bibenzimidazoles was carried out:

1) in weakly acidic media (pH > 1), [Cu(II)]$_{feed}$ = 0.1 or 0.4 M, and at (i) a constant water activity (a_w = 0.62), [LiCl] + [LiNO$_3$] + [Mg(NO$_3$)$_2$] = 6 M, [LiCl] = 0.1-6 M, (ii) [LiCl] = 8 M, (iii) [LiCl] = 10 M;

2) in strongly acidic media at [HCl] = 0.5-4.0 M, [Cu(II)]$_{feed}$ = 0.01 M, and at (i) [HCl] + [LiCl] = 6 M, (ii) [HCl] + [LiCl] = 7 M, (iii) [HCl] + [LiCl] = 8 M, (iiii) [LiCl] = 4 M.
Each organic solution contained a 0.2 M extractant.

2.4 Calculations

The copper(II) concentration in the aqueous solutions before and after the extraction, and after the stripping were analysed by AAS. The concentration of copper(II) ions in the organic phase was determined by mass balance. The distribution ratio of copper(II) ions (D$_{Cu}$) and extraction percentage (%E) were calculated from the following equations (assuming that the phase volumes did not change):

$$D_{Cu} = \frac{[Cu(II)]_{(o)}}{[Cu(II)]_{(aq)}} = \frac{[Cu(II)]_{feed} - [Cu(II)]_{(aq)}}{[Cu(II)]_{(aq)}} \tag{1}$$

$$\%E = \frac{[Cu(II)]_{(o)}}{[Cu(II)]_{feed}} \times 100\% = \frac{[Cu(II)]_{feed} - [Cu(II)]_{(aq)}}{[Cu(II)]_{feed}} \times 100\% \tag{2}$$

where [Cu(II)]$_{feed}$ is the total metal concentration in the aqueous phase before extraction, [Cu(II)]$_{(o)}$ and [Cu(II)]$_{(aq)}$ are the total metal concentration in the organic and aqueous phase after extraction, respectively. The confidence interval for the extraction percentage of Cu(II) was estimated for ten parallel extraction at a confidence level of (1-α) = 0.95. It was equal to 17.5 ± 0.7(%).

3. Results and discussion

3.1. Diluent

A mixture of toluene and benzyl alcohol in a volume ratio of 3:2 was used as a diluent in weakly acidic systems (pH$_{feed}$ > 1). Hydrophobic dialkyl derivatives of 2,2'-bibenzimidazole are well soluble in toluene but their complexes with Cu(II) precipitate in weakly acidic aqueous/toluene systems. Decan-1-ol, 2-ethylhexan-1-ol, 4-methylpentan-2-one, and benzyl alcohol were used as modifiers of the toluene phase (Table 1). A good result was obtained for chloroform, but due to its toxicity and low boiling temperature, further work with the diluent was discontinued. The best results were obtained for benzyl alcohol as an organic phase modifier. In the presence of other modifiers, an emulsion formation or a precipitation of the complex after extraction was observed. Increasing amount of benzyl alcohol do not only increases the percentage of extraction, but it also improves the solubility of the complex being formed with copper(II) (Table 1, and items 3 and 7 in Table 2). This mixture of toluene and benzyl alcohol in a volume ratio of 3:2 was used in the further preparation of the extractants' solutions. In strongly acidic systems ([HCl]$_{feed}$ ≥ 0.5 M), toluene was used as a diluent.

Table 1. Influence of diluents on copper(II) elimination from chloride solutions with diC10
([extractant] = 0.2 M, [Cu(II)]$_{feed}$ = 0.4 M)

[LiCl]$_{feed}$, M	Solvent (v/v)	Percentage of Cu(II) elimination from aqueous feed, %
8.0	toluene	24.7[a]
	toluene : decan-1-ol = 5 : 1	30.5[a]
	toluene : decan-1-ol = 3 : 2	emulsion
	toluene : 2-ethylhexan-1-ol = 5 : 1	23.1[a]
	toluene : 2-ethylhexan-1-ol = 3 : 2	emulsion
	toluene : 4-methylpentan-2-one = 5 : 1	7.4[a]
	toluene : 4-methylpentan-2-one = 3 : 2	12.5[a]
	toluene : benzyl alcohol = 3 : 2	30.7
	chloroform	38.1
10.0	toluene	emulsion
	toluene : benzyl alcohol = 9 : 1	34.7[a]
	toluene : benzyl alcohol = 7 : 3	44.6[a]
	toluene : benzyl alcohol = 3 : 2	50.3

[a] Complex precipitates; it was possible to determine the percentage of copper(II) elimination from aqueous feeds because the volume of the aqueous phase after the solvent extraction did not change in all the experiments.

3.2. Extraction of copper(II) from chloride solutions at pH > 1

Basic extraction studies were carried out for 1,1'-didecyl-2,2'-bibenzimidazole (diC10). The acid transfer to the organic phase by diC10 was investigated and reported in our earlier work (Mądrzak-Litwa and Borowiak-Resterna, 2018). It was found that both, the acid concentration, and the presence of salt (e.g. LiCl) have an impact on HCl transfer to the organic phase. For $[HCl]_{feed} \leq 0.1$ M, the extractant is not protonated. Therefore, it can be concluded that diC10 is a weak organic base, and in weakly acidic media (pH > 1), can form complexes with metal ions as a solvating extractant.

In chloride solutions copper(II) forms chloro-complexes $CuCl_i^{2-i}$ where i = 1-4. Based upon the stability constants of copper(II) chloro-complexes, obtained at a_w = 0.62 and σ = 12 M (Cote et al., 1994), the influence of chloride concentration on the molar fractions of the complexes $CuCl_i^{2-i}$ is shown in Fig. 1. The molar fraction of the complex $CuCl_2$ increases with an increase in the Cl$^-$ concentrations of up to about 2 M, and at higher chloride concentrations, the content of $CuCl_2$ is rather constant. Furthermore, at $[Cl^-] \geq 0.5$ M the complex $CuCl_2$ dominates in the solutions, which is important because diC10 forms solvating complexes with neutral $CuCl_2$.
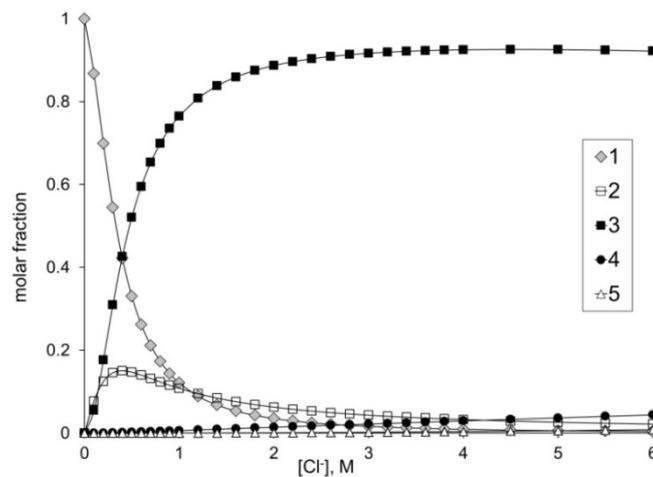
Fig. 1. Influence of chloride concentration on molar fractions of complexes $CuCl_i^{2-i}$ at a_w = 0.62 and σ = 12 M (1 – Cu^{2+}, 2 – $CuCl^+$, 3 – $CuCl_2$, 4 - $CuCl_3^-$, 5 - $CuCl_4^{2-}$)
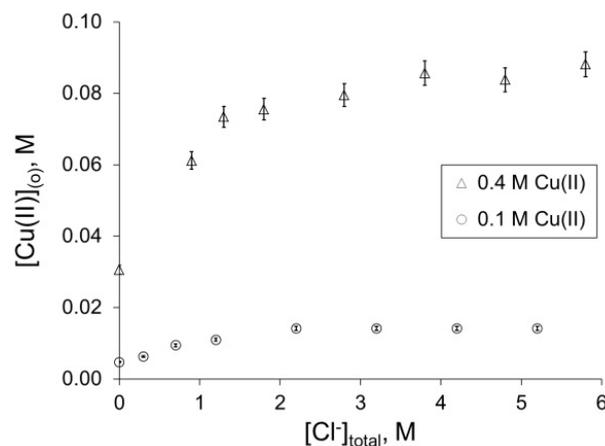
Fig. 2. Influence of chloride and copper(II) ions concentration on copper(II) extraction from aqueous chloride/nitrate solutions with diC10 ([diC10] = 0.2 M; pH_{feed} > 1)

Fig. 2 presents the effect of chloride concentration on the extraction of copper(II) from chloride/nitrate solutions at a_w = 0.62. Lithium chloride, and lithium and magnesium nitrates were used to adjust the activity of water. Keeping a_w at a constant level eliminates the influence of the composition of the aqueous phase on the activity coefficients of ions and molecules in the extraction media (Cote et al., 1994).

The data in Fig. 2 show that the concentration of chloride ions has a significant influence on Cu(II) extraction with diC10 in the range of 0-2 M Cl$^-$. At [Cl$^-$]$_{feed}$ > 2 M, the extraction of Cu(II) does not change because the molar fraction of a neutral CuCl$_2$ complex in the feed is rather constant. When [Cl$^-$]$_{total}$ = 0 M, copper(II) can form complexes with nitrate ions ([NO$_3^-$]$_{feed}$ = 6.85 M). The extraction percentage of copper(II) in the absence of chloride ions in the extraction system is equal to 4 and 8% at 0.1 and 0.4 M Cu(II) in the feed, respectively. Although Cu(NO$_3$)$_i^{2-i}$ complexes are less stable than CuCl$_i^{2-i}$ (Davis and Chong, 1972; Cote et al., 1994), it should be assumed that at low concentrations of chloride ions and high concentrations of nitrate ions, nitrate or mixed chloride-nitrate complexes can be formed in such systems. The data presented in Fig. 2 show also that the copper(II) extraction percentage rises with an increasing the metal ions concentration in the feed.

Table 2 illustrates the influence of the concentration of salts (LiNO$_3$/NaNO$_3$ and LiCl/NaCl) on the copper(II) extraction percentage. Copper complexes with chloride ions are more stable than with nitrate ions, which is confirmed by the extraction results. In a system containing 0.8 M chloride ions (from 0.4 M CuCl$_2$), the extraction yield is almost 11% higher, compared with a system without these ions (Table 2, items 1 and 2). At the constant concentration of chloride ions in the aqueous feed, copper(II) extraction rises with an increase in LiNO$_3$ concentration (Table 2, items 3 and 4). However, a lower extraction efficiency of copper(II) ions is obtained when lithium salts are replaced by sodium salts (Table 2, items 3, 5, and 6). A strong hydration of lithium ions causes a better salting-out effect of Li$^+$ (Cl$^-$ / NO$_3^-$) in comparison with Na$^+$ (Cl$^-$ / NO$_3^-$).

Table 2. Influence of salts concentration in the feed on copper(II) extraction with diC10 ([diC10] = 0.2 M; diluent - toluene:benzyl alcohol = 3:2 (No. 1-6), toluene (No. 7); [Cu(NO$_3$)$_2$]$_{feed}$ (No. 1) and [CuCl$_2$]$_{feed}$ (No. 2-7) = 0.4 M)

No.	[NaCl], M	[LiCl], M	[Cl$^-$]$_{total}$, M	[LiNO$_3$], M	[NaNO$_3$], M	Ionic strength	E, %
1	-	-	-	7	-	8.2	8.0
2	-	-	0.8	7	-	8.2	18.8
3	-	1	1.8	6	-	8.2	33.7
4	-	1	1.8	3	-	5.2	3.8
5	1	-	1.8	6	-	8.2	20.6
6	1	-	1.8	-	6	8.2	6.9
7	-	1	1.8	6	-	8.2	5.3

1,1'-Dialkyl derivatives of 2,2'-bibenzimidazole in weakly acidic chloride solutions can form complexes only as neutral bidentate ligands, extracting copper(II) as a neutral molecule CuCl$_2$. The extraction of copper(II) ions in these conditions can be described by the solvation mechanism:

$$m\,Cu^{2+} + 2m\,Cl^- + n\,L_{(o)} \Leftrightarrow (CuCl_2)_m L_{n(o)} \tag{3}$$
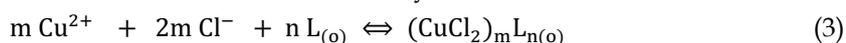
where L denotes the non-protonated extractant molecule, the subscript "o" does the organic phase, and the unsubscripted terms – the aqueous phase. The concentration extraction constant for reaction (3) is described by Eq. (4):

$$K_{ex} = \frac{[(CuCl_2)_m L_n]_{(o)}}{[Cu^{2+}]_{free}^m\,[Cl^-]^{2m}\,[L]_{(o)}^n} \tag{4}$$

where [Cu^{2+}]$_{free}$, [Cl$^-$] and [L]$_{(o)}$ are concentrations in the equilibrium state. The concentration of all copper(II) ions in the aqueous phase is given by Eq. (5):

$$[Cu(II)] = [Cu^{2+}]_{free}(1 + \sum_1^4 \beta_i [Cl^-]^i) \tag{5}$$

where β_i denotes the stability constants of CuCl$_i^{2-i}$. Conversion of the Eqs. (4) and (5) allows to obtain a dependence given by Eq. (6):

$$\log \frac{[Cu(II)]_{(o)}}{[Cu(II)]^m} = \log m + \log K_{ex} + 2m\log[Cl^-] - m\log(1 + \sum_1^4 \beta_i [Cl^-]^i) + n\log[L]_{(o)} \tag{6}$$

Fig. 3 shows the influence of diC10 concentration on copper(II) extraction from weakly acidic solutions at the constant concentration of chloride ions and copper(II) in the aqueous feed. Assuming that a 1:1 (mol Cu(II):mol diC10) complex is formed, according to Eq. (6) and for m = 1 a straight line with a slope of 1 ought to be obtained. As shown in Fig. 3, the slope of this straight line is 1.64, which does not confirm the formation of the CuCl$_2$L complex. However, for m = 2, a straight line with a slope of 1.96

was obtained. Therefore, it can be assumed that, under the studied conditions, a binuclear complex with the composition $(CuCl_2)_2L_2$ (m = n = 2) is formed.
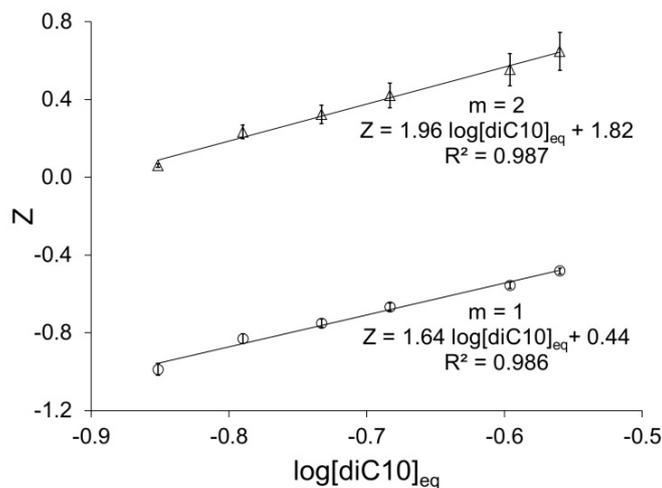
Fig. 3. Influence of diC10 concentration on copper(II) extraction from weakly acidic solutions
($Z = \log ([Cu(II)]_{(o)} / Cu(II)]^m)$; $pH_{feed} > 1$; $[Cu(II)]_{feed} = 0.1$ M; $[Cl^-]_{feed} = 6.2$ M)

The electronic spectra of the organic phase, after copper(II) extraction from chloride solutions, in the visible range show a broad band at 735-771 nm with the shoulder in the 620-635 nm region (Fig. 4). This means that, in the studied extraction systems, probably one type complexes can be formed. Two absorption bands in the visible spectra of organic phases suggest that in these complexes, the central ion, Cu(II), is coordinated at least by three chloride ions (Davies et al., 1985; Dieck, 1973). This would mean that, in the formed complexes, adjacent copper(II) ions are connected by chloride bridges. However, the presence of two broad bands in the visible region can also result from the equilibrium of the two isomeric structures of the complex with a similar stability, e.g. with a trigonal bipyramidal and tetragonal pyramidal geometry. The obtained spectral data do not allow to unequivocally propose the structure of the complexes formed. Such information can be obtained after comprehensive experimental and computational research.
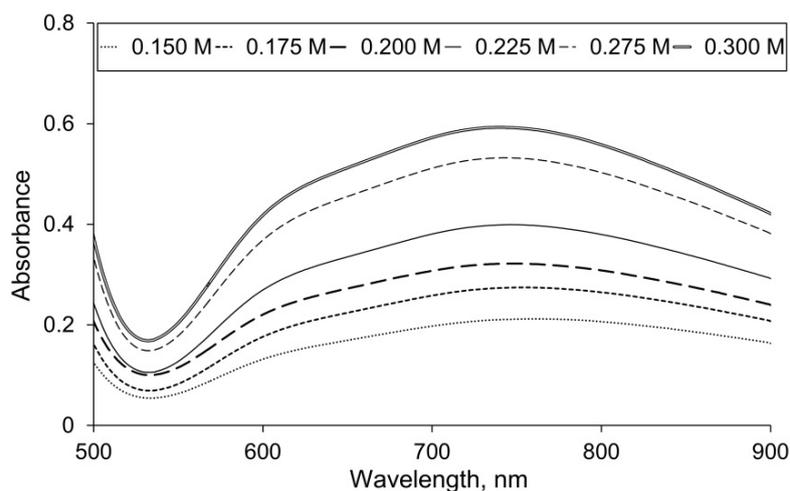
Fig. 4. Electronic spectra of organic solutions after Cu(II) extraction from chloride solutions by diC10 ($[Cu(II)]_{feed} = 0.1$ M, $[Cl^-]_{feed} = 6.2$ M; $pH_{feed} > 1$; $[diC10] = 0.150-0.300$ M; toluene/benzyl alcohol 3:2 v/v)

The Cu(II) loading test for diC10 was performed for 0.2 M extractant solution in toluene-benzyl alcohol at [LiCl] = 8 M and $[CuCl_2] = 0.4$ M in the aqueous feed. After the first extraction, the phases were separated and the organic phase was shaken again with the fresh aqueous feed. The maximum

capacity, 0.91 mol Cu(II)/mol diC10, was reached after four extraction stages. It seems that the complex in which the ratio of the copper(II) ion to the extractant is 1 (mol/mol) is dominant in these conditions.

The extraction isotherm describes the distribution of copper(II) between the organic and aqueous layers. It was obtained by contacting the copper(II) aqueous solutions ($[LiCl]_{feed}$ = 8 M) and 0.2 M diC10 toluene-benzyl alcohol solution at different $[Cu(II)]_{feed}$. The McCabe–Thiele diagram in Fig. 5 shows that, at a phase ratio O/A = 5 and after two extraction stages, it is possible to reduce the copper(II) ions concentration from 25.0 g/dm^3 in the feed to approx. 5 g/dm^3 in the aqueous phase after extraction.
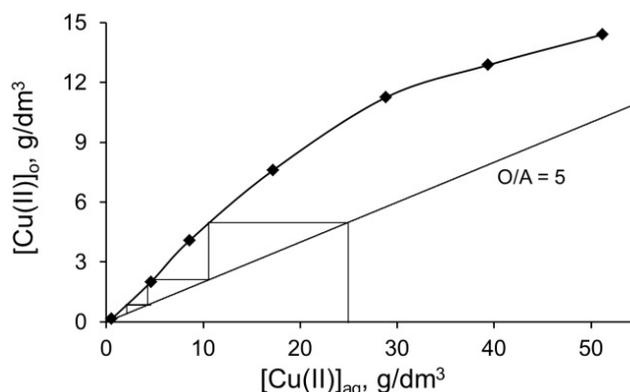
Fig. 5. Copper(II) extraction isotherm and the McCabe-Thiele diagram

The effect of the alkyl chain length in 1,1'-dialkyl-2,2'-bibenzimidazoles on the extraction of copper(II) from weakly acidic chloride/nitrate solutions is illustrated in Table 3. These results indicate that the extraction ability of the studied compounds rises with an increasing concentration of chloride ions in the aqueous feed. Comparable amounts of copper(II) are removed from the aqueous phase by diC10, diC8, and diC6 but only Cu(II) complexes with diC10 are well soluble in toluene-benzyl alcohol in all studied range 0.9-5.8 M Cl-.

Table 3. Copper(II) elimination from chloride solutions with 1,1'-dialkyl-2,2'-bibenzimidazoles
([extractant] = 0.2 M, $[Cu(II)]_{feed}$ = 0.4 M, a_w = 0.62, pH of feed > 1)

$[Cl^-]_{feed}$, M	Percentage of Cu(II) elimination from aqueous feed, %		
	diC10	diC8	diC6
0.9	16.1	19.4	19.4
1.3	19.4	19.4	21.0
2.8	20.6	22.6[a]	24.2[a]
3.8	22.6	22.6[a]	27.4[a]
5.8	22.4	23.0[a]	–

[a] Complex precipitates; it was possible to determine the percentage of copper(II) elimination from aqueous feeds because the volume of the aqueous phase after the solvent extraction did not change in all the experiments.

After extraction from weakly acidic media, the stripping of copper(II) ions from diC10 solutions can be carried out quantitatively with water with pH 1 at the water/organic phase volume ratio of 1:1. Pure water also can be used for the stripping stage although the ratio A:O > 1 ought to be applied (Table 4).

3.3. Extraction of copper(II) from acidic chloride solutions

The extraction of copper(II) from strongly acidic chloride solutions was also investigated. Toluene was used as a diluent. The data demonstrated in Fig. 6 show that the extraction of copper(II) ions by diC10 increases with increasing acidity of the aqueous phase.

Another significant factor affecting the extraction abilities of diC10 is the concentration of lithium chloride. At 1 M HCl, an increase in the concentration of LiCl in the feed from 4 to 7 M increases the extraction percentage of Cu(II) from 0 to 84%, respectively. When [HCl] + [LiCl] = 6 M and at high HCl concentration in the feed (4 M), the Cu(II) extraction ceases to take place because the concentration of

lithium chloride in the aqueous feed is too low. However, when [HCl] + [LiCl] = 7 or 8 M, at the same HCl concentration, 86% and 95% of copper(II) ions is efficiently extracted from the feed, respectively.

Table 4. Stripping of copper(II) from organic solutions after extraction from weakly and strongly acidic solutions with 0.2 M diC10

Extraction		Stripping		
$[HCl]_{(aq)}$, M	$[Cu(II)]_{(o)}$, M	Agent used in stripping	Phases ratio (v/v) A:O	Stripping percentage
6.30×10^{-2}	0.132	water	1:1	85
			2:1	89
			3:1	96
		water, pH 1	1:1	100
1.00	0.010	$1\ M\ NH_3$	1:1	88
		$1\ M\ NH_3$	3:1	100
2.00	0.007	$2\ M\ NH_3$	1:1	90
		$3\ M\ NH_3$	1:1	93
		$5\ M\ NH_3$	1:1	99
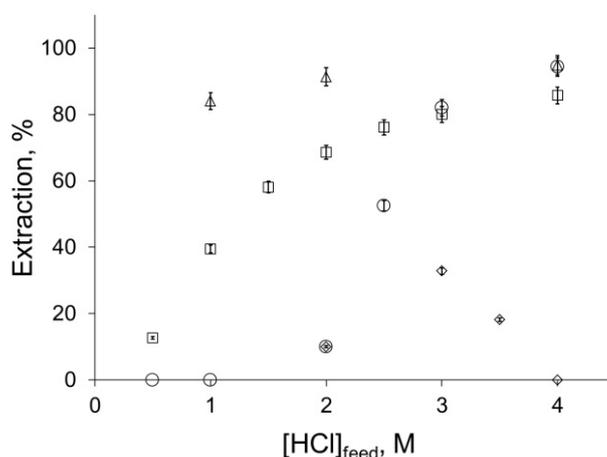
Fig. 6. Influence of hydrochloric acid and lithium chloride concentration on copper(II) extraction from aqueous solutions ([diC10] = 0.2 M, [CuCl₂]$_{feed}$ = 0.01 M, ◊ [HCl] + [LiCl] = 6 M, □ [HCl] + [LiCl] = 7 M, Δ [HCl] + [LiCl] = 8 M, ○ [LiCl] = 4 M)

The studies on HCl transfer by diC10, as described in our earlier work (Mądrzak-Litwa and Borowiak-Resterna, 2018), indicate that, for 0.2 M diC10 in toluene, the concentration of HCl transferred into organic phase increases from $2.8 \cdot 10^{-3}$ M to $1.2 \cdot 10^{-1}$ M at 1 M HCl and 3 M HCl, respectively, in the feed. Therefore, it can be presumed that under the test conditions, mainly the monohydrochloride of diC10 is present in the system. At high Cl⁻ concentration, the protonated diC10 (LH⁺) is able to form ion pairs with anionic copper(II) chloro-complexes according to the reactions:

$$x\,L_{(o)} + H^+ + CuCl_3^- \iff [(LH^+)(CuCl_3^-)L_{x-1}]_{(o)} \tag{7}$$

$$x\,L_{(o)} + 2H^+ + CuCl_4^{2-} \iff [(LH^+)_2(CuCl_4^{2-})L_{x-2}]_{(o)} \tag{8}$$
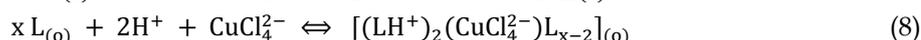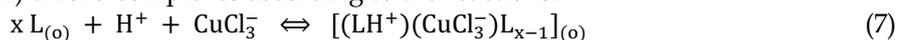
The Eq. (9), for the distribution ratio of Cu(II), is obtained when the concentration extraction constant (K'_{ex}) and the stability constants of $CuCl_i^{2-i}$ (β_i, i = 1-4) are inserted in Eq. (1):

$$\log D_{Cu} = x\,\log[L]_{(o)} + y\,\log[H^+] + \log K'_{ex} + \log(\beta_j[Cl^-]^j) - \log(1 + \sum_1^4 \beta_i[Cl^-]^i) \tag{9}$$

where y = 1 and j = 3 for the reaction (7), y = 2 and j = 4 for the reaction (8), K'_{ex} is the concentration extraction constant for the reaction (7) or (8), $[L]_{(o)}$ is the equilibrium concentration of diC10 in organic phase. When ionic strength and chloride concentration are constant, Eq. (9) can be written as:

$$\log D_{Cu} = x\,\log[L]_{(o)} + y\,\log[H^+] + const \tag{10}$$

Which of the reactions, (7) or (8), will take place during the extraction of Cu(II) in strongly acidic media can be found out when Eq. (10) is used. Figs. 7 and 8 show the relationship between copper(II) distribution ratio and the HCl or extractant concentration, respectively. The slopes of the straight lines suggest that at $[Cl^-]_{feed}$ = 7 M, diC10 forms complexes with Cu(II) in which the metal:hydrogen:extractant molar ratio is 1:2:3. Taking this into account, it is presumed that, in this system, diC10 forms with Cu(II) ion pair $(LH_2^+)_2(CuCl_4^{2-})L$.
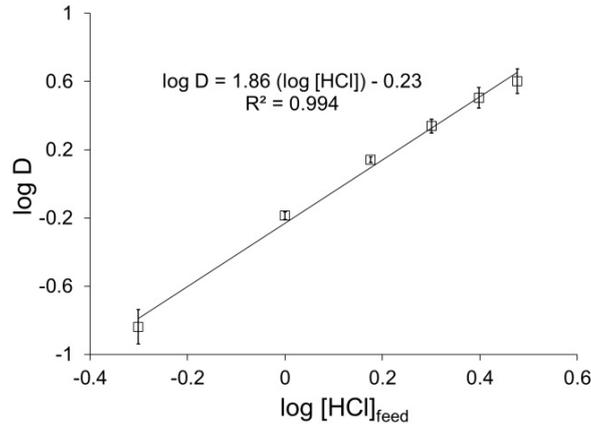
Fig. 7. Influence of HCl concentration on copper(II) distribution ratio ([diC10] = 0.2 M,
$[Cu(II)]_{feed}$ = 0.01 M, [HCl] + [LiCl] = 7 M)
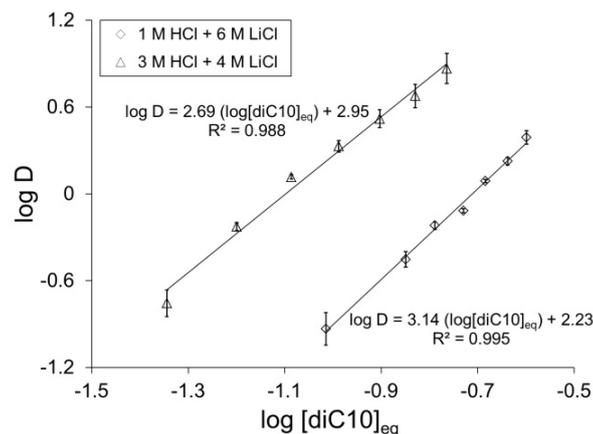
Fig. 8. Influence of diC10 concentration on copper(II) distribution ratio in acidic system
($[Cu(II)]_{feed}$ = 0.01 M, $[Cl^-]_{feed}$ = 7 M)

The studies of copper(II) extraction from strongly acidic chloride solutions with three dialkyl derivatives of 2,2'-bibenzimidazole show that diC8 has slightly better complexing properties than does diC10. It should also be noted that diC6 cannot be used in strongly acidic systems for copper(II) extraction, due to the limited solubility of its complexes with Cu(II) in the organic phase.

The recovery of copper(II) ions after the extraction from strongly acidic systems is possible when ammonia solution is used (Table 3). When $[HCl]_{feed}$ = 1 M, a diluted solution of ammonia (1 M) can be used at A:O = 3:1 for the complete stripping of copper(II). But when the concentration of HCl increases in the feed and in the organic phase after the extraction stage (Mądrzak-Litwa and Borowiak-Resterna, 2018), a solution having a higher concentration of ammonia must be used in the stripping stage.

3.4. Extractant re-utilization

Five successive extraction–stripping stages were carried out with 0.2 M diC10 in the appropriate diluent using a fresh aqueous solution in each stage. The stability of the tested diC10 extractant has been studied for both weakly (0.4 M Cu(II), 6.0 M LiCl) and strongly (0.1 M Cu(II), 2.0 M HCl, 5.0 M LiCl) acidic solutions. No decrease in the extraction and stripping efficiency was observed after any of the stages.

3.5. Copper(II) separation from zinc(II) in low acidity system

In our previous work (Mądrzak-Litwa and Borowiak-Resterna, 2018), we found that the separation of zinc(II) from copper(II), cadmium(II) and nickel(II) ions is possible in weakly acidic media (pH_{feed} > 1) at $[Cl^-]_{feed}$ < 2 M, when $LiNO_3$ and $Mg(NO_3)_2$ are present in the feed for keeping a constant water activity, and when diC10 in toluene is used as an extractant. However, our present studies have shown that the selective extraction of copper(II) in the presence of zinc(II) may be performed when benzyl alcohol is used as a modifier of the organic phase. This modifier improves the extraction efficiency of both metal ions. However, in systems with low chloride ion concentrations, the selectivity of the separation of zinc(II) from copper(II) significantly decreases when toluene is replaced with a toluene-benzyl alcohol mixture (Table 5, items 1 and 2). Therefore, the presence of benzyl alcohol in this type of systems is disadvantageous. On the other hand, replacing toluene with a mixture of toluene and benzyl alcohol has a very positive effect on the selective separation of copper(II) in the presence of zinc(II) from solutions with a higher concentration of chloride ions ($[LiCl]$ = 4 M; Table 5, item 3). A further increase in chloride ion concentration ($[LiCl] \geq 6$ M) improves the extraction efficiency of copper(II), and zinc(II) extraction does not exceed 4% (Table 5, items 4 and 5). We can, therefore, conclude that the proposed extractant may be useful in the selective recovery of these two metal ions from liquid industrial waste and secondary materials.

Table 5. Extraction of copper(II) and zinc(II) ions from chloride solutions by 1,1'-didecyl-2,2'-bibenzimidazole in various diluents ($[diC10]$ = 0.2 M, $[Cu(II)]_{feed} = [Zn(II)]_{feed}$ = 0.4 M)

No	$[LiCl]_{feed}$, M	$[NO_3]_{feed}$, M	Metal ions extraction from feed, %			
			TOL		TAB	
			Cu	Zn	Cu	Zn
1	0.1	6.7[a]	0	33.3	6.4	41.5
2	0.5	6.3[a]	0.6	27.3	12.3	35.9
3	4.0	2.3[a]	1.2	3.0	23.44	6.1
4	6.0	0	-	-	26.2	2.4
5	8.0	0	-	-	40.8	3.5

[a] $LiNO_3$ and $Mg(NO_3)_2$ used for preparation of the feed;

TOL – toluene as a diluent; TAB – toluene-benzyl alcohol mixture as a diluent

Sometimes, the extractant can also be used for the recovery of copper(II) from chloride solutions after leaching sulfide ores. Concentrated chloride solutions (5-10 M Cl^-) in which the Cu(II) and Zn(II) concentrations are high (25-50 and 30-80 g/L, respectively), are obtained by ferric-chloride leaching of complex sulfide concentrates as chalcopyrite (Dalton et al., 1984). An exemplary chloride solution after leaching, from which Dalton et al. (1984) separated copper(II), contains mainly ions of three metals: approx. 0.4 M Cu(II), 0.4 M Zn(II), and 1.24 M Fe ions, including approx. 0.01 M Fe(III). The concentration of HCl is probably 0.5 M or less. Thus, the total concentration of chloride ions is equal to approx. 5 M.

The results of the studies on the extraction of Cu(II), Zn(II), Fe(III) and Fe(II) from chloride solutions, previously published by Mądrzak-Litwa and Borowiak-Resterna (2018) and some not published ones show that from the chloride solution, with the composition described above, it will be possible to selectively and completely separate Fe(III) with 0.2 M diC10 in toluene. Fe(II), Cu(II) and Zn(II) ions will remain in the raffinate. Based on the results presented in the current work (Table 5), it can be concluded that after decreasing the acidity of the obtained raffinate (pH about 1) and increasing the concentration of chloride ions to about 6-7 M, the selective extraction of Cu(II) ions will be possible using 0.2 M diC10 in toluene with benzyl alcohol as a modifier.

4. Conclusions

The ability of 1,1'-dialkyl-2,2'-bibenzimidazoles to extract copper(II) from the aqueous chloride solution was investigated. The presented results indicate that extraction depends mainly on the presence of the

organic phase modifier (benzyl alcohol), copper(II), inert salt, and chloride ions concentration in the feed, and acidity of the feed. The dialkyl derivative of 2,2'-bibenzimidazole with decyl alkyl chains (diC10) turns out to be the most useful of the extractants tested, because the solubility of its complexes in the studied solutions is the best.

From the solutions with $pH_{feed} > 1$, the extraction percentage of Cu(II) increases with an increase in chloride and copper(II) ions concentration. The use of benzyl alcohol as an organic phase modifier in these systems improves the extraction efficiency and prevents precipitation of the complex of copper(II) with the extractant. The conducted studies in the low acidity media indicate that a binuclear complex $(CuCl_2)_2L_2$ (L = diC10) is formed in these conditions.

When $[HCl]_{feed} \geq 1$ M, the extractant can be protonated and it forms an ion pair with an anionic chloro-complex of copper(II). Experimental data seem to indicate that a complex with the composition $(LH^+)_2(CuCl_4^{2-})L$ is formed. From the strongly acidic solutions, almost 100% of copper(II) ions can be removed by diC10 in toluene.

The selection of the appropriate conditions for the extraction process enables the selective recovery of copper(II) in the presence of zinc(II) from binary solutions at $pH_{feed} > 1$. The selectivity of the separation of Cu(II)/Zn(II) increases with increasing concentration of chloride ions.

The analysis of the experimental results allows to state that 1,1'-didecyl-2,2'-bibenzimidazole turns out to be a good extractant of copper(II) ions. The regenerated extractant does not lose its extraction abilities and can be re-used in the next extraction cycles. Therefore, we can assume that the proposed extractant can be useful in the selective recovery of Cu(II) from liquid industrial waste and secondary materials, also in the presence of Zn(II).

Acknowledgments

References

ALGUACIL, F.J., ALONSO, M., 1999. *Recovery of copper from ammoniacal/ammonium sulfate medium by LIX 54.* J. Chem. Technol. Biotechnol. 74, 1171-1175.

ALGUACIL, F.J., REGEL-ROSOCKA, M., 2018. *Hydrometallurgical treatment of hazardous copper Cottrell dusts to recover copper.* Physicochem. Probl. Miner. Process. 54, 771-780.

AMINIAN, H., BAZIN, C., 2000. *Solvent extraction equilibria in copper(II)-iron(III)-LIX984 system.* Miner. Eng. 13, 667-672.

ASGHARI, H., SAFARZADEH, M.S., ASGHARI, G., MORADKHAM, D., 2009. *The effect of impurities on the extraction of copper from sulfate medium using LIX®984N in kerosene.* Russ. J. Non-Ferr. Met. 50, 89-96.

ASHISH, B., NEETI, K., HIMANSHU, K., 2013. *Copper toxicity: A comprehensive study.* Res. J. Recent Sci. 2, 58-67.

BOGACKI, M.B., ZHIVKOVA, S., KYUCHOUKOV, G., SZYMANOWSKI J., 2000. *Modeling of copper(II) and zinc(II) extraction from chloride media with KELEX 100.* Ind. Eng. Chem. Res. 39, 740-745.

BOROWIAK-RESTERNA A., 1999. *Extraction of copper(II) from acid chloride solutions by N-dodecyl- and N,N-dihexylpyridinecarboxamides.* Solvent Extr. Ion Exch. 17, 133-148.

BOROWIAK-RESTERNA, A., LENARCIK, B., 2004. *Effect of the alkyl chain length in N,N-Dialkylpyridine-3-carboxamides upon their extraction of copper(II) from aqueous chloride solutions.* Solvent Extr. Ion Exch. 22, 913-931.

COTE, G., JAKUBIAK, A., BAUER, D., SZYMANOWSKI, J., MOKILI, B., POITRENAUD, C., 1994. *Modeling of extraction equilibrium for copper(II) extraction by pyridinecarboxylic acid esters from concentrated chloride solutions at constant water activity and constant total concentration of ionic or molecular spieces dissolved in the aqueous solution.* Solvent Extr. Ion Exch. 12, 99-120.

DAI, D., HRUBY, D.E., BOLKEN, T.C., AMBERG, S.M., WARREN, T.K., 2009. *Antiviral drugs for treatment of arenavirus infection.* WO Patent 2009/123776.

DALTON, R.F., BURGESS, A., 1993. *ACORGA ZNX50 - a novel reagent for the selective solvent extraction of zinc from aqueous chloride solutions.* In: Logsdail, D.H. and Slater, M.J. (Eds), Solvent Extr. Process Ind., Proc. ISEC'93, Elsevier Applied Science, London, 3, 1279-1286.

DALTON, R.F., BURGESS, A., QUAN, P.M., 1992. *ACORGA ZNX50 - a new selective reagent for the solvent extraction of zinc from chloride leach solutions.* Hydrometallurgy 30, 385-400.

DALTON, R.F., DIAZ, G., PRICE, R., ZUNKEL, A.D., 1991. *The Cuprex metal extraction process: Recovering copper from sulfide ores.* JOM 43, 51-56.

DALTON, R.F., PRICE, R., HERMANA, E., HOFFMAN, B., 1988. *Cuprex - new chloride based hydrometallurgy to recover copper from sulfide ores.* Min. Eng. 40, 24-28.

DALTON, R.F., PRICE, R., QUAN, P.M., TOWNSON, B., 1984. *Novel solvent extractants for recovery of copper from chloride leach solutions derived from sulphide ores.* Reagents Miner. Ind., Pap. 181-188.

DALTON, R.F., PRICE, R., QUAN, P.M., STEWART, D., 1982. *Process for the extraction of metal values and novel metal extractants.* US Patent US4525330 A.

DAVIES, G., EL-TOUKHY, A., ONAN, K.D., VEIDIS, M., 1985. *Synthesis, structure and properties of the isomeric dinuclear complexes [(DENC)$_2$CuX$_2$]$_2$ (DENC = N,N-diethylnicotinamide; X = Cl or Br) and the kinetics of their reactions with DENC in methylene chloride.* Inorg. Chim. Acta 98, 85-94.

DAVIS, A.R., CHONG, C., 1972. *A laser Raman study of aqueous copper nitrate solutions.* Inorg. Chem. 11, 1891-1895.

DIECK, H.T. 1973. *Tetranuclear complexes of trigonal-bipyramidal copper(II). III. Electronic and infrared spectra.* Inorg. Chim. Acta 7(C), 397-403.

DZIWIŃSKI, E., SZYMANOWSKI, J., WRZESIEŃ, E., 2000. *Composition of ACORGA ZNX 50.* Solvent Extr. Ion Exch. 18, 895-906.

EL-HEFNY, N.E., DAOUD, J.A., 2007. *Extraction of copper(II) by CYANEX 302 in kerosene from different aqueous media.* Solvent Extr. Ion Exch. 25, 831-843.

FENG, Q., ZHAO, W., WEN, S., 2018. *Surface modification of malachite with ethanediamine and its effect on sulfidization flotation.* Appl. Surf. Sci. 436, 823-831.

FENG, Q., WEN, S., BAI, X., CHANG, W., CUI, C., ZHAO, W., 2019. *Surface modification of smithsonite with ammonia to enhance the formation of sulfidization products and its response to flotation.* Miner. Eng. 137, 1-9.

GALÁN-MASCARÓS, J.R., DUNBAR, K.R., 2003. *A self-assembled 2D molecule-based magnet: The honeycomb layered material {Co$_3$Cl$_4$(H$_2$O)$_2$[Co(Hbbiz)$_3$]$_2$}.* Angew. Chem. Int. Ed. 42, 2289-2293.

HU S.-Y.B., WIENCEK J.M., 2000. *Copper − LIX 84 extraction equilibrium.* Sep. Sci. Technol. 35, 469-481.

HUANG, W.-K., CHENG, C.-W., CHANG, S.-M., LEE, Y.-P., DIAU, E.W.-G., 2010. *Synthesis and electron-transfer properties of benzimidazole-functionalized ruthenium complexes for highly efficient dye-sensitized solar cells.* Chem. Commun. 46, 8992-8994.

HÜBNER, H., 1881. *Ueber Anhydroverbindungen.* Justus Liebigs Ann. Chem. 209, 339-384.

ISMAEL, M.R.C., GAMEIRO, M.L.F., CARVALHO, J.M.R., 2004. *Extraction equilibrium of copper from ammoniacal media with LIX 54.* Sep. Sci. Technol. 39, 3859-3877.

KLONOWSKA-WIESZCZYCKA, K., OLSZANOWSKI, A., PARUS, A., ZYDORCZAK, B., 2009. *Removal of copper(II) from chloride solutions using hydrophobic pyridyl ketone oximes.* Solvent Extr. Ion Exch. 27, 50-62.

KUL M., OSKAY K.O., 2015. *Separation and recovery of valuable metals from real mix electroplating wastewater by solvent extraction.* Hydrometallurgy 155, 153-160.

KYUCHOUKOV, G., KOUNEV, R., 1994. *Copper transfer from hydrochloric acid into sulphuric acid solution by means of Kelex 100®.* Hydrometallurgy 35, 321-342.

LIN, S., CHEN, L.-J., XU, H.-H., SU, J.-B., HUANG, H., 2010. *Two 2D metal-organic frameworks based in 2,2'-bibenzimidazole ligand with (6,3) net topology.* Inorg. Chem. Commun. 13, 1347-1349.

LOSSIN, A., 2002. *Copper, vol. 10 of Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH: Verlag GmbH.

MĄDRZAK-LITWA, I., BOROWIAK-RESTERNA, A., 2018. *Solvent extraction of zinc from chloride solutions using dialkyl derivatives of 2,2'-bibenzimidazole as extractants.* Hydrometallurgy 182, 8-20.

MĄDRZAK-LITWA, I., TURGUŁA, A., RUSIŃSKA-ROSZAK, D., BOROWIAK-RESTERNA, A., 2016. *The synthesis of hydrophobic 1-alkyl-1H,1'H-2,2'-benzo[d]imidazoles.* Heterocyclic Commun. 22, 99-102.

MCDONALD, R.G., MUIR, D.M., 2007. *Pressure oxidation leaching of chalcopyrite. Part I. Comparison of high and low temperature reaction kinetics and products.* Hydrometallurgy 86, 191-205.

MO, H.-J., ZHONG, Y.-R., CAO, M.-L., OU, Y.-C., YE, B.-H., 2009. *Hydrothermal syntheses and structural diversity of cobalt complexes with 2,2'-bibenzimidazole ligand by temperature tuning strategy.* Cryst. Growth Des. 9, 488-496.

OCIO, A., ELIZALDE, M.P., 2006. *Copper(II) extraction from phosphoric acid media by 5-dodecylsalicylaldoxime (LIX 622).* Solvent Extr. Ion Exch. 24, 861-875.

OWUSU, G., 1999. *Selective extraction of copper from acidic zinc sulfate leach solution using LIX 622.* Hydrometallurgy 51, 1-8.

PANIGRAHI, S., PARHI, P.K., SARANGI, K., NATHSARMA, K.C., 2009. *A study on extraction of copper using LIX 84-I and LIX 622N.* Sep. Purif. Technol. 70, 58-62.

PARK, K.H., MOHAPATRA, D., REDDY, B.R., 2006. *A study on the acidified ferric chloride leaching of a complex (Cu-Ni-Co-Fe) matte.* Sep. Purif. Technol. 51, 332-337.

RADZYMINSKA-LENARCIK, E., WITT, K., 2018. *Copper recovery from model chloride solution using polimer inclusion membranes with 1-decyl-2,4-dimethylimidazole.* IOP conf. Ser.: Mater. Sci. Eng. 427, 012005.

REGEL-ROSOCKA, M., 2018. *Electronic wastes.* Phys. Sci. Rev. 3 (5).

REIS, M.T.A., ISMAEL, M.R.C., 2018. *Electroplating wastes.* Phys. Sci. Rev. 3 (6).

RÚA, M.S., ALMELA, A., ELIZALDE, M.P., 2006. *Aggregation equilibria of the components of the commercial extractants LIX 622 and LIX 622N in toluene and n-heptane.* Fluid Ph. Equilibria. 244, 111-116.

SASTRE, A., ALGUACIL, F., 2001. *Co-extraction and selective stripping of copper(II) and molybdenum(VI) using LIX 622.* Chem. Eng. J. 81, 109-112.

SCHLESINGER, M.E., KING, M.J., SOLE, K.C., DAVENPORT, W.G., 2011. *Extractive metallurgy of copper*, 5th Ed.; Elsevier: Oxford, UK.

SENGUPTA, B., BHAKHAR, M.S., SENGUPTA, R., 2007. *Extraction of copper from ammoniacal solutions into emulsion liquid membranes using LIX 84 I.* Hydrometallurgy 89, 311-318.

SHAH, K., GUPTA, K., SENGUPTA, B., 2017. *Selective separation of copper and zinc from spent chloride brass pickle liquors using solvent extraction and metal recovery by precipitation-stripping.* J. Environ. Chem. Eng. 5, 5260-5269.

SOLE, K.C., HISKEY, J.B., 1995. *Solvent extraction of copper by Cyanex 272, Cyanex 302 and Cyanex 301.* Hydrometallurgy 37, 129-147.

SRIDHAR, V., VERMA, J.K., KUMAR, S.A., 2009. *Selective separation of copper and nickel by solvent extraction using LIX 984N.* Hydrometallurgy 99, 124-126.

WANG, L., LI, Q., SUN, X., WANG, L., 2019. *Separation and recovery of copper from waste printed circuit boards leach solution using solvent extraction with Acorga M5640 as extractant.* Sep. Sci. Technol. 54, 1302-1311.

WEI, T., LIU, J., YAO, H., LIN, Q., XIE, Y., SHI, B., ZHANG, P., YOU, X., ZHANG, Y., 2013. *Selective chemosensor of Fe^{3+} based on fluorescence quenching by 2,2'-bisbenzimidazole derivative in aqueous media.* Chinese J. Chem. 31, 515-519.

WIECZOREK, D., KWAŚNIEWSKA, D., 2018. *Economic aspects of metals recover.* Phys. Sci. Rev. 3 (4).

WIESZCZYCKA, K., 2018. *Wastes generated by mineral extraction industries.* Phys. Sci. Rev. 3 (6).

WOJCIECHOWSKA, A., WIESZCZYCKA, K., WOJCIECHOWSKA, I., 2017. *Efficient recovery of copper from aqueous solutions with pyridine extractants (oxime, ketone) and their quaternary pyridinium salts.* Sep. Purif. Technol. 185, 103-111.