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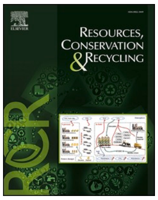

Review

Towards sustainable recycling of critical metals from e-waste: Bioleaching and phytomining

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ABSTRACT

Critical metals are indispensable components of our daily lives, becoming increasingly scarce due to their irreplaceable functions in electronics. As technological progress fuels demand, the reevaluation of end-of-life devices and electronic waste presents a sustainable approach to ensuring metal supplies. However, the extraction of critical metals from electronic waste necessitates careful management to mitigate material loss and address environmental concerns. Conventional large-scale hydrometallurgical and pyrometallurgical methods lack targeted selectivity for critical metals like Ga, In, and REEs. These metals are often lost in pyrometallurgical processes or require extensive purification following chemical leaching. Consequently, attention has shifted to emerging bioleaching and phytomining technologies as alternative selective recovery methods that adhere to sustainability criteria without excessive capital investment. Nevertheless, knowledge of these recovery mechanisms remains limited, and their application faces challenges such as longer processing times and slower yields. This review article seeks to provide insights into these novel technologies for recycling critical metals from end-of-life materials by examining their mechanisms and key parameters, exploring potential optimization strategies, and assessing trade-offs to evaluate their feasibility and sustainability in large-scale operations.

1. Introduction

Electronic waste (e-waste) is an umbrella term for discarded electric and electronic devices, classified into six categories per Annex III of the EU WEEE Directive (Directive 2018). These categories encompass namely, temperature exchange equipment, screens and monitors, lamps, large appliances such as dishwashers, and tumble dryers, small equipment such as e-cigarettes, electric kettles and calculators, and small IT and telecommunication equipment (Directive 2018, Priya, 2024, Baldé et al.).

As electronic devices have become ubiquitous devices in daily life, their usage increased during the Sars-Cov-2 pandemic due to changes in work environments, rendering many to transition into home-office and remote studies (Botelho Junior et al., 2024). Due to the ever-growing demand for electric and electronic devices, e-waste generation peaked at 62 billion kg in 2022 but only 13.8 billion kg is collected and recycled (Baldé et al.). Moreover, by the year 2030, e-waste generation is anticipated to reach 82 billion kg [3].

E-waste comprises ferrous, non-ferrous, plastic, glass, and ceramic parts, of their composition diversifies per unit kg (Tesfaye et al., 2017). Generally speaking, e-waste streams contain precious metals (Ag, Au, Pt, Pd) and technology-critical metals (Ga, In, rare earth elements, and so on) and other metals (Fe, Cu, Zn, and so on) (Sahu et al., 2022, Fornalczyk et al., 2022, Wahlström et al., 2017). Technology critical elements Ga, In, Ta, rare earth elements (REE), platinum group, Nb, and Ta constitute important electronic components, which are provided in a periodic table in Fig. 1, according to the classification regarding the EU and US guidelines. The concentration of technology-critical elements in discarded electronics can range from 0.01 up to 100 mg/kg (Nd: >100 mg/kg) (Işıldar et al., 2018, Ballinger et al., 2020, European Commission 2020). However, their supply is at risk considering their natural abundance and limited primary production, which might be hampered by the volatile economic, environmental, and political conditions (Abdou et al., 2023, Walton et al., 2021). Considering the built-in obsolescence of electronic devices, and the conundrum of supply and demand for critical metals, their extraction from e-waste is considered a vital aspect of e-waste management (Işıldar et al., 2018, Bakas et al., 2016, Xavier et al., 2023).

Nevertheless, precious and base elements remain the main driver for e-waste recycling due to their abundance in electronic components and

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their monetary value, undermining the concentrations of technology-critical metals in e-waste matrices (Zamprogno Rebello et al., 2020, Sagrillo Pimassoni et al., 2023). As exemplified in a simulation study by Reuter and van Shaik (2015), recovery rates were quantified for Ag, Au, Al, Cu, and Fe, whereas the critical metals in the waste LED lamp matrix such as Ga, In, and REE were disregarded (Reuter and van Schaik, 2015). This gap in the recovery for the vital fraction of critical metals underscores the need for more targeted recovery efforts for these elements.

Although efforts have been made to address critical metals in e-waste management, current industrial practices primarily employ pyrometallurgical and hydrometallurgical techniques or a combination of both. Pyrometallurgical recovery, a well-established method, involves thermal treatment through incineration, smelting, or roasting (Thakur and Kumar, 2020). A notable example is the ISASMELT process, used in large-scale e-waste facilities such as Auribis AG in Lünen and Umicore in Hoboken, Belgium (Alvear F and Nikolic, 2013). ISASMELT is a selective smelting process targeted at metals, in which the impurities are liberated from the precursor by taking advantage of the selective oxidation phenomenon (Alvear F and Nikolic, 2013). Despite attaining higher recovery efficiencies in one-pot large-scale reactors, the recovery is usually targeted at base elements, meanwhile, technology-critical metals often end up in the slag phase during smelting due to their thermodynamic properties, leading to their loss along the process (Hasan et al., 2022, Chu et al., 2022, Binnemans et al., 2013).

Hydrometallurgical recovery is a less energy-intensive alternative to the pyrometallurgical processes, involving a leaching process (Thakur and Kumar, 2020). Leaching is a mass transfer-driven process, revolving around the extraction of solid phase by a chemical reagent (Ray, 2023). In general, the leaching processes are influenced by the particle size of the material, temperature, mixing, and the choice of a suitable solvent, after which the extracted solid phase can be recovered through ion exchange, solvent extraction, or electrowinning (Ray, 2023, Murali et al., 2022). The commonly used leaching agents are sulfuric acid, nitric acid, aqua regia, and hydrochloric acid for the recovery of elements from e-waste (Dass et al., 2023, Xie et al., 2023, Illés and Kékesi, 2023). These reagents are excellent solvents for recovery, yet they not only lack selectivity which requires multiple purification steps for the recovery of small fractions but also pose challenges in the waste management of toxic and concentrated acid residual liquids (Li et al., 2019, Rice, 2016, Cheng et al., 2024). Considering the low recovery of technology-critical metals via conventional methods, the search for sustainable and selective alternatives has become more urgent than ever.

Bioleaching and phytomining emerge as promising technologies in the quest for alternative yet promising metal recovery methods. Bioleaching involves using microbial leaching liquor for extracting metals from ore or e-waste matrices, eliminating the need for concentrated and toxic chemicals while operating at lower temperatures (Brown et al., 2023). Nguyen and Lee (2015) reported a significantly higher leaching efficiency of bioleaching with the mixed culture of *A.ferrooxidans* and *A. thiooxidans* than the chemical leaching with sulfuric acid in the recovery of Mn, As, Fe, and Cu. Moreover, Pourhossein et al. (2022) also highlighted the superior extraction efficiency of biogenic leaching over chemical leaching due to the presence of biogenic metabolites such as amino acids, thiosulfates, glycine, etc.

Phytomining, on the other hand, harnesses the metal uptake and sequestration abilities of hyperaccumulator plants (Chaney et al., 2004, Dinh et al., 2022, Merlot et al., 2018). Due to the exceptional selective metal accumulation abilities of hyperaccumulators, phytomining has become a viable option for metal extraction (Wang et al., 2020). In a study, *Acacia mangium* inoculated with *Bacillus amyloliquefaciens* showed Ni accumulation at 825.50 mg/kg in the roots (Joradon et al., 2023). Preliminary research on *Eleocharis acicularis* by Ha et al. (2011) also demonstrated its potential for In and Ag phytomining. Yet, at present, phytomining cannot replace conventional recovery methods or traditional mining technologies (Akinbile et al., 2023). It can, however, be combined with phytoremediation processes to make the process financially more viable and can be considered as an accompanying procedure (Ha et al., 2011, Robinson et al., 2003). For instance, plants growing near e-waste dumping sites can be evaluated for their potential in phytomining. Additionally, leachates, sludges, and wastewater from processed e-waste can be incorporated in a hydroponic bath treatment with hyperaccumulators in a controlled environment to reduce the environmental burden of e-waste processing sites, as illustrated in the graphical abstract (Singh and Kumar, 2022).

Considering various factors, bioleaching and phytomining show great potential in the circular recycling of critical and precious metals. However, the scalability of these alternative technologies faces certain limitations, which often confine the current research to laboratory-scale or smaller reactor volumes. For instance, bioleaching has slower kinetics, necessitates a pre-culture period, and demands substantial amounts of nutrients and water, as well as increased energy consumption due to sterilization (Alipanah et al., 2020, Thompson et al., 2018). The process also typically necessitates multi-step reactor configurations, which increases space requirements and makes one-pot applications challenging (Lee et al., 2024, Tezyapar Kara et al., 2023). Similarly, phytomining remains under-explored and presents its own set of

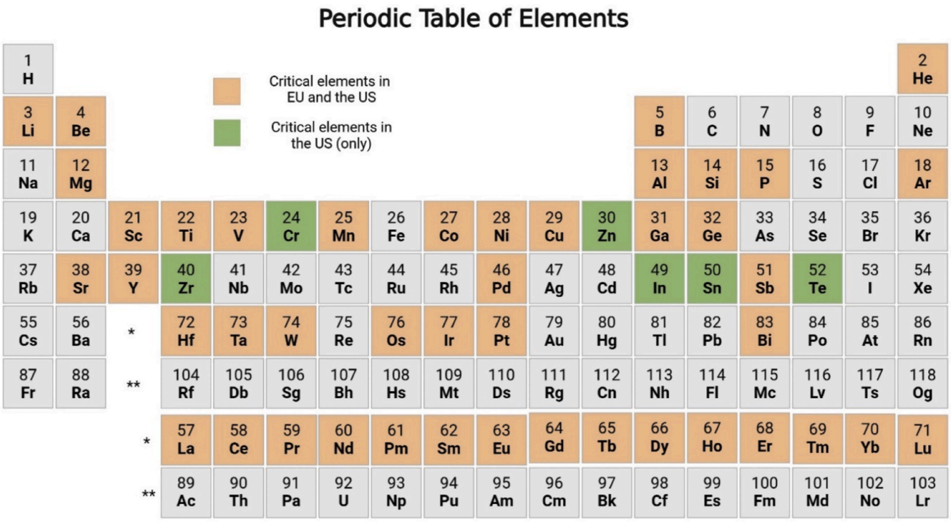

Fig. 1. The latest critical elements are listed in the periodic table, according to the reports by the EU (2023) (European Commission, 2023) and the US Geological Survey (2022) (Final List of Critical Minerals 2024).

challenges, including a lengthy uptake process influenced by environmental factors and the need for vast areas of arable land (Robinson et al., 2015). In comparison with the conventional methods, they also fall short in several aspects. The conventional methods are well-established and are operated on a large scale without the need for an extensive spatial volume, as they rely on more compact process equipment. This makes them more efficient and practical for widespread operations.

While bioleaching and phytomining may not match the efficiency of conventional technologies, plausible environmental and cost aspects, combined with their untapped potential, call for more extensive research and investment. A comprehensive analysis and a thorough understanding of key parameters, coupled with optimization strategies and hybrid methods that incorporate both thermal and physical pretreatment of e-waste, may potentially enhance metal recovery rates for critical metals (Parsa et al., 2024, Ilkhani et al., 2024, Dolker and Pant, 2019). This approach offers promising avenues for sustainable e-waste management solutions.

This paper presents a critical evaluation of alternative methods for recovering metals, focusing on bioleaching and phytomining, and aiming to provide new insights into their potential as viable alternatives to conventional technologies for recycling critical metals from electronic waste. The review examines the biological mechanisms and key parameters that drive these processes and offers a comprehensive analysis of optimization strategies to enhance efficiency. The study aims to address existing research gaps and establish a solid foundation for future research and innovation in the field.

2. Pretreatment of the e-waste

As raw e-waste materials cannot be directly used in the chemical / thermal and possibly in biological treatments for the recovery, the waste precursor should undergo a series of operations encompassing dismantling, size reduction, milling, sieving, screening, and further separation processes such as magnetic, electrostatic, and density separation (Castro and Bassin, 2022, Kumar et al., 2022). Pre-processing is a crucial step in the recovery of critical and valuable elements. The selectivity of solvents/leaching liquors for the desired elements in the waste matrix is impaired by the presence of interfering metals since the mass transfer is mainly driven by the concentration gradient (Cussler, 2009). Anaya-Garzon et al. (2021) reported that the presence of interfering and toxic metals in the leaching medium retarded the microbial growth, hindering the bioleaching efficiency. Hence, a favored strategy to preprocess e-waste not only enhances the diffusion rate of desirable elements but also reduces the need for excessive amounts of chemicals, and prolonged operations.

Size reduction, a crucial parameter in attaining suitable particle size, is usually achieved through shredding and grinding. This is evident in the case of shredded waste PCB samples, in which the REE content was enriched below 0.25 mm sieving size (Baez et al., 2022). As for the LED waste, a notable concentration of Ga, Al, Au, and Ag below 600 μm sieve fraction was observed (Zhang et al., 2023). This observation is also consistent with the findings of Nagy et al. (2017), who detected a concentration of 254 ppm of Ga in the 106–1000 μm fraction followed by the grinding of LED waste. Size reduction not only enables a selective fractionation for the biorecovery, but also enhances the area-to-volume ratio for metal leaching, and bioavailability. Díaz Martínez et al. (Díaz Martínez et al., 2018). observed higher bioaccumulation in the *L.perenne* roots, which were exposed to ground PCBs of smaller particle sizes.

Magnetic separation is commonly utilized to segregate ferromagnetic elements such as Fe and Ni from nonferromagnetic elements in an e-waste matrix (Suponik et al., 2019). Magnetic separation is often paired with electrostatic separation technologies, in which corona or eddy-current separation can be counted among them, facilitating the isolation of conductive fractions, predominantly Cu, from other non-conductive fractions (Kumar et al., 2022, de Souza and Veit, 2023). (Baniasadi et al., 2021) separated the ceramic and plastic fractions from the ground waste PCBs with the help of the electrostatic separator, which later remarkably increased the bioleaching rate with *A. ferrooxidans*.

Ultimately, the prior processing of e-waste plays an immense role in enhancing recovery rates. As there is a wide spectrum of plausible configurations, notable gaps persist in current research. Therefore, the emphasis should be placed on coupling mechanical or mechanochemical treatment techniques with further leaching, and separation processes to optimize the long-term recycling efficiencies of critical elements. This will also pioneer in mitigating environmental concerns, associated with energy consumption and the use of chemicals.

3. Bioleaching

Bioleaching is an alternative technology, that utilizes microorganisms such as bacteria, fungi, or archaea to leach metal ions from ore surfaces or e-waste particles (Adetunji et al., 2023). Cyanogenic, sulfur-oxidizing bacteria and filamentous fungi have been utilized to recover precious and critical metals from various precursors such as red mud or waste from electrical and electronic equipment (WEEE) (Qu et al., 2019, Li et al., 2020, Parsa et al., 2024). Bioleaching behavior in microorganisms diversifies into two categories bioleaching by heterotrophic and chemolithotrophic organisms, respectively. Heterotrophs such as *Aspergillus Niger* and cyanogenic bacteria *Bacillus megaterium* secrete secondary metabolites to immobilize metals through metabolizing organic carbon sources (Ertan, 2023, Karim and Ting, 2022). Whereas, chemolithotrophic microorganisms such as *A. ferrooxidans* and *A. thiooxidans* obtain energy by reducing inorganic compounds, which consequently produce biogenic acids such as sulfuric acid (Tezyapar Kara et al., 2023).

3.1. Heterotrophic bioleaching

Heterotrophic microorganisms, such as cyanogenic bacteria (e.g., *Pseudomonas spp., Bacillus mageterium*) and filamentous fungi (e.g., *Aspergillus sp., Penicillium sp.)* require organic compounds as their carbon source (Madigan et al., 2022). These microorganisms are not only capable of impressive metal extraction but also possess the ability to withstand various abiotic stresses, including temperature, pH changes, and metal toxicity (Crecca et al., 2023, Dusengemungu et al., 2021, Naseri and Mousavi, 2022). Bioleaching by heterotrophs consists of three steps: acidolysis, where secreted organic acids are deprotonated and cations are removed; complexolysis, where dissolved cations are complexed by deprotonated organic acids; and redoxolysis, where insoluble metals are reduced through oxidation–reduction reaction (Mulligan et al., 1999, Trivedi et al., 2022, Srichandan et al., 2020).

3.2. Chemolithotrophic bioleaching

Chemolithotrophs (rock-eating microorganisms) use inorganic sources such as H_2S, pyrite, and FeS_2 as energy sources to be used in respiratory processes (Madigan et al., 2022, Ji et al., 2022). Chemolithotrophs that use CO_2 as an energy source are considered autotrophs (Madigan et al., 2022). Due to their adaptability in various abiotic settings, chemolithotrophic bioleaching is considered a viable approach for recovering metals from ores and e-waste matrices (Priya and Hait, 2018, Wang et al., 2017). As shown in Fig. 2, chemolithotrophic bioleaching occurs through two primary mechanisms: direct and indirect. In the direct mechanism, bacteria adhere to the metal surface by secreting extracellular polymeric substances (EPS), where metals are dissolved through enzymatic reactions (Wang et al., 2009, Vera et al., 2022, Srichandan et al., 2019). The indirect mechanism involves metal degradation through the oxidation–reduction cycle of Fe (Srichandan et al., 2020, Nestor et al., 2001).

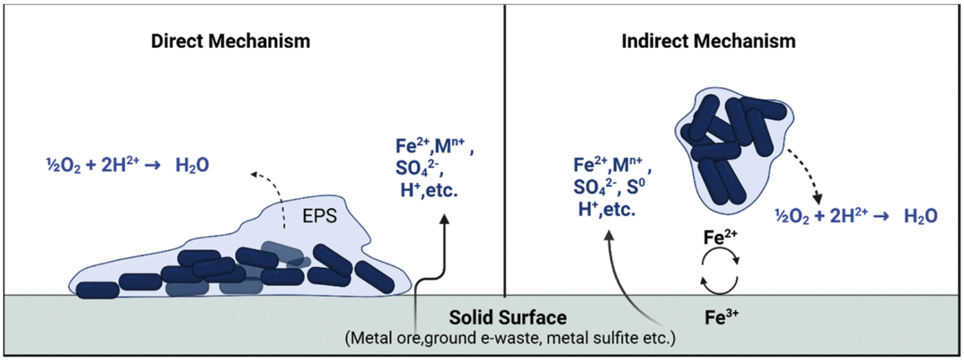

Fig. 2. Chemolithotrophic metal bioleaching from metal ores, e-waste materials, sulfite moieties, etc. (Adapted from Srichandan et al . (2019) (Srichandan et al., 2020). Created with Biorender.

3.3. *Key parameters*

Bioleaching is a process that involves various parameters, including pH, temperature, energy source, method of bioleaching, and pulp density (Sarkodie et al., 2022). Furthermore, the operational mode, or the selection of a specific strain for metal extraction, can significantly influence the process. Given that the mechanisms of heterotrophic and chemolithotrophic bioleaching differ, it is essential to select appropriate criteria to achieve higher efficiencies. Moreover, time is a critical factor in bioleaching, necessitating a comprehensive understanding of the key parameters and kinetics involved in optimizing the process.

3.3.1. *Strain*

The selection of suitable strains is a crucial step in bioleaching. Owing to the presence of various metals in the bioleaching matrix, the reaction mechanisms of strains differ, as well. Therefore, one-size-fits-all solutions are not applicable in the context of bioleaching. Chemolithotrophic acidophiles are effective for leaching sulfide minerals and pyrites, while heterotrophs are preferred for their shorter lag phase, tolerance to toxic metals, and wide pH adaptability (Aghazadeh et al., 2023, Horeh et al., 2016). Given the typically alkaline nature of e-waste, the bioleaching medium for chemolithotrophs must be adjusted to a pH below 2 to promote microbial growth and redox potential, often necessitating substantial use of concentrated HCl (Wang et al., 2009).

Chemolithotrophic microorganisms efficiently extract base, critical, and precious metals (Pourhossein et al., 2021, Pourhossein and Mousavi, 2023). Abhilash et al. (2021) found that a chemolithotrophic mixture of *A. ferrooxidans* and *A. thiooxidans* achieved significant leaching efficiencies, extracting 93 % of Cu and 94 % of Fe from PCBs, whereas heterotrophic *A. niger* extracted only 66 % of Cu and 78 % of Fe. Ni, Co, and Al recovery rates were comparable between the bioleaching setups, highlighting the superior performance of chemolithotrophs for base metals. Conversely, heterotrophic microorganisms selectively leach REEs and other critical metals by secreting organic acids (Di Piazza et al., 2017, Shen et al., 2023). For instance, *Penicillium expansum* leached terbium and lanthanum from e-waste up to 1520 ppm and 390 ppm, respectively (Di Piazza et al., 2017). Under optimal conditions (initial pH of 7.5, 0.1 mM phosphate concentration without a buffering agent), *Penicillium expansum* extracted 41.3 % La, 61.3 % Pr, 57.6 % Nd, and 46.4 % Tb from waste PCB (Baez et al., 2024). Yet, selective recovery of critical and precious metals relies on metabolic activity and secreted metabolites in the bioleaching medium (Kang et al., 2020, Suyamud et al., 2020). Understanding the strain's selectivity for certain metals requires analyzing its metabolic pathways during cultivation (Naderi et al., 2023). Optimizing organic acid production can facilitate selective critical metal recovery from e-waste without requiring post-processing to separate targeted elements from recycled base metals. This enhances the appeal of heterotrophic bioleaching over chemolithotrophic bioleaching (Bahaloo-Horeh and Mousavi, 2024, Gavrilescu, 2022). Table 1 details the bioleaching capabilities of various strains, including information on secreted metabolites and precursors.

3.3.2. *Energy source*

Organic carbon sources and inorganic compounds as energy sources in the metabolism of microorganisms play a crucial role in metal leaching. In the case of *A. ferrooxidans*, elemental sulfur as a sole energy source showed better efficiencies than iron (II) sulfate (He et al., 2019). However, in the context of heterotrophic bioleaching, its strategic use of energy sources such as sucrose or glucose, galactose, and so on becomes even more important considering the dependence of secondary metabolite production on these mono/di-saccharides (Naseri et al., 2023). Bahaloo-Horeh and Mousavi (2024) observed that among the various sugars investigated, glucose emerged as the most effective in promoting metabolite production, with the highest quantity of oxalic acid secreted. Whereas, sucrose, xylose, galactose, and lactose followed in descending order of effectiveness. This can be attributed to the faster processing of monosaccharides than disaccharides, leading to higher flux rates through glycolysis. Another exemplary study indicated a higher yield of organic acid in a sugar cane molasses medium than in a sucrose medium attaining also higher Mn and Li recovery from spent coins (Naseri et al., 2023). These findings, which revolve more on metabolite production, may be of interest to researchers in the field.

3.3.3. *Initial pH-value*

The metabolism, microbial colonization, microbial growth, and secondary metabolite production are all influenced by the initial pH value of the culture medium (Dusengemungu et al., 2021, Peng et al., 2019, Wang et al., 2018). Microorganisms tend to have a specific pH range, in which they can grow and leach the metals at higher rates. Metal mobility usually increases with a decrease in pH and an increase in the redox potential (Kamizela and Worwag, 2020). By way of illustration, the acidophilic *A.manzaensis* strain showed a higher copper dissolution from jarosite at lower pH values and the highest recovery at the pH of 1.25 (Liu et al., 2016). On the other hand, initial pH takes on a different dimension in fungal bioleaching, where secondary metabolite production comes into play. A drop in the pH after the initial growth period of filamentous fungi is closely associated with organic acid production (Naderi et al., 2023). According to Walaszczyk et al. (2018), oxalic acid is secreted mostly at neutral to lower pH (∼ 6), whereas citric acid reached its peak at the initial pH of the sucrose medium at 3. Owing to having a higher dissociation constant than the other carboxylic acids, oxalic acid is an important leaching reagent in the complexation reaction with metals (Zhou et al., 2019). Even though a pH close to 6 favors the overall oxalic acid secretion, acidolysis may be the controlling step, which requires an acidic medium to dissolve the metals (Bahaloo-Horeh and Mousavi, 2024). Hence, it is essential to strike a balance between the final pH of the solution and the frequency of buffering the medium at specific intervals to favor the secretion of the ideal carboxylic acid for

Table 1
Bioleaching efficiencies of various strains in studies dealing mainly with the recycling of critical metals from e-waste.

Microorganism	E-waste material	Process conditions	Leaching agent	Leaching efficiency	Reference
A.niger	Waste fluorescent lamp (< 60 μm)	One-step bioleaching, Inoculation: 1 % (v/v) Pulp density: 1 % (w/v), Stirring rate: 150 rpm, Initial pH: 5.3, Temperature: 30 °C	1.2 mM oxalic acid, 3.6 mM citric acid, and 34 mM gluconic acid in the presence of waste powder after 4 days	13.43 % Y, 11.99 % Eu, 0.86 % La, 0.70 % Ce, 0.74 % Tb after 7 days	(Castro et al., 2023)
A mixture of *A.niger* & *A.tubingensis*	Waste PCBs (< 1 mM)	Two-step bioleaching, Inoculation: 5 % (v/v) Pulp density: 3 % (w/v), Stirring rate: 170 rpm, Initial pH: 5.7, Temperature: 30 °C	16.3 g/L citric acid, 8.4 g/L oxalic acid, 0.5 g/L malic acid	86 % Cu, 51 % Ni, 100 % Zn after 33 days	(Trivedi and Hait, 2024)
A.niger	Waste LCD (≤ 74 μm)	Indirect bioleaching, Inoculation: 1 % (v/v) Pulp density: 1 % (w/v), Stirring rate: 160 rpm, Initial pH: 7.5, Temperature: 70 °C	14,880 mg/L oxalic acid, 1180 mg/ L gluconic acid, 904 mg/L citric acid, 391 mg/L malic acid	81.4 % Al, 69.1 % As, 60 % In, 33.3 % Sr after 29 h	(Parsa et al., 2024)
A mixture of *A. thiooxidans, A. ferrooxidans*	Waste LED monitors (<75 μm)	One-step bioleaching, Inoculation: 1.5 % (*A. ferrooxidans)*, 0.5 % (*A. thiooxidans)* (v/v) Pulp density: 6 % (w/v), Stirring rate: 160 rpm, Initial pH: 2, Temperature:30 °C	~ 7.2 g/L sulfate ion	99 % In after 18 days	(Khezerloo et al., 2023)
Alcaligenes aquatilis	Waste PCBs (d_{50} = 0.175 mM)	One-step bioleaching, Inoculation: 5 % (v/v), Pulp density: 2 % (w/v), Stirring rate: 160 rpm, Temperature: 28 ± 3 °C	n.a.[a]	47.99 % Cu after 84 hours	(Madhavan et al., 2023)
A.ferrooxidans	Waste PCBs (75μm<ϕ<100 μm)	Two-step bioleaching, Inoculation: 10 % (v/v) Pulp density: 0.22 % (w/v), Stirring rate: 100 rpm, Initial pH: 1.8, Temperature: 30 °C	n.a.[a]	100 % Al, 83.82 % Cu, 98.27 % Pb after 10 days	(Silva et al., 2023)
Pseudomonas aeruginosa	Waste PCBs (< 2 mM)	Two-step bioleaching, Inoculation: 5 % (v/v) Pulp density: 1 % (w/v), Stirring rate: 150 rpm, Initial pH: 8, Temperature: 30 °C	~ 10 mg/L cyanide after 20 h from 1 g/L glycine	90 % Ag, 20 % Au after 7 days	(Merli et al., 2022)
Acidithiobacillus ferrooxidans	Waste LEDs (≤75 μm)	Multi-step indirect bioleaching,	Biogenic ferric ion concentration of 4–5 g/L	83 % Ga, 97 % Cu,	(Pourhossein and Mousavi, 2019)

(*continued on next page*)

Table 1 (*continued*)

Microorganism	E-waste material	Process conditions	Leaching agent	Leaching efficiency	Reference
		Pulp density: 2 % (w/v), Stirring rate: 140 rpm, Initial pH: 2.11, Temperature: 29 °C		84 % Ni after 15 days	
Penicillium citrinum	Waste LIB powder	Indirect bioleaching, Inoculation: 1 % (v/v) Pulp density: 7 % (w/v), Stirring rate: 140 rpm, Initial pH: ~5, Temperature: 40 °C	40.12 g/L citric acid	79 % of Mn, 90 % of Li after 6 days	(Naseri et al., 2023)
Acidithiobacillus thiooxidans	WEEE	Two-step bioleaching, Inoculation: 10 % (v/v) Pulp density: 1 % (w/v), Stirring rate: 150 rpm, Initial pH: 3.5, Temperature: 30 °C	Biogenic sulfuric acid of unknown concentration	99 % of Ce, Eu, N, ~80 % of La, Y after 8 days	(Marra et al., 2018)
A.niger	Waste autocatalyst powder	Indirect bioleaching, Inoculation: 1 % (v/v) Pulp density: 0.5 % (w/v), Stirring rate: 130 rpm, Initial pH: 6, Temperature: 30 °C	11,366 mg/L oxalic acid	33% of Pt, and 57 % of Pd after 24 h	(Bahaloo-Horeh and Mousavi, 2024)
A.niger	Spent LIB	Indirect bioleaching, Inoculation: 1 % (v/v) Pulp density: 1 % (w/v), Stirring rate: 130 rpm, Initial pH: 6, Temperature: 30 °C	8078 mg/L citric acid, 1170 mg/L oxalic acid,1251 mg/L malic acid, 2126 mg/L gluconic acid	100 % of Cu, 95 % of Li, 70 % of Mn, 65 % of Al, 45 % of Co, 38 % of Ni after 16 days	(Horeh et al., 2016)
A mixture of *A. thiooxidans, A. ferrooxidans*	Waste PCBs < 150 µm	One-step bioleaching, Inoculation: 10 %, (v/v) Pulp density: 8% (w/v), Stirring rate: 120 rpm, Initial pH: 2, Temperature:35 °C	~ 7.2 g/L sulfate ion	93% of Cu, 70 % of Ni, 69 % of Co, 94 % of Fe, 41 % of Al after 10 days	(Abhilash et al., 2021)
A mixture of *A. niger, Bacillus megaterium*	Waste PCBs	Indirect bioleaching, Inoculation: n.a.[1] Pulp density: 1 % (w/v), Stirring rate: 160 rpm, Initial pH: 4.6, Temperature: 60 °C	7460 mg/L oxalic acid	100 % of Mn, 100 % of Pt, 70.7 % of Pd, 50.8 % of Fe, 48.3 % of Co, 21.8% of Al after 24 h	(Vakilchap and Mohammad Mousavi, 2024)
A. thiooxidans	Spent LED lights < 75 µm	Multi-step indirect bioleaching, Inoculation: 2 % (v/v) Pulp density: 4 % (w/v), Stirring rate: 140 rpm, Initial pH: 2, Temperature: 29 °C	biogenic sulfuric acid ranging from 9000 to 11,000 mg/L	100 % of Ga, 100 % of Cu, 100 % of Ni after 10 days	(Pourhossein et al., 2022)
B.megaterium	Bio-pretreated ground LED powder	Direct hybrid bioleaching, Pulp density: 1 % (w/v), Inoculation: 2 % (v/	15 mg/L biogenic cyanide	93 % of Ag, 91 % of Au, 98 % of Ni, 87 % of Cu, and 84 % of Ga after 4 days	(Pourhossein et al., 2021)

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Table 1 (*continued*)

Microorganism	E-waste material	Process conditions	Leaching agent	Leaching efficiency	Reference
		v), Glycine concentration: 2.5 g/L, Methionine concentration: 10 g/L, Stirring rate: 150 rpm, Initial pH: 7, Temperature: 30 °C			
Cellulosimicrobium funkei	Ground thin-film GaAs solar cell waste	indirect bioleaching, Pulp density: 20 % (w/v), Inoculation: 4 % (v/v), Stirring rate: 150 rpm, Initial pH: 7, Temperature: 30 °C	Growth supernatant at death phase (after 3 days) containing amino acids	70 % of Ga after 15 days	(Maneesuwannarat et al., 2016)
Arthrobacter creatinolyticus	Ground GaN powder < 38 μm	indirect bioleaching, Pulp density: 20 % (w/v), Inoculation: 4 % (v/v), Stirring rate: 150 rpm, Initial pH: 7, Temperature: 30 °C	Growth supernatant (after 3 days) containing amino acids, peptides, proteins	18 % of Ga after 15 days	(Maneesuwannarat et al., 2016)
A.niger	Waste PCBs < 150 μm	Two-step bioleaching, Pulp density: 1 % (w/v), Inoculation: 1 % (v/v), Stirring rate: 130 rpm, Initial pH: 5.15, Temperature: 30 °C	Mainly biogenic oxalic acid of unknown concentration	97 % of Cu, 97 % of Ni	(Arshadi et al., 2020)
A.ferrooxidans	Waste OLED touch screens < 75 μm	Two-step bioleaching, Pulp density: 1.5 % (w/v), Inoculation: 5 % (v/v), Stirring rate: 140 rpm, Initial pH: 1.1, Temperature: 29 °C	Biogenic sulfuric acid of unknown concentration	100 % of In, 5 % of Sr after 30 days	(Pourhossein et al., 2021)
A.niger	Thermally treated ground waste LCDs ≤ 74 μm (at 1100 °C)	Indirect bioleaching, Inoculation: 1 % (v/v) Pulp density: 1 % (w/v), Stirring rate: 160 rpm, Initial pH: 7.5, Temperature: 70 °C	15,103 mg/L biogenic oxalic acid	82.6 % of Al, 70,8 % of As, 64.5 % of In, 36.2 % of Sr after 2 days	(Parsa et al., 2024)
Penicillium expansum	Waste PCBs < 0.5 mM	Two-step bioleaching, Inoculation: 1 % (v/v) Pulp density: 1 % (w/v), Stirring rate: 150 rpm, Initial pH: 7.5, Temperature: 25 °C	>70 mM gluconic acid,8 mM acetic acid, 3 mM citric acid, 5 mM succinic acid, 4 mM malic acid, <0.02 mM fumaric acid	~ 70 % of Pr, Nd, Gd, 50 % of Tb, 40 % of La after 24 h	(Baez et al., 2024)

[a] n.a.: not available data

metal mobilization.

3.3.4. Temperature

Temperature is one of the most influential parameters in bioleaching studies, which is frequently tested in response surface methodology (RSM) studies to evaluate the influence of temperature on metal leaching (Manikkampatti Palanisamy et al., 2023, Tian et al., 2022). Primarily, the temperature utilized in bioleaching studies averaged at ambient temperature, so most bioleaching studies were conducted at a temperature lower than 40 °C (Mokarian et al., 2022). As an example, *Leptospirillum ferriphilum* showed the highest efficiency in leaching Zn at 40 °C, whereas *A.niger* could leach heavy metals mostly at 30 °C (Sundramurthy et al., 2020, Zeng et al., 2015). Nevertheless, the ideal temperature for leaching various metals is typically species-specific and varies in the processes involved. Therefore, the temperature is usually optimized with other bioleaching parameters such as pulp density, stirring speed, initial pH, etc. (Tian et al., 2022, Naseri et al., 2023).

3.3.5. *Aeration and mixing*

Aeration and mixing are critical parameters, as their interaction ensures adequate oxygen for cell metabolism and suspends pellets in large vessels (Wang and Wang, 1979). In shake flasks, oxygen transfer occurs through orbital rotation (Peter et al., 2006), but in larger systems, the presence of media components, e-waste pulp, and viscosity fluctuations can limit oxygen uptake, making proper aeration and mixing essential for both mass transfer and microbial growth (Ilyas and Lee, 2014, Maiorano et al., 2020). Research has demonstrated that improper mixing rates can decrease biomass and metal leaching efficiency, most likely due to cell damage caused by mechanical forces (Qu et al., 2022, Ilyas and Lee, 2014). Moreover, Nili et al. (2022) found that exacerbated attrition resulting from increasing pulp density led to reduced dissolved oxygen and microbial growth, indicating the need for optimized aeration in bioleaching processes, where aerobic microorganisms are often used (Ni'am et al., 2019).

The volumetric oxygen transfer coefficient (K_La) defines the efficiency of oxygen transfer in bioreactors and fermenters, typically ranging from 0.02 s^{-1} to 0.25 s^{-1} in larger-scale settings (Doran, 2013). Enhancing KLa through increased stirring, gas flow rate, and higher partial pressure can improve mass transfer due to the improved gas hold-up and residence time of bubbles. However, this approach comes at the cost of higher capital expenses and energy demands (Doran, 2013). Although aeration coupled with mixing is more beneficial in terms of energy costs by 60–65 % compared to stand-alone mixing, overall energy demand and capital costs still increase with the scaling-up(Wang and Wang, 1979).

3.3.6. *Method*

The bioleaching method diversifies primarily into one-step, two-step, and indirect bioleaching. The one-step method involves the simultaneous interaction of metals with microorganisms (Srichandan et al., 2019), while the two-step method requires a preliminary growth stage (Naseri et al., 2019). In indirect bioleaching, biogenic liquid is separated from microorganisms after reaching the desired growth stage to subsequently leach metals. Indirect bioleaching has been gaining ground in application for advantages such as not having metal stress on microorganisms, flexibility such as easier biomass separation, and scalability in operation since no microorganisms are found in the leaching medium (Chu et al., 2022, Tian et al., 2022). A good example of this is the indirect bioleaching of GaAs powder with *Cellulosimicrobium funkei*, in which the supernatant solution at the death stage was utilized, and as a result, 79 % of gallium could be leached (Maneesuwannarat et al., 2016). As demonstrated in Table 1, an extensive range of options are available for the efficient extraction of critical and precious metals. Due to the slower processing rates encompassing days or even months to recover one metal to its attainable limit, the volumetric recovery rate is currently unable to be achieved on smaller scales. As a result, larger vessels or multiple configurations in series processes are necessary to compensate for the low efficiency in prolonged times. However, as the size of the vessel increases, so does the mixing time proportionally (Wang and Wang, 1979). Therefore, to maintain a consistent mixing time, larger impellers and higher stirring speeds must be used, which in turn increase energy and capital demands (Doran, 2013). Owing to this, comprehensive research encompassing various methodologies for targeted and enhanced metal extraction in line with reasonable energy and capital costs is noteworthy. Given these challenges, further research is needed to explore and enhance targeted metal extraction processes that are cost-effective in terms of energy and capital.

3.3.7. *Pulp density*

Pulp density, the ratio of solid to liquid, is a crucial parameter affecting bioleaching efficiency, immensely. Even though toxicity influence does not apply to the process of indirect bioleaching, the increasing pulp densities might retard the availability of deprotonated organic acids, leading to lower bioleaching efficiencies (Petrus et al., 2018). Pulp density was found to be the most influential parameter in the recovery of scandium from Bauxite residue, in which the highest recovery could be attained with 1 % pulp density in one-step *A.niger* bioleaching (Kiskira et al., 2023). Increasing pulp density beyond this threshold decreased the leaching efficiency. The study by Rouchalova et al. (Rouchalova et al., 2020) also suggested that increasing pulp densities decreased the bioleaching efficiency of Cu, Pb, Zn, and Fe in one-step bioleaching with *A.ferroxidans*, which possibly stems from the toxicity of precursors on microorganisms in contact bioleaching mechanisms. However, through the adaptation of microorganisms with stepwise incorporation of pulp, the toxicity can be alleviated. For instance, multi-step incorporation of the waste LED pulp up to 20 g/L resulted in higher efficiencies (Pourhossein and Mousavi, 2018).

3.3.8. *Particle size*

Grinding waste materials to smaller diameters enhances mass transfer, as it increases the contact surface area, facilitating the attainment of higher bioleaching efficiencies (Olubambi et al., 2008). The immobilization of Cu from waste PCBs using *Alcaligenes aquatilis* could be optimized at 169.45 mg/g in shake flasks, in which the smallest particle size of 0.175 mm was added (Madhavan et al., 2023). Nonetheless, by further grinding below the critical particle size threshold such as 25 μm or 75 μm, bioleaching does not seem to improve and shows a rather negative trend, which has to do with the particle-particle attrition, damaging the cell structure (Olubambi et al., 2008, Nemati et al., 2000).

3.4. *Bioleaching: overall assessment*

All in all, bioleaching can be considered a viable technology for the recovery of critical metals from e-waste, but it is important to acknowledge the challenges associated with it. For instance, bioleaching has slower reaction rates than chemical leaching, which requires constant monitoring of parameters to ensure efficiency, resulting in increased capital expenses for larger vessels or more vessels and impellers, as well as higher energy demands due to the need for larger equipment and increased gas flow rates. Therefore, prior economic assessment and identification of cost drivers within the system boundaries have become a primary focus for revenue forecast in recovery processes (Lin et al., 2020). The examination of the economic and technical aspects of bioleaching and phytomining necessitates a thorough evaluation, which should also take into account any direct and indirect expenses that may arise during the design of such processes.

Scaling up from shake flasks to large vessels is often not easy to translate, as maintaining constant parameters across different scales is difficult. Additionally, there is a risk of contamination and dependence on specific energy sources, incurring more expenses to the overall production costs. Thompson et al. (2018) identified the energy source of glucose as the largest cost, which accounted for 44 % of the total expenses. As a result, the cost of raw materials is a critical factor in determining the feasibility of bioleaching processes. Additionally, the pulp density of metal sludges or e-waste governs the profitability of bioleaching (Thompson et al., 2018). As reported by Van Yken et al. (2023), higher metal extraction rates were achieved with lower pulp densities, which necessitated a higher generation of lixiviant, leading to increased total capital costs. Therefore, it is more profitable to use higher pulp densities per operation. Deng et al. (2020) also reported an increased annual profit of $1.08m in 2020 by incorporating higher pulp density at 50 %. Thus, the primary focus ought to be on enhancing metal extraction rates within a reasonable timeframe, while reducing capital expenditures and energy consumption, particularly by maximizing the volumetric production rate within minimal volume, without requiring extensive production capacity.

Despite the limitations, bioleaching is an innovative and environmentally friendly technology for critical metal recycling. Further research is required to optimize the kinetics and key parameters for efficient recycling of critical metals, particularly during the fermentation stage of cultivation to increase the yield of organic acids in the medium before leaching, as well as an assessment of the feasibility of hybrid chemical-biological leaching technologies. Future research should also concentrate on scale-up engineering to adapt parameters from small-scale experiments with smaller bioreactors equipped with stirrers and spargers to larger vessels while maintaining optimal recycling yields, minimizing plant volume, and controlling capital costs, all while considering sustainability in terms of emissions and energy demands.

4. Phytomining

Phytomining is a novel technology, utilizing hyperaccumulator plant species to recover metals for financial gains (Chaney et al., 2018). Phytomining entails the utilization of hyperaccumulator plant species to immobilize, translocate, and sequester trace metals in their vacuoles, culminating in harvesting to capitalize on the extracted metals (Yan et al., 2020). This process of phytoextraction, which commences in the rhizospheric environment, is fundamental to phytomining and facilitates economic returns through the extraction of metals.

Hyperaccumulator plant is an umbrella term for plants that can accumulate metals in their shoots more than 10,000 mg/kg than non-hyperaccumulator plant species (Dai et al., 2022, Baker et al., 2000). However, this threshold value might differ in hyperaccumulators for specific elements (Baker and Whiting, 2002). For example, a suggested total REE hyperaccumulation threshold was specified in the range of 100–1000 $\mu g\ g^{-1}$ (van der Ent et al., 2021), whereas the threshold values are specified to 1000 $\mu g\ g^{-1}$ for Ni, 1 $\mu g\ g^{-1}$ for Au (Nemutandani et al., 2006), and 100 $\mu g\ g^{-1}$ for Tl in dry weight (van der Ent et al., 2013). The hitherto discovered hyperaccumulator species are confined to 761 species on a global scale, largely dominated by 523 nickel hyperaccumulators, followed by 28 zinc, 22 rare earth elements, and 7 cadmium hyperaccumulator species (Balafrej et al., 2020, Liu et al., 2018, Liu et al., 2023).

4.1. Uptake mechanism of hyperaccumulators

Although hyperaccumulation in plants is an acknowledged process, the mechanism behind it, as well as the evolutionary process, remains shrouded in mystery. Several hypotheses attempted to shed light on the phenomenon of hyperaccumulation towards elements and their translocation to aerial tissues. The elemental defense strategy suggests hyperaccumulation as a protection mechanism against pathogens and herbivores (Cappa and Pilon-Smits, 2014, Hörger et al., 2013). In contrast, the inadvertent uptake hypothesis considers hyperaccumulation as a by-product of physiological processes (Boyd and Martens, 1998). In other words, the uptake of ultra-trace elements such as Ga, In, REE, etc. is not intentional but rather a consequence of the shared similarities with essential nutrients or the shared pathways (van der Ent et al., 2021, Meindl et al., 2021). Nkrumah and van der Ent (2023) observed a Ga accumulation of 150 $mg\ kg^{-1}$ (DW=dry weight) in the Al accumulator *C. sinensis*, denoting the consequential uptake of Ga through Al transporter channels (Nkrumah and van der Ent, 2023). Similarly, REE accumulation was also attested in *P. Americana,* through the uptake of essential elements such as Mn, Fe, Ca, and so on (Liu et al., 2021, Yuan et al., 2017).

4.2. Steps, transporter systems, organic acid complexations

As mentioned earlier, plant transport systems play a pivotal role in the consequential uptake of non-essential elements, which encompasses the uptake of critical as well as other non-essential elements through the pathways of nutrients (Matzen and Pallud, 2023). The plant transporters are the main actors in the metal uptake, accumulation, translocation, detoxification, and sequestration of essential and non-essential elements (Memon, 2016). Apart from controlling vital nutrients like iron, phosphate, nitrate, and potassium, there are also plant transporters that manage the flow of metals by expressing transport genes, which help regulate the uptake process and prevent the negative impact of excessive metals on plants (Ahad et al., 2022, Final List of Critical Minerals 2008).

The upregulation of transporter genes varies depending on the accumulated metal species as well as strategies taken for dealing with toxicity coming from these elements (Gong et al., 2003). Prevalently encountered transporters in the regulation of detoxification and uptake mechanisms are known to be ZIP, MATE, ABC, YSL1, and NRAMP (Song et al., 2014). A well-known ZIP transporter family, also known as, Zinc regulated transporter (ZRT) and IRT (Iron-regulated transporter) stimulates the uptake of essential metals such as Zn and Fe, and the inadvertent uptake of non-essential heavy metals by hyperaccumulators (Thakur et al., 2022). The study by Ding et al. (2017) pointed out the proactive role of the ZIP 6.2 transporter in the uptake of the non-essential element Cadmium in *Populus* × *canescens*. In addition, the multidrug toxic compound extrusion (MATE) family tackles heavy metal stress by releasing detoxification agents into the environment to later expel them from plant cells (Kar et al., 2022). Members of the MATE family were held accountable for secreting citric acid under Al stress for dealing with Reactive Oxygen Species (ROS) triggered by Al and other potentially toxic elements (Yang et al., 2019). Moreover, ATP-Binding Cassette (ABC) family transporters are more involved in the translocation of phytohormones as well as in the uptake of divalent metals (Jalmi, 2022). The Yellow-striped like1 (YSL1) family, another transport protein, is responsible for the long-distance translocation of Fe and Cd by forming metal-nicotianamine complexes and utilizing natural resistance-associated macrophage proteins (NRAMP) to mediate homeostasis and the transport of divalent elements from the apoplast to the cytosol (Ball et al., 2022, Ghosh et al., 2022, He et al., 2022, Kumar et al., 2023, Tian et al., 2021). In addition to these common metal transporters, recent research by Zheng et al. (2023) has identified a novel REE transporter, NRAMP REE Transporter 1 (NREET1), which further supports the hypothesis of shared similarities between Al and REE, Ga, In, and so on. The elucidation of the biological function of transporters and their identification in the uptake process for targeted elements presents novel opportunities in the context of phytomining of critical and valuable elements. Following a discussion of the essential biological principles and mechanisms in hyperaccumulator plants, the following chapter tackles the key factors that influence the success of phytomining.

4.3. Key parameters

Previous research, thus far has provided valuable insights into the mechanisms by which hyperaccumulators take up trace metals, as well as potential strategies to enhance the yield of hyperaccumulation. However, the uptake of non-essential elements, such as REE, Ga, In, and other critical metals, can be challenging due to their scarcity in the rhizosphere (Jensen et al., 2018, Wiche and Heilmeier, 2016). As a result, the phytomining potential of these metals may be more viable when combined with phytoremediation strategies, such as recovering from industrial wastewater or harvesting plants near e-waste dumping facilities or tailing storage facilities, as illustrated in the graphical abstract (Ha et al., 2011).

Most studies concerning the metal recycling from e-waste material are confined to the phytoremediation processes taking place in the

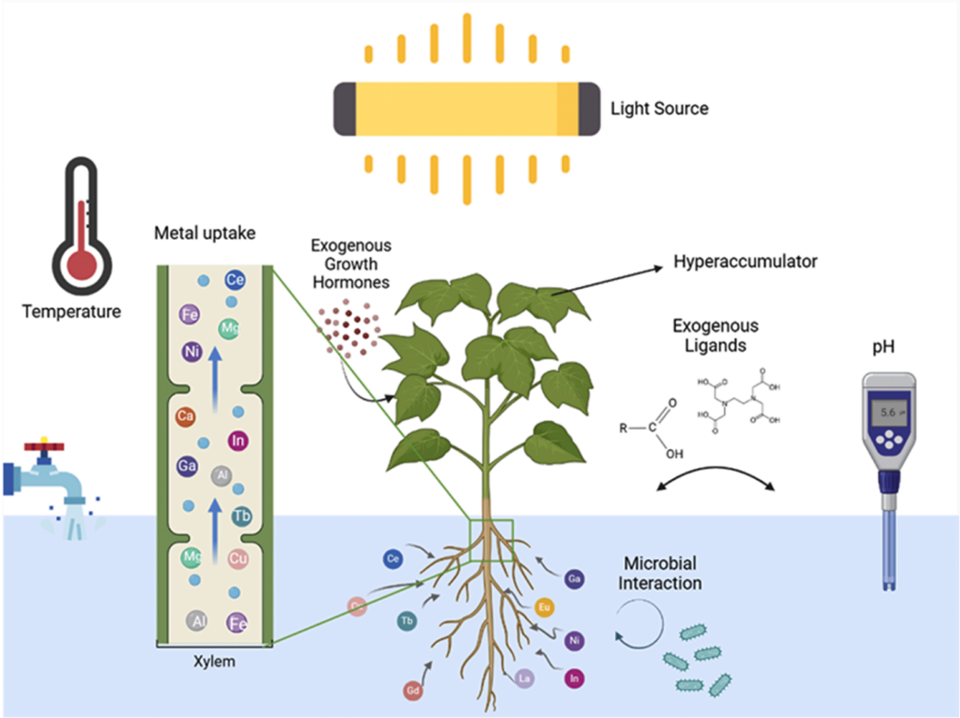

Fig. 3. Main parameters influencing the phytoextraction in hyperaccumulators. Created with BioRender.com.

vicinity of e-waste contaminated sites, so the research gap persists in the context of phytomining of critical and precious elements from ground e-waste materials in hydroponic and pot experiments (Kriti et al., 2023, Luo et al., 2018, Xu et al., 2024). In Table 2, the preliminary findings centering on the phytoextraction of critical metals via hyperaccumulators from pure solutions in a controlled environment are presented. As suggested in Fig. 3, the uptake of these elements is underscored by various key parameters such as the selected plant species, abiotic factors, exogenous agents, and so on, which will be explored within this subchapter for establishing a plausible framework for the phytomining of critical metals.

4.3.1. *Hyperaccumulator species*

Opting for a suitable “plant family” is one of the most crucial parameters in hyperaccumulation (Shi et al., 2023). As presented in Table 2, various species can accumulate certain elements at varying uptake rates. The sought-after criteria for hyperaccumulators can be listed as higher selectivity for targeted elements (exceeding the nominal assigned threshold values), high biomass yield within short periods, and resistance to interfering toxic metals (Nkrumah et al., 2021). Bioconcentration factor (BCF) is a good indicator in the selection of suitable hyperaccumulator candidates, which is a ratio of accumulated metal content in plant tissues from the contaminants. Higher BCF values than 1 denote a potential hyperaccumulator candidate (Maiti et al., 2022). Upadhyay et al. (Upadhyay et al., 2021) identified a hyperaccumulation of In from an LCD slurry consisting of 353 mg/L at a BCF of 147.69 ± 14.49 by *Eleocharis acicularis*. Nguyen et al. (2019) also reported a metal uptake by *Eleocharis acicularis* for Ga, In, Ag, Tl, and Cu, constituting the BCF values of, 1230, 777, 179, 264, 1690 after 21 days, respectively. Therefore, selecting a suitable hyperaccumulator of high metal selectivity commensurate with high biomass yields helps attain the assigned threshold values in the phytomining (van der Ent et al., 2021, Mohsin et al., 2022, Shen et al., 2022).

4.3.2. *Light and temperature*

Light and temperature regulate plant metabolism and various enzymatic activities, which are deemed to correlate with the uptake efficiencies in hyperaccumulators (Seydel et al., 2022, Tang et al., 2022). Light is the main energy source of plants, regulating nutrient uptake, photosynthesis, transpiration, and transport of genes, and as well as it is also known to influence the development of branch and aerial tissues (Karimi et al., 2022, Lintner et al., 2023, Mao et al., 2023, Mohammadi et al., 2023, Prasad et al., 2023, Sathasivam et al., 2023). Chen et al. (2021) revealed the correlation between the light combination of blue and red with higher biomass production, accompanied by enhanced uptake of Cd (up to 121.6 mg/kg) in *Arabidopsis thaliana*.

As for temperature, the optimal temperature for most terrestrial and aquatic plants has been found to fall between 10 and 30 °C for photosynthesis, and other biochemical activities (Nievola et al., 2017). Temperature influences plant growth while regulating the uptake of nutrient elements, functioning of transporters, root exudates, and bioavailability of metals (Hooda and Alloway, 1993, Kawasaki et al., 2014, Pramanik et al., 2000, Xu et al., 2018). Cd accumulation was proved to be a temperature-dependent first-rate reaction between the temperatures of 5 and 10 °C, in which the total Cd accumulation in *Arabidopsis helleri* ssp. *gemmifera* has risen from 7.9 ± 1.6 to 11.1 ± 1.9 μg (Kudo et al., 2023) . Ever-changing environmental conditions in open-field experiments challenge metal accumulation efficiencies in hyperaccumulators. Yet, growing chambers present a viable alternative for having controlled environmental conditions in the context of light and temperature. As it is shown in Table 2, temperature, illuminance as well as day/night cycle can be adjusted for tailoring certain hyperaccumulation schemes.

4.3.3. *Initial pH value*

The bioavailability of metal species is directly influenced by the pH fluctuations in the rhizosphere matrix. Adamczyk-Szabela and Wolf (2022) investigated the speciation of Mn, Zn, and Cu under various pH levels spanning from 4.7 to 8.5, which pointed out the pH dependence of the translocation factor of these metals in the rhizosphere. Rhizosphere pH controls metal speciation, promoting the release of certain metals, and reducing the solubility of other metals, thus aiding hyperaccumulators in absorbing metals. Fluctuation in the rhizosphere pH is attributed to respiratory CO_2 release, secretion of organic acids in the roots, and microbial activity, influencing the uptake of metals at the root

Table 2

Relevant experimental studies as to the uptake of critical metals via phytoextraction.

Hyperaccumulator	Exposure	Process parameters	Accumulation (mg/g DW)[a]	Reference
Hypnum cupressiforme	Al (0,40,400 µM)	Type: Hydroponic Nutrient Medium: Hoagland pH: 4 Duration: 4 weeks Light-dark period: 16/8 h PAR: 300 µmol.m^{2-}.s^{-1} Temperature (day/night): 27/16 °C Relative Humidity: 70–80 %	2500 mg/kg Al at 400 µM spike in old leaves of. *H. cupressiforme*	(Hajiboland et al., 2023)
Cannabis sativa L.	Li (0,50,150,300 mg/L)	Type: in vitro Nutrient Medium: Murashige-Skoog Medium with 30 g/L Sucrose + 0.8 % Agar pH: 5.7 Duration: 2 weeks Light-dark period: 16/8 h PAR: 60 µmol.m^{2-}.s^{-1} Temperature (day/night): n.a.[b] Relative Humidity: n.a.[2]	2400 mg/kg Li at 300 mg/L spike in micro shoots	(Zacchini et al., 2023)
C.sinensis	Al (500 µM),Ga (500µM), In (500 µM), Al+ Ga (250 µM, each), Al+ In (250 µM, each)	Type: Hydroponic Nutrient Medium: ½ modified Hoagland pH: 4.5 or 5.8 Duration: 8 weeks Light-dark period: 12/12 h PAR: 350 µmol.m^{2-}.s^{-1} Temperature (day/night): 26/20 °C Relative Humidity: n.a.[b]	150 (Ga), < 20 (In), 300 (Al)	(Nkrumah and van der Ent, 2023)
Phytolacca americana L.	REE (0, 1, 10, 50, 100 and 250 µM)	Type: Hydroponic Nutrient Medium: Modified Hoagland pH: 5.3 ± 0.1 Duration: 28 days Light-dark period: 14/10 h PAR: 350 µmol. m^{2-}.s^{-1} Temperature (day/night): 25 °C Relative Humidity: 75 %	~ 1250 mg/kg ($\sum$ REE at 50 µM spike)	(Yuan et al., 2017)
Eleocharis acicularis	In, Ga, Ag, Tl (0.5 mg/L each)	Type: Hydroponic Nutrient Medium: MiliQ Water Exogenous agent: Silicon at 4 mg/L pH: 5.5 Duration: 21 days Light-dark period: 16/8 h PAR: 54 µmol. m^{2-}.s^{-1} Temperature (day/night): 24 ± 1 °C Relative Humidity: n.a.[b]	Roots, Shoots (mg/kg): 239, 538 mg/kg In, 886, 340 mg/kg Ga, 68.4, 111 mg/kg Ag, 117, 146 mg/kg Tl	(Nguyen et al., 2019)
Arabidopsis thaliana	Ga (0, 6, 30,150,250,500,750 µM)	Type: Hydroponic Nutrient Medium: ½ Murashige-Skoog with (1 % Sucrose) pH: 5.7 Duration: 8 days Light-dark period: 16/8 h PAR: 70 µmol. m^{2-}.s^{-1} Temperature (day/night): 22 °C Relative Humidity: n.a.[b]	Ga in roots: 1000 > x > 80 mg/g In shoots: 200 > x > 150 mg/kg(at 500 µM)	(Chang et al., 2017)
Eleocharis acicularis	ITO Powder (300,600 Indium mg/L) and 800 g/L LCD waste	Type: Hydroponic Nutrient Medium: Saline solution (1:1 (w/w), NaCl and $CaCl_2$) pH: 5 and 3 Duration: 15 days Light-dark period: 16/8 h PAR: 12,000 cd. sr/ m^{2-} Temperature (day/night): 24 ± 1 °C Relative Humidity: n.a.[b]	58.9 mg/g (300 mg In/L), 122.4 ± 13.8 mg/kg (600 mg/L), 52.8 ± 0.9 mg/kg (800 g/L LCD)	(Upadhyay et al., 2021)
Eleocharis acicularis	In (0,0.1,0.2,0.3,0.4 mg/L)	Type: Hydroponic Nutrient Medium: MiliQ Water pH: 5.5 Duration: 15 days Light-dark period: 16/8 h PAR: 54 µmol. m^{2-}.s^{-1} Temperature (day/night): 24 ± 1 °C Relative Humidity: n.a.[b]	477 mg/g In in roots, 353 mg/kg In in shoots (at 0.4 mg/L spike)	(Ha et al., 2011)
Silene latifolia	Tl (0,0.5,1,6, and 12 mg/L)	Type: Hydroponic Nutrient Medium: ½ Hoagland pH: 5.5 Duration: 16 days	12,900 ± 4140 µg/g Tl (at 6 mg/L spike), 16,700 ± 2810 (at 12 mg/L spike) in young leaves	(Corzo Remigio et al., 2022)

(continued on next page)

Table 2 (*continued*)

Hyperaccumulator	Exposure	Process parameters	Accumulation (mg/g DW)[a]	Reference
		Light-dark period: 12/12 h PAR: 350 μmol. m^{2-}.s^{-1} Temperature (day/night): 26/20 °C Relative Humidity: n.a.[b]		
Boehmeria nivea L.	∑ REE (0, 1.6, 8, 16, 80, 160, 400, 800 μmol/L)	Type: Hydroponic Nutrient Medium: ½ Hoagland pH: 5.5 ± 0.1 Duration: 16 days Light-dark period: 14/10 h PAR: 350 μmol. m^{2-}.s^{-1} Temperature (day/night): 25/20 °C Relative Humidity: 70 %	249 mg /kg REE (at 80 μmol/L); ∑ LREE/∑ HREE = 0.51	(C. Liu et al., 2022)
Lolium perenne L.	Ga (0,15,31,63,125,250,500, 1000, and 2000 mg/kg), In (0,1.5,3,6,13,25,50,100, and 200 mg/ kg)	Type: Pot Nutrient Medium: Soil pH: 5.95 Duration: 6 weeks Light-dark period: 16/8 h PAR: 800 μmol. m^{2-}.s^{-1} Temperature (day/night): 20/12 °C Relative Humidity: 70 %	11.6 mg/kg Ga at 2000 mg/kg spike, 0.02 mg/kg In at 100 mg/kg spike	(Jensen et al., 2018)

[a] Unless it is specified, it denotes the highest accumulation in the leaf section

[b] n.a. = not available data

interface (Rengel, 2003). Most metals tend to be more soluble under acidic conditions, whereas the mobilization of cations is favored under alkaline conditions for amphoteric metals (Król et al., 2020). As an example, at alkaline pH, the bioavailability of Pb and Cr decreases (Pang et al., 2023). Whereas, at low pH, proton exchange capacity increases, thus leading to the release of heavy metals in the rhizosphere matrix. As can be deduced, metal migration in the plant matrix is rather specific to metals as well as to the nature of plants (Zhang et al., 2023). In this respect, Pourbaix diagrams can be utilized as a compass for understanding metal speciations to optimize metal uptake mechanisms (Gailer and Turner, 2022). For example, the affinity of divalent metal ions in the soil matrix towards organic matter is listed as Cu > Ni > Pb > Co > Ca > Zn > Mn > Mg (Mcbride, 1989). If the pH is found at elevated levels, the proton deposit retards, reducing the bioavailability of metals (Zhang et al., 2023). (Gao et al., 2019) observed a significant decrease in the dissolution rate for Cu by 30.36 % at an elevated pH level from 5.9 to 6.8, whereas another study showed the promoting effect of increasing pH for more cation release of Mn under alkaline conditions (Sato et al., 2017). Due to the pH dependence of bioavailability and translocation behavior, adjusting the pH will play a key role in comprehending the mobility of trace elements, especially the critical metals, in the rhizosphere matrix.

4.3.4. *Chelating agents*

Adding chelating agents as well as other exogenous substances is a common strategy to increase metal bioavailability and reduce metal toxicity for hyperaccumulators in phytoextraction (Solanki, 2022). Chelates can be divided into synthetic amino polycarboxylic acids such as EDTA, natural amino polycarboxylic acids such as Ethylenediamine-*N, N'*-succinic acid (EDDS), and natural low molecular weight organic acids i.e. citric acid, and oxalic acid (Mellor, 1964, Ranđelović et al., 2022). EDTA is reported to increase the translocation and bioaccumulation efficiency in pot experiments, yielding an enhanced accumulation of targeted trace elements (Hosseinniaee et al., 2023). Nevertheless, due to environmental concerns regarding artificial chelators in downstream processing, attention is now turning to more biodegradable alternatives such as citric acid oxalic acid, nitrilotriacetic acid (NTA), and so on (Gluhar et al., 2020, Greipsson, 2022, Nörtemann, 1999). Organic chelators of acetic acid, malic acid, and citric acid enhanced the La uptake by barley by 4.3, 2.8, and 1.5 times the control, respectively (Han et al., 2005). Similarly, Liu et al. (2022) reported an enhanced uptake of Y in the roots of *P.americana* through exogenous maleic and citric acid supplements, resulting in an increase in the translocation efficiencies by 51 % and 49 %, respectively. Hence, chelates can be strategically incorporated to enhance the metal extraction yields in the context of phytoextraction and phytomining.

4.3.5. *Plant growth regulators*

Exogenous application of plant growth regulators (PGRs) promotes biomass production and metal uptake in plants (Tassi et al., 2008). PGRs comprise auxins, cytokinins, abscisic acid, gibberellins, jasmonic acids, salicylic acid, and so on (Bulak et al., 2014, George et al., 2008, Zahid et al., 2023). Auxins are the main actors in regulating cell elongation, differentiation, and division, in which cytokinins are also involved (George et al., 2008). Whilst, cytokinins play a role in maturation and senescence, as well as in resistance to abiotic stresses (George et al., 2008). Furthermore, gibberellins are known to promote elongation in stems as well as govern seed germination, sex determination, and fruit development (George et al., 2008). A recent study by Vaz et al. (2023) demonstrated the contribution of auxin to phytoremediation, in which varying concentrations of auxin from 1.4 to 3 μM achieved a removal higher than 15 mg L $^{-1}$ for fluoride and 6.42 mg L^{-1} for phosphate. In another study, exposure to cytokinin resulted in significant growth in the ramets of *E. acicularis* (Sato et al., 2017).

4.3.6. *Plant growth promoting microorganisms*

Plant growth-promoting microorganisms (PGPM) improve trace metal bioavailability, growth in biomass, translocation of metals as well as endurance to abiotic stress, by siderophore production, nitrogen fixation, release of phytohormones, 1-aminocyclopropane-1-carboxylate (ACC) deaminase, and phosphate solubilization (Alves et al., 2022, Jing et al., 2007). As the composition of root exudates differs vastly, hyperaccumulators respond differently to the promoting effects of PGPM (Vocciante et al., 2022, Xiong et al., 2016).

Siderophore-generating microorganisms are dominantly used in studies for their potential to increase metal uptake by plants. Siderophores are small molecules secreted by microorganisms to increase the iron solubility in soil for its uptake by plants, which also improves the bioavailability of other metals and metalloids (Roskova et al., 2022). This is evident in the case of gallium, in which the inoculation of the bacterial strain improved the mobility of Ga compared to the commercial metallophore solution Desferrioxamine B (Schwabe et al., 2017). In a similar case regarding Ge and REE (REE = La, Nd, Gd, Er), the supernatants of rhizobacteria *Kocuria rosea* ATW4 and *Arthobacter oxydans* ATW2 also increased the mobility of these elements accompanied by a growth in biomass (Schwabe et al., 2021). In another study, Luo et al.

(2012) pointed out that, IAA-producing Endophyte Bacillus sp. SLS18 promoted metal uptake by 65.2 % for Mn and 40 % for Cd, accompanied by increased plant biomass.

Rhizobacteria are also reported to secrete low molecular organic acids such as citric acid, and oxalic acid, which influences consequently the bioavailability of metals (Archana et al., 2012). This phenomenon has been utilized in the study by Virk et al. (2022) to increase nickel availability through pH-lowering Bacterium Bacillus sp. ZV6. In the study, acidification of soil by 0.98 units via organic acids led to an increase in the influx of cations through roots of *Salix alba*, enhancing the nickel uptake in aerial parts from 81.4 mg kg^{-1} to 102.3 mg kg^{-1}. In Table 3, related studies centering on PGRM influence on phytoextraction are provided. Based on these findings, the symbiotic relationship between plants and PGPMs can be immensely beneficial for phytomining to boost the bioaccumulation factor of desired elements in plants' biomatrices.

4.4. Phytomining: overall assessment

Phytomining is a multi-step approach to recovering metals from the biomass of hyperaccumulators process that requires a thorough understanding of its mechanisms and correlational parameters to be successful. The use of innovative phytomining has been explored, but it is crucial to recognize the limitations and technical challenges. One significant challenge is the limited extraction capacity, particularly from e-waste, which restricts recycling efforts primarily to wastewater from leachate (O. et al., 2015). The incorporation of phytoremediation in leachate waters from e-waste processing facilities or the areas within the proximity of tailing ponds, e-waste contaminated sites might alleviate the burden on the ongoing recycling process as well as biological treatments and at the same time, might help secure the supply of critical metals. Therefore, feasibility studies are often conducted in open fields to identify metal-laden sites and to plant suitable hyperaccumulators that exhibit fast growth and higher biomass yields (Anderson et al., 2005, Wilson-Corral et al., 2011, Krisnayanti et al., 2016). However, arable areas for phytoextraction are confined to remote regions with low land values, whereas in developed regions the application is not feasible due to the high land values and longer harvesting periods (Wang and Aghajani Delavar, 2023). Moreover, irrigation, manuring, chelation, and exogenous treatments also increase the phytoextraction cost in long-term processing (Wang and Aghajani Delavar, 2023). Biomass conversion and following purification processes also play a critical role in the recovery of metals from phytoextraction, which requires a wide range of unit operations (Kaksonen and Petersen, 2023). For instance, the high energy costs associated with biomass conversion, amounting to $215 per ton in 2015, affected the profitability of rhenium phytomining, resulting in a profit of 3906 $ ha^{-1} $harvest^{-1}$ (Novo et al., 2015).

The cost of phytoextraction includes expenses related to planting and cultivation, production costs, the value of ore-containing biomass as an asset, metal extraction costs, and market prices for the extracted metals (Harris et al., 2009, Kuppens et al., 2018). Therefore, to thoroughly assess the scalability of phytoextraction in the context of e-waste recycling, techno-economic and life cycle assessments are necessary. While lab environments enable the achievement of optimal metal accumulation yields, the downstream processing for the recovery of small concentrations in the context of critical metal recycling from e-waste poses challenges and hinders the overall feasibility. The slower processing times compared to other methods raise questions about its scalability in the long run, making it crucial to evaluate the trade-offs involved. Due to the limitations in terms of lower metal accumulation rates as well as slower processing and requiring extensive spatial area as well as energy input related to conversion processes as well as transport costs, phytomining can be phytomining can be conceptualized as a complementary procedure conducted in open-field experimental areas proximal to mining or electronic waste disposal sites (Robinson et al., 2015, Vigil et al., 2022). In the context of metal fluctuations and the low recovery yield of critical metals from the e-waste, the recovery of precious elements such as silver and gold remains an economic driver in phytoextraction (Robinson et al., 2015).

5. Conclusion and outlook

This review paper examined the emerging technologies of bioleaching, and phytomining for recycling critical metals from e-waste. By taking a critical stance, it aimed to identify potential improvements for enhancing recovery yields through strategic optimization of key parameters, while also acknowledging the challenges associated with large-scale implementation.

The co-extraction of valuable and critical metals by bioleaching and phytomining could significantly enhance the sustainability profile, positioning them as promising alternatives to conventional metal extraction methods. Indirect fungi bioleaching shows promise with its reliability and selectivity.Further studies are needed to enhance organic acid production and to upscale bioleaching, involving experiments in small bioreactors and evaluating scalability. Additionally, the scaling-up aspect of bioleaching also needs to be explored. The common methods and empirical correlations used for scaling up, such as maintaining constant volumetric power input or oxygen transfer rate, often do not apply when transitioning from smaller volume shake flasks to large vessels with a capacity of up to 100,000 liters. This can limit small-scale experimental studies to strain selection or suitable nutrient media development, making existing findings only applicable on a smaller scale. To achieve optimal results in scale-up, future studies should consider using smaller bioreactors with stirrers and aeration on a laboratory scale, and thoroughly investigate the bioleaching limitations on a representative scale concerning slower processing and lower recovery yields. By doing so, researchers can directly apply the recovery rates obtained from experimental studies to larger scales. This approach may help avoid material, capital, energy, utility, and time costs and investments, which can significantly impact the overall process. Therefore, thorough techno-economic evaluations and bottom-up analyzes are vital for assessing bioleaching's integration with current industrial processes.

In phytomining, significant research gaps in extracting critical

Table 3
Inoculated PGRM in relevant phytoextraction studies and their influence on metal uptake in the context of critical metal recycling.

Microorganism	Metal	Mechanism of action	Impact on plant growth	Impact on metal uptake	Reference
Variovorax paradoxus	Ni	Siderophore, auxin, and ACC deaminase production	Increased in the biomass of root and shoot	Enhanced Ni uptake in the roots up to 105.8 %, and in the shoots up to 79.6 %	(Durand et al., 2016)
Arthrobacter oxydans and *Kocuria rosea*	Ge, REE	Mobilization of elements through the release of desferrioxamine, bacillibactin, and surfactin-like compounds	Increased biomass yield and nutrient availability with Ge and REE	Increased Ge uptake in the shoots with 163 %, and up to 12.2 ± 1.3 μg La accumulation by *A. oxydans*	(Schwabe et al., 2021)
Bacillus amyloliquefaciens	Ca, Cu, Co, REEs	Secretion of IAA and ACC deaminase	Higher shoot yield	For F.esculentum: increased uptake in REE, and much more significant with Ca, Cu, and Co by 40 %, 383 %, and 2042 %, respectively	(Okoroafor et al., 2022)
Bacillus amyloliquefaciens	Ni	Release of IAA, siderophore, ACC deaminase, and phosphate solubilization	Increased root length and total biomass weight	Enhanced Ni uptake in roots up to 825.50 mg/kg	(Joradon et al., 2023)

metals from e-waste remain. Future research should concentrate on isolating critical, rare, and precious metals from diverse sources, finding new hyperaccumulator species, and employing genome editing to increase metal absorption. These advancements could broaden the application of phytoextraction, either as a stand-alone process or in conjunction with existing processes for treating e-waste leachate and wastewater, or in recovering metals from foliage in polluted regions. To fully evaluate the potential of phytomining in the context of metal recovery while closing the loop, comprehensive techno-economic assessments and life cycle studies are necessary.

All in all, these initiatives, bioleaching and phytomining are imperative to foster sustainable resource utilization, ensuring the supply continuity, while mitigating waste generation. The primary goal is to stimulate innovation in metal recovery methodologies and contribute to more efficient and environmentally sustainable management of electronic waste.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the author(s) used ChatGPT 3.5 to search for alternative/ proper wording in certain sentences to avoid repetitiveness. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

CRediT authorship contribution statement

Aylin Nur Erkmen: Writing – review & editing, Writing – original draft, Visualization, Resources, Project administration, Methodology, Investigation, Conceptualization. **Roland Ulber:** Writing – review & editing, Validation, Supervision. **Thomas Jüstel:** Writing – review & editing, Supervision. **Mirjam Altendorfner:** Writing – review & editing, Validation, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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