

Article

Extraction of Cu(II), Fe(III), Zn(II), and Mn(II) from Aqueous Solutions with Ionic Liquid R₄NCy

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Abstract: The leaching of copper ores produces a rich solution with metal interferences. In this context, Fe(III), Zn(II), and Mn(II) are three metals contained in industrial copper-rich solutions in high quantities and eventually can be co-extracted with the copper. The purpose of the current study was to determine the feasibility of solvent extraction with the use of ionic liquid methyltri-octyl/decylammonium bis (2,4,4-trimethylpentyl)phosphinate (R₄NCy) as an extractant of Cu(II) in the presence of Fe(III), Zn(II), and Mn(II). In general terms, the results showed a high single extraction efficiency of all the metals under study. In the case of Fe(III) and Zn(II), the extraction was close to 100%. On the contrary, the stripping efficiency was poor to Fe(III) and discrete to Zn(II), but very high to Cu(II) and Mn(II). Finally, the findings of this study suggest that the ionic liquid R₄NCy is feasible for the pre-treatment of the copper solvent extraction process to remove metal impurities such as Fe(III) and Zn(II).

Keywords: ionic liquids; solvent extraction; green chemistry; mining



Citation: Castillo, J.; Toro, N.; Hernández, P.; Navarro, P.; Vargas, C.; Gálvez, E.; Sepúlveda, R. Extraction of Cu(II), Fe(III), Zn(II), and Mn(II) from Aqueous Solutions with Ionic Liquid R₄NCy. *Metals* **2021**, *11*, 1585. <https://doi.org/10.3390/met11101585>

Academic Editors: Antoni Roca and Antonije Onjia

Received: 12 August 2021

Accepted: 1 October 2021

Published: 5 October 2021

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1. Introduction

Hydrometallurgy is an important technique used in mineral processing to obtain pure metal from ores. The hydrometallurgical route commonly involves ore leaching, solvent extraction (SX), and pure metals' electrowinning [1–3]. SX is a technique with several advantages, it is a continuous operation, efficient, high production, low cost, and employs of simple equipment to recover valuable elements from impurities [4,5]. Opposite, SX has industrial-scale severe problems, such as emulsification, solvent volatilization, or degradation of extractant. The negative effect of SX results in decreased production, an increase of production cost, low quality of final products, and environmental implications, mainly by loss of volatile compounds. Hydroxyoxime type extractants are one of the large-scale copper extractants. Currently, a variety of hydroxy oximes are used for the copper industry, either ketoxime or aldoxime or a combination of both [6,7].

The recent advance in metal extraction with SX finds to improve the separation, extraction efficiencies, and selectivity, mainly involving the use of synergistic extractants, ionic liquids, and both, that is, a mixture of extractant and ionic liquids [8–10].

Ionic liquids (ILs) are a green kind of reagents, comprising organic cations and organic/inorganic anions, with a high potential to reduce or replace the hazardous organic solvents [11–13]. The properties of ILs have globally captured the attention, negligible

vapor pressure, high solvating power, thermal and electrochemical stability, good conductivity, and recyclability. The application of ILs is extensive, ranging from refrigeration, lubricants to solvents [14–16]. ILs are proposed in several industrial applications, for example, metal dissolution, metal and organic extraction, electrolytes for batteries, water treatment, and environmental processes [17–22].

In the case of metal extraction with ILs, the list is too long; several elements are studied with these green reagents, for example, molybdenum, rare earth, precious metals, chromium, iron, copper, cobalt, lead, and zinc [23–33].

Some ILs (e.g., based on imidazolium cations) have solubility and decomposition problems in some solvent extraction systems. To resolve the problems described above, ILs based on quaternary ammonium and phosphonium ions are proposed [34–36]. In this context, Swain et al. [37] used trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) and trioctylmethylammonium chloride (Aliquat 336) for cadmium recovery. The results have shown 99% of cadmium extraction using 0.4 M of Cyphos IL 101, and 0.2 M of Aliquat 336. The stripping performance was 70 and 75% from Cyphos IL 101, and Aliquat 336, respectively, used 0.1 M of EDTA. In 2020, Deferm and coworkers reported the separation of In(III) and Zn(II) using Cyphos IL 101. The elements were extracted from ethylene glycol since the amount of IL in the chloride solution was inefficient [38]. Padhan and Sarangi extract Nb and Pr from the magnet with conventional extractant and ionic liquid-based of this same extractant. The efficiency of different extractants Nd and Pr extraction followed the order $R_4NCy > R_4ND > Cyanex\ 272 > D2EHPA > Aliquat\ 336$ [39]. Jing and coworkers recovered cobalt selectively from lithium batteries using the ionic liquid $[C_8H_{17}NH_2]$ [Cyanex 727]. The system has a good performance and produces a final product $CoSO_4 \times 7H_2O$, with high purity (99.7%) [24]. Rybka and Regel-Rosocka report Ni(II) and Co(II) extraction with the use of Cyphos IL 101 and Cyphos IL 104 in chloride media. Both ILs are only very efficient to extract Co(II), with an extraction rate over 95% with Cyphos IL 104, Ni(II) extraction up 20% as maximum [40].

In the present investigation, ionic liquids were synthesized by reacting the commercial extractants Aliquat 336 and Cyanex 272 to investigate the extraction of Cu, Fe, Zn, and Mn from sulfate solutions. The mono and multielement extraction were studied under the following experimental conditions: IL concentration, O/A ratio, and pH. As a final step, the elements loaded in the IL were stripped, varying the sulfuric acid solution and O/A ratio.

2. Materials and Methods

2.1. Reagents and Synthesis of Ionic Liquids

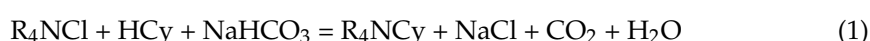
The SX experiments were carried out by a synthetic pregnant leach solution (PLS). The PLS was prepared according to the information of Chilean mining reported by Quijada-Maldonado et al. [41]. The concentrations of Cu(II), Zn(II), Mn(II), and Fe(III) of the PLS are summarized in Table 1. The reagents used in the aqueous phases were copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), Fe(III) sulfate hydrate ($Fe_2(SO_4)_3 \cdot nH_2O$), Mn(II) sulfate monohydrate ($MnSO_4 \cdot H_2O$), Zn sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$), sulfuric acid, and distilled water. All reagents used in aqueous phases were analytical grade purchased from Merck.

Table 1. Concentration of metals in PLS.

Metal	Concentration (mg/L)	
	Literature Report [41]	This Study
Cu(II)	3360	3360
Fe(III)	1570	1570
Mn(II)	>1000	1000
Zn(II)	107	110

The reagents used in the organic phase were the commercial extractants trialkyl methylammonium chloride (Aliquat 336), bis 2,4,4-trimethylpentylphosphinic acid (Cyanex 272), kerosene, and sodium hydrogen carbonate. All the reagents were provided by Sigma-Aldrich (St. Louis, MO, USA), except Cyanex 272, provided by Solvay (Santiago, Chile). Aliquat 336 and Cyanex 272 (commercial grade) were used without further purification; all other used compounds were analytical grade.

Ionic liquid methyltriethyl/decylammonium bis 2,4,4-(trimethylpentyl)phosphinate denoted as R_4NCy was synthesized according to procedures published in the literature [35,36], mixing equimolar ratio of Cyanex 272 (HCy) and Aliquat 336 (R_4NCl), and dissolved the mixture in kerosene to obtain the desired IL concentration. The mixture of Cyanex 272 and Aliquat 336 was washed twice with sodium bicarbonate 0.5 M to remove the chloride anion and the proton from the organic phase. The general reaction of ionic liquid formation is shown in the following equation [39]:



Schematic structures of the ionic liquids and reagent used in this work are depicted in Figure 1. To identify the formation of R_4NCy , the FT-IR spectra was performed on the IL synthesized. The concentration of IL in kerosene was 0.1 M. The frequencies of the characteristic stretching vibrational bands of this extractant in kerosene are presented in Figure 2.

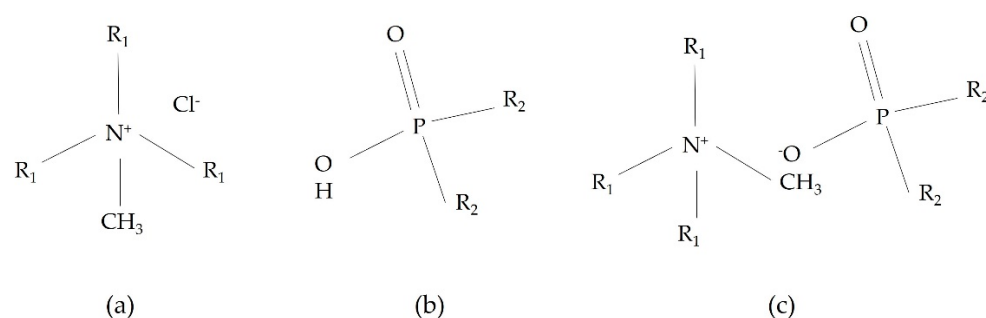


Figure 1. Molecular structure of the reagents and IL used in this work (a) Aliquat 336 (b) Cyanex 272, and (c) R_4NCl .

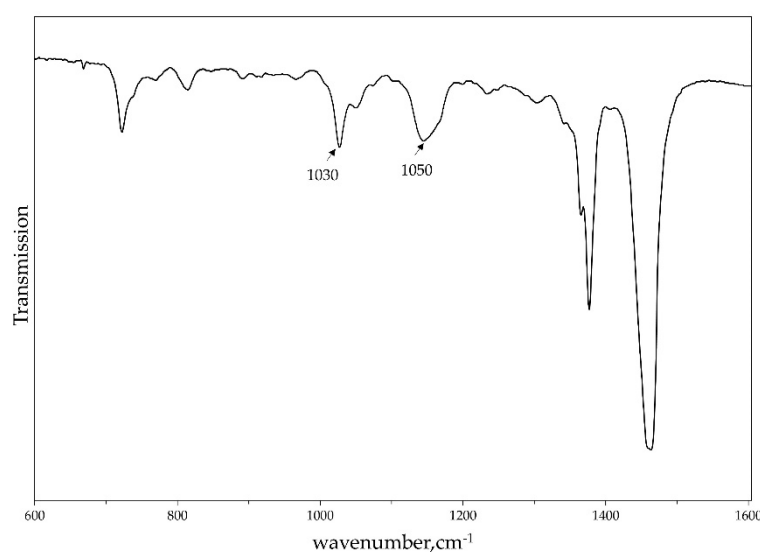


Figure 2. FT-IR of R_4NCy LiCY in kerosene. IL concentration 0.1 M.

2.2. Liquid/Liquid Extraction

The solvent extraction tests were performed in shake flasks (50 mL), at ambient temperature (22 ± 1 °C), with a magnetic stirring set to 200 rev/min for 20 min. The elemental analysis was measured in an aqueous solution by atomic absorption spectrometry (PinAAcle 900F, Perkin Elmer, Waltham, MA, USA). For extraction tests, 10 mL of aqueous phase containing metal was contacted 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 aqueous sample was analyzed for metal concentration. 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 (2)–(4) as the extraction percentage, the stripping percentage, and distribution ratio of the specie (D). The stripping procedure was similar to that of extraction tests. The mass balance was confirmed by measuring the concentration of the metals in the stripped aqueous phase:

$$\text{Extraction (\%)} = ([M]_i - [M]_{aq})/[M]_i \times 100 \quad (2)$$

$$\% \text{ Stripping} = ([M]_{aq}^*/[M]_{org}) \times 100 \quad (3)$$

$$D = ([M]_i - [M]_{aq})/[M]_{aq} \quad (4)$$

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 aqueous phase after stripping, 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 Extraction

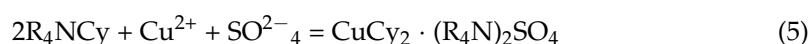
Table 2 shows the single metals extraction as a function of the different molar concentrations of R_4NCy in the organic phase. It is observed that R_4NCy strongly extracts Fe (III) and Zn(II) in all ranges of concentration of IL. In the case of Cu(II) and Mn(II), the extraction increases when the concentration of R_4NCy increases, from 44.14% and 30.63% with 0.1 M of extractant to achieving 97.64% and 93.22% respectively with 0.54 M of extractant. These results are totally surprising, considering that the purpose of the current study was to determine the feasibility of solvent extraction with the use of ionic liquid R_4NCy as an extractant of Cu(II) in the presence of Fe(III), Zn(II), and Mn(II). Therefore, the R_4NCy would not replace the commercial extractants, for example, LIX and ACORGA type, widely used in the hydrometallurgical copper industry. Anyway, the more efficient extraction of Fe and Zn could be positive, considering that are potential impurities that could affect the process SX.

The trend to the high efficiency of extraction of Fe(III) and Zn(II) over the Cu(II) and Mn(II), is reported in literature using similar ILs. Devi [42], despite working with lower copper and ionic liquid concentrations, reported that some ILs showed a similar tendency for Cu extraction. In the case of Fe(III) and Zn(II), Regel-Rosocka et al. [43] report high extraction percentage in chloride media using phosphonium ILs (Cyphos IL 101 and Cyphos IL 104). Another study similar to the previous one, Baczyńska et al. [44], uses three phosphonium ILs (Cyphos IL 101, Cyphos IL 104, and Cyphos IL 167) to extract Zn(II) and Fe(III) in membrane process, the result showed a good extraction efficiency. In the case of extraction of Mn(II) and Fe(III), Ola et al. [45] report a similar tendency, the Fe(III) is extracted more efficiently than Mn(II). Ola et al. used Cyphos IL 101 in chloride media. Finally, Nguyen and Lee report good extraction of Mn(II) with R_4NCy from leaching solution containing Co(II), Ni(II), Mn(II), and Li(I) [46].

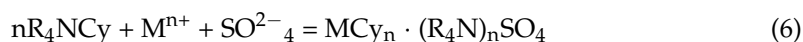
Table 2. Effect concentration of R_4NCy on extraction efficiency and distribution ratio of the species. Experimental conditions: initial pH = 2, O/A = 1, 400 min^{-1} , and 20 min of stirring time.

Metal	IL Concentration [M]	E(%)	D
Cu(II)	0.1	44.14	0.79
	0.27	84.73	5.54
	0.54	97.64	41.4
Fe(III)	0.1	99.77	435
	0.27	99.82	559
	0.54	99.73	372
Mn(II)	0.1	30.63	0.44
	0.27	71.58	2.51
	0.54	93.22	13.7
Zn(II)	0.1	95.55	21.4
	0.27	96.09	24.6
	0.54	92.82	12.9

The mechanism of metal extraction with R_4NCy involves both the metal and the medium in which the tests are carried out. Previous work [35] reported of Cu(II) extraction mechanism with R_4NCy as shown below:



This mechanism can be generalized to the rest of the metals in this study, as shown below:



3.2. Effect of Initial pH in Metal Extraction

The results shown in Figure 3 indicate two hugely different single metal extraction performance tendencies with R_4NCy . In the case of Fe(III) and Zn(II), the efficiency of extraction is not influenced by initial pH in the range 1 to 3; this result confirms the affinity of R_4NCy for Fe(III) and Zn(II).

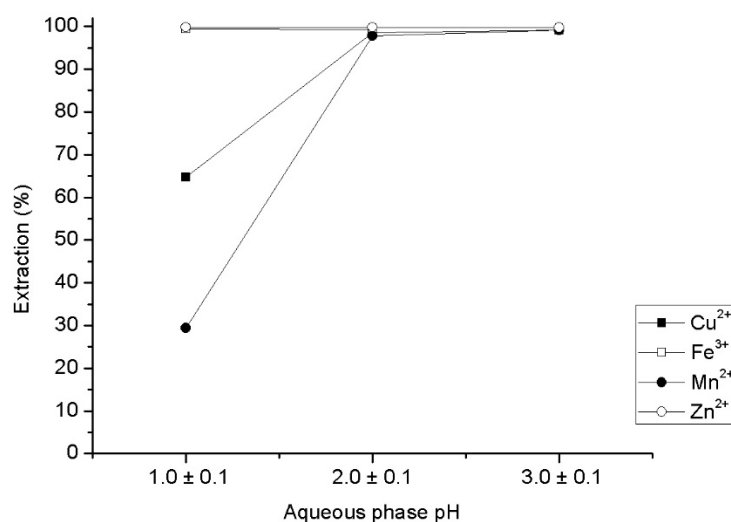


Figure 3. Effect of initial pH on the single extraction percentage of metals from aqueous solution. Experimental conditions: $[R_4NCy] = 0.54\text{ M}$, O/A = 1, 400 min^{-1} , and 20 min of stirring time.

On the contrary, the efficiency of extraction of Cu(II) and Mn(II) is clearly influenced by the initial pH of the aqueous solution, decrease the percentage from close 97% at pH 2 and 3 to 65% and 30% at pH 1, respectively. This makes it possible to carry out a multi-element

extraction at pH values from 2 or, failing that, selective extraction of Fe(III) and Zn(II) at pH 1, like a pretreatment of Cu PLs or recovery of Fe and Zn.

Previous work [35] demonstrates the influence of pH on the Cu(II) extraction using R_4NCy . A similar tendency of pH effect on Cu extraction is reported by Devi [42]. This research uses the same IL for Cu(II) extraction in a diluted system with low IL concentration. The results are very similar in this study; the efficiency of Cu(II) extraction decrease at low pH. This fact is because the solutions with acid pH and high sulfate concentrations produce the undissociated neutral molecule $CuSO_{4aq}$. In the case of Zn(II) and Mn(II), Zhu et al. [47] report a higher Zn(II) extraction over Mn(II) as a function of pH. This research used Cyphos IL 101 as extractant.

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

The results show in Table 3 show a total extraction of Fe(III) and Zn(II). This result is impressive because the 1/6 is a high O/A ratio, and the extraction is not affected, again the R_4NCy demonstrates the high affinity for these cations. On the other hand, Cu(II) and Mn(II) extraction efficiency decreases significantly with the increment of the O/A ratio. The results of these sets of tests show a clear tendency to the high efficiency of extraction of Fe(III) and Zn(II) over the Cu(II) and Mn(II). In this context, to study the O/A ratio, Foltova et al. [48] used quaternary ammonium ionic liquids to extract Co and Sm. The results of Foltova show a similar tendency of this study, the Cu extraction efficiency decay when the O/A relationship is under 0.25 (or 1/4).

Table 3. Effect of O/A ratio on extraction efficiency and distribution ratio of the species. Experimental conditions: $[R_4NCy] = 0.27$ M, initial pH = 2, 400 min^{-1} , and 20 min of stirring time.

Metal	O/A Rate	E(%)	D
Cu(II)	1:1	84.73	5.54
	1:3	28.60	0.40
	1:6	9.08	0.09
Fe(III)	1:1	99.82	559
	1:3	99.82	540
	1:6	91.40	10.6
Mn(II)	1:1	71.58	2.51
	1:3	22.70	0.29
	1:6	11.90	0.13
Zn(II)	1:1	96.09	24.58
	1:3	96.73	29.55
	1:6	82.73	4.78

3.4. Effect of Sulfuric Acid in Metal Stripping

Each loaded organic phase contained 3.25 g/L Cu(II), 1.55 g/L Fe(III), 0.96 g/L Mn(II), and 0.106 g/L Zn(II). Figure 4 shows the stripping performance as a function of the sulfuric acid. It is observed that the sulfuric acid concentration of 2 M all metals are removed over 90% of organic phases. If the acid concentration is reduced to 1 and 0.5 M, the performance decrease significantly in the case of Fe(III); the other metals maintain the best stripping efficiency.

The most interesting aspect of this graph is sensitivity to acid concentration for the stripping Fe(III) loaded IL and the contrast with the stripping performance of the other metals in the study. Cu(II), Zn(II), and Mn(II) were easily stripped from loaded ILs for all acid concentrations studied. In the case of Fe(III), the stripping efficiency is near 95% for 2 M of H_2SO_4 but decreases significantly at 1 and 0.5 M of acid concentration (65% and 20% respectively). This result is relevant for subsequent studies since it is possible to perform a selective stripping of iron concerning the remaining metals extracted in the IL but at higher sulfuric acid concentrations.

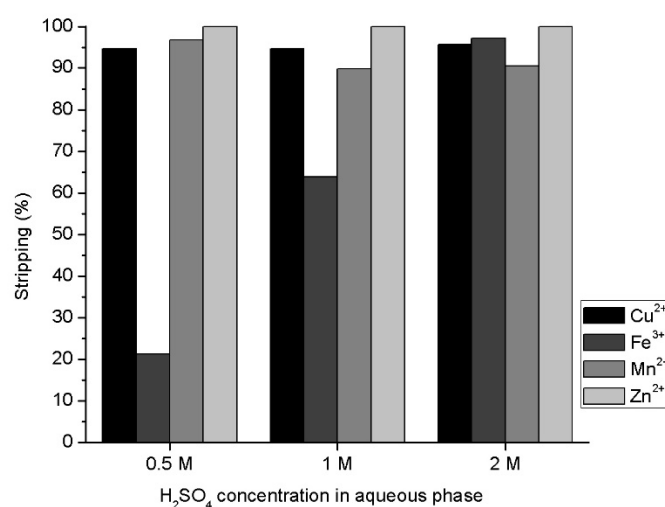


Figure 4. Effect of sulfuric acid on the stripping percentage of metals from the loaded organic phases. Experimental conditions: $[R_4NCy] = 0.54\text{ M}$, $O/A = 1$, 400 min^{-1} , and 20 min of stirring time.

In the literature it has been reported that HNO_3 , HCl , and H_2SO_4 solutions can strip the metals in this study from the loaded ionic liquids. In this context, Nguyen and Lee report the stripping of $Mn(II)$ from $ALiCY$ with HCl , and the best performance of 1 M of acid [46]. Tran et al. reported the stripping tests for $Fe(III)$ loaded ILs using 3 M of H_2SO_4 and HCl . The ILs used by the researchers were $[C4min][N88SA]$, $[C4Py][N88SA]$, $ALiCy$, $ALiD2$, and $ALiPC$. The results of the stripping tests are very heterogeneous, but in general terms, the best performance of stripping from $Fe(III)$ loaded ILs was using H_2SO_4 [49].

3.5. Effect of O/A in Metal Stripping

The loaded organic phases were similar to the previous point. To concentrate the metals in stripping solution, the O/A ratio was investigated from 1/1 to 6/1 (Figure 5). The tests showed a different high performance for metals in the study. It is possible to obtain relatively high stripping efficiency for $Mn(II)$ and $Cu(II)$, even at high O/A ratios (6/1), which reach 60% and 30%, respectively. For $Zn(II)$ and $Fe(III)$, the stripping at 3/1 of O/A ratio were 20% and 2%, respectively, and for 6/1 ratio, both metals were not stripped.

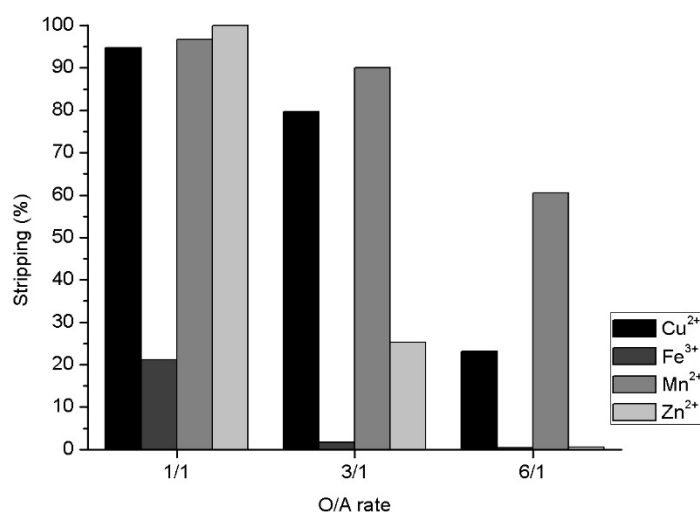


Figure 5. Effect of O/A ratio on the stripping percentage of metals from the organic loaded phases. Experimental conditions: $[R_4NCy] = 0.54\text{ M}$, $[H_2SO_4] = 1\text{ M}$, 400 min^{-1} , and 20 min of stirring time.

To evaluate the effect of the O/A ratio in the stripping efficiency, the relation of organic and aqueous phases was variate from 1/1 to 6/1. Figure 5 shows a clear trend of decreasing

stripping efficiency when increasing the O/A ratio from 1/1 to 6/1, but at the same time, the aqueous phase is concentrated with the discharged metals. The Cu(II) and especially the Mn(II) maintain relative ease for being stripped of the organic phase. On the other hand, Zn(II) and Fe(III) have a poor stripping efficiency; both metals practically are not stripped from load IL over 3/1 O/A ratio.

This result is not entirely evident in solvent extraction systems. For example, Quijada et al. [41] reported a stripping efficiency of Fe(III) close to 50% for similar operational conditions, but in this case, the researchers used TFA as extractant and a Bmim-based ionic liquid as diluent. Finally, these results may be useful to design a selective process of separation of metals contained in a PLS of copper, or a pretreatment of this solution to remove Fe(III) and Zn(II).

4. Conclusions

The present research aimed to evaluate the extraction and stripping of ionic liquid R_4NCy in the presence of a simulated commercial PLS of copper industry containing Cu(II), Mn(II), Zn(II), and Fe(III). The main conclusions are the following:

- (1) The extraction tests showed a strongly selective extraction of Fe(III) and Zn(II) over Cu(II) and Mn(II). A practically total extraction of Fe(III) and Zn(II) was obtained for all the conditions under study. In the case of Cu(II) and Mn(II), the extraction efficiency is strongly influenced by the R_4NCy concentration, the PLS pH, and the O/A ratio.
- (2) The use of 2 M of H_2SO_4 produces a very efficient stripping of all metals loaded into the ionic liquid. The efficiency does not decline as acid concentration decreases, except for Fe(III). The stripping efficiency of iron loaded into the ionic liquid is close to 20% for 0.5 M of sulfuric acid. This result is very promising because it would allow developing a very selective process concerning Fe(III).
- (3) Despite its exploratory nature, this study offers a clear insight into the strong affinity of ionic liquid R_4NCy for Fe(III) and Zn(II) over Cu(II) and Mn(II). This fact opens the possibility of using the ionic liquid R_4NCy in the pre-treatment of copper-rich solutions, removing the impurities as Fe(III) and Zn(II).

Author Contributions: Conceptualization, P.N. and C.V.; methodology, P.H. and E.G.; validation, N.T.; formal analysis, P.H. and E.G.; investigation, J.C. and R.S.; data curation, N.T.; writing—original draft preparation, J.C. and R.S.; writing—review and editing, J.C. and R.S.; visualization, C.V.; supervision, P.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: This work was supported by the Universidad de Atacama (project DIUDA 22317). The proofreading was supported by the project “FIUDA 2030”. The FTIR spectra collections was supported by project “FT-IR Thermo Nicolet iS50, DIUDAQUIP-2017 UDA”.

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

References

1. Cao, X.; Zhang, T.A.; Zhang, W.; Lv, G. Solvent Extraction of Sc(III) by D2EHPA/TBP from the Leaching Solution of Vanadium Slag. *Metals* **2020**, *10*, 790. [[CrossRef](#)]
2. Sekisov, A.; Rasskazova, A. Assessment of the Possibility of Hydrometallurgical Processing of Low-Grade Ores in the Oxidation Zone of the Malmyzh Cu-Au Porphyry Deposit. *Minerals* **2021**, *11*, 69. [[CrossRef](#)]
3. Mahmoudi, A.; Shakibania, S.; Rezaee, S.; Mokmeli, M. Effect of the Chloride Content of Seawater on the Copper Solvent Extraction Using Acorga M5774 and LIX 984N Extractants. *Sep. Purif. Technol.* **2020**, *251*, 117394. [[CrossRef](#)]
4. Rao, M.; Zhang, T.; Li, G.; Zhou, Q.; Luo, J.; Zhang, X.; Zhu, Z.; Peng, Z.; Jiang, T. Solvent Extraction of Ni and Co from the Phosphoric Acid Leaching Solution of Laterite Ore by P204 and P507. *Metals* **2020**, *10*, 545. [[CrossRef](#)]

5. Ying, Z.; Ren, X.; Li, J.; Wu, G.; Wei, Q. Recovery of Chromium(VI) in Wastewater Using Solvent Extraction with Amide. *Hydrometallurgy* **2020**, *196*, 105440. [\[CrossRef\]](#)
6. Zhang, W.; Xie, X.; Tong, X.; Du, Y.; Song, Q.; Feng, D. Study on the Effect and Mechanism of Impurity Aluminum on the Solvent Extraction of Rare Earth Elements (Nd, Pr, La) by P204-P350 in Chloride Solution. *Minerals* **2021**, *11*, 61. [\[CrossRef\]](#)
7. Shakibania, S.; Mahmoudi, A.; Mokmeli, M.; Rashchi, F. The Effect of the Chloride Ion on Chemical Degradation of LIX 984N Extractant. *Miner. Eng.* **2020**, *159*, 106628. [\[CrossRef\]](#)
8. Wang, L.Y.; Guo, Q.J.; Lee, M.S. Recent Advances in Metal Extraction Improvement: Mixture Systems Consisting of Ionic Liquid and Molecular Extractant. *Sep. Purif. Technol.* **2019**, *210*, 292–303. [\[CrossRef\]](#)
9. Hong, T.; Liu, M.; Ma, J.; Yang, G.; Li, L.; Mumford, K.A.; Stevens, G.W. Selective Recovery of Rhenium from Industrial Leach Solutions by Synergistic Solvent Extraction. *Sep. Purif. Technol.* **2020**, *236*, 116281. [\[CrossRef\]](#)
10. Hidayah, N.N.; Abidin, S.Z. The Evolution of Mineral Processing in Extraction of Rare Earth Elements Using Liquid-Liquid Extraction: A Review. *Miner. Eng.* **2018**, *121*, 146–157. [\[CrossRef\]](#)
11. Keskin, S.; Kayrak-Talay, D.; Akman, U.; Hortaçsu, Ö. A Review of Ionic Liquids towards Supercritical Fluid Applications. *J. Supercrit. Fluids* **2007**, *43*, 150–180. [\[CrossRef\]](#)
12. Park, J.; Jung, Y.; Kusumah, P.; Lee, J.; Kwon, K.; Lee, C.K. Application of Ionic Liquids in Hydrometallurgy. *Int. J. Mol. Sci.* **2014**, *15*, 15320–15343. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Weng, J.; Wang, C.; Li, H.; Wang, Y. Novel Quaternary Ammonium Ionic Liquids and Their Use as Dual Solvent-Catalysts in the Hydrolytic Reaction. *Green Chem.* **2006**, *8*, 96. [\[CrossRef\]](#)
14. Quijada-maldonado, E.; Olea, F.; Sepúlveda, R.; Cabezas, R.; Merlet, G.; Romero, J. Possibilities and Challenges for Ionic Liquids in Hydrometallurgy. *Sep. Purif. Technol.* **2020**, *251*, 117289. [\[CrossRef\]](#)
15. Lee, J.; Yeo, C.-D.; Hu, Z.; Thalangama-Arachchige, V.D.; Kaur, J.; Quitevis, E.L.; Kumar, G.; Koh, Y.P.; Simon, S. Friction and Wear of Pd-Rich Amorphous Alloy (Pd43Cu27Ni10P20) with Ionic Liquid (IL) as Lubricant at High Temperatures. *Metals* **2019**, *9*, 1180. [\[CrossRef\]](#)
16. Alguacil, F.J.; López, F.A. Permeation of AuCl_4^- Across a Liquid Membrane Impregnated with $\text{A324H}^+\text{Cl}^-$ Ionic Liquid. *Metals* **2020**, *10*, 363. [\[CrossRef\]](#)
17. Diabate, P.D.; Dupont, L.; Boudesocque, S.; Mohamadou, A. Novel Task Specific Ionic Liquids to Remove Heavy Metals from Aqueous Effluents. *Metals* **2018**, *8*, 412. [\[CrossRef\]](#)
18. Rodríguez, M.; Ayala, L.; Robles, P.; Sepúlveda, R.; Torres, D.; Carrillo-Pedroza, F.R.; Jeldres, R.I.; Toro, N. Leaching Chalcocopyrite with an Imidazolium-Based Ionic Liquid and Bromide. *Metals* **2020**, *10*, 183. [\[CrossRef\]](#)
19. Salar-García, M.J.; Ortiz-Martínez, V.M.; Hernández-Fernández, F.J.; de los Ríos, A.P.; Quesada-Medina, J. Ionic Liquid Technology to Recover Volatile Organic Compounds (VOCs). *J. Hazard. Mater.* **2017**, *321*, 484–499. [\[CrossRef\]](#)
20. Carlesi, C.; Cortes, E.; Dibernardi, G.; Morales, J.; Muñoz, E. Ionic Liquids as Additives for Acid Leaching of Copper from Sulfidic Ores. *Hydrometallurgy* **2016**, *161*, 29–33. [\[CrossRef\]](#)
21. Jin, Y.; Zhang, J.; Song, J.; Zhang, Z.; Fang, S.; Yang, L.; Hirano, S.I. Functionalized Ionic Liquids Based on Quaternary Ammonium Cations with Two Ether Groups as New Electrolytes for Li/LiFePO₄ Secondary Battery. *J. Power Sources* **2014**, *254*, 137–147. [\[CrossRef\]](#)
22. Egashira, M.; Okada, S.; Yamaki, J.I.; Yoshimoto, N.; Morita, M. Effect of Small Cation Addition on the Conductivity of Quaternary Ammonium Ionic Liquids. *Electrochim. Acta* **2005**, *50*, 3708–3712. [\[CrossRef\]](#)
23. Matsumoto, M.; Yamaguchi, T.; Tahara, Y. Extraction of Rare Earth Metal Ions with an Undiluted Hydrophobic Pseudoprotic Ionic Liquid. *Metals* **2020**, *10*, 502. [\[CrossRef\]](#)
24. Jing, X.; Wu, Z.; Zhao, D.; Li, S.; Kong, F.; Chu, Y. Environmentally Friendly Extraction and Recovery of Cobalt from Simulated Solution of Spent Ternary Lithium Batteries Using the Novel Ionic Liquids of $[\text{C}_8\text{H}_{17}\text{NH}_2][\text{Cyanex 272}]$. *ACS Sustain. Chem. Eng.* **2021**, *9*, 2475–2485. [\[CrossRef\]](#)
25. Łukomska, A.; Wiśniewska, A.; Dąbrowski, Z.; Domańska, U. Liquid-Liquid Extraction of Cobalt(II) and Zinc(II) from Aqueous Solutions Using Novel Ionic Liquids as an Extractants. *J. Mol. Liq.* **2020**, *307*, 112955. [\[CrossRef\]](#)
26. Tran, T.T.; Liu, Y.; Lee, M.S. Recovery of Pure Molybdenum and Vanadium Compounds from Spent Petroleum Catalysts by Treatment with Ionic Liquid Solution in the Presence of Oxidizing Agent. *Sep. Purif. Technol.* **2021**, *255*, 117734. [\[CrossRef\]](#)
27. Binnemans, K. Lanthanides and Actinides in Ionic Liquids. *Compr. Inorg. Chem. II Second. Ed. Elem. Appl.* **2013**, *2*, 641–673. [\[CrossRef\]](#)
28. Maria, L.; Cruz, A.; Carretas, J.M.; Monteiro, B.; Galinha, C.; Gomes, S.S.; Araújo, M.F.; Paiva, I.; Marçalo, J.; Leal, J.P. Improving the Selective Extraction of Lanthanides by Using Functionalised Ionic Liquids. *Sep. Purif. Technol.* **2020**, *237*, 116354. [\[CrossRef\]](#)
29. Devi, N.; Sukla, L.B. Studies on Liquid-Liquid Extraction of Yttrium and Separation from Other Rare Earth Elements Using Bifunctional Ionic Liquids. *Miner. Process. Extr. Metall. Rev.* **2019**, *40*, 46–55. [\[CrossRef\]](#)
30. Rzelewska-Piekut, M.; Regel-Rosocka, M. Separation of Pt(IV), Pd(II), Ru(III) and Rh(III) from Model Chloride Solutions by Liquid-Liquid Extraction with Phosphonium Ionic Liquids. *Sep. Purif. Technol.* **2019**, *212*, 791–801. [\[CrossRef\]](#)
31. Sepúlveda, R.; Romero, J.; Sánchez, J. Copper Removal from Aqueous Solutions by Means of Ionic Liquids Containing a β -Diketone and the Recovery of Metal Complexes by Supercritical Fluid Extraction. *J. Chem. Technol. Biotechnol.* **2014**, *89*, 899–908. [\[CrossRef\]](#)

32. Kim, B.K.; Lee, E.J.; Kang, Y.; Lee, J.J. Application of Ionic Liquids for Metal Dissolution and Extraction. *J. Ind. Eng. Chem.* **2018**, *61*, 388–397. [\[CrossRef\]](#)
33. Valdés Vergara, M.A.; Lijanová, I.V.; Likhonova, N.V.; Olivares Xometl, O.; Jaramillo Viguera, D.; Morales Ramirez, A.J. Recycling and Recovery of Ammonium-Based Ionic Liquids after Extraction of Metal Cations from Aqueous Solutions. *Sep. Purif. Technol.* **2014**, *155*, 110–117. [\[CrossRef\]](#)
34. Nguyen, V.N.H.; Le, M.N.; Lee, M.S. Comparison of Extraction Ability between a Mixture of Alamine 336/Aliquat 336 and D2EHPA and Ionic Liquid ALi-D2 from Weak Hydrochloric Acid Solution. *Metals* **2020**, *10*, 1678. [\[CrossRef\]](#)
35. Castillo, J.; Coll, M.T.; Fortuny, A.; Navarro Donoso, P.; Sepúlveda, R.; Sastre, A.M. Cu(II) Extraction Using Quaternary Ammonium and Quaternary Phosphonium Based Ionic Liquid. *Hydrometallurgy* **2014**, *141*, 89–96. [\[CrossRef\]](#)
36. Fortuny, A.; Coll, M.T.; Sastre, A.M. Use of Methyltrioctyl/Decylammonium Bis 2,4,4-(Trimethylpentyl)Phosphinate Ionic Liquid (ALiCY IL) on the Boron Extraction in Chloride Media. *Sep. Purif. Technol.* **2012**, *97*, 137–141. [\[CrossRef\]](#)
37. Swain, S.S.; Nayak, B.; Devi, N.; Das, S.; Swain, N. Liquid-Liquid Extraction of Cadmium(II) from Sulfate Medium Using Phosphonium and Ammonium Based Ionic Liquids Diluted in Kerosene. *Hydrometallurgy* **2016**, *162*, 63–70. [\[CrossRef\]](#)
38. Deferm, C.; Onghena, B.; Nguyen, V.T.; Banerjee, D.; Franssaer, J.; Binnemans, K. Non-Aqueous Solvent Extraction of Indium from an Ethylene Glycol Feed Solution by the Ionic Liquid Cyphos IL 101: Speciation Study and Continuous Counter-Current Process in Mixer-Settlers. *RSC Adv.* **2020**, *10*, 24595–24612. [\[CrossRef\]](#)
39. Padhan, E.; Sarangi, K. Recovery of Nd and Pr from NdFeB Magnet Leachates with Bi-Functional Ionic Liquids Based on Aliquat 336 and Cyanex 272. *Hydrometallurgy* **2017**, *167*, 134–140. [\[CrossRef\]](#)
40. Rybka, P.; Regel-Rosocka, M. Nickel(II) and Cobalt(II) Extraction from Chloride Solutions with Quaternary Phosphonium Salts. *Sep. Sci. Technol.* **2012**, *47*, 1296–1302. [\[CrossRef\]](#)
41. Quijada-Maldonado, E.; Romero, J.; Osorio, I. Selective Removal of Iron(III) from Synthetic Copper(II) Pregnant Leach Solutions Using [Bmim][Tf2N] as Diluent and TFA as Extracting Agent. *Hydrometallurgy* **2016**, *159*, 54–59. [\[CrossRef\]](#)
42. Devi, N. Solvent Extraction and Separation of Copper from Base Metals Using Bifunctional Ionic Liquid from Sulfate Medium. *Trans. Nonferrous Met. Soc. China* **2016**, *26*, 874–881. [\[CrossRef\]](#)
43. Regel-Rosocka, M.; Nowak, Ł.; Wiśniewski, M. Removal of Zinc(II) and Iron Ions from Chloride Solutions with Phosphonium Ionic Liquids. *Sep. Purif. Technol.* **2012**, *97*, 158–163. [\[CrossRef\]](#)
44. Baczyńska, M.; Regel-Rosocka, M.; Coll, M.T.; Fortuny, A.; Sastre, A.M.; Wiśniewski, M. Transport of Zn(II), Fe(II), Fe(III) across Polymer Inclusion Membranes (PIM) and Flat Sheet Supported Liquid Membranes (SLM) Containing Phosphonium Ionic Liquids as Metal Ion Carriers. *Sep. Sci. Technol.* **2016**, *51*, 2639–2648. [\[CrossRef\]](#)
45. Ola, P.D.; Kurobe, Y.; Matsumoto, M. Solvent Extraction and Stripping of Fe and Mn from Aqueous Solution Using Ionic Liquids as Extractants. *Chem. Eng. Trans.* **2017**, *57*, 1135–1140. [\[CrossRef\]](#)
46. Nguyen, V.N.H.; Lee, M.S. Separation of Co(II), Ni(II), Mn(II) and Li(I) from Synthetic Sulfuric Acid Leaching Solution of Spent Lithium Ion Batteries by Solvent Extraction. *J. Chem. Technol. Biotechnol.* **2021**, *96*, 1205–1217. [\[CrossRef\]](#)
47. Zhu, Z.; Yoko, P.; Cheng, C.Y. Recovery of Cobalt and Manganese from Nickel Laterite Leach Solutions Containing Chloride by Solvent Extraction Using Cyphos IL 101. *Hydrometallurgy* **2017**, *169*, 213–218. [\[CrossRef\]](#)
48. Sobekova Foltova, S.; vander Hoogerstraete, T.; Banerjee, D.; Binnemans, K. Samarium/Cobalt Separation by Solvent Extraction with Undiluted Quaternary Ammonium Ionic Liquids. *Sep. Purif. Technol.* **2019**, *210*, 209–218. [\[CrossRef\]](#)
49. Tran, T.T.; Iqbal, M.; Lee, M.S. Comparison of the Extraction and Stripping Behavior of Iron (III) from Weak Acidic Solution between Ionic Liquids and Commercial Extractants. *J. Korean Inst. Met. Mater.* **2019**, *57*, 787–794. [\[CrossRef\]](#)