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Hydroxy-Carboxylic Acids as Green and Abundant Ligands for Sustainable Recovery of Copper from a Multimetallic Powder: A Proof of Concept

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The recovery of copper and other valuable metals had become increasingly strategic for the future of the global economy, particularly in regions lacking abundant mineral resources, such as most European countries. In this study, we investigated the viability of utilizing environmentally friendly, cost-effective, abundant and bio-based ligands, specifically carboxylic acids and their derivatives, for copper leaching in a low-temperature hydrometallurgical process. Our investigation focused on elucidating the impact of substituents in the α position of hydroxy-carboxylic acids on copper solubilization efficacy. Notably, hydroxy-carboxylic acids, like malic acid and lactic acid, were evidenced as particularly promising ligands for leaching copper from a custom-made multimetallic powder. By thoroughly characterizing the obtained complexes (Raman, UV-Vis) and by supporting the experimental efforts by a Design of Experiment (DoE) approach, we optimized the leaching process. The influence of experimental parameters such as pH, temperature, leaching time, and Cu/ligand molar ratio on process yield (determined through Inductively Coupled Plasma – Optical Emission Spectroscopy, ICP-OES, analysis) was thoroughly investigated. Additionally, we developed a subsequent copper recovery step by precipitating copper (II) hydroxide in an alkaline environment, guided by speciation diagrams tailored for each copper-ligand system.

Introduction

The recovery of copper and other valuable metals is becoming increasingly vital for the future of the global economy, especially in regions with limited mineral resources, like many European countries. With copper being essential for electrical wiring, electronics, and renewable energy technologies, its demand is rising, highlighting the importance of efficient recovery methods.[1] European Union, in particular, faces significant challenges due to the relative scarcity of raw materials in Europe, including critical and strategic metals essential for various industries, such as copper, platinum group metals (PGM) and rare earths.[2] Because of its technological relevance, copper has been inserted in 2023 in the list of Strategical Raw Materials by the European Union.[3]

This scarcity requires innovative and more sustainable approaches to metal recovery, emphasizing the utilization of alternative sources and environmentally friendly processes. The current state of the art in copper recovery predominantly relies on traditional pyrometallurgical and hydrometallurgical techniques.[4–6] The former involves high-temperature smelting processes to extract copper from sulfide ores, producing significant emissions and requiring substantial energy inputs.[7–8] On the contrary, the latter utilizes aqueous solutions to dissolve copper from ores or concentrates, offering lower energy consumption and reduced environmental impact by exploiting methods like acid leaching, solvent extraction, and electrowinning.[5] While these methods have been effective, they often involve the use of harsh chemicals (e.g. mineral acids such as hydrochloric acid, nitric acid, sulfuric acid and mixtures thereof) and generate large volumes of wastewater, posing environmental and economic challenges.[7] However, hydrometallurgical methods can also rely on more sustainable leaching agents, offering a promising avenue for metal extraction, by substituting strong mineral acids with bio-based ligands such as carboxylic acids and their derivatives.[9–10] These ligands do not only facilitate metal dissolution, but also comply with the principles of green chemistry, minimizing environmental impact and enhancing resource efficiency.[11–12] In a typical hydrometallurgical process for secondary copper recovery, once copper(II) is dissolved in water by means of mineral acids, it then undergoes a solvent extraction step in kerosene, in which phenolic oximes are employed as ligands to form

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copper complexes in the organic phase.[13] After that, the organic phase is counter-extracted with an acidic water solution (mainly hydrochloric or sulfuric acid solution), which is then used as electrolytic bath for the copper electrorefinement process.[13] The oximes employed in the solvent extraction step form very stable complexes with copper (II) ions, in a selective way.[14] In particular, phenolic oximes allow the formation of a six member ring complex, with copper being one of the vertexes of the hexagon, bound directly to the phenolic hydroxyl group and to the nitrogen atom.[15] The efficiency of metal binding and selectivity of the oximes towards copper can be tuned through the specific substituents, or by controlling the pH and counter anions present in the metal leachate.[13] However, when dealing with copper-based raw materials containing high amount of impurities (both metals and anions), as secondary copper sources are, oximes become much less effective, and are often decomposed during the process.[15] Furthermore, in order to achieve the target copper concentration in the electrolytic bath, more solvent extraction and counter-extraction procedures would be required, also due to the fact that, in future, copper ores will be of lower grade.[16] Oximes, however, were found to be less able to withstand these repeated extractions, which resulted in their deterioration.[15] Despite this, the coordination geometry of copper (II) oximes complexes is a good starting point for defining the steric and compositional requirements of a ligand to be effective in a hydrometallurgical process for the recovery of copper. As far as the latter point is concerned, nature and number of functional groups, electrodonating/withdrawing properties of these and geometry of the ligand are relevant factors to be considered to implement effective ligand development strategies for selective metal recovery.

Among potential and abundant alternative to expensive and demanding coordination agents, carboxylic acids and their derivatives have emerged as viable ligands for metal leaching due to their biodegradability, low toxicity, and economic affordability.[17–20] By harnessing the complexing abilities of these bio-based ligands, it is possible to enhance the dissolution of metals from various sources, including ores and electronic waste.[21–22] Notably, the number, position and nature of substituents on the carboxylic acid molecule can significantly influence its effectiveness as a metal leaching agent.[23] Our study focuses on investigating the feasibility of employing carboxylic acids, particularly those with hydroxy-functionalities such as malic acid and lactic acid, for the leaching of copper in a low-temperature hydrometallurgical process. The aim is to elucidate the impact of substituents in the α position of the carboxylic acids on the efficacy of copper solubilization. Understanding the structure-activity relationship of these ligands is crucial for optimizing the leaching process and enhancing the metal recovery efficiency. To achieve this goal, a systematic exploration of the experimental parameters space supported by a Design of Experiment (DoE)[24] methodology was employed. The influence of key experimental parameters, including pH, temperature, leaching time, and Cu/ligand molar ratio, on the leaching process yield[25] was thoroughly investigated. Remarkably, the developed process does not require a solvent extraction step, avoiding the use of harmful organic solvents, and lowering the number of steps of the whole process.

Results and Discussion

The first step of the experimental activity was devoted to identifying the most promising ligands to be further tested. For the selection of the most promising ligands, we considered the stability of the corresponding complex formed with copper. The formation of stable complexes is correlated to the possibility of separating copper from other metals. The formation of a labile complex with Cu could lower the efficiency of the process, both in terms of yield of the process (i.e. the amount of copper leached from the powder) and selectivity. However, also the formation of a too strong complex could be an issue for what concerns the post-leaching separation of copper from the ligand for the final metal recovery.

The screening of the ligands was performed by treating copper (II) sulfate with different carboxylic acids, as described in the experimental section. The carboxylic acids employed were succinic (SA), L-aspartic (AA), DL- malic (MA), DL-tartaric (TA) and DL-lactic acid (LA), whose structures are reported in Figure 1.

Even though the carboxylic acids reported in Figure 1 could be found in different stereoisomers, we did not consider this as a relevant parameter in our study. Carboxylic acids, and in

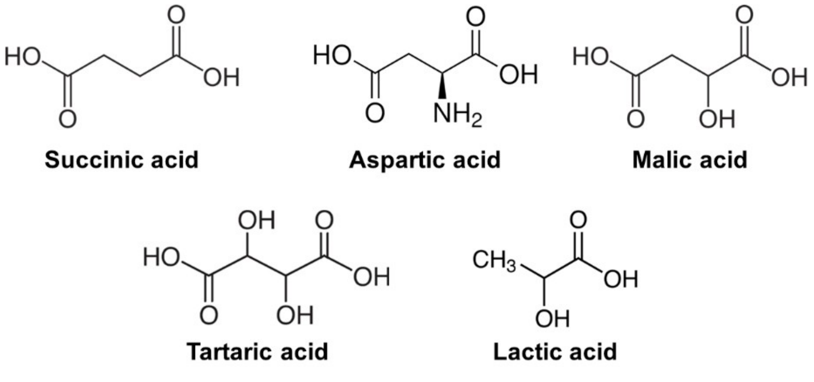


Figure 1. Structure of the employed carboxylic acids.

particular hydroxy-carboxylic acids, are known to form different complexes with metals according to the pH of the solution.[23,26] Furthermore, also the solubility of such complexes is usually determined by the pH.[26] For these reasons, the formation of complexes between copper and the acids reported in Figure 1 was evaluated as a function of the pH of the solution (vide infra in experimental part), by performing the reaction between a stoichiometric amount of Cu^{2+} and the selected ligand. In literature, hydroxy-carboxylic acids are reported to form complexes with metals, and in particular with copper (II), in which the metal cation is bound to the ligand through one oxygen atom from the carboxylate and the alcoholic oxygen.[26–27]

When mixing cupric sulfate and succinic acid in a 1:1 molar ratio in water the native pH was 2.3, and the visible spectrum of the obtained solution was superimposable to the spectrum of cupric sulfate at the same pH (Figure 2a). At pH 2.3, succinic acid is mainly present in water in the undissociated form ($pK_{a,1} = 4.07$),[28] which cannot interact with Cu^{2+} cations and form the complex. By adding dropwise a solution of NaOH 2 M, we observed the formation of a pale blue precipitate at pH 3, attributed to the formation of insoluble copper (II) succinate, as confirmed by the Raman spectrum of the precipitate (Figure 2b). Benitha et al[29] reported a polymeric structure for copper (II) succinate, in which the succinate moieties form a bridge between two Cu(II) cations, in an overall neutral structure which is proven to be insoluble in water.

To further test the solubility of the copper complex, we performed an analogous reaction between Cu^{2+} and aspartic acid, which bears a $-NH_2$ moiety on the α-position with respect to succinic acid. In this case, the amine group was supposed to participate in the formation of the complex with copper, as reported by Rani et al.[30] Indeed, we observed a blue-shift in the visible spectrum of the Cu^{2+}/aspartate system at different pH from 2.8 (native pH) to about 9, which was compliant with the formation of a complex (Figure 2c). However, at pH 5 we also observed the formation of a precipitate of copper (II) aspartate, as confirmed by the Raman spectrum reported in Figure 2d, which shows signals from the ligand and Cu–O and Cu–N stretching, confirming that aspartate binds copper both with carboxylate and amine groups. Although at pH 5 the amine group of aspartate should be protonated ($pK_{a,3} = 9.85$),[31] probably, during the formation of the complex, the proton bound to the nitrogen is substituted by a Cu(II) cation, resulting in the formation of a neutral and insoluble complex. This finding is supported by the work of Rani et al[30] who reported a structure for this complex in which Cu^{2+} is bound to the aspartate through the oxygen atoms from the carboxylic groups and to the nitrogen atom of the amine group, replacing the protons.

The introduction of an electron-donating group in the α position (i.e. amine group) of succinic acid resulted anyway in the formation of a more stable complex with copper (II). Therefore, in order to better understand the effect of substituents on the α position of the carboxylic acid, we employed malic acid as ligand, which presents a hydroxyl moiety in place of the amine. Alcoholic groups are weaker bases with respect to amines, therefore the hydroxyl group of malic acid in the form of free ligand is not supposed to undergo relevant acid/base equilibria. By mixing the copper sulfate solution with a stoichiometric amount of malic acid (1:1 molar

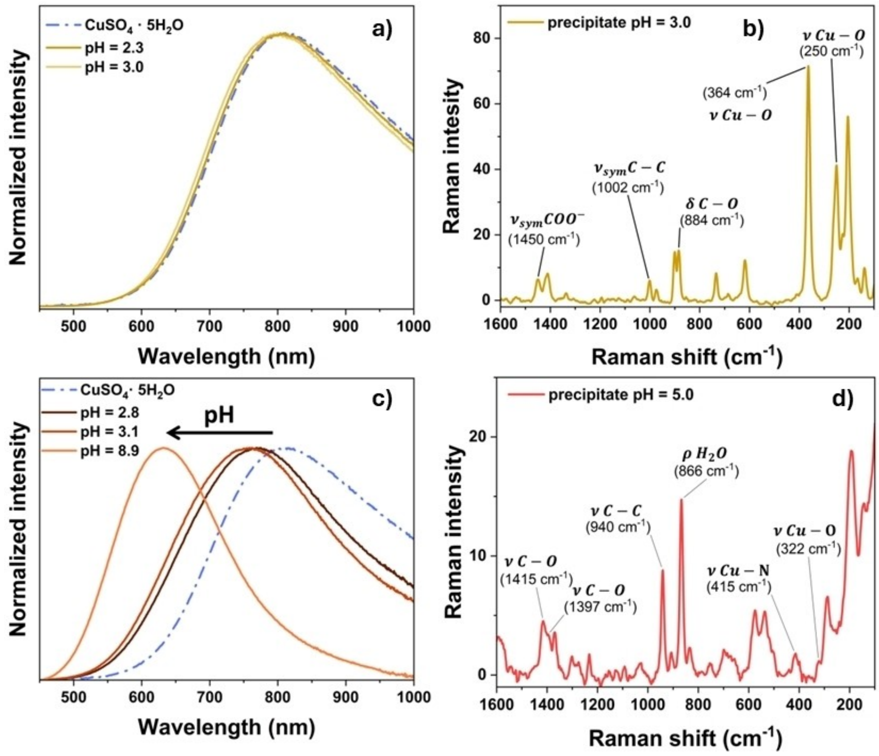


Figure 2. Visible and Raman spectra of copper (II) succinate (a, b) and copper (II) aspartate (c, d) systems.

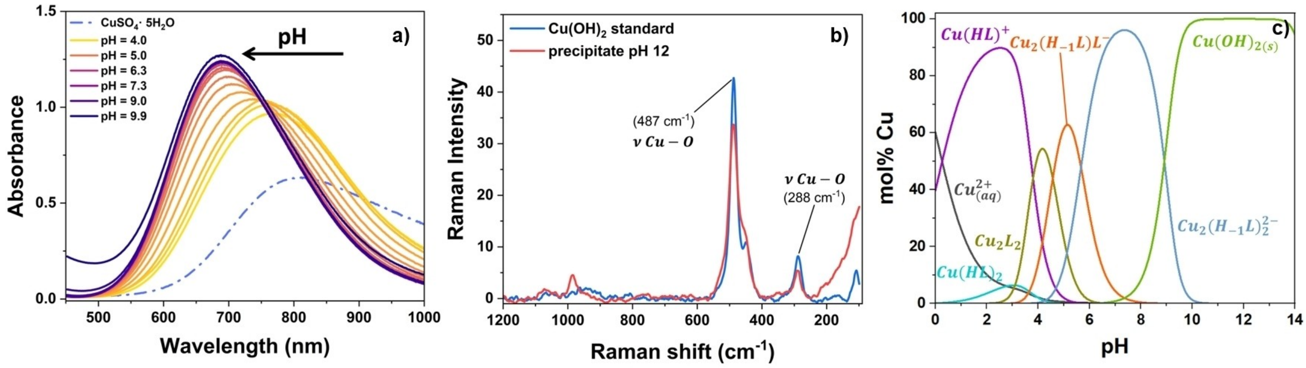


Figure 3. Visible and Raman spectra (a, b, respectively), and distribution diagram (c) of copper (II) malate system.

ratio Cu^{2+}/MA) we were able to obtain stable complexes in a wide range of pH from 1.8 (autogenic) to 12. The visible spectrum recorded for the obtained solutions (Figure 3a) showed a blue-shift of the maximum of absorption, and an increase of its intensity by increasing the pH, indicating the formation of more stable and less symmetric complexes.[32] This finding well fits with the speciation diagram we obtained for the Cu^{2+}/malic acid system in 1:1 molar ratio (vide infra experimental part), and total Cu^{2+} concentration of 0.1 M (Figure 3c).

In the diagram above (Figure 3c), L represents malic acid (the ligand), HL^- is the malic acid only once deprotonated and the species $H_{-1}L^{3-}$ is a molecule of malic acid with also the alcoholic group deprotonated. Thanks to the interaction with the metal cation, the alcoholic group in the α position in turns becomes more acidic and can be deprotonated at relatively low pH, thus forming more stable and soluble complexes.

According to the diagram in Figure 3c, at $pH > 10$, the main copper species should be hydroxide, and indeed we observed the presence of a blue precipitate which was confirmed to be copper hydroxide from Raman spectroscopy (Figure 3b). This kind of interaction between the metal center and the ligand was very promising for the copper recovery process, because it allowed a sufficiently stable and soluble complex to be formed between copper (II) and malic acid, and then for copper hydroxide to precipitate, resulting in the recovery of both the metal and the ligand. In this perspective we also tested lactic acid and tartaric acid as the monocarboxylic and di-hydroxycarboxylic counterpart of malic acid, respectively (Figure 1). In particular, tartaric acid gave similar results with respect to malic acid (visible spectra recorded at increasing pH are reported in Figure 4a), however we were not able to precipitate copper (II) hydroxide at high pH. This was probably due because of the presence of two alcoholic groups on the molecule, which could be both deprotonated, leading to a too strong interaction with Cu^{2+}, inhibiting the formation of the hydroxide. Since in the process of copper recovery the separation of the metal cation from the ligand is a necessary step, we excluded tartaric acid from further investigations.

On the other hand, lactic acid resulted to be reliable for the copper recovery process, enabling the formation of stable and soluble complexes, and the precipitation of copper hydroxide at pH 12 (visible and Raman spectra in Figure 4b, c, respectively). However, the copper hydroxide precipitated already at pH about 7, which is almost the only difference with respect to what we observed in the copper/MA system. Since lactic acid is monocarboxylic, we used a 1:2 molar ratio between Cu^{2+} and lactic acid, to be compared to the results obtained for malic acid. In Figure 4d the speciation diagram we obtained for the Cu^{2+}/LA system is reported.

In the diagram above, L represents lactic acid (the ligand), L^- is the lactic acid only once deprotonated and the species $H_{-1}L^{2-}$ is a molecule of lactic acid with also the alcoholic group deprotonated. This behavior is very similar to the one of MA (Figure 3), and it fits with our experimental findings. For this reason, further leaching experiments on multi-metallic powder were conducted using only malic and lactic acid.

Since during a leaching experiment several parameters are involved, such as pH, leaching time, temperature and molar ratio between metals and ligand, in order to better rationalize the effects of each parameter on the leaching behavior, we adopted a Design of Experiment approach (see the experimental part for further details).[24] We employed a full factorial design with four factors, three of them varied between two levels and one on three levels. Table 1 shows the design.

For all the experiments, we set the liquid/solid ratio, i.e. the ratio of the volume of the leaching solution to the mass of the sample powder, at 25 mL/g and the total volume of the solution at 15 mL. We obtained a set of 24 randomized experiments with one replicate to be performed, and we set the copper concentration in the leachate solution (expressed as ppm) as the output of the DoE. The employed ligand was malic acid, since it showed both a high Cu recovery percentage and the

Table 1. Design summary of the Design of Experiment.

Parameter	Level 1	Level 2	Level 3
Temperature	40 °C	80 °C	–
Time	1 h	4 h	–
pH	$< pK_{a,1}$	$pK_{a,1} < pH < pK_{a,2}$	$pH > pK_{a,2}$
Cu^{2+}/MA molar ratio	1:1	1:2	–

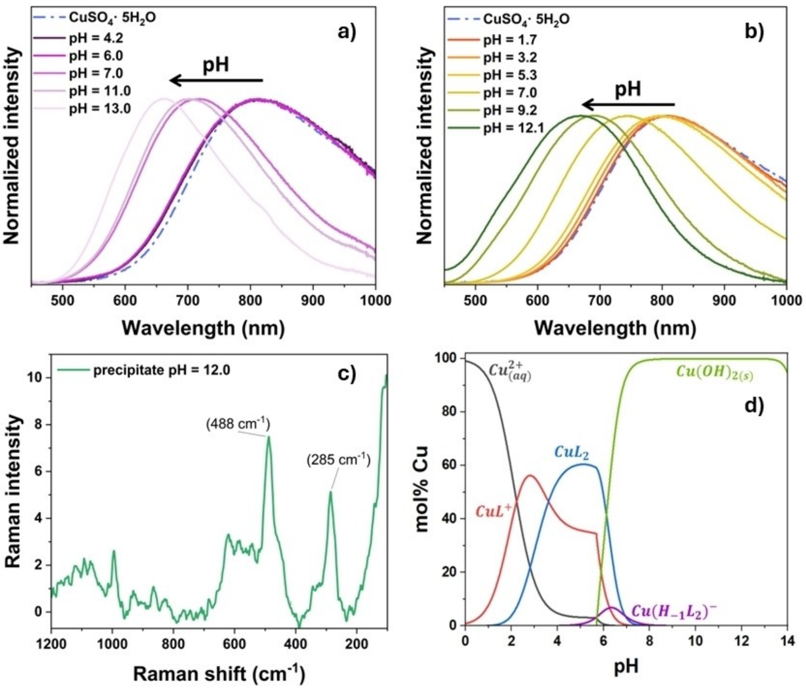
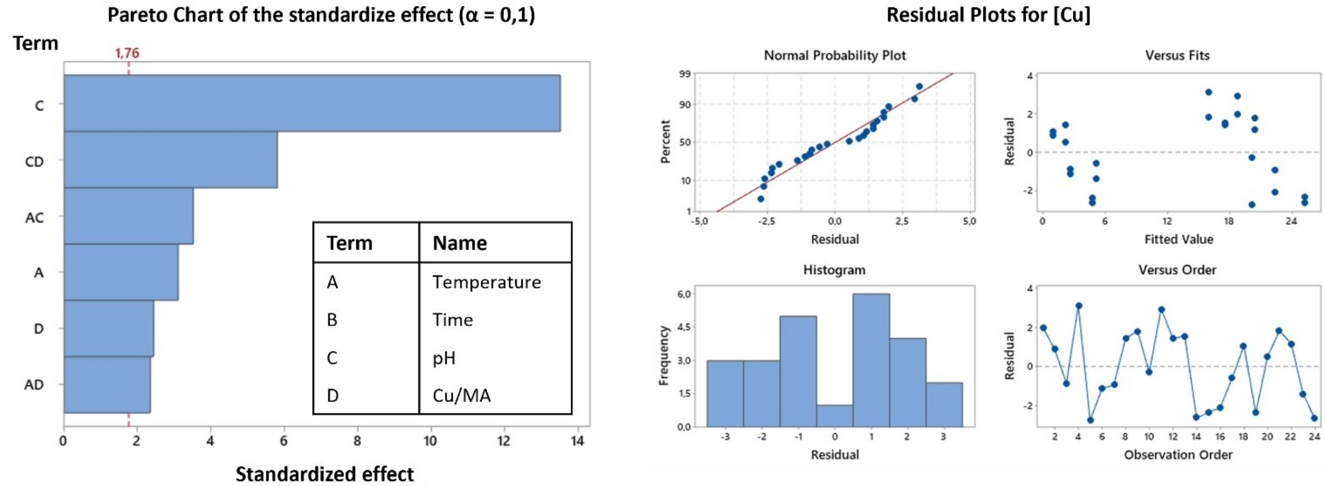


Figure 4. Visible spectrum of the CuTA system (a). Visible and Raman spectra (b, c, respectively), and distribution diagram (d) of CuLA system.

possibility to vary the pH in a wider range, and monobasic copper (II) carbonate ($Cu_2(OH)_2CO_3$, *Malachite*) as copper (II) source, a water insoluble source of naturally occurring copper. From the statistical analysis made by the DoE we obtained the following Pareto chart:[24,33]

In the Pareto Chart (Figure 5, on the left), with a resolution of V, we included the effect of the single parameters and the pair interactions between them. The temperature, pH and Cu/MA single factors are significant, as well as the combinations pH*Cu/MA, temperature*pH and temperature*Cu/MA. It is possible to observe that the pH was the parameter most affecting the yield of the leaching experiments, while the effect of time was negligible (time did not compare in the Pareto chart), also in the pair interactions. These results reflect the leaching mechanism of malic acid towards malachite: malachite is an alkaline mineral, which in a first approximation can react with MA through an acid/base neutralization between protons from MA and hydroxide and carbonate from malachite. Moreover, the pH also drives the formation of a variety of complexes, each of them with a different stability. Furthermore, the complex geometry, and thus its stability, is driven also by the molar ratio between the metal and the ligand; to this purpose we obtained a distribution diagram for the Cu^{2+}/MA system in a 1 : 2 molar ratio (Figure S3). The obtained diagram showed the



Term	Name
A	Temperature
B	Time
C	pH
D	Cu/MA

Figure 5. Pareto Chart (on the left) obtained from the DoE and Residual Plots for [Cu] analysis (on the right).

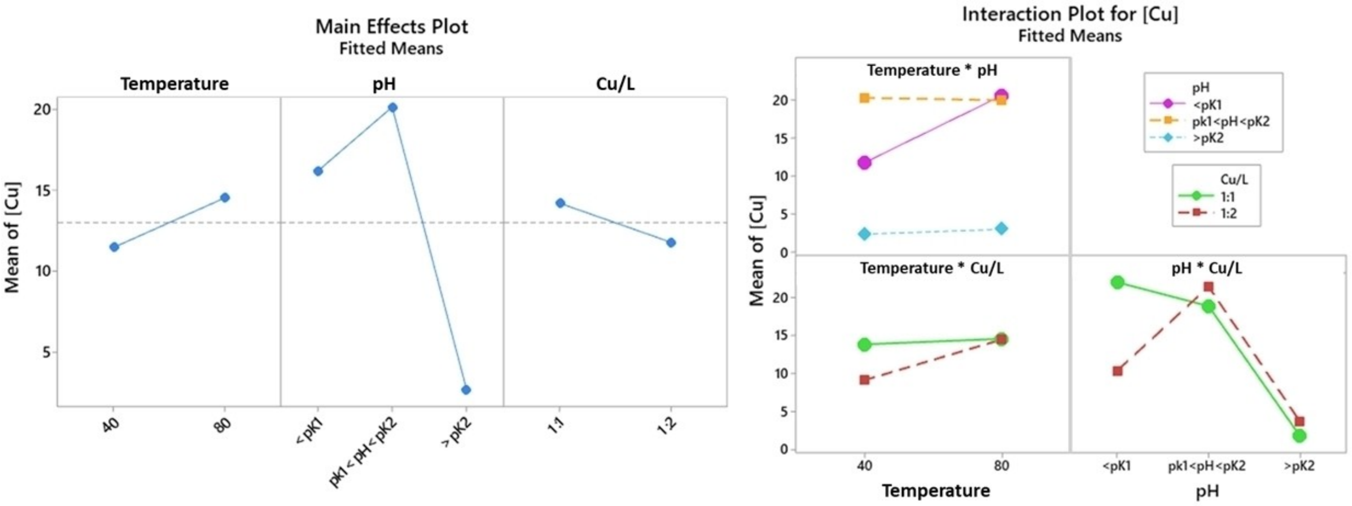


Figure 6. Factorial Plots for copper concentration recovery, showing the effects of the single factors on the leaching process and their interactions.

same coordination as for the 1:1 Cu^{2+}/MA molar ratio, but with different stability and distribution against the pH, highlighting the importance of the pair interaction between pH and copper/ligand molar ratio.

By considering the Normal Probability Plot (Figure 5, on the right) it is possible to underline the normally distribution of the dataset, without any presence of outliers. The Factorial Plots are reported in Figure 6.

Regarding the single factors (Figure 6, on the left) it can be seen that the pH has the highest influence on the copper concentration in the leachate solution; moreover, the combination of a high temperature and a $pH < pK_{a,1}$ showed a synergic interaction, leading to a high copper recovery (Figure 6, on the right), coupled with the combination of a $pH < pK_{a,1}$ and a Cu/MA ratio of 1:1.

The effect of the temperature on leaching efficacy was lower than the effect of pH, and this is probably due to the kinetic effect of the temperature on the leaching experiments. At 80 °C, the reaction between copper hydroxy-carbonate and MA could be fastened, resulting in a higher copper concentration in the leached solution in a shorter time. Hence, the optimized conditions for the leaching experiments are reported in Table 2:

The optimized pH was actually the autogenic pH after the addition of malic acid to the solution (i.e., 1.8), and within these conditions 100% of the initial amount of copper contained in the malachite was leached.

Table 2. Optimized parameters for the leaching experiments obtained from the DoE.

Parameter	Value
Temperature	80 °C
Time	1 h
pH	$< pK_{a,1}$
Cu^{2+}/MA molar ratio	1:1

One of the biggest challenges in metal recycling is the heterogeneous composition of the input flow of waste.[9] For example, electronic waste (e-waste) is composed of a variety of metals like Cu, Ag, Au and PGMs, depending on both the source of the e-waste (e.g. smartphones, computers or other appliances) and the country in which e-waste is produced.[34]

To mimic the heterogeneous nature of input materials flow typically encountered in recovery of metals from waste, we prepared *ad hoc* a multimetallic powder. To assess the selectivity of the ligands towards copper, we firstly prepared a multimetallic powder composed of copper (II) hydroxy-carbonate, iron (III) oxide and aluminium oxide (CuFeAl powder); then we prepared a second multimetallic powder composed of copper (II) hydroxy-carbonate, manganese (II) ferrite (spinel ferrite, $MnFe_2O_4$), zinc oxide, aluminum oxide and calcium sulfate (CuFeAlMnCaZn powder). In particular, as leaching conditions we only tested the one optimized by the DoE (see Table 2) with both malic and lactic acid, exploiting the same setup used for the malachite leaching experiments. In Table 3 the compositions of the multimetallic powders determined by ICP-OES analysis are reported.

The composition of the multimetallic powders was chosen in order to prove the selectivity of the ligands towards copper in presence of both trivalent cations (Fe^{3+} and Al^{3+}), and bivalent cations (Mn^{2+}, Ca^{2+} and Zn^{2+}). The histograms in Figure 7 show the percentage of metal recovery from the leaching experiments.

Table 3. Composition of multimetallic powders.

Powder	Cu (% wt)	Fe (% wt)	Al (% wt)	Mn (% wt)	Ca (% wt)	Zn (% wt)
CuFeAl	31	15	9	–	–	–
CuFeAlMnCaZn	24	4	3	2	5	14

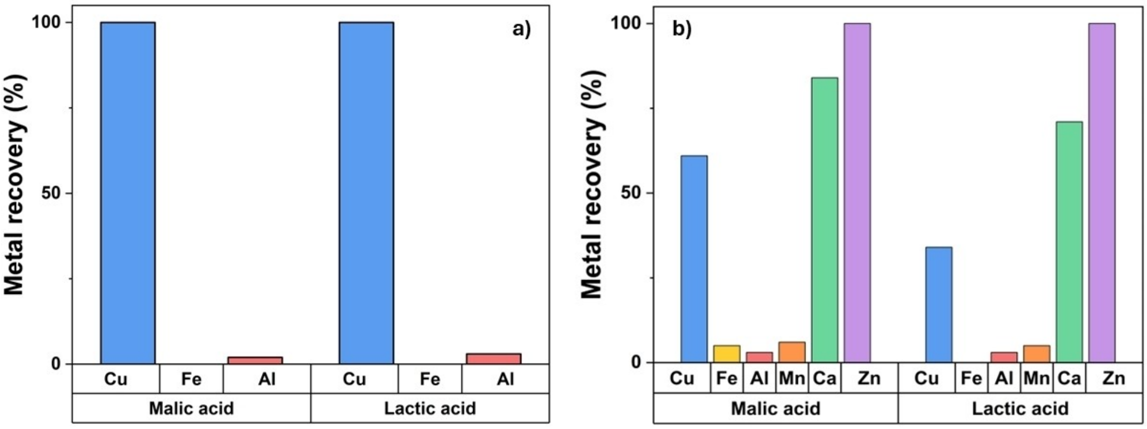


Figure 7. Metal recovery from CuFeAl powder (a) and CuFeAlMnCaZn powder (b).

Remarkably, according to the histograms in Figure 7a, the copper recovery (assessed by ICP-OES analyses) was quantitative (100 %) with both ligands. Additionally, the selectivity of the ligands towards Fe(III) and Al(III) was almost negligible. Although both iron and aluminum are known to form complexes with malate ligands[35–36], with association constant slightly higher than copper,[35–37] in their oxide form they are almost inert, and with a very sluggish kinetics towards this reaction.[38–39] Indeed, since the leaching time was just 1 h, only malachite, which was the most prone to acid attack, completely dissolved. Since the ligands were employed in the acidic form at a native pH of about 2, the leaching mechanism probably involves a first acid/base reaction with metal oxides or malachite, followed by the complexation reaction. Indeed, during the leaching reaction with malic acid, the pH raised from 2 to 3.6, while with lactic acid the final pH was 4.8, and the solution turned blue in both cases, indicating the formation of Cu(II) complexes. This was even more evident in the leaching of the CuFeAlMnCaZn powder, where during the leaching the pH raised from 2 to 4.7 and 5.4 for malic and lactic acid respectively. Histograms in Figure 7b show a dramatic decrease in copper selectivity (61 % and 34 % recovery with malic and lactic acid respectively), whilst Zn recovery was 100 %, and Ca recovery was 85 % and 70 % with malic and lactic acid, respectively. As expected, the recovery of Fe, Al and Mn was very low, in a range between 0 to 6 %, perfectly in accordance with what we already observed for iron and aluminum, and with the association constant of Mn(II) with malate and lactate which is much lower compared to the one of the other metals.[40–41] These results contribute to understand the leaching mechanism, highlighting the acid/base contribution in the leaching reaction. While iron and aluminum oxides precipitate at pH about 2.5 and 5 respectively, zinc oxide precipitate at pH about 8,[42] showing higher reactivity. Moreover, Zn(II) is known to form stable complexes with hydroxy-carboxylic acids, such as malic and lactic acid,[26,43–44] with association constant very close to those of copper,[40–41] accounting for the high recovery obtained from the leaching experiments. Although calcium sulfate is water insoluble ($K_{sp} = 4.93 \cdot 10^{-5}$),[45] calcium showed recovery higher than 70 % with both ligands. This was probably due to the protonation of the sulfate anion in acidic environment (sulfuric acid, $pK_{a,\ 2} = 1.99$[45]), which enhanced calcium sulfate solubility,[46] and despite the association constant being very low compared to the one of other metals,[47–48] probably the equilibrium was further shifted thanks to the formation of malate or lactate complexes.[47–48]

As a way to assess the effect of the ligands on the leaching of metals in the conditions used for both the reference multimetallic powders, a control experiment was performed by involving simply deionized water as "leaching" agent (pH = 5.5). The ICP-OES analysis outlined as only calcium was leached in a significant amount (35 % recovery), whereas other metals were almost not present in the post-leaching solution. This result confirmed the effectiveness of the ligand for the leaching of the metals, especially for copper which, in the form of malachite, is insoluble in water ($K_{sp} = 10^{-32}$).[49]

Despite different approaches to free copper from the ligand (e.g. precipitation, cementation, electrodeposition) are reported, we decided to exploit the alkaline precipitation for practical reasons. First of all, copper hydroxide is a very versatile source of copper, which can easily react to form other copper compounds, or be dissolved in acidic environment and then used to produce metallic copper, by reduction with a suitable reducing agent (e.g. metallic zinc), or by electrochemical reduction. Moreover, the variation in pH is a versatile and easy to handle tool to separate different metals according to the solubility product of their hydroxides. Finally, sodium hydroxide is a very easy to handle reagent that, after the precipitation of copper hydroxide, forms a solution of the sodium salt of the ligand. With this perspective, the recovery of the ligand could be enabled as well.

Within this framework, to separate copper from the other metals in the leached solution of the CuFeAlMnCaZn powder, we increased the pH of the solution to about 12 by adding dropwise a solution of 2 M NaOH, precipitating a pale blue powder of copper (II) hydroxide. However, from the ICP analysis of the precipitate, iron, aluminum and calcium were precipitated together with copper, underling the necessity of improvement of the separation of metals in a future work.

Conclusions

This study successfully demonstrated the viability of using environmentally friendly, bio-based ligands, specifically hydroxy-carboxylic acids such as malic acid and lactic acid, for the hydrometallurgical recovery of copper. The research highlighted that these ligands were effective in leaching copper from custom home-made multimetallic powders, achieving high recovery rates under optimized conditions, thanks to the formation of sufficiently stable complexes, which were soluble in the optimized pH range, and allowed the precipitation of copper hydroxide at alkaline pH. Notably, 100% recovery was achieved from CuFeAl powder, showcasing the potential of these ligands. The role of pH was found to be critical in the leaching process, significantly influencing the formation and stability of copper-ligand complexes. Optimal leaching was attained at an autogenic pH of 1.8, which facilitated complete copper dissolution from malachite. This emphasizes the importance of precise pH control in maximizing recovery efficiency. Particularly significant was the application of Design of Experiments (DoE) methodology, which played a key role in optimizing the leaching conditions. By systematically varying parameters such as ligand concentration, temperature, and pH, DoE allowed for the identification of optimal conditions that maximized copper recovery while minimizing the consumption of reagents and time. The screening of various bio-based ligands was another important component of this study.

Through extensive ligand screening, hydroxy-carboxylic acids like malic acid and lactic acid were identified as the most effective for copper recovery. This screening process was essential in selecting ligands that not only demonstrated high efficacy but also aligned with the principles of green chemistry. In experiments involving CuFeAlMnCaZn powder, the selective recovery of copper was still significant and comparable with state of the art processes,[50] although competition from other metals, particularly zinc and calcium, reduced the overall recovery rate. This suggests that further refinement of the process is necessary to enhance selectivity and yield. The use of DoE can be particularly valuable in this context, as it can help fine-tune the process parameters to improve selectivity. Post-leaching, the study demonstrated the feasibility of recovering copper from the leachate by precipitating copper (II) hydroxide through pH adjustment. However, co-precipitation with other metals such as iron, aluminum, and calcium indicated the need for improved and more effective separation steps in future research. Overall, the use of bio-based ligands presents notable environmental and economic benefits. The optimized approach offers a sustainable alternative to traditional hydrometallurgical processes that rely on harsh chemicals, potentially reducing environmental impact and operational costs. The findings provide a strong foundation for developing greener, more efficient methods for copper recovery. Future work should aim to enhance ligand selectivity and optimize separation techniques to improve overall process efficiency further, leveraging the power of DoE to systematically refine and perfect the recovery process.

Materials and Methods

Materials

Copper sulfate pentahydrate $CuSO_4 \cdot 5H_2O$ (99.5% grade) was supplied by Manica S.p.A. Aqueous ammonia (28–30% wt), sodium hydroxide ($\geq$ 98% wt), succinic acid, DL-malic acid, malachite, hydrochloric acid (37% wt), zinc oxide (99.9% grade) and isopropanol (technical grade) were purchased from Sigma Aldrich. DL-lactic acid was purchased from SAFC. L-aspartic acid was purchased from Acros Organics. Nitric acid (69.5% wt) was purchased from Scharlau. Sulfuric acid (95–97% wt) was purchased from VWR Chemicals. Ferric nitrate nonahydrate and tartaric acid were purchased from Merck. Aluminum oxide and anhydrous calcium sulfate were purchased from Carlo Erba. Manganese ferrites (Fe_2MnO_4), $Cu(OH)_2$ and Fe_2O_3 were produced in our laboratory. For all the solutions of ligands, metals and precipitating agents (NaOH and ammonia), and all the leaching experiments deionized water was used as a solvent.

Characterization Techniques

UV-Vis Spectroscopy

The UV-Vis spectra were recorded with a Cary50 spectrophotometer, in the range between 1000–450 nm with medium scan speed (600 nm/min), and baseline correction with deionized water.

Raman Spectroscopy

Raman spectra were collected with a Thermo Scientific DXR instrument in micro-Raman configuration with 532 nm wavelength laser and equipped with CCD detector. Spectra were collected in the range 100–1200 cm^{-1} with 2 cm^{-1} resolution. The power of the incident beam was varied between 1–7 mW to obtain the best signal.

Inductively Coupled Plasma – Optical Emission Spectroscopy

Multi-elemental analyses on the leachate solutions were carried out with a PerkinElmer Optima 4200 DV ICP-OES equipped with two-dimensional CCD array; the plasma source is dual-view RF generator, i.e. it can be viewed both axially and radially. The calibration curve was performed before each series of analyses.

Standard Preparation and Characterization

The ligands screening was performed by preparing standard compounds using copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$). Each standard was prepared by adding copper sulfate pentahydrate to a solution of ligand under stirring. Then, a solution of NaOH 2 M was added dropwise to study the complexation at increasing pH values, monitored with a pH meter. All the standards were prepared considering a 1:1 molar Cu/ligand ratio and the total concentration of copper to be 0.1 M (0.01 M only for copper aspartate for aspartic acid solubility reasons). After NaOH addition, the solution was stirred until either solubilization, or precipitation of the complex was observed. In case of precipitation, the solid was filtered on Buchner filter, washed first with deionized water and isopropanol, and finally it was let air dried. The solution was then analyzed by UV-Vis, while the solid was analyzed by Raman spectroscopy.

A detailed pH study was performed on the copper malate complex. This was done by mixing a 0.04 M solution of sodium malate with copper sulfate pentahydrate in a molar Cu/ligand ratio of 1:1. A solution of NaOH 2 M was added dropwise, and UV-Vis spectra were obtained each time.

The synthesis of the $Cu(OH)_2$ standard was carried out by adding a NH_3 solution to a copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) one until the soluble Cu-NH_3 complex formed (clear dark blue solution obtained). Then NaOH pellets were added in a Cu : NaOH 1:2 molar ratio and stirred for 15 min. At the end, a blue precipitate was obtained, filtered through filter paper, washed with cold deionized water and then with isopropanol. Finally, the solid was air dried.

The Fe_2O_3 standard, was prepared by adding dropwise a solution of NH_3 into a solution of iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9\ H_2O$) until a red precipitate was formed. The resulting solid was filtered on a Büchner filter, washed with cold deionized water, and calcinated in a muffle at 400 °C overnight.

Manganese ferrite $MnFe_2O_4$ was prepared according to a well-established procedure in our laboratory, by the coprecipitation of Mn^{2+} and Fe^{3+} oxalates in presence of Tetraethylammonium hydroxide (TEAOH), followed by a hydrothermal treatment in a closed autoclave at 135 °C for 4 h.[51]

The multimetallic powders were prepared by mixing the calculated amount of each solid (i.e. metal compound) and grinding for 15 minutes to obtain a homogeneous powder. For CuFeAl powder, malachite, iron (III) oxide and aluminum oxide were used, while for CuFeAlMnCaZn powder, malachite, manganese ferrites, aluminum oxide, anhydrous calcium sulfate and zinc oxide were used. The actual metal concentration in the powder was determined by ICP-OES.

Leaching Experiments and Copper Hydroxide Precipitation

The experimental setup used for leaching of malachite or multimetallic powder consists of a flask heated by a hot plate stirrer through an oil bath. The temperature was measured by placing a thermometer inside the bath, which also allowed to minimize solution loss. First, the solution of the leaching agent was prepared by dissolving the suitable amount of ligand in deionized water and adjusting the pH with a 2 M NaOH solution. The total volume was calculated considering for each sample the solid/liquid weight ratio of 1:25. The solution was placed in the flask and, after reaching the target temperature, the metallic powder was added under constant stirring. Then, the system was allowed to cool to room temperature and the remaining powder was separated from the solution by filtration and/or centrifugation. Then the solution was prepared for ICP-OES analysis.

The effectiveness of the ligands for the leaching of metals was tested by using just deionized water as leaching agent. The experiment was conducted in the same experimental conditions of the leaching of the multimetallic powders.

The second part of the recovery consists of precipitating copper hydroxide at alkaline pH. For this purpose, a known volume of 2 M NaOH solution was added drop by drop, under stirring to the previously weighted leached solution. The addition was continued until the pH was in the range 12–12.5. The flask was stirred for 30 minutes, and the precipitate was separated by filtration with a Buchner filter, washed with deionized water and isopropanol in sequence, and air dried.

Design of Experiments and Speciation Diagrams

The design of experiment was carried out using the Minitab19 software, applying a general full factorial design with 4 factors (temperature, time, pH and Cu:Ligand molar ratio) and 2 level each except for pH which was 3. The design also includes randomization and replicates of 2 experiments to analyze the reproducibility. Then, the analysis concerned the output of concentration determined by ICP-OES and the terms were included up to order 2 (linear A, B, C, D and two-way interactions AB, AC, AD, BC, BD, CD). The backward elimination option was also selected with $\alpha = 0{,}01$.

The speciation diagram was created by using the open source software HySS 2009 (*Hyperquad Simulation and Speciation*)[52] by using the following general reaction for chemical equilibria:

$$\mathrm{oM} + \mathrm{pL} + \mathrm{qH} = \mathrm{M_oL_pH_q}$$

in which M is the metal, L the ligand e H the hydrogen atom. From this the total stability constant was defined as following:

$$\beta = \frac{[M_oL_pH_q]}{[M]^o[L]^p[H]^q}$$

The analysis includes the stability constants of the complexes found in the literature, the hydrolysis constants of the metal ions, and the ionic product of water ($pK_W = 13.77$) already provided by the software.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: carboxylic acids · copper recovery · circular economy · hydrometallurgy · sustainability

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