



# Biosorption as green technology for the recovery and separation of rare earth elements

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## Abstract

Rare earth elements (REE) have great demand for sustainable energy and the high-end technology sector. The high similarity of REE owing to the nature of their electronic configurations increases the difficulty and costs of the development of chemical processes for their separation and recovery. In this way, the development of green technologies is highly relevant for replacing conventional unit operations of extractive metallurgy, viz. precipitation, liquid–liquid and solid–liquid extraction, and ion-exchange. Biosorption is a physicochemical and metabolically-independent biological process based on a variety of mechanisms including absorption, adsorption, ion-exchange, surface complexation and precipitation that represents a biotechnological cost-effective innovative way for the recovery of REE from aqueous solutions. This mini-review provides an overview and current scenario of biosorption technologies existing to recover REE, seeking to address the possibilities of using a green technology approach for wastewater treatment, as well as for the recovery of these high valued elements in the REE production chain.

**Keywords** Biosorption · Rare earth elements · Recovery

## Rare earth elements

The rare earth elements (REEs) are listed in the periodic table located in the lanthanide series ( $Z=57$  to  $71$ ), including yttrium ( $Z=39$ ) and scandium ( $Z=21$ ), which have very similar chemical and physical properties. On the basis of their atomic weight, REEs are divided into light REE (LREEs)—lanthanum through gadolinium ( $Z=57$  to  $64$ ); and heavy REE (HREEs)—terbium through lutetium ( $Z=65$  to  $71$ ). The high similarity comes from the nature of its electronic configurations that result in a highly stable  $3+$  oxidation state (Richard and Fan 2018; Owens et al. 2019).

The numerous applications of REEs are due to their spectroscopic and magnetic properties and involve different areas of knowledge. The LREEs have been applied to the manufacture of permanent magnets, phosphors (i.e., substances that emit luminescence), magnetic resonance imaging, battery alloys, fluid catalytic cracking, ceramics, polishing powders, catalysts, and metallurgy excluding batteries. In

turn, the HREEs are used in permanent magnets, ceramics, phosphors, portable X-ray devices, and as glass additives (Chararlampides et al. 2015; Suli et al. 2017; Giese 2018; Balaram 2019).

The high market value of REEs is due to the high cost and the extreme difficulty of separating these elements in high purity form (Silva et al. 2018). These elements have been extracted from primary ores in limited regions of the world by energy-intensive processes. Extraction of REEs from bastnasite ((La,Ce)FCO<sub>3</sub>), monazite ((Ce,La,Y,Th)PO<sub>4</sub>) and xenotime (YPO<sub>4</sub>) have been performed using physical processes through particle size separation, flotation and magnetic separation. Classic methods of hydrometallurgy have been used for the separation, preconcentration or removal of trace REEs from various matrices. After the beneficiation steps, REEs are then separated by chemical processes involving hydrometallurgical methods based on liquid–liquid (solvents) or solid–liquid (ion-exchange resins) extraction (Suli et al. 2017).

Recent reports classify REEs as Critical Raw Materials because they are not available in most geographical locations. China provides 95% of the world's supply of REEs; on the other hand, developed countries whose manufacturing or technology base depends upon imported REEs have

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commenced seeking alternative secondary sources. Since these countries import REEs and manufacture a number of electrical and electronic equipment, these countries also discard sizeable quantities of *e*-waste materials that can be in “urban mines” rich in precious metals and REEs (Xavier et al. 2019). Consequently, urban mining of REEs is emerging as a sustainable alternative to primary ore mining (Wang et al. 2017).

Recovery of REEs from secondary sources is also possible, but remains a technological and economic challenge. Impediments on recovering strategic minerals from both primary ores and *e*-waste are identified with traditional processes, such as pyrometallurgical and hydrometallurgical systems, which are fast and efficient, but cause environmental contamination and are often not economically viable (Das and Das 2013). Although the strategies mentioned above are efficient, innovative work is being conducted to improve the extraction of REEs from different sources, as well as to improve selective separation of each element in the REEs series (Yesiller et al. 2013).

## Biosorption as green technology processes in recovering REEs

Biosorption is considered an economical, simple and environmentally-friendly process that has been studied as an alternative to hydrometallurgy for the preconcentration, or as a separation of high-demand and high-valued metals from ores and waste solutions. Over the past decade, a number of significant contributions to the adsorption of REEs using biosorbents have been made (Das and Das 2013; Gupta et al. 2019). In this sense, the use of biosorbents is promising because it also presents as a viable cost-effective industrial process at the expense of the environmental impact of similar technologies (Volesky 2007).

Biosorption is a term that describes “the removal of metal ions, radioisotopes or REE elements by their passive binding to active, or dead, biomass materials in aqueous solutions”. In this process, the ion-biomass interaction is based on the chemical properties of biosorbent cell coatings and not on their biological activity (Gadd 2008; Beni and Esmaili 2020).

The use of biosorption within an industrial process is encouraged by the lower cost of operation as well as biosorbent material. Other advantages include the high efficiency in the removal of metal ions in solutions containing low metal concentrations, the easy regeneration of the biosorbent for recycling and reuse, and the recovery potential of the biosorbed elements, as well as the minimization of residues and rapid adsorption kinetics (Olukanni et al. 2014; Gupta et al. 2019).

In addition to serving as a preconcentration tool, recovery and selective separation of REEs, biosorption is an eco-friendly approach to eliminate REEs from waste streams as a priority concern due to their accumulation and exertion of toxic effects on living systems. Physicochemical methods such as coagulation, membrane separation and solvent extraction have historically carried out the recovery of heavy metals from aqueous solutions; however, some of the traditional processes are expensive and inefficient at low metal concentrations and also generate unwanted secondary residues (Hisada and Kawase 2018).

Presently, biosorption remains exclusive for the removal of heavy metals or textile dyes from the industrial wastewaters; however, the progressive approach of developing an efficient and selective biosorption process at a viable economic cost has extended the recovery and separation of REEs. Recent published studies by Ponou et al. (2014), Kucuker et al. (2017), Piazza et al. (2017) and Ramasamy et al. (2018) demonstrated respectively, the possibility of biosorption for industrial applications to recover REEs from clay minerals, hard-disk drive magnets, *e*-waste, and acid mine drainage. Further investigations are anticipated to comprehend the selectivity of biosorption of REEs for their recovery from solutions containing multiple elements (Gupta et al. 2019).

## Mechanism of REE biosorption

Overall, the uptake mechanism of REE is not an easy issue to tackle. Because of their capacity for complexation by different types of ligands, these metals possess rich solution chemistry. It has been reported that in the presence of OH ligands, a variety of lanthanide species might form, which including  $\text{Ln}(\text{OH})^{2+}$ , e.g., in addition to polymeric species (Wood 1990). Unless the concentration of hydroxide is high, 3+ is the dominant state of oxidation of REEs in aqueous solution. This high state of oxidation makes REEs behave as strong acids that can strongly bind to groups of oxides and metal hydr(oxy) REE bonds are expected to primarily have an electrostatic rather than a covalent character in such complexes. Furthermore, it was suggested that REEs are taken up on oxide surfaces on heteronuclear surface sites. Such reactions can produce a variety of surface species depending on the conditions of operation, surface nature, and chemical REE form. In this scenario, it is suggested to include two charged and two neutral sites per adsorbed metal (Yesiller et al. 2013).

In addition, biosorbents have been found to be highly specific to certain elements of particular interest and often have a high capacity for adsorption. Biosorption of REE elements can be considered mostly as an ion-exchange process based on the functional groups present on the surface of organisms.

Substances present on microbial cells, such as polysaccharides, glycoproteins and lipids can act as functional groups in the uptake of REEs through binding sites such as carboxyl, amino, sulfhydryl, phosphate and hydroxyl groups, among others as shown in Fig. 1.

Different types of algal biomass (red, brown and green) have cellulose, carrageen, and alginate as their constituents. These polysaccharides have functionalities such as  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{NH}_2$ , and  $-\text{SH}$ , and are responsible for selectively binding metal ions (Cheng et al. 2019). Fungi are eukaryotic organisms that have chitin (a carbohydrate biopolymer composed of N-acetylglucosamine repeat units) as a constituent of their cell wall. The fungal cell wall is filled with functionalities such as amine, imidazole, phosphate, sulfate, thiol and hydroxyl (Beni and Esmaeili 2020).

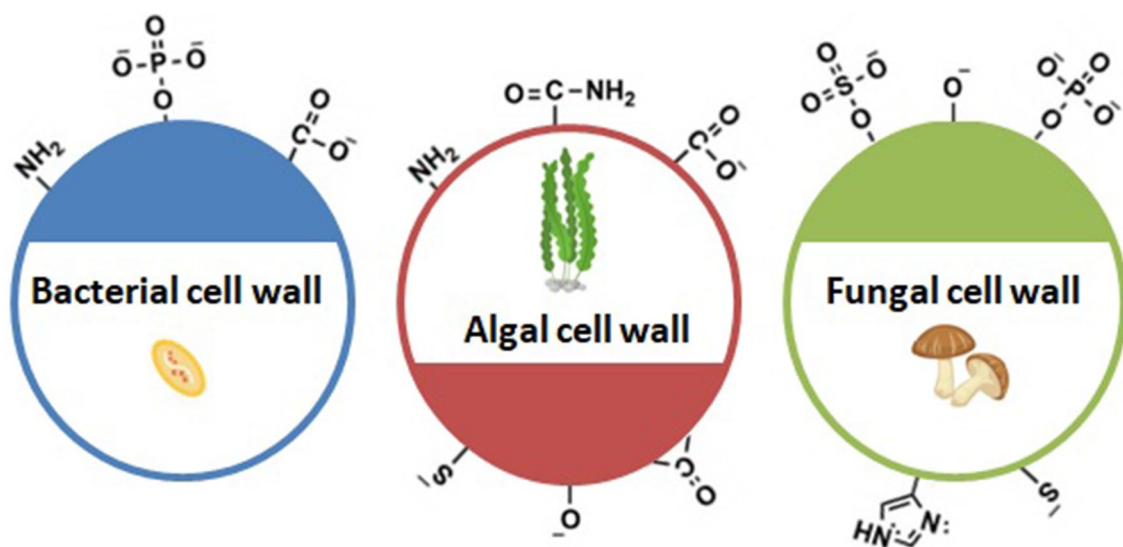
The total adsorption cycle is entirely dictated by the distribution of active sites on a biosorbent surface. Since adsorption is a surface process, a biosorbent with a very large surface area favours metal ion adsorption, as it provides a large area of contact for the interaction of metal ions (Beni and Esmaeili 2020). The biosorbent used in the biosorption process must be metabolically inactive. This characteristic of the material is important because it allows the recovery of REEs and enables their reuse. The advantage of using inactivated biomass as biosorbents is that living cells have growth limitations, mainly due to the toxicity of the cells by the REEs in solution, in addition to the environmental conditions of the biosorption process, such as the pH of the medium, which tends to be acidic to ensure the solubility of REE ionic species (Andrès et al. 2003).

In algae, specifically, the cell wall matrix is composed of a variety of polysaccharides and proteins, some of which contain anionic functional groups, e.g., carboxylic, sulfate

and phosphate groups for biosorption (Klimmek et al. 2001). Since lanthanides are considered strong acids (Brookins 1989), these ions will preferentially bind to strong bases containing oxygen as the electron-donating atom. This means that REEs bind weakly to weak bases, such as those that have S or P as ion donors. Among the ligands on the algal cell surface, the dominant ligand that contains at least one donor oxygen atom are the carboxylic and hydroxyl ionic groups (Birungi and Chirwa 2014; Diniz and Volesky 2005).

Diniz and Voleski (2005) demonstrated that the  $\text{Ca}^{2+}$  ions exchange for  $\text{La}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Yb}^{3+}$  binding in *Sargassum polycystum*, and occurs in the ratio of 1:1. The cationic exchange was also observed by Vijayaraghavan et al. (2010) using energy-dispersive X-ray spectroscopy (ED-XRF) analysis, and demonstrated that  $\text{Ca}^{2+}$  peaks on the cell surface of brown algae, *Turbinaria conoides*, were reduced when new  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Yb}^{3+}$  and  $\text{Eu}^{3+}$  peaks biosorbed were present.

Chemical modification of biomass is generally intended to increase biosorption capacity and affinity for an ion of interest. In general, modification procedures include pretreatment, enhancement of the binding site, modification of binding sites and polymerization (Vijayaraghavan and Balasubramanian 2015). Acid pretreatment is one of the most common methods for cleaning biomass, but it is also possible to perform alkaline treatment, ethanol and acetone (Zhang et al. 2010; Rehman et al. 2013; Giese and Jordão 2019). In order to inactivate the biomass to be used as biosorbent, drying, heating and freezing processes are routinely used—the lyophilization process does not compromise the biomass adsorption capacity. Maintaining the integrity of the cell wall lining during the inactivation process is essential to preserve the biosorptive characteristics of biomass (Ribeiro et al. 2010).



**Fig. 1** Active functional groups of microbial cell surfaces involved in the biosorption of rare-earth elements

## Factors affecting REE biosorption

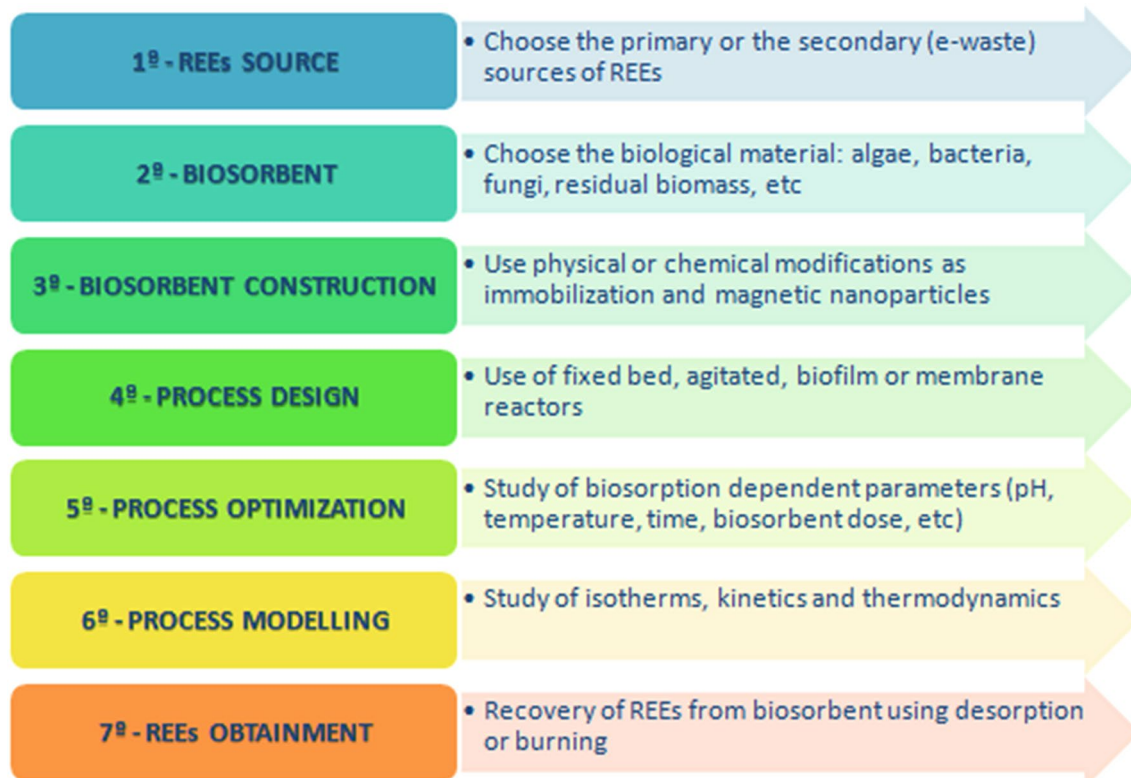
Application of biosorbents for the preconcentration of REEs is greatly justified as the process is environmentally benign, simple and can be economic (Gupta et al. 2019). Figure 2 summarizes the biosorption process technology for REE ions. A huge range of biosorbents have been used for the adsorption and recuperation of REEs, and biosorption of REEs was governed by certain parameters, viz., contact time, pH, biosorbent dosage, temperature, ionic strength; and must be optimized using statistic designed methods for maximizing absorption effectiveness, and recovery.

In most cases, metal binding occurs by electrostatic interaction, surface complexation, ion transfer, and precipitation that can occur individually or in combination. Biomass (living or non-living cells), biomaterial shapes, chemical properties of metal solutions, environmental conditions, such as pH, influences the biosorption of REEs (Gadd 2008; Gupta et al. 2019).

The solution pH is an important factor regulating the biosorption process, which affects the speciation of REEs

in solution through hydrolysis, complexation and redox reactions (Coimbra et al. 2017; Heidelmann et al. 2017; Hisada and Kawase 2018). The temperature also influences metal ion biosorption, and during the sorption process, several studies have suggested different views on the temperature effects.

An increase in the concentration of biosorbent dose usually increases the amount of REE adsorbed once the number of binding sites is rising due to the increased surface area of the biosorbent. On the other hand, the amount of biosorbent adsorbed ion per unit weight decreases as the biosorbent dose increases, which may be due to the complex interaction of several variables (Gadd 2008; Das and Das 2013; Gupta et al. 2019). Finally, pore distribution controls the internal diffusion of metal ions contributing to intracellular metal accumulation in biosorbents. REE' adsorption in a biosorbent depends on the size and volume of the pore. The pore entry of REE ions is highly feasible when the pore size is comparatively larger than the size of the hydrated REE ion. This is also the pore width, these REE ions it can handle, which ultimately leads to higher adsorption efficiency (Beni and Esmaeili 2020).



**Fig. 2** The biosorption process, summarizing for the biosorption of rare-earth elements



## Microbial biosorbents for recovery of REEs

Due to their high adsorption capacity and easy availability, algal biomass has been used for the adsorption of heavy metal ions and other toxic pollutants from industrial wastewater. In the case of lanthanides, the concentration of REEs adsorbed on macroalgae such as seaweed can reach  $10^2$ – $10^6$ -fold above that found in seawater (Sakamoto et al. 2008). REEs can be found at 1.3  $\mu\text{g}$  per seaweed (Xiao-Jun et al. 1998) which is considered a high concentration when compared to the concentration found in the environment, between  $10^{-3}$  and  $10^{-1}$   $\mu\text{g/L}$  (Sahoo et al. 2012; Liang et al. 2014; Richards and Mullins 2013).

Among the algae studied, the group most used in REE biosorption studies has been the brown marine macroalgae, mainly of the *Sargassacea* family. These algal species contain high concentrations of alginate that comprise abundant carboxylic groups capable of capturing cations metallic species present in solution (Davis et al. 2003). Additionally, in laboratory studies for  $\text{La}^{3+}$  biosorption, the freshwater green microalgae *C. reinhardtii* was able to recover 1.03 mmol/g within 5 h (Birungi and Chirwa 2014), which was very close to 1.11 mmol/g in 6 h for the brown marine *Turbinaria conoides* (Vijayaraghavan et al. 2010). The same can be observed for  $\text{Nd}^{3+}$ , where studies have shown that microalgae *Ankistrodesmus gracilis* and *Monoraphidium* sp. biosorbed 0.98 and 0.94 mmol/g, respectively (Palmieri et al. 2000), while the best result found for brown macroalgae *Sargassum* spp. was 0.70 mmol/g in 40 min (Oliveira and Garcia 2009).

Bacteria are widely studied for their potential as biosorbents because they have a high surface area in relation to their small size, which facilitates the process of adsorption of metal ions present in solution (Vijayaraghavan and Yun 2008). Among the bacterial strains studied as biosorbents for REEs, are those belonging to the genera *Bacillus* (Coimbra et al. 2017, 2019; Giese and Jordão 2019), *Streptomyces* (Tsuruta 2006), *Pseudomonas* (Andrès et al. 2000; Texier et al. 2002), *Myxococcus* (Merroun et al. 2003) and *Agrobacterium* (Xu et al. 2011).

Pretreatment of bacterial cells with NaCl, HCl or NaOH solutions may be necessary for the active cell surface sites to have sufficient negative charge density to favor interaction between the cells. For *Bacillus subtilis*, for example, pretreatment with 1 M NaOH favored the  $\text{La}^{3+}$  sorption process, which was equal to 100% within 40 min with 100  $\mu\text{M}$   $\text{La}^{3+}$  solution at pH 3.0. With cells pretreated with 1 M HCl, the maximum sorption was only 34% in 60 min (Giese and Jordão 2019). On the other hand, both alkaline and acid pretreatments did not promote an increase of  $\text{La}^{3+}$  and  $\text{Ce}^{3+}$  biosorption by *Agrobacterium* sp. HN1 (Xu et al. 2011).

Takahashi et al. (2005) observed that the distribution coefficient ( $K_d$ ) between the *B. subtilis* cell wall and the REE solution tends to increase proportionally to the cellular concentration (at a fixed pH value), as well as proportionally to pH values (in a fixed cell concentration). The dependence of  $K_d$  values on pH solution indicated that phosphate groups participated in the interactions between REE and biomass at higher pH values (Bonificio and Clarke 2016).

Higher rates of metal percentage removal in diluted solutions have been observed in the literature for some fungal and yeast strains. Muraleedharan et al. (1994) evaluated the use of pulverized biomass (particle size 600–1200  $\mu\text{m}$ ) from the fruiting body of *Ganoderma lucidum*, a wood-decomposing basidiomyceteous fungus, on REE biosorption. The authors simulated a synthetic effluent from the monazite process consisting of  $\text{Th}^{4+}$ ,  $\text{RCl}_3$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{F}^-$  and  $\text{PO}_4^{3-}$  ions, and used *G. lucidum* biomass packed in a fixed-bed reactor for the treatment of this effluent. The use of biosorbent decreased the concentration of REE ( $<0.15$  mg/L) and thorium ( $<0.1$  mg/L) to lower levels.

Recently, Giese et al. 2019 described the  $\text{La}^{3+}$  and  $\text{Sm}^{3+}$  biosorption by *Botryosphaeria rhodina*, a fungus used in the industrial production of  $\beta$ -glucan. The maximum uptake capacity of  $\text{La}^{3+}$  was observed at low amounts of La ions in solution, decreasing from 100 to 25% when the initial lanthanide concentration increased from 15 to 100 mg/L. The scaled-up production of  $\beta$ -glucan by this fungus results in the production of large amounts of mycelial biomass as an industrial by-product that represents a potentially cost-effective biosorbent for REEs (Giese et al. 2019), and heavy metals (Muñoz et al. 2019).

Vlachou et al. (2009) evaluated the biosorption capacity of *Kluyveromyces marxianus*, *Candida colliculosa* and *Debaryomyces hansenii*, and compared them to *Saccharomyces cerevisiae*. These yeast species are present as waste streams originating from breweries, wineries, and bakeries, and can be used as low-cost biosorbents. The authors described the biosorption behavior of  $\text{Nd}^{3+}$  by adsorption isotherms at pH 1.5 with the initial concentration of  $\text{Nd}^{3+}$  between 10 and 200 mg/L, where the  $q_{\text{max}}$  value was from 10 to 12 mg/g, and a  $K_f$  value of 0.9–1.2. The analysis of the mathematical model indicated the existence of two types of  $\text{Nd}^{3+}$  ion binding sites that were common to the four yeast strains evaluated. The same behavior was also observed for the bacterium, *Mycobacterium smegmatis*, cells for REE ions  $\text{La}^{3+}$ ,  $\text{Eu}^{3+}$ , and  $\text{Yb}^{3+}$  biosorption (Andrès et al. 1993).

Two strains of *S. cerevisiae*, one wild type the other a mutant (rim20 $\Delta$ ), were evaluated for the capacity of biosorption of  $\text{La}^{3+}$ . Di Caprio et al. (2016) observed that for both strains, ion-biomass interactions occurred through bonding to carboxylic, amino and phosphate groups on the yeast surface. Both processes reached equilibrium between 10 and

**Table 1** Important data from the literature on the biosorption of Rare Earth Elements by various microbial species

REEs	Organism	REE uptake	pH	Time	References
Algae and microalgae					
Nd	<i>Ankistrodesmus gracilis</i>	0.99 mmol/g	1.5	24 h	Palmieri et al. (2000)
	<i>Ankistrodesmus densus</i>	0.74 mmol/g	1.5	24 h	
	<i>Monoraphidium</i> sp.	0.95 mmol/g	1.5	24 h	
	<i>Chlorella minutissima</i>	0.71 mmol/g	1.5	24 h	
La	<i>Chlorella vulgaris</i>	1.11 mg/g	3.0	20 min	Heidelmann et al. (2017)
Nd	<i>Euglena gracilis</i>	0.018 mmol/g	N.D	30 min	Guo et al. (2000)
	<i>Euglena gracilis</i>	0.26 mmol/g	N.D	30 min	
Er	<i>Sargassum</i> sp.	0.63 mmol/g	N.D	N.D	Palmieri et al. (2001)
Yb	<i>Sargassum</i> sp.	0.66 mmol/g	N.D	N.D	
La	<i>Sargassum fluitans</i>	0.29 mmol/g	4.0	45 min	Palmieri and Garcia (2001)
		0.53 mmol/g	5.0	45 min	
Eu	<i>Chlorella vulgaris</i>	$8.5 \times 10^{-5}$ M	4.0	20 min	Ozaki et al. (2003)
		$6.0 \times 10^{-5}$ M	5.0	20 min	
		$4.5 \times 10^{-5}$ M	6.0	20 min	
La	<i>Sargassum polycustum</i>	0.8 mmol/g	3.0	24 h	Diniz and Volesky (2005)
		0.9 mmol/g	4.0	24 h	
		1.0 mmol/g	5.0	24 h	
Eu	<i>Sargassum polycustum</i>	0.8 mmol/g	3.0	24 h	
		0.9 mmol/g	4.0	24 h	
		0.97 mmol/g	5.0	24 h	
Yb	<i>Sargassum polycustum</i>	0.7 mmol/g	3.0	24 h	
		0.8 mmol/g	4.0	24 h	
		0.9 mmol/g	5.0	24 h	
La + Eu + Yb	<i>Sargassum polycustum</i>	La 0.29 mmol/g Eu 0.41 mmol/g Yb 0.28 mmol/g	4.0	24 h	
La	<i>Sargassum</i> sp.	0.66 mmol/g	5	N.D	Oliveira and Garcia (2009)
Nd	<i>Sargassum</i> sp.	0.70 mmol/g	5	N.D	
Eu	<i>Sargassum</i> sp.	0.63 mmol/g	5.0	N.D	Oliveira et al. (2011)
Gd	<i>Sargassum</i> sp.	0.67 mmol/g	5.0	N.D	
Sm	<i>Sargassum</i> sp.	0.34 mmol/g	5.0	30 min	
Pr	<i>Sargassum</i> sp.	0.29 mmol/g	5.0	30 min	
Sm + Pr	<i>Sargassum</i> sp.	Sm 0.39 mmol/g Pr 0.33 mmol/g	5.0	30 min	
La	<i>Turbinaria conoides</i>	1.11 mmol/g	4.9	6 h	Vijayaraghavan et al. (2010; 2011)
Ce	<i>Turbinaria conoides</i>	1.09 mmol/g	4.9	6 h	
Eu	<i>Turbinaria conoides</i>	0.91 mmol/g	4.9	6 h	
Yb	<i>Turbinaria conoides</i>	0.70 mmol/g	4.9	6 h	
REE ore	<i>Promidium</i>	La 335 mg/Kg Pr 50 mg/Kg Nd 193 mg/Kg Sm 33 mg/Kg Gd 18 mg/Kg Dy 13 mg/Kg	5.6	30 min	Kim et al. (2011)
La	<i>Sargassum</i> sp.	0.57 mmol/g	5.0	N.D	Oliveira et al. (2012)
Nd	<i>Sargassum</i> sp.	0.55 mmol/g	5.0	N.D	
La + Nd	<i>Sargassum</i> sp.	La 0.23 mmol/g Nd 0.28 mmol/g	5.0	N.D	
La	<i>Sargassum hemiphylum</i>	0.70 mmol/g	4.0	24 h	Kano et al. (2013)
Eu		0.78 mmol/g	4.0	24 h	

**Table 1** (continued)

REEs	Organism	REE uptake	pH	Time	References
Yb		0.77 mmol/g	4.0	24 h	
La	<i>Ulva pertusa</i>	0.93 mmol/g	4.0	24 h	
Yb		0.72 mmol/g	4.0	24 h	
La	<i>Schizymenia dubyi</i>	0.65 mmol/g	4.0	24 h	
Eu		0.98 mmol/g	4.0	24 h	
Yb		0.93 mmol/g	4.0	24 h	
La	<i>Chloroidium saccharophilum</i>	0.93 mmol/g	6.0	300 min	Birungi and Chirwa (2013)
	<i>Stichococcus bacillaris</i>	0.36 mmol/g	6.0	300 min	
	<i>Desmodesmus multivariabilis</i>	0.72 mmol/g	6.0	300 min	
	<i>Chlorella vulgaris</i>	0.53 mmol/g	6.0	300 min	
	<i>Scenedesmus acuminatus</i>	0.79 mmol/g	6.0	300 min	
La	<i>Chlamydomonas reinhardtii</i>	1.03 mmol/g	6.0	300 min	Birungi and Chirwa (2014)
Nd	<i>Chlamydomonas reinhardtii</i>	0.26 mmol/g	N.D	3 h	Heilmann et al. (2015)
	<i>Anthonema africanum</i>	0.19 mmol/g	N.D	3 h	
	<i>Calothrix brevissima</i>	0.48 mmol/g	N.D	3 h	
	<i>Chlorella sorokiniana</i>	0.16 mmol/g	N.D	3 h	
	<i>Euglena gracilis</i>	0.22 mmol/g	N.D	3 h	
	<i>Euglena mutabilis</i>	0.35 mmol/g	N.D	3 h	
	<i>Euglena stellata</i>	0.24 mmol/g	N.D	3 h	
	<i>Euglena viridis</i>	0.19 mmol/g	N.D	3 h	
	<i>Galdieria sulphuraria</i>	0.19 mmol/g	N.D	3 h	
	<i>Lynghya taylori</i>	0.31 mmol/g	N.D	3 h	
	<i>Nostoc ellipsosporum</i>	0.17 mmol/g	N.D	3 h	
	<i>Nostoc punctiforme</i>	0.13 mmol/g	N.D	3 h	
	<i>Porphyridium purpureum</i>	0.22 mmol/g	N.D	3 h	
	<i>Prymnesium saltans</i>	0.18 mmol/g	N.D	3 h	
	<i>Taselmis chuii</i>	0.35 mmol/g	N.D	3 h	
	<i>Arthrospira platensis</i>	0.18 mmol/g	N.D	3 h	
Pr	<i>Turbinaria conoides</i>	0.93 mmol/g	5.0	60 min	Vijayaraghava and Jegan (2015)
	<i>Sargassum wightii</i>	0.78 mmol/g	5.0	60 min	
	<i>Turbinaria conoides</i>	1.04 mmol/g	5.0	60 min	
	<i>Sargassum wightii</i>	0.84 mmol/g	5.0	60 min	
Nd	<i>Chlorella vulgaris</i>	123.82 mg/g	4	90 min	Kücüker et al. (2016)
		157.21 mg/g	5	90 min	
Bacteria, yeast and fungi					
La, Ce, Pr, Nd, Pm, Sm, Eu Gd, Tb Dy, Ho, Er, Tm, Yb, Lu, Y	<i>Bacillus subtilis, Escherichia coli</i>	N.D	2.5–4.5	90 min	Takahashi et al. (2005)
La, Eu, Yb	<i>Pseudomonas aeruginosa</i>	La 397 µmol/g Eu 290 µmol/g Yb 326 µmol/g	5.0	60 min	Texier et al. (1999)
Nd	<i>Kluyveromyces marxianus</i> <i>Candida colliculosa</i> <i>Debaromyces hansenii</i> <i>Saccharomyces cerevisiae</i>	10–12 mg/g	1.5	60 min	Vlachou et al. (2009)
La	<i>Saccharomyces cerevisiae</i>	70 mg/g 80 mg/g	4.0 6.0	20 min	Di Caprio et al. (2016)
La, Ce	<i>Agrobacterium</i> sp. HN1	La 23.26 mg/g Ce 31.15 mg/g	6.8	60 min	Xu et al. (2011)
Sc, La, Sm, Y	<i>Candida utilis</i>	N.D	4.0–6.0	20 min	Korenevsky et al. (1999)
Ce	<i>Aspergillus niger</i> <i>Aspergillus flavus</i>	6.84% 7.01%	N.D	7 days	Sallam et al. (2014)

**Table 1** (continued)

REEs	Organism	REE uptake	pH	Time	References
Tb	<i>Caulobacter crescentus</i>	N.D	6.1	20 min	Park et al. (2016)
La, Sm	<i>Bacillus subtilis</i>	N.D	3.0	20 min	Giese and Jordão (2019)
La, Sm	<i>Bacillus subtilis</i> -alginate	La 81.10 mg/g Sm 83.51 mg/g	3.0	20 min	Coimbra et al. (2017)
La, Sm	<i>Bacillus subtilis</i> -alginate	La 3.62 L/mg Sm 4.22 L/mg	3.0	20 min	Coimbra et al. (2019)
Eu	<i>Bacillus thuringiensis</i>	160 mg/g	4.0	N.D	Pan et al. 2017
La, Sm	<i>Botryosphaeria rhodina</i>	La 1.011 mg/g Sm 1.041 mg/g	3.0	20 min	Giese et al. (2019)

N.D. not determined

20 min, with a  $q_{\max}$  of 70 mg/g at pH 4.0 for the wild type strain, and 80 mg/g at pH 6.0 for the mutant strain.

Table 1 summarizes some data from the literature on the biosorption of REEs by various microbial species. Further studies are needed to understand the behavior of biosorption using microbial biosorbents in real wastewater and leachate solutions, where selective adsorption of REEs from an element matrix develops the technology towards large-scale application of the method of biosorption. Although REEs partitioning from multi-element solutions has been achieved by tailoring chelating ligands to the biosorbent surface, selectivity among REEs still needs future work (Gupta et al. 2019).

## Final considerations

Currently, the biggest challenge in the REE industry is to separate and retrieve the elements to obtain pure REE compounds, as a result of the high chemical similarity between the group elements. Biosorption offers an economically-feasible technology for efficient removal and recovery of REEs from diluted leachates combining biotechnology with extractive hydrometallurgy, as a potential alternative for REE concentration through interactions between REEs and certain active sites present in the biosorbent.

In general, studies involving biosorption of REEs by algae, bacteria, fungi and yeasts are still at an early stage, with few species of organisms exploited, and not all REEs have been studied. The use of packed-bed column technology with immobilized biomass is an economically and operationally viable alternative that could be employed in REE biosorption processes, and feasibility studies of this type of bioprocess should be conducted. The use of fixed or fluidized bed reactors is preferred because of the easier recovery of the treated effluent. For this purpose, successful bacterial immobilization on different matrices is required.

The development of a bioprocess to make up the REEs production chain promising and innovative is for the mineral

sector. Alternative routes and clean technologies for REE extraction and separation are needed to fit current trends seeking better performance of hydrometallurgical facilities. Researchers progressive approach to developing an effective, selective, and stable biosorbent at minimal cost, should also be extended to preconcentration for REE. The move from the laboratory to an industrial scale of the biosorption process is difficult for preconcentration of REEs.

There are two trends for the use of biosorption as an industrial process of REE removal and separation: (a) use of hybrid technologies using active biomass, and (b) efficient biomaterials as biosorbents for reuse and recycling. Industry and the bioeconomy will strengthen investigative biases for the application of tools, such as molecular biotechnology, which can be used in future to construct manipulated microorganisms with higher sorption capacities and specificity for each REE species.

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