



Recovery of critical metals using biometallurgy

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The increased development of green low-carbon energy technologies that require platinum group metals (PGMs) and rare earth elements (REEs), together with the geopolitical challenges to sourcing these metals, has spawned major governmental and industrial efforts to rectify current supply insecurities. As a result of the increasing critical importance of PGMs and REEs, environmentally sustainable approaches to recover these metals from primary ores and secondary streams are needed. In this review, we define the sources and waste streams from which PGMs and REEs can potentially be sustainably recovered using microorganisms, and discuss the metal–microbe interactions most likely to form the basis of different environmentally friendly recovery processes. Finally, we highlight the research needed to address challenges to applying the necessary microbiology for metal recovery given the physical and chemical complexities of specific streams.

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branches in the biometallurgical field, and are employed worldwide at large scales. Biomining (or bioleaching) facilitates the extraction and recovery of metals from ores and waste materials [2] while bioremediation focuses on the removal or immobilization of hazardous contaminants such as radionuclides and heavy metals from contaminated sites [3]. However, biometallurgy has the potential to make novel contributions to a sustainable world that should rapidly eclipse current biomining and bioremediation applications. Indeed, worldwide changes in metal cycling have opened up a plethora of opportunities and challenges for biometallurgical technologies. More specifically, the central roles critical metals play in the emergent technologies needed to transition to, for example, a low carbon energy system, which is already driving expansions in secondary and urban mining, will only amplify demand to develop novel biometallurgy-based technologies to extract, separate, purify and recover critical metals [1]. Therefore, this overview focuses on metals whose supply has been deemed critical, reviewing possible sources and waste streams from which they can be recovered using microorganisms, the most promising microbe–metal interactions, and potential new biotechnologies on the horizon.

Selection of critical metals

Europe and the US are increasingly confronted with potential shortages of critical raw materials, that is, materials for which the risk of supply shortage resulting in adverse impacts on the economy are high. The European Union defined a list of 20 critical raw materials that includes bulk metals, industrial minerals, platinum group metals (PGMs) and rare earth elements (REEs) [4]. One of the most powerful forces influencing their economic importance is the growing demand for these materials by emerging low-carbon energy technologies. In a similar review conducted by the US Department of Energy, five REEs (dysprosium, terbium, europium, neodymium and yttrium) were identified to be critical to the development of ‘clean’ emerging energy technologies [5]. These government reports along with further analyses [6,7] highlighted the inevitable need for metallurgical research to develop efficient methods to recover these critical materials, with specific focus on PGMs and REEs. The criticality of these materials is pushing society to expand capacity to mine and extract these materials from primary ores and concentrates as well as to optimize recovery and recycle from residues and scrap from preconsumer products, end of life consumer goods, and landfilled waste streams [6,7]. We envision biotechnologies playing an important role in all of these activities.

Introduction

Biometallurgy is a term used to describe biotechnological processes that involve interactions between microorganisms and metals or metal-bearing minerals [1]. Biomining and bioremediation have been the two most studied

The potential for biomining PGMs and REEs

Biomining of primary ores has mainly been practiced for copper, nickel and gold using bio-heap leaching or bio-oxidation in stirred tank bioreactors which are technologies that have been described in details [2]. The microbial processes that power current industrial biomining are the autotrophic utilization of sulfide and ferrous iron minerals [8]. The application of autotrophic biomining for PGMs and REEs, however, must overcome a number of challenges related to their source materials. REEs are typically mined as carbonates (bastnäsite) or phosphates (monazite and xenotime) from igneous and alkaline rocks, or as ions absorbed on clay minerals. To our knowledge, DNI Metals in Alberta Canada operates the only REE bio-heap leaching project. It seemed that DNI relies on the high content of polymetallic sulfides in the Buckton shale deposits to recover economically viable quantities of Sc, which occurs in a 'metallized zone' of the shale at $\sim 5 \text{ g ton}^{-1}$. In contrast to REEs, PGMs are generally mined from Ni or Cu deposits with Pt, Pd and Rh concentrations at $1\text{--}10 \text{ g ton}^{-1}$ [9]. Most of these deposits are sulfide minerals, and Ni and Cu have been successfully biomined at full scale via heap leaching technologies. The PGM sulfides, however, are more stable than the base metal sulfides, and are therefore more difficult to oxidize [10]. For example, bioleaching of flotation concentrate from the Stillwater Complex, which contained pentlandite ($(\text{Fe,Ni})_9\text{S}_8$), released Ni, but Pd as PdS, and other PGMs required further chemical leaching such as pressurized cyanidation [10]. Concentrates that had not undergone biological treatment, released none or very little PGMs, perhaps suggesting a role for bioleaching of PGMs if the process could be improved.

Besides proton-induced disassociation of metallic ores, metals can also be liberated from solid materials by ligand-induced solubilization. The broad diversity of solubilizing heterotrophic microorganisms, including yeasts, fungi and bacteria have been extensively described as well as the ligands they produce which are mainly organic acids such as citric, oxalic and gluconic acids [11,12,13*]. To our knowledge, no industrial processes using heterotrophic microorganisms have been demonstrated. The probable reason for this is the continuous requirement for significant quantities of carbon and energy sources in the lixiviant (i.e. leaching solution) to support the growth and activity of the leaching microorganisms. This is in contrast with the autotrophic leaching which requires only small amounts of a few inexpensive inorganic nutrients. Although limited research has been performed on heterotrophic extraction of PGMs or REEs from primary ores using organic ligands, we believe that the high value of the product can justify the additional cost of heterotrophic bioleaching. This idea has been partially demonstrated by the Bio-HeapTM technology from Western Areas Ltd. that uses exogenous cultures acclimated to hypersaline and high

temperature environments to conduct more effective bioleaching processes. It is not hard to imagine that similar technologies using heterotrophic microorganisms can be adopted to mine PGMs and REEs. By combining with other advantages from biometallurgy, such as cutting out froth flotation or ultrafine grinding steps with environmental advantages such as low carbon footprint, absence of noxious gases (sulfides, As) production and on-site treatment, biomining can make an interesting economic case under growing stringent regulations. It is envisioned that increased efforts in research can progress biomining of PGMs and REEs from primary ores significantly.

From biomining to biorecovery

A recent comprehensive review defined three major waste streams that present opportunities for effective metal recovery: (1) preconsumer manufacturing scrap/residues; (2) recycling (urban mining) of end-of-life products; and (3) landfill mining of urban and industrial waste residues [6*]. The first two waste streams have been the primary focus of both industrial attention and academic research targets because these waste streams are often found to have high contents of REEs and PGMs. Permanent magnets, nickel metal hybrid batteries, lamp phosphors, spent car catalysts and electric and electronic waste are the most interesting sources within the first two waste streams due to their high metals content and physical consistencies within each category. Consequently, more energy intensive pyrometallurgical techniques or chemical-intensive hydrometallurgical techniques can be used for high efficient metals recovery from these wastes and biometallurgical techniques seem to have very little utility for them currently. On the other hand, although urban and industrial waste residues contain much lower critical metal concentrations, their volumes can be enormous. Examples include, but are not limited to, bauxite mine residues, phosphogypsum, incinerator ash, metallurgy slags, acid mine drainage, and industrial and municipal wastewaters. Biometallurgical technologies are most likely to find their niches in recovering critical metals from these waste residues.

Liquid waste streams

Many wastewaters are currently being considered as energy or nutrient sources, and thus the research paradigm has shifted from simply organic and nutrient removal to resource recovery [14]. In contrast, metal recovery from wastewaters has hardly been considered. Wastewaters have not commonly been characterized for their PGM and REE content. This can be attributed to the fact that utilities and industries primarily focus on the metals included in environmental quality standards imposed by environmental legislation when monitoring the quality of their wastewaters. The few full-scale biotechnologies applied to waste streams from mining or metal refining industries today were primarily developed to remove

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