

Article

Solvent Extraction of Metal Ions from Synthetic Copper Leaching Solution Using R_4NCy

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Abstract: Recent works suggest that the use of ionic liquids in the copper solvent extraction industry is feasible. However, the reports did not use real solutions (or synthetic solutions with various elements). This fact remains poorly established, and the interaction efficiencies are still under study. The objective of this research is to explore the extraction and stripping of the four major elements present in a copper industrial pregnant leach solution (Cu(II), Fe(III), Mn(II), and Zn(II)) using the methyltrioctyl/decylammonium bis(2,4,4-trimethylpentyl)phosphinate (R_4NCy) ionic liquid as an extractant. The work conditions studied in extraction were ionic liquid concentration, initial pH, and O/A ratio, and in stripping were H_2SO_4 concentration and O/A ratio. The test was carried out at room temperature and ambient pressure. High efficiency and selectivity (99.82% and 113,755 over Cu(II), respectively) were observed for Fe(III) extraction over the other elements. Moreover, after the extraction test, significant difficulty in stripping Fe(III) loaded in the ionic liquid was observed (28.7% at 0.5 M of H_2SO_4). Finally, the present study demonstrates that the R_4NCy ionic liquid is not suitable for copper extraction because it has a higher selectivity for Fe(III) and Zn(II).

Keywords: ionic liquid; leaching; hydrometallurgy; green chemistry



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1. Introduction

Solvent extraction (SX) is an essential unit operation to obtain highly pure copper cathodes in the copper hydrometallurgy route. SX is a liquid/liquid process that uses an organic extractant diluted in a diluent to transfer the metals and complexes selectively from the pregnant solution into the organic phase. Hydroxyoxime (ketoxime and aldoxime) is one of the reagents used in large-scale copper extractants. Ketoximes and aldoximes are very selective for the extraction of copper over impurities from sulfate, nitrate, and perchlorate solutions [1–5].

SX is a large-scale technique that has been used in the copper industry since the 1970s. However, it has had several challenges over the years, such as the addition of high concentrations of chloride ions [6,7], presence of nitrate ions [8], increased impurities [9], organic phase degradation, and reuse of wastewaters and brines [10–18]. Nevertheless, despite time's passage, hydroxyoxime has adapted and remained with minimal modifications in its chemical composition (mainly by adjusting mixtures between aldoximes and ketoximes). Although hydroxyoximes have demonstrated adaptability to changing operating conditions, further research still has potential. Therefore, the opportunity is to develop new

reagents that are resistant to degradation, more selective, and highly reusable. That said, ionic liquids (ILs) emerge as potential candidates to be incorporated into industrial copper solvent extraction processes.

Ionic liquids (ILs) are a relatively new generation of reagents. The ILs are very adaptable and are proposed in several industrial applications. ILs are organic salts in a liquid state, many even at room temperature, and they are considered a green kind of reagent. ILs comprise organic cations and small organic/inorganic anions, and their properties depend on the cation/anion combination. Thus, ILs are called tunable reagents or task-specific ionic liquids. The study of ionic liquids is overgrowing while new compounds are being synthesized. Non-volatility, thermal stability, high conductivity, and recyclability are some aspects of ILs [19–22]. ILs based on ammonium or phosphonium are reported in the literature as good extractants in metal SX systems [23–25]. These ILs have attracted the attention of metal recovery because of their low volatility, thermal stability, good extraction for metal, and chemical stability [26–28]. The use of Aliquat 336, or ILs based on this commercial reagent, demonstrates fast extraction kinetics for zinc, cobalt, nickel, and rare earth, among others [29–34]. On the other hand, the Cyphos ILs family was used in several systems reported in the literature. Cyphos IL 101 (trihexyl(tetradecyl)phosphonium chloride), Cyphos IL 102 (trihexyl(tetradecyl)phosphonium bromide), and Cyphos IL 104 (trihexyl(tetradecyl)phosphonium bis 2,4,4-(trimethylpentyl)phosphinate) are reported in SX of cadmium, palladium, iron, cobalt, manganese, zinc, nickel, boron, molybdenum, and vanadium, from sulfate or chloride solutions [35–43].

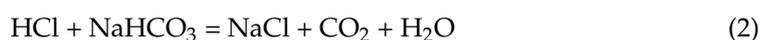
Finally, some authors reported the use of IL synthesis for the mixture of Cyanex 272 and Aliquat 336, called R_4NCy , [A336][C272] or ALiCY. For example, the Co(II) and Ni(II) separation or co-extraction is possible as a possible function of HCl concentration. At low HCl concentration, both metals are extracted, and at high HCl concentration, only Ni(II) is extracted [44]. Other applications are the selective separation of tungsten over molybdenum from sulfate solutions [45]. Padhan and Sarangi extract Nb and Pr from the electronic residues with the conventional extractant R_4NCy and other ionic liquids. The efficiency of extractants Nd and Pr extraction was in the order: $R_4NCy > R_4ND > Cyanex\ 272 > D2EHPA > Aliquat\ 336$ [29]. Castillo et al. report the individual extraction of Cu(II), Fe(III), Zn(II), and Mn(II) with the ionic liquid R_4NCy . Results showed a strong affinity of ionic liquid R_4NCy for Fe(III) and Zn(II) over Cu(II) and Mn(II) [46].

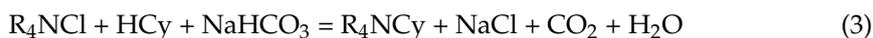
Despite the hydroximes being well known and widely used in solvent extraction, Ionic liquids have many advantages and many more to be investigated. Therefore, they deserve an opportunity to be studied in copper SX systems. Thus, in the present research, R_4NCy was studied for solvent extraction of Cu(II), Fe(III), Zn(II), and Mn(II). Metal extraction was performed in synthetic solutions. Metals ion extraction and stripping were studied under the following conditions: IL concentration, O/A ratio, and sulfuric acid concentration.

2. Materials and Methods

The commercial extractants (without further purification) trialkylmethylammonium chloride (Aliquat 336) and bis 2,4,4-trimethylpentylphosphinic acid (Cyanex 272) were provided by Sigma-Aldrich and Solvay, respectively. Kerosene and sodium hydrogen carbonate are analytical grades by Merck.

Ionic liquid methyltrioctyl/decylammonium bis 2,4,4-(trimethylpentyl)phosphinate denoted as R_4NCy was synthesized according to procedures published in the literature [35,36], mixing an equimolar ratio of Cyanex 272 and Aliquat 336. The mixture of extractants was dissolved in kerosene to obtain the desired concentration of IL, and subsequently, they were washed twice with sodium bicarbonate solution 0.5 M to remove the chloride anion and the proton from the organic phase. The synthesis of ionic liquid is shown in Equations (1) and (2), and the global reaction is shown in Equation (3) [29].





Copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), iron(III) sulfate hydrate ($Fe_2(SO_4)_3 \cdot nH_2O$), manganese(II) sulfate monohydrate ($MnSO_4 \cdot H_2O$), zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$), and sulfuric acid (H_2SO_4) are analytical grade from Merck. The salts were dissolved in distilled water. The synthetic pregnant leach solution (PLS) was prepared according to previous work [46] and simulated a PLS from SX process of copper. The concentrations of Cu(II), Zn(II), Mn(II), and Fe(III) of the PLS are summarized in Table 1.

Table 1. Concentration of metals in synthetic solution (pH = 2, sulfate = 8.65 g/L).

Metal	Concentration (mg/L)
Cu(II)	3360
Fe(III)	1570
Mn(II)	1000
Zn(II)	110

Liquid/Liquid Extraction

All experiments were conducted at room temperature (22 ± 1 °C) in shake flasks (50 mL) and with a magnetic stirring set to 200 rev/min for 20 min. A solution of 1 M sulfuric acid was used to adjust the pH of the aqueous phase. The metal concentration was measured in an aqueous solution by atomic absorption spectrometry (PerkinElmer PinAAcle 900F, Waltham, MA, USA). For tests, 10 mL of aqueous phase containing metal was mixed with a volume of the organic phase to obtain the organic/aqueous phase ratio (O/A). After extraction, two phases were centrifuged at 3000 rpm for 5 min for total phase separation. The liquid–liquid extraction tests were carried out in duplicate and a standard deviation of $\pm 2\%$ was obtained for all the tests. The performance of the liquid–liquid extractions was determined by Equations (4)–(7) as the extraction percentage, the stripping percentage, distribution ratio of the species (D), and the selectivity of the species over b (β_{ab}). The stripping procedure was similar to that of the extraction tests. The mass balance was confirmed by measuring the concentration of metals in the stripped aqueous phase.

$$\text{Extraction (\%)} = ([M]_i - [M]_{aq}) / [M]_i \times 100 \quad (4)$$

$$\% \text{ Stripping} = ([M]_{aq}^* / [M]_{org}) \times 100 \quad (5)$$

$$D = ([M]_i - [M]_{aq}) / [M]_{aq} \quad (6)$$

$$\beta_{ab} = D_a / D_b \quad (7)$$

where $[M]_i$ and $[M]_{aq}$ are the initial and final concentrations of metal in the aqueous solution, and $[M]_{org}$ and $[M]_{aq}^*$ are the concentrations of a metal ion in the loaded organic phase before stripping and in the aqueous phase after stripping, D_a and D_b are distribution ratios of species a and b, respectively. The concentration of metals in the loaded organic phase was determined by mass balance ($[M]_{org} = [M]_i - [M]_{aq}$). The equations shown above are valid for a 1/1 phase relationship. Otherwise, the mass balances incorporate the phase volumes.

3. Results and Discussion

3.1. Effect of the R_4NCy Concentration in Metal Ions Extraction

The extraction capability of R_4NCy for Cu(II), Fe(III), Zn(II), and Mn(II) was studied by varying the IL concentration in organic phase, from 0.1 to 0.54 M. In Table 2, it is observed that the extraction of Fe(III) was higher than the other elements in all IL range of concentrations. The tendency of IL extraction for metals is clear: Fe(III) > Zn(II) > Cu(II) > Mn(II). Fe(III) ever is more highly extracted than the other elements, and this tendency is more evidenced at a low IL concentration. Thus, at 0.1 M of R_4NCy , about 100% of Fe(III) is removed, and only about 17% of Mn(II), and 10% of Zn(II) and Cu(II) are not extracted. At

higher IL concentrations, all elements are extracted in some proportion. Fe(III) and Zn(II) are totally removed from the aqueous solution.

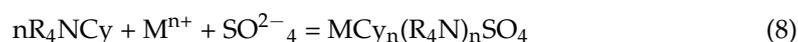
Table 2. Effect concentration of R₄NCy on extraction efficiency, distribution ratio and selectivity of the species. Experimental conditions: initial pH = 2, O/A = 1, 400 min⁻¹, and 20 min of stirring time.

Metal	IL Concentration (M)	E(%)	D	β _{Cu(II)}	β _{Fe(III)}	β _{Mn(II)}	β _{Zn(II)}
Cu(II)	0.10	0.00	0.0	-	113,755.00	702.70	373.20
	0.27	37.93	0.61	-	884.20	0.80	275.30
	0.54	85.82	6.05	-	55.30	0.1.	60.40
Fe(III)	0.10	99.70	336.63	0.00	-	0.00	0.00
	0.27	99.82	540.38	0.00	-	0.00	0.30
	0.54	99.70	336.63	0.02	-	0.00	1.10
Mn(II)	0.10	17.30	0.21	0.00	1609.20	-	0.50
	0.27	32.50	0.48	1.27	1122.30	-	349.40
	0.54	47.10	0.89	6.79	375.70	-	410.70
Zn(II)	0.10	10.00	0.11	0.00	3029.70	1.9	-
	0.27	99.41	168.23	0.00	3.2	0.00	-
	0.54	99.73	365.67	0.02	0.9	0.00	-

Relative to the data in Table 2, overall, these results indicate that iron and zinc are distributed preferentially in the IL. The D coefficient is a lower number for copper and manganese. This fact implicates that these elements tend to remain in the aqueous phase. Regarding selectivity, this study refers to the copper industry. Therefore, the selectivity of copper, iron, zinc, and manganese are presented in Table 2. The selectivity of copper over other elements is really low. It can be observed that under the system in this study, copper is not extracted selectively from the rest of the elements. On the contrary, the selectivity of iron is much higher than that of the other elements. For example, iron is extracted with selectivity up to one hundred thousand times over copper (113,755 exactly). Furthermore, the selectivity of zinc over copper and manganese is hundreds of times higher (373.2 and 410.7, respectively). It is essential to note the high selectivity of the ionic liquid for iron and zinc over copper and manganese. This fact can be explained based on previous results [46]. The extraction of the individual elements clearly showed that the performance was more efficient for the extraction of iron and zinc than for copper and manganese under all the conditions under study. Therefore, the individual species extraction efficiency performance would be the cause of the selectivity presented by the ionic liquid in the collective extraction.

The high efficiency of extracting Fe(III) and Zn(II) over Cu(II) and Mn(II), is reported in the literature using ILs as extractants. Alves-Lima et al. extracted selectively Zn(II) over Cr(III) using Aliquat 336. In the best conditions, the reaches recover about 99% of Zn(II) [34]. Regel-Rosocka et al. reported zinc and iron extraction using Cyphos IL 101 and Cyphos IL 104. The results of this research support the idea that the phosphonium ILs studies effectively remove zinc and iron from hydrochloric solutions [47]. The mixtures of Cyanex302 and Cyphos IL101 were used to separate Cu(II)/Co(II). The evidence from the study of Zang suggests that the mixture of Cyanex 302 and Cyphos IL 101 in different ratios can improve the separation of Cu(II) over Co(II) [48].

The mechanism of metal extraction with R₄NCy was reported in previous work [46] and can be generalized to all metals in this study, as shown below.



This simple extraction mechanism, based on ion exchange, is proposed. The support of the proposal is because the elements studied are found in ionic form and do not form other types of compounds. For example, more complex extraction mechanisms can be found in studies with metals in chloride medium [49]. In a chloride medium, metals form

various stable compounds (chloro-compounds); therefore, the mechanism is more complex than in the system of the present study.

3.2. Effect of Initial pH in Metal Ions Extraction

The results obtained from the initial pH in metal ions extraction are summarized in Figure 1. From the chart, the tendency of R_4NCy in the extraction of Fe(III) and Zn(II) is higher than the other ions in almost all pH ranges studied. At pH values 2 and 3, iron, zinc, and copper extraction are favored, with efficiencies close to 100% for the first two and close to 80% for copper. Manganese extraction is only 21.2% at pH = 3. This scenario changes completely at pH 1, where the extraction of copper and manganese reaches 19.2% and 3.05%, respectively. Iron and zinc extraction remained above 99%. However, there is a slight decrease in zinc extraction (from 99.7% at pH = 2 to 99.1% at pH = 1). Finally, when the pH is lowered to 0.5, there is a significant decrease in copper, manganese, and zinc extraction, with the first two species decreasing to zero and the third to 9.7%.

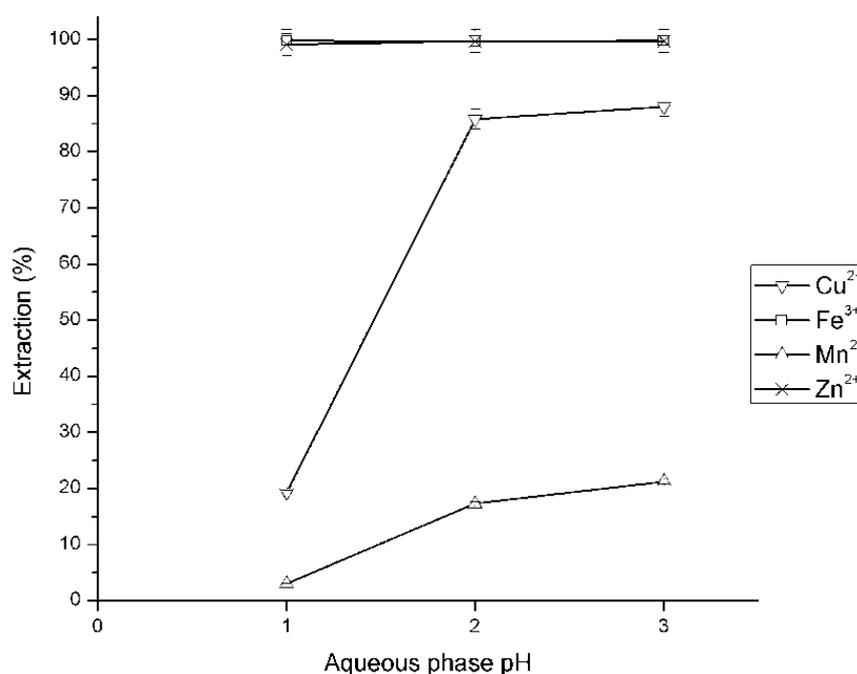


Figure 1. Effect of initial pH on the extraction percentage of metals from aqueous solution. Experimental conditions: $R_4NCy = 0.54$ M, O/A = 1, 400 min^{-1} , and 20 min of stirring time.

Previous work [24,46] demonstrates the influence of pH on the Cu(II), Fe(III), Zn(II), and Mn(II) extractions using R_4NCy . The above results showed that all the elements had an extraction efficiency close to 100% at pH 2 and 3. However, at pH 1, the extraction efficiency maintained this level only for Fe(III) and Zn(II), decreasing to about 60% for Cu(II), and 30% for Mn(II), respectively. On the other hand, the current research results indicate that, surprisingly, the extraction of Fe(III) and Zn(II) approaches 100%, even though the solution contains four elements simultaneously. Perhaps the most interesting finding is the strong affinity of R_4NCy for Fe(III) and Zn(II) over Cu(II) and Mn(II). Thus, removing Fe(III) and Zn(II) from PLS is feasible at pH 1. Another alternative is the removal of Mn(II) selectively at pH 2 or 3.

3.3. Effect of O/A Ratio in Metal Ions Extraction

The first approach to Figure 2 reveals a clear tendency to efficient extraction of Fe(III) for all O/A ratios. When the O/A ratio is 1/1, there is a high extraction of copper, iron, and zinc, with values of 85.8%, 99.7%, and 99.4%, respectively. However, the extraction of manganese is low, obtaining 17.3%. This behavior may be due to the high selectivity of the ionic liquid, displacing its extractive capacity towards iron, zinc, then copper, and finally

manganese. In the case of the O/A ratio of 1/3, an abrupt decrease in the extraction of copper (9.35%) and a null extraction of manganese were observed. However, the extraction of iron and zinc was maintained above 99%. A similar effect is observed with an O/A ratio of 1/6. Over 99% of the iron and zinc are removed, and the copper and manganese are not extracted. These working conditions mean that all the available extractants are destined to extract iron and zinc.

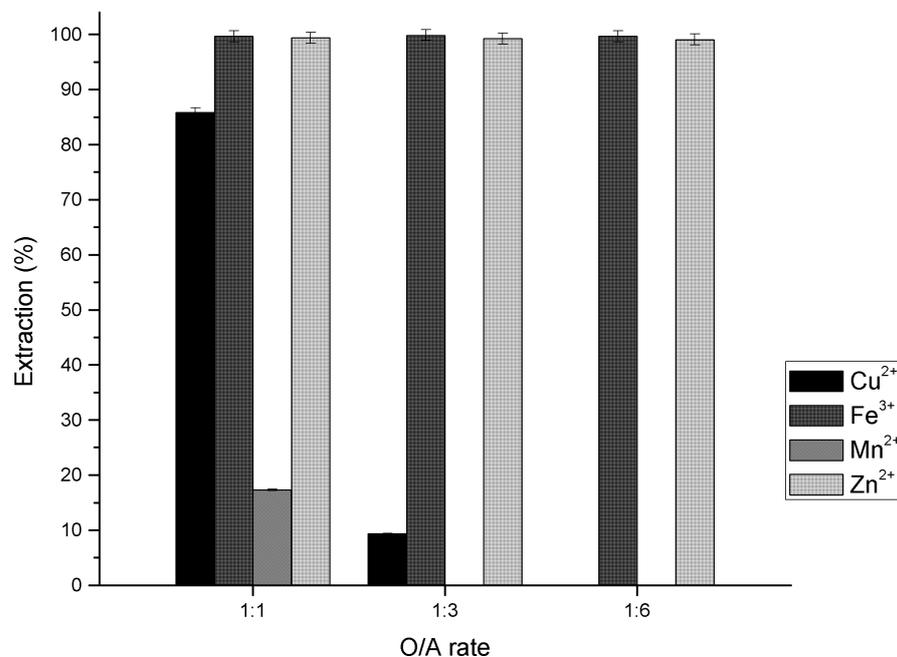


Figure 2. Effect of O/A ratio on extraction percentage of metals from aqueous solution. Experimental conditions: $R_4NCy = 0.54$ M, pH = 2, 400 min^{-1} , and 20 min of stirring time.

This result of Figure 2 can be considered favorable, for example, to remove Fe(III)/Zn(II) from PLS, in addition to a significant saving of the organic phase. Finally, with an O/A ratio of 1/6, there is a slight decrease in iron extraction (94%) and a considerable decrease in the case of zinc (34.2%). This result is attributed to the low amount of ionic liquid in relation to the aqueous phase, causing all its extractive capacity to be used to extract iron.

3.4. Effect of Sulfuric Acid in Metal Ions Stripping

The stripping tests aimed to evaluate the ease or difficulty of recovering the metals loaded into the ionic liquid in the aqueous phase. To perform the stripping tests, the ionic liquid was loaded with the different metals using an extractant concentration of 0.54 M, an O/A phase ratio of one, and pH 2. The stirring time was maintained at 20 min at a stirring speed of 400 min^{-1} . The loaded IL contained 2912.3 mg/L Cu(II), 1560.0 mg/L Fe(III), 226.7 mg/L Mn(II), and 110 mg/L Zn(II). The results shown in Figure 3 suggest the following. First, zinc stands out above the other elements, with stripping efficiency of 100% for the entire range of sulfuric acid concentration under study. This result is interesting because zinc is extracted and stripped very efficiently. Thus, it is worthwhile to carry out future studies with higher concentrations of this element. In the case of copper and manganese, the stripping performance would not change when varying the sulfuric acid concentration. Copper has an approximate efficiency of 87.5%. In the case of manganese, the re-extraction efficiency is close to 80%. Finally, in the case of iron, a low stripping efficiency (close to 30%) is observed at a sulfuric acid concentration of 0.5 M. As the acid concentration increases, the stripping efficiency increases, reaching 96.6% to 2 M. This result supports that iron's ionic liquid has an exceptional extractive force since it produces an excellent metal extraction and a difficult re-extraction.

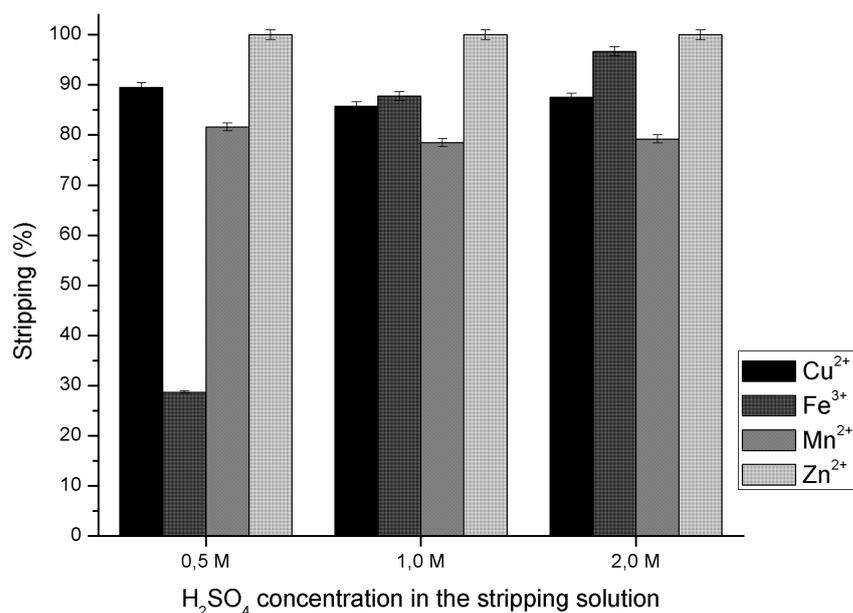


Figure 3. Effect of sulfuric acid on the stripping percentage of metals from loaded organic phase. Experimental conditions: $R_4NCy = 0.54$ M, $O/A = 1$, 400 min^{-1} , and 20 min of stirring time.

In general terms, R_4NCy is quite efficient in the stripping stage (except for Fe(III)); therefore, it meets the requirements of a metal extracting. That is, it can extract and re-extract metallic species in solutions. Recent evidence suggests that the copper industry still has several challenges, such as seawater use and the high concentrations of chlorides in the PLS. This scenario generates problems in extracting and stripping copper [1,7]. Therefore, it is possible that the use of ionic liquids can contribute to solving part of the current and future problems in SX.

3.5. Effect of O/A in Metal Ions Stripping

The results in Table 3 show how copper is stripped with acceptable efficiency. When the phase ratio is 1/1, the maximum stripping efficiency of 88.7% is achieved. The performance of copper gradually decreases when the presence of IL increases compared to aqueous phase. In the case of iron (except when O/A ratio is 1/1), the stripping was close to 0%. This fact reaffirms the great extractive force of IL with iron. This result is not very promising (under the studied conditions) since the stripping operation becomes complicated, even more so if it is considered that more species are co-extracted in the extraction stage. Manganese performance shows a slight decline in stripping efficiency, which is explained by the presence of more species in the loaded organic and the low affinity of IL by Mn(II). Finally, zinc stripping is extremely sensitive to variations in the O/A ratio, going sharply from 100% extraction when the ratio is 1/1 to 21.2% when the ratio is 3/1, and only 2% for 6/1. This performance is perhaps the most promising for future research. In addition, zinc stripping can be adjusted by varying the O/A ratio, allowing highly selective extraction of species in a few steps.

The most interesting aspect of Table 3 is that copper has become a significant player, as it is relatively easy to strip and can be concentrated in the aqueous solution. For an O/A ratio of 1:1, copper reaches a concentration of 2497 mg/L in the aqueous solution. In the case of O/A 3:1 and 6:1, the final solution reaches copper concentrations of 6391 mg/L and 7569 mg/L. These results indicate that it is possible to concentrate copper almost three times in a single stripping step. A similar trend is observed with manganese, as it is concentrated more than twice for an O/A ratio of 1:6. In the case of iron, the result is the opposite since stripping under the conditions studied is inefficient. The final aqueous solutions contain very little Fe(III), especially when the O/A phase ratio is 1:3 and 1:6. A similar performance to iron is obtained for zinc.

Table 3. Effect of O/A ratio on the stripping of metals from the organic loaded phase. Experimental conditions: R₄NCy = 0.54 M, [H₂SO₄] = 0.5 M, and 20 min of stirring time.

Metal	O/A Rate	Metal Concentration in Loaded IL (mg/L)	S(%)	Metal Concentration in Aqueous (mg/L)
Cu(II)	1:1	2912.3	85.7	2497.0
	3:1		73.1	6391.0
	6:1		43.3	7569.0
Fe(III)	1:1	1560.0	28.7	447.3
	3:1		0.6	28.1
	6:1		0.5	42.4
Mn(II)	1:1	226.7	81.6	185.0
	3:1		63.3	430.4
	6:1		41.9	570.0
Zn(II)	1:1	110.0	100.0	110.0
	3:1		21.3	70.2
	6:1		2.4	15.6

4. Conclusions

The purpose of the current study was to determine the performance of solvent extraction of Cu(II), Fe(III), Zn(II), and Mn(II) using ionic liquid R₄NCy. The main conclusions are the following. The extraction tests showed a high affinity of ionic liquid R₄NCy with Fe(III) and Zn(II). Cu(II) and Mn(II) are poorly extracted. Almost total Fe(III) extraction was obtained for most conditions under study. In the case of Zn(II), Cu(II), and Mn(II), the extraction efficiency is strongly influenced by the R₄NCy concentration, pH, and the O/A ratio. A very efficient stripping of all metals loaded into the ionic liquid was observed. The stripping performance is not affected by acid concentration, except for Fe(III). Fe(III) is only stripped at high acid concentrations. Finally, the results of this study show that the Cu(II) extraction is insignificant with the R₄NCy in the presence of Fe(III), Zn(II), and Mn(II). On the other hand, all the available extractant is mainly destined to extract Fe(III) and Zn(II). However, this finding is not considered as a failure; on the contrary, significant progress has been made in an eco-friendly process for removing Fe(III)/Zn(II) from copper PLS.

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