The Role of Microorganisms in Mobilization and Phytoextraction of Rare Earth Elements: A Review

Jihen Jalali and Thierry Lebeau*

Laboratory of Planetology and Geodynamics of Nantes, UMR 6112 CNRS, Faculty of Sciences and Technology of Nantes, Nantes, France

Rare earth (RE) elements are a group of 17 chemical elements including the 15 lanthanides plus Yttrium and Scandium. RE have been identified as critical elements due to their special properties (e.g., catalytic, metallurgical, nuclear, electrical, magnetic, and luminescent) and various applications in many modern technologies, environment and economic areas. Thus, the demand for RE has increased significantly during the last decades. This demand has induced an increase in mining activities and consequently a release of RE into the surrounding environment, causing a potential threat to human health and the environment. Therefore, investigations leading to new solutions for the RE recycling from alternate resources like electronic, mining and industrial wastes, has been rapidly growing. In spite of that, recycling stays extremely difficult, expensive and is currently not seen as a significant solution. The concept of phytomanagement is a promising solution when conventional mining methods are no longer cost-effective, not to mention all the ecosystem services provided by plants. The phytoextraction service allows the extraction and recovery of RE from soils or industrial wastes (e.g., phosphogypsum from phosphoric acid production) with the prospect of economic added value. To date, some twenty hyperaccumulator plant species (almost ferns such as Dicranopteris dichotoma) accumulate high concentrations of RE especially in their aerial parts. While the potential roles of native bacteria in mobilization of RE from ores remains slightly documented, those of Plant Growth Promoting Rhizobacteria (PGPR) is much less. PGPR are indeed able to mobilize metals and/or to stimulate plant development in the aim to increase the amount of RE extracted by the plant with then a higher phytoextraction efficiency. Yet to date, only a few studies have been devoted to RE using coupled bioaugmentation-phytoextraction. This review summarizes the data regarding 1) the source of RE (RE-accumulating sediments, soils naturally rich in RE, wastes) and their bioavailability in these matrices, 2) plants identified as RE hyperaccumulator and their potential for RE phytomining, 3) isolation and selection of indigenous bacteria stemming from RE contaminated matrices, such as soil, for their potential ability to increase phytoextraction performances and 4) bioaugmentation-assisted phytoextraction studies dealing with RE.

Keywords: bioaugmentation, bioavailability, hyperaccumulator, phytomanagement, phytomining, rare earth elements, soil
INTRODUCTION

The rare earth elements (RE) are strategic metals because of their increasing importance in high technology applications and renewable energy. RE is relatively abundant in the earth’s crust and widely distributed around the world, but is rarely concentrated, as is the case with most metals, in mines, making it economically viable to exploit. Currently, RE are extracted mostly in China which supplies more than 85% of the World’s RE, to meet the growing global demand. The RE demand increased significantly during the last decades, which will put great pressure on the current RE supply chain. This continuously demand has induced an increase in mining activities and consequently a release of RE into the soil especially surrounding mining areas, causing a potential threat to human health and the environment. Currently, conventional hydrometallurgical extraction of RE is realized by using harsh acidic and basic conditions at high temperature (Zhang and Edwards, 2013), which release a large amounts of toxic and radioactive waste. Furthermore, the extraction efficiency is dependent on ores containing high concentrations of RE, which restricts the possibility of recovery. Therefore, investigations leading to new solutions for the RE recycling from alternate resources like electronic, mining and industrial wastes, has been rapidly growing. In spite of that, recycling stays extremely difficult, expensive and is still quite limited and was calculated in 2011 to be around one per cent of RE supply. This had led to the development of processes which are more economically feasible and environmentally friendly. On the one hand, phytoremediation (i.e., phytoextraction) appears as an innovative solution that may help to reduce the high levels of RE in soils through the use of RE hyperaccumulating plants. On the other hand, the use of bacteria (bioaugmentation) capable of mobilizing RE and/or stimulating plant growth (PGPR – Plant Growth Promoting Rhizobacteria — properties) could serve to increase the quantity of RE extracted by the plant and consequently, improve phytoextraction efficiency. The association of these two techniques (bioaugmentation and phytoextraction) may offer an attractive alternative to conventional processes in yielding a cost-effective and ecological solution. To the best of our knowledge, no research coupling bioaugmentation and phytoextraction has yet to be implemented to treat RE.

This study provides an overview of the current literature relating to various aspects of RE in the soil environment. RE properties, main applications, resources, recovery from waste and potential health and environmental risk are characterized. The main focus in this review is about the analysis of the RE phytoextraction process, the ability of plants to hyperaccumulate RE and the possibility of enhancing phytoextraction process with the use of microorganisms (bioaugmentation) to mobilize RE and/or to promote plant growth.

DEFINITION AND PROPERTIES OF RARE EARTHS

Rare earths, are diversely abbreviated to as rare earths (RE), rare-earth elements (REE), rare-earth metals (REM), rare earth oxides (REO) and total rare-earth oxides (TREO) (Massari and Ruberti, 2013; Mehmood, 2018). Hereinafter referred to as RE are a group of 17 chemically similar elements in the periodic table as defined by International Union of Pure and Applied Chemistry (IUPAC) (Massari and Ruberti, 2013; Balaram, 2019). They are the scandium (Sc) (Z = 21), yttrium (Y) (Z = 39) and 15 lanthanides with numbers successive atomic numbers from 57 to 71 from the periodic table of elements: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium ( Tb), dysprosium (Dy), holmium (Ho), erbi (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). Scandium and yttrium belonging to group IIIA of the transition metals, are not lanthanides. They are usually included in RE because they occur naturally in the same minerals and have similar physical and chemical properties: e.g., in the crystalline compounds, they generally have the +III oxidation state, despite some can also have a +II or +IV oxidation state, the coordination numbers in compounds are usually greater than six and decrease across the series. RE bind preferably with oxygen or fluorine as strong electronegative elements. All RE except promethium occur in nature (Henderson, 1984; Mehmood, 2018). They have high electrical conductivity and there are very small differences in solubility and complex formation between these metals (Voncken, 2015). In addition, RE are generally similar in their electronic configuration and ionic radius, so that they have a similar chemical and physical properties (Krishnamurthy and Gupta, 2016). Based on their location in the periodic table and their atomic weights, RE are divided into light RE (i.e., those with a lower mean atomic mass, Z = 57 up to 62) and heavy RE (i.e., those with a higher mean atomic mass, Z = 63 up to 71 (Damhus, 2005)]. Heavy RE are different from light RE in that they have “paired electrons” (counter-clockwise spinning electrons) (Voncken, 2015). Yttrium, although light (Z = 39), is included with the heavy RE group because of its similar chemical and physical properties in terms of compressibility at high pressures and the behavior of the ratio of the Wigner–Seitz radius to the ionic radius as a function of pressure (Chakhmouradian and Wall, 2012; USGS, 2014). Some authors include europium and gadolinium within the group of heavy RE but there is no consensus. Generally, the heavy RE are more used and less concentrated because of their lower crustal abundances and limited reserves. In the Earth’s crust, there is a general trend of decreasing abundance of RE with increasing atomic number. (Xiao et al., 2015). From other studies a third class, medium-RE, includes europium and gadolinium and samarium (Hatch, 2011; Zhanheng, 2011). RE do not exist as individual native metals in nature such us a gold. They are extracted from ores such as bastnæsites, monazites and xenotimes (Zhang et al., 2015).

RARE EARTH APPLICATIONS

RE were used in many applications in the past and they are becoming more popular in high-tech industry nowadays. Their unique physical and chemical properties (such as unique
TABLE 1 | Main application of rare earth.

| Element      | Applications* b, c |
|--------------|-------------------|
| Lanthanum    | Battery alloys, metal alloys, auto catalysts, petroleum refining, polishing powders, glass additives, phosphors, ceramics, optics, electron microscopic tracer, studio lighting, laptop batteries, camera lenses and hybrid car batteries. |
| Cerium       | Battery alloys, metal alloys, auto catalysts (emissions control), petroleum refining, polishing powders, glass additives, phosphors, and ceramics, carbon-arc lighting, TV color, screen, fluorescent lighting, catalytic converter. |
| Praseodymium | Battery alloys, metal alloys, auto catalysts, polishing powders, glass additives, and coloring ceramics, nickel metal hydride (NiMH) in hybrid cars, glass goggels for glass blowers and welders, high-intensity carbon arc lights. |
| Neodymium    | Permanent magnets, battery alloys, metal alloys, auto catalysts, glass additives, and ceramics, neodymium magnets also known NIB (computers, hand phones, medical equipment, motors, wind turbines and audio systems), specialized goggels for glass blowers. |
| Promethium   | Watches, pacemakers, and research, atomic batteries for spacecraft and guided missiles. |
| Samarium     | Magnets, ceramics, and radiation treatment (cancer), Magnets for headphones, small motors and pickups for some electric guitars, absorber in nuclear reactors, cancer treatment. |
| Europium     | Phosphors, anti-forgery marks on euro bank notes, nuclear reactor control rods, compact fluorescent bulbs. |
| Gadolinium   | Ceramics, nuclear energy, and medical (magnetic resonance imaging, X-rays), microwave, magnetic resonance imaging (MRI), color television picture tubes. |
| Terbium      | Fluorescent lamp phosphors, magnets especially for high temperatures, and defense, magnet for wind turbine and hybrid car motor, speaker UV light for euro bank notes. |
| Dysprosium   | Permanent magnets, speakers, compact discs and hard discs, medium source rare-earth lamps (MSRs) within the film industry. |
| Holmium      | Permanent magnets, nuclear energy, and microwave equipment, yellow or red coloring for glass, cubic zirconia, nuclear reactor control rods, solid-state lasers for non-invasive medical procedures treating cancers and kidney stones. |
| Erbium       | Nuclear energy, fiber optic communications, glass coloring, nuclear reactor. control rods, coloring agent in glazes and glasses. Laser for skin (remove tattoo) |
| Thulium      | X-rays (medical) and lasers, laser, euro banknotes for its blue fluorescence under UV. |
| Ytterbium    | Cancer treatment and stainless steel, stress gauges to monitor ground deformations caused by earthquakes or under-ground explosions, catalyst, fiber laser amplifiers. |
| Lutetium     | Dating rocks and minerals, petroleum refining, catalyst, detectors in positron emission tomography (PET). |
| Yttrium      | Battery alloys, phosphors, ceramics, microwave filter, red color in color television tubes, high-temperature super-conductor YBCO. |
| Scandium     | High strength, low weight aluminum scandium alloys, aerospace industry components and for sports equipment such as bicycle frames, fishing rods, golf iron shafts and baseball bats. |

*Guyonnet et al. (2015),
*Suli et al. (2017),
*Ganguli and Cook (2018).

magnetic and optical properties) have made them essential for a growing number of critical technologies, i.e., those subject to trade disputes such as semiconductors and computers. (Migaszewski and Galuszka, 2015; Suli et al., 2017; Ganguli and Cook, 2018; Balaram, 2019; Seaman, 2019).

The applications of RE concern traditional and high-tech sectors. Traditional sectors include the metallurgy industries, glass, ceramics, as well as the oil and chemical industry. RE can be in the form of a mixture of metals, oxides or salts. High-tech sectors, which developed over the past 40 years, include the industries of phosphorus, permanent magnets, batteries [hydrogen storage material, nickel-metal hydride (NiMH)], polishing powders and the nuclear industry. For these applications, RE often need to be in the form of high purity oxides (Zhang et al., 2016). The main industrial applications of RE are briefly summarized in Table 1. In addition, RE have been used in the China agriculture for about 20 years as fertilizers. The yield and quality for several crops have been improved (Pang et al., 2002; Balaram, 2019). Zhenhong and Hong (1996) reported that the RE can raise the output of wheat 4–10% every year in a continuous ten-year period after applications of RE of 600 g/ha-yr. Pang et al. (2002) summarized the effects of RE on main crops.

Due to all these applications, the RE demand increased manifold during the last decades and the trend appears to be for a continued increase in the use of RE. Zhou et al. (2017) reviewed current and predicted 10-years market demand for RE. It is reported that RE demand from clean technologies will reach 51.9 thousand metric tons (kt) REO in 2030. Scenarios on future demand for the RE (Nd, Dy, Pr, and Tb) can be found in the literature up to the year 2035 (Marscheider-Weidemann et al., 2016). Worldwide RE demand is growing rapidly. The annual demand for RE doubled up to 125,000 tons in 15 years, and the demand is projected to reach 315,000 tons in 2030, driven by increasing uptake in green technologies, e.g., global wind show a strong growth in demand and their capacity reached 870 GW in 2021 and could grow to greater than 1330 GW by 2026. Though other applications for NdFeB magnets in renewable energy production will become more important, as governments make efforts to meet stringent global warming and emissions standards.

This demand has induced an increase in mining activities and consequently a release of RE into the surrounding environment, causing a potential threat to human health and the environment.

ENVIRONMENTAL AND HUMAN HEALTH RISKS

The massive use of RE in various industries has induced serious contaminations of the surrounding environment which could, in turn, cause negative effects on human health. Despite the growing interest raised by RE, the information that has become available over the last two decades regarding RE is relatively recent and scarce, which has led to the current controversy regarding the health benefits at low concentrations vs. toxic effects at high.
concentrations. RE have previously been considered to be not toxic and to be readily excreted by animals and human after ingestion. The highest RE concentration was measured in the liver of fattening bulls amounted to 22–482 μg/kg DM for La, 37–719 μg/kg DM for Ce and 4–73 μg/kg DM for Pr and the lowest La, Ce and Pr concentrations with 3–5 μg/kg DM, 5–7 μg/kg DM and 0.5–0.7 μg/kg DM, respectively (Schwabe et al., 2012). Nevertheless, recent publications have reported toxic effects of RE in human health (Li et al., 2013; Rim et al., 2013; Gwenzi et al., 2018), in aquatic organisms (Malhotra et al., 2020), in aquatic microbes (Wilde, 2001), animals (Briner et al., 2000; Rim, 2016) and plants (Babula et al., 2009). The determination of RE concentrations reporting non-toxic and toxic effects in living organisms vary according to the total concentration of these elements in the environment and among different species and the bodyweight of individuals, which in turn depends on age. Moreover, it’s depended on short and long-term exposure. The risks of RE pollution due to mining, transportation and processing as well as from the improper disposal of materials containing these compounds could potentially lead to elevated levels within the environment, that may have very serious environmental and occupational risks. These studies show that the solvent extraction used in the RE mining process [e.g., versatic, naphthenic and phosphoric acids (Xie et al., 2014)] have been responsible for the disease and occupational poisoning of workers and local residents, water pollution, and the contamination of agricultural area. The processing of RE rich monazite rocks for the production of phosphate fertilizers and the subsequent applications of these fertilizers could further increase RE soil concentrations, especially in agricultural areas (Turra and Bacchi, 2011). The amount of RE used in Chinese agriculture has been increasing continuously, reaching some thousands of tons per year. A detailed description of the RE contents reported in the worldwide literature for the main phosphate fertilizers and other products of relevant use in agriculture effects on performance parameters is published by Ramos et al. (2016). Li et al. (2013) reported that RE soil pollution due to tailings from an RE processing plant in China can travel up to approximately 7 km before soil concentrations stabilize to natural levels. In addition, most RE deposits contain radioactive materials (thorium and uranium especially), which impose the risk of radioactive dust emissions. Due to the high mobility in tailings, RE readily disperse into surrounding agricultural soil through water flow and wind. Li et al. (2013) indicated that, fortunately, the risk assessment of the consumption of vegetables containing RE should not lead to an excess of the daily intake considered harmful to human health. There is still a lack of knowledge about the large-scale effects of RE in the environment, as well as their spatial distribution in urban contexts, where these areas are potentially most at risk.

RARE EARTH RESOURCES, SPECIATION AND RECOVERY PROCESSES

Natural Resources

They are known as “rare earths” because their history dates back to the end of the 18th century when the name “earth” was used for describing alkaline metal oxides and “rare” because they were found in low concentrations in the earth’s crust, insufficient to allow their exploitation (Migaszewski and Galuszka, 2015). Yet some RE are relatively abundant in the earth’s crust relative to other metals (Table 2). For comparison, average crustal abundances for gold, silver, lead, and copper are 0.004, 0.075, 14, and 60 mg/kg, respectively (USGS, 2014). Each RE has different abundance in the earth crust. The most abundant element is cerium with concentrations higher than those of copper or lead. Disregarding the extremely rare RE, i.e., promethium, all other elements are more abundant than silver, gold or platinum (Van Gosen et al., 2014). Ce are five times as much as lead, 880 times as much as silver and 16,500 as much as gold.

Although most RE are not currently rare in terms of total amounts in the earth’s crust, they are unevenly distributed and rarely occurred in sufficient abundance in a single location for their mining to be economically exploitable (Mehmood, 2018). In addition, they are usually found within other minerals such as phosphates, carbonates, fluorides and silicates and occur especially in pegmatites, granites and related metamorphic igneous rocks (Tyler, 2004), making extraction from the ore and processing both highly difficult and expensive. In addition, due to their similar chemical and physical properties, as mentioned above, it makes difficult to separate RE using common chemical methods relies on either an alkaline process that uses concentrated sodium hydroxide or an acidic process that uses concentrated sulfuric acid, both at high temperatures (Jha et al., 2016; Zhang et al., 2016).

Out of 200 known minerals containing RE (Walters and Lusty, 2011), only three are considered to be the main mineral deposits exploitable for extraction, (Gupta and Krishnamurthy, 2004; Tyler, 2004; Binnemans et al., 2013; Xie et al., 2014) i.e., 1) bastnaesites ((Ce, La) (CO₃) F) deposits in China and United States. They generally contain mostly light RE and provide more than 70% w/w of RE oxides, 2) monazites [(Ce, La, Nd, Th) PO₄; provide 35–71% w/w of RE oxides] deposits in Australia, Brazil, China, India, Malaysia, South Africa, Sri Lanka, Thailand, and the United States. They contain mostly heavy RE and a small amount of the light RE phosphate, 3) xenotimes (YPO₄; provide 52–67% w/w of RE oxides). Other instances of minerals known to contain RE include secondary monazite, ion absorption clays, spent uranium solutions, apatite, cheralite, eudialyte, loparite, phosphorites (Zhang et al., 2015; Jha et al., 2016).

According to estimates by the U.S. Geological Survey (2018), the worldwide reserves of RE by principal countries such as China, Brazil, Vietnam, Russia, India and Australia (in decreasing order of available reserves) are approximately 132 million metric tons in terms of rare earth oxides. Most of these reserves are located within China, and are estimated at some 44 million metric tons (US Geological Survey, 2018). China represents one third of the total global mining reserves in RE (33.33%), Brazil and Vietnam concentrate 16.67% of world reserves, followed Russia (13.64%), India (5.23%) and Australia (3.40%) (US Geological Survey, 2018; Balaram, 2019). The main sites current operations are in China (Bayan Obo, Inner Mongolia), United States (Mountain Pass, California) and Australia (Mount...
TABLE 2 | List of the rare earth (RE) found in natural deposits, classification and their abundance in the earth’s crust [in parts per million (mg/kg)].

| Element     | Symbol | Atomic number | Ionic radius (Å)b | Classificationb, c | Crustal abundance Min-max,d (means)* (mg/kg) |
|-------------|--------|---------------|-------------------|-------------------|------------------------------------------|
| Lanthanum   | La     | 57            | 1.03              | Light             | 5–39 (35)                                |
| Cerium      | Ce     | 58            | 1.01              | Light             | 20–70 (66)                               |
| Praseodymium| Pr     | 59            | 0.99              | Light             | 3.5–9.2 (9.1)                            |
| Neodymium   | Nd     | 60            | 0.98              | Light             | 12–41.5 (40)                             |
| Promethium  | Pm     | 61            | 1.85              | Light             |                                          |
| Samarium    | Sm     | 62            | 0.96              | Light             | 4.5–8 (7.0)                              |
| Europium    | Eu     | 63            | 0.95              | Light/Heavyb      | 0.14–2 (2.1)                             |
| Gadolinium  | Gd     | 64            | 0.94              | Light/Heavyb      | 4–8 (6.1)                                |
| Terbium     | Tb     | 65            | 0.92              | Heavy             | 0.65–2.5 (1.2)                           |
| Dysprosium  | Dy     | 66            | 0.91              | Heavy             | 3–7.5 (4.5)                              |
| Holmium     | Ho     | 67            | 0.90              | Heavy             | 0.7–1.7 (1.3)                            |
| Erbium      | Er     | 68            | 0.89              | Heavy             | 2.1–6.5 (2.5)                            |
| Thulium     | Tm     | 69            | 0.88              | Heavy             | 0.2–1 (0.5)                              |
| Ytterbium   | Yb     | 70            | 0.87              | Heavy             | 0.3–3 8 (3.1)                            |
| Lutetium    | Lu     | 71            | 0.86              | Heavy             | 0.35–1.7 (0.8)                           |
| Yttrium     | Y      | 39            | 0.90              | Heavy             | 24–70 (31)                               |
| Scandium    | Sc     | 21            |                   | Light             | 5–22 (ND)                                |

ND: Not Determined.
aShannon (1976).
bChakhmouradian and Wall (2012).
cLide (2004).
dGanguli and Cook (2018).
eGreenwood and Earnshaw (1984).
fPromethium is a radioactive metal and does not occur naturally on earth. It is artificially created for applications.

Weld, Australia-Western). While the United States was the world’s dominant producer through the 1980s, China’s low production cost for RE since the mid-1990s significantly reduced the prices of RE globally and has become the greatest world supplier which reportedly produces more than 95% of total RE oxide (Rüttinger and Feil, 2010; Zhang, 2013). As a result, many other mines worldwide stopped extracting these elements (Stone, 2009).

Currently, to protect its industry and to decrease the environmental impacts that may result from RE mining, China has reduced its production and restricted the supply of RE through quotas (Golev et al., 2014; Langkau and Erdmann, 2020). Thus, RE are currently placed on the list of “critical” resource for high technology industrial applications due to importance for strategic sectors of the economy and risks of supply shortage (Massari and Ruberti, 2013; Grabas et al., 2014).

Secondary Rare Earth Resources

The risk of missing RE led many countries to require secondary resources to meet their needs.

Currently, several secondary resources have been identified as having high RE concentrations including recycling of RE from manufacturing RE scrap and residues (Binnemans et al., 2013; Peelman et al., 2016). Also, recycling of RE from end-of-life products containing RE such as NiMH batteries, permanent magnets, fluorescent lamp phosphors, Fe-Nd-B magnets, Sm-Co magnets, voice coil motors and computer monitors (Binnemans et al., 2013; Zhang et al., 2015). In addition, the extraction of RE from mine waste or industrial landfill by-products (apatite rock, phosphogypsum waste, red mud, RE mineral mine tailings metallurgical slags, coal ash, incinerator ash and waste water streams) has been the focus of a number of studies (Binnemans et al., 2013; Hammas-Nasri et al., 2016; Antonick et al., 2019; Gasser et al., 2019; Masmoudi-Soussi et al., 2019; Jalali et al., 2020a).

RE can also be extracted from trace RE associated with minerals such as uranium ore, fluorite, sea sediments, and phosphate rocks (Chen and Graedel, 2015; Wu et al., 2018). Another way to manage the balance problem is to researching out new RE ore deposits or reopening pre-existing RE mine (Long et al., 2012). However, as above mentioned, RE are very dispersed due to their geochemical characteristics and not usually found concentrated as rare earth minerals in economically exploitable ore deposits (Balaram, 2019). Substitutes of RE in most cases either are inferior alternatives or still undiscovered.

Rare Earth Recovery Processes

Usually, the treatment of RE minerals involves two operation steps, i.e., a physical treatment and a chemical treatment: 1) Physical processing, also known as mineral enrichment, consists of separating the RE minerals from the gangue minerals to produce a RE concentrate, 2) The chemical treatment (Lin et al., 2017), which includes the extraction and separation processes, converts the RE mineral concentrate into a compound which is either a final or an intermediate product for the subsequent production of individual RE or other compounds. RE extraction processes use one or more regents to decompose the minerals and leach the RE into solution. For the RE separation, several processes can be used such as solvent extraction, ion exchange or chemical precipitation to produce
mixed or individual RE oxides (REO). Separation of mixed REO into the individual RE can partially be achieved by multiple recrystallization as double salts, and ultimately by multi-stage solvent extraction (Zhang et al., 2013; Haque et al., 2014).

RE production process must go through a series of complex separation processes to produce each individual element. Although there are several costs associated with RE, it is the separation process that largely dictates the cost of RE production. Recycling of RE from secondary resources offers great opportunities for countries with no primary resources. The different RE processes developed are based on acid or basic leaching stages depending on the type of resource treated, followed by a precipitation step to produce a solid of RE usable for various applications. It is clear that in addition to mitigating some supply risks, recycling of RE can minimize environmental problems related to their extraction and processing. Innovative and profitable technologies, which reduce considerably the environmental impact of all recycling streams compared to the primary extraction route, should be developed.

The costliest processes for primary RE mining route are physical separation and chemical leached of minerals (EPA, 2012), similar processes are also required for many recycling methods (Tanaka et al., 2013). However, the recycling can offer an opportunity to recover the desired elements, specifically targeting products with high concentration of certain valuable RE, on the contrary, with the mining where all the RE elements have to be extracted. Another advantage of RE recycling vs. mining is likely to be associated with the treatment and disposal of radioactive wastes arising from the processing of ore raw materials. Even though there has been minimal study to assess the real significance of radioactive pollution arisen from RE processing (Schmidt, 2013), it is evident that taking into account this issue would position recycling as more advantageous (EPA, 2012).

Recycling, cannot replace primary extraction of minerals and satisfy growing RE demand alone, due in particular to the delay induced by end-of-life products behind current requirements. Consequently, any global analysis of mineral raw material supply should consider both types of resources (Grosse, 2010). In addition, the advantages of producing RE concentrates as a secondary resource are that mining operating costs are low. This processing provides also environmental benefits by neutralizing acid producing steps and reducing the volume of waste storage. However, currently, most of these secondary resources are restricted to academic research due to the difficulties of collection, technique and economy (Borra et al., 2015; Davris et al., 2016).

**Speciation of Rare Earths in Different Matrices**

As above mentioned, the total RE contents of soils vary considerably, depending on the type of soil and of the parent rock from which they are issued (Liu et al., 1988; Xin et al., 2006). In addition, other RE sources in soils are atmospheric depositions (rainwater, atmospheric particles and snow) and spreadsings (fertilizers, waste especially phosphogypsum, irrigation and sewage waters (Aubert et al., 2002). The RE content in various components of the environment are shown in Table 3.

The effectiveness of phytoextraction is highly dependent on the availability of metals for plant uptake. In general, a higher availability of RE in soil induce a higher RE uptake by plants, as for all trace elements. The RE availability in soils is related to the water soluble and exchangeable fractions of RE, and thus is dependent on physico-chemical of soil properties such as pH, redox potential (Eh), cation exchange capacity (CEC), and clay content (Shan et al., 2002). For instance, the desorption of RE decreased with increasing equilibrium solution pH (Shan et al., 2002). The adsorption capacity of RE is significantly correlated with the CEC of soil (Shan et al., 2002). Johannesson and Lyons (1995) pointed out the important role of complexing RE with various ligands at different pH levels. RE complexation with carbonate ions predominates in the majority of natural waters with moderate to high pH where carbonates are the main component. Thus RE carbonate complexes dominate and typically account for more than 99% of all RE complexes in solution. At neutral pH, the speciation of the RE in complexes with carbonate includes LnHCO$_3^{-}$, LnCO$_3^{2-}$, and Ln(CO$_3$)$_2^{-}$, and that with phosphate LnH$_2$PO$_4^{-}$, LnHPO$_4^{2-}$, Ln(HPO$_4$)$_2$, and LnPO$_4$. In water with a acidic pH, free metal ions dominate the speciation of HRE (Ln$^{3+}$ account for 60% of total Ln and dominate the LnSO$_4^{2+}$ complexes) (Johannesson et al., 1996). RE release increases as redox potential and pH decrease (Jones, 1997; Cao et al., 2001). The mobilization of La, Gd, and Y depend mainly upon pH value, whereas the mobilization of Ce depends both upon pH and Eh. RE mobilization is positively correlated with that of Fe and Mn (Cao et al., 2001). Due to their higher mobility in soils, LRE are more easily absorbed and accumulated by plants than heavy RE since the latter form much more stable complexes in soil solution (Brioschi et al., 2013; Grosjean et al., 2020). Indeed, roots preferentially absorb free ions rather than dissolved complexes (Brioschi et al., 2013).

**PHYTOEXTRACTION AS A SUSTAINABLE SOLUTION FOR RE RECYCLING**

The decontamination of soils enriched with RE still requires costly techniques that sometimes generate associated pollution (use of acids). Phytotechnologies are a relevant alternative, suitable for in situ depollution, making possible to preserve the properties of soils which can then regain their vocation as a support for food production or at least to support plantations. Phytotechnologies go beyond the simple “soft” remediation function of plants for risk management and are more broadly integrated into the concept of phytomanagement (Cundy et al., 2013; Song et al., 2019), which brings together all the benefits that humans can derive from plants. This may involve maintaining or even improving biodiversity in the soil (fauna, micro-organisms), as well as preserving the integrity of the environment (fauna, flora and micro-organisms of concern), the physical integrity of the soil, e.g., by limiting erosion through revegetation. Plant biomass can be harvested and incinerated to recover target metals or to be
converted into renewable energy such as biofuel, biochar, charcoal, and essential oils. Plants help to sequester CO₂, to regulate its concentration in the atmosphere and limit global warming. Finally, plant management integrates cultural services with the possible reuse of vacant areas up to the creation of vegetated recreational spaces.

**Uptake of RE by Plants**

**Stimulating Vs. Adverse Effects of RE on the Plant Growth**

RE are not known to be essential for plants (Grosjean et al., 2019) but they can compete with calcium in a number of calcium-mediated biological processes, which could explain for some of the toxicity to plants (Brown et al., 1990). Due to their divalent charges and thus lesser charge density, Ca can probably be displaced by the trivalent RE (Ce, Eu, Gd, Ho, La, Nd, Pr, Tb and Y) at Ca-binding sites in biological molecules. Generally, RE toxicity is considered low. Therefore, at present there are no maximum permissible concentrations or threshold limits in the literature (Thomas et al., 2014).

In general, like other minerals, RE exhibit stimulating action on plant growth at low doses and their toxicity increases with concentration. The concentration of RE to become toxic vary according to the elements (Emmanuel et al., 2010; Zhang et al., 2014). In order to evaluate the effect and toxicity of RE on plant growth, the literature provides a certain amount of information concerning the physiological effects of RE on germination and plant growth (Table 4). A greater number of studies have been performed under hydroponic conditions that are not necessarily representatives of real conditions in soil (Thomas et al., 2014).

**Distribution of RE in the Different Parts of the Plants**

The main route of RE absorption, as most trace metals (TE), is mainly through root absorption of free ionic forms. After dissolving metal in the rhizosphere, two transport mechanisms

### TABLE 3: Concentration of rare earth elements (RE) in different components of the environment.

| Element | Air (pg/m³) | Soils (mg/kg) | Plants (µg/kg) | RE mining areas world average (µg/kg) | Tunisian phosphogypsum (mg/kg) |
|---------|-------------|---------------|----------------|-------------------------------------|-----------------------------|
| Light RE |             |               |                |                                     |                             |
| Lu      | Spitsbergen 0.4–3 | 0.06–0.45     | Vegetables 0.01–60; grass 3; pine needles 2 | 40 | 0.34 |
| Er      | 24          | 0.02–2        | Vegetables 0.5–2; pine needles 6; blue berry–leaves 1.5–8 | 0.6 | 3.89 |
| Ho      | 13          | 0.02–1        | Vegetables 0.06–0.1; grass <20; pine needles 4–5 | 2 | 1.32 |
| Tb      | Greenland 1–5; Germany 10; United States 20–35 | 0.05–1       | Vegetables 0.1–2; grass 9; pine needles 20 | 5 | 1.10 |
| Tm      | 4           | 0.03–0.05     | Vegetables 0.02–4; grass 50; pine needles 1.5 | 3 | 0.47 |
| Y       | Atmospheric dust 0.02–2 mg/kg. | World 5–24. Poland 5–12 | Different 0.01–3.5; lichens and briophytes 200 | — | 44.48 |
| Yb      | >10         | 0.07–2.5      | Vegetables 0.01–20; grass 20; pine needles 8 | 0.4 | 3.31 |
| Dy      | 40          | 1–5           | Vegetables 20; blue berry–leaves 21 | 0.6 | 6.62 |
| Sc      | South Pole 0.06–0.2; Spitsbergen 0.01–5; United States 80–3,000 | World; podzolic loam 5; brown 8; mold 10. Poland; sandy soils 2; clay 6 | Different 8–700; tea 10–140; fungi 2–300 | — | — |
| Heavy RE |            |               |                |                                     |                             |
| Gd      | 1           | 0.7–5         | Vegetables <2; grass 35; pine needles 25 | 0.7 | 7.20 |
| Ce      | South Pole. 0.8–5; Spitsbergen 20–60; Great Britain 330–550 | 2–75         | Vegetables 2–50; grass 330; pine needles 370 | 7 | 49.99 |
| Sm      | South Pole 0.03–0.1; Great Britain 20–40; United States 70–1,000 | 0.2–6        | Vegetables 0.2–100; grass 53; pine needles 32 | 1 | 7.14 |
| La      | South Pole 0.2–1.4; Spitsbergen 5–30; United States 500–9,000 | 1.5–40       | Vegetables 0.4–2,000; grass 170; pine needles 1–30 | 50 | 35.86 |
| Nd      | –300        | 1–30          | Vegetables 10; grass 150; pine needles 160 | 4.5 | 52.63 |
| Pr      | 60          | 1.5–9         | Vegetables 1–2; grass 40; pine needles 60–130 | 35 | 8.90 |
| Eu      | South Pole 0.004–0.02; Spitsbergen 1–2; Germany 5–80 | <1–1.5        | Vegetables 0.04–70; grass 8; pine needles 5 | 4 | 1.68 |

References: Kabata-Pendias and Pendias (1999) Kabata-Pendias and Pendias (1999) Kabata-Pendias and Pendias (1999) Wang et al. (1989) Hammas-Nasri et al. (2016)
of metals within plant have been identified. These are either through the apoplastic (passive diffusion) or symplastic pathways (active transport) (Shan et al., 2003). RE are transferred later to the erial parts (AP) in soluble form. The concentrations and distribution patterns are controlled by wall adsorption cell and phosphate precipitation of RE in the roots or at the roots surface (Ding et al., 2005). This process also partly determines the fractionation of RE in AP. The transfer of metal ions to AP is

| TABLE 4 | Physiological effects of rare earths on seed germination and plant root elongation. |
|---------|--------------------------------------------------------------------------------|
| Element | Species                        | Culture media            | Concentration | Effect                                      | References            |
| Nd      | Cassia obtusifolia             | BS solid medium          | 1 mg/L        | -↑ Seed germination                         | Zhang et al. (2013)  |
|         |                                |                          | 5 mg/L        | -↑ Seed germination                         |                      |
|         |                                |                          | 3 mg/L        | -↑ Optimal concentration                    |                      |
|         | Astragalus Angelica sinensis   | 10, 50, 80 et 100 mg/L   | -↑ Seed germination | Germination rate is optimal (57%) at Nd³⁺ concentrations around 80 mg/L |                      |
| La      | Bleé                           | Germination papers       | 1.3 à 1.389   | -↓ Germination                              | D’Aquino et al. (2009) |
| La + Eu | Eriobotrya japonica            | 1.0–3.0 mM               | -↑ Root length |                                           | Zhang et al. (2013)  |
| La      | Huperzia serrata               | 10 µM                    | -↑ Root growth |                                           |                      |
| Ce      | Dioscorea zingiberensis        | 50–100 µM                | -↑ Root growth |                                           |                      |
| Ce      | Arabidopsis thaliana           | 100 µmol/L               | -↑ The formation of root tissues and inhibits it in high concentrations- Disrupts the nutrients intrinsic balance |                      |
| La      | Triticum aestivum              | Hydroponic               | 0.5–25 mg/L   | -↓ Primary roots elongation                 | Hu et al. (2002)     |
| La + Ce | Hydrangea serrata              | 1.0–3.0 mM               | -↑ Root growth |                                           |                      |
| Ce      | Arabidopsis thaliana           | 0.5–10 mM                | -↓ Primary roots elongation                  | He and Loh (2000)    |
| La      | Zea mays                       | Continuous flowing solution | 0.2 µM     | Stage 17 days after germination: -No Effect |                      |
| La + Ce | Vigna radiata                  | 5.0 µM (0.2 µM)          | -↓ Zn and Mo accumulation in the roots      |                      |
| Ce      | Oryza sativa                   | 0.2 µM                   | -↓ K, Ca and Fe accumulation in the roots   |                      |
| Ce      | Zea mays                       | MES/Tris buffer          | 0.2 µM       | -↓ Growth: necrosis, chlorosis              |                      |
| Ce      | Zea mays                       | Containers with nutrient solution | 13.89 mg/L | -↑ 28% of root growth                      | Liu and Hasenstein (2005) |
| Ce      | Zea mays                       | Containers with nutrient solution | 138.9 mg/L | -↑ 42% of root growth                      |                      |
| Ce      | Zea mays                       | Containers with nutrient solution | 1,389 mg/L | -↑ 55% of root growth                      |                      |
| Ce      | Zea mays                       | Containers with nutrient solution | 2.7 mg/L   | -↑ 28% of root growth                      | Von Tucher et al. (2001) |
| Ce      | Zea mays                       | Containers with nutrient solution | 27 mg/L    | - No Effect                                |                      |
| Y       | Nymphoides peltata             | Hydroponic               | 1–15 mg/L    | -↑ Catalase activity                       | Fu et al. (2014)     |
| Ce      | Oryza sativa                   | Soil                     | 0–500 mg/L   | -↑ Lipid peroxidation; fatty acid and lignin content |                      |
|         |                                |                          |              | - Electrolyte leak                          |                      |
|         |                                |                          |              | -↑ H₂O₂ (oxidative stress)                 |                      |

MS: Murashige and Skoog Medium.
mainly carried out through the xylem (Marschner et al., 2012). Xylem cells have strong cation exchange capacities. Therefore, the combination with a ligand (organic acids and amino acids such as aspartic acid, glutamic acid, citric acid, malic acid and histidine) promotes the RE absorption and translocation from roots to aerial parts. Aspartic acid, asparagine and glutamic acid stimulate the lanthanum and yttrium transport in the xylem of Phytolaccaceae (Wu et al., 2009). Histidine increases LRE (such as La, Ce Nd, and Pr) desorption from soil, their uptake into the soil solution and their transport to the upper parts of Dicranopteris dichotoma (Shan et al., 2003). Zygyophyllum album a wild plant growing in soils in the vicinity to PG stockpiles in Tunisia was shown to be a promising candidate in RE phytoextraction, notably for La (Translocation Factor of 6.12) (Jalali et al., 2019). While the uptake and transport of RE in plants have attracted attention during the last decade, the available information on the functioning of the soil-plant system enriched with these elements is scarce (Hu et al., 2004).

The uptake of RE may be facilitated by increased levels of nitrogen and potassium fertilization. Hypotheses supporting the increase in RE uptake in the presence of Na and K maybe due to direct competition between RE and Ca at uptake sites or perhaps soil interactions prior to uptake but is more probably due to increased plant growth. While there was no such effect in the presence of phosphate fertilization, Brown et al. (1990).

The Use of Hyper-Accumulative Plants in the Context of Phytomining

Originally, the main objective of phytoextraction was the depollution of contaminated soils allowing polluted sites and soils rehabilitation (salt et al., 1995). Currently, the domain is more interested in cultivating hyperaccumulators plants to recover accumulated economically valuable metals (Rodrigues et al., 2016). These economic and environmental issues conduct to the creation of a new concept called “phytomining.” It is a phytotechnology that aims to rehabilitate contaminated or naturally metal rich soils by recovering metals of high economic value such as nickel or gold, from cultivated hyperaccumulator plants, that can absorb these elements and transfer them to their AP where they are accumulated, and then to reutilize these metals for industrial purposes (Van der Ent et al., 2015). Phytomining aims to develop a chain of an environmentally friendly process, as it is based on plant growth and recovery that minimizes the impacts on resources (Rodrigues et al., 2016). Initially, this chain consists of developing new agronomic practices to select the best hyperaccumulators plants allowing to optimize the extraction yields of valuable metals from the soil and to maximize the economic income (Brooks, 1998; Barbaroux et al., 2012; Van der Ent et al., 2015). Secondly, hydrometallurgical processes are developed and optimized to transform biomass into marketable metal compounds. The phytomining effectiveness depends on the amount of metals that accumulate in harvested biomass as well as the biomass yield that can be cultivated per year or per season.

To date, phytomining technology has been applied intensively in Ni phytoextraction (Barbaroux et al., 2012; Ye-Tao et al., 2012; Bani et al., 2018), but less attention has been paid to the study of accumulation RE mechanisms and phytomining potential of these elements. It is thus possible to consider the possibility of applying this concept for RE, in particular for the development of hydrometallurgical processes for the recovery and upgrading of metals from biomass. The first discovery of the RE accumulation in plants was reported by Robinson in 1943 in the leaves of Carya calathensis that reached 2,296 mg/kg DW of total RE (Robinson, 1943). Later, high concentrations of RE have been reported in different plant species. There are difficulties in applying the concept of hyperaccumulator thresholds to the RE (Van der Ent et al., 2021), some study in the literature reported concentrations of total RE whereas others focus on individual elements. Nevertheless, some publications have referred to hyperaccumulation of RE based on a criterion of 0.1 wt% [i.e., 1,000 mg/kg of dry matter (DM)] for the sum of all 17 RE of the AP (Wang et al., 1997; Shan et al., 2003). According to this criterion, to date, 10 species belonging to five families have been identified worldwide as RE hyperaccumulators: Blechnaceae, Gleicheniaceae, Juglandaceae, Phytolaccaceae and Thelypteridaceae (Table 5). In another research, the threshold concentration for RE hyperaccumulators could potentially be lowered to 100 mg/kg DM. Moreover, they are two indexes that describe respectively the metal accumulation ability from soil to plant and the metal transfer ability from roots to AP (Brooks, 1998): The Bioconcentration Factor (BCF) and the Translocation Factor (TF) whereby BCF is the RE concentration in the xylem plant and the metal transfer ability from roots to AP (Brooks, 1998; Brown et al. (1990), Dicranopteris dichotoma (3,358 mg/kg DW of Ce, La, Pr, and Nd mixture; Wang et al., 1997). To a lesser extent, other ferns could also accumulate RE, such as Carya tomentosa (1,350 mg/kg DW of total RE; Thomas, 2011), Pronephrium simplicifolium (1,234 mg/kg DW of total RE; Lai et al., 2005), Pronephrium triphyllum (1,027 mg/kg DW of total RE; Xue, 2009), Blechnum orientale (1,022 mg/kg DW of La, Ce, Nd, Sm, Eu, Tb, Yb and Lu mixture; Xiao et al., 2003) and Carya spp. (859 mg/kg DW of total...
TABLE 5 | Concentrations of rare earth element (RE) in hyperaccumulator plants (mg/kg)—A hyperaccumulation threshold of 1,000 and 100 mg/kg was adopted for the first 10 species and three species respectively.

| Element | Latin name | Family | Maximum contents in leaves (mg/kg) | BCF | References |
|---------|------------|--------|------------------------------------|-----|------------|
| Σ RE    | Blechnum orientale | Blechnaceae | 1,022 | ND | Xiao et al. (2003) |
|         | Caraya cathayensis | Juglandaceae | 2,296 | ND | Robinson (1943) |
|         | Caraya glabra | Juglandaceae | 2,300 | ND | Robinson et al. (1938) |
|         | Cary tamasota | Juglandaceae | 3,150 | ND | Thomas (2011) |
|         | Dicranopteris dichotoma | Gleicheniaceae | 3,358 | ND | Xiao et al. (2003) |
|         | Dicranopteris linearis | Gleicheniaceae | 7,000 | ND | Shan et al. (2003) |
|         | Phytolacca americana | Phytolaccaeae | 1,012 | ND | Yuan et al. (2017) |
|         | Phytolacca icosaandra | Phytolaccaeae | 13,000 | ND | Grosjean et al. (2019) |
|         | Proenephrum simplex | Thelypteridaceae | 1,234 | ND | Lai et al. (2005) |
|         | Proenephrum triphyllum | Thelypteridaceae | 1,027 | ND | Xue (2009) |
|         | Atryrium yokosence | Atryriaceae | 202 | ND | Ichinashi et al. (1992) |
|         | Stenoloma chusana | Lindaeaceae | 725 | ND | Xiao et al. (2003) |
|         | Woodwardia japonica | Blechnaceae | 367 | ND | Xiao et al. (2003) |
| La      | Adriantum monochlamys | Adriantaceae | 11 | >1 | Ozaki et al. (2000) |
|         | Aspleniun honoendae | Aspleniaceae | 14 | >1 | Ozaki et al. (2000) |
|         | Aspleniun filipes | Aspleniaceae | 25 | >1 | Ozaki et al. (2000) |
|         | Aspleniun ritoense | Aspleniaceae | 12 | >1 | Ozaki et al. (2000) |
|         | Aspleniun ruprechtii | Aspleniaceae | 40 | >1 | Ozaki et al. (2000) |
|         | Aspleniun subnomaile | Aspleniaceae | 14 | >1 | Ozaki et al. (2000) |
|         | Aspleniun trichomanes | Aspleniaceae | 21 | >1 | Ozaki et al. (2000) |
|         | Adriantum monochlamys | Adriantaceae | 11 | >1 | Ozaki et al. (2000) |
|         | Blechnum ripicium | Blechnaceae | 9.7 | >1 | Ozaki et al. (2000) |
|         | Dicranopteris strigoze | Gleicheniaceae | 12 | >1 | Ozaki et al. (2000) |
|         | Dryopteris erythrosora | Dryopteridaceae | 32 | | Ozaki et al. (2000) |

Σ RE: Total of the sum of 17 RE.

BCF: Bioconcentration Factor, i.e., the metal concentration in plant to the concentration in the soil ratio.

ND: Not Determined.

RE; Wood and Grauke, 2011). Phytolacca americana is a high biomass plant that is naturalized worldwide, and is able to accumulate RE up to 1,040 mg/kg of total RE in dry leaves, (Yuan et al., 2018).

As for most trace elements, the RE distribution among the main organs of vascular plants differs considerably. The roots generally accumulate the most RE. For example, the roots of Zea mays accumulate La concentrations 20–150 times higher than the leaves (Diatloff et al., 1999). Many studies have shown a decrease in RE concentrations in the order: root > leaf > stem > grain or fruits in a variety of crops such as corn, wheat, rice and paprika. In trees like those that produce, e.g., citrus fruits, the highest concentrations of RE are generally found in roots too. The same is true in seven species of tropical trees (Jureima-branca (Piptadenia stipulacea), Faveleira (Cnidoscolus phyllacinthus), Jureima-preta (Mimos hostilis), Caatingueira (Caesalpinia pyramidals), Manisoba (Mannihotea glaziovii), Burra-leiteira (Sapitm cicitricosum), and Umbu (Phytolacca dioica L.), where RE are also accumulated in the roots except cerium that tends to be concentrated in the bark (Nakanishi et al., 1997; Tyler, 2004). Among the plants identified, the natural perennial fern D. dichotoma (syn. D. linearis) grown in acidic soil in southern China, is the one that accumulates the most RE in mining areas of China. Li et al. (2010), first reported the accumulation of RE in this plant species in southern Jiangxi province in China. For many years, this plant has proven to be an ideal material for the study of RE in plants (Fa-Shui et al., 1999; Liang et al., 2014). In this plant, the Ce, Dy, La and Nd concentrations are in the order leaf > root > stem while those of Eu, Gd, Ho, Pr, Sm, and Y are in the order root > leaf > stem (Fa-Shui et al., 1999).

Hyperaccumulators such as D. dichotoma often adopt different mechanisms such as a defense strategy against metal stress, e.g., compartmentation of metals in vacuoles (Lasat et al., 1998; Yuan et al., 2001), complexing of metal ions with organic ligands (Lee and Kim, 1997) and coordination with histidine (Krämer et al., 1996). The identification of new fern species that are able to accumulate RE is of great interest. A recent study identified new accumulating species RE using a screening method for ferns grown on RE contaminated substrate. Three species reached more than 200 mg/kg: Onoclea sensibilis, Athyrium othophorum and Athyrium flax-femina (Grosjean et al., 2020).

Associating Microorganisms With Plant for Increasing the Phytoextraction Performance of RE

For non-hyperaccumulating plants, i.e., bioindicator plants, whose accumulation level depends on the pool of RE in the soil solution, one way to improve phytoextraction performances consists in promoting the mobilization of RE with the help of microorganisms to increase its pool in solution. In addition to that, microorganisms, in particular the Plant Growth Promoting Rizobacteria (PGPR), may improve the plant growth and health.
Mobilization of Rare Earth by Rhizosphere Bacteria

Microorganisms are involved in all geochemical cycles of TE including RE. While lanthanides can substitute for Ca$^{2+}$ in some enzymes and tissues, because their similarities in terms of ionic radius (Lim and Franklin, 2006; Pagano et al., 2015), scientists have long considered RE to be inert because of the low solubility of these elements in the environment. Since 2011, it has been discovered that RE such as Ce$^{3+}$ and La$^{3+}$ are required for the activity of methanol dehydrogenase enzyme used by some bacteria to oxidize methanol for carbon and energy (Hibi et al., 2011; Pol et al., 2014). Thus, many studies have been undertaken for a better understanding of the interactions between microorganisms and RE, such as RE mobilization from solids through metabolic reactions (Brandl et al., 2016) and RE immobilization from liquids through sorption by biomass. The mobilization of TE by microorganisms from all solid matrix including those containing RE occurs thanks to three mechanisms 1) proton induced solubilization (acidolysis) with the mobilization by formation of organic/inorganic acids, 2) ligand induced solubilization (complexolysis) with the mobilization of RE from mineral surfaces by excretion of complexing agents, and 3) oxidation/reduction reactions (redoxolysis) resulting from the mobilization of RE by oxidative or reductive reactions (Brandl, 2001). Various parameters such as pH, oxidation-reduction conditions, the presence and nature of mineral and organic colloids as well as the presence and activity of microorganisms influence this mobility (Cao et al., 2001).

Since microorganisms have different optimum growth pH, it is essential to identify pH conditions that promote the production of the most beneficial microbial agents for the leaching of RE. For example, under controlled conditions, a fungus isolated (but no identified) from a carbonate rock was shown to be able to mobilize Ce and Eu of a dolomite at acidic pH (Dou and Lian, 2010) while Arthrobacter sp. leads, between pH 6.5 and 7.5, to mobilize all the RE from hornblende (Brantley et al., 2001).

In another example, it has been shown that at low pH values of bioleaching cultures (<2) Aspergillus niger produces mainly citric acid, while at higher pH values (>4) it tends to produce gluconic and oxalic acids (Brisson et al., 2016; Rasoulinia and Mousavi, 2016). These acids are well known for their ability to mobilize TE among which RE.

Since most of the RE are found in oxidation state III, they are quickly adsorbed by a large variety of bearing phases in soil, such as oxides and metallic hydroxides. For example, manganese oxides (Mn(III), Mn(IV)) strongly adsorb trivalent RE, in particular Ce(III), much more than La and Pr, and oxidize it to Ce(IV) (Takahashi et al., 2000; Ohta and Kawabe, 2001). These adsorption reactions and oxidation-reduction will also be influenced by the organic matter content and the competition phenomena between ligands. Once mobilized, bacterial interactions with RE will modify their behavior and transfer in the environment. Ohnuki et al. (2015) showed that the adsorption of Ce by P. fluorescens in Ce(III) form prohibited its subsequent oxidation to Ce(IV) by manganese oxides, thus modifying its transfer.

In an attempt to understand the fundamental mechanisms of monazite bioleaching by Enterobacter ergonos, Fathollahzadeh et al. (2018) has demonstrated that the contact of bacteria with minerals can have a significant effect on their capacity to increase mineral dissolution. The ability of phosphate-solubilizing microorganisms to solubilize RE-phosphate minerals can occur by contact mechanisms, non-contact mechanism, or a combination of both. In contact leaching, attached cells solubilize phosphate within a matrix of extracellular polymeric substances and mobilize RE(III) into the solution. Organic acid anions secreted by the cells from organic substrates (e.g., glucose) may complex RE(III). Following proton dissociation of organic acids, free protons also attack the ore surface resulting in further phosphate solubilization. Incorporation of phosphate into the biomass enhances RE(III) solubility. Alternatively (non-contact leaching), attached cells may play a role in organic acid production while suspended cells incorporate phosphate from solution increasing RE(III) solubility.

The potential roles of native bacteria in mobilization of RE from ores, in which the density of these elements is low, are only slightly documented. The extremely varied metabolisms of microorganisms allow them to interact closely with the mineral component of their environment. Microbial extracellular polysaccharides can increase the RE dissolution by complexing the ions of the solution thus lowering the saturation level of the latter (Banfield et al., 1999; Welch et al., 1999). The bacteria can solubilize the metals or increase their bioavailability by the production of siderophores and afterward adsorb the metals on their biomass, on metal-induced outer membrane proteins and by bioprecipitation (Diels et al., 2009). Loges et al. (2012) have shown that siderophores have a very strong affinity for Ce (IV). The formation of RE (La, Sc and Y)-siderophore complexes was observed in Mycobacterium smegmatis by Andrés et al. (1991), as well as the sorption of Eu, La, Th and Yb on the same bacterial cells (Andrés et al., 1993; Andrés et al., 1995). These same authors observe the sorption of Gd in Bacillus subtilis, Pseudomonas eruginosa, Ratstonia metallidurans CH34 (renamed Cupriavidus metallidurans CH34), M. smegmatis and Saccharomyces cerevisiae (Andrès et al., 2000), La, Eu and Yb in P. eruginosa (Texier et al., 2000; Texier et al., 2002), Ce and Nd in Bacillus cereus, Sc and Sm in Arthrobacter luteolus isolated from an environment rich in RE (Emmanuel et al., 2011; Emmanuel et al., 2012).

Many phosphate solubilizing microorganisms (PSM), such as E. ergonos, Pantoea agglomerans, Pseudomonas putida have demonstrated to grow in the presence of natural RE phosphate minerals, releasing RE, iron and thorium (Corbett et al., 2017). Qu et al. (2019), studied the RE bioleaching performance of chemoheterotrophic bacterium (Acetobacter sp.) from red mud. The results showed that the leaching ratios of Al, Lu, Sc, Th, and Y were 55, 53, 61, 52 and 53% respectively under one-step process at 2% red mud pulp density. Other studies reported that the highest percentages of bioleached total RE from monazite and (Th-U) concentrate directly by Aspergillus ficuum, are found to be 75.4 and 63.8% at a pulp density 0.6 and 1.2% (w/v), respectively, after 9 days and 63.5 and 52.6% by Pseudomonas eruginosa after 8 days (Hassanien et al., 2014). Also, fungal strains able to solubilize...
phosphate minerals such as *A. niger* have shown potential for RE bioleaching from monazite (Castro et al., 2020). Several other fungal strains have been also used to leach monazite releasing RE to the aqueous phase such as *Aspergillus terreus*, *Paccilomyces* spp. and *Penicillium* sp. that can release a total concentration of 12.32 mg/L RE (Ce, La, Nd, and Pr) from the weathered monazite after 8 days (Castro et al., 2020). Another study with *A. niger* reported that the highest rates of RE from monazite were obtained when the fungus was cultivated on minimal medium with the mineral as the sole phosphorous source.

Concentrations of RE leached by other fungal species, such as *A. niger* and *Aspergillus tubigenis*, were 24 times lower than *Penicillium* sp. (0.44 and 0.43 mg/L, respectively). Bacterial species such as *P. agglomerans*, *E. erogenes*, and *P. putida* released round RE into solution at also quite low concentrations (1.63, 1.93, and 1.45 mg/L, respectively). While the complexity of the process is low, other bacteria have demonstrated that they were more able to solubilize Ce and La from monazite ore: ca. 5.7 mg/L of Ce (0.13% of leaching efficiency) and ca. 2.8 mg/L of La (0.11%) were leached by *Acetobacter aceti*, and *Azospirillum brasilense*, *Azospirillum lipoferum*, *Pseudomonas rhizosphaerae* and *Mesorhizobium cicer* leached 0.5–1 mg/L of both Ce and La (Shin et al., 2015).

In addition, anaerobic bacteria have been applied for the mobilization of RE from solid waste such as phosphogypsum. Almost 80% of Yttrium was mobilized from phosphogypsum in a fixed-bed reactor by *Desulfovibrio desulfuricans* (Dudaney and Sbai, 1993). Total RE was mobilized from gibbsite samples by *Acidithiobacillus ferrooxidans* with efficiencies of 67.6% (Brandl et al., 2016).

The combination of native consortia presents on the ore with the inoculation of a PSM leached a greater amount of RE than a single PSM or than the native population alone, due to a syntrophic effect between populations (Corbett et al., 2018). In addition, PSM produce both alkaline and acid phosphatases, either intracellular or secreted extracellularly, enabling the hydrolysis of phosphoric compounds and the release of RE into the leachate. The combination action of acid phosphatase activity and organic acids increase RE solubilization in monazite (Corbett et al., 2018). More information for microbial RE mobilization from solid matrices were reviewed by Brandl et al. (2016).

**Effect of Microorganisms (PGPR) on the Plant Growth**

The rhizosphere contains 10–100 times more microorganisms per gram of soil than the non-rhizospheric soil, due to the release of carbon and nitrogen compounds belonging to rhizodeposits (Cunningham and Ow, 1996). Thus, plants have close interaction with rhizospheric microbes, some of which being able to improve their growth and development by increasing the absorption of nutrients and their tolerance to telluric pathogens and various other stresses (Lebeau et al., 2008). Rhizospheric microorganisms can also modify the mobility and availability of metals present in the soil (Abou-Shanab et al., 2003; Bani et al., 2007; Lebeau et al., 2008). PGPR (which stands for Plant Growth-Promoting Rhizobacteria) play a key role in stimulating plant growth and improving the tolerance to abiotic stresses (Dimkpa et al., 2009; Aransiola et al., 2019). Generally, PGPR isolated from the rhizosphere belong to different bacterial families, including *Achromobacter*, *Arthrobacter*, *Azotobacter*, *Azospirillum*, *Bacillus*, *Burkholderia*, *Enterobacter*, *Micrococcus*, *Pseudomonas*, *Rhizobium* and *Serratia* (Gray and Smith, 2005; De Zelicourt et al., 2013). These bacteria possess the capacity to increase the plant biomass and/or to mobilize the soil metals. Processes such as chelation and protonation are the main drivers for the mobilization of TE to which RE belong (Kidd et al., 2009; Cabello-Conejo et al., 2014). Some bacteria produce organic acids (oxalate, malate and citrate . . .) capable to dissolving silicates, thus making metal more available (Khan, 2005; Lebeau et al., 2008; Braud et al., 2009). Thus, the interactions between plant and microorganisms influence the RE mobility and their availability for plants (Sessitsch et al., 2013), promoting the transfer of RE from rhizosphere to plant and therefore contribute to improving phytoextraction performance.

The stimulation of plant biomass results from two actions, the first of which being the production of phytohormones like indole acetic acid (IAA) (Patten and Glick, 2002). A small concentration of IAA in the rhizosphere stimulates the elongation of primary roots (within the young shoots), whereas stronger concentrations inhibit this elongation while promoting a lengthening of the lateral and adventive roots (Xie et al., 1996). The second justification entails the production of enzymes like 1-amino cyclopropane-1-carboxylate (ACC) deaminase. Many PGPR are capable of splitting the ACC produced by plants, a precursor of ethylene, a phytohormone involved in modulating the growth and cellular metabolism of plants (Ping and Boland, 2004). Hence ACC deaminase contribute to reduce the ethylene content for plants subjected to stress, e.g., TE-related stress (Belimov et al., 2005). On average, the use of PGPR reduces the rate of ACC and ethylene by a factor of 2 up to 4 (Belimov et al., 2005).

Modifying metal mobility in the soil can be explained by microbial complexation with microbial metabolites, such as siderophores, some small molecules with a molecular weight ranging from 150 to 2,000 Da. These siderophores are known for their very high affinity for iron from 1023 up to 1052 M−1 (Hernlem et al., 1996; Hider and Kong, 2010; Khan et al., 2018). They are produced by various microorganisms when iron is in short supply [<10 μM (De Villegas et al., 2002; Braud et al., 2009)] for the purpose of solubilizing and acquiring this vital metal of limited bioavailability. The roots can thus incorporate the iron from bacterial siderophore-iron complexes by a mechanism of either chelator degradation accompanying the iron release or a direct incorporation of these complexes (Rajkumar et al., 2010). The siderophores, like pyoverdine and pyochelin, can also complex other metals, e.g., copper (Cu) and nickel (Ni) (Braud et al., 2009).

**Bioaugmentation Coupled With Phytoextraction for the Treatment of Rare Earth**

The slowness of phytoextraction constitutes its main drawback, which is sometimes prohibitive. Among various solutions to increase the phytoextraction rates, the association of microorganisms (bioaugmentation) with plants (phytoextraction),...
in particular PGPR has been the subject of growing interest for the past ten years (Lebeau et al., 2008; Sessitsch et al., 2013; Xu et al., 2014). In both natural and anthropized ecosystems, bacteria associated with plants, in addition to stimulating their growth, play a key role in the adaptation of their hosts to changing environments (Ma et al., 2011). Different direct mechanisms (solubilization of phosphorus and potassium, nitrogen fixation, iron sequestration by siderophores, hormone production) or indirect (reduction in the number of pathogens by the production of antibiotics as well as the iron available in the rhizosphere for phytopathogens) are involved (Glick, 1995; Lucy et al., 2004). The production of phytohormones by bacteria associated with plants, such as auxin (indole-3-acetic acid, AIA), cytokinins and gibberellins, frequently leads to stimulation of germination, growth and reproduction while by protecting the plant from both biotic and abiotic stresses (Taghavi et al., 2009). Although several conditions, including stimulation of plant growth, accumulation and tolerance to metals, can effectively enhance phytoextraction rates, the concentration of metals available in the rhizosphere greatly influences the amount of metals accumulated in the plants. Indeed, a significant proportion of TE is generally related to organic or inorganic constituents in polluted soils and their phytoavailability is closely linked to their chemical speciation (McBride, 1989). Nevertheless, the metabolites released by bacteria in the rhizosphere (siderophores, acids organic, plant growth regulators) can promote or, on the contrary, alter the uptake by the plant. According to the literature, in a contaminated medium the plant/bacteria association can increase, in 60% of studies, the biomass of the plant by 1.2–4 times and/or the metal concentration in the leaves from 1.1 to 3.1 times (Lebeau et al., 2008). The microorganisms used in bioaugmentation can result from selections made from environmental samples (soil, sediment, waste, sludge, etc.) (Vogel, 1996). The use of bacteria capable of mobilizing TE and/or stimulating plant development (PGPR properties) may serve to increase the amount of TE extracted in this manner and hence the efficiency of phytoextraction. The microorganisms used for the bioaugmentation of metal-contaminated soil may be sourced using selections among environmental samples (Bois et al., 2011; Lebeau, 2011). They are then cultivated and inoculated in either their native environment or another environment. For RE, Jalali et al. (2020a) selected bacteria derived from contaminated soils in the vicinity of phosphogypsum stockpiles for TE including RE (Ce, La, Nd and Y) mobilization (siderophore production) and plant growth promotion (IAA, ACC deaminase production). Attention has also been paid to the use of genetically modified microorganisms for bioaugmentation, but their introduction into the environment must be carefully controlled (Sayler and Ripp, 2000).

Despite the growing concern on the environmental impact of an increasing use of RE in agriculture and their effects on plant growth and productivity (Reddy et al., 2001; Tyler, 2004; Balaram, 2019), only a few studies have been devoted to extraction RE using coupled bioaugmentation-phytoextraction which have taken into account, only the effect of bacteria on the biomass. Treatment with Arbuscular mycorrhizal fungi significantly increase N, P, and K content in shoots and roots of Astragalus sinicus and growth of Zea mays and Sorghum bicolor in soil enriched with RE (Chen and Zhao, 2009; Guo et al., 2013). The dry weight biomass of the investigated plants increase by 211% up to 387% in shoots and roots as compared with the non-inoculated treatment. Trifi et al. (2017) revealed that Pannoza sp. BM17, an isolated bacterium of Tunisian phosphogypsum, produces siderophores, IAA and ACC deaminase. Its addition to a soil amended with 2% PG has enabled increasing the biomass of the stems and roots of cultivated Brassica napus. A recent study by Jalali et al. (2020a, 2020b) reported that Bacillus as PGPR promoted barley seedlings growth mainly via production of organic acid, ACC deaminase and the association of Trifolium pratense, with Bacillus sp. stimulate the growth of this plant (i.e., factors of 3.7 for in AP and 3.1 in roots) and while increasing the Cd, Sr and RE (Ce, La, Nd, Sr and Y) concentrations respectively by factors of 6.4, 0.6, 0.93, 0.58 and 5.5 in AP. Also, Bacillus sp. strain is especially promising, in association with Helianthus annuus, for Ce, La, Nd and Y, with plant concentrations being raised by factors of 4.4, 38.3, 3.4 and 21, respectively in the AP. A major increase was also observed in the AP biomass of H. annuus by factors of 3.36. In addition, the translocation factor was increased for all MTE and is ranged between 1.1 for Sr and 6.8 for Y.

**CONCLUSION**

Conventional extraction and recovery of RE by physico-chemical methods has three major limitations: 1) extraction of RE is via chemical treatment using strong acidic and alkali solutions at high temperature, 2) RE are found mixed in the ore, and thus chemical separation of each element leads to an overall inefficient recovery, and 3) the extraction efficiency is dependent on ores containing high concentrations of RE, which prevents the recovery of less concentrated sources of RE. Green and efficient extraction techniques are receiving increasing attention. Bioaugmentation-enhanced RE phyтомining is an innovative technology that offers an alternative to physico-chemical methods of recycling RE, which could contribute to a more sustainable world and help to avoid risks of supply disruption and market dependencies.

Based on the limited reports of the association of bioaugmentation with phytoextraction for the treatment of RE, the review highlights the need for more detailed studies on this process. It has been shown the phytoextraction potential of various plants, but from a more fundamental point of view, the study of the mechanisms involved in its tolerance to RE could be investigated more in depth. It would especially be relevant to study more accurately the mobilization of RE by bacteria. Their ability to survive, colonize the soil, and maintain their PGPR and RE mobilization activities must be specified. From an application point of view of the process associating bioaugmentation with phytoextraction, several studies can be undertaken, in particular the identification of local spontaneous plant species with high biomass capable of accumulating RE and...
implementing technical routes (from seed collection to sowing and harvesting). Also, the use of wild plant growing in soils containing RE could increase the efficiency of phytoextraction.

As the main factor of failure of bioaugmentation is the stress to which the microorganisms inoculated in the soil or the growing medium are subjected, the optimization of the survival of these microorganisms and their colonization of the rhizosphere is of paramount importance. Inoculation modalities could be tested such as the inoculation technique (free or immobilized microorganisms); the direct coating of the seeds would also be tested.

A final perspective would be to develop and optimize processes for valuing the plant biomass collected and recovering RE, like what has been developed for nickel (phytoming, agromining and recovery of Ni sulfate).

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JL wrote the first draft of the review. TL has initiated this review, helped structure it, proofread it, correct and complete it.

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