

Selective Bioprecipitation of Rare Earth Elements from Bioleachates: The Role of Biorefining

Siti Nur Amala¹ and Siti Khodijah Chaerun^{1,2,3*}

¹Laboratory of Biomining and Biometallurgy, Department of Metallurgical Engineering, Faculty of Mining and Petroleum Engineering, Institut Teknologi Bandung, Bandung 40132, Indonesia

²Department of Metallurgical Engineering, Institute Technology of Bandung, Indonesia 40132

³Geomicrobiology-Biomining & Biocorrosion Laboratory, Microbial Culture Collection Laboratory, Directorate of Research and Innovation, Institut Teknologi Bandung, Bandung 40132, Indonesia

Abstract. The selective recovery of Rare Earth Elements (REEs) from red mud leachates is a major challenge due to the presence of interfering metals such as Fe, Al, Ca, and Mg. This review examines microbial bioprecipitation as a promising strategy to improve selectivity in REE recovery. Microorganisms can produce metabolites, such as phosphates, carbonates, and oxalates, that help selectively precipitate REEs from solution, while sulfate-reducing bacteria can remove competing metals through sulfide precipitation. Although research on similar waste streams exists, studies specifically addressing red mud bioleachates are still limited. Key factors affecting selectivity are discussed, including pH, competing ions, metabolite specificity, and microbial strain selection. Integrating microbial bioprecipitation into broader biorefinery processes could enhance the sustainable and efficient recovery of REEs from red mud, contributing to circular economy goals. This review also identifies important research gaps and suggests future directions for scaling up this approach in metallurgical applications.

1 Introduction

Rare Earth Elements (REEs) are a group of 15 lanthanides with yttrium (Y) and scandium (Sc), are important parts in modern technologies [1]. Rare earth elements (REEs), particularly rare earth element magnets (Nd, Pr, Dy, and Tb), become important since they produce high-performance permanent magnets used throughout a variety of advanced applications, including electric vehicles (EVs) and wind turbines [2]. Global demand for REE magnets from 2015 to 2024 has nearly doubled. By 2050, demand possibly may increase also. That increase will almost double [2]. The surging of demand combined with the supply risks from primary mining and environmental concerns emphasized the need for more sustainable secondary sources [3].

Red mud, the highly alkaline waste produced during alumina extraction via the Bayer process, represents one such promising secondary source. With global stockpiles exceeding 4 billion tons and annual generation of ~175 million tons [4], red mud contains substantial REE ranges from 0.05% to 0.17% by weight [5]. Transforming red mud from an environmental liability into a strategic REE resource supports both circular economy goals and critical raw material supply security.

Among emerging recovery technologies, bioleaching has gained increasing attention due to its ability to mobilize rare earth elements (REEs) from red mud through microbial metabolism and the production of organic acids. Bioleaching is considered an efficient and environmentally benign alternative for the recovery of base and precious metals compared with energy-

intensive hydrometallurgical and pyrometallurgical processes. However, bioleaching alone is insufficient, as it produces complex bioleachates containing mixed REEs together with interfering elements such as Fe, Al, Si, and Ca, which create substantial challenges for downstream separation [6,7].

To address this obstruction, microbial bioprecipitation, which exploits microbially generated metabolites to selectively precipitate REEs, has emerged as a promising downstream strategy [8]. While direct studies on bioprecipitation REEs from red mud bioleachates have not been explored, success in analogous waste systems provides transferable mechanistic insights. This mini-review explores the potential of microbial bioprecipitation for selective REE recovery from red mud bioleachates, identifies key challenges, and outlines opportunities for integration into broader biorefining strategies.

2 Microbial Bioprecipitation: Concepts and Mechanisms

2.1 Definition of Bioprecipitation

Bioprecipitation is a biologically mediated process in which microorganisms promote the formation of insoluble metal(loid) phases. Microbial activity facilitates precipitation by inducing chemical conditions favourable for mineral formation, often resulting in hydroxide, carbonate, phosphate, or sulfide precipitates. This process is driven by microbial-

* Corresponding author: skchaerun@gmail.com; skchaerun@itb.ac.id

metabolites such as organic acids, electron donors, and enzymes, which influence metal speciation and solubility. Through metabolic activity, microorganisms modify local environmental conditions, particularly pH and redox potential, thereby enabling or enhancing metal(loid) precipitation [9].

2.2 Major Bioprecipitation Mechanisms of Rare Earth Elements

Bioprecipitation occurs through two primary mechanisms: biologically controlled mineralisation (BCM) and biologically induced mineralisation (BIM). BCM is governed by intracellular microbial processes, whereas BIM results from extracellular reactions driven by microbial activity. Microorganisms regulate ion transport and metabolite release, thereby influencing mineral formation within intracellular, intercellular, or extracellular environments. In BIM, negatively charged functional groups on the microbial cell wall, such as carboxyl and phosphoryl groups, attract metal(loid) cations, promoting the formation of insoluble compounds. The cell surface also serves as a nucleation site, facilitating mineral growth and precipitation [9].

2.2.1 Oxalate Precipitation (Organic Acid-Mediated)

Fungi such as *Aspergillus niger* produce a range of organic acids, including oxalic, citric, and gluconic acids, during the metabolism of carbohydrate substrates [10]. Among these, oxalic acid shows a particularly strong affinity for rare earth elements (REEs), forming highly stable and poorly soluble rare earth oxalates. This property enables the selective precipitation of REEs from solution, often with high recovery efficiency and purity, even under acidic conditions. Oxalate precipitation is most effective at low pH, typically in the range of 1.5 – 2 [11]. As a result, oxalic-acid-producing fungi such as *Aspergillus niger* play an important role in the biorecovery of REEs, including yttrium and europium [10].

2.2.2 Phosphate Precipitation

Microorganisms can promote the precipitation of REEs by releasing inorganic phosphate into solution. This process is often mediated by enzymatic activity, such as that of alkaline phosphatase [8]. REEs interact with the released phosphate ions. High insolubility rare earth phosphates are produced by the process [8]. Bacteria such as *Methylobacterium extorquens* AM1 use polyphosphate metabolism within the cell in order to sequester and store REEs in cytoplasmic granules [12]. This buildup may be augmented through genetic engineering that suppresses polyphosphate-degrading enzymes [12].

2.2.3 Carbonate Precipitation

Microorganisms facilitate carbonate precipitation through the elevation of pH levels and the concentration of dissolved inorganic carbon [9]. Ureolytic bacteria generate urease, an enzyme that breaks down urea and produces carbonate and ammonium ions. This process increases alkalinity, leading to the precipitation of calcium carbonate. The resulting carbonate minerals provide effective nucleation sites and reactive surfaces for the immobilisation of metal ions, including rare earth elements. *Lysinibacillus* sp. DW018 demonstrates the ability to induce CaCO₃ precipitation, which encapsulates REE ions such as Tb³⁺ via co-precipitation mechanisms and interactions with the formation of carbonate crystals [13].

2.2.4 Hydroxide Precipitation

Microbial metabolic activity can increase pH and modify local environmental conditions, thereby promoting hydroxide precipitation. When dissolved metal ions reach supersaturation, they form less soluble hydroxide phases that precipitate from solution [9]. Through the alteration of the extracellular environment and the provision of biomass surfaces as nucleation sites, microbes function as catalysts that enhance the rate of chemical precipitation [9]. This hydroxide precipitation process may serve as a valuable method for immobilizing multivalent metal ions, using microbial approaches [9].

2.2.5 Sulfide Precipitation (Indirect Selectivity Enhancement)

Sulfate-reducing bacteria (SRB) play an important role in the bioremediation of acid mine drainage (AMD) by reducing sulfate to sulfide, although they are less directly involved in REE precipitation. The sulfide produced reacts with dissolved metal ions, leading to the precipitation and immobilisation of heavy metals such as iron, copper, zinc, and nickel [9]. Sulfide precipitation removes competing heavy metal ions, thereby indirectly improving both the selectivity and purity of REE recovery. Sulfate-reducing bacteria play an important role in this process by selectively precipitating heavy metals, although direct sulfide precipitation of REEs is generally limited. Consequently, effective treatment of complex bioleachates may require a multi-stage recovery strategy, potentially combined with co-culture systems.

2.3 Influencing Factors

A few of the parameters do critically influence all of the efficiency of microbial bioprecipitation. For microbial bioprecipitation, selectivity also depends upon those parameters.

- pH: pH controls precipitate solubility, microbial activity, and metal speciation. An acidic range of pH 1.5 – 2 is optimal for oxalate precipitation, as supported by reported studies [11].
- Temperature: Temperature influences microbial growth, enzyme activity, metabolic rates, and the solubility of metal complexes. Optimal temperatures vary among microbial species. For example, *Lysinibacillus* sp. DW018 exhibits optimal mineralization activity at 35 – 40 °C [13].
- Competing metals: High concentrations of non-REE metals such as calcium (Ca), aluminium (Al), iron (Fe), magnesium (Mg), manganese (Mn), zinc (Zn), and lead (Pb) can inhibit REE precipitation or cause co-precipitation, thereby reducing both the selectivity and purity of the target REEs [11].
- Metabolites and microbial species: Different microorganisms produce distinct metabolites, such as organic acids, enzymes, and REE-binding ligands (e.g., lanthanophores). Consequently, microbial species selection strongly influences REE affinity and precipitation selectivity [14].
- REE concentration: Uptake rates and precipitation efficiency depend on REE concentrations in the leachate. Excessively high concentrations may be toxic and inhibit microbial activity, whereas suitable concentrations can enhance microbial growth and metabolite production. In some cases,

higher REE concentrations can also lead to precipitates with greater purity [14].

3 Bioprecipitation of REEs from Other Waste Streams: Transferable Insights

Although bioprecipitation from red mud bioleachates remains underexplored, studies on other REE-bearing waste streams have shown promising results. These systems provide valuable insights into microbial mechanisms, metabolite-driven precipitation, and key operational parameters, which can be adapted for application to red mud bioleachates.

Engineered *Methylobacterium extorquens* has demonstrated highly selective intracellular accumulation of rare earth elements (REEs) from NdFeB magnet swarf [12]. Fungi such as *Aspergillus niger* enable oxalate-mediated precipitation with high selectivity for yttrium (Y) and europium (Eu) [10]. In addition, urease-producing bacteria, including *Lysinibacillus* sp., induce calcium carbonate precipitation that can encapsulate REE ions such as Tb³⁺ [13].

Mechanistically, REE recovery in these systems is primarily driven by microbial production of ligands such as oxalate, carbonate, and phosphate. High recovery efficiency and selectivity are achieved under well-controlled operating conditions [10,12,13]. Representative systems are summarized in Table 1.

Table 1. Summary of REE bioprecipitation studies

Waste Source	Microorganism	Mechanism	Result	Ref.
E-waste (NdFeB magnets, smartphones)	<i>Methylobacterium extorquens</i> (engineered)	Intracellular polyphosphate storage	High selectivity; up to 202 mg/g REE	[12]
E-waste (fluorescent lamp)	<i>Aspergillus niger</i>	Oxalate precipitation	Highly selective for Yttrium (Y) and Europium (Eu)	[10]
Acid mine drainage (AMD)	<i>Lysinibacillus</i> sp. DW018	Urease-induced carbonate precipitation	98% recovery of Tb in 10 minutes and co-precipitation with CaCO ₃	[13]

4 Bioprecipitation from Red Mud Bioleachates: Challenges and Integration into Biorefining

4.1 Challenges in Applying Bioprecipitation to Red Mud Leachates

Red mud bioleachates are chemically complex solutions containing not only REEs, but also high concentrations of major elements such as Fe, Al, Mg, Mn, and Ca, [6]. Although microbial activity during bioleaching can reduce the extreme alkalinity of raw red mud to more neutral or acidic values [6,7], the resulting leachate remains challenging for selective REE recovery due to ionic competition, metal toxicity, and variable solubility of precipitates [11].

A key limitation is the lack of direct studies on bioprecipitation from red mud bioleachates. Most existing research focuses on the bioleaching step, with few efforts addressing the downstream separation

challenge. Additionally, the presence of competing ions can lead to co-precipitation, reducing REE purity and recovery efficiency [11]. High metal concentrations may also inhibit microbial activity or alter metabolite production [7], requiring the selection of strains with adequate metal tolerance.

To address these diverse challenges, Table 2 provides a comparative synthesis of various microbial strains that have been studied for REE bioprecipitation from other waste streams. This table focuses on parameters that are crucial for red mud applications, such as optimal pH range, and an assessment of each strain’s potential suitability for use in red mud bioleachates. These insights are intended to help guide future research and identify the most promising microbial candidates for overcoming the unique obstacles associated with red mud.

Table 2. Comparison of microorganisms for bioprecipitation of REEs

Microorganisms	pH Range	Selectivity vs Other Metals	Implications for Red Mud Bioleachate
<i>Aspergillus niger</i>	2.0 – 6.0	High	Highly suitable for red mud bioleachate applications. Capable of selectively separating REE (Rare Earth Elements) from other metals.
<i>M. extorquens</i> AM1	5.0 – 7.0	High	Although it produces high REE purity due to specific biological mechanisms, further testing is required to evaluate if this strain is suitable for complex environments such as red mud bioleachates.
<i>Lysinibacillus</i> sp. DW018	8.0 – 9.5	Low	Less suitable for complex red mud bioleachate applications due to its low selectivity.

The choice of microorganisms for the recovery of REE from red mud bioleachate is mostly determined by their pH tolerance and intrinsic selectivity. *Aspergillus niger* is the most promising candidate because of its capacity to flourish in acidic conditions (pH 2.0 – 6.0) and its excellent selectivity, enabling the efficient separation of REE from predominant contaminants. *M. extorquens* AM1 provides remarkable purity via specialized enzymatic processes; nonetheless, its use is constrained by the requirement for neutral conditions and additional validation in intricate industrial matrices. In contrast, *Lysinibacillus* sp. DW018 is less suitable for treating complex bioleachates because its low selectivity under alkaline conditions leads to substantial co-precipitation of undesired metals, thereby complicating downstream purification.

4.2 Integrating Bioprecipitation into Biorefining Systems

4.2.1 Biorefining Concept: Multi-component Recovery from Waste in a Systemic and Sustainable Manner

Biorefining represents a significant shift from linear resource use to a more sustainable approach that ensures the continuous availability of resources. The emphasis is on transforming waste streams into valuable resources through various methods. This concept views industrial waste not merely as refuse to discard, but as intricate raw materials that can be transformed into a variety of valuable products, simultaneously benefiting the environment and the overall system. The goal is to get a high degree of "atom economy," which means that every part of the waste is used, which leads to less waste being made and better use of resources. This method fits well with global goals for sustainability and is a strong way to ensure a steady supply of important raw materials by reducing reliance on primary mining and outside political factors. Even in the face of shortages due to political issues, biorefineries have the ability to adapt and fulfill the current demands of the energy and product market.

4.2.2 Biorefining Scheme for REEs Recovery from Red Mud

A conceptual biorefining scheme for REE recovery from red mud is illustrated in Fig. 1.

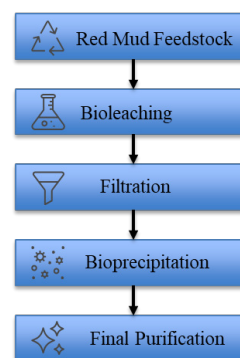


Fig. 1. Schematic flow diagram illustrating the integrated biorefining process for REE recovery from red mud

This flowchart shows the order of the integrated biological and physicochemical stages, which are explained below:

1. Red mud feedstock: The process begins with red mud as the primary feedstock for rare earth element (REE) recovery.
2. Bioleaching: Microorganisms that produce organic acids are applied to solubilise REEs and other metals into the liquid phase. This step also reduces the inherently high alkalinity of red mud, facilitating subsequent processing.
3. Solid-liquid separation: Following bioleaching, residual solid material is removed by filtration, yielding a complex bioleachate containing dissolved REEs together with other metal ions.
4. Bioprecipitation: Microorganisms or their metabolites are used to selectively precipitate target REEs from the bioleachate. This may involve microbially induced pH adjustment or the production of organic acids, such as oxalic acid, to form insoluble REE oxalates and concentrate the metals.
5. Final purification: Additional hydrometallurgical steps are applied to achieve the purity required for commercial applications. Overall, this integrated strategy combines biological and chemical processes to enhance recovery efficiency and sustainability.

4.2.3 Advantages of Bioprecipitation Systems in Biorefining

Incorporating bioprecipitation into biorefining methodologies presents several significant benefits, improving the sustainability and economic feasibility of REE recovery.

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Incorporating bioprecipitation into biorefining methodologies presents several significant benefits, improving the sustainability and economic feasibility of REE recovery.

1. **Environmental sustainability:** Bioprecipitation operates under mild, ambient conditions, substantially reducing energy consumption and avoiding the use of harsh or toxic chemicals commonly associated with conventional processes. This leads to a lower carbon footprint and reduced generation of hazardous waste [9].
2. **Reduced Operational Expenses:** Utilizing natural microbial processes, bioprecipitation can markedly decrease energy and reagent expenditures in comparison to high-temperature furnaces or harsh chemical treatments, hence enhancing the economic feasibility of recovering REEs from low-grade waste streams [8].
3. **Improved Selectivity:** Microorganisms can provide targeted binding and precipitation for REEs [8]. This intrinsic biological selectivity can significantly streamline subsequent purification operations, minimizing the number of necessary stages and the usage of supplementary chemicals.
4. **Resource Circularity:** Bioprecipitation facilitates resource circularity by extracting valuable REEs from industrial waste, such as red mud, thus converting a significant waste liability into a valuable asset and prolonging the utility of existing resources.
5. **Waste Minimization and Environmental Rehabilitation:** This method recovers valuable materials, reduces overall waste generation, and contributes to environmental rehabilitation by stabilizing harmful substances within the original waste matrix.
6. **Strategic Security:** Employing previously unprofitable deposits and mining tailings via bioprecipitation diversifies REE supply sources, hence mitigating geopolitical risks linked to dependence on a restricted number of primary suppliers.

5 Conclusion

The growing global demand involving REEs, underscoring the urgency for sustainable recovery technologies, is coupled with the huge underutilized potential of red mud. Bioleaching enables the mobilization of REEs from red mud in an environmentally friendly way, but selectively separating downstream remains a critical challenge.

Microbial bioprecipitation shows strong potential as a selective and environmentally compatible recovery strategy. Although direct studies on red mud

bioleachates remain limited, insights from analogous systems such as e-waste and acid mine drainage provide a valuable foundation for process development. Key factors influencing performance include pH, the presence of competing ions, microbial tolerance, and metabolite specificity.

Future research should prioritize the development of multi-stage bioprocesses to manage complex leachate chemistries, combined with robust microbial strains or consortia tailored to red mud matrices. Integrating bioprecipitation within a biorefining framework offers a holistic approach for REE recovery while supporting circular economy objectives. To validate industrial feasibility and long-term sustainability, this approach must be advanced from laboratory-scale studies to pilot-scale implementation.

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