Interaction of *Rhodococcus* with Metals and Biotechnological Applications

Alessandro Presentato, Elena Piacenza, Martina Cappelletti, and Raymond J. Turner

Contents

Abstract In studies of environmental stresses caused by metals, *Rhodococcus* species are routinely identified as part of a beneficial microbial rhizosphere community. These bacterial strains, inhabiting diverse ecological niches, possess a variety of enzymatic activities to carry out relevant biodegradation reactions, such as degradation of organic pollutants in some cases using them for both carbon and energy. In this context, most *Rhodococcus* strains have been found to have very high

---

A. Presentato (✉)
Environmental Microbiology Laboratory, Department of Biotechnology, University of Verona, Verona, Italy
e-mail: alessandro.presentato@univr.it

E. Piacenza · R. J. Turner (✉)
Department of Biological Sciences, University of Calgary, Calgary, AB, Canada
e-mail: elena.piacenza@ucalgary.ca; turnerr@ucalgary.ca

M. Cappelletti
Unit of General and Applied Microbiology, Department of Pharmacy and Biotechnology, University of Bologna, Bologna, Italy
e-mail: martina.cappelletti2@unibo.it

H. M. Alvarez (ed.), *Biology of Rhodococcus*, Microbiology Monographs 16,
https://doi.org/10.1007/978-3-030-11461-9_12

levels of metal resistance. Thus, these microorganisms are not only capable of metabolizing various organic pollutants in the presence of co-contaminating heavy metals, but they can also bioadsorb and/or bioconvert various metals and metalloids [metal(loid)s]. Indeed, some *Rhodococcus* exploit these metal(loid) compounds to generate biogenic nanoscale materials of intriguing physical-chemical properties, which can find applications in biotechnology.

This book chapter has the focus in overviewing the biotechnological relevance of the *Rhodococcus* genus relationship with metal(loid)s, the bioprocesses elicited by these microorganisms in handling metal(loid)s' toxicity, and the importance of these actinomycetes in the context of the bioremediation and bionanotechnology fields.

1 Introduction

Metal elements such as aluminum (Al), cadmium (Cd), cesium (Cs), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), silver (Ag), strontium (Sr), zinc (Zn), and uranium (U) and the metalloids arsenic (As), selenium (Se), and tellurium (Te) are naturally occurring throughout the Earth's crust, being defined "heavy" as both their atomic weight and density are higher than water (Fergusson 1990). Although some of these elements (e.g., Fe, Se, Zn, Cu) are essential in traces for living organisms, the overdose of these and exposure to some others (e.g., As, Pb, Hg, whose toxicity is undisputed) can be severely toxic (Chang et al. 1996; Tchounwou et al. 2008). Indeed, the global human concern toward these contaminants relies mostly on their mutagenicity and carcinogenicity, negatively impacting the quality of life of both flora and fauna in different habitats (i.e., aquatic, terrestrial, and atmospheric) (Chakraborty et al. 2017). This aspect is exacerbated by the intense industrial progress in several fields (i.e., engineering, biomedicine, agriculture, metallurgy, microelectronics, mining operations, etc.), as well as unjustified waste disposal processes, which inexorably add to environmental pollution. The result is that there are sites in almost every community on the planet with a buildup of substantial amounts of recalcitrance toxic metal(loid)s in diverse ecological niches (Chakraborty et al. 2017). In this context, a prolonged exposure to metal(loid) compounds is often associated to human poisoning, as well as to their biomagnification at successively high levels in the food chain (Phillips and Rainbow 2013).

Toxicity of a metal to an organism depends on a variety of physical-chemical and biological parameters influencing the metal ion speciation and bioavailability. Chemical parameters include temperature, pH, redox potential, and presence/absence of compounds capable of chelating or binding to the metal. Some biological parameters include the metal-lipid solubility, physiological state of the organism, presence/absence of key metal interacting proteins, and any physiological adaptation of the organisms. The combination of such parameters and their interplay contribute to the environmental resiliency of metal(loid)s (Hamelink et al. 1994). Focusing the attention at the molecular level, it is generally believed that proteins are the primary targets of metal(loid)s. Indeed, malfunctioning of proteins in their native conformation can be attributed to (1) the binding of metals to protein ligands such as free thiols (RSHs), imidazoles, amines, or carboxylates, (2) the displacement of essential metal ions in metalloenzymes, (3) the oxidation of the amino acid side chains, and (4) their interaction with non-folded proteins causing their aggregation and, therefore, impairing protein homeostasis in living organisms (Beyersmann and Hartwig 2008; Sharma et al. 2011; Lemire et al. 2013).

As dramatic as the above picture may appear, human beings have evolved the concept of *environmental remediation*, which combines physical-chemical and biological knowledge for strategies aimed to decrease the concentration of metal (loid) compounds into the environment, restoring its ecological fitness. Overall, biological methods, exploiting the natural catabolic abilities of bacteria, fungi, and plants to clean up diverse contaminated matrices in a *green* and cost-effective manner (Strong and Burgess 2008), are generally preferred over physical-chemical approaches, as the latter often have cost-prohibitive and non-efficient results at low metal(loid) environmental load (Ali et al. 2013).

Aerobic non-sporulating microorganisms belonging to the *Rhodococcus* genus are known for their environmental robustness and persistence, as they can physiologically adapt (i.e., modification of the cell membrane composition, formation of intracellular inclusions) to several stressful conditions (e.g., pH, desiccation, low nutrient availability, presence of xenobiotic compounds, etc.) (Martínková et al. 2009; Alvarez and Steinbüchel 2010; Presentato et al. 2018a). This allows members of this genus to populate diverse ecological niches. Although much less is known about the *Rhodococcus* genus potential to resist toxic metal(loid) compounds, recently the unique capacity of some rhodococci to overcome environmental stresses like the presence of antimicrobials and very high concentrations of metal(loid)s such as tellurite [Te (IV)], arsenate [As (V)], and selenite [Se (IV)] has been described (Orro et al. 2015; Cappelletti et al. 2016; Presentato et al. 2016, 2018b). Such findings highlight how these microorganisms are worth exploring as candidates for bioremediation of metal(loid)-polluted sites. Further, it has been reported that bacteria are able to convert toxic metal(loid) ion/oxyanions into less/nontoxic metal forms, generating discrete structures at the nanometer scale (1×10^{-9} m) with different shapes, i.e., nanoparticles (NPs) and nanorods (NRs) (Turner et al. 2012). To this aim, different *Rhodococcus* strains have been studied and exploited as cell factories for nanotechnological purposes, proving the specific proficiency of rhodococci to biosynthesize high-quality biogenic metal(loid) nanostructures with relevant biotechnological applications (Ahmad et al. 2003; Otari et al. 2012; Kundu et al. 2014; Presentato et al. 2016, 2018b, c). Thus, this chapter will overview the interaction between *Rhodococcus* genus and metal(loid)s in terms of bacterial resistance and strategies adopted to counteract metal(loid) toxicity, as well as their remarkable ability in generating biogenic nanomaterials.

2 Microbial Interaction with Metal(loid)s

A large number of organisms are capable of thriving in the presence of high metal (loid) load, being this feature ascribed to intrinsic and/or induced biochemical mechanisms combined with environmental factors (Gadd 1992a). In this respect, bacteria are defined to be tolerant as they are not killed by the toxicity exerted by metal(loid) compounds through their intrinsic properties yet do not grow or proliferate, while those that are resistant show the ability to live because of the induction of detoxification mechanisms implemented in response to the presence of metal(loids) (Gadd 1992b). Bacteria have evolved uptake mechanisms in order to exploit diverse nutrients, which enable them to survive even under extreme and adverse environmental conditions (Brooks et al. 2011). Because microorganisms have coevolved with the geochemistry of the planet and inhabit all possible niches, many can utilize even toxic metal(loid) compounds (i.e., As, Cd, Te, Se, etc.) (Gadd 2010). For instance, bacterial cells can encounter metal(loid) ions from either aqueous or solid matrices, using them as (1) energy source, (2) terminal electron acceptor during microbial respiration, and (3) cofactors in metalloproteins and enzymes (Ehrlich 1997; Valls and de Lorenzo, 2002). Thus, microbial scavenging and biotransformation of metal(loid) elements can be related to either detoxification processes or resistance phenomena, which are carried out as parallel events related or not with bacterial growth (Park et al. 2018).

The different mechanisms exploited by microbes to cope with metal(loid)s' toxicity can rely on their transformation by means of either redox processes or alkylation reactions (Ledin 2000). Bacterial cells can sequester metal(loid) ions onto their cell wall either in a passive and metabolism-independent manner (biosorption) or through active mechanisms (bioaccumulation), which is a metabolism-dependent process based on the actual metal(loid) uptake (Ledin 2000). Further, metal(loid) ions can be trapped outside bacterial cells through interaction with (1) surface proteins, (2) carbohydrates, (3) cell wall polymers, and (4) extracellular polymeric substance (EPS) often produced when bacteria grow as a biofilm. Finally, there may be chelation (precipitation and/or complexation) through the production of either siderophores or specific metalloproteins (Gupta and Diwan 2017). All these strategies occur in the microbial world; hence, the exploitation of the microbial catabolic abilities represents a powerful tool to abate the metal(loid) load polluting the environment.

2.1 Rhodococcus *Tolerance/Resistance Toward Metal(loid)s*

Bacterial strains belonging to the *Actinomycetales* order, which include *Rhodococcus* genus, exploit different mechanisms enabling them to highly tolerate metal(loid) compounds (Pavel et al. 2013). For instance, the reduction of cellular sensitivity, the intracellular sequestration of metal ions and oxyanions, their complexation with siderophores, the alteration of the membrane permeability, mutations, and repairing mechanisms of the DNA responsible for both plasmid and chromosomal DNA stability are some of the mechanisms implemented by bacteria to tolerate and/or resist to metalloids' toxicity (Stillman 1995; Garbisu and Alkorta 2003; Figueira et al. 2005). A primary mechanism through which metal(loid) compounds can exert their toxicity toward bacteria relies on the alteration of the cellular thiol chemistry. Indeed, the reaction of metal(loid)s with cell thiols leads to the depletion of glutaredoxin and thioredoxin from their activity of reducing metal (loid) compounds and becoming oxidized (Turner 2001). Thus, such reactions can cause an increase in the intracellular content of reactive oxygen species (ROS), which can ultimately cause cellular death (Turner et al. 1999). This process is even more emphasized if we consider the presence of oxygen as terminal electron acceptor in the case of strictly aerobic microorganisms, as in the case of *Rhodococcus* strains. This process is even more emphasized if we consider the presence of oxygen as terminal electron acceptor in the case of strictly aerobic microorganisms, such as in the case of *Rhodococcus* strains. However, instead of having the redox buffer molecule glutathione (GSH), actinomycetes are mostly characterized by the presence of genes involved in the synthesis of mycothiols (MSHs), which are more stable and less prone to oxidation (Newton et al. 1996). Thus, the potential of actinomycetes in resisting the toxicity exerted by metal(loid)s overall derives from the *redox stability* of these microorganisms. Rhodococci investigated for metal tolerance to date are listed in Table 1 along with their resistance levels. It is noteworthy to highlight that among the metal(loid) elements listed in Table 1, tellurium in the form of oxyanion tellurite (TeO_3^{2-}) is typically the most toxic, with minimal inhibitory concentrations (MIC) as low as 1 $\mu g\ mL^{-1}$ (Taylor 1999). This concentration is several orders of magnitude lower than other metal(loid) compounds (Nies 1999; Harrison et al. 2004), and yet *R. aetherivorans* BCP1 strain showed to be highly resistant to this oxyanion (Presentato et al. 2016, 2018c).

In nature microorganisms are found in a close relationship to each other and adhering to a surface forming a complex community known as biofilm. Within a biofilm, the bacterial cells are overprotected by a heterogeneous surrounding matrix defined as extracellular polymeric substance (EPS), which is mostly constituted by water, proteins, polysaccharides, lipids, and extracellular DNA (e-DNA) (Harrison et al. 2005). Thus, a bacterium living within a biofilm has the advantage of resisting and adapting to harsh environmental conditions (this topic has been reviewed by Harrison et al. 2007). In line with this, Adhami et al. (2017) described two different *Rhodococcus* strains with an enhanced metal resistance against Cd, Cr, Cu, Pb, and Zn supplied as salts when these bacterial cells were grown as biofilms in comparison with those grown as planktonic cultures (Adhami et al 2017).

Table 1 Minimal inhibitory concentration (MIC) of different metal(loid)s of *Rhodococcus* species

MICs of metal(loid)s of *Rhodococcus* spp. (mM)										
Strain		Cd	Cr	Cu	Hg	Pb	Se	Te	Zn	References
R. RS67		ND[a]	ND	ND	ND	0.5	ND	ND	0.2	Perelomov et al. (2018)
R. rhodochrous		8	1	4	ND	8	ND	ND	8	Adhami et al. (2017)
	MBEC[b]	16	4	8	ND	16	ND	ND	16	
	MBIC[c]	4	0.5	1	ND	4	ND	ND	2	
R. rhodnii		8	1	4	ND	8	ND	ND	8	
	MBEC	16	4	8	ND	16	ND	ND	16	
	MBIC	4	0.5	2	ND	2	ND	ND	1	
R. aetherivorans BCP1		ND	ND	ND	ND	ND	500	11.2	ND	Presentato et al. (2016, 2018b, c)
R. strain 3		8–10	ND	8–16	ND	>16	ND	ND	8–16	Vela-Cano et al. (2014)
R. ruber	AC239	ND	>1.8	3.7	0.28	ND	ND	ND	ND	Fleck et al. (2000)
	AC74	ND	>1.8	1.5	0.17	ND	ND	ND	ND	
	AC87	ND	>1.8	3.5	0.28	ND	ND	ND	ND	
R. erythropolis	AC272	ND	>1.8	3	0.21	ND	ND	ND	ND	
	AC265	ND	>1.8	0.1	0.03	ND	ND	ND	ND	

[a] Not determined
[b] Minimum biofilm eradicating concentration
[c] Minimum biofilm inhibitory concentration

3 Metal(loid) Biosorption in *Rhodococcus*

Biosorption is recognized as an emerging and *eco-friendly* approach for metal(loid)s' or radionuclides' removal from polluted environments or in biomining, as it is cost-effective, is highly efficient, and can be specific. This technique relies on the application of different microbial biomasses (i.e., microalgae or bacterial cells of the genera including *Bacillus*, *Pseudomonas*, *Streptomyces*, etc.) as biosorbents, which possess a natural affinity toward metal(loid) compounds, contributing to a feasible and economic way toward the purification of metals from contaminated matrices (Volesky 1990; Wilde and Benemann 1993). From an engineering perspective, bacteria are considered good biosorbents as their small size offer a high surface-to-volume ratio, conferring a large surface area of interaction with metal(loid)s. Several molecular mechanisms are possible for biosorption performed by bacteria (Gadd and White 1993), dependent on factors, such as capacity, affinity, and specificity of the biomass and/or biosorbent considered, as well as the physical-chemical conditions of a given environmental niche and the metal of interest.

3.1 Parameters Influencing Metal(loid) Biosorption

The biosorption of metal(loid)s by bacteria depends on the characteristics of the surface structural chemistry of the cell wall and membrane (i.e., charge and orientation of the metal(loid) binding functional groups), as well as the chemistry and speciation of the considered metal(loid) (Ledin 2000). A given bacterial cell surface can be composed of lipids, peptidoglycan, lipopolysaccharides, lipoproteins, and enzymes, being featured by carboxyl (COO^-), sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), amino (NH_2^+/NH_3^+), carbonyl (CO^-), and hydroxyl (OH^-) functional groups as well as the acyl chains of membranes. Thus, the amphoteric behavior of a cell wall depends on the presence of these anionic and cationic groups, being those anionic predominant over the cationic ones (Plette et al. 1995; van der Wal et al. 1997).

Restricting the focus onto rhodococci, it has been reported that these microorganisms have a cell wall characterized by polysaccharides, carboxylic acids, lipid groups, and mycolic acids, which are responsible for the amphoteric behavior of the cellular surface (Stratton et al. 2002; Botero et al. 2007). Moreover, Plette et al. (1995) showed that the isolated cell wall material deriving from *R. erythropolis* A177 was featured by a chemical heterogeneity due to the existence of at least three different proton group binding sites (i.e., carboxylic, phosphate, and amino types), therefore leading to a surface charge dependent on the pH and salt level (Plette et al. 1995). A reasonable explanation for the effect of the pH on the sorption capability of a given biosorbent relies on the pKa of the biosorbent molecules and the combined isoelectric point of all biosorbent molecules and the number of active sites present as well as the speciation state of the metal ion. Therefore, at pH values lower than the biosorbent isoelectric point, its surface will be positively charged because of the association with hydronium (H_3O^+) ions, determining a repulsion of metal cations. By contrast, the biosorbent surface will be negatively charged for pH values higher than its isoelectric point; hence, it favors the adsorption of cations. Furthermore, at pH values above the pKa of a given biosorbent, its functional groups will be dissociated, enabling proton exchange with the metal(loid) in solution (Cayllahua and Torem 2010). In line with this, Cayllahua and Torem (2010) reported that the biosorption capability of a *R. opacus* strain toward Al (III) ions was optimal at pH of 5, as its isoelectric point was c.a. 3.26. Similar observations were also reported for ions of Pb (II), Cr (III), Cu (II), Cd (II), and Zn (II) (Sheng et al. 2004; Vasquez et al. 2007; Bueno et al. 2008). Thus, depending on the type of metal(loid)s to be removed (i.e., anions or cations), it must be considered the characteristics of the biosorbent and the pH of the system at which the metal(loid)s' sorption occurs.

In natural settings, a variety of different metal(loid) ions other than those targets of bioremediation can be found, leading to a competition for the available binding sites present on the surface of bacterial cells, therefore interfering with the remediation of polluted sites. Calcium [Ca (II)], for example, is known as the major bivalent ion competitor for metal(loid) sorption in soil (Doyle et al. 1980; Xue et al. 1988; Flemming et al. 1990). However, it is noteworthy to mention that the cell wall material isolated from *R. erythropolis* A177 showed an enhanced Cd (II) sorption in the presence of Ca (II) ions. Indeed, the binding of Ca (II) ions to the cell wall can cause (1) the breaking of cross-linkages that normally occurs between different groups (e.g., COO^- and NH_3^+) of the cell wall and (2) the disruption of bonds occurring between phosphate groups of the phospholipids and others present in the peptidoglycan layer. These effects cause a drastic change of the cell surface and wall morphology leading to an increased availability of the number of accessible and active binding sites for other bivalent cations, such as Cd (II). Thus, since the binding of Ca (II) to the cell wall enhances the binding of Cd (II), in this case Ca (II) can be considered as a cooperative acting ion toward Cd (II), influencing in a salt-dependent manner the sorption potential of *R. erythropolis* A177-derived cell wall (Plette et al. 1996).

The concentration of the biosorbent in a given environment is another parameter of crucial importance, as the sorption capability of a biosorbent tends to decrease when its concentration rises. This aspect might be related to the cross-linkages occurring among the functional groups as described above (Koch 1990). Indeed, the cell wall material recovered from *R. opacus* strain was capable of efficiently adsorbing Al (III), Cd (II), and Zn (II) ions, while their sorption dropped down when the biosorbent concentration was increased (Vasquez et al. 2007; Cayllahua and Torem 2010).

3.2 EPS-Mediated Extracellular Biosorption

Another modality through which microorganisms can interface with metal(loid) compounds relies on the production of biological exudates featured by a high adsorption potential. Overall, these biologically active compounds are known as EPS (see Sect. 2), which includes polysaccharides and their derivatives, proteins, peptides, metabolites, nucleic acids, and lipids. These microbial-derived compounds showed to have an efficient adsorptive property (Jixian et al. 2015; Zheng-bo et al. 2015), due to the presence of different functional reactive groups [i.e., OH^-, COO^-, acetamido ($AcNH^+$), NH_3^+] characterizing the polymer chains, which in turn confer to EPS: (1) high hydrophilicity, (2) polarity, and (3) structural flexibility (Crini 2005). Moreover, the amount of functional binding groups featuring EPS reflects its actual biosorption potential, working also as enhancer for the metal(loid) binding to microbial cell surfaces (Liu and Fang 2002; Wei et al. 2011). Since the treatment of metal(loid)-polluted sites via EPS is based on the binding of ions, the pH values at which the sorption process occurs are of fundamental importance as discussed above with the cell surface. Indeed, the competition between protons and metal(loid) ions to bioadsorb onto the active and accessible sites present in the EPS surface should be controlled, in order to maintain the appropriate electronic state allowing for chelation or complexation (Lamelas et al. 2006; Guibaud et al. 2008).

The EPS composition will be highly dependent on the bacterial species/strain, and thus its adsorption properties might be influenced by different protocols applied, reagents utilized, and physical-chemical (e.g., sonication, ionic exchange resin) method adopted for the extraction (Liu and Fang 2002; Comte et al. 2005). This leads toward the challenge that every system will be different and optimization strategy will need to be empirically determined. This reflects the importance of fundamental microbiology research to expand the knowledge on the possible microbial factories implied for this purpose.

3.3 Parameters Influencing EPS Biosorption

As biosorption EPS-mediated appears an attractive and *green* choice to develop new eco-sustainable strategies of environmental remediation, researchers have focused their attention in exploiting a variety of microorganisms belonging to diverse families (i.e., *Cyanobacteriaceae*, *Bacillaceae*, *Pseudomonadaceae*, *Myxococcaceae*) as cell factories for the production and extraction of EPS to test against different metals (e.g., Cd, Cu, Pb, Mn, Ni, Zn, Hg) (Merroun et al. 2003; Salehizadeh and Shojaosadati, 2003; Freire-Nordi et al. 2005; Lau et al. 2005; Paperi et al. 2006). Among rhodococci, Dobrowolski et al. (2017) studied the sorption capability of EPS material derived from *R. opacus* and *R. rhodochrous*, revealing a fast adsorption rate (between 1 and 30 min) of Ni (II), Pb (II), Co (II), Cd (II), and Cr (VI) for EPS material from both strains, which supports their application in flow adsorption systems (Dobrowolski et al. 2017).

The application of microbial EPS is highly influenced by the pH values at which the metal(loid)s' sorption occurs. Indeed, the best biosorption of Ni (II) mediated by the EPS recovered from either *R. opacus* or *R. rhodochrous* strains occurred at pH values ranging from 3 to 4, as, decreasing the content of H_3O^+ ions, the EPS surfaces resulted more negatively charged and thus more prone to bind this divalent cation. By contrast, an increase of the pH value (>4) resulted in a decreased EPS sorption potential, as the two prominent species of Ni (II) ions in solution (i.e., $Ni(OH)_2$ and $Ni(OH)_3^-$) could not be adsorbed onto the negatively charged surfaces characterizing EPS. Similar observations can be drawn for Pb (II) and Co (II), while sorption up to a pH value of 7.5 was observed in the case of Cd (II), as cadmium hydroxyl $[Cd_x(OH)_y]$ was the major species of Cd present in solution at this pH (Dobrowolski et al. 2017).

Temperature is another parameter to experimentally control for the optimization of a biosorption process, as it can influence the ionization of the EPS functional groups and influence the formed biosorbent-metal(loid) complex, as well as the diffusion and equilibrium kinetics. Generally, an increase in the temperature can cause (1) a decrease of the biosorption extent in the case of an exothermal process, (2) a destruction of the biosorbent's active sites, and (3) a faster ion motion, which enhances off-rates of the metal(loid)s to bioadsorb (Dobrowolski et al. 2017).

Other than EPS, humic substances (HSs) present in the soil and aquatic environments can mitigate the toxicity of metal(loid)s and organic compounds, which is due to the complex chemistry of HSs thus providing sorption properties (Boguta and Sokołowska 2016). Further, the network generated among metal(loid) compounds, bacteria, and environment can influence (1) the speciation and bioavailability of metal(loid)s, (2) the sorption phenomenon, (3) the metabolic capacity of bacteria toward xenobiotics, and (4) the biochemical/physiological functions of bacteria (Perminova and Hatfield 2005). Although the comprehension of this process is difficult and poorly investigated, Perelomov et al. (2018) described different bacteria capable of tolerating higher amounts of Zn (II) and Pb (II) consequently to the copresence of HSs and derivative fractions (i.e., humic acids, hymatomelanic acids). Indeed, a study employing infrared spectroscopy revealed that humic acids and hymatomelanic acids possess different functional active sites represented by alcohols, phenols, amines, amides, and carboxylic acids, which can be either free or intermolecularly bonded (Rodrigues et al. 2009), enabling HSs to bind cations (Kar et al. 2011). Thus, the addition of 200 mg L^{-1} of HSs (mixture of humic and hymatomelanic acids) resulted in an enhanced tolerance to Zn (II) in the case of *Pseudomonas fluorescence* 142NF and *R.* sp. RS67, which were five- and fourfold more tolerant, respectively, as compared to the non-HSs amended cultures (Perelomov et al. 2018). This effect originates from the stable HS-Zn complex formed (Perminova et al. 2006), which is not bioavailable to the bacteria. Similar results were achieved in the case of Pb (II), therefore highlighting the importance of HSs in attenuating metal(loid)s' toxicity and bioavailability. However, this also limits the ability to remediate a site of the metal pollutant.

As discussed in this section, biosorption is a powerful biotechnological tool that can be exploited for the remediation of metal(loid)-polluted sites. The process relies on the binding, complexation, ion exchange, crystallization, and/or precipitation of the metal(loid) in the biochemical context of a given cell wall. The parameters (i.e., pH, salt level, temperature, and biosorbent concentration) described are crucial and must be optimized according to the physical-chemical characteristics of both metal (loid) and biosorbent, particularly focusing on its amphoteric behavior, in order to take advantage of biosorbents for bioremediation purposes.

4 Metal(loid) Bioaccumulation in *Rhodococcus*

As opposed to biosorption, metal(loid) accumulation is an energy-demanding and metabolic-dependent process, as it requires an active uptake transporter by a living organism and, therefore, it occurs slower as compared to the above described biosorption phenomenon (Mowll and Gadd 1984). In this respect, Mirimanoff and Wilkinson (2000) showed that the initial Zn adsorption performed by *R. opacus* C125 occurred in less than 1 min; on the other hand, microorganisms have evolved specialized uptake systems for essential metal(loid)s that are needed for the cell biochemistry. Specific ion channels or carriers facilitate uptake for the ion down its concentration gradient and active transporters using either ATP or the electrochemical gradient as energy for transport. Such transporters are key to charge metalloenzymes that exploit transition metals as cofactors. For example, molybdenum (Mo) is actively taken up, in the form of oxyanion (MoO_4^{2-}), either by an ATP-binding cassette (ABC) transporter with high affinity or through low affinity carrier systems, which have been both evolved by those microorganisms that use Mo for nitrogenases and/or oxidoreductases featured by molybdopterin as cofactor, respectively (Pau et al. 1997).

A common route for toxic heavy metal accumulation is mediated by transporters of essential metals, which facilitate the transport of closely related elements. For example, the molybdate ABC transporter will also transport tungsten (W) as WO_4^{2-}, in this way nonessential elements can be bioaccumulated. Bacteria can take up divalent cations such as Co (II), Zn (II), and Ni (II) exploiting the magnesium [Mg (II)] transport system, although this strategy only weakly contributes to the uptake of transition metals in the presence of magnesium (Smith and Maguire 1998). Thus, bacterial strains featured by genes coding for enzymes dependent on Ni (II) as cofactor exploit specific transporters for Ni (II), which constitute a family of permeases featured by eight transmembrane segments with high affinity for this cation but a very low transport capacity, while *Escherichia coli* cells exploiting an ABC transporter represents an exception (Hausinger 1997; Eitinger and Friedrich 1997). These permeases for Ni (II) have been identified in different bacterial genera (i.e., *Bradyrhizobium*, *Alcaligenes*, *Helicobacter*) (Fu et al. 1994; Eitinger et al. 1997; Fulkerson et al. 1998). Among actinomycetes, *Mycobacterium tuberculosis* relies on this permease to accumulate Ni (II), supporting the activity of a Ni-dependent urease, which is also an important virulence factor for this microorganism (Cole et al. 1998).

Concerning rhodococci, Komeda et al. (1997) studied in *R. rhodochrous* strain J1 the NhlF transporter for Co (II), which is responsible to provide Co (II) for nitrile hydratases containing non-corrin Co as cofactor (Komeda et al. 1997). Nitrile utilization by *R. rhodochrous* strain M8 was dependent on the nitrile hydratase activity as well, whose expression was enhanced by the presence of Co (II) in the growth medium as compared to Co-limiting conditions, suggesting that Co (II) deficiency could lead to either a weak expression of the nitrile hydratase coding gene or to a fast nitrile hydratase transcript (mRNA) degradation (Pogorelova et al. 1996). However, the NhlF transporter is highly similar at amino acid sequence level to the Ni (II) transporter HoxN of *Alcaligenes eutrophus* (Wolfram et al. 1995). Although both NhlF and HoxN transporters share similar membrane topology, Co (II) uptake NhlF-mediated was impaired by the copresence of Ni (II), thus indicating that NhlF could also transport Ni (II) (Komeda et al. 1997). Later, Degen et al. (1999) demonstrated that HoxN was able to mediate the transport of Ni (II) and incapable of taking up Co (II), while NhlF had a promiscuous binding ability toward these divalent cations (Degen et al. 1999). Indeed, NhlF transporter could mediate Ni (II) uptake, as demonstrated by the enhanced Ni-dependent urease activity of recombinant *Escherichia coli* clones expressing *nhlF* gene grown under Ni-limiting conditions, as well as cross-complementing Ni deficiency due to the deletion of the *hoxN* gene in *Alcaligenes eutrophus*. Nevertheless, the Ni (II) uptake by NhlF was markedly reduced when *R. rhodochrous* strain J1 was cultured in the presence of both nickel and cobalt salts, therefore suggesting that Co (II) was the preferred cation-binding substrate, as well as the NhlF transporter was featured by a certain level of ion selectivity toward two similar transition metals (Degen et al. 1999).

4.1 Metal(loid) Homeostasis in Microbial Bioaccumulation

In addition to metal(loid) uptake, the efflux system is a biologically relevant phenomenon responsible for the control of toxin accumulation in the cell, and examples exist to control metal(loid) accumulation, as well as its homeostasis between intra- and extracellular environment, highlighting a sort of "microbial metal toxicity care". This is the case for *R. opacus* C125 cells that accumulated at most c.a. 6 μmol g^{-1} (dry weight) of Zn (II) after 20 min exposure to 5 μM Zn (II), which with time drastically decreased. When Zn-loaded *R. opacus* C125 cells were exposed to either additional 5 μM Zn (II) or Cd (II), cellular Zn concentrations decreased, therefore suggesting both an inducible and cross-inducible efflux mechanism by Zn (II) and Cd (II), respectively, as well as the existence of Zn-binding ligands capable of mediating the accumulation of this transition metal in the first place (Mirimanoff and Wilkinson, 2000).

Overall, nonessential metal(loid)s can be taken up by microorganisms, and the amount of these compounds accumulated varies as function of the species and the type of metal(loid) considered. An example is given by cesium (Cs), which became a metal of pollutant interest after the Chernobyl accident in 1986, attracting the research interest in both the removal and the fate of radioactive Cs. In this respect, Tomioka et al. (1994) investigated two different *Rhodococcus* strains (i.e., *R. erythropolis* CS98 and *R.* sp. CS402) capable of tolerating and growing in the presence of Cs and rubidium (Rb) supplied in a mineral salt medium up to concentrations of 1 mM. It was found that Cs uptake by both *Rhodococcus* strains was negatively influenced by the presence of monovalent cations such as K (I) and Rb (I). Reasonably, Cs (I) and Rb (I) may substitute K (I) in bacteria growing under K-limiting conditions due to the poor specificity of the K (I) transport systems (Avery et al. 1991, 1992). This idea was reported earlier in the case of other bacterial strains (i.e., *Rhodopseudomonas capsulata*, *Escherichia coli*, and *Rhodococcus* spp.; Rhoads and Epstein 1977; Jasper 1978; Tomioka et al. 1994).

If the biosorption phenomenon is the first event occurring when bacterial cells interface metal(loid)s, the active bioaccumulation of these ions within the intracellular environment would be a complementary event. To date we are still at early stages to appreciate the diversity and mechanisms for most metal uptake systems. However, the microbial potential in handling metal(loid)s' toxicity goes beyond the above depicted strategies, as metal(loid) bioconversion and/or biotransformation reactions may take place, leading to either biomineralization or production of valuable metal(loid) products. Indeed, the next section will overview this aspect of the microbial world that crosses and merges itself with the nanotechnology field.

5 Nanotechnology: A Physical-Chemical Perspective

Nanotechnology is the science related to the world of *very small material*, which implies the manipulation of matter at molecular or atomic level (Horikoshi and Serpone 2013). The prefix *nano* is referred to structures defined as intermediate states between molecules and bulk materials (Yuwen and Wang 2013). The uniqueness of nanostructures relies on the possibility to manipulate physical-chemical properties of the materials scaled down to the nanorange (1–100 nm) (Yuwen and Wang 2013), conferring them fundamental and peculiar features as high surface-to-volume ratio and large surface energy with high spatial confinement (Cao 2004a). These peculiar characteristics allow in turn innovative chemical, catalytic, mechanical, electrical, and opto-magnetic properties in the nanomaterials (Appenzeller 1991; Yuwen and Wang 2013), making them suitably manipulated for applications in multidisciplinary fields, such as biomedicine/biotechnologies, energy production, environmental engineering, material science, and optoelectronics (Cao 2004a; Horikoshi and Serpone 2013).

In the past few decades, the nanoscience field has exponentially grown in terms of study and implementation, leading to the development of new methods for nanomaterial production (Rao et al. 2004). In this context, we have witnessed the generation of nanostructures having various compositions and morphologies, of which the most exploited to date are *zero-dimensional* (0D) nanoparticles (NPs), nanocrystals and cluster quantum dots (QDs), *one-dimensional* (1D) nanorods (NRs), nanowires (NWs), nanotubes (NTs) and nanobelts (NBs) (or ribbons), nanoporous solids, *two-dimensional* (2D) arrays of NPs, thin films, and *three-dimensional* (3D) structures (superlattices) (Rao et al. 2004).

Although the physical-chemical methods to synthesize nanomaterials are efficient and available for a scaled-up production, they require the use of toxic substances that are converted during the fabrication process into hazardous waste requiring specialized disposal or are released to the environment (Zhang et al. 2006, ACS Nano 2011; CDC 2014). Moreover, several of these production procedures require expensive equipment and chemicals, affecting the production costs. Therefore, these drawbacks led to a demand for the generation of novel cost-effective and *eco-friendly* methods of nanomaterial production (Ankamwar et al. 2005).

5.1 Microbial Nanotechnology

To date, the new and *green* frontier in nanostructure synthesis is constituted by the exploitation of the natural ability of biological systems (i.e., plants, bacteria, fungi, yeasts, and algae) to bioconvert toxic metal(loid) ions into their less toxic elemental forms producing nanostructures (Suresh et al. 2004; Bhainsa and D'Souza 2006; Song and Kim 2009). Particularly, bacteria are among the organisms that have been the most explored for nanomaterial generation, due to their ability to populate different environmental niches that has led to unique biochemistry and physiology features (Li et al. 2011; Pantidos and Horsfall 2014). Indeed, in nature, the production of metal(loid), metal sulfide, and oxide nanostructures by bacterial cells is achieved through either aerobic detoxification processes or the use, under anaerobic conditions, of metal(loid) ions as terminal electron acceptors to produce energy (Li et al. 2011).

Among the diverse bacterial species that can biosynthesize nanostructures, those belonging to the *Actinomycetales* order recently gained interest in the nanoscience field, as they previously showed their proficiency to produce bioactive compounds, such as antibiotics and biocides (Duraipandiyana et al. 2010). Thus, several *Streptomyces*, *Thermoactinomyces*, and *Nocardia* strains have been investigated for the production of intra- or extracellular gold (Au), silver (Ag), zinc oxide (ZnO), copper oxide (CuO), or selenium (Se) NPs upon their growth and/or exposure to the metal(loid) precursor salts (Forootanfar et al. 2014; Manimaran and Kannabiran 2017). For example, Fig. 1 shows the different cellular localizations of metalloid nanomaterials generated by *R. aetherivorans* BCP1 as a result of metal(loid) oxyanion (i.e., SeO_3^{2-} and TeO_3^{2-}) bioconversion into their elemental forms (i.e., Se^0 and Te^0). The intracellular biosynthesis of metal(loid) NPs by actinomycetes is mainly ascribed to either (1) electrostatic interactions occurring between metal cations and $R\text{-}COO^-$ groups of enzymes associated with the bacterial cell membrane (Manimaran and Kannabiran 2017) or (2) a Painter-type reaction between RSH groups of cellular enzymes and metalloid oxyanions (Tan et al. 2016). As a result, these reactions can reduce the metal(loid) ions, leading to the formation of elemental metal(loid) nuclei, which in turn aggregate forming nanomaterials of defined shape (Ahmad et al. 2003; Sunitha et al. 2013). On the other hand, it is proposed that soluble secreted enzymes are responsible for the reduction of metal cations into their elemental forms in the case of the extracellular generation of metal-based nanomaterials (Manivasagan et al. 2016).

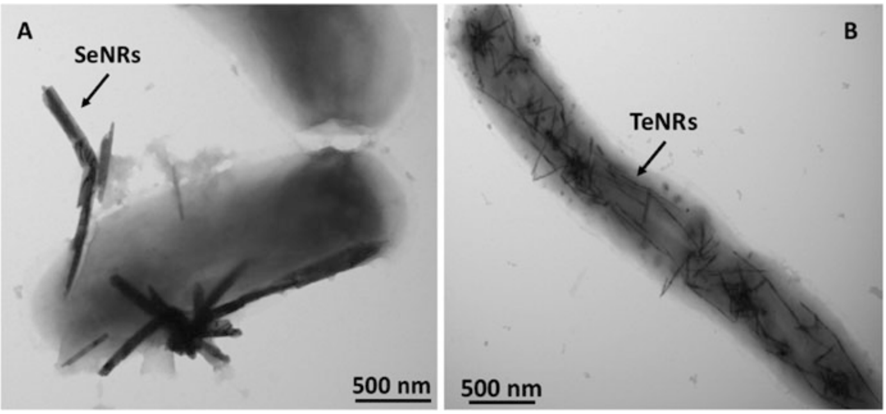

Fig. 1 Electron micrographs of *R. aetherivorans* BCP1 cells featured by the presence of (**a**) selenium nanorods (SeNRs) and (**b**) tellurium nanorods (TeNRs). Data not published, Dr. Alessandro Presentato, University of Calgary (2017)

5.2 Rhodococcus *Strains as Cell Factories for Nanotechnological Purposes*

Considering the great potential of the *Rhodococcus* genus for biotechnological purposes, recently a few research groups started to evaluate the ability of these microorganisms to produce metal(loid) nanomaterials through the bioconversion of metal(loid) salts. Although this research field is only in its infancy, various *Rhodococcus* strains revealed their capability of generating both intra- and extracellular Au-, Ag-, ZnO-, Se-, and Te-based nanostructures (Ahmad et al. 2003; Otari et al. 2012; Kundu et al. 2014; Presentato et al. 2016, 2018b, c), whose key features are summarized in Table 2, while an example of different biogenic nanomaterial shapes is shown in Fig. 2. A common property of these biogenic metal(loid) nanomaterials is their natural thermodynamic stability, which is in contrast with the behavior of those chemically synthesized (Piacenza et al. 2018). Indeed, materials at the nanoscale are generally unstable from a thermodynamic point of view, as they possess a high surface energy (Goldstein et al. 1992). To overcome their instability, nanostructures tend to either combine forming bigger aggregates (Ostwald ripening process) or agglomerate each other without altering individual particles (Cao 2004b). Since the unique properties of nanosized materials are strictly dependent on their small size, it is imperative to avoid their aggregation, making it necessary to use expensive and hazardous substances to stabilize chemically produced nanostructures prior their use (Cao 2004a; Piacenza et al. 2018). By contrast, the natural thermodynamic stability of metal(loid) nanomaterials generated by *Rhodococcus* species is a fundamental feature for the application of these nanostructures in different fields. Moreover, these biogenic nanomaterials resulted in being stabilized by biomolecules (e.g., proteins, enzymes, or surfactant-like molecules) produced by the bacterial strains themselves (Kundu et al. 2014,

Table 2 Production of metal(loid) nanomaterials by *Rhodococcus* spp. and their characterization

Strain	Core	Localization	Shape	Size (nm)	Reducing agents/ stabilizers	References
Rhodococcus sp.	Au	Intracellular	Spherical	5–15	Cellular proteins	Ahmad et al. (2003)
R. NCIM 2891	Ag	Intracellular	Spherical	ca. 100	NADH-dependent nitrate reductases	Otari et al. (2012)
R. pyridinivorans NT2	ZnO	Extracellular	Spherical porous	100–120	Extracellular proteins, heterocyclic compounds	Kundu et al. (2014)
R. aetherivorans BCP1	Te	Intracellular	Rod-shape	200–450	MSHs, biosurfactants	Presentato et al. (2016)
R. aetherivorans BCP1	Se	Intracellular	Spherical	50–90	MSHs, biosurfactants	Presentato et al. (2018a)
			Rod-shape	400–600		
R. aetherivorans BCP1	Te	Intracellular	Spherical	100–900	MSHs, surfactant-like molecules	Presentato et al. (2018b)

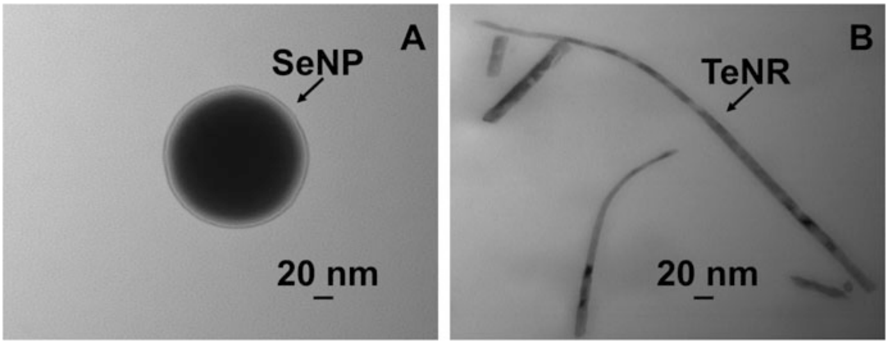

Fig. 2 Electron micrographs of (**a**) selenium nanoparticles (SeNPs) and (**b**) tellurium nanorods (TeNRs) recovered from *R. aetherivorans* BCP1 selenite- and tellurite-grown cells, respectively. Data not published, PhD Student Elena Piacenza, University of Calgary (2017)

Presentato et al. 2016, 2018b, c), therefore constituting a *greener* choice as compared to the compounds used for the stabilization of chemical nanostructures.

To date, metal(loid) nanomaterials generated by *Rhodococcus* spp. have been mainly investigated for their potential use in biomedicine. Indeed, AgNPs produced by *R.* sp. NCIM 2891 were found to be efficient as both antimicrobials toward

Escherichia coli and *Bacillus subtilis* pathogenic indicator strains and anticancer agents limiting the proliferation of A549 lung cancer cell line (Subbaiya et al. 2014). Similarly, ZnO NPs biosynthesized using *R. pyridinivorans* NT2 have been used as coating for cotton textile surfaces intended for the production of footwear (Kundu et al. 2014). As a result of this conjugation process, the cotton fibers acquired long-term UV-protective, photocatalytic, and antimicrobial properties, whose efficacy was evaluated against *Staphylococcus epidermidis* ATCC 12228, an opportunistic pathogen of the sole of the foot (Kundu et al. 2014). Moreover, ZnO NPs showed their proficiency as an in vitro drug delivery system of an anticancer compound (i.e., anthraquinone) toward HT-29 colon carcinoma cell line, without exerting cytotoxic effects on normal peripheral blood mononuclear cells (PBMCs) (Kundu et al. 2014). Finally, the potential of using metal(loid) nanomaterials generated by *Rhodococcus* strains in other fields rather than biomedicine has been recently explored (Presentato et al. 2018c). Particularly, since Te is a well-known narrow band gap *p*-type semiconductor (Araki and Tanaka 1972) exhibiting high photoconductivity, piezo, and thermoelectricity (Araki and Tanaka 1972; Tangney and Fahy 2002; Suchand Sandeep et al. 2010), TeNRs obtained from resting (not growing) cells of *R. aetherivorans* BCP1 were studied for the ability to conduct electrical current. As a result, these TeNRs revealed electrical conductivity approaching the values established for chemically produced TeNRs, highlighting the potential of these biogenic nanomaterials in the development of electrical components or devices (Presentato et al. 2018c).

6 Summary

Rhodococcus is a bacterial genus with strong resilience in handling metal(loid)s' toxicity, applying different strategies to tolerate and/or resist metal(loid) compounds (i.e., biosorption, bioaccumulation, efflux, extracellularly chelation) regardless their form (i.e., anions, cations, oxyanions). This is in part related with the rhodococci's innate and adaptive mechanisms, enabling them to survive and thrive, even under typically unfavorable conditions. The intense study and efforts devoted to comprehending how bacteria interface metal(loid)s led to understanding that *Mother Nature* can be respectfully exploited for different purposes, such as the bioremediation of metal(loid)-polluted environmental matrices and the generation of *eco-friendly* strategies to expand the nanotechnology field without negatively affecting the environment. Thus, this kind of research implies that the knowledge of both the microbiology and the physical-chemical characteristics of metal(loid)s must be used in a conscious way, as the system represented by the *real life* is complicated through a variety of different factors constantly interacting each other. Only by awareness of this complex picture it is possible to predict the biological effects occurring in natural systems.

Acknowledgments Natural Science and Engineering Research Council of Canada (NSERC) is gratefully acknowledged for the support of this study (Grant/Award Number: 216887-2010).

References

Adhami E, Aghaei SS, Zolfaghari MR (2017) Evaluation of heavy metals resistance in biofilm cells of native *Rhodococcus* spp. isolated from soil. Arch Hyg Sci 6:235–243

Ahmad A, Senapati S, Khan MI, Kumar R, Ramani R, Srinivas V, Sastry M (2003) Intracellular synthesis of gold nanoparticles by a novel alkalotolerant actinomycete, *Rhodococcus* species. Nanotechnology 14:824–828. https://doi.org/10.1088/0957-4484/14/7/323

Ali H, Khanb E, Sajad AM (2013) Phytoremediation of heavy metals-concepts and applications. Chemosphere 91:869–881. https://doi.org/10.1016/j.chemosphere.2013.01.075

Alvarez HM, Steinbüchel A (2010) Physiology, biochemistry and molecular biology of triacylglycerol accumulation by *Rhodococcus*. In: Alvarez HM (ed) Biology of *Rhodococcus*, Microbiology monographs, vol 16. Springer, Heidelberg, pp 263–290. https://doi.org/10.1007/978-3-642-12937-7_10

American Chemistry Society (ACS) NANO(2011) Green nanotechnology challenges and opportunities. http://greennano.org/sites/greennano2.uoregon.edu/files/GCI_WP_GN10.pdf

Ankamwar B, Chaudhary M, Sastry M (2005) Gold nanoparticles biologically synthesized using tamarind leaf extract and potential application in vapor sensing. Synth React Inorg Met Org Nano Met Chem 35:19–26. https://doi.org/10.1081/SIM-200047527

Appenzeller T (1991) The man who dared to think small. Science 254:1300–1300. https://doi.org/10.1126/science.254.5036.1300

Araki K, Tanaka T (1972) Piezoelectric and elastic properties of single crystalline Se-Te alloys. Appl Phys Expr 11:472–479. https://doi.org/10.1143/JJAP.11.472

Avery SV, Codd GA, Gadd GM (1991) Cesium accumulation and interactions with other monovalent cations in the cyanobacterium *Synechocystis* PCC 6803. J Gen Microbiol 137:405–413. https://doi.org/10.1099/00221287-137-2-405

Avery SV, Codd GA, Gadd GM (1992) Replacement of cellular potassium by cesium in *Chlorella emersonii*: differential sensitivity of photoautotrophic and chemoheterotrophic growth. J Gen Microbiol 138:69–76. https://doi.org/10.1099/00221287-138-169

Beyersmann D, Hartwig A (2008) Carcinogenic metal compounds: recent insight into molecular and cellular mechanisms. Arch Toxicol 82:493–512. https://doi.org/10.1007/s00204-008-0313-y

Bhainsa KC, D'Souza SF (2006) Extracellular biosynthesis of silver nanoparticles using the fungus *Aspergillus fumigatus*. Colloids Surf B Biointerfaces 47:160–164. https://doi.org/10.1016/j.colsurfb.2005.11.026

Boguta P, Sokołowska Z (2016) Interactions of Zn(II) ions with humic acids isolated from various type of soils. Effect of pH, Zn concentrations and humic acids chemical properties. PLoS One 11:1–20. https://doi.org/10.1371/journal.pone.0153626

Botero AEC, Torem ML, de Mesquita LMS (2007) Fundamental studies of *Rhodococcus opacus* as a biocollector of calcite and magnesite. Miner Eng 20:1026–1032. https://doi.org/10.1016/j.mineng.2007.03.017

Brooks AN, Turkarslan S, Beer KD, Lo FY, Baliga NS (2011) Adaptation of cells to new environments. Wiley Interdiscip Rev Syst Biol Med 3:544–561. https://doi.org/10.1002/wsbm.136

Bueno BYM, Torem ML, Molina F, de Mesquita LMS (2008) Biosorption of lead (II), chromium (III) and copper (II) by *R. opacus*: equilibrium and kinetic studies. Miner Eng 21:65–75. https://doi.org/10.1016/j.mineng.2007.08.013

Cao G (2004a) Chapter 1: Introduction. In: Cao G (ed) Nanostructures & nanomaterials, synthesis, properties and applications. Imperial College Press, London, pp 1–14

Cao G (2004b) Chapter 2, Physical chemistry of solid surfaces. In: Cao G (ed) Nanostructures & nanomaterials, synthesis, properties and applications. Imperial College, London, pp 15–48

Cappelletti M, Fedi S, Zampolli J, Di Canito A, D'ursi P, Orro A, Viti C, Milanesi L, Zannoni D, Di Gennaro P (2016) Phenotype microarray analysis may unravel genetic determinants of the stress response by *Rhodococcus aetherivorans* BCP1 and *Rhodococcus opacus* R7. Res Microbiol 167:766–773. https://doi.org/10.1016/j.resmic.2016.06.008

Cayllahua JEB, Torem ML (2010) Biosorption of aluminum ions onto *Rhodococcus opacus* from wastewaters. Chem Eng J 161:1–8. https://doi.org/10.1016/j.cej.2010.03.025

Centers for Disease Control and Prevention National Institute for Occupational Safety and Health (CDC) (2014) Current strategies for engineering controls in nanomaterial production and downstream handling processes. https://www.cdc.gov/niosh/docs/2014-102/pdfs/2014-102.pdf

Chakraborty J, Dash AR, Das S (2017) Metals and their toxic effects. An introduction to noxious elements. In: Das S, Dash HR (eds) Handbook of metal-microbe interactions and bioremediation. CRC, Boca Raton, FL, pp 3–17. ISBN: 9781498762434

Chang LW, Magos L, Suzuki T (1996) Toxicology of metals. CRC, Boca Raton, FL. ISBN: 9780873718035

Cole ST, Broch R, Parkhill J, Garnier T, Churcher C, Harris D, Gordon SV, Eiglmeir K, Gas S, Barry CE 3rd, Tekaia F, Badcock K, Basham D, Brown D, Chillingworth T, Connor R, Davies R, Devlin K, Feltwell T, Gentles S, Hamlin N, Holroyd S, Hornsby T, Jagels K, Krogh A, McLean J, Moule S, Murphy L, Oliver K, Osborne J, Quail MA, Rajandream MA, Rogers J, Rutter S, Seeger K, Skelton J, Squares R, Squares S, Sulston JE, Taylor K, Whitehead S, Barrell BG (1998) Deciphering the biology of *Mycobacterium tuberculosis* from the complete genome sequence. Nature 393:537–544. https://doi.org/10.1038/31159

Comte S, Guibaud G, Baudu M (2005) Relation between extraction protocols of the activated sludge extracellular polymeric substances (EPS) and EPS complexation properties. Part I. Comparison of the efficiency of eight EPS extraction properties. Enzyme Microb Technol 38:237–245. https://doi.org/10.1016/j.enzymictec.2005.06.016

Crini G (2005) Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. Prog Polym Sci 30:38–70. https://doi.org/10.1016/j.progpolymsci.2004.11.002

Degen O, Kobayashi M, Shimizu S, Eitinger T (1999) Selective transport of divalent cations by transition metal permeases: the *Alcaligenes eutrophus* HoxN and the *Rhodococcus rhodochrous* NhlF. Arch Microbiol 171:139–145. https://doi.org/10.1007/s002030050

Dobrowolski R, Szcześ A, Czemierska M, Jarosz-Wikołazka A (2017) Studies of cadmium(II), lead (II), nickel(II), cobalt(II) and chromium(VI) sorption on extracellular polymeric substances produced by *Rhodococcus opacus* and *Rhodococcus rhodochrous*. Bioresour Technol 225:113–120. https://doi.org/10.1016/j.biortech.2016.11.040

Doyle RJ, Matthews TH, Streips UN (1980) Chemical basis for the selectivity of metal ions by the *Bacillus subtilis* wall. J Bacteriol 143:471–480

Duraipandiyana V, Sasi AH, Islam VHI, Valanarasu M, Ignacimuthu S (2010) Antimicrobial properties of actinomycetes from the soil of Himalaya. J Med Mycol 20:15–20. https://doi.org/10.1016/j.mycmed.2009.11.002

Ehrlich HL (1997) Microbes and metals. Appl Microbiol Biotechnol 48:687–692. https://doi.org/10.1007/s002530051

Eitinger T, Friedrich B (1997) Microbial nickel transport and incorporation into hydrogenases. In: Winkelmann G, Carrano CJ (eds) Transition metals in microbial metabolism. Harwood, Amsterdam, pp 235–256

Eitinger T, Wolfram L, Degen O, Anthon C (1997) A Ni^{2+} binding motif is the basis of high affinity transport of the *Alcaligenes eutrophus* nickel permease. J Biol Chem 272:17139–17144. https://doi.org/10.1074/jbc.272.27.17139

Fergusson JE (1990) The heavy elements: chemistry, environmental impact and health effects. Pergamon, Oxford. https://doi.org/10.1016/0269-7491(91)90124-F

Figueira EMAP, Lima AIG, Pereira SIA (2005) Cadmium tolerance plasticity in *Rhizobium leguminosarum* bv. *viciae*: glutathione as a detoxifying agent. Can J Microbiol 51:7–14. https://doi.org/10.1139/w04-101

Fleck LC, Bicca FC, Ayub MAZ (2000) Physiological aspects of hydrocarbon emulsification, metal resistance and DNA profile of biodegrading bacteria isolated from oil polluted sites. Biotechnol Lett 22:285–289. https://doi.org/10.1023/A:1005607112566

Flemming CA, Ferris FG, Beveridge TJ, Bailey GW (1990) Remobilization of toxic heavy metals absorbed to wall-clay composites. Appl Environ Microbiol 56:3191–3209

Forootanfar H, Zare B, Fasihi-Bam H, Amirpour-Rostami S, America A, Shakibaie M, Nami MT (2014) Biosynthesis and characterization of selenium nanoparticles produced by terrestrial actinomycete *Streptomyces microflavus* strain FSHJ31. RRJMB 3:47–53. e-ISSN: 2320-3528

Freire-Nordi CS, Vieira AAH, Nakaie CR, Nascimento OR (2005) Effect of polysaccharide capsule of the microalgae *Staurastrum iversenii* var. *americanum* on diffusion of charged and uncharged molecules, using EPR technique. Braz J Phys 36:75–82. https://doi.org/10.1590/S0103-97332006000100013

Fu C, Javedan S, Moshiri F, Maier RJ (1994) Bacterial genes involved in incorporation of nickel into a hydrogenase enzyme. Proc Natl Acad Sci USA 91:5099–5103. https://doi.org/10.1073/pnas.91.11.5099

Fulkerson JF Jr, Garner RM, Mobley HLT (1998) Conserved motifs and residues in the NixA protein of *Helicobacter pylori* are critical for the high affinity transport of nickel ions. J Biol Chem 273:235–241. https://doi.org/10.1074/jbc.273.1.235

Gadd GM (1992a) Microbial control of heavy metal pollution. In: Fry J, Gadd GM, Herbert RA, Jones CW, Watson-Craik IA (eds) Forty-eighth symposium of the society for general microbiology. Cambridge Univ. Press, The University of Cardiff, Cardiff, pp 59–88

Gadd GM (1992b) Metals and microorganisms: a problem of definition. FEMS Microbiol Lett 100:197–204. https://doi.org/10.1111/j.1574-6968.1992.tb14040.x

Gadd GM (2010) Metals, minerals and microbes: geomicrobiology and bioremediation. Microbiology 156:609–643. https://doi.org/10.1099/mic.0.037143-0

Gadd GM, White C (1993) Microbial treatment of metal pollution—a working biotechnology? Trends Biotechnol 11:353–359. https://doi.org/10.1016/0167-7799(93)90158-6

Garbisu C, Alkorta I (2003) Basic concepts on heavy metal soil bioremediation. Eur J Miner Process Environ Prot 3:58–66

Goldstein AN, Echer CM, Alivisatos AP (1992) Melting in semiconductor nanocrystals. Science 256:1425–1427. https://doi.org/10.1126/science.256.5062.1425

Guibaud G, Bordas F, Saaid A, D’abzac P, Hullebusch EV (2008) Effect of pH on cadmium and lead binding by extracellular polymeric substances (EPS) extracted from environmental bacterial strains. Colloid Surf B Biointerfaces 63:48–54. https://doi.org/10.1016/j.colsurfb.2007.11.002

Gupta P, Diwan B (2017) Bacterial Exopolysaccharide mediated heavy metal removal: a review on biosynthesis, mechanism and remediation strategies. Biotechnol Rep 13:58–71. https://doi.org/10.1016/j.btre.2016.12.006

Hamelink J, Landrum PF, Bergman H, Benson WH (1994) Bioavailability: physical, chemical and biological interactions. CRC, Boca Raton, FL. ISBN: 9781566700863

Harrison JJ, Ceri H, Stremick CA, Turner RJ (2004) Biofilm susceptibility to metal toxicity. Environ Microbiol 6:1220–1227. https://doi.org/10.1111/j.1462-2920.2004.00656.x

Harrison JJ, Turner RJ, Marques LLR, Ceri H (2005) Biofilms: a new understanding of these microbial communities is driving a revolution that may transform the science of microbiology. Am Sci (6):508–515

Harrison JJ, Ceri H, Turner RJ (2007) Multimetal resistance and tolerance in microbial biofilms. Nat Rev Microbiol 5:928–938. https://doi.org/10.1038/nrmicro1774

Hausinger RP (1997) Metallocenter assembly in nickel-containing enzymes. J Biol Inorg Chem 2:279–286. https://doi.org/10.1007/s007750050

Horikoshi S, Serpone N (2013) Chapter 1, General introduction to nanoparticles. In: Horikoshi S, Serpone N (eds) Microwaves in nanoparticle synthesis: fundamentals and applications. Wiley-VCH, Weinheim, pp 1–24

Jasper P (1978) Potassium transport system of *Rhodopseudomonas capsulate*. J Bacteriol 133:1314–1322

Jixian Y, Wei W, Shanshan P, Fang M, Ang L, Dan W, Jie X (2015) Competitive adsorption of heavy metals by extracellular polymeric substances extracted from *Klebsiella* sp. J1. Bioresour Technol 196:533–539. https://doi.org/10.1016/j.biortech.2015.08.011

Kar S, Maity JP, Jean JS, Liu CC, Nath B, Lee YC, Bundschuh J, Chen CY, Li Z (2011) Role of organic matter and humic substances in the binding and mobility of arsenic in a Gangetic aquifer. J Environ Sci Health A 46:1231–1238. https://doi.org/10.1080/10934529.2011.598796

Koch AL (1990) Growth and form of the bacterial cell wall. Am Sci 78:327–341

Komeda H, Kobayashi M, Shimizu S (1997) A novel transporter involved in cobalt uptake. Proc Natl Acad Sci USA 94:36–41. https://doi.org/10.1073/pnas.94.1.36

Kundu D, Hazra C, Chatterjee A, Chaudhari A, Mishra S (2014) Extracellular biosynthesis of zinc oxide nanoparticles using *Rhodococcus pyridinivorans* NT2: multifunctional textile finishing, biosafety evaluation and in vitro drug delivery in colon carcinoma. J Photochem Photobiol B 140:194–204. https://doi.org/10.1016/j.jphotobiol.2014.08.001

Lamelas C, Benedetti M, Wilkinson KJ, Slaveykova VI (2006) Characterization of H^+ and Cd^{2+} binding properties of the bacterial exopolysaccharides. Chemosphere 65:1362–1370. https://doi.org/10.1016/j.chemosphere.2006.04.021

Lau TC, Wu XA, Chua H, Qian PY, Wong PK (2005) Effect of exopolysaccharides on the adsorption of metal ions by *Pseudomonas* sp. CU-1. Water Sci Technol 52:63–68

Ledin M (2000) Accumulation of metals by microorganisms-processes and importance for soil systems. Earth Sci Rev 51:1–31. https://doi.org/10.1016/S0012-8252(00)00008-8

Lemire JA, Harrison JJ, Turner RJ (2013) Antimicrobial activity of metals: mechanisms, molecular targets and applications. Nat Rev Microbiol 11:371–384. https://doi.org/10.1038/nrmicro3028

Li X, Xu H, Chen ZS, Chen ZS, Chen G (2011) Biosynthesis of nanoparticles by microorganisms and their applications. J Nanomater. https://doi.org/10.1155/2011/270974. Article ID 270974

Liu H, Fang HH (2002) Characterization of electrostatic binding sites of extracellular polymers by linear programming analysis of titration data. Biotechnol Bioeng 30:806–811. https://doi.org/10.1002/bit.10432

Manimaran M, Kannabiran K (2017) Actinomycetes-mediated biogenic synthesis of metal and metal oxide nanoparticles: progress and challenges. Lett Appl Microbiol 64:401–408. https://doi.org/10.1111/lam.12730

Manivasagan P, Venkatesan J, Sivakumar K, Kim SK (2016) Actinobacteria mediated synthesis of nanoparticles and their biological properties: a review. Crit Rev Microbiol 42:209–221. https://doi.org/10.3109/104084X.2014.917069

Martínková L, Uhnáková B, Pátek M, Nesvera J, Kren V (2009) Biodegradation potential of the genus *Rhodococcus*. Environ Int 35:162–177. https://doi.org/10.1016/j.envint.2008.07.018

Merroun ML, Ben Chekroun K, Arias JM, González-Muñoz MT (2003) Lanthanum fixation by *Myxococcus xanthus*: cellular location and extracellular polysaccharide observation. Chemosphere 52:113–120. https://doi.org/10.1016/S0045-6535(03)00220-0

Mirimanoff N, Wilkinson KJ (2000) Regulation of Zn accumulation by a freshwater Gram-positive bacterium (*Rhodococcus opacus*). Environ Sci Technol 34:616–622. https://doi.org/10.1021/es990744g

Mowll JL, Gadd GM (1984) Cadmium uptake by *Aureobasidium pullulans*. J Gen Microbiol 130:279–284. https://doi.org/10.1099/00221287-130-2-279

Newton GL, Arnold K, Price MS, Sherrill C, delCardayre SB, Aharonowitz Y, Cohen G, Davies J, Fahey RC, Davis C (1996) Distribution of thiols in microorganisms: mycothiol is a major thiol in most *actinomycetes*. J Bacteriol 178:1990–1995. https://doi.org/10.1128/jb.178.7.1990-1995.1996

Nies D (1999) Microbial heavy-metal resistance. Appl Microbiol Biotechnol 51:730–750. https://doi.org/10.1007/s002530051

Orro A, Cappelletti M, D'Ursi P, Milanesi L, Di Canito A, Zampolli J, Collina E, Decorosi F, Viti C, Fedi S, Presentato A, Zannoni D, Di Gennaro P (2015) Genome and phenotype microarray analyses of *Rhodococcus* sp. BCP1 and *Rhodococcus opacus* R7: genetic determinants and metabolic abilities with environmental relevance. PLoS One 10(10):e0139467. https://doi.org/10.1371/journal.pone.0139467

Otari SV, Patil RM, Nadaf NH, Ghosh SJ, Pawar SH (2012) Green biosynthesis of silver nanoparticles from an actinobacteria *Rhodococcus* sp. Mater Lett 72:92–94. https://doi.org/10.1016/j.matlet.2011.12.109

Pantidos N, Horsfall LE (2014) Biological synthesis of metallic nanoparticles by bacteria, fungi and plants. J Nanomed Nanotechnol 5:5. https://doi.org/10.4172/2157-7439.1000233

Paperi R, Micheletti E, De Philips R (2006) Optimization of copper sorbing-desorbing cycles with confined cultures of the exopolysaccharide-producing cyanobacterium *Cyanospira capsulata*. J Appl Microbiol 101:1351–1356. https://doi.org/10.1111/j.1365-2672.2006.03021.x

Park JH, Kim BS, Chon CM (2018) Characterization of iron and manganese minerals and their associated microbiota in different mine sites to reveal the potential interactions of microbiota with mineral formation. Chemosphere 191:245–252. https://doi.org/10.1016/j.chemosphere.2017.10.050

Pau RN, Klipp W, Leimkühler S (1997) Molybdenum transport, processing and gene regulation. In: Winkelmann G, Carrano CJ (eds) Transition metals in microbial metabolism. Harwood, Amsterdam, pp 217–234

Pavel VL, Sobariu DL, Tudorache-Fertu ID, Statescu F, Gaverilescu M (2013) Symbiosis in the environment biomanagement of soils contaminated with heavy metals. Eur J Sci Theol 9:211–224

Perelomov LV, Sarkarb B, Sizovad OI, Chilachava KB, Shvikina AY, Perelomova IV, Atroshchenkoa YM (2018) Zinc and lead detoxifying abilities of humic substances relevant to environmental bacterial species. Ecotoxicol Environ Saf 151:178–183. https://doi.org/10.1016/j.ecoenv.2018.01.018

Perminova IV, Hatfield K (2005) Remediation chemistry of humic substances: theory and implications for technology. In: Perminova IV, Hatfield K, Hertcorn N (eds) Use of humic substances to remediate polluted environments: from theory to practice. Springer, Dordrecht, pp 3–36. https://doi.org/10.1007/1-4020-3252-8_1

Perminova IV, Kulikova NA, Zhilin D, Grechischeva M, Kovalevskii DV, Lebedeva GF, Matorin DN, Venediktov PS, Konstantinov AI, Kholodov VA, Petrosyan VS, (2006) Mediating effects of humic substances in the contaminated environments. Concepts, results, and prospects. In: Twardowska I, Allen HE, Haggblom MH, Stefaniak S (Eds) Viable methods of soils and water pollution monitoring, protection and remediation, Krakow, Poland, pp 249–273. https://doi.org/10.1007/978-1-4020-4728-2_17

Phillips DJ, Rainbow PS (2013) Biomonitoring of trace aquatic contaminants, vol 37. Springer, New York. ISBN: 978-94-011-2122-4

Piacenza E, Presentato A, Turner RJ (2018) Stability of biogenic metal(loid) nanomaterials related to the colloidal stabilization theory of chemical nanostructures. Crit Rev Biotechnol 25:1–20. https://doi.org/10.1080/07388551.2018.1440525

Plette ACC, van Riemsdijk WH, Benedetti MF, van der Wal A (1995) pH dependent charging behavior of isolated cell walls of a Gram-positive soil bacterium. J Colloid Interface Sci. 173:354–363. https://doi.org/10.1006/jcis.1995.1335

Plette ACC, Benedetti MF, Vanriemsdijk WH (1996) Competitive binding of protons, calcium, cadmium, and zinc to isolated cell walls of a Gram-positive soil bacterium. Environ Sci Technol 30:1902–1910. https://doi.org/10.1021/es950568l

Pogorelova TE, Ryabchenko LE, Sunzow NI, Yanenko AS (1996) Cobalt-dependent transcription of nitrile hydratase gene in *Rhodococcus rhodochrous* M8. FEMS Microbiol Lett 144:191–195. https://doi.org/10.1016/0378-1097(96)00361-8

Presentato A, Piacenza E, Anikovskiy M, Cappelletti M, Zannoni D, Turner RJ (2016) *Rhodococcus aetherivorans* BCP1 as cell factory for the production of intracellular tellurium nanorods under aerobic conditions. Microb Cell Fact 15:204. https://doi.org/10.1186/s12934-016-0602-8

Presentato A, Cappelletti M, Sansone A, Ferreri C, Piacenza E, Demeter MA, Crognale S, Petruccioli M, Milazzo G, Fedi S, Steinbüchel A, Turner RJ, Zannoni D (2018a) Aerobic growth of *Rhodococcus aetherivorans* BCP1 using selected naphthenic acids as the only carbon and energy sources. Front Microbiol 9:672. https://doi.org/10.3389/fmicb.2018.00672

Presentato A, Piacenza E, Anikovskiy M, Cappelletti M, Zannoni D, Turner RJ (2018b) Biosynthesis of selenium-nanoparticles and -nanorods as a product of selenite bioconversion by the aerobic bacterium *Rhodococcus aetherivorans* BCP1. New Biotechnol 41:1–8. https://doi.org/10.1016/j.nbt.2017.11.02

Presentato A, Piacenza E, Darbandi A, Anikovskiy M, Cappelletti M, Zannoni D, Turner RJ (2018c) Assembly growth and conductive properties of tellurium nanorods produced by *Rhodococcus aetherivorans* BCP1. Sci Rep. https://doi.org/10.1038/s41598-018-22320-x

Rao CNR, Muller A, Cheetham AK (2004) Chapter 1, Nanomaterials. In: Rao CNR, Muller A, Cheetham AK (eds) The chemistry of nanomaterials: synthesis, properties and applications. WILEY-VCH, Weinheim, pp 1–11

Rhoads DB, Epstein W (1977) Energy coupling to net K+ transport in *Escherichia coli* K-12. J Biol Chem 252:1394–1401

Rodrigues A, Brito A, Janknecht P, Proenca MF, Nogueira R (2009) Quantification of humic acids in surface water: effects of divalent cations, pH, and filtration. J Environ Monit 11:377–382. https://doi.org/10.1039/B811942B

Salehizadeh H, Shojaosadati SA (2003) Removal of metal ions from aqueous solution by polysaccharide produced from *Bacillus firmus*. Water Res 37:4231–4235. https://doi.org/10.1016/S0043-1354(03)00418-4

Sharma SK, Goloubinoff P, Christen P (2011) Non-native proteins as newly identified targets of heavy metals and metalloids. In: Bánfalvi G (ed) Cellular effects of heavy metals. Springer, Heidelberg, pp 263–274. https://doi.org/10.1007/978-94-007-0428-2_12

Sheng PX, Tan LH, Chen JP, Ting YP (2004) Biosorption performance of two brown marine algae for removal of chromium and cadmium. J Disper Sci Technol 25:679–686. https://doi.org/10.1081/DIS-200027327

Smith RL, Maguire ME (1998) Microbial magnesium transport: unusual transporters searching for identity. Mol Microbiol 28:217–226. https://doi.org/10.1046/j.1365-2958.1998.00810.x

Song JY, Kim BS (2009) Rapid biological synthesis of silver nanoparticles using plant leaf extracts. Bioprocess Biosyst Eng 32:79–84. https://doi.org/10.1007/s00449-008-0224-6

Stillman MJ (1995) Metallothioneins. Coord Chem Rev 144:461–571. https://doi.org/10.1016/0010-8545(95)01173-M

Stratton H, Brooks P, Griffiths P, Seviour R (2002) Cell surface hydrophobicity and mycolic acid composition of *Rhodococcus* strains isolated from activated sludge foam. J Ind Microbiol Biotechnol 28:264–267. https://doi.org/10.1038/sj/jim/7000241

Strong PJ, Burgess JE (2008) Treatment methods for wine-related and distillery wastewaters: a review. Bioremediat J 12:70–87. https://doi.org/10.1080/10889860802060063

Subbaiya R, Preetha L, Gayathril S, Swarnalatha WA, Selvam MM (2014) Synthesis and characterization of silver nanoparticles from *Rhodococcus*-2891 and its antitumor activity against lung cancer cell line (A549). In: International conference on science, engineering and management research (ICSEMR 2014), ISBN: 978-1-4799-7613-3

Suchand Sandeep CS, Samal AK, Pradeep T, Philip R (2010) Optical limiting properties of Te and Ag_2Te nanowires. Chem Phys Lett 485:326–330. https://doi.org/10.1016/j.cplett.2009.12.065

Sunitha A, Isaac RSR, Geo S, Sornalekshmi S, Rose A, Praseetha PK (2013) Evaluation of antimicrobial activity of biosynthesized iron and silver nanoparticles using the fungi *Fusarium oxysporum* and *Actinomycetes* sp. on human pathogens. Nano Biomed Eng 5:39–45. https://doi.org/10.5101/nbe.v5i1.p39-45

Suresh K, Prabagaran SR, Sengupta S, Shivaji S (2004) *Bacillus indicus* sp. nov., an arsenic-resistant bacterium isolated from an aquifer in West Bengal, India. J Syst Evol Microbiol 54:1369–1375. https://doi.org/10.1099/ijs.0.03047-0

Tan Y, Yao R, Wang R, Wang D, Wang G, Zheng S (2016) Reduction of selenite to Se (0) nanoparticles by filamentous bacterium *Streptomyces* sp. ES2-5 isolated from a selenium mining soil. Microb Cell Fact 15:157. https://doi.org/10.1186/s12934-016-0554-z

Tangney P, Fahy S (2002) Density-functional theory approach to ultrafast laser excitation of semiconductors: application to the A1 phonon in tellurium. Phys Rev B 14:279. https://doi.org/10.1103/PhysRevB.65.054302

Taylor DE (1999) Bacterial tellurite resistance. Trends Microbiol 7:111–115. https://doi.org/10.1016/S0966-842X(99)01454-7

Tchounwou P, Newsome C, Williams J, Glass K (2008) Copper-induced cytotoxicity and transcriptional activation of stress genes in human liver carcinoma cells. Metal Ions Biol Med 10:285–290

Tomioka N, Uchiyama H, Yagi O (1994) Cesium accumulation and growth characteristics of *Rhodococcus erythropolis* CS98 and *Rhodococcus* sp. strain CS402. Appl Environ Microbiol 60:2227–2231

Turner RJ (2001) Tellurite toxicity and resistance in Gram-negative bacteria. Recent Res Dev Microbiol 5:69–77

Turner RJ, Weiner JH, Taylor DE (1999) Tellurite-mediated thiol oxidation in *Escherichia coli*. Microbiology 145:2549–2557. https://doi.org/10.1099/00221287-145-9-2549

Turner RJ, Borghese R, Zannoni D (2012) Microbial processing of tellurium as a tool in biotechnology. Biotechnol Adv 30:954–963. https://doi.org/10.1016/j.biotechadv.2011.08.018

Valls M, de Lorenzo V (2002) Exploiting the genetic and biochemical capacities of bacteria for the remediation of heavy metal pollution. FEMS Microbiol Rev 4:327–338. https://doi.org/10.1111/j.1574-6976.2002.tb0018.x

van der Wal A, Norde W, Zehnder AJB, Lyklema J (1997) Determination of total charge in the cell walls of Gram-positive bacteria. J Colloids Surf B Biointerfaces 9:81–100. https://doi.org/10.1016/S0927-7765(96)01340-9

Vasquez TGP, Botero AEC, de Mesquita LMS, Torem ML (2007) Biosorptive removal of Cd and Zn from liquid streams with a *Rhodococcus opacus* strain. Miner Eng 20:939–944. https://doi.org/10.1016/j.mineng.2007.03.014

Vela-Cano M, Castellano-Hinojosa A, Vivas AF, Toledo MVM (2014) Effect of heavy metals on the growth of bacteria isolated from sewage sludge compost tea. Adv Microbial 4:644–655. https://doi.org/10.4236/aim.2014.410070

Volesky B (1990) Biosorption and biosorbents. In: Volesky B (ed) Biosorption of heavy metals. CRC, Boca Raton, FL, pp 3–6. ISBN: 9780849349171

Wei X, Fang L, Cai P, Huang Q, Chen H, Liang W, Rong X (2011) Influence of extracellular polymeric substances (EPS) on Cd adsorption by bacteria. Environ Pollut 159:1369–1374. https://doi.org/10.1016/j.envpol.2011.01.006

Wilde EW, Benemann JR (1993) Bioremoval of heavy metals by the use of microalgae. Biotechnol Adv 4:781–812. https://doi.org/10.1016/0734-9750(93)9000-6

Wolfram L, Friedrich B, Eitinger T (1995) The *Alcaligenes eutrophus* protein HoxN mediates nickel transport in *Escherichia coli*. J Bacteriol 177:1840–1843. https://doi.org/10.1128/jb.177.7.1840-1843.1995

Xue HB, Stumm W, Sigg L (1988) The binding of heavy metals to algal surfaces. Water Res 22:917–626. https://doi.org/10.1016/0043-1354(88)90029-2

Yuwen L, Wang L (2013) Chapter 11.5, Nanoparticles and quantum dots. In: Devillanova F, Du Mont WW (eds) Handbook of chalcogen chemistry: new perspectives in sulfur, selenium and tellurium, 2nd edn. The Royal Society of Chemistry, Cambridge, pp 232–260

Zhang B, Ye X, Dai W, Hou W, Zuo F, Xie Y (2006) Biomolecule-assisted synthesis of single-crystalline selenium nanowires and nanoribbons via a novel flake-cracking mechanism. Nanotechnology 17:385–390. https://doi.org/10.1088/0957-4484/17/2/007

Zheng-Bo Y, Qing L, Chuan-chuan L, Tian-hu C, Jin W (2015) Component analysis and heavy metal adsorption ability of extracellular polymeric substances (EPS) from sulfate reducing bacteria. Bioresour Technol 194:399–402. https://doi.org/10.1016/j.biortech.2015.07.042