

# Bridging the Bottlenecks in Biohydrometallurgy: Enhancing Kinetics, Resource Utilization, and Sustainability for Scalable Metal Recovery

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**Abstract.** Biohydrometallurgy provides eco-friendly alternatives for extracting metals from primary and secondary resources. However, its industrial scalability is limited due to slow bioleaching kinetics, a lack of process adaptability to complex waste, and insufficient integration of sustainability assessments. This review addresses these challenges by examining recent advances in redox-controlled systems, microbial consortia engineering, and hybrid bioleaching techniques that enhance reaction rates and selectivity. The application of biohydrometallurgy to complex matrices, such as electronic waste and tailings, remains underexplored, necessitating the development of selective bioprocesses and robust microbial communities. Scalable and continuous bioreactor systems are also lacking, hindering commercial adoption. Moreover, few studies incorporate life cycle assessment (LCA) and techno-economic analysis (TEA), leaving uncertainties about environmental and economic performance. The inefficient recovery of critical raw materials such as rare earth elements and precious metals via biotechnological methods presents an additional gap. Addressing these bottlenecks through interdisciplinary innovations can transition biohydrometallurgy from laboratory scale to industrial viability. This review contributes to the IPMC 2025 theme by highlighting practical and sustainable approaches to improve metal recovery from low-grade and complex resources through biological processes.

## 1 Introduction

Biohydrometallurgy, the use of microbiological processes to extract metals from ores and wastes, represents a sustainable alternative to traditional hydrometallurgical and pyrometallurgical methods. By leveraging microorganisms such as *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, and *Sulfobacillus* species, biohydrometallurgy facilitates the leaching of metals like copper, gold, silver, and rare earth elements (REEs) from primary resources (e.g., sulfide ores) and secondary sources (e.g., electronic waste, mine tailings) [1]. This approach reduces energy consumption, minimizes greenhouse gas emissions, and decreases reliance on toxic chemicals, aligning with global sustainability goals. The growing demand for critical raw materials driven by technologies such as electric vehicles, wind turbines, and electronics underscores the need for efficient recovery from low-grade and complex resources [2].

Despite its promise, biohydrometallurgy faces significant barriers to industrial scalability. Slow bioleaching kinetics limit processing efficiency, while the heterogeneous nature of secondary wastes like e-waste poses challenges for process adaptability [3]. The lack of scalable bioreactor designs and insufficient integration of life cycle assessment (LCA) and techno-economic analysis (TEA) further hinders commercial

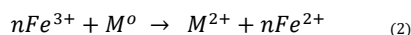
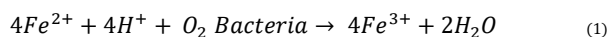
adoption [4]. Moreover, the inefficient recovery of REEs and precious metals highlight a critical gap in biotechnological methods. This review focuses on the recent advances in the bioleaching approaches, such as microbial consortia engineering and hybrid techniques, to address these bottlenecks. It explores applications to complex matrices, proposes selective bioprocesses, and emphasizes sustainability assessments to bridge the gap between laboratory and industrial scales.

## 2 Fundamentals of Biohydrometallurgy

Biohydrometallurgy encompasses bioleaching, where microorganisms oxidize metal sulfides to release metals, and biooxidation, which pre-treats ores to enhance subsequent extraction [5]. The process relies on acidophilic bacteria and archaea that thrive in low-pH environments, producing sulfuric acid and ferric iron as leaching agents [6]. For instance, *Acidithiobacillus spp.* oxidize ferrous iron to ferric iron, which acts as an oxidant for sulfide minerals. Bioleaching mechanisms include direct (microbial attachment to mineral surfaces) and indirect (solubilization via excreted metabolites) pathways. Ferric iron ( $\text{Fe}^{3+}$ ) plays a crucial role in bioleaching by serving as both an electron donor for bacterial energy production (Eq. 1) and an electron acceptor for metal dissolution (Eq.2). This cyclical

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regeneration of ferrous iron ( $\text{Fe}^{2+}$ ) continues the bioleaching process (Eq.2) [7].



Compared to hydrometallurgy, which uses aggressive chemicals like cyanide or sulfuric acid, biohydrometallurgy offers lower environmental impact but slower rates. Pyrometallurgy, involving high-temperature smelting, is energy-intensive and generates emissions, whereas biohydrometallurgy operates at ambient temperatures. Recent studies [8, 9] highlight its potential for low grade ores, yet scalability remains a challenge due to kinetic and adaptability limitations.

### 3 Bottleneck in The Biohydrometallurgical Process

This process is environmentally promising, encounters significant technical and operational hurdles that impede its industrial scalability. These bottlenecks span slow reaction kinetics, challenges in resource utilization, and sustainability limitations, each requiring targeted research to bridge the gap between laboratory success and commercial viability.

#### 3.1. Slow Reaction Kinetics

The slow rate of the microbial extraction of metals against other hydrometallurgical processes is still a main limitation, especially for intractable minerals and complicated wastes. The limitations and influential factors are explained in this section.

##### 3.1.1. Limitations of Classical Bioleaching

The relatively low rate of kinetic solubilization of metals in contrast to that of more conventional chemical leaching methods is inherent in classical bioleaching, which largely uses naturally existing acidophilic microorganisms (including *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*) to solubilize metals. As an example, the bioleaching of chalcopyrite ( $\text{CuFeS}_2$ ) averages an extraction of copper at the rate of 0.1 to 0.5 percent a day [11] compared to 5% or more a day by chemical leaching using sulfuric acid in optimized conditions under a hydrometallurgical process. This difference is exaggerated through lower reactive substrates, like sphalerite ( $\text{ZnS}$ ), or alternative sources such as electronic waste, where recent research results [3] estimate leaching timescales up to several days and weeks. These long processing periods do have a tremendous impact on economic feasibility and throughputs in large scale operations. The inherent restriction is the dependence on the metabolic functioning of microbes, as directed by growth kinetics, redox potential control, and resilience to fluctuations in the environment, including pH, temperatures, and toxicity to metals [10]. Also, the bioleaching process is even more hampered in complex or passivated mineral

matrices, which do not allow microbial attachment or biofilm formation. This elongated leaching time requires a larger volume of bioreactors with high residence time, which demands a lot of capital and operational costs. As a result, these aspects jointly limit the industriality and economic applicability of classical bioleaching, particularly in the case of low-grade or heterogeneous waste streams.

##### 3.1.2. Factors Determining Bioleaching Rate

The kinetics of bioleaching are governed by multiple interrelated factors, each acting as a potential bottleneck:

- Microbial Growth/Density and Metabolic Activity: The rate of metal solubilization is directly proportional to microbial biomass and activity. Low initial cell densities or inhibited metabolism due to nutrient limitations can reduce efficiency [12].
- Substrate Accessibility: Particle size, mineral crystallinity, and surface passivation (e.g., formation of jarosite or elemental sulfur layers) restrict microbial access to target metals. For example, fine grinding ( $< 75 \mu\text{m}$ ) can enhance leaching rates by 20 – 30%, yet increases energy costs [13].
- Mass Transfer: Efficient transfer of oxygen, carbon dioxide, and metabolites is critical. Oxygen limitation in deep bioreactors can decrease reaction rates by up to 40% [14]. Poor mixing or substrate diffusion further exacerbates this issue.
- Environmental Stresses: Optimal pH (1.5 – 2.5), temperature (25 – 40 °C for mesophiles, 50 – 80 °C for thermophiles), and salinity are essential. Toxic by products (e.g., heavy metals, organic inhibitors) and extreme conditions can halve microbial activity [1].

The bioleaching of electronic waste (e-waste) introduces additional layers of complexity. The heterogeneity of matrices comprising metals, ceramics, and plastics, coupled with the formation of intermetallic compounds (e.g., Cu-Sn alloys) and the presence of hazardous organics or brominated flame retardants, significantly impairs microbial efficacy. Adetunji (2023) report that flame retardants can reduce gold leaching rates by 15 – 20% due to toxicity, necessitating pre-treatment strategies to mitigate these effects.

#### 3.2. Resource Utilization Challenges

Effective resource utilization is pivotal for biohydrometallurgy's success, yet several obstacles persist in harnessing secondary resources.

##### 3.2.1. Substrate Variation

Secondary sources such as e-waste, spent lithium-ion batteries, and mine tailings exhibit wide compositional variability and contaminant loads. Tembhare (2022) note that e-waste PCB composition can range from 20 – 40% metals to 30 – 50% plastics, with contaminant levels (e.g., lead, cadmium) varying by 10 – 15% across batches. Biswal further emphasize that spent Li-ion batteries contain inconsistent concentrations of cobalt (5

– 20%) and lithium (2 – 7%), which complicates process optimization.

### 3.2.2. Process Integration

Integrating biohydrometallurgical units into existing flowsheets poses significant challenges, particularly for co-recovery with hydrometallurgical or physicochemical steps. Ngoma (2025) highlights that aligning bioleaching with solvent extraction or electrowinning requires precise pH and redox control, often leading to 10 – 20% metal loss due to incompatibility. The lack of standardized protocols further hinders seamless integration.

### 3.2.3. Metal Selectivity

Many bioleaching microorganisms exhibit metal-specific affinities. For instance, *Acidithiobacillus* preferentially leaches copper over zinc, necessitating consortia or sequential processes for multi-metal recovery. Phogat (2025) demonstrate that mixed cultures can achieve 80% copper and 60% zinc recovery, but the added complexity increases operational costs by 15 – 25%.

## 3.3. Sustainability Limitations

While biohydrometallurgy offers reduced energy and chemical demands, sustainability challenges persist, impacting its long-term viability.

### 3.3.1. Process Duration and Infrastructure

Extended processing times increase land use for reactors and storage, with land requirements potentially doubling compared to hydrometallurgy [19]. This escalation raises costs and environmental footprints.

### 3.3.2. Uncontrolled Emissions

Bio-generated gases such as hydrogen sulfide (H<sub>2</sub>S) and sulfur oxides (SO<sub>x</sub>) can escape if emission controls are inadequate. Studies estimate that uncontrolled H<sub>2</sub>S emissions can contribute 5 – 10% of the process's total environmental impact [20].

### 3.3.3. Life-Cycle Impacts

Downstream processing and effluent management introduce uncertainties. Phogat (2025) note that effluent treatment can account for 20 – 30% of the energy use, opposing some environmental benefit. Comprehensive LCA studies are scarce, limiting impact assessments.

### 3.3.4. Social and Regulatory Gaps

Novel biological processes face public scepticism and regulatory hurdles. The lack of standardized guidelines for genetically modified microbes in industrial settings

delays approval, with compliance costs potentially adding 5 – 10% to project budgets.

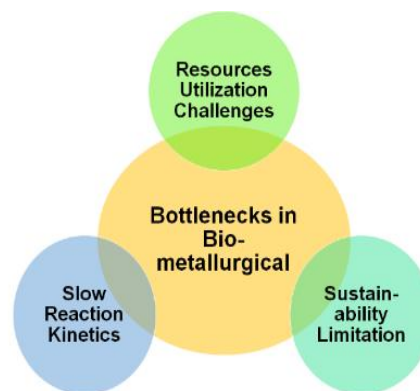


Fig. 1. Bottleneck factors in the bio-metallurgical process

## 4 Innovative Approaches to Overcome Biohydrometallurgy Bottlenecks

Biohydrometallurgy transition to industrial scalability hinges on addressing its inherent limitations, including slow kinetics, poor adaptability to complex waste matrices, and inefficient recovery of critical metals. Recent innovations in redox controlled systems, microbial consortia engineering, and hybrid bioleaching techniques offer promising solutions to these bottlenecks. These approaches enhance reaction rates, improve selectivity, and integrate sustainability, paving the way for practical applications in metal recovery from low grade ores and secondary resources like electronic waste (e-waste) and mine tailings.

### 4.1. Redox-Controlled Bioleaching Systems

Redox controlled bioleaching systems leverage the manipulation of oxidation-reduction potentials to optimize microbial activity and metal solubilization. The introduction of controlled electron acceptors (e.g., oxygen, ferric iron) and donors (e.g., organic substrates) directs microbial metabolism, accelerating the dissolution of metal sulfides and oxides [1]. Bioelectrochemical systems (BES), where microbes interact with anodes and cathodes, represent a significant advancement. These systems facilitate electron transfer, enhancing the oxidation of ferrous iron to ferric iron, a key oxidant in bioleaching. For instance, studies using *Acidithiobacillus ferrooxidans* in BES have reported a 30 – 40% increase in copper recovery from chalcopyrite compared to traditional bioleaching, attributed to sustained redox potentials of +600 to +700 mV [27].

The application of BES extends to e-waste, where precious metals like gold and palladium are solubilized through microbial reduction processes. However, challenges remain, including electrode fouling and energy costs. Recent pilot-scale trials suggest integrating renewable energy sources (e.g., solar) to power BES, reducing operational costs by up to 15%

[21]. Future research should focus on scaling electrode surface areas and optimizing Microbial electrode interfaces to enhance efficiency for industrial adoption. Table 1 shows the different studies done on redox-controlled bioleaching to improve the slower kinetics.

**Table 1.** Redox Potential Control as a Solution to Slow Leaching Kinetics in Bioleaching: Insights from Experimental Studies

Study / Condition	Redox Control Method	Microorganisms Used	Redox Range / ORP	Key Outcome / Copper Recovery	Notable Observations	References
Normalized-based redox study	Normalized redox potential (Normat)	<i>Sulfobacillus</i> spp., <i>Acidithiobacillum ferrooxidans</i> , <i>Acidiplasma</i> sp.	Enomal: 0 to 1 (opt. -0.35 mV)	>75% Cu (optimal); <50% (at Enomal >1)	Weak iron oxidizers prevent passivation; jarosite forms at high redox	Masaki et al. (2018)
Chalcocite constant redox	Nitrogen sparging to maintain ORP	<i>Acidithiobacillus</i> spp.	<760 mV vs SHE	90-90% Cu (10% Fe)	Oxygen limitation favors sulfur oxidizers, improving redox balance	Wu et al. (2014)
Pyrite-assisted redox	Pyrite addition (3:1 mass ratio)	<i>Leptospirillum ferriphilum</i>	350-370 mV vs Ag/AgCl	70% Cu	Pyrite acts as redox buffer; chalcocite forms, and faster dissolution	Hong et al. (2021)
Potentiostat bioelectrode	Controlled air supply to fix ORP	<i>At. ferrooxidans</i>	380 mV vs Ag/AgCl	52-61% Cu (vs <30% without control)	Oxygen-limited bioleaching enhances efficiency	Thard et al. (2002)
<i>Sulfobacillus</i> vs <i>Leptospirillum</i>	Microbial selection	<i>S. thermophilus/ferrooxidans</i> vs <i>L. ferriphilum</i>	Lower ORP with <i>S. thermophilus/ferrooxidans</i>	Higher Cu recovery with weak Fe oxidizer	Transcriptomics showed suppressed iron oxidation genes	Christel et al. (2018)
WMPPCB fed-batch vs batch	High vs low redox in a stirred tank	Mixed acidophiles	Higher in fed-batch (exactly not specified)	97-98% Cu	Fed-batch required 1.35x less H <sub>2</sub> O <sub>2</sub> ; both followed 1st-order kinetics	Gung et al. (2020)
Mechanical activation + ORP control	Surface activation + Fe <sup>3+</sup> system	<i>A. caldus</i> , <i>S. thermophilus/ferrooxidans</i>	Controlled by the Fe <sup>2+</sup> /Fe <sup>3+</sup> ratio	Up to 95.3% Cu	Activated surfaces improved bioleaching; sulfur oxidizers beneficial	Li et al. (2025)
Low pH/high acid tolerance	Low pH with & without redox control	<i>Sulfobacillus</i> L-15, <i>At. ferrooxidans</i>	L-15: ORP -100-150 mV lower than <i>At. ferrooxidans</i>	Active at pH 0.8-1.0	L-15 survives extreme acid and low ORP, promising for harsh environments	Yabu et al. (2002)
Electrochemical redox control	Electrochemical setpoints (SCE)	Mixed thermophilic consortia	420-440 mV (SCE)	Increased Cu from ~39% to >69%	Bioleaching accelerated by redox control	Loftalan et al. (2015)
Pilot-scale bioleaching	Multi-stage with & without redox control	Moderate & thermophilic consortia	420 mV (at 45°C); 70°C (no control)	97% Cu (with control); >95% (at 70°C)	Redox control boosts kinetics at lower temp; high T also effective	Genicke et al. (2010)

#### 4.2. Engineering Microbial Consortia for Enhanced Adaptability

Monocultures of bioleaching microorganisms often exhibit limited adaptability to the chemically heterogeneous nature of complex wastes, thereby constraining their efficiency. In contrast, mixed microbial consortia comprising both autotrophic species, such as *Leptospirillum ferrooxidans*, and heterotrophic bacteria, like *Pseudomonas fluorescens*, demonstrate enhanced metal solubilization and efficiency under challenging conditions [32]. Autotrophs facilitate the oxidation of metal sulfides, while heterotrophs contribute to the degradation of organic constituents and detoxification of secondary metabolites, resulting in a more robust and efficient leaching system. Experimental findings suggest that such synergistic interactions in consortia can lead to a 20 – 25% increase in zinc recovery from mine tailings compared to monocultures [33].

The integration of synthetic biology offers a transformative avenue for optimizing microbial consortia by enabling precise genetic modifications. Tools such as CRISPR-Cas9 allow for the overexpression of genes encoding metal-binding proteins (e.g., metallothioneins) and organic acid synthases, thereby enhancing metal recovery performance [34]. These engineered consortia can be tailored for specific waste types, including rare earth element-rich electronic waste and arsenic-laden tailings. Nevertheless, challenges persist in ensuring genetic stability, especially under industrially relevant, non-sterile conditions, and in mitigating the risks associated with horizontal gene transfer.

To address these issues, ongoing research focuses on quorum sensing based regulatory systems to control interspecies communication and behavior within consortia, thereby enhancing their scalability and functional reliability. While most synthetic biology efforts to date have focused on clonal populations, it is increasingly proposed that engineering synthetic consortia can facilitate the execution of more complex biochemical tasks in industrial settings [35, 36]. Applications in biomining [37] and heavy metal bioremediation [38] stand to benefit significantly from such advancements, given the established roles of natural consortia in these processes.

Notably, hybrid consortia comprising both genetically engineered and naturally occurring bioleaching microorganisms have not yet been reported in the literature. Although some bioleaching species, particularly within the *Acidithiobacillus* genus, have been successfully transformed, their genetic modification remains a technical challenge due to low transformation efficiencies [39]. To date, only two gene knockouts and two expression mutants have been described, one involving an *A. ferrooxidans* strain overexpressing the *rus* gene, and another *A. caldus* strain expressing the *mer* operon for mercury resistance [40].

Ultimately, the deployment of engineered microbial consortia in large-scale heap and tank leaching operations holds significant promise for enhancing bioleaching and biooxidation processes. However, as emphasized by Rawlings & Johnson (2007), any introduced consortia must be capable of competing with indigenous microbial communities in open, non-sterile environments, which remains a critical consideration for successful industrial implementation.

#### 4.3. Hybrid Bioleaching Techniques

Hybrid bioleaching integrates biological processes with chemical or physical treatments to overcome the limitations of standalone bioleaching. Thermal pre-treatment (e.g., 200 – 300 °C) disrupts waste matrices, increasing metal bioavailability by breaking down organic coatings and exposing metal phases [15]. A study on e-waste demonstrated that pre-treating printed circuit boards (PCBs) with mild heating followed by *Acidithiobacillus thiooxidans* bioleaching improved copper recovery from 60% to 85% [42].

Sequential or simultaneous coupling with hydrometallurgy further enhances efficiency. Bioleaching followed by solvent extraction or electrowinning allows for higher recoveries with cleaner outputs. For instance, Baez (2024) reported this by integrating bioleaching with ionic liquid extraction, achieving 88% REE recovery from tailings with minimal iron co-extraction. These hybrid systems mitigate kinetic limitations and adapt to complex matrices, though they require optimization of pre-treatment conditions and integration costs. Future developments should explore automated process control to balance biological and chemical stages, ensuring scalability and sustainability.

Hybrid bioleaching integrates microbial and chemical processes to enhance the recovery of critical metals from electronic waste and metallurgical residues, offering an environmentally sustainable alternative to conventional smelting, which emits hazardous chemicals and heat. Pourhossein (2021) use this approach to microbial metabolisms, such as those of *Acidithiobacillus ferrooxidans* and *Bacillus megaterium*, alongside chemical agents like citric acid or hydrogen peroxide, to achieve high metal extraction efficiencies while minimizing secondary pollution, such as jarosite formation. For spent LED lamps, a hybrid acidic-cyanide bioleaching process utilizing *A. ferrooxidans* for bio-pretreatment followed by *B. megaterium*-mediated cyanide production yielded 93% Au, 91% Ag, 98% Ni, 87% Cu, and 84% Ga under optimized conditions (pH 7, 2.5 g/L glycine, 10 g/L L-methionine, 10 g/L pulp density) [13]. Brar (2024) performed sequential oxidative-reductive bioleaching of acid-pretreated copper smelter slag with *A. ferrooxidans*, achieving 80% Cu, 77.1% Zn, and 65.3% Al extraction, with the reductive phase mitigating surface passivation. Enzymatic bioleaching in a 5 L stirred tank reactor, optimized via response surface methodology and artificial neural network modeling, extracted 90% Cu, 95% Ni, 96% Pb, and 99% Zn from mobile phone PCBs at 395 rpm and 5 g/L pulp density, with > 98% metal recovery via chemical precipitation [45]. Hybrid bioleaching of PCBs with *A. ferrooxidans* and 0.2 M citric acid achieved 94% Cu, 92% Zn, 64% Pb, and 81% Ni, enhanced by exopolymeric substances [46]. Liu (2020) conducted an experiment on high-pressure acid leaching residue, a thermophilic microbial consortium with citric acid, Fe(II), and sulfur, extracted 87.91% Co and 58.52% Cu. Additionally, *Acidiphilium acidophilum* with H<sub>2</sub>O<sub>2</sub> leached 100% Cu from PCBs, enabling the synthesis of an organic-inorganic hybrid for 95% phenol degradation [48]. Originating from 1950s copper dump leaching, hybrid biohydrometallurgy has evolved to address diverse waste streams, demonstrating economic viability and environmental benefits through efficient metal recovery and reduced ecological impact.

## 5 Key Equations in Biohydrometallurgy

### 5.1. Leaching Kinetics Shrinking Core Model

Kinetics studies in biohydrometallurgy are essential for elucidating the mechanisms and rate limiting processes involved in bioleaching. Two primary kinetic models—diffusion controlled and chemically controlled both models have been widely applied to describe heterogeneous metal dissolution during bioleaching, assuming a homogeneous, spherical ore particle and isothermal conditions. These models delineate five sequential steps: (i) diffusion of lixiviant through the liquid boundary layer, (ii) diffusion across the solid product layer, (iii) interfacial chemical reaction between lixiviant and solid, (iv) diffusion of reaction products

through the solid product layer, and diffusion of products through the liquid boundary layer. Under high agitation in bioleaching systems, the boundary layer diffusion steps (i and v) are negligible, rendering the interfacial chemical reaction (step iii) or product layer diffusion (step ii) as the dominant rate-controlling mechanisms [49-51].

In diffusion-controlled leaching, also known as the shrinking core model, a porous product layer forms on the particle surface, where diffusion through this layer becomes rate-limiting as the chemical reaction at the unreacted core proceeds more rapidly than mass transport. Thus, this diffusion kinetics within the product layer can be estimated using Eq. (3)

$$1 - \frac{2}{3} \cdot \alpha - (1 - \alpha)^{\frac{2}{3}} = \frac{2 \cdot M \cdot D \cdot C}{\beta \cdot \rho \cdot r_0^2} \cdot t \quad (3)$$

Here,  $\alpha$  = Metals fraction leached, M = Molecular weight of solid, D = Diffusion constant, C = Leach solution concentration, t = Time, r<sub>0</sub> = Original particle radius,  $\rho$  = Density,  $\beta$  = Stoichiometric coefficient.

Similarly, the diffusion coefficient (D) can be calculated by plotting the right-hand side of Eq. (3) vs time (t), assuming constant values for M, C,  $\rho$ , and  $\beta$ .

In chemically controlled leaching, also known as the shrinking particle model, the surface chemical reaction proceeds more slowly than intraparticle diffusion between the solid matrix and reactant species; consequently, the reactant concentration at the solid-liquid interface equilibrates with the bulk lixiviant concentration (Eq. 4).

$$1 - (1 - \alpha)^{\frac{1}{3}} = \frac{k \cdot C}{r_0 \cdot \rho} \cdot t \quad (4)$$

Here,  $\alpha$  denotes the fractional metal leached, k is the rate constant, r<sub>0</sub> is the initial particle radius, C is the lixiviant concentration,  $\rho$  is the particle density, and t is time. With constant C, r<sub>0</sub>,  $\rho$ , the rate constant k is derived from the slope of the right-hand side of Eq. (4) vs time (t).

### 5.2. Study of the Rate of Reaction (First and Second Order Kinetics)

Kinetics modelling is essential for process design and scale up, as it is well known to explain the rate of metal dissolution mediated by lixiviant (either ferric or proton ions). Several models, including first- and second-order kinetics, were evaluated to identify the most suitable description of the leaching kinetics.

First-order kinetic model: expressed linearly as Eq. (5):

$$\ln C = \ln C_0 - Kt \quad (5)$$

Second-order kinetic model: - Linearized as (Eq. 6):

$$\frac{1}{C} = C_0 + Kt \quad (6)$$

Where C and C<sub>0</sub> represent dissolved metal concentration at time t (h) and t = 0, respectively, and K is the second-order rate constant (L (mol min)<sup>-1</sup>). The

rate constant,  $K$ , is determined from the slope of  $1/C$  vs  $t$ , as depicted in Eq. (6).

## 6 Future Directions and Research Needs

- Advanced microbial engineering to increase leaching rates and metal selectivity.
- Process intensification by combining bioleaching with electrochemical and physical methods.
- Modular, digitalized bioreactors with real-time monitoring and AI-driven control.
- Comprehensive sustainability assessments incorporating environmental, social, and economic dimensions.
- Pilot and demonstration-scale deployments of integrated bioleaching systems targeting diverse feedstocks.

## 7 Conclusions

Biohydrometallurgy offers a transformative approach for sustainable metal recovery from electronic waste and metallurgical residues, addressing resource scarcity and environmental challenges inherent in conventional smelting. The bottleneck of slow leaching kinetics in bioleaching, often governed by the shrinking core model and particle leaching kinetics, can be overcome through targeted innovations. The shrinking core model describes the progressive dissolution of metal-bearing particles, where reaction rates are limited by diffusion through a product layer or surface reaction kinetics, often following first-order kinetics for initial rapid leaching or second-order kinetics for complex interactions involving microbial and chemical synergies. Optimizing these kinetics involves employing robust microbial consortia (e.g., *Acidithiobacillus ferrooxidans* paired with *Bacillus megaterium* for cyanide production), hybrid processing with chemical enhancers like citric acid or hydrogen peroxide, and advanced reactor designs optimized via machine learning. These strategies enhance microbial activity, increase biomass and exopolymeric substance production, and mitigate passivation effects, such as jarosite formation, thereby accelerating metal solubilization. By integrating sequential oxidative-reductive bioleaching or chelate-assisted processes, hybrid biohydrometallurgy aligns with circular economy principles, maximizing resource recovery while minimizing ecological impact. Sustained efforts in research translation, comprehensive sustainability assessments, and supportive regulatory frameworks are critical to scaling biohydrometallurgy, ensuring its industrial viability to meet future metal demands sustainably.

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