

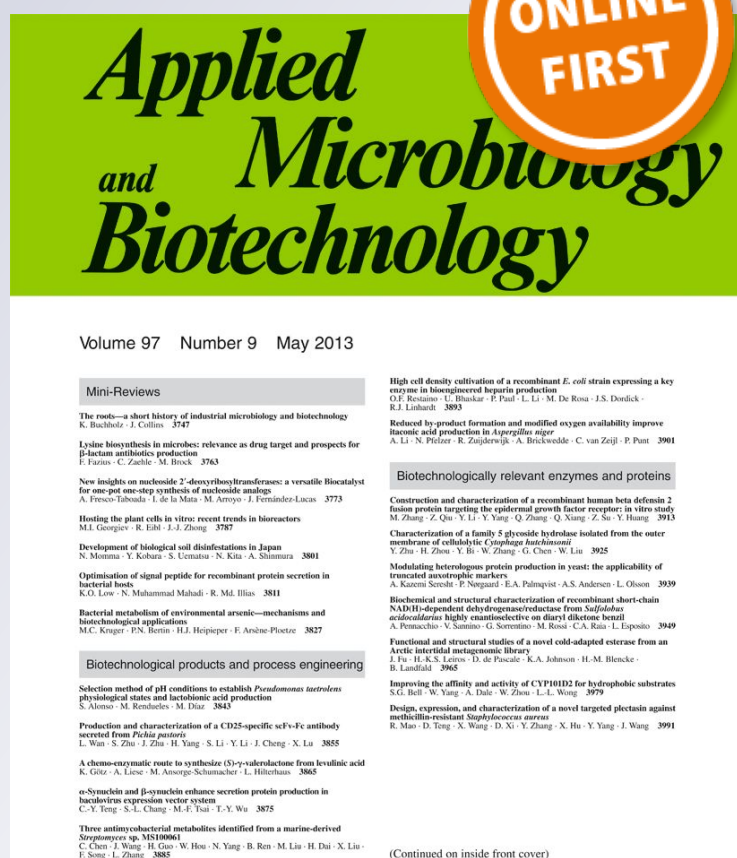
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# Role of microorganisms in bioleaching of rare earth elements from primary and secondary resources

Homayoun Fathollahzadeh<sup>1,2</sup> · Jacques J. Eksteen<sup>1</sup> · Anna H. Kaksonen<sup>2</sup> · Elizabeth L. J. Watkin<sup>3</sup>

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## Abstract

In an era of environmental degradation, and water, and mineral scarcity, enhancing microbial function in sustainable mining has become a prerequisite for the future of the green economy. In recent years, the extensive use of rare earth elements (REEs) in green and smart technologies has led to an increase in the focus on recovery and separation of REEs from ore matrices. However, the recovery of REEs using traditional methods is complex and energy intensive, leading to the requirement to develop processes which are more economically feasible and environmentally friendly. The use of phosphate solubilizing microorganisms for bioleaching of REEs provides a biotechnical approach for the recovery of REEs from primary and secondary sources. However, managing and understanding the microbial-mineral interactions in order to develop a successful method for bioleaching of REEs still remains a major challenge. This review focuses on the use of microbes for the bioleaching of REEs and highlights the importance of genomic studies in order to narrow down potential microorganisms for the optimal extraction of REEs.

**Keywords** Phosphate solubilizing microorganisms · Monazite bioleaching · Rare earth elements · Sustainable mining

## Introduction

In view of escalating environmental degradation, water scarcity, and the depletion of high-grade mineral deposits, the need for a new integrated approach towards sustainable mining has become more urgent. In addition, market demands for green and digital high technology including

but not limited to wind energy, electric cars, and smart phones are growing at an accelerated rate (Goodenough et al. 2018). Rare earth elements (REEs) are known to critical for green economy, modern life, and society (Jowitt et al. 2018). However, annual global demand of REEs has not yet exceeded the annual supply, which ranged from 120,000 to 140,000 t (Klinger 2018).

Recent advances in biomining reflect the exciting potential of developing microbial miners to mobilize a range of metals (Watling 2016). The diversity and capabilities of bioleaching microorganisms for mineral dissolution are ample, providing adaptability of these microorganisms to extreme and challenging environments (Watling et al. 2010).

This review summarizes the fundamental understanding of the interactions of REEs with the microorganisms as well as microbial processes related to the mobilization of REEs to provide insight into the potential application of microorganisms in the extraction of REEs from REEs-bearing minerals. Subsequently, the studies on the use of phosphate solubilizing bacteria in the bioleaching of REEs from primary and secondary resources will be reviewed, and the current state and future outlook will be discussed.

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## Global situation of rare earth elements: turning crisis into opportunity

REEs are an essential component in most modern technologies. The current development of electric vehicles and wind turbines relies extensively on dysprosium and neodymium in REEs magnets (Deady et al. 2016). It is anticipated that further development of these technologies will result in a disproportionate increase in the demand for REEs (Alonso et al. 2012). On the one hand, there are limited recycling technologies available for REEs and less than 1% of the REEs in end-of-life consumer products are recycled globally (Tkaczyk et al. 2018). On the other hand, global primary resources of REEs are limited due to geopolitical controls (i.e., limiting of export quotas for REEs by China in 2010), and they have been identified as critical metals (DOE 2011; Hoatson et al. 2011; Jaireth et al. 2014). It has been found that REEs are relatively abundant in the Earth's crust (Zepf 2013). However, the concentrated forms suitable for viable extraction are less common and separation procedures for REEs are more difficult compared to most other exploited metals (Hoatson et al. 2011).

REEs are typically complexed with chemical groups including oxides [Anatase:  $(\text{Ti}, \text{REEs})\text{O}_2$ ], carbonates [Bastnäsite:  $(\text{Ce}, \text{La})(\text{CO}_3)\text{F}$ ] or phosphates [Monazite:  $(\text{Ce}, \text{La}, \text{Nd}, \text{Th})\text{PO}_4$ ; Xenotime:  $\text{YPO}_4$ ] (Jaireth et al. 2014). Of the 250 known REEs minerals, only three major REEs-bearing minerals (bastnäsite, monazite, and xenotime) are currently exploited commercially (Jordens et al. 2013). The main operating mines are Bayan Obo in China, Mountain Pass in the USA, and Mount Weld in Australia with China producing 70–90% of the global REEs supply (Binnemans et al. 2018). Since the REEs crisis in 2010 and the current control by China's of REEs supply, countries with a high dependency on REEs products have pursued multiple measures to transform the industry and secure their REEs supply (Klinger 2018). The decrease in global supply and an ever increasing demand for REEs, offer potential opportunities for Australia to become a major player in the REEs industry as Australian deposits are known as the richest deposit of REEs in the world (Haque et al. 2014).

Currently, industrial extraction of REEs requires significant processing, and the conventional REEs production relies on either an alkaline process that utilizes concentrated sodium hydroxide or an acidic process that utilizes concentrated sulfuric acid and high temperatures. These generate large amounts of toxic waste containing thorium, uranium, hydrogen fluoride, and acidic wastewater (Abreu and Morais 2010; Hurst 2010). Chemical leaching efficiencies of 85% for La, Nd, and Sm have been reported (Kim et al. 2009). In Australia, until 1995 REEs were largely produced from mineral sands containing monazite associated with high thorium content (Hoatson et al. 2011). The Chinese REEs production has resulted in environmental pollution that was attributed to

the imposition of an export quota by the Chinese government in 2010 (Vahidi et al. 2016).

Indeed, the environmental life cycle impact of REE production through chemical leaching is significantly higher compared to other metals (Haque et al. 2014; Thompson et al. 2017; Vahidi and Zhao 2016). Therefore, alternative approaches offering environmental benefits have received increased attention. Regrettably, in contrast to the biomining of sulfide minerals, much less effort has been devoted to studying the interaction of REEs with microorganisms in bioleaching systems and the application of biohydrometallurgy to REE-bearing resources. To date, there are no available reports on the bioleaching of bastnäsite and xenotime, and only a few studies on monazite bioleaching. Nevertheless, there is considerable incentive to establish green technologies for the recovery of REEs which may contribute to a more sustainable process (Barnettler et al. 2016).

## Rare earth elements: connecting chemistry to biology

While the first REE in an oxide form ( $\text{Y}_2\text{O}_3$ ) was discovered in 1794, non-radioactive REEs were not characterized/separated until 113 years later, as these elements are highly insoluble and scarce in pure form (Bünzli 2014). In 1891, Karl Auer von Welsbach used a mix of various lanthanide oxides, thorium, and other metals for the first gas mantles (Bünzli 2014).

According to recommendations by the International Union of Pure and Applied Chemistry (IUPAC), REEs include 17 elements with special chemical and physical properties, namely yttrium (Y) and scandium (Sc) as well as lanthanides such as lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). The REEs are commonly divided into light (LREEs) and heavy (HREEs). However, there is no absolute agreement on which elements are included in each category, the LREEs being commonly referred to as the first six elements of REEs series, namely La, Ce, Pr, Nd, Pm, and Sm and the HREEs being Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y (Ramos et al. 2016; Šmuc et al. 2012). Y is grouped with the HREEs as its ionic radius is nearly identical to that of Ho (Chakhmouradian and Wall 2012). The LREEs have lower atomic numbers and masses but larger ionic radius, higher solubility, and alkalinity, whereas the group of HREEs has higher atomic numbers and masses but smaller ionic radius and lower alkalinity (Li et al. 2017; Ramos et al. 2016).

REEs have very similar chemical and physical properties, and this uniqueness stems from their electronic configuration (mainly f orbitals), generally forming a particularly stable

oxidation state (3+) (e.g.,  $\text{Ce}^{3+}$  with electron configuration  $[\text{Xe}] 4f^1$ ), and a very small but regular decrease in the ionic radius, with an increase in atomic number (from La to Lu), known as “lanthanide contraction” (Aide and Aide 2012). However, Ce and Eu usually present in the oxidation state (3+) and may also occur as  $\text{Ce}^{4+}$  and  $\text{Eu}^{2+}$  under oxidizing and reducing conditions, respectively. The significance of the lanthanide contraction phenomena is observed in the greater stability of hydrolysis and complex constants with increasing atomic number (from the LREEs to HREEs). The higher stability behavior of HREEs can also be explained by Pearson’s rule (Pearson 1963) which suggested that hard cations (e.g.,  $\text{REE}^{3+}$ ) will preferentially bond with hard anions (i.e., ligands such  $\text{F}^-$ ,  $\text{OH}^-$ , and  $\text{PO}_4^{3-}$ ), through ionic bonds, whereas soft or polarizable cations will bond with soft anions through covalent bonds.

Due to similarities between  $\text{Ce}^{3+}/\text{La}^{3+}$  and  $\text{Ca}^{2+}$  in terms of ionic radius, coordination environment and ligand preferences, REEs have been used as analogues for multiple applications (Lim and Franklin 2006; Pagano et al. 2015; Pang et al. 2002). Although, displacement of  $\text{Ca}^{2+}$  by  $\text{Ce}^{+3}$  and  $\text{Ga}^{+3}$  ions for bone tissue engineering has long been applied (Deliormanlı 2015), only a few recent studies suggest a biological role for REEs. Until recently, the biologists and enzymologists believed REEs to be inert because of the low solubility of these elements in the environment. However, in 2011, it has been discovered that  $\text{Ce}^{3+}$  and  $\text{La}^{3+}$  are required for the activity of the enzyme methanol dehydrogenase (MDH) in some bacteria to oxidize methanol for carbon and energy (Hibi et al. 2011; Pol et al. 2014; Skovran et al. 2011).

Furthermore, it has been postulated that REEs may play pivotal roles not only in biogeochemical processes of single carbon compounds but may also be involved in the metabolism of a broader range of compounds, in a wide range of microorganisms (Chistoserdova 2016). Thus, recent studies on the biological roles of REEs have emerged as a new field which may contribute to the isolation of potential strains for biomining of REEs (Shiller et al. 2017; Skovran and Martinez-Gomez 2015).

## Why do we need biomining?

Due to the growth in the numbers of hybrid electric vehicles (HEVs) and full electric vehicles (EVs), the use of REEs by the automotive industry is forecasted to increase (Goodenough et al. 2018). The production of HEVs and EVs is estimated to increase from 2.3 million units in 2016 to over 10.1 million units in 2026, which is likely to drive an increased demand for neodymium-iron-boron (NdFeB) magnets (Roskill 2017).

Currently, the opportunities for major improvement in the mining, extraction, and recovery of REEs are increasingly

limited by three factors: (1) the extraction of REEs is achieved by using harsh acidic and/or alkaline conditions with either concentrated sulfuric acid and/or sodium hydroxide extraction at high temperature, which release toxic and radioactive waste; (2) REEs are found mixed in the ore, and thus chemical separation of each type leads to an inefficient overall recovery; and (3) the extraction efficiency is dependent on ores containing high concentrations of REEs, which limits potential sources of recovery (Zhuang et al. 2015).

The environmental life cycle impacts of REEs production through chemical treatments are higher than those for other metals currently measured with life cycle assessment tools (Vahidi and Zhao 2016). Consequently, due to environmental issues, sustainable mining, and production are now encouraged on environmental grounds in many countries. Biomining is successfully used in industrial operations, to extract several metals such as copper, nickel, cobalt, and zinc, with 20% of the world’s copper production originating from heap or dump/stockpile bioleaching (Jerez 2017). Bioleaching methods offer environmentally friendly alternatives to classical approaches, when properly executed. A variety of microbial groups has the potential to be applied for bioleaching of REEs from solid matrices (Barmettler et al. 2016). In most of these studies, phosphate-solubilizing microorganisms (PSMs) were used to solubilize REEs from REEs-containing materials (Hopfe et al. 2018).

## Phosphate-solubilizing microorganisms

Most studies to date on the bioleaching of REEs have been carried out with PSMs. However, the majority of the previous research on PSMs has been conducted in agricultural systems. The reason may be the simplicity of using PSMs to liberate insoluble phosphate from organic and inorganic (mineral) phosphate resources present in soil for enhanced crop production derived after hundreds year of agronomic studies (Goldstein and Krishnaraj 2007). A large number of studies have been conducted over the last hundred years on the isolation and characterization of PSMs, mainly using tricalcium phosphate (TCP) as model phosphate mineral. However, it has recently been reported that TCP is unreliable as a universal selection factor for isolating and testing the direct contribution of biological P solubilization (Bashan et al. 2013). Perhaps, this is the main reason why among potential isolated PSMs, a low number of isolates proved to be successful in the direct mobilization of phosphate (Banik and Dey 1983). These discrepancies suggest that other processes and variables of considerable importance, as will be discussed in the following sections, also control the rates of P solubilization.

Gram-negative bacteria have been found to be more efficient at dissolving mineral phosphates than Gram-positive bacteria (Sashidhar and Podile 2010). A large range of

Gram-negative bacterial species including *Klebsiella*, *Enterobacter*, *Pseudomonas*, *Bacillus*, *Rhizobium*, *Erwinia*, *Agrobacterium*, *Flavobacterium*, *Enterobacter*, *Micrococcus*, *Thiobacillus*, *Acetobacter*, *Burkholderia* spp., *Clavibacter*, *Serratia*, and *Streptomyces* are capable of P solubilization as well as some fungi such as *Penicillium*, *Aspergillus*, *Rhizopus*, and *Fusarium* (Illmer and Schinner 1992; Rodríguez and Fraga 1999; Zhao and Lin 2001).

In this review, the term “PSMs” is used in recognition of the fact that microorganisms are capable of transforming insoluble phosphate into more soluble form which directly and/or indirectly contributes to the metabolism of microorganism via increasing phosphate availability in the cell-mineral interface and the solution. Phosphate minerals are dissolved by acidification (Goldstein and Krishnaraj 2007). Therefore, any microorganism that acidifies the media can potentially release some level of phosphate and hence REEs which are in a phosphate mineral matrix.

## Mechanisms of phosphate and REEs solubilization

It is well established that the solubilization of phosphate from poorly soluble mineral phosphates is mainly related to the production of organic acids (Babu-Khan et al. 1995; Goldstein and Krishnaraj 2007; Goldstein 2007); however, the precise mechanism of P solubilization by different PSMs still remains poorly understood (Park et al. 2009). The following sections will address a number of proposed theories to explain the mechanism of phosphate solubilization.

### Organic acid release

As heterotrophic microorganisms in bioleaching systems rely mainly on organic carbon sources (e.g., glucose), heterotrophic metabolism (biologic oxidation of organic compounds to yield ATP) lowers the pH of the leachate either by  $H^+$  extrusion (Illmer and Schinner 1995) or by the secretion of organic acids such as gluconic, citric, acetic, lactic, malic, succinic, tartaric, 2-ketogluconic, and oxalic acids (Bolan et al. 1994). The proton release from the cytoplasm to the outer surface occurs in exchange for a cation (Sashidhar and Podile 2010). The addition of a various carbon sources has been shown to affect the type of secreted organic acids by *Penicillium rugulosum*. With sucrose, most of the glucose molecules were converted to gluconic acid while fructose was strongly associated with the production of citric acid through the tricarboxylic acid cycle (Reyes et al. 1999). While some of the organic acids are responsible for energy production as intermediates in the tricarboxylic (TCA) cycle (e.g., citrate, malate), others are primarily present in cells for cation-charge balancing or for

maintaining osmotic potential (e.g., malate, malonate, oxalate) (Jones 1998).

In most heterotrophic bacteria and fungi, the release of low molecular weight organic acids has been demonstrated to be the most common reason for phosphate solubilization (Rodríguez and Fraga 1999). The heterotrophic leaching involves several mechanisms but organic acids play a dominant and central role in the overall process, supplying both protons and REEs-complexing organic acid anions. Therefore, the ability of organic acid production by PSMs could be considered a phenotype, defined as “a specific characteristic of the microorganism” (Goldstein and Krishnaraj 2007). Beyond organic acids, Illmer and Schinner (1995) also reported that the proton excretion associated with ammonium ion assimilation could be another mechanism of P solubilization without organic acid production.

Although, organic acids have been suggested as the principal mechanism of P solubilization, it has been demonstrated that the higher amount of free organic acids was not directly correlated with higher phosphate solubilization (Banik and Dey 1983; de Oliveira Mendes et al. 2014). Among 57 fungal strains (with a clear predominance of *Penicillium* and *Aspergillus* species), it has been found that phosphate solubilization mechanisms not only differ between strains but are also dependent on the applied P sources where solubilization rate increased as follows:  $TCP > AlPO_4 > FePO_4 > Rock$  phosphate (de Oliveira Mendes et al. 2014).

The rate of P mobilization during phosphate minerals bioleaching varied based on (i) the microbial strains, (ii) the concentration and types of organic acid produced, (iii) and the physicochemical properties of the mineral which is governed by the chemical composition, surface chemistry, phosphate uptake rate by microorganisms, co-precipitation of phosphate, and growth rate of the biomass (Brisson et al. 2016; Corbett et al. 2017). It may be seen that any member of PSMs community either from a same or different family, may release different metabolites including organic acids depending on the solubility of the phosphate mineral and the growth media condition (Table 1). Buch et al. (2008) have described the metabolic flexibility of two *Pseudomonads* strains related to gluconic acid secretion and P solubilization. Under P-deficient conditions, both *Pseudomonas* strains produced only gluconic acid. However, under P-sufficient conditions, the production of pyruvic and acetic acids in addition to gluconic acid by both strains suggested increased carbon flow through the phosphorylative pathway of glucose oxidation (Buch et al. 2008). Under normal metabolic conditions, three different strains of a well-known PSMs family, *Enterobacter (E.) aerogenes* have been reported to produce similar range of gluconic acid up to 1 mM (Stella and Halimi 2015). However, in another recent study, the type and levels of secreted organic acids by the same strain (*E. aerogenes* ATCC 13048) on the same monazite have been found to be different, even though the concentration of

**Table 1** Biological phosphate mobilization and secreted organic acids by phosphate solubilizing microorganisms from various phosphate resources

| Microbial strain                         | Final concentration of organic acids (mM)                                   | P released (mM) | Organic substrate, phosphate source, final pH and leaching time | Reference                     |
|------------------------------------------|-----------------------------------------------------------------------------|-----------------|-----------------------------------------------------------------|-------------------------------|
| <i>Pseudomonas aeruginosa</i> P4         | Gluconic acid: 46                                                           | 0.44            | 100 mM glucose, rock phosphate, final pH = 4.80, 96 h           | (Buch et al. 2008)            |
| <i>Burkholderia cepacia</i> CC-A174      | Gluconic acid: 16, 2-keto gluconic acid: 3.8                                | 2.10            | 29 mM sucrose, tri-calcium phosphate, final pH = 3, 199 h       | (Lin et al. 2006)             |
| <i>Burkholderia caribensis</i> FeG103    | Gluconic acid: 31, acetic acid: 0.02                                        | 8.17            | 55 mM glucose, hydroxy apatite, final pH = 4.04, 168 h          | (Delvasto et al. 2009)        |
| <i>Burkholderia ferrariae</i> FeG101     | Gluconic acid: 0.03, acetic acid: 0.04                                      | 5.07            | 55 mM glucose, hydroxy apatite, final pH = 4.82, 168 h          | (Delvasto et al. 2009)        |
| <i>Enterobacter asburiae</i> PSI3        | Acetic acid: 55                                                             | 0.89            | 75 mM glucose, rock phosphate, final pH = 4, 60 h               | (Sharma et al. 2005)          |
| <i>Serratia marcescens</i> CTM 50650     | Acetic acid: 229                                                            | 19              | 55 mM glucose, hydroxy apatite, final pH = NR, 48 h             | (Farhat et al. 2009)          |
| <i>Serratia marcescens</i> CTM 50650     | Citric acid: 56                                                             | 3.42            | 55 mM fructose, hydroxy apatite, final pH = NR, 48 h            | (Farhat et al. 2009)          |
| <i>Enterobacter aerogenes</i> ATCC 13048 | Gluconic acid < 0.01, formic acid < 0.01, citric acid: 0.10                 | < 0.02          | 166 mM glucose, monazite, final pH = 3.8, 192 h                 | (Corbett et al. 2017)         |
| <i>Pseudomonas aeruginosa</i> DSMZ 50071 | Gluconic acid < 0.01, formic acid < 0.01, citric acid: 0.16                 | < 0.02          | 166 mM glucose, monazite, final pH = 4, 192 h                   | (Corbett et al. 2017)         |
| <i>Aspergillus niger</i> DSMZ 821        | Gluconic acid: 0.27, acetic acid: 1.4, formic acid < 0.01, malic acid: 0.04 | < 0.02          | 166 mM glucose, monazite, final pH = 2, 192 h                   | (Corbett et al. 2017)         |
| <i>Aspergillus terreus</i> ML3-1         | Itaconic acid > 20, succinic acid: 4                                        | 0.48            | 55 mM glucose, monazite, final pH = 2–2.8, 168 h                | (Brisson et al. 2016)         |
| <i>Gluconobacter oxydans</i> NRRL B58    | Gluconic acid: 233                                                          | Not reported    | 222 mM glucose, waste materials, final pH = 2.14, 40 h          | (Thompson et al. 2017)        |
| <i>Enterobacter aerogenes</i> ATCC 13048 | Gluconic acid: 1, acetic acid: 1, malic acid: 11                            | < 0.02          | 166 mM glucose, monazite, final pH = 3.4, 72 h                  | (Fathollahzadeh et al. 2018a) |

the principle metabolite, glucose (3% w/v) was similar (Corbett et al. 2017; Fathollahzadeh et al. 2018a) (Table 1).

## Phosphatase activity

Recently, it has been reported that besides organic acids, phosphatases produced by PSMs may contribute to monazite solubilization (Corbett et al. 2018). The authors suggested that the higher solubilization of REEs in the presence of phosphatases can be attributed to the incorporation of phosphate into the biomass shifting the monazite dissolution reaction and increasing REE<sup>3+</sup> solubility (Corbett et al. 2018). The authors concluded that the action of acid phosphatase activity accompanied with organic acids enhanced REEs solubilization in monazite (Corbett et al. 2018).

## The importance of bacterial attachment

Successful and efficient interaction of microbial strains and mineral surfaces are another key component that control mineral dissolution (Sand and Gehrke 2006). Adhesion and then microbial colonization of the mineral surfaces for nutrient acquisition are a survival mechanism (Busscher and van der Mei 2012). However, the extent to which measured REEs concentration over biomobilization and biomineralization attributed to the bacterial attachment on a phosphate mineral has not been studied until recently. Although, a few studies have been conducted to investigate the role of attachment of bacteria on the dissolution of phosphate- and silicate-based minerals such as apatite, fluorapatite, and feldspar (Feng et al. 2011; Hutchens 2009; Hutchens et al. 2003, 2006), no report of the role of bacterial attachment in the monazite dissolution was available until recently.

To improve bioleaching performance, it is essential to have a detailed understanding of the bioleaching mechanism. In an attempt to understand the fundamental mechanisms of monazite bioleaching by *E. aerogenes*, it has been demonstrated that the contact of bacteria with minerals can have a significant effect on their capacity to enhance mineral dissolution, even though the same types of organic acids with similar concentration were observed in non-contact leaching (Fathollahzadeh et al. 2018a). It has been suggested by Fathollahzadeh et al. (2018a) that the ability of PSMs to solubilize REEs-phosphate minerals is by contact mechanisms, non-contact mechanism, or a cooperative mechanism (a combination of both) (Fig. 1). In contact leaching (Fig. 1a), attached cells solubilize phosphate within a matrix of extracellular polymeric substances (EPS) and mobilize REE<sup>3+</sup> into the solution. Organic acid anions (OA) secreted by the cells from organic substrates (e.g., glucose) complex with REE<sup>3+</sup>. Following proton dissociation of organic acids, free protons also attack the ore surface

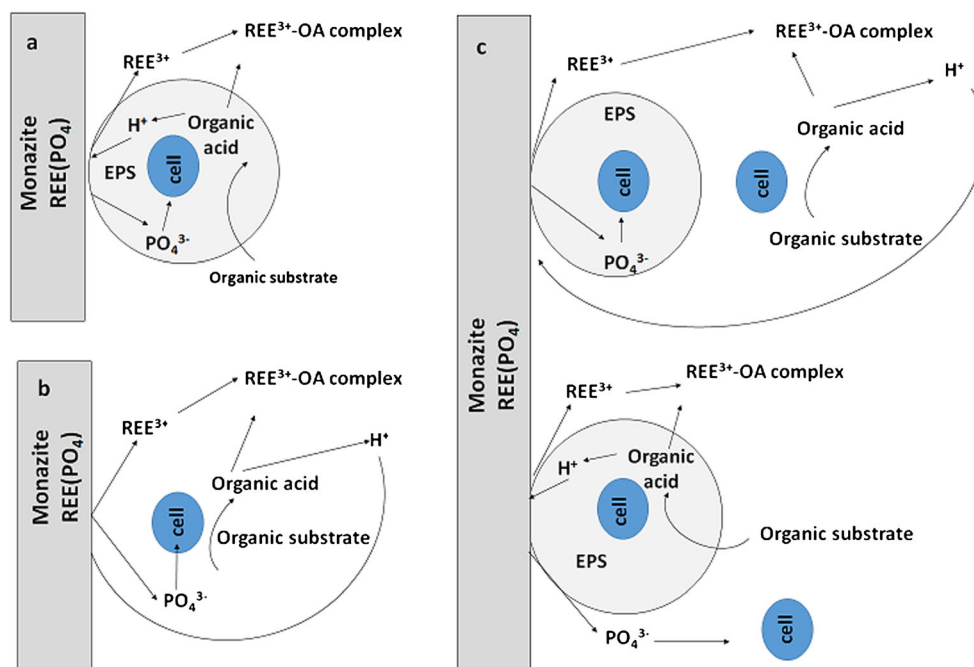


**Fig. 1** a Schematic illustration of the proposed mechanisms of monazite bioleaching. In contact, leaching attached microbial cells solubilize phosphate ( $\text{PO}_4^{3-}$ ) within a matrix of extracellular polymeric substances (EPS) mobilizing REE cations ( $\text{REE}^{3+}$ ) into solution. Organic acids (OA) secreted by the cells from organic substrates complex  $\text{REE}^{3+}$ . Following proton dissociation of organic acids, free protons also attack the ore resulting in further  $\text{PO}_4^{3-}$  dissolution. Incorporation of  $\text{PO}_4^{3-}$  into the cells increases  $\text{REE}^{3+}$  solubility. b In non-contact mechanism, suspended cells form  $\text{REE}^{3+}$ -organic acid complex and incorporate  $\text{PO}_4^{3-}$  into cells

increasing  $\text{REE}^{3+}$  solubility. The protons dissociated from organic acids attack the mineral surface resulting in further  $\text{REE}^{3+}$  and  $\text{PO}_4^{3-}$  solubilization. c In cooperative mechanisms, attached cells solubilize  $\text{PO}_4^{3-}$  from monazite and incorporate it into cells releasing  $\text{REE}^{3+}$  while suspended cells accompany organic acids- $\text{REE}^{3+}$  complex and excretion of protons dissociated from organic acids attack the ore. Alternatively, attached cells may play a role in organic acid production while suspended cells incorporate  $\text{PO}_4^{3-}$  from solution increasing  $\text{REE}^{3+}$  solubility. Reprinted from (Fathollahzadeh et al. 2018a) with permission from Elsevier

resulting in further phosphate solubilization. Incorporation of phosphate into the biomass enhances  $\text{REE}^{3+}$  solubility. Under the non-contact condition (Fig. 1b), suspended cells form  $\text{REE}^{3+}$ -organic acid complex and biologically incorporate phosphate increasing  $\text{REE}^{3+}$  solubility. The protons dissociated from organic acids attack the mineral surface resulting in further  $\text{REE}^{3+}$  and phosphate solubilization. Within the cooperative mechanism (Fig. 1c), attached cells solubilize phosphate from the monazite and incorporate it into cells mobilizing  $\text{REE}^{3+}$  while suspended cells produce organic acid- $\text{REE}^{3+}$  complexes and excretion of protons dissociated from organic acids attack the mineral surface. Alternatively, attached cells may play a role in organic acid production while suspended cells incorporate phosphate from solution increasing  $\text{REE}^{3+}$  solubility.

## Spent medium and abiotic leaching

Apart from direct leaching, where bioleaching is achieved in the presence of the organism, efforts have been made to investigate the effects of metabolites present in spent media, where cells have been removed as well as abiotic leaching

with synthesized organic acids (Brisson et al. 2016; Fathollahzadeh et al. 2018a; Hassanien et al. 2013).

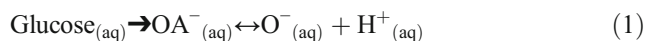
When investigating the possible leaching mechanisms of REEs from monazite, it has been demonstrated that monazite spent medium leaching resulted in lower REEs leaching compared to biotic contact and non-contact leaching (Fathollahzadeh et al. 2018a). The authors suggested that as no phosphate consumption occur during spent media leaching, the precipitation and formation of secondary phosphate minerals increased, resulting in a decrease in overall REEs solubilization. Furthermore, as microorganisms are not present in the system, organic acids are not continually produced in the spent media. These findings suggested that the lower REEs leaching in spent media and abiotic than in the inoculated system was related to the presence and attachment of bacteria (Fathollahzadeh et al. 2018a).

It has also been demonstrated that abiotic leaching of REEs from Egyptian monazite (0.6% pulp density) with synthesized organic acids (chemical leaching using 74 mM citric and 14 mM oxalic acids) resulted in lower recovery, of 58.8% compared to 75.4% with bioleaching directly by *Aspergillus ficuum* (Hassanien et al. 2013). In another study, the solubilized REEs concentrations from monazite sand by all detected

organic acids and with cell-free spent medium were substantially lower than those observed for the active cultures (*Aspergillus terreus* strain ML3-1 and a *Paecilomyces* spp. strain WE3-F.), confirming applied strains secreted as yet unidentified metabolites into solution that are more effective than the identified organic acids at solubilizing phosphate and REEs from monazite (Brisson et al. 2016). This also suggests that to some extent the synthesized organic acids may substitute conventional lixiviants in REEs mineral leaching, whereas in the presence of the microbes and biogenic organic acids, the overall leaching efficiency for REEs can be increased (Corbett et al. 2017, 2018; Fathollahzadeh et al. 2018a). These results emphasize the importance of implementing contact leaching in the bioleaching of REEs from monazite.

## Processes related to the mobilization of REEs

As mentioned previously, PSMs can acidify the medium naturally and therefore are able to release phosphate and REEs present in a phosphate mineral matrix. In most heterotrophic bioleaching systems, proton substitution reactions rely on the production of organic acids (OA) as follows:



The proton activity is a key parameter affecting the dissolution of REEs-phosphate minerals. It has been reported that the normalized dissolution rate of La and Ce (by increasing acidity from 0.1 M to 1 M HNO<sub>3</sub>) increased by one and two order of magnitude, respectively (Gausse et al. 2018).

A complex formation between OA anions and metal cations depends on the number and position of carboxylic (COOH) and hydroxy (OH) functional groups in the organic acids (Bolan et al. 1994). Depending on the dissociation properties and the number of these functional groups, organic acids can carry different negative charges, thereby allowing the complexation of REEs cations in solution and the displacement of anions from the bioleaching matrix (reactions 1 and 2). Therefore, it is reasonable to assume that the higher degree of protonation of the organic molecules is associated with (i) provision of a lower pH condition which helps to maintain the stability of dissolved REEs<sup>3+</sup> in solution; (ii) affecting the degree of proton and ligand attack on the mineral surface; and (iii) influencing the kinetics and strength of the complex formed with the relevant ligands, either in solution or at the bacterial-mineral surface interfaces.

Overall, during the biosolubilization process of monazite, the organic acids secreted by PSMs with differing numbers of donating protons governs the leaching behavior of REEs and

phosphate. Naturally occurring organic ligands secreted by microorganisms, such as acetate, gluconate, citrate, malate, formate, oxalate, and succinate, play a crucial role in the mobility of REEs (Goyne et al. 2010).

From chemistry point of view, the solubility of the trivalent REEs phosphates is very low ( $10^{-13}$  M in pure water) compared to calcium phosphate minerals (Firsching and Brune 1991). The equilibrium solubility products ( $K_{\text{sp}}$ ) expression for the equilibrium reaction of monazite dissolution is as follows:



Apart from the complexity of REEs-phosphate minerals, PSMs may stimulate or suppress mineral dissolution by the transport of solubilized inorganic phosphate for intercellular metabolism. As mentioned previously, according to the reaction (3), the incorporation of phosphate into the biomass shifts the reaction to the right and increases REE<sup>3+</sup> solubility. Also, the precipitation (formation of secondary phosphate minerals), adsorption, and desorption (formation of aqueous REE<sup>3+</sup>/PO<sub>4</sub><sup>3-</sup>) control the concentration of phosphate ions in the solution. It has been well established that the level of released P should not be relied upon as an indicator of ore solubilization as microbial incorporation of inorganic phosphorus from the pregnant solution for immediate use in metabolic processes lowers the soluble P concentration (Brisson et al. 2016; Corbett et al. 2017). The diffusion of released phosphate into microorganisms influences phosphate concentrations in solution and promotes the dissolution and desorption reactions. Thus, phosphate regulation between the cell-mineral interface and the solution through biosorption, precipitation, and coprecipitation may influence REEs dissolution rate during bioleaching. Additionally, it has been reported that the low molecular weight organic acids can be rapidly degraded by microorganisms (Corbett et al. 2017). The retention mechanisms of citric and malic acids have demonstrated that higher Fe concentration under acidic conditions reduced the biodegradation of citric acid and malic acid (Yang et al. 2016). Therefore, the presence of Fe either originating from the mineral or regenerated during bio-oxidation in the bioleaching system can modulate the stability of organic acids by complexolysis, and hence prolong their complexing capacity with REEs (Fathollahzadeh et al. 2018b). Moreover, iron supplementation can be used for phosphate removal, by forming FePO<sub>4</sub> precipitate (Bunce et al. 2018).

Apart from the abovementioned factors associated with REEs mobilization, perhaps the more urgent challenge is a better understanding of the molecular genetics of mineral phosphate solubilization mechanisms and the associated metabolic pathways to phosphate regulation in response to P

stress to develop efficient and environmentally friendly processing pathways, for bioleaching of REEs-phosphate minerals. Therefore, the following section focuses on the phosphate (Pho) regulon, the unique mechanism responsible for the regulation of phosphate and phosphate solubilization in the bacteria.

## Utilizing omics for enhanced bioleaching

Inorganic phosphate is an essential nutrient for energy, nucleic acid, and phospholipid biosynthesis in microorganisms. Microbial communities have evolved appropriate regulatory mechanisms to survive and adapt rapidly to changes in phosphate availability through the presence of a “Pho regulon.” The characterization of the Pho regulon was first reported for *Escherichia coli*, and later for many other bacterial species (Wanner and Chang 1987). The Pho regulon in Gram-negative bacteria is controlled by a two-component regulatory system (phoR-phoB) which involves an inner-membrane histidine kinase sensor protein (phoR) and a cytoplasmic transcriptional response regulator (phoB) (Santos-Beneit 2015). The *phoB* gene encodes the soluble DNA-binding response regulator and the *phoR* encodes the cytoplasmic membrane-associated sensor kinase (White and Metcalf 2007). The P signaling pathway requires seven proteins (phoB, phoR, pstS, pstC, pstA, pstB, phoU), all of which probably interact in a membrane-associated signaling complex (Hsieh and

Wanner 2010). Inorganic extracellular phosphate depletion in the medium has been highlighted to be essential for the activation of the pho regulon and P signaling pathway in bacteria (Hsieh and Wanner 2010). Figure 2 represents a model for  $P_i$  signal transduction of the *E. coli* pho regulon, showing how it is activated in response to P levels (Hsieh and Wanner 2010).

With excess extracellular P ( $> 4 \mu\text{M}$  for *E. coli*) (Fig. 2a), the pstSCAB complex transports P across the membrane into the cytoplasm, where phoU proteins forms a complex with pstSCAB transporter system and the phoR histidine kinase, which inhibits auto phosphorylation of the kinase caused by the interaction with phoU, a chaperon-like phoR-phoB inhibitory protein. When external P is low ( $< 4 \mu\text{M}$  for *E. coli*) (Fig. 2b) and the pstSCAB complex is inactive, phoU dissociates and autophosphorylation of phoR occurs. The phosphorylated phoR triggers the transcription factor phoB, which then activates the transcription of at least 31 genes, where one of activated genes, *phoA*, encodes the phoA protein (bacterial alkaline phosphatase). This protein is transported across the membrane into the periplasm to degrade organic polyphosphates to release P which is then taken up into the cell to overcome the P stress (Blätke et al. 2012). When the cell's P requirement is met, this system is switched off again and phoBP is dephosphorylated (Fig. 2c) (Hsieh and Wanner 2010; Wanner 1996).

A recent study has demonstrated that the distinct organization of the master regulator, *phoBR*, in *Acidithiobacillus*

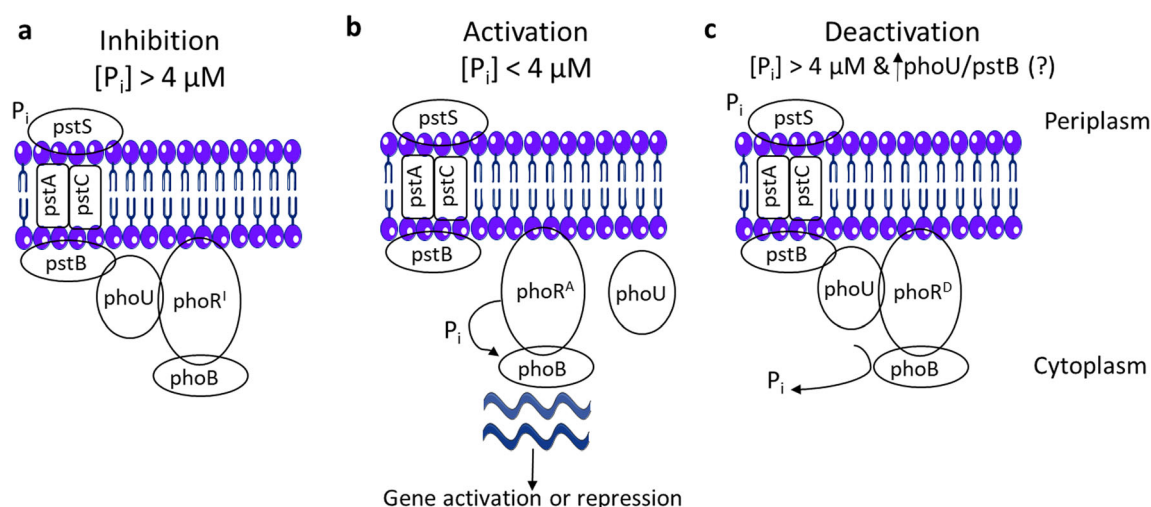


**Fig. 2** Biogeochemical model for sensing extracellular inorganic phosphate ( $P_i$ ) and transduction of the signal to control gene expression in *Escherichia coli* (adapted from (Hsieh and Wanner 2010)). The signaling processes of inhibition, activation, and deactivation are proposed to correspond to different states of phoR: an inhibition state (phoR<sup>I</sup>), an activation state (phoR<sup>A</sup>), and a deactivation state (phoR<sup>D</sup>). With excess extracellular P ( $> 4 \mu\text{M}$  for *E. coli*) (a), the pstSCAB complex transports P across the membrane into the cytoplasm, where phoU proteins forms a complex with pstSCAB transporter system and the phoR histidine kinase, which inhibits auto phosphorylation of the kinase caused by the interaction with phoU, a chaperon-like phoR-phoB inhibitory protein. When

external P is low ( $< 4 \mu\text{M}$  for *E. coli*) (b) and the pstSCAB complex is inactive, phoU dissociates and auto phosphorylation of phoR occurs. The phosphorylated phoR triggers the transcription factor phoB, which then activates the transcription of at least 31 genes, where one of activated genes, *phoA*, encodes the phoA protein (bacterial alkaline phosphatase). This protein is transported across the membrane into the periplasm to degrade organic polyphosphates to release P which is then taken up into the cell to overcome the P stress (Blätke et al. 2012). When the cell's P requirement is met, this system is switched off again and phoBP is dephosphorylated (c). Reprinted from (Hsieh and Wanner 2010; Wanner 1996) with permission from Elsevier

*ferrooxidans* compared to *E. aerogenes* led to more efficient stress response which potentially increased the overall REEs dissolution from monazite (Fathollahzadeh et al. 2018b). Furthermore, previous research on several PSMs as well as *E. coli* have identified a variety of different genes/operons with homology to those which play a role in phosphate uptake, regulation, and solubilization mechanisms of mineral phosphate, including *pqq*, *phoR*, *phoB*, *pstC*, *pstA*, *pstB*, *pstS*, *phoU*, *phoR*, *pKKY*, *pK1M10*, and *gabY* (Chhabra et al. 2013; Rodríguez et al. 2006; Tsurumaru et al. 2015). These may have pivotal roles in the solubilization of phosphates and, therefore, in the recovery of REEs through phosphate bioleaching.

In addition to the *pho* regulon, gene-cloning studies have also revealed that genes directly or indirectly involved in organic acid synthesis as well as expression and regulation of direct oxidation pathways participate in phosphate mobilization (Babu-Khan et al. 1995; Rodríguez et al. 2006). Among organic acids, gluconic acid was highlighted as the metabolic basis of inorganic phosphate solubilization, through the oxidation of glucose by a periplasmic glucose dehydrogenase (*gdh*) enzyme (encoded by *gcd* gene) that requires pyrroloquinoline quinone (PQQ) as a redox cofactor (An and Moe 2016). The second periplasmic oxidation, catalyzed by gluconate dehydrogenase (*gad*) results in the production of 2-ketogluconic acid ( $pK_a = 2.6$ ) while minimizing the respiratory chain component PQQ and bypassing the NADPH-generating glucose-6-phosphate dehydrogenase (G6PD) (Ebert et al. 2011). In addition to providing carbon for intracellular metabolism, the direct oxidation of glucose to gluconic acid produces a transmembrane proton motive force (PMF) that may be used for bioenergetics and/or membrane transport functions which results in the uptake of exogenous amino acids and other compounds (Goldstein 2007). Moreover, several acid phosphatase genes (*acp*) from Gram-negative bacteria have been characterized for improving organic phosphate solubilization from organic compounds in soil (Rossolini et al. 1998). It has been suggested that acid phosphatase generated by isolated PSMs does not act directly on inorganic P solubilization. However phosphatase activity may participate in lowering the pH of the culture medium by the dephosphorylating action and the production of organic acids (Achal et al. 2007; Park et al. 2011) corresponding to no significant correlation between the concentration of phosphate, phosphate solubilization, and the phosphatase activity (Braz and Nahas 2012; Mihalache et al. 2015).

Extending beyond genomic studies, transcriptome profiling also provides potential in identifying molecular mechanisms that affect bioleaching. For example, transcriptome profiling of PSM strain *Burkholderia multivorans* at three levels of exogenous soluble phosphate (0, 0.5, and 20 mM) identified 446 differentially expressed genes, among which 44 genes were continuously upregulated when soluble phosphate

concentration was increased and 81 genes were continuously downregulated (Zeng et al. 2017). Furthermore, genes involved in glucose metabolism were continuously downregulated, which indicated that metabolic channeling of glucose towards the phosphorylative pathway was negatively regulated by soluble phosphate, which may in turn might affect the organic acid secretion and subsequently the phosphate-solubilizing activity (Zeng et al. 2017).

Altogether, a better understanding of complex interactions among PSM genotypes, phenotypes, environmental conditions, and microbiome structure provides indispensable information in their metabolic properties and helps to identify novel strains and genes for optimum biological REEs/phosphate mobilization. Alongside REEs/phosphate solubilization tests with conventional strains, novel omics techniques are enabling the discovery of the core genetic elements that increasingly drive the regulation of PSMs adaptation strategies/physiological responses based on the growth media and the types of mineral. This genetic material has the potential to be transferred to other microorganisms in order to enable them to solubilize phosphate and REEs. Despite the great potential of applying omics to construct microbial communities with modified phosphate starvation-responsive genes for bioprocessing of REE-phosphate minerals, the exploration of opportunities in which core microbiomes can be integrated into “smart bioleaching” is only emerging.

## Current status of bioleaching of REEs from primary and secondary resources

Microorganisms are effective in the mobilization of elements mainly through three principles including acidolysis (formation of organic/inorganic acids), complexolysis (excretion of complexing agents), and redoxolysis (oxidation/reduction reactions) (Brandl 2008). Biotechnological mineral processing approaches where microorganisms generate bio-lixiviants have been demerged as a sustainable alternative to chemical processing of primary and secondary ores and waste streams (Watling 2016). Bioleaching processes are generally occur at relatively low temperature and atmospheric pressure, without relying on expensive and aggressive reagents common in hydrometallurgical processing, or high temperature, energy cost, and gas emissions related to pyrometallurgical processing (Bryan et al. 2015). There have been several studies and patents published recently addressing the interactions of microorganisms and REEs including both REEs mobilization from solids and immobilization from liquids (Barmettler et al. 2016). However, the role of microorganisms in REEs immobilization is not included in the scope of this review as most of available and economical resources of REEs are present as solid matrices and the current bioleaching efforts are directed to releasing REEs from minerals. In the following sections,

the latest studies on bioprocessing of REEs from primary and secondary REEs resources will be discussed.

## Primary resources

Prominent currently operating mines with primary REEs minerals (i.e., monazite, bastnasite, and xenotime) are Mount Weld in Australia, Bayan Obo in China, and recently reopened Mountain Pass in the USA (Haque et al. 2014). The Mount Weld deposit, Laverton, in Western Australia has been identified as the richest and highest grade known deposit of REEs in the world dominated with secondary REEs phosphate (monazite) encapsulated in iron oxide minerals (Haque et al. 2014).

In 2017, the laboratory bioleaching studies of Mount Weld Monazite (MWM) (500-mL shake flasks containing 0.5% ore (w/v) with 3% glucose and modified PVK media, initial pH = 7, for 14 days at 130 rpm, at either 30 or 37 °C depending on the inoculum species) demonstrated that a number of traditional PSMs could solubilize REEs from a lateritic monazite concentrate into the leachate (Corbett et al. 2017). After 8 days, *Penicillium* sp. released a total concentration of 12.32 mg L<sup>-1</sup> of Ce, La, Nd, and Pr with little release of Th and Fe into solution (Corbett et al. 2017). Furthermore, bioleaching experiments conducted on non-sterile MWM with a known PSM (*Penicillium* sp.CF1) (8 days and pulp density of 0.5% w/v) resulted in greater mobilization of REEs into solution (23.7 mg L<sup>-1</sup>) in comparison to experiments conducted on sterile monazite (Corbett et al. 2018). The authors suggested that the presence of indigenous microbes (*Firmicutes*) on the non-sterile monazite increased the bioleaching of MWM by PSMs at rates greater than what was recorded with either the indigenous organisms or the PSMs separately (Corbett et al. 2018). This syntrophic effect of indigenous and inoculated microorganisms was in good agreement with enhanced REEs bioleaching from monazite with a co-culture system (up to a final concentration of 40 mg L<sup>-1</sup> REEs) (Fathollahzadeh et al. 2018b).

The two mine deposits outside of Australia (Bayan Obo in China and Mountain Pass in California) principally contain bastnasite where in Bayan Obo bastnasite and monazite co-occur in ore minerals (Haque et al. 2014). Bioleaching of some REEs (Y, La, Ce, and Nd) from bastnasite-bearing rock by Gram-positive *Actinobacteria* isolated from a Chinese REEs mine has been investigated (Zhang et al. 2018). Utilizing a nutrient-rich growth medium, the total concentration of REEs ranged from 56 to 342 µg L<sup>-1</sup>. However, *Streptomyces* species in an oligotrophic medium and in the presence of the bastnasite (0.5% w/v), bioleached up to 548 µg L<sup>-1</sup> of total REEs (Zhang et al. 2018). Coincidentally, the authors suggested a combination of low solubility of the mineral, the formation of new REEs

precipitate minerals, the accumulation of leached REEs to cell, and the resorption of leached REEs on mineral surfaces may explain the observed low leaching efficiency (<0.1%) (Zhang et al. 2018).

Despite many known deposits available for the evaluation of the bioleaching of REEs from primary minerals, the other available published studies have reported REEs bioleaching efficiencies for monazite sand or synthesized and poorly characterized REEs matrices (Brisson et al. 2016; Hassanien et al. 2013). The use of synthesized REEs matrices for studying the solubilization mechanisms of REEs/phosphate has disadvantages because of a variety of factors such chemical composition and surface chemistry.

An enrichment culture of heterotrophic REEs–phosphate solubilizing fungi was established with 10 g L<sup>-1</sup> glucose and NdPO<sub>4</sub> (Brisson et al. 2016). A 1-mL aliquot of a spore suspension of the three isolated fungal strains (*A. niger*, *A. terreus*, and *Paecilomyces* spp.) were incubated for 6 days in 250-mL Erlenmeyer flasks at room temperature, 250 rpm, with 1% pulp density of synthesized monazite sand. Bioleaching efficiencies were tested in comparison to abiotic leaching (HCl, organic acid, and spent medium). Cell-free spent medium and active cultures leached REEs to concentrations 1.7–3.8 and 5 times higher than those of HCl solutions of comparable pH (3% of leaching efficiency for the cell-free spent medium and 5% of leaching efficiency for active cultures), indicating that metabolites secreted by these organisms contribute substantially to REEs leaching.

In another study, the feasibility of 10 species of PSMs to develop a bioleaching process of REEs from a monazite bearing ore was determined by halo zone formation on agar media, where *Pseudomonas fluorescens*, *P. putida*, *P. rhizosphaerae*, *Mesorhizobium ciceri*, *Bacillus megaterium*, and *Acetobacter aceti* formed halo zones, with the zone of *A. aceti* being the widest (Shin et al. 2015). Furthermore, with respect to higher Ca and phosphate solubilization of *Ac. aceti* from TCP comparing to the other strains, this strain was used for further REEs bioleaching experiments. The strain released up to 5.7 mg L<sup>-1</sup> of Ce on day 4 (0.13% of leaching efficiency).

## Secondary resources

To tackle the REEs supply challenge, extraction of REEs from secondary resources and waste streams has been proposed (Binnemans et al. 2013). However, up to 2011, less than 1% of the REEs were recovered (Tkaczyk et al. 2018). In contrast to recycling of REEs from the REEs waste streams and/or the low grade ores such as mineral sands, more attention has been devoted to red mud (bauxite residue), waste electrical and electronic equipment (WEEE) shredding, waste phosphors/cracking catalysts, and fluorescent powder (Hopfe et al. 2017; Marra et al. 2018; Qu and Lian 2013; Reed et al. 2016).

A filamentous, acid-producing fungi named RM-10, identified as *Penicillium tricolor*, was isolated from red mud and the fungal bioleaching efficiency of REEs from red mud was investigated under various bioleaching processes (one-step and two-step) and pulp densities (2, 5, and 10% w/v) (Qu and Lian 2013). Higher production of citric and oxalic acids with the increased pulp density of red mud in both processes demonstrated that both acids played major roles in the bioleaching of REEs from red mud with leaching efficiencies varying from 36 to 78%.

Marra et al. (Marra et al. 2018) proposed a two-step bioleaching process for the extraction of REEs from WEEE dust with *Acidithiobacillus thiooxidans* and *P. putida*. The first leaching step with *A. thiooxidans* showed yields of > 99% for Ce and Eu, and > 80% for La and Y while pH of the leaching solution dropped from 3.5 to 1.0 (with 1% pulp density after 8 days). In the second step, the cyanide producing *P. putida* released 48% of gold within 3 h from the residue of the first step (Marra et al. 2018). As sulfur was not present in the WEEE dust, the production of biogenic sulfuric acid from elemental sulfur was responsible for the solubilization of the REEs contained in WEEE. The leaching efficiency of Y in this study was higher than in a study where a mixed culture of acidophiles leached up to 70% of Y from fluorescent powder (with 10% pulp density after 16 days) (Beolchini et al. 2012).

The potential of *Gluconobacter oxydans* in bioleaching of REEs from spent fluid catalytic cracking (FCC) catalyst and retorted phosphor powder (RPP) was demonstrated to be controlled by the production of gluconic acid. The leaching efficiency was up to 49% of the total REEs from the FCC material and up to 2% of total REEs from the RPP (Reed et al. 2016). The optimized batch process (agitation intensity, oxygen levels, glucose concentrations, and nutrient additions) increased leaching efficiency of REEs from FCC up to 56% (Thompson et al. 2017). As a result, the authors suggested that microorganisms producing gluconic and other organic acids can effectively leach REEs from waste materials, and that increasing organic acid production will improve the overall recovery. Another readily accessible secondary resource of REEs, fluorescent phosphor (FP) which contains about 10% of REE-oxides has been bioleached by Kombucha metabolites (i.e., acetic and gluconic acid) with leaching efficiency of up to 8% (Hopfe et al. 2017). These studies revealed that the interaction of the different microorganisms and the sample material contribute to the leaching behavior of REEs. Bioleaching could also potentially be applied to other waste products.

## Mining of REEs and sustainability: the missing link

In a world of metal scarcity, the development of new sustainable technologies for REEs extraction from both primary and

secondary resources would be extremely beneficial. It must be realized that in a market where the global consumption of a resource grows by more than 1% per annum, REEs recycling cannot replace primary mining of REE ores (Binnemans et al. 2013), thereby recycling, investigating new potential REEs resources, and primary mining of rare earths are complementary activities for securing long-term REEs supply. Among the available processes, bioleaching can be a sustainable technique for extracting these elements (Ilyas et al. 2017).

The major drawback of bioleaching compared to conventional REEs extraction is lower leaching yield and need for a growth substrate for microbial growth, particularly in heterotrophs. However, the magnitude and the tolerance of bioleaching microorganisms in bioleaching of REEs are still unclear. Further studies using higher solid/liquid ratio with different pure and mixed cultures are required to better understand whether the inadequate yields is due to low solid/liquid ratio or some inhibitory compounds accumulate to the leach liquor that might lead to lower the overall yield. A techno-economic analysis showed glucose to be the single largest expense for the heterotrophic bioleaching process of REEs, constituting 44% of the total cost (Thompson et al. 2017). Therefore, lower expenditure on carbon and energy in addition to an improved leaching efficiencies with core PSMs would increase the overall profit.

## Challenges and future prospects

Until recently relatively little research has been conducted on the solubilization of REEs from phosphate minerals with only a few papers focusing on the biomining of REEs having been published. In addition, knowledge of the underlying metabolic basis of phosphate solubilization is limited with no information on the fate of phosphate and REEs within the bacteria-mineral-solution interface being available. One study has determined the concentration of P in the biomass of a Gram-positive PSM, *Staphylococcus aureus*, (grown on  $K_2HPO_4$ ) (Mechler et al. 2015); however, the method does not reflect the complex multicomponent thermodynamics of monazite. Moreover, due to the low solubility of REEs, the biological functions of these elements have not been extensively studied. As a result, the understanding of the biochemistry of these elements is limited. The rate of biomass growth is governed by nutrient availability including phosphate (Rodríguez and Fraga 1999; Rodríguez et al. 2006) as well as environmental stress such as low pH, other contaminants in the pregnant solution and REEs toxicity which may suppress further REEs solubilization. Further studies using different pure and mixed cultures are required to better understand the mechanisms of phosphate diffusion to and from the mineral and the effects of toxic elements (e.g., fluoride) in bioleaching of REEs.

The mineralogy of monazite governs the dissolution and transport of REEs and phosphate due to its very low solubility compared to other mineral types, such as apatite and/or orthophosphates are more susceptible to leaching. The mobility of REEs, Th, and U is also controlled by their oxidation state. Nevertheless, limited information on the characteristics of the different oxidation states of REEs and their mobility and transition in biogeochemical processes is available in the literature.

REEs-phosphate minerals are made up of inorganic P that can be utilized by PSMs for metabolic purposes. It has been demonstrated that the mineral composition together with the speciation of elements in the phosphate minerals is one key factor influencing the proliferation of microbial communities in the bioleaching systems (Fathollahzadeh et al. 2018b). Studying the effects of bioleaching on REEs mobility from monazite has demonstrated that during REEs mobilization from different fractions of REEs, solubilized REEs does not necessary remain in the solution but shifts to the other fractions in the residue. In this context, the geochemical behavior and mobility of REEs and phosphate in monazite is interpreted to stem from phase association of the REEs (distribution of labile and non-labile REE), microbial activity, attachment of bacteria on the surface, and which physiochemical and biological processes (Fathollahzadeh et al. 2018b) these phases are subjected to.

Another aspect of the mineralogical challenge is the shift of REEs phases in the REEs-phosphate minerals. Sequential extraction procedures (SEP) provide evidence on the fractionation of elements of interest for evaluating their potential mobility and bioavailability (Fathollahzadeh et al. 2014, 2015). A method for REEs fractionation has only recently been proposed (Mittermüller et al. 2016). It has been demonstrated that bacteria are capable of modulating the fate and speciation of metals in contaminated sediments (Fonti et al. 2015); however, the effects of bioleaching on REEs mobility from phosphate minerals have only recently been reported (Fathollahzadeh et al. 2018b).

## Conclusions

Bioleaching of REEs is considered a greener and environmentally friendly technology than conventional techniques. Although a number of endeavors have been made to investigate the effects of PSMs on the bioleaching of phosphates and REEs from phosphate minerals, there are not enough studies of the mechanisms responsible for the mobilization of REEs. As REEs exist as either primary or secondary resources, it is mandatory to study the viability of different strains for bioleaching. Organic acids, phosphatases, bacterial attachment, phosphate regulation, the fractionation of REEs, and mineralogy determine the fate and mobility of REEs and phosphate, which is crucial for the optimal extraction of

REEs. Metagenomic, transcriptomic, proteomic, and metabolic studies are needed to unveil the biochemical and molecular mechanisms used by PSMs during bioleaching.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

**Ethical approval** This article does not contain any studies with human participants or animals performed by any of the authors.

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