



A short critique on biomining technology for critical materials

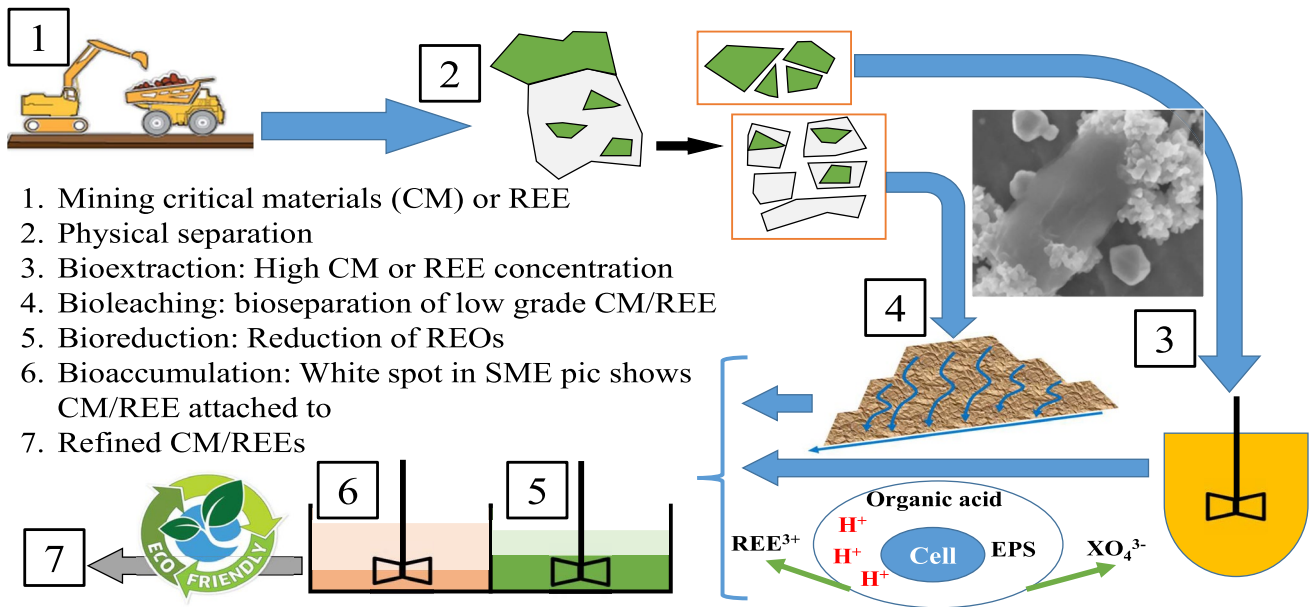
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Abstract

Being around for several decades, there is a vast amount of academic research on biomining, and yet it contributes less to the mining industry compared to other conventional technologies. This critique briefly comments on the current status of biomining research, enumerates a number of primary challenges, and elaborates on some kinetically-oriented strategies and bottom-up policies to sustain biomining with focus on critical material extraction and rare earth elements (REEs). Finally, we present some edge cutting developments which may promote new potentials in biomining.

Graphic abstract



Keywords Bioextraction · Recovery rate · Bottom-up policies · Kinetically-oriented strategies

Introduction: current state

Caveat

There exists an inconsistency on the definition of “biomining” in the scientific literature but herein it literally refers to extraction of minerals via biological systems. In this definition, phytomining is subcategory of biomining.

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Having to work with biological systems in biomining adds extra complications beyond what investors and miners often deal with. This stems from the following factors: (1) biomining, as a whole, is a slow process (Senthil Kumar et al. 2018) (extraction and separation), (2) extreme conditions of traditional mining processes conflict with the sensitive nature of biological systems, and (3) typical mining infrastructures are not designed for bio-processes, and changing it requires high capital investments. Economic pressures for a faster return on invested capital (ROIC) have slowed progress in developing sustainable biomining opportunities. Mining companies mainly invest in pre-examined technologies, some of which have been refined over centuries, such as pyrometallurgical technologies (Johnson 2014). On the other hand, majority of experimental/theoretical studies on bioextraction make simplifications that are not well-suited to biological systems (e.g., linear extrapolation), resulting in misestimations of the kinetic and thermodynamic efficiency of the process (Jin et al. 2017; Thompson et al. 2018). Albeit, those results remain largely unproven, especially at scale. As an example, bioextraction of rare earth elements (REEs) and critical materials are portrayed as a promising method, but still needs validation at a commercial scale (Vahidi and Zhao 2016). Due to this significant gap between research and practice, biomining is still a minor contributor to the entire mining industry; with 15–20% contribution in extraction of copper and 5% of gold at best (Fathollahzadeh et al. 2019; Johnson 2014). With the ROIC being the major concern, slow recovery rate seems to be a bottleneck for the technology readiness level (TRL) of the emerging technologies in biomining. What is the bottleneck of that recovery rate? To answer this question, we shall revisit biomining from the perspective of its constituent elements: (1) bio; the primitive element (bottom), and (2) mining; the derivative element (top).

Biology

From an evolutionary perspective, surviving through gradual and catastrophic terrestrial changes, microorganisms are considered the most successful living organisms on Earth (Francis 2017; Nath et al. 2018). In fact, many microorganisms readily adapt to the slightest environmental changes (Govil et al. 2020; Prado et al. 2019). For instance, bacteria can sense negligible gravitational gradients within small altitudinal variations and adjust their motility (gravitaxis) (Thomas et al. 2018). Owing to this adaptability, microorganisms have been considered for their potential to be used on other planets for the purpose of space mining (Jakhu et al. 2017; Valtonen et al. 2016). Cyanobacteria are one of the most promising microorganisms for self-sustained biomining because of being autotrophs (Mazard et al. 2016). It has

been demonstrated that competition between living species requires taking advantage of the fast kinetics of electron-transfer processes, which in turn is promoted by metal ions present in different minerals (Bauer et al. 2007; Sun et al. 2017). Having free electrons and different oxidation states, multivalent metal ions (e.g., transition metal ions) promote diversity in electron-transfer processes in living systems. Electron exchange between extracellular minerals and microorganisms occurs via external receptors as microbial cells are not permeable/conductive to minerals/electrons (Shi et al. 2016). Those external receptors have evolved to selectively attach to specific metals, in a process known as biosorption. For example, *S. oneidensis* (strain MR-1) is capable of using minerals that contain Fe^{3+} , Mn^{3+} or Mn^{4+} as terminal electron acceptors (Shi et al. 2016). Microorganisms exchange electron with metal ions as: (1) energy source, (2) energy sink, (3) electron transfer (electrical signaling), and (4) electron storage to electrically support their own metabolism (Shi et al. 2016). As majority of multivalent metal ions have positive oxidation states, extraction of these ions is preferably made by biooxidation versus bioreduction (e.g., copper and gold). The recent discovery on the role of Ce^{3+} and La^{3+} in the enzyme methanol dehydrogenase (MDH) to oxidize methanol to carbon and energy (in some microbes such as *Methylacidiphilum fumarolicum* SolV) has renewed interests in using microorganisms for bioextraction of REEs (Pol et al. 2014; Skovran and Martinez-Gomez 2015). Bioaccumulation is the intracellular counterpart of biosorption to extract/collect metals. Compared to the relatively well-known mechanisms of outward electron transfer to extracellular minerals, mechanisms of inward electron transfer are yet to be understood, that is in turn very critical to better understand the nature of bioaccumulation (Shi et al. 2016).

Thriving on far-from-equilibrium stability, thermodynamic efficiency is not the only priority in living systems; $\sim 10 \text{ k}_B\text{T/cycle}$ is the lower bound of energy dissipation in macromolecular biological machinery (Feng and Crooks 2008; Procacci 2017; Riechers and Crutchfield 2017). However, biomining is restricted less by efficiency (energy) and more by effectivity (time); it is a kinetically controlled rather than a thermodynamically controlled process (Johnson 2014; Senthil Kumar et al. 2018). As an examples, a vast number of microorganisms used in biomining gain (versus consuming) energy by oxidizing metals (Johnson 2014). As the result, biooxidation processes can be more lavish in exploring energy intensive strategies in exchange for enhancement of the process rate, which in turn serves the overall success of biomining. With this in mind, an effective strategy triggers tight competitions among microbial species (single/multiple) over common targets (single/multiple) within natural cell approaches (NCA). Those strategies are based on providing highly competitive environments that select for organisms

that carry “selfish genes” that help them outcompete others in a specific mineral rich environment (Silva and Gatenby 2011). Within laboratory-bound experiments (i.e., evolution in action), one not only could devise adaptation strategies to give privilege to survival of desired species (Table 1) but also could drive a population of species to adapt new diets (Blount et al. 2012). We argue that carrier-focused strategies are promising candidates to address the slow recovery rate of biomining (Table 1) as they adapt effective/fast species; eat more in less time (Smulek et al. 2019; Zdarta et al. 2020). A proposed strategy is to start with multispecies assemblages with enough food only for a few generations to adjust, and gradually reducing the food to pass on more selfish genes. As a rule of thumb, diversity improves adaptation in natural biological processes (e.g., multi-species/target) but not necessarily selectivity (Carratalà et al. 2017; Vignuzzi et al. 2006).

While NCA is being gradually explored, sudden breakthroughs rely on *engineered cell approaches* (ECA). Relatively speaking, the latter (micro-controlled) is complementary to the former (macro-controlled), and faster within certain criteria (Table 2). Nonetheless, successful ECA strategies should eventually be customized within NCA strategies.

Highly selective microbial strategies become more kinetically favorable along with declining ore grades as they simply ignore what is not considered their target. For such cases, an alternative is engineering of a scaffold protein with a specific metal binding domain to enrich for specific targets (i.e., biosorption). This approach includes adding metal binding domains to proteins that form inclusion bodies, and thereby provide a novel strategy to sequester bound elements into an insoluble cellular fraction (Singh and Panda 2005). While inclusion bodies are often considered a problem to be avoided when purifying functional proteins, we suggest that this limitation actually represents a unique opportunity to express

insoluble proteins that can sequester bound elements. Inclusion bodies are dense particles comprised of aggregated protein and range in size from 0.15 to 1.3 μm with a density of $\sim 1.3 \text{ mg/ml}$ (Singh and Panda 2005). They can easily be fractionated from other cellular components by a high-speed centrifugation step. Despite their high density, they are hydrated and have a porous architecture. While proteins trapped in inclusion bodies are typically blocked from folding into complex secondary and tertiary structures, small hydrophilic metal binding motifs are more resilient. Thus, inclusion bodies derived from polypeptides with short metal binding motifs offer a powerful strategy to bind excess metals and sequester those metals inside a cell. The ability of inclusion bodies to sequester elements also creates an expectation that the microorganisms should gain some degree of resistance to otherwise toxic levels of specific elements. Thus, this biosorption strategy provides a flexible engineering platform in which other novel proteins can be designed to specifically bio-enrich different target elements. However, because genetically manipulated strains cannot be simply dumped into the environment, there are additional environmental constraints that need to be dealt with in scaling up this technology. Hence, ECA has drawn less attentions in biomining compared to other biotechnologies (Johnson 2014). However, this problem has environmentally safe solutions. The harvesting and processing of bacteria can be done in contained environments. For extracting metals that are sequestered in microorganisms, the organism will be killed as a part of the harvesting process.

In recent years researches were used OMICs (genomics, proteomics, transcriptomics, metabolomics) to identify genes and proteins involved in bioleaching (Buetti-Dinh et al. 2020). Understanding the genetic basis for cell attachment on metal and what gene expression patterns are enriched in a microbial community will help in the design of strategies to stimulate bioleaching rates, speed up the initiation of bioleaching operations, and improve the persistence of active cells in heap bioleaching operations (Christel et al. 2017).

Mining

Traditional (bio)mining has a top-down structure in the following order: (1) decision makers issue a list of so-called “critical materials” based on provisional policies, (2) investors outline future directions for organizations, and (3) organizations adjust their own policies accordingly. In this picture, it is the supreme order, i.e., the list, which guides policies from top to bottom. On the other hand, nature functions in a bottom-up fashion. As

Table 1 NCA adaptation strategies

NCA strategies	Effect on carrier species	Effect on other species
Win–win	Positive	Positive
Altruistic	Negative	Positive
Carrier-focused	Positive	Negative

Table 2 Criteria for employing natural/engineered cell approaches

Cell approach	Selectivity	Kinetics	Planning	Primary target	Stimuli	Modification
NCA	Low	Slow	Stepwise planning	Ensemble of cells	External	Evolutionary
ECA	High	Fast	Careful planning	Single cell	Internal	Induced

far as bioextraction is concerned, minerals have been naturally concentrated based on the needs at the bottom level; i.e., what is critical for microorganisms, versus that of human decision makers. Consequently, we argue that sustainable biomining should emphasize (1) finding pre-existing ecosystems that already concentrate minerals of interest (bottom up approach) or (2) developing new artificial ecosystems (for example, with organisms engineered to accumulate a specific metal). In a bottom-up perspective, bioextraction processes are inherently more selective than those based on a general dissolution of the surrounding matrix, particularly in extraction of low-grade minerals, such as REEs and gold. From the operational perspective, current strategies are based on proper selection and adaptation of microorganisms to meet the harsh mine conditions. However, we suggest consideration should be given to alternative mining strategies that better accommodate growth requirements for different bioextracting microorganisms.

Sustainable biomining and its outlook

Taken together, as a natural way of extracting minerals, the use of bioextraction has the potential to be a major and sustainable addition to traditional mining. Here, we enumerate some reasons for such claim: (1) compared to other extraction techniques, bioextraction can be more energy conservative and environmentally friendly (Johnson 2014), (2) rich primary resources for many minerals are increasingly being exhausted or becoming cost prohibitive, especially for critical and REEs, and (3) inspired by the fact that many minerals are already bioextracted by living organisms, biomining only needs to expedite this process within kinetically-oriented strategies that combine top-down policies with bottom-up processes.

Biomining has gazed at the most recent explorations in the forefront of science and technology. For example, scholars are in continuous search to find microorganisms which can survive at high temperatures, where biomining might be faster and more selective (e.g., selective oxidation of iron over sulfur) (Johnson 2014; Mbye et al. 2020). Within resources containing an abundance of sulfide minerals, an active area of research is on how to hinder the oxidation of sulfide all the way to sulfate as it releases a lot of sulfuric acid in the environment (Engelbrektson et al. 2018). In the field of microbiology, there exists an ongoing search on how electron transfers occur from extracellular minerals to internal electron acceptors of microorganisms, while energy remains conserved within such processes (Shi et al. 2016). Inspired by the fact that the active sites of proteins are very specific and selective, one can invest on refining this selectivity within ECA, as already discussed. Albeit, biosafety is a major concern for ECA alternatives, as there exist very strict limitations when engineered cells are potentially

released into terrestrial environments. These biosafety-related concerns are less of a constraint in the context of engineering biosystems for space biomining projects, such as BioRock (Loudon et al. 2018; Raafat et al. 2013). Biomining is considered as one of the better economical viable options for mining celestial bodies (e.g., asteroids). As an example, the long-term objective of BioRock (by NASA) is to enable in-situ 3D printing of machinery directly from the minerals extracted by pre-cultivated microorganisms, rather than launching that machinery from earth to space (Loudon et al. 2018; Raafat et al. 2013). A parallel line of investigation has emerged based on cutting edge developments in the field of nonequilibrium chemistry. Promising research in this area has progressively thinned the border between chemistry and biology, i.e., living and nonliving systems (Dhiman et al. 2017; Intoy and Halley 2017; Nakouzi and Steinbock 2016). New (bio)materials are being developed to make proper adjustments in response to environmental changes (Derkus et al. 2020; Dhiman et al. 2020; Huang et al. 2020; Li et al. 2019). Such (bio)materials could ideally be tailored to selectively extract minerals, eliminating biosafety concerns. As an example, macrocyclic/bio-inorganic receptors have been recently designed for highly selective extraction of precious metals, such as gold, platinum, or palladium (Liu et al. 2018). Although, application of life-like materials that mimic biological structures have been extensively investigated, their capability for bioextraction or hyperaccumulation of critical materials have not been reported.

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Declarations

Conflict of interest The authors declare no competing financial interest.

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