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A Mature Tool to Address New Challenges: Harnessing Coordination Chemistry for The Sustainable Copper Recovery from Industrial and E-Waste in The Age of Energy Transition

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Copper is arguably one of the most strategic metals for the energy transition, particularly in the shift from fossil fuel-based engines to sustainable and renewable energy sources, with related and broader electrification efforts. While global copper mineral resources are far from depleted, their uneven distribution poses significant supply risks, especially in regions like Europe. In 2023, the European Union (EU) recognized this risk by designating copper as a strategic raw material (SRM), highlighting the need for innovative copper recovery processes. Copper recovery from industrial and electronic waste has been approached through various methods, primarily categorized into pyrometallurgy and solvo- and hydrometallurgy. The latter offers greater tunability and potential for sustainability, particularly when leveraging coordination chemistry. This review focuses on the most promising hydrometallurgical processes for copper recovery from industrial and e-waste (i.e., electronic waste), with a special emphasis on the role of coordination chemistry in supporting these methods. We posed particular focus on the adaptability and versatility of the coordination chemistry-based processes to the highly heterogenous composition of the copper-containing wastes.

1. Introduction

Coordination chemistry is a well-established tool in the production of copper from primary sources, particularly through hydrometallurgical processes where chelating agents, like oximes, are used to selectively extract copper from ores.[1–3] These methods, which involve leaching of ores by acidic lixiviants (e.g. sulfuric acid, hydrochloric acid) to solubilize copper which is then extracted in organic solvents,[2,4] have proven effective and widely adopted in the industry.[1,3] However, as the global demand for copper increases, driven by the energy transition and the proliferation of electronic devices,[4–7] there is a growing need to implement these processes targeting greater sustainability and to extend their application to secondary sources like industrial and electronic waste.[8–10] The increasing demand for copper driven by the energy transition and electrification is paralleled by a rising production of waste, particularly from copper refinement processes (i.e., copper slag)[11] and Waste Electrical and Electronic Equipment (WEEE).[12,13] As a result, recovering copper from these waste streams is not only crucial for mitigating supply risks, but also presents a strategic opportunity to address the growing challenge of waste management.[13] By extracting copper and other valuable materials from WEEE and industrial by-products, we can significantly reduce environmental pollution,[14,15] conserve natural resources,[16] and promote a circular economy.[17,18] This approach transforms waste from a liability into a resource, aligning economic and environmental objectives in a sustainable manner.

While the concepts of copper recovery and recycling are still gaining traction, with fewer than 2,000 publications between 1960 and 2024 [Source: Scopus database, www.scopus.com (accessed September 2024)], approximately 1,600 of these were published in the last 25 years, reflecting a growing interest in the field. In contrast, coordination chemistry has consistently maintained its significance, with over 34,000 publications in the same 25-year period, underscoring its established role and ongoing relevance in various scientific and industrial applications.

Among the various techniques developed for copper recovery, including pyrometallurgy[19] and hydrometallurgy, the latter stands out as the most promising approach due to its ability to deliver high yields while adhering, in most cases, to green chemistry principles.[20] Notably, the coordination chemistry underlying hydrometallurgical processes is both complex and versatile, making it particularly well-suited to handle the heterogeneous nature of waste streams.[21–23]

The authors note that there is often ambiguity and confusion regarding the terminology used in metal recovery and recycling, particularly regarding terms such as leaching, recovery, and recycling. Given that these terms will be frequently used throughout this review, we aim to clarify each

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term with precise definitions based on EU regulations, IUPAC terminology, and standard chemical practice:

Leaching: a chemical process in which metals are dissolved from a solid matrix, such as ores or waste materials, into a solvent (often water) through a reaction with a leaching agent, which can be acids, bases, or complexing agents (ligands[24]).

Recovery: the process of extracting valuable metals or materials from waste or by-products to create secondary raw materials. For instance, copper recovery involves extracting copper from e-waste to produce pure copper ingots or compounds for further use.[25,26]

Recycling: the process of converting waste materials into new products or materials. For example, copper recycling might involve using recovered copper from e-waste to manufacture new printed circuit boards (PCBs) or other products.[25,26]

2. Growing Demand for Copper

The central focus of the energy transition is the shift from fossil-fuel-based engines to electricity-driven systems, powered by renewable energy sources.[27] In this context, copper emerges as a strategic element.[28] Although copper may not be directly involved in renewable or sustainable energy generation (such as in nuclear power), it is indispensable for the efficient transportation of electricity.[27] For instance, in wind turbines, copper is vital not only for the electrical cables that transport power, but also as a material in the construction of turbine blades.[29,30] Similarly, copper plays a crucial role in solar panels, facilitating both the conversion of solar energy into electricity and its subsequent transmission.[31] Furthermore, electric vehicles require approximately three times more copper than traditional internal combustion engine vehicles.[32,33] These are just examples to illustrate the growing importance of copper, with demand projected to nearly double by 2050, reaching an estimated 44 million tons.[4,34]

The growing demand for copper is not just a matter of increasing production rate and capacity, but also poses serious concerns across the entire production and supply chain.[5,35] Copper is mainly extracted from ores (about 84% wt of copper production in 2022[4]), requiring from 30 to 90 GJ of energy per ton of copper cathode, depending on the refinement process (i.e. hydro- or pyrometallurgical).[35,36] More than half of the energy demand is due to the mining and concentration steps, in which copper-bearing minerals are extracted from the mine and then separated from other minerals, respectively.[35,37] In Figure 1, a graphical representation of the energy demand for copper production is reported.

On the other hand, the production of copper from secondary sources enables saving about 80% of energy, especially the energy required for mining and concentrating.[4,36] Although copper recycling allows a significant energy saving, it alone will not suffice to meet the future demand.[5,36] As the global appetite for copper continues to grow, recycling efforts, although essential, are limited by the availability of recyclable material.[6] This limitation stems from several factors: challenges in the collection of scrap materials,[38] the difficulty of accessing copper embedded within complex products, inadequate waste management policies and regulations,[5] and the absence of efficient and sustainable recycling technologies.[39–41] This means that primary extraction from ores will remain unavoidable to bridge the gap. However, a significant challenge in relying on primary copper production is the declining grade of copper ores.[42–44] As high-grade deposits become increasingly scarce, mining operations are forced to process larger volumes of lower-grade ore to extract the same amount of copper. This not only increases the energy required for mining and concentration, but also amplifies environmental impacts such as waste generation and land degradation.[44] Despite its refractory nature, chalcopyrite ($CuFeS_2$) remains the most extensively exploited mineral for copper extraction,[45,46] and numerous pyrometallurgical and hydrometallurgical processes have been developed to efficiently extract copper from this challenging ore.[47–49]

A further major challenge for copper mining and future demand is the uneven global distribution of copper deposits, with most high-grade reserves concentrated in regions like South America, especially Chile and Perú.[4,50] This imbalance creates supply chain vulnerabilities for countries without domestic resources.[51] Additionally, the geopolitical stability of

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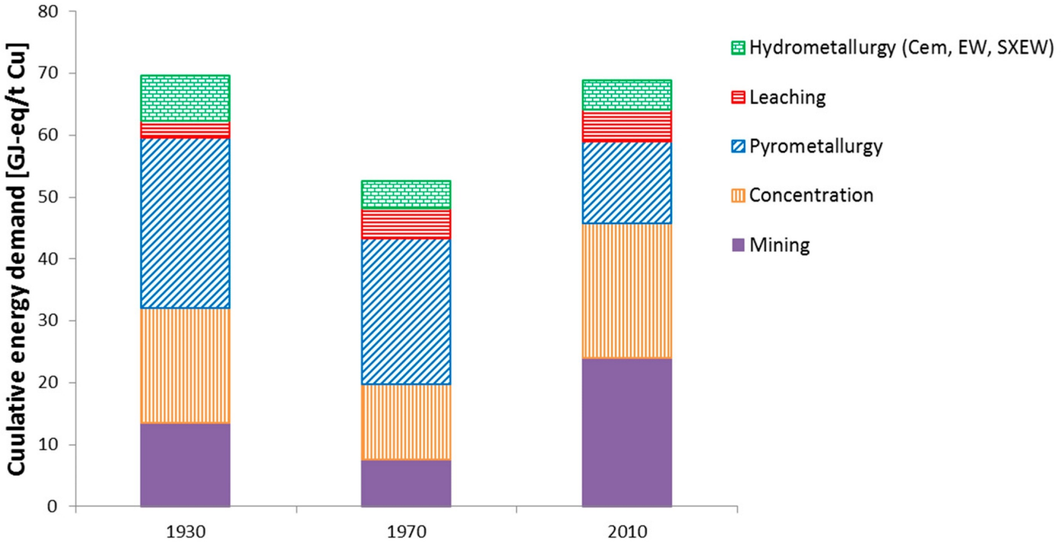

Figure 1. Contribution of the individual process step to the energy demand for copper production. With permission of *Resources* **2020**, 9, 44.

these copper-rich regions is crucial for maintaining a reliable supply.[52]

Technological advancements in copper recycling from secondary sources are essential to meet increasing demand, with coordination chemistry playing a key role. It enables efficient copper recovery from complex industrial and e-waste through eco-friendly processes.[8]

3. Sustainable Copper Recovery

Copper recovery from industrial by-products and electronic waste involves various methods, each with distinct advantages and challenges. Even if they are not treated in this review, in the framework of copper recovery from waste, also pyrometallurgical processes have been developed.[19] **Pyrometallurgy** employs high-temperature processes to separate copper from other elements, effectively treating large volumes of waste but often with significant energy consumption and environmental impact.[19]

On the other side, **hydrometallurgy** uses chemical solutions to leach copper, which can be tailored to various types of waste, offering more control over the recovery process. In this framework, **coordination chemistry** is increasingly crucial in optimizing and refining these methods, particularly in enhancing the effectiveness of hydrometallurgical processes and recycling technologies.[8]

3.1 Industrial and E-Waste Treatment

3.1.1. E-Waste Composition and Processing

One of the major challenges in copper recovery from waste is the highly heterogeneous composition of these materials.[10,53,54]

This complexity arises from the big variety of elements, both metallic and non-metallic, present in the waste, as well as the complex matrices of plastics and supports in which copper and other metals are embedded.[8,54]

The metal fraction in e-waste typically accounts for about 30% by weight, while the remaining 70% consists of non-metallic materials such as plastics, resins, and glass.[55–57] The specific elemental composition of these fractions varies depending on the type of device - such as printed circuit boards (PCBs), mobile phones, or laptops - and the specific components within those devices, like displays, central processing units (CPUs), random access memory (RAM), and smart cards.[58] Table 1 summarizes the average composition of the metal fraction of selected e-waste.

Table 1 highlights also that e-waste is an exceptionally rich source of metals, with concentration of Au, Ag, Pd and Cu being tens of times higher than those found in traditional ore deposits. For instance, the average copper concentration in mines is around 3 g/kg, while gold is found in the range from 300 – 500 mg/t[64]; in e-waste, copper and gold could be found in concentrations up to 350 g/kg and 3500 g/t, respectively.[8] This abundance is the basis for the term "urban mining" used to describe the recovery and recycling of metals from e-waste and other scraps produced by urban environment.[65] Nevertheless, the huge variety of metals poses significant challenges for the metal recovery efficiency, and so for the economical sustainability of the processes.

To enhance metal recovery yields from e-waste, various pretreatment processes have been developed. The initial step involves disassembling electrical appliances to extract reusable components and isolate metal-rich sections from non-metallic materials.[66] This process is crucial not only for maximizing recovery, but also for safely removing hazardous substances and batteries, which can pose environmental risks and fire hazards during subsequent processing.[8] Once metal-rich

Table 1. Average composition of the metal fraction of selected e-waste.

Source	Valuable Metals*	Rare Earth Elements	Other Metals	Reference
PCB	Au, Ag, Pd, Cu	Sc, Y, La, Ce, Dy, Er, Eu, Nd, Yb, Pr, Ho, Gd	Fe, Ni, Pb, Sn, Al, Co, Mn, Zn	[8,59–61]
CPU	Au, Ag, Pd, Cu	–	Fe, Ni, W, Mo, Pb, Sn, Al, Co, Zn, Cr	[8]
Ink-jet printer cartridges	Au, Cu	–	Ta, Al	[8]
Sim and smart cards	Au, Cu	–	Ni	[8]
Permanent magnets**	Cu	Nd, Dy, Tb	Fe, B, Co, Al, Ga	[62]
LED***	–	La, Ce, Eu, Tb, Y, Sc	Ba, Ca, Mg, Si, Al, Ga	[63]

*Valuable metals have been chosen according to their high concentration in e-waste and for their economical and strategical value
**Permanent magnets are not strictly e-waste, however they are essential to the function of devices like speakers and electrical motors
***Light Emitting Diode

components are separated (PCBs, wires, tubing, etc…), they undergo crushing and pulverizing operations.[67] This comminution is essential to drive the separation between metals and non-metal components, like plastics and glasses. Then, the metal fraction is separated from plastics and glasses by exploiting different physical properties, such as electric conductivity, density and magnetism.[8] Many authors highlight the importance of pre-treatment in boosting metal recovery efficiency, particularly the role of scrap size. Reducing scrap to the proper size ensures optimal contact between metals and lixiviants, greatly enhancing dissolution and extraction processes.[57,58]

3.1.2 Industrial Waste Composition and Processing

This section provides an overview of the composition and processing of copper-bearing industrial waste, highlighting key sources of valuable copper and outlining the necessary pre-processing steps.

Most copper-bearing industrial wastes arise from by-products of copper production processes, such as smelting slag,[68] mining tailings,[69] spent acid from pickling[70,71] and spent electrolytes.[72,73] Another valuable source is spent copper catalysts, commonly used in petrochemical refining[74] and methanol production.[75] In the case of smelting slag, copper recovery is typically conducted on-site due to the relatively low copper content (about 2% by weight),[76] but the sheer volume of slag - projected to reach 20 million tons[76,77] - makes recovery economically viable. It is also worth to mention that copper slag is used also for other applications without further metal recovery.[78] In contrast, spent copper catalysts, though produced in smaller quantities, can contain up to 70% copper by weight,[75] making them highly attractive for copper extraction despite their lower production volume.

The composition of copper slag varies depending on several factors, including the type of ore processed, the operating temperature, and the presence of impurities.[76,77,79] Copper can be found in multiple forms within the slag, such as metallic copper, copper sulfides,[79] or copper oxides,[77] underscoring the need for tailored recovery processes to efficiently and selectively extract the metal. The primary components of copper slag are iron oxides, a by-product of chalcopyrite smelting, and silicates, introduced during the purification process through the addition of silica.[2,77] Other oxides, such as aluminum oxide, calcium oxide, and magnesium oxide, are also commonly present.[77] Given this complex composition, pre-treatment steps are necessary to concentrate the copper compounds before proceeding with the recovery process.

The pre-treatment processes for concentrating copper compounds from slag largely mirror those used in the concentration of copper ores in primary production, with flotation being the most common technique.[76] In flotation, slag is first mixed with water and additives, such as surfactants or polymers, which interact selectively with the metal compounds present in the slag.[2] These additives work by altering the surface properties of the slag's components, effectively helping to differentiate between copper compounds and the other materials. Once this interaction takes place, gas is injected into the mixture, creating bubbles. The metal compounds, having been rendered hydrophobic by the additives, attach themselves to the gas bubbles, which then rise to the surface, forming a froth. This froth, enriched with copper-containing particles, can be skimmed off and collected for further processing.[2] Since mining tailings are the residues of the mining processes, similar considerations and processes apply also to them.[69]

Pickling liquors are acidic solutions used for surface treatment of metal products, particularly those made from copper and brass, which are prone to form oxide layers when exposed to air.[71,80] These oxides, especially copper oxide with its characteristic black appearance, cause tarnishing, a discoloration that degrades the aesthetic and surface properties of the metal. To remove this oxide layer, the metal items are immersed in sulfuric or hydrochloric acid baths. For example, brass pickling liquors typically contain significant concentrations of copper and zinc, often in the range of grams per liter, along with trace amounts of metals such as iron, aluminum, tin, and nickel, measured in parts per million. Chloride and sulfate ions are also present, originating from the acids used in the pickling process.[71] Due to the relatively high concentration of dissolved metals, these liquors generally do not require extensive pre-treatment, and metal recovery can proceed directly from the solution.

On the contrary, electrolyte wastewaters from electrorefining processes require pre-treatment before metal recovery can occur. During the electrorefining process, two electrodes are immersed in the electrolytic bath bearing the metal to be refined. Then, an electrical current passes through the electrodes and the solution causing the reduction of metal ions (e.g. Cu^{2+}) on the cathode, and the evolution of oxygen at the anode.[81] These spent electrolytes contain valuable metals like copper, gold, silver, and nickel, but they also hold hazardous elements and compounds such as arsenic, lead, hexavalent chromium (Cr(VI)), and cyanide. Proper pre-treatment is essential to remove these toxic substances, ensuring both the safety of the recovery process and the efficient extraction of the valuable metals.[72,73,82,83] There are lots of pre-treatment processes aimed both to the removal of dangerous substances and the regeneration of electrolytic baths. Among these methods, neutralization, crystallization, evaporation, electrodialysis, ion-exchange are the most employed.[84] For example, Dutra et al. reported an electrochemical method for cyanide oxidation as an alternative to the well-known chlorination with hypochlorite, allowing at the same time the recovery of copper.[72]

The pre-treatment process for recovering copper from spent catalysts is not well-established and is scarcely covered in the literature. Some authors have reported the use of calcination to remove organic matter, followed by grinding to enhance the leaching process.[85,86] The lack of detailed pre-treatment methods could be attributed to modern catalyst designs, which aim to minimize harmful components, reducing the need for extensive pre-treatment steps. Additionally, the recovery of valuable metals from spent catalysts is an emerging field, with still not many published works.[87]

3.2 The Role of Coordination Chemistry

Coordination chemistry, as powerful and well-established methodological tool, plays a pivotal and versatile role in numerous copper recovery processes. Through the careful tailoring and informed variation of the ligands chemical composition, structure and stereochemistry, and of their properties such, for instance, of hard/soft properties and redox potential, enhancement of the recovery rate and selectivity, while at the same time minimizing the environmental impact of the overall process, can be pursued. A single ligand can be used across different techniques and substrates, offering flexibility for tailored approaches in treating both industrial waste and e-waste. For example, citric acid is used in both the leaching of copper from Cu(II)-bearing substrates,[88,89] forming copper citrate complexes, and in the leaching of metallic copper from e-waste, where the same complexes are exploited to enhance the oxidation power of hydrogen peroxide, as a green oxidant.[90]

That's why the authors decided to split the discussion into traditional and innovative methods, rather than according to the substrate. In particular, section 3.2.1 encompasses all those methods which employ old fashioned ligands such as oximes and oximes derivatives, di(2-ethylhexyl)phosphoric acid (D2EHPA) and other apolar ligands, which require a solvent extraction step for the purification of copper, usually performed in kerosene. On the contrary, in section 3.2.2 processes involving greener ligands and oxidants, e.g. carboxylic acids and hydrogen peroxide, and greener solvents, e.g. Deep Eutectic Solvents (DES), are reviewed.

As stated in the end of Section 1, the role of coordination chemistry is considered in all the steps of the hydrometallurgical processes (leaching and recovery or recycling), that is why also works which employ coordination chemistry just in one of the steps have been considered.

Achieving high selectivity in metal recovery processes is a significant challenge, as it requires precise control over chemical conditions to selectively extract target metals from complex mixtures, particularly when the chemical reactivity and behavior of the species are similar. This is critical for enhancing efficiency, minimizing waste, and ensuring the purity of the final product, making it a key focus in the development of more sustainable extraction technologies.

3.2.1. Traditional Methods

In Table 2, a summary of the traditional methods employed for the recovery of copper is presented.

Traditional methods typically involve leaching the copper-bearing substrate with various inorganic acids such as hydrochloric, sulfuric and nitric acids,[91] or their mixtures (e.g., aqua regia), or other oxidants such as hypochlorite and chlorine

Table 2. Summary of the traditional methods for copper leaching and recovery.

Lixiviant(s)*	Post-leaching Cu species	Separation process	Ligand(s)*
HNO_3, H_2SO_4	$[Cu(H_2O)_6]^{2+}$	Solvent extraction – pH swing	Hydroxyoximes, hydrophobic carboxylic acids
H_2SO_4	$[Cu(H_2O)_6]^{2+}$	Electrowinning	-
HCl, $FeCl_3$, Cl_2, ClO^-, aqua regia	$[CuCl]^+$	Solvent extraction – pH swing	Hydroxyoximes
HCl, $FeCl_3$, Cl_2, ClO^-	$[CuCl_x]^{2-x}$, $2 \leq x \leq 4$	Solvent extraction – pH swing or anion swing	Trialkylamines, tetraalkylammonium chlorides, dialkyl-thiophosphinic acids, hydrophobic carboxylic acids
NH_3	$[Cu(NH_3)_x]^{2+}$	Solvent extraction – pH swing	β-diketones

*Lixiviants and ligands reported are just examples of the category of compounds employed. More details are given in the text.

gas, or Fe(III) ions.[8] The choice of acid depends on the nature of the substrate, particularly the oxidation state of copper. For example, if copper is present as element, Cu(0), nitric acid is the only acid capable of dissolving it due to its oxidizing power, according to the following equation[8]:

$$3Cu_{(s)} + 8HNO_{3(aq)} \rightarrow 3Cu(NO_3)_{2(aq)} + 2NO_{(g)} + 4H_2O_{(l)} \qquad (1)$$

When copper is embedded in an organic matrix, or when the substrate contains noble metals (NM), a mixture of hydrochloric and nitric acid (aqua regia) is used, as it can also dissolve gold, palladium, and platinum by forming complexes with chloride.[8] As shown in equation 1, when nitric acid acts as the oxidant, colorless nitrogen monoxide is produced, which is further oxidized by air to form nitrogen dioxide, evidenced through its typical brownish color. This poses several concerns to the use of nitric acid as oxidant in large scale processes, because nitrogen dioxide is very harmful both for humans and to the environment.[92] The same applies to the employment of aqua regia, which produces also chlorine gas, as well as the use of mixtures of hydrochloric acid and hypochlorite.[8] That is why, more innovative processes are aimed to exploit greener and safer oxidants such as oxygen, ozone, hydrogen peroxide, ferric ions, halides, combined with coordination compounds (see Section 3.2.2 for further details).[8]

In other cases, when copper is present as cupric ions, sulfuric acid is the most employed acid for the leaching of the substrates.[93] Sulfuric acid offers numerous advantages in copper recovery, as it is more selective toward copper, forming soluble copper sulfate while precipitating impurities like lead as insoluble sulfates, and its resulting solutions can be directly used in electrorefining processes, enabling efficient copper purification.[2] This is why in processes which involve a solvent extraction (SX) step, whatever the acid used for the leaching of copper, the stripping from the organic phase is made with a sulfuric acid solution.[1,2]

When acidic leaching proves inefficient for copper dissolution due to refractory matrices or when the matrix composition complicates metal separation, hydrochloric acid is often employed as the preferred leaching agent.[1] With respect to sulfuric and nitric acids, hydrochloric acid is able to form stable chloride complexes with almost all transition metals, and in particular copper chloride complexes of stoichiometry $[CuCl_x]^{2-x}$ for Cu(II) and $[Cu_xCl_y]^{x-y}$ for Cu(I) are known.[94] The former are particularly exploited in the solvent extraction process of copper with oximes ligands,[95] while the latter are exploited in the stabilization of Cu(I) species in the leaching of metallic copper.[96]

Once copper is leached from the substrate, usually a solvent extraction step is required to separate it from other metals and impurities.[2] In hydrometallurgy, solvent extraction relies on the formation of complexes between metals and organic ligands that are soluble in nonpolar solvents, facilitating the transfer of metals into the organic phase for efficient separation and recovery. There is a wide plethora of well-established ligands, which can bind to metals in a selective and effective way, like alkyl oximes, phenolic oximes, phosphoric, phosphonic and phosphinic acids, carboxylic acids, β-diketones, amines (primary, secondary and tertiary), ammonium derivatives, phosphine and derivatives, and more exotic ligands such as ditopic ligands, which are used to extract metal salts rather than metal cations or metalates.[1,97]

All the reactions involved in the SX process can be categorized into "load" reactions, where metals are transferred from the aqueous solution (the leachate) into the organic phase by complexation, and "strip" reactions, where the metals are subsequently counter-extracted from the organic phase into an acidic aqueous solution for further refinement and recovery.[97] In particular, all these reactions are equilibrium reactions based either on cation exchange or pH- or anion-swing mechanisms.[97] The cation exchange mechanism is the simplest, and involves the exchange between metal cations in the aqueous solution and protons from the ligand, typical of oximes as reported in Figure 2.

In this case, the efficiency and the selectivity of the process can be controlled by the pH of the leachate, the acidity of the phenolic protons, the complex stabilization through inter-ligand hydrogen bonds, and the size of the cavity in which metal ions are accommodated.[97] The pH of the leachate can be easily tuned according to the specific ligand involved, and can be also changed during the extraction process to stepwise recovery different metals.[98] The acidity of phenolic protons, the hydrogen bond network and the size of the cavity can be tuned by the change of the substituents R and R', as well as the position of such substituents.[97] As reported by Turkington and coworkers, the inter-ligand H bonding plays a pivotal role in determining the stabilization of the complexes, especially when the *ortho* position of the phenolic oxygen is substituted with a hydrogen bond acceptor, like Cl, Br or methoxy groups.[97]

When either hydrochloric acid or HCl/$FeCl_3$ systems are employed as lixiviant, the loaded solution (the leachate) contains chloridometalates, and in this case the metal recovery proceeds through the extraction of the metal-chloride complex.[1] The recovery of metalates can be driven either by a pH- or anion-swing mechanism: in the former, trialkylamines and trialkylphosphine oxides are the most used, while in the latter trialkylammonium or trialkylphosphonium salts are employed.[97] In a pH-swing process employing amines as ligands, protons are needed for the formation of the

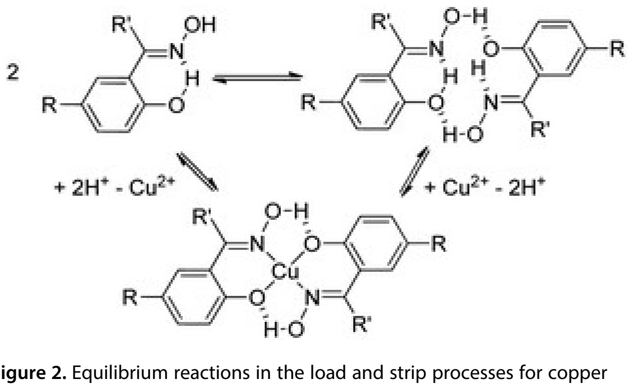

Figure 2. Equilibrium reactions in the load and strip processes for copper recovery. With permission of *Chem. Comm.* **2013,** 49, 1891-1899.

ammonium salt of the ligand and the metalate acts as counterion[97]:

$$xH^+_{(aq)} + xNR_{3(org)} + [MCl_y]^{x-} \rightleftarrows [(HNR_3)_x MCl_y]_{(org)} \tag{2}$$

As shown in equation 2, in the pH-swing process, the extraction is controlled by the pH of the aqueous phase, as protons are necessary to form neutral complexes. However, this kind of process is mostly employed for the extraction of platinum, palladium or rhodium chloride complexes which are much more stable than those of copper.[99,100]

On the other hand, copper chloride is conveniently extracted in anion-swing processes, in which the concentration of chloride is the driving force for the formation of $[CuCl_x]^{2-x}$ species:

$$n[L^+Y^-]_{(org)} + [MCl_y]^{n-} \rightleftarrows [L_nMCl_y]_{(org)} + nY^- \tag{3}$$

$$Cu^{2+} + 2L_{(org)} + 2Cl^- \rightleftarrows [CuCl_2(L)_2]_{(org)} \tag{4}$$

The reaction reported in equation 4 is particularly exploited in the CUPREX process for the extraction of copper from sulfide ores.[101] As reported in Figure 3, by tuning the chloride concentration in solution, it is possible to obtain copper chloride complexes with different stoichiometry. Indeed, Xing and co-workers exploited the reactions reported in Figure 2, equation 2 and equation 4 for the selective recovery of copper (II) and silver (I) from anode slimes leachate with LIX 63, Alamine and Cyanex 301.[102] LIX 63 is an alkyl-α-hydroxyoxime, which Xing reported to be able to bind both to Cu(II) ions and to $CuCl^+$ ions in concentrated HCl solutions according to the reaction scheme reported in Figure 2. According to the authors, LIX 63 binds to copper when it is in its Cu^{2+} or $CuCl^+$ form, and they reported an increase of copper extraction with increasing HCl concentration from 0.5 to 5 M. At higher HCl concentrations copper extraction failed due to the formation of anionic copper-chloride complexes which inhibited the interaction with LIX 63. The other category of extractant employed by Xing and co-workers are alamines, a group of trialkylamines which are used to extract mainly metalate complexes or metal salts.[1,102] In this case, copper (II) was extracted through a pH-swing mechanism (see equation 2), in which HCl is needed both for the formation of the ammonium salt of the extractant and for the formation of metalate complexes. However, this kind of process was not selective due to the formation of similar $[MCl_y]^{x-}$ complexes of Cu (II), Ag (I) and Zn (II) which were present in the leachate and have been extracted together. Despite this, the authors obtained a selective stripping of loaded metals from the organic phase by employing different stripping solutions. In particular, high stripping efficiency and selectivity was achieved by using a solution of ammonium thiocyanate, which formed stable complexes selectively with Ag(I). The last extractant used by Xing and co-workers to selectively extract copper was Cyanex 301, which is a dialkylthiophosphinic acid.[1,102] The extraction of copper (II) with Cyanex 301 occurs through the mechanism reported in equation 4, in which copper is extracted into the organic phase as neutral $CuCl_2$ by forming an adduct with the extractant.[1,102]

A similar process was developed by Zhu and co-workers for the selective separation of copper (II) from iron (III) and aluminum (III), exploiting the formation of chloridometalates in the aqueous phase to be extracted in the organic phase with a mixture of LIX 63 and Versatic acid 10.[103] Versatic acid 10 is a hydrophobic carboxylic acid with a branched alkyl chain, which can form both mono- and binuclear metal complexes as reported in Figure 4.

In the reaction scheme in Figure 4, Y represents a neutral molecule like water or a protonated carboxylic acid.[1] However, hydrophobic carboxylic acids are not very often employed due to the lack of selectivity and poor pH-swing mechanism.[1,101]

Jun and co-workers reported the use of phenolic oximes for the recovery of copper from industrial waste without the need of the formation of chloridometalates.[104] Copper was present in the industrial waste as Cu_2O, therefore they performed an

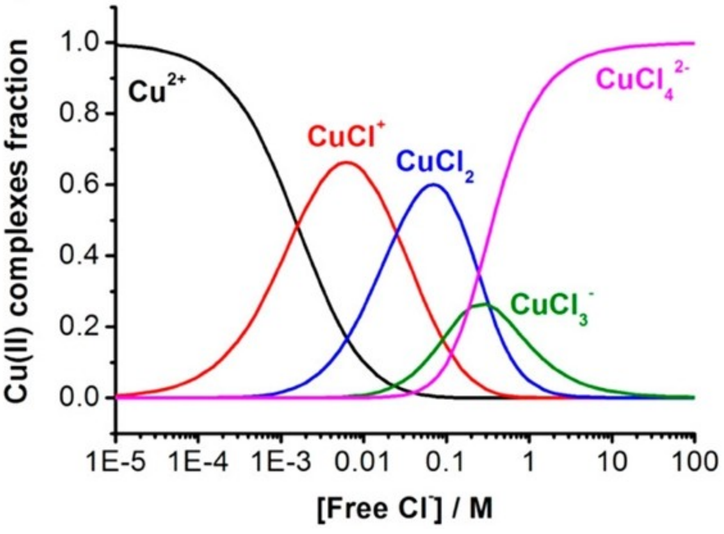

Figure 3. Distribution of Cu-Cl species as function of chloride concentration. Adapted from *Anal. Chem.* **2013**, 85, 16, 7696–7703.

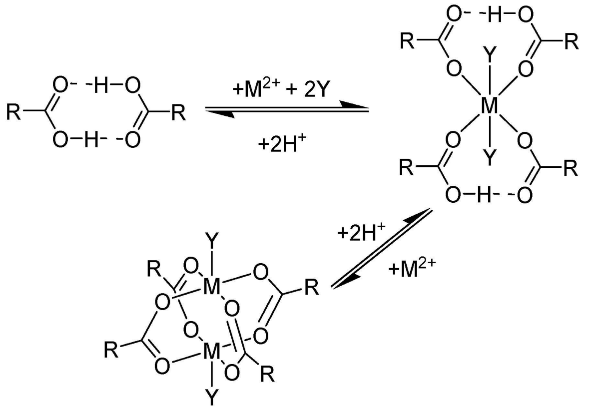

Figure 4. Equilibrium reactions in the load and strip processes for copper recovery with hydrophobic carboxylic acids. With permission of *Chem. Soc. Rev.* **2014**, 43, 123-134.

acidic leaching of the industrial waste with nitric acid, aimed at solubilize copper as Cu^{2+}. Then, a first solvent extraction was performed with di(2-ethylhexyl)phosphoric acid (D2EHPA) as extractant for the removal of iron (III) from the leachate. The extraction of copper (II) was performed with LIX 84-I, which is a phenolic oxime recognized as selective for copper and resistant to degradation. The extraction was studied in the pH range from 0.5 to 3.2, showing increasing copper concentration in the organic phase as the pH increased, while other metals were not extracted, and evidencing as a simple parameter as pH can also be exploited to enhance selectivity. The other metal present were Ca^{2+} and Al^{3+}, and according to the authors, calcium was not extracted due to weaker interaction with the extractant with respect to copper. LIX 84-I acts as a bidentate ligand through the phenolic oxygen and the nitrogen atom of the oxime group, as reported in Figure 2. Since each LIX 84-I molecule carries one proton, two extractant molecules are required to form a neutral complex with Cu^{2+}, resulting in a tetragonal coordination around the metal center, again highlighting the relevance of structure and ligand spatial arrangement in pursuing selectivity. In contrast, Al^{3+}, which requires six coordination sites to complete its coordination sphere, would theoretically need a third LIX 84-I molecule. However, due to the significant steric hindrance of LIX 84-I, the coordination of a third molecule around aluminum is not possible, preventing its extraction into the organic phase.[104]

As already reported, the extraction of metals in organic solvent through the formation of complexes can be controlled both by the pH of the leachate and the concentration of anions like chloride. This is particularly helpful to improve the selectivity of the processes, by exploiting the specific reactivity of a metal cation. For instance, the exploitation of the higher stability of chloridometalates of Cu^{2+} over Ni^{2+} allows the selective extraction of copper.[102] In a similar way, Zn^{2+} forms stronger anionic chloride complexes with respect to copper (II), preventing the extraction of zinc with hydroxyoximes.[71]

On the other hand, the extraction of chloridometalates could be an issue for the last step of the copper refinement, that is the electrorefining.[71,81] In this case, the extraction of copper as Cu^{2+} is preferred, so that the stripping can be performed with sulfuric acid which is the best choice for the electrorefining baths.[2] As an alternative, the refinement of copper can be performed in other ways, and different stripping agents can be employed. For example, Shah and co-workers reported an effective stripping of copper and zinc from the organic phase by oxalic acid solutions.[71] In this case, oxalic acid is used both as a source of H^+ for the stripping of copper from the organic phase, and as precipitating agent. Although copper was extracted into the organic phase as chloride complex, the precipitation of insoluble copper oxalate was not affected by this. After the precipitation of oxalates, the authors calcinated the powders at 400 °C to obtain pure copper oxide, which is a versatile raw material.[71]

When dealing with the recovery of copper from e-waste where metals are present in their elemental form, the leaching step plays a pivotal role to enhance the selectivity and the yield of the whole process.[105] The selective leaching can be achieved by exploiting redox activities and coordination chemistry of the lixiviants. Base metals, like Cu, can be leached through acidic leaching with nitric acid, leaving noble metals like Au in their elemental form. Then, by the addition of halides like chloride or bromide, gold can be dissolved thanks to the formation of halide complexes.[105] Another example of the selective leaching of metals, is the chlorination process, in which chlorate is used as oxidant.[106] In this case, the redox potential of the leaching solution is tuned by the concentration of chlorate in presence of sulfuric acid, which can selectively dissolve copper or gold, due to the different reduction products of chlorate, that are chlorine or chloride. The latter, together with the addition of sodium chloride to the leaching solution can dissolve metal by the formation of the respective chloridometalates which have a lower reduction potential, making the dissolution of metals from e-waste easier.[106]

So far, all the cited extractant and extraction processes were performed in acidic media, however there are also extractant which work under alkaline conditions, like β-diketones. In Figure 5, the generic structure of β-diketones and their acid base equilibrium are reported.

The unique structure of β-diketones enables the stabilization of the negative charge generated after proton removal, thanks to resonance delocalization across the molecule. This is highly exploited for the formation of meal complexes, where β-

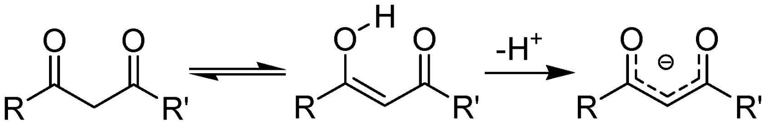

Figure 5. Structure and acid base equilibrium of β-diketones. With permission of *Chem. Soc. Rev.* **14**, 43, 123-134.

diketonates act as bidentate chelating ligands in a pseudo-aromatic six-member ring coordination. In particular, the acidity of the α-protons is sufficiently high to be easily removed in alkaline conditions, or by reacting with metal hydroxides or hydroxo-complexes.[107]

For what concerns the solvent extraction of metals, the chemical nature of the R substituents is crucial in determining the selectivity of the extractants and their solubility in the organic phase. Usually, one of the substituents is a phenyl group, while the other is an aliphatic chain, which can be either linear or branched.[1]

This kind of extractants have been employed for the extraction of copper (II) from alkaline solutions of ammonia and glycine.[108,109] In particular, Tanda and co-workers compared the extraction capacity of two different β-diketones Mextral 84H (2-hydroxy-5-nonylacetophenone oxime) and Mextral 54–100 (1-benzoyl-2-nonyl ketone), both containing phenyl and aliphatic substituents. High extraction yield was achieved with both extractant in kerosene, with neglectable extraction of glycine in the organic phase, limiting its loss. Then copper was easily stripped with sulfuric acid solutions, recovering also the extractants.[109]

Although being well-established, the metal extraction processes lack of sustainability and are not fully compliant with green chemistry, as for the use of kerosene and harmful chemicals.[20] Moreover, even if in the majority of the SX processes ligands are recovered after the stripping of metals, when dealing with metal recovery from waste, more than one extraction step could be needed in order to concentrate metals. Because of this, the above-mentioned ligands can undergo degradation, especially when put into contact with leachate containing nitric acid,[110] or in the case of β-diketones which can be degraded by ammonia while recovering metals from ammoniacal baths.[108]

Despite this, SX is still widely used as purification technique thanks to the numerous and well-established ligands, which well adapt to the specific composition of leachates, and offer high selectivity and yield.[111]

3.2.2 Innovative Methods

With respect to traditional methods, innovative methods are designed to avoid the use of toxic and oil-based organic solvents and ligands for metal extraction, as well as strong mineral acids like nitric acid as oxidant for metal leaching. Moreover, innovative methods are aimed at reducing the number of steps in the recovery processes, by maintaining good selectivity and high yields.[8]

This specific section devoted to innovative methods focus on replacing traditional, often hazardous, extraction materials and processes with eco-friendly alternatives. One of the most remarkable way to exploit coordination chemistry is the oxidative leaching, where coordination chemistry is combined with greener oxidants—such as oxygen-based oxidants (e.g., hydrogen peroxide and ozone) or the iodate/iodine/iodide system—to oxidize and dissolve copper. This approach prevents the use of harsh oxidants like nitric acid or chlorine gas by forming stable metal complexes that facilitate oxidation at milder conditions. Additionally, this section covers the use of sustainable solvents, such as Deep Eutectic Solvents (DES) and Ionic Liquids (ILs), often combined with the design of copper coordination compounds, as well as of bioleaching, which leverages on microorganisms for metal recovery. Together, these advancements aim to streamline copper extraction by reducing process steps, toxic solvent usage, and environmental footprint, compliant with green chemistry principles.

Within this framework, coordination chemistry plays a key role not only in designing new ligands, but also in finding new strategies for exploiting the already well-known chemistry of transition metals. A great example of how coordination chemistry can be exploited for the green and sustainable recovery of metals and copper in particular, is the leaching of e-waste.[8]

As already stated, e-waste contains metals in their elemental form, the most valuable of them being electronegative metals like Cu, Ag, Au and PGMs (Platinum Group Metals), which cannot be leached just by direct acidic or alkaline leaching. The leaching of these metals must be a so called oxidative leaching, in which an oxidant and a ligand are employed together.[8] During oxidative leaching, the oxidant used may or may not have a higher reduction potential compared to the metal being leached. However, the formation of complexes can lower the metal's reduction potential, facilitating its oxidation.[112] This is also true for oxidants like oxygen, which has a high reduction potential (1.23 V vs RHE[113]), but its reduction has sluggish kinetics due to the 4 electron transfer process.[114] Moreover, the reaction between oxygen and metals is an heterogeneous reaction between a gas and a solid, which is intrinsically challenging.[115] In addition, during oxidation, metals often covers with an oxide layer, i.e. passivation layer, which prevents further oxidation of bulk metals.[115]

The formation of complexes can favor the oxidation of metals, and can be rationalized by considering the equilibrium of complex formation (eq. 5 and 6) and the Nernst equation (eq 7–8–9):

$$M^{z+} + xL^{y-} \rightleftarrows [ML_x]^{z-xy} \tag{5}$$

$$K^{*}_{eq} = \frac{\left[ML_x^{z-xy}\right]}{\left[M^{z+}\right]\left[L^{y-}\right]^x} \rightarrow \left[M^{z+}\right] = \frac{\left[ML_x^{z-xy}\right]}{K^{*}_{eq}\left[L^{y-}\right]^x} \tag{6}$$

$$M^{z+} + ze^- \rightleftarrows M \tag{7}$$

$$E = E^0 - \frac{RT}{nF}\ln\frac{1}{\left[M^{z+}\right]} = E^0 - \frac{0.0592}{n}\log\frac{1}{\left[M^{z+}\right]} \tag{8}$$

$$E = E^0 - \frac{0.0592}{n}\log K^{*}_{eq} - \frac{0.0592}{n}\log\frac{\left[L^{y-}\right]^x}{\left[ML_x^{z-xy}\right]} \tag{9}$$

Where M is the metal, L is the ligand, K^{*}_{eq} is the overall formation constant of the complex, $[ML_x]^{n-xy}$ is the complex, R the gas constant, T the absolute temperature and n is the number of exchanged electrons.

From equation 9 it is easy to understand that the stronger the complex, i.e. the higher K_{eq}^{*}, and so the higher the $\left[ML_x^{n-xy}\right]$, the lower the reduction potential E. Since K_{eq}^{*} is usually known, as well as E^0, the first two terms in equation 9 are often grouped in a "conditional" standard reduction potential $E^{0'}$, which for example for the reduction of the $[Cu(NH_3)_4]^{2+}_{(aq)}$ complex to metallic copper is -0.05 V,[116] compared to $+$ 0.34 V[113] of $Cu^{2+}_{(aq)}$.

This is a very well-known principle, adopted since the latest XIX century for the leaching of gold and silver from mines through cyanidation,[117] and recently also copper.[118] During the gold cyanidation process, and similarly for silver, the metal is leached from its elemental form using oxygen as oxidant in presence of an alkaline solution of cyanide. The reaction is favored by the formation of $[Au(CN)_2]^-$ complex which is strong enough to reduce the reduction potential of gold from 1.68 V to -0.60 V.[8] However, due to the poisonous nature of cyanide, this process is becoming less used, and replaced with safer reagents.

Nowadays, one of the most employed oxidants for the recovery of copper (at least in the laboratory scale) is hydrogen peroxide, H_2O_2, often in presence of an acid or a ligand.[8] The acidic environment is necessary for hydrogen peroxide to act as strong oxidant[113]:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad E^0 = +1.77\ V \tag{10}$$

In addition, the acidic environment prevents the formation of a passivating layer on top of the metal which would limit the oxidation. For this reason, mixtures of hydrogen peroxide and sulfuric acid have widely been used for the leaching of copper from e-waste. In this case, sulfuric acid provides the acidic environment needed for reaction 10 to occur, and at the same time assist the dissolution of copper which otherwise would precipitate as oxide.[119,120] Also hydrochloric acid/chloride systems have been employed for the oxidation of copper with hydrogen peroxide, through copper (I) intermediates.[121]

Good alternatives to sulfuric and hydrochloric acid are citric acid or glycine, naturally occurring acids that are sufficiently strong to create the necessary acidic environment for hydrogen peroxide to work as effective oxidant, while also promoting the formation of stable metal complexes, which enhance metal solubility.[90,122,123] Hydrogen peroxide has been employed also in neutral and alkaline environment for the dissolution of copper in presence of ammonia and ammonium oxalate, highlighting the effectiveness of combining a powerful oxidant and coordination chemistry for greener leaching of metals.[124,125]

Hydrogen peroxide is a powerful and green oxidant, as its reduction results in the formation of water (see reaction 10). However, hydrogen peroxide is also an unstable compound that tends to decompose into water and oxygen, limiting its employment in industrial environment.[126] Moreover, hydrogen peroxide is readily decomposed in presence of most transition metals and metal complexes,[127] making its use as oxidant for metals still more complicated, and in fact it has to be used always in large excess.[90,123–125]

As an alternative to hydrogen peroxide, molecular oxygen or ozone can be effectively used for the oxidation of copper from e-waste. While the reaction between oxygen and copper is typically difficult to carry out, combining oxygen with acidic solutions of sulfuric acid enables the complete leaching of metallic copper.[128,129] According to Park and co-workers, the leaching mechanism of copper with Cu^{2+}/O_2 mixture involves Cu^+ intermediates[129]:

$$Cu^{2+}_{(aq)} + Cu_{(s)} \rightleftarrows 2Cu^+_{(aq)} \tag{11}$$

$$4Cu^+_{(aq)} + O_{2(g)} + 4H^+_{(aq)} \rightleftarrows 4Cu^{2+}_{(aq)} + 2H_2O_{(l)} \tag{12}$$

The presence of oxygen is necessary for the oxidation of the cuprous ions formed by reaction 11, which otherwise would disproportionate in sulfuric acid solution to Cu(0) and Cu(II), leading to the formation of Cu(II).[129] On the other hand, since reaction 12 produce Cu(II) ions, the amount of Cu(II) ions at the beginning of the reaction can be very small, just to trigger the reaction.[129]

A more powerful version of oxygen is its allotrope ozone, which has a much higher reduction potential in acidic environment[113]:

$$O_{3(g)} + 2H^+_{(aq)} + 2e^- \rightarrow O_{2(g)} + H_2O_{(l)} \quad E^0 = 2.076\ V \tag{13}$$

In alkaline environment ozone is still a good oxidant with a reduction potential of 1.24 V compared to 0.40 V of oxygen in alkaline solution.[113] For the leaching of metals from e-waste, ozone is employed in acidic environment to boost reaction 13 and making the solubilization of metals easier.[130] The advantages of using ozone over oxygen include the ability to operate at ambient pressure and temperature, as well as the possibility of generating ozone in situ through the UV treatment of air.[131,132]

Taking a step to the right on the periodic table, we move from oxygen-based oxidants to halogens, in particular to the system $IO_3^-/I_2/I^-$. Actually, iodine-based oxidants are mostly used for the leaching of gold, thanks to the formation of gold iodide complexes that lower gold reduction potential.[133] However, Serpe and co-workers developed a process for the stepwise recovery of copper, silver and gold from e-waste by exploiting the $IO_3^-/I_2/I^-$system and coordination chemistry approaches.[58,116] In particular, after the leaching of base metals (Sn, Pb, Zn and Ni) with citric acid, the remaining scraps were rich in copper and NMs. The leaching of the solid residue was obtained by the combined action of IO_3^-, I^- and an ammonia/ammonium sulfate solution. Iodate and iodide were obtained by dissolving iodine in a solution of NaOH 1.5 M thanks to these reactions:

$$I_{2(s)} + 2OH^-_{(aq)} \rightarrow I^-_{(aq)} + IO^-_{(aq)} + H_2O_{(l)} \tag{14}$$

$$IO^-_{(aq)} + O_{2(g)} \rightarrow IO^-_{3(aq)} \tag{15}$$

The standard reduction potential of the couple $IO_3^-/\ I^-$ is only 0.26 V in alkaline environment,[113] which would not be sufficient for oxidizing copper. However, since the leaching was conducted in an ammonia solution, the formation of copper (II) ammino complex lowered the reduction potential of copper, allowing for the formation of soluble Cu(II) species. Similar applies for the leaching of silver, which through the formation of insoluble AgI precipitate, its reduction potential was lowered to -0.152 V,[113] allowing to separate it from copper. Finally, gold remained as precipitate, since the redox couple IO_3^-/ I^- is not strong enough to oxidize it, also if considering the formation of gold-iodide complexes.[116] Moreover, the authors proposed also a way to recover also ligands (ammonia) and iodine. For doing this, they treated the solution containing Cu(II) ammino complex with Zn powder, obtaining metallic copper; then ammonia was recovered by bubbling the distillation vapors in water, leaving a precipitate of $Zn(OH)_2$ which can be recovered as it is. The remaining solution containing iodide was finally treated with H_2O_2 at acidic pH, with the production of I_2 vapors that were cooled, obtaining solid I_2.

The use of the $IO_3^-/I_2/I^-$system offers advantages over hydrogen peroxide as an oxidant, allowing for safer handling since all reagents are stable solids, eliminating the formation of byproducts, and providing the option to recycle them at the end of the process. Moreover, compared to hydrogen peroxide, iodine can act as an oxidant, a precipitating agent, and a ligand, allowing for the selective leaching of metals rather than leaching all metals together and separating them afterward.[58,116]

As already mentioned, the leaching of copper can be performed also by exploiting Cu(II) ions in chloride medium in presence of oxygen.[96,128,129,134] An alternative to Cu(II) ions are Fe(III) ions, which have a higher reduction potential, that for the couple Fe(III)/Fe(II) is 0.77 V.[113] In this case, the direct reaction between ferric ions and copper can be performed obtaining ferrous and cupric ions in the end[135]:

$$2Fe^{3+}_{(aq)} + Cu_{(s)} \rightarrow 2Fe^{2+}_{(aq)} + Cu^{2+}_{(aq)} \quad (\Delta E^0 = +0.33\ V) \tag{16}$$

However, the hexa-aquaion of iron (III) has a relatively low pK_a, about 2.2,[136] so that the reaction has to be performed in acidic environment to prevent the precipitation of iron hydroxides. The selection of the acid can be done according to the specific substrate to be leached, but usually sulfuric or hydrochloric acids are employed.[137] Yazici and co-workers proposed a process for the leaching of copper and other metals from printed circuit boards (PCBs) by employing ferric sulfate as lixiviant in sulfuric acid solutions. In particular, the main reaction of the process was the one reported in equation 16, nevertheless they explored the post-leaching regeneration of Fe(III) by oxidation of Fe(II) with oxygen or hydrogen peroxide. The former resulted the most suitable oxidant, because hydrogen peroxide underwent Fenton reaction producing oxygen gas, thus posing issues in its handling.[137] The authors also reported that by adding chloride ions in the leaching solution of ferric sulfate and sulfuric acid, they were able to solubilize silver and palladium thanks to the formation of their chloridometalates, lowering the reduction potential.[137] Despite this, the post-leaching recovery of copper remains challenging due to the presence of relatively high concentration of iron species. Sethurajan and co-workers suggested the use of sodium sulfide for the precipitation of copper sulfide, however with scarce selectivity due to the competitive precipitation of iron.[135]

In some cases, the above-described reactions can be performed *in situ* by exploiting the metabolism of many microorganisms. For example, similar reactions are exploited also for the bioleaching of metals by iron oxidizing bacteria like *Acidithiobacillus ferroxidans, Leptospirillum ferroxidans* and *Leptospirillum ferriphilum*.[138–142] Bioleaching is a process in which microorganisms (mainly bacteria and fungi) are involved in the leaching of metals, with different mechanisms of action.[143–145] Historically, two mechanisms were recognized, direct and indirect mechanism according to the fact that microorganisms were or not in contact with the substrate.[143] In other cases, the direct mechanism was considered when metals were leached by reacting with compounds produced by microorganisms' metabolism, otherwise the mechanism was considered indirect.[144] However, this was an ambiguous definition, and we prefer to adopt the more conservative description of bioleaching mechanisms proposed by Dong and co-workers.[145] In Figure 6 the main bioleaching mechanisms are reported.

As reported in Figure 6, the main mechanisms are acidolysis, complexolysis, redoxolysis and bioaccumulation. Through acidolysis, microorganisms secrete organic acids in the leaching solution as metabolites, such as oxalic, gluconic, malonic, lactic, acetic, succinic, malic, citric and other acids, which dissolve metal oxides.[146] In addition, the production of carboxylic acids by microorganisms can be coupled with metal oxidation by dissolved oxygen, as reported by Johnson for the dissolution of copper from chalcocite (Cu_2S)[147]:

$$2Cu_2S_{(s)} + 5O_{2(g)} + 4H^+_{(aq)} \rightarrow 4Cu^{2+}_{(aq)} + 2SO^{2-}_{4(aq)} + 2H_2O_{(l)} \tag{17}$$

Complexolysis involves extracellular polymeric substances (EPS) produced by microorganisms which can complex metal ions. This is possible thanks to hydroxyl, carboxylic and amino groups present on EPS,[148] that complex metals, possibly after acidolysis of metal compounds.[145]

During redoxolysis, microorganisms can either come into contact with metal substrate and perform redox reactions through enzymes inside the cell, or by secreting enzymes which react with metals.[145] For example, the mechanism of action of metal sulfide oxidizing bacteria involve both the oxidation of sulfide to sulfate performed by bacteria, and the *in situ* formation of Fe(III) by bacterial oxidation of Fe(II).[149] The former is the case of *Acidithiobacillus thiooxidans* and *Acidithiobacillus caldus*,[139,140] while the latter is common of *Acidithiobacillus ferroxidans, Leptospirillum ferroxidans* and *Leptospirillum ferriphilum*.[138–142]

Finally, bioaccumulation involves the intracellular accumulation of metals by active metabolic reactions in which metals are used as cation exchangers, typical of fungi like *Aspergillus niger*.[145]

For what concerns the leaching of copper, and in general of metals from their oxidized form, acidolysis and complexolysis are the most exploited mechanisms, while for the leaching of

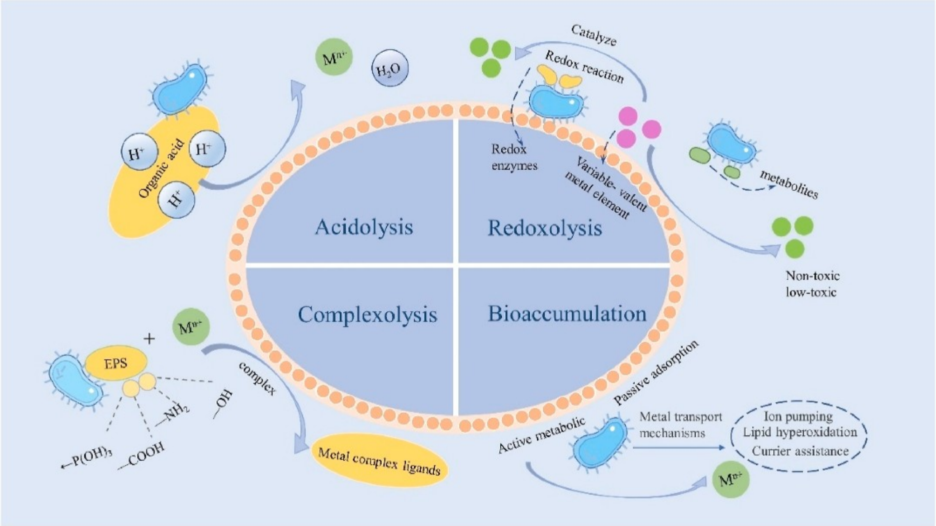

Figure 6. Main bioleaching mechanisms. With permission of *J. Environ. Manage.* **2023**, 344, 118511.

copper from is elemental form is achieved through redoxolysis.[145,150] There are also microorganisms which convert amino acids into cyanide, which is then conveniently exploited in cyanidation of metals for their recovery from e-waste.[151]

Despite these interesting features, a broader use of bioleaching is hampered by a major drawback: bioleaching is usually not a selective process, and requires further purification steps, like solvent extraction.[111] Moreover, the bioleaching processes are often slower than common chemical approaches, posing issues at an industrial scale development.[145]

A step further for the sustainable leaching and recovery of copper is the use of carboxylic acids and amino acids, especially those that are naturally occurring. Carboxylic acids can act as chelating agents in copper recovery by forming complexes with copper ions. This facilitates the dissolution of copper, and the process typically operates under mild conditions, such as moderate pH levels. The organic nature of carboxylic acids makes them attractive for use in green chemistry as they tend to be less aggressive than strong mineral acids, leading to reduced environmental harm.[152]

We already mentioned the use of a combination of citric acid and hydrogen peroxide for the leaching of copper and other metals from e-waste,[90] but also other carboxylic acids have been employed for the same purpose, like acetic,[153] malonic,[154] oxalic[155] acids, glycine[156] and thiourea.[155] In all these cases, the role of the ligands is providing an acidic environment (organic acids), but more importantly they form stable complexes with metals which stabilize them in solution in their oxidized form.[90,153–156] All the mentioned ligands can form different complexes with different metals and also with the same metal, but with different stoichiometry. The metal-ligand interaction is governed mostly by the pH of the solution and the molar ratio between metal and ligand,[157] and this can be exploited for improving the selectivity of the leaching process toward a specific metal.[155]

On the other hand, carboxylic acids and amino acids can be employed also for the leaching and recovery of copper in its oxidized form Cu(II), thanks to the formation of various complexes with these ligands. For example, citric and oxalic acids have been employed as ligands for the recovery of copper from copper slag. The slag is composed of metal oxides and silicates, and copper in particular is mainly present as Cu(II). In this case, the mechanism of copper recovery involves the acidic leaching of copper oxide from the slag and the formation of soluble complexes.[158] The formation of soluble complexes was recognized of primary importance to enhance the recovery of copper, that is why citric acid was preferred over oxalic acid. Copper and citric acid can form a wide variety of complexes with different stoichiometric ratios, including charged species, according to the pH of the solution. On the contrary, oxalic acid mostly forms insoluble species with metals, reducing the recovery percentage.[158] However, this process was not selective enough, due to the fact that citrate can form several stable complexes with also other metals present in the slag, and further purification and separation steps are required for the recovery of copper.[158]

Within this framework, we very recently published a paper in which we demonstrated the possibility of using hydroxycarboxylic acids as green and abundant ligands for the recovery of copper from a multimetallic powder. In particular we explored the formation of copper complexes with succinic, malic, lactic, aspartic and tartaric acids, evaluating the effect of the substituent in α-position of the carboxylate moiety.[159] We emphasized the significance of forming sufficient stable and soluble copper complexes to attain a high leaching yield while also allowing for the potential breakdown of these complexes for the final recovery of copper. In particular, we observed that malic and lactic acid were the most promising ligands, which allowed for the formation of soluble complexes with copper, and the precipitation of copper hydroxide at pH 12. These ligands showed high selectivity when copper hydroxycarbonate was mixed with iron and aluminum oxides, while lower selectivity was observed when Mn(II), Ca(II) and Zn(II) were added to the multimetallic powder. Despite this, we proposed a new approach for the recovery of copper, by also employing a Design of Experiment approach (DoE) which allowed us to limit the number of experiments, and so limiting the waste of time and materials.[159,160]

There are additional examples of utilizing carboxylic acids and amino acids for leaching copper as Cu(II) from diverse sources, along with other ligands like ethylenediaminetetraacetic acid (EDTA), both through traditional chemical methods and biometallurgical approaches, all underscoring the versatility of coordination compounds for efficient leaching and recovery of copper and other metals.[85,86,151,161]

The use of carboxylic acids and amino acids as green ligands for copper recovery in aqueous environments presents a promising approach. Yet, there is an innovative and unique way to exploit coordination chemistry that not only serves as a ligand but also acts as a solvent with ionic liquids (ILs).[162–164] These salts, which remain liquid at temperatures below 100 °C, provide non-volatility, thermal stability, and tunable chemical properties, making them highly versatile for various industrial applications.[8,162,165] In the realm of metal recovery, particularly copper, ILs offer improved selectivity, efficient leaching, and environmentally friendly electrochemical processes.[166] Compared to traditional SX processes, ILs allow for greater flexibility in tuning their affinity for metal ions, enhancing both extraction efficiency and selectivity while reducing the risk of aqueous-phase contamination.[167]

In Figure 7 the basic structures of the most used cation and anion in ILs are reported.

Due to their remarkable versatility, and in particular thanks to the possibility of being employed both in solvent extraction processes and in electrochemical treatments, ILs have been used for the recovery of copper from a wide range of substrate, including waste waters,[168–171] industrial waste[172,173] and e-waste.[166,174,175]

When employed as extractants, the mechanism of copper extraction with ILs is very closed to the one for the traditional SX (see equations 2, 3 and 4), in which copper is extracted into the IL phase by forming stable complexes with one of the components of the IL.[176,177] This occurs particularly with a special category of ILs that are the protic ILs (PILs), formed by a protonated trialkylamine (i.e., trialkylammonium) and an aliphatic carboxylic acid with more than six carbon atoms. Therefore, the formed IL is apolar and can be exploited both as an extractant and a solvent for the recovery of copper from aqueous phases. In this case, the mechanism of extraction involves the cation exchange between the proton of the trialkylammonium and copper (II), which is extracted into the IL phase[168]:

$$2HNR^{+}_{3(IL)} + Cu^{2+}_{(aq)} \rightarrow 2H^{+}_{(aq)} + [Cu(NR_3)_2]^{2+}_{(IL)} \tag{18}$$

Furthermore, since ILs are ionic compounds, they can also solvate copper (II) ions and its counterion by keeping the charge balance[168]:

$$Cu^{2+}_{(aq)} + \frac{2}{n}X^{n-}_{(aq)} \rightarrow Cu^{2+}_{(IL)} + \frac{2}{n}X^{n-}_{(IL)} \tag{19}$$

The two mechanisms described in equations 18 and 19 can occur simultaneously. However, which mechanism predominates depends on the specific ionic liquid (IL) and, for instance, can be influenced by adjusting the length of the amine's alkyl chain.[168]

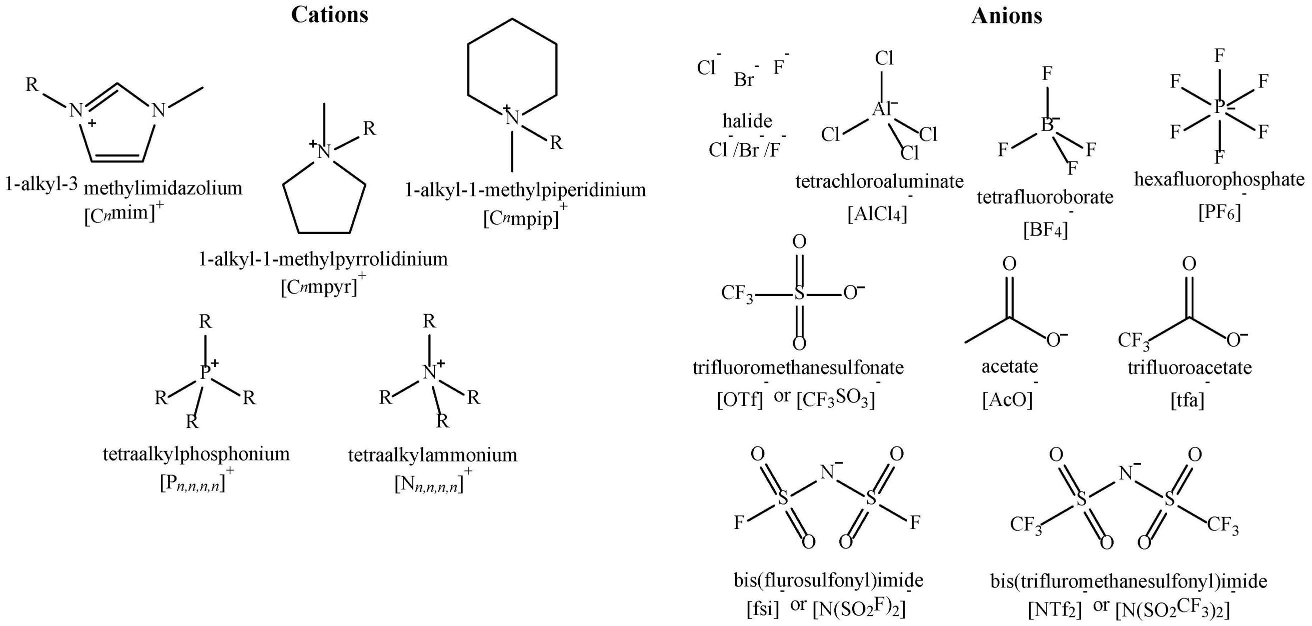

Figure 7. Structures of cations and anions employed in ILs. With permission of *Molecules*, **2020**, 25(21), 5207.

The recovery of copper using ILs from e-waste (i.e., copper present as Cu(0)) has been conducted both in the absence and presence of an added oxidant. Notably, higher yields were achieved when hydrogen peroxide was employed as the oxidant.[174,175,178] In the absence of an added oxidant, copper was leached after oxidation by dissolved oxygen and subsequent solubilization by the IL.[175] Conversely, when hydrogen peroxide was present, it served as the oxidant for metallic copper, which was then dissolved by the IL.[174,175] After leaching, copper can conveniently be recovered from the IL solution either by electrochemical deposition or precipitation. Due to their ionic nature, electrodeposition can be conducted directly in ionic liquid solutions, facilitating both the recovery of copper and the regeneration of the ILs simultaneously.[175] On the other hand, Li and co-workers proposed a method for the post-leaching precipitation of copper with oxalate, forming insoluble copper oxalate, which was further thermally decomposed to yield CuO nanoparticles.[178]

A good example of the possibility of tailoring ILs for specific purposes was given by Papaiconomou and co-workers, which they functionalized the alkyl chain of imidazolium, pyridinium, piperidinium and pyrrolidinium based ILs to improve their selectivity towards transition metals.[169] In particular, to achieve selectivity towards copper, the alkyl chain of the cations was functionalized with disulfides which are known to interact with copper (II).[169]

Although ionic liquids are powerful tools widely used and generally recognized as "green solvents" due to their low volatility, they have been found to not fully adhere to the principles of green chemistry.[179] The synthesis of the components of the most common ILs usually starts from fossil sources, and involves harmful and dangerous reagents. Moreover, the constituents of the final IL can be harmful themselves, as in the case of methyl-imidazolium derivatives, and are not biodegradable.[179] However, there is a wide literature about the production of ILs deriving from renewables and natural feedstocks,[180–188] each of them with still some issues about green principles.[179] Furthermore, several eco-friendly processes have been developed for the recovery and recycling of ionic liquids after use, enabling the same IL to be employed in multiple cycles.[179]

This poses some concerns when considering the sustainability and greenness of processes, because, even if they may not be eco-friendly, ILs can be used for green and sustainable purposes, like the recovery and recycling of metals.[179] Additionally, from a sustainability perspective, a process that facilitates the recovery of the reagents or solvents used should be preferred over one that employs only green chemicals but does not allow for their recovery.

A concrete step forward in terms of both sustainability and greenness was made by Abbott and co-workers in the early 2000s with the development of Deep Eutectic Solvents (DES).[189] DES are a greener alternative to ionic liquids, produced by combining a hydrogen bond donor (HBD), typically containing functional groups such as hydroxyls, amines, or carboxyls, with a hydrogen bond acceptor (HBA), often composed of quaternary ammonium salts or similar compounds. The interaction between these components results in a eutectic mixture with a lower melting point than the individual substances.[190] Compared to ILs, DES are more sustainable, offering lower toxicity, better biodegradability, and easier preparation from inexpensive, naturally derived materials. DES can be classified into four categories, according to the nature of the HBD and HBA, and are summarized in Table 2[191]:

It is easy to observe that Type I and II eutectics are actually analogous of well-known ionic liquids formed by combining ammonium derivatives and chloridometalates, as reported in Figure 8.[192] However, the most interesting category of DES for the recovery of metals, and in particular copper, are Type III eutectics, since they are formed by the interaction of two organic molecules which can act as complexing agent towards metals.[191] In Figure 8, examples of HBD and HBA used in Type III DES are reported.

As reported in Figure 8, many of the hydrogen bond donors are carboxylic acids, which we have already mentioned as suitable ligands for the recovery of metals from various sources. However, DES offer a versatile and sustainable approach for copper recovery through various mechanisms. They can effectively leach **Cu(II)** ions from ores or waste materials, providing an eco-friendly alternative to conventional solvents.[193] In **e–waste recovery**, DES can dissolve copper with the aid of an oxidant, converting metallic copper to a soluble ionic form. Additionally, by combining hydrophobic HBD and HBA it is possible to obtain another subgroup of DES, called hydrophobic DES (HDES), which can serve as apolar solvents in solvent extraction processes, selectively recovering copper from aqueous solutions while maintaining low volatility and biodegradability, making them an attractive green alternative to traditional extraction methods.[194–197]

DES typically result in a highly viscous state due to the formation of a wide network of hydrogen bonds, making them more challenging to handle, particularly on large scales.[198] However, several attempts have been made in order to overcome the viscosity issue, like working at higher temperatures, adding controlled amount of water or with improved stirring equipment.[191] An interesting solution was found by Rivera and co-workers which employed ultrasounds for enhancing metal leaching from e-waste, with a hydrated calcium chloride – ethylene glycol-based DES. The substrate was a gold coated PCB with a layered structure in which copper was covered with a nickel layer. In order to oxidize copper, they added to the DES copper chloride to exploit the reaction reported in equations 11 and 12, in which Cu(II) oxidizes Cu(0), forming Cu(I), which is stabilized by the high chloride concentration as chloride complex, and then further oxidized to Cu(II) by dissolved oxygen. Gold was not solubilized due to its too high reduction potential in these conditions, while nickel was leached only in small amount probably due to the formation of a passivating layer. They also demonstrate that the etching rate of copper was nearly five order of magnitude higher when ultrasounds were applied, mainly due to the removal of the passivating layer of insoluble CuCl formed on the surface of copper.[199] Similar results were obtained by Doche and co-workers, which applied ultrasounds for the leaching of copper in a ethylene

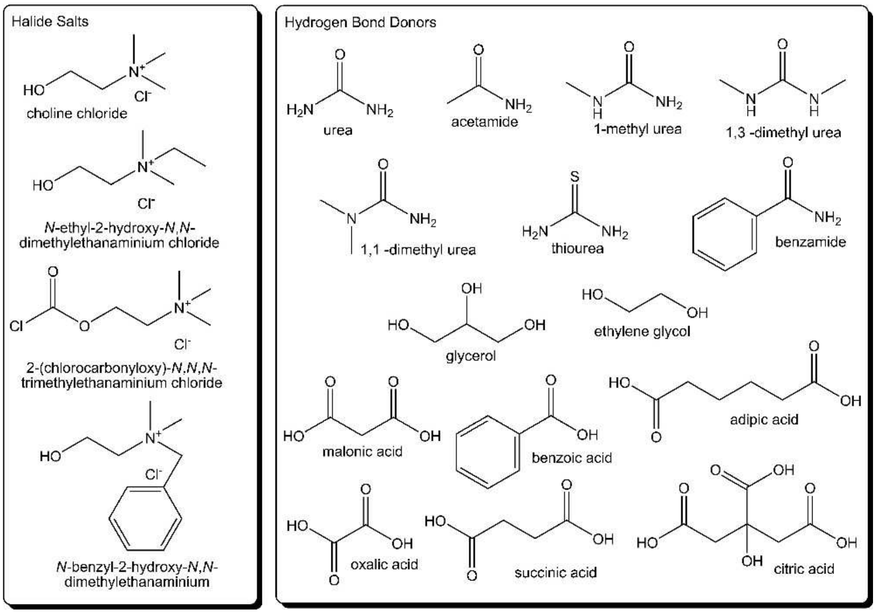

Figure 8. Examples of HBD and HBA employed in Type III DES. With permission of *Chem. Rev.* **2014**, 114, 21, 11060–11082 (pubs.acs.org/doi/10.1021/cr300162p, further permissions should be directed to ACS).

glycol – choline chloride-based DES, implementing also a recovery step through electrodeposition of copper.[200]

As a completely different approach, Schaeffer and coworkers prepared a library of HDES by combining menthol or thymol with various long chain saturated carboxylic acids, from C_8 to C_{18}, to be used as hydrophobic phase for the extraction of Cu(II) form an aqueous solution.[196] The authors demonstrated that the extraction of copper was increased by decreasing the length of the alkyl chain of the carboxylic acid, obtaining the highest extraction with capric acid. According to the authors, this was due to the lower mole fraction of acid with increasing chain length.[197] Interestingly, authors observed an increase of copper extraction by increasing pH of the aqueous phase from 3 to 4.9, indicating that the extraction mechanism involved the cation exchange between the protons of the carboxylic acid and copper (II). However, according to the author, copper was extracted as hydroxo complex like $Cu(OH)^+$ rather than Cu^{2+}, and this was verified also by the fact that copper extraction was near 100 % when additive salts of organic acids were added to the aqueous solution, indicating the formation of copper complexes. In the end, the HDES was recovered by stripping copper with a dilute sulfuric acid solution, preserving the HDES composition in multiple cycles.[196]

Finally, in literature, some more attempts to boost the above-reported coordination chemistry approaches are reported, like hydrothermal,[201] sono-[202] and mechanochemical[203] approaches. Although these methods are not yet well-established, they help broaden the landscape of metal leaching and recovery.

4. Summary and Outlook

This review explores the role of coordination chemistry in advancing sustainable copper recovery, critical for meeting the growing demand driven by the global energy transition. Copper is essential for electrification, renewable energy infrastructure, and electric vehicles. Although primary copper sources remain abundant, their uneven distribution and the environmental impact of mining have highlighted the need for alternative recovery methods from secondary sources such as industrial by-products and e-waste.

Hydrometallurgy offers a promising approach for copper recovery due to its flexibility in processing varied waste streams. Coordination chemistry enables the use of selective ligands to efficiently recover copper from complex, multimetallic matrices. Traditional ligands like oximes and carboxylic acids have long been used for solvent extraction, providing efficient separation of copper from other metals.

However, these traditional methods often rely on the use of toxic solvents and strong acids, making them environmentally unsustainable. Recent advancements have focused on greener alternatives, such as using organic carboxylic acids and amino acids as ligands. These molecules form stable copper complexes, offering an eco-friendlier approach to both leaching and solvent extraction.

Ionic liquids (ILs) and deep eutectic solvents (DES) present innovative, greener alternatives to traditional organic solvents. These solvents are tunable, biodegradable, and offer high selectivity for copper recovery. ILs can be tailored to target specific metals, while DES—often made from natural components like bio-based carboxylic acids—provide a sustainable, low-toxicity solution. Both show potential for scalable industrial applications, with DES being particularly appealing due to their ease of preparation and lower cost.

Bioleaching, another innovative method, uses microorganisms to extract copper from waste. Although slower and less selective than chemical methods, bioleaching has the advantage of requiring lower energy and being suitable for low-grade ores. It holds promise for industrial applications, but still faces selectivity and scalability challenges.

In addition to these emerging techniques, mechanochemical and hydrothermal methods are also being explored. While not yet widely adopted, these methods offer the potential to improve process efficiency and sustainability by reducing energy consumption and reliance on harmful chemicals.

The selectivity of a chemical process for copper recovery, and metal recovery in general, is not solely determined by the choice of the reagents and of the related experimental parameters (e.g. pH, temperature, molar ratios…). Indeed, the composition of the waste material itself plays a crucial role, often dictating the effectiveness and efficiency of the recovery process. Each waste matrix presents a unique blend of elements, phases, and impurities, whose interactions and reactivity dramatically affect the resulting selectivity. Consequently, a process highly effective for one specific waste composition may be entirely ineffective for another one, as the varying interactions can drastically alter recovery outcomes and metal-specific selectivity. Understanding the waste composition in detail is thus essential to tailor and adjust the approaches that target maximization of copper recovery while minimizing interference from other metals and materials.

Overall, while traditional hydrometallurgical methods are effective, a shift towards greener, more sustainable processes is necessary. Coordination chemistry remains a powerful methodological tool for developing selective, efficient recovery methods, particularly when paired with greener solvents and ligands. Future research should focus on optimizing these processes for large-scale use, balancing efficiency, selectivity, environmental impact, and cost. By advancing these innovative approaches, the industry can meet the rising demand for copper while minimizing the environmental footprint associated with traditional mining.

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Conflict of Interests

The authors declare no conflict of interest.

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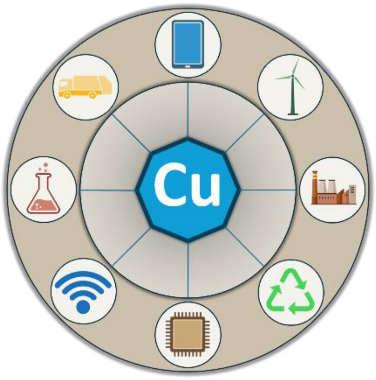
REVIEW

Copper is a fundamental transition metal with wide-ranging applications in chemistry, technology, and society. Its recovery and recycling are vital to support the increasing demands of energy transition and digitalization. In this context, coordination chemistry plays a crucial role in developing sustainable and environmentally friendly processes for extracting and reusing copper from various waste sources.



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