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Microbial recovery of metallic nanoparticles from industrial wastes and their environmental applications

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Abstract

In recent years, metallic nanoparticles (NPs) have been produced by biological methods using bacteria and have been used with remarkable environmental applications. This paper emphasizes the basic aspects of microbial synthesis of metallic nanoparticles, from the election of the strain to the settings of reaction parameters. Mechanisms involved in the microbial production of NPs are also discussed, summarizing general findings and implications in the process. There is also a section dedicated to the identification of wastes as a source of precious metals and the production of metallic NPs from waste streams containing ionic metals to give a vision of the opportunities to implement microbial synthesis as a treatment-recovery technology. Environmental applications of biogenic NPs are reviewed in detail indicating that the implementation of these nanomaterials enable to achieve higher removal efficiencies and greater extent of transformation of recalcitrant compounds in wastewater treatment systems. Under this scenario and based on the information reviewed concluding remarks and futures perspectives are enunciated.

Keywords: Bioremediation; nanomaterials; microbial synthesis; recovery; wastewater treatment; nanoparticle; mechanisms.

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INTRODUCTION

Nanomaterials have attracted a great interest nowadays, mainly because of their wide range of applications in fields such as energy, medicine, electronics, space and pharmaceutical industries. Among nanomaterials, particles between 1 and 100 nm in size, called nanoparticles (NPs), have gained scientific and technological interest. Their nanometric size results in unique physicochemical characteristics, such as high surface area to volume ratio, which potentially yield high reactivity.

Although examples of nanostructured materials date since the 4th century, those were based on craftsmen's empirical understanding and manipulation of materials[1]. At the present time, it is possible to use different methods to synthesize NPs and characterize them by advanced techniques, which contribute to understand and study in more detailed the nanostructure.

However, now the challenge is to obtain specific properties in NPs linked to their applications and many of them are size- and shape-dependent; hence the synthesis process is crucial. Regarding methods of synthesis, NPs are produced by physical, chemical and biological methods. Yet, nanomaterial synthesis protocols of some chemical and physical methods involve the use of toxic chemicals and hence the generation of residues, which have also been associated with toxic effects[2,3]. In consequence, there has been much interest in the development of reliable, nontoxic, clean and environmentally friendly methods and protocols for the synthesis of NPs, which is reflected in the emergence of biological methods as an option to conventional approaches. Currently, several microorganisms and plant extracts have been explored for their ability to produce NPs[4–6].

This paper provides an overview highlighting the main aspects of the microbial synthesis of metallic NPs by bacteria, such as parameters of synthesis, mechanisms reported, source of the precursor as well as environmental relevance and applications in water treatment systems, metal recovery and contaminants degradation. Each section summarizes fundamental information to give elements in order to discuss and conclude advances and gaps regarding nanoparticle synthesis by bacteria and their environmental applications.

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MICROBIAL SYNTHESIS OF METALLIC NPs

The formation of mineral phases by a number of living organisms is known since many years ago through a process referred to as biomineralization. Indeed, the term biologically induced biomineralization (Lowenstam 1981) refers to the biological formation of minerals without any apparent regulatory control[7]. Biominerals form as incidental byproducts of interactions between microorganisms and their immediate environment. This process is characterized by bulk extracellular and/or intercellular mineral formation, without the elaboration of organic matrices. Minerals produced through this passive process have crystal habits and chemical compositions similar to those produced by precipitation under inorganic conditions.

Therefore, the natural occurrence of inorganic nanomaterials in microorganisms encourages the use of microorganisms as possible eco-friendly factories for nanoparticle synthesis routes, alternative to chemical methods[8]. The metal reduction potential of several bacteria has been known for at least 20 years. Microbial metabolism can change the oxidation state of inorganic species by oxidation and reduction of metals[9]. For instance, dissimilatory metal reducers and sulfate reducers play a key role in metals biogeochemistry[8]. Bacteria have been used in metal bioremediation due to their ability to survive at high concentrations of heavy metals by several types of mechanisms to tolerate the uptake of heavy metal ions.

Mechanisms of microbial resistance includes: (i) hydrogen sulfide production (by driving the formation of insoluble metal sulfides), (ii) production of organic compounds (by binding or chelating the metal), (iii) uptake and accumulation (nonspecific binding or metabolism-dependent intracellular uptake), (iv) metal transformation (valence changes) and (v) genetically determined metal resistance (by genes or plasmids)[10].

In the last years, several bacteria have been used for the synthesis of metal NPs, which is divided in extra- and intracellular synthesis according to the location: inside (by transporting ions into the microbial cell) or outside (by trapping the metal ions on the surface) of the cell, respectively. For practical purposes, extracellular formation of NPs is desired in order to avoid further steps for their recovery.

The typical methodology for the synthesis of metallic NPs by bacteria implies deciphering three elements: bacterial strain, metal salt and incubation conditions (Figure 1). Microorganisms are cultured and harvested at the optimal growth period. In this stage, it is important the selection of the strain (oxidation or reduction process, aerobic or anaerobic conditions) and the cellular concentration that will be exposed to the metal. In

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practice, the process usually starts with the aim to obtain a specific metallic nanoparticle, hence bacteria are selected according to their abilities to change or transform the metals. Depending on the objective, the metallic salt needs to be carefully chosen and special consideration to the metal speciation and solubility has to be made as chemical aspects are crucial to achieve metals reduction. The incubation period is the main part of the process since, during this time, NPs are formed. The parameters mentioned in Figure 1, such as pH, temperature, electron donor, and those regarding bacteria and metals selection (mentioned before) are determinant to achieve NPs production. In the next section, key factors affecting the microbial synthesis of metallic NPs are discussed.

To date, many NPs have been synthesized by bacteria. In this paper, we summarize the information reported on metallic NPs biosynthesis from this century (from 2000 to date). As can be observed in Table 1, most investigations have been focused on the synthesis of iron (Fe_3O_4, Fe_2O_3, Fe_3S_4), precious metals (Au, Ag, Pd, Pt), rare elements, such as Se and Te (Se, Te, Cu_2Se), as well as specific metallic NPs, such as TiO_2, ZnS, CdS, Bi_2S_3; all of them with a wide range of applications. Table 1 summarizes recent investigations regarding 32 strains and enriched consortia, which include different bacteria: aerobes, anaerobes, Gram +, Gram -, isolated strains, metal-reducers, sulfur-reducers and several others. Among them, *Geobacter sulfurreducens* and *Shewanella oneidensis* are, to date, the most studied strains as both are reported to synthesize four different metallic NPs (iron, Pd^0, Au^0 and Ag^0). Also, it can be confirmed that different strains synthesize the same type of metallic NPs, but size and location (intra- or extracellular) could differ. Moreover, biologically generated NPs are not only synthesized, but they are also proved to have applications in different fields with the same or even better performance than their chemically synthesized counterparts.

It is worth to mention that all the studies reported in Table 1 refer to the use of whole cells, as a culture, but currently there are special interest on using culture supernatants, purified enzymes, and excreted biomolecules[57,58]. This strategy is specially pursued to make sure that NPs are uniformly dispersed and to avoid an extra step to separate them from the cells.

KEY FACTORS AFFECTING THE MICROBIAL SYNTHESIS OF METALLIC NPs

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Besides the strain, the process to obtain metallic NPs by biological methods implies different factors. Table 2 summarizes the main conditions affecting the microbial synthesis of NPs, including cells growth phase, reaction medium, pH, temperature, reaction time, aerobic or anaerobic conditions and cells concentration.

According to the literature, most studies have performed experiments with resting cells, which means that late exponential, early- and stationary-phase bacterial cultures have been used. However, sometimes the metal serves as terminal electron acceptor for the anaerobic growth of bacteria and NPs are obtained as a product of this respiratory process[46].

Regarding the reaction medium used in the experiments, it has been proved that buffers (i.e., phosphate), mineral salt medium and even aqueous solutions can be successfully used. Moreover, growth media can be used and/or adjusted in order to obtain metallic NPs. Regarding the medium and the pH, it must be considered that the presence and concentration of some chemical compounds could chelate, form metal complexes, etc., altering the metal speciation, hence affecting the bioavailability of metals.

The pH is an important factor to consider in the microbial synthesis of NPs. It can be inferred that neutral conditions apply for most strains, except for acidophiles, especially if the process depends on the integrity and metabolism of microorganisms. Moreover, the pH value can also influence the shape and size of NPs[29].

Temperature requirements depend on the type of strain used; most of the synthesis protocols are successful at intervals between 30 and 37°C. However, there are reports of different temperatures, mainly when this parameter is adjusted in order to optimize the formation of NPs. A special case is the combination of temperatures when two methods are used, for example biological and physicochemical synthesis, each of them carried out at an optimum value[59].

Concerning time scale, the process to obtain metallic NPs can vary from a few hours to weeks, the time needed can be related to the bacterial strain, metal and cells concentrations, or the addition of a redox mediator, which has been documented to increase the reduction rate[60,62]. However, if the reaction time is overestimated it can lead to undesirable results, such as NPs aggregation[16].

As shown in Table 2, the parameter related to cells concentration is expressed in two ways, as inoculum (when cells growth is expected to occur) or as catalyst (when cells are used to trigger the synthesis and as scaffold). For that reason, this parameter is reported in different units, such as mg cells/L, number (10^n) of cells/volume, mL of culture, v/v, cell dry weight, etc.; clearly this disparity in units avoids comparison among

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the experiments performed. Generally, it is always needed to use an excess of cells and a low concentration of metals; this ratio must be determined by experiments, to avoid damage to cells (toxicity) and to guarantee NPs production.

The synthesis process is reported according to metal reduction rate, size and shape of NPs, location (intra- or extracellular), composition and crystalline structure (Table 1). The studies performed under different experimental conditions allowed to investigate the mechanisms involved since physicochemical aspects can be very influential. The use of molecular techniques provides further information to propose details on specific genes involved. To date, different findings have been reported which are summarized in Table 2.

Proteins have been found to play an important role in the synthesis of NPs and some of them have been isolated[29,51,63]. Also amino and carboxylate groups have been reported to be responsible for the reduction and stabilization of NPs acting as capping agents[23,26,31,50]. Other reported mechanisms specify the interactions governing the process, some of them have referred to complexes formation, film diffusion or electrostatic interactions as the first step, followed by pore diffusion or ligand substitution until bioreduction is achieved and nucleation occurred as a final step[23,28,60]. However, it cannot be assumed that these mechanisms are general or applicable for all conditions, since it can vary according to experimental conditions, physicochemical parameters, strain used, metabolic pathways, etc.

Advances in the development of NPs synthesis protocols have led to combined processes, such as biological-chemical or biological-natural-oxidation[59,61]. Fusion of methods allows the production of metallic NPs while overcoming limitations of single processes.

MECHANISMS INVOLVED IN THE MICROBIAL SYNTHESIS OF NPs

Several studies performed under different experimental conditions have elucidated some mechanisms involved in the microbial synthesis of NPs. The use of molecular techniques also contributed with further information to propose details on specific genes involved in the reduction pathway of metals. To date, different findings have been reported regarding the mechanisms involved in the microbial synthesis of NPs, and they are summarized in Table 2.

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The mechanisms reported have been explained in terms of (i) enzymes and proteins, (ii) extracellular substances, (iii) addition and/or participation of redox mediators, (iv) metabolites and secondary metabolites and (v) specific gene clusters. The main mechanisms reported are summarized in Figure 2.

Proteins have been found to play an important role in the synthesis of NPs. FT-IR spectra of biosynthesized NPs have shown peaks in the amide I (1629.85 cm^{-1}) and amide II (1535.34 cm^{-1}) regions, characteristic of proteins/enzymes. Therefore, results from most studies indicate binding of metals to free amino or carboxylate groups of proteins secreted or located in the bacterial cell membrane.

Outer membrane c-type cytochromes have also been linked to metal reduction by transferring electrons to metals via direct contact, but their abundance and participation strongly depends on the strain[17,18,60]. Besides, some studies reported the induction of specific proteins due to exposure of bacteria to metal solutions leading to metal reduction and production of metallic NPs[11]. Moreover, experiments with isolated proteins presumably involved in metals reduction have been performed and the results have shown that metals reduction is linked to those specific proteins[11,29,51]. In addition, proteins have been reported to be responsible for the reduction and stabilization of NPs acting as capping agents[23,26,31,50].

Enzymes, such as reductases, flavoenzymes, oxidoreductases, hydrogenases, amylases, etc., have been associated with metals reduction. Enzyme activity in culture supernatant evinced participation of extracellular enzymes in metallic NPs biosynthesis[49]. However, the proteins and/or enzymes involved are specific of the strain. Efforts have been done, but complete enzymatic pathways have not been fully understood or explained yet because of the complexity of the process.

Extracellular substances, such as reduced sugars, proteins/peptides and other biomolecules produced by bacteria under metal stress, have also been reported to participate in metals reduction through their interaction with functional groups, such as amine and carboxyl groups[16,26,39,44].

Metabolites and secondary metabolites (e.g. glycyl-L-proline) have also been reported as responsible of bioreduction, stabilization and as capping agents of NPs by interacting with functional groups, such as carboxylic, aldehyde, alcohols, primary amines and phenols, among others.[51]

Results have also demonstrated that the presence of a redox mediator either excreted by cells or artificially added to the medium (e.g. anthraquinone-2,6-disulfonate, AQDS) increases the rate of NPs production and enhances the kinetics of metals reduction.[15,18]

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Some reported mechanisms specify the interactions governing the process; for instance, complexes formation, film diffusion or electrostatic interactions as the first step, followed by pore diffusion or ligand substitution until bioreduction is achieved and nucleation occurs as a final step[23,28,60].

The different mechanisms or elements involved in the biosynthesis of metallic NPs explained above cannot be assumed applicable for all experimental conditions since they can vary according to physicochemical parameters, strain used, metabolic pathways, metals solution, etc. The complexity of the process and the multiple and variable factors connected make difficult the full description, but the identification of key elements offers the advantage to control and optimize the process. For example, the combination of methods allows the production of metallic NPs, while overcoming limitations of detached processes; hence, advances in the development of NPs synthesis protocols have led to combined processes, such as biological-chemical or biological-natural-oxidation[54,59].

WASTES AS A SOURCE OF PRECIOUS METALS

Mining activities are currently constrained by limited high-grade ores due to depletion of local resources together with restrictions in the import of precious metals as a result of regulations on metal-exporting countries[64,65]. Thus, recycling of precious metals from waste streams has emerged as a possible solution that can alleviate the disproportion between supply and demand[66].

A variety of wastes generated from different human activities contain significant amounts of precious metals, such as Pt, Pd, Cu, Zn, Ni, Mo, among others (Table 3). These wastes derive from abandoned mines, geothermal fluids, leachates, as well as effluents generated from metallurgic industries and hospitals. Recently, Westerhoff et al. (2015)[67] made a nationwide survey to assess the recovery opportunities and valuation of metals in municipal sludges from U. S. wastewater treatment plants (WWTPs). For a community of 1 million people, metals in biosolids were valued at up to US$13 million annually. The most lucrative identified elements were Ag, Cu, Au, P, Fe, Pd, Mn, Zn, Ir, Al, Cd, Ti, Ga and Cr accounting for a combined value of US$280 per ton of sludge. Thus, there is a great potential to recover valued metals from biosolids generated at WWTPs. Furthermore, wastewaters containing metal ions are generated in several anthropogenic activities (mining, metallurgic operations, burning fossil fuels, cement production, electroplating, leather

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tanning) and products (manufacturing plastics, fertilizers, pesticides, anticorrosive agents, Ni-Cd batteries, paints, pigments, dyes, photovoltaic devices)[68].

Several technologies have been explored for the recovery of precious metals from wastewaters for a long time. These technologies include hydroxide (lime) and sulfide precipitation, adsorption processes, ion exchange, solvent extraction, as well as membrane and electrochemical technologies[79]. Nevertheless, the main limitation for recovering precious metals from those wastewaters is that the level of these valued elements is usually quite low. Therefore, most of these recovery options are not economically attractive and there is an urgent need to develop and apply low-cost and environmental-friendly methods to recover precious metals from wastewaters[66]. In the following sections the main microbial biotechnologies reported for the recovery of precious metals will be discussed.

MICROBIAL APPROACHES TO RECOVER PRECIOUS METALS FROM WASTES

The capacity of microorganisms to change the redox state of several elements can be taken as strategy to recover precious elements from waste streams. In the following sections the main microbial processes explored for the recovery of precious metals will be discussed.

Recovery under sulfate-reducing conditions

Sulfate-reducing bacteria (SRB) have intensively been explored not only for metals removal from wastewaters, but also for their selective recovery in a variety of bioreactor configurations[79]. Many mine effluents contain high sulfate concentrations derived from sulfide oxidation. SRB convert sulfate to hydrogen sulfide (H_2S) and dissociated sulfides (HS^- and S^{2-}) that are removed from water via volatilization of H_2S, or preferentially, precipitation as poorly soluble metal sulfides. Passive and active technologies (requiring active management with either or both energy and chemicals) are currently available at full scale for water treatment[79].

Several abiotic and biological mechanisms contribute to the removal of sulfate, metals and acidity in passive SRB systems, such as compost bioreactors, infiltration beds and permeable reactive barriers[79]. These passive systems are particularly suitable for long-term bioremediation at abandoned mining sites[80]. Nevertheless, metals removal is less selective and predictable than in active systems, and they are generally insufficient for the recovery of precious metals[79].

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Metal ions can precipitate as sulfides (Pd^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}), hydroxides (Fe^{3+}, Cr^{3+}, Al^{3+}), and carbonates (Fe^{2+}, Mn^{2+}), whereas in active sulfidogenic bioreactors, metal hydroxides and carbonates represent only a minor fraction of the precipitates as compared to the predominant sulfides[79,81]. In passive systems, neutralization of acidic mine wastewater is often improved by using limestone crush[79].

High-rate active systems can present different configurations to achieve metals recovery with biogenic sulfide. In a single-stage flow sheet, sulfate reduction and metals sulfide precipitation proceed simultaneously in one reactor. Optimal environmental conditions, such as circumneutral pH and a temperature of 20-40 °C, should be maintained. Moreover, an excess sulfide concentration (200-400 mg S L^{-1}) must be kept in the bioreactor in order to prevent accumulation of inhibitory dissolved metals[82]. However, metals sulfide crystallization may not occur optimally under these conditions. Most of the common heavy metals, such as Fe, Co, Ni, Cu, Zn and Pb, will precipitate below discharge standards under such conditions, but the relatively high sulfide concentration promotes the formation of colloidal precipitates with poor settling and dewatering characteristics[83]. Also, extracellular polymeric substances excreted by SRB might interfere with crystallization, although these phenomena are still poorly understood. The advantage of the single-stage process is that it represents a simple and cheap option as compared to more complex arrangements. However, it is less suitable when metals concentrations are low (<50 mg L^{-1}) because the process easily becomes hydraulically limited, resulting in poor metals recovery. The single-stage flow sheet has already been applied at full-scale for sulfate and Zn removal from polluted groundwater at the Pasminco Budel Zink refinery in The Netherlands [84]. Another example of the single-stage scheme is the conversion of lead waste from car batteries, mainly consisting of $PdSO_4$ to PdS[85,86].

In two-stage systems, biological sulfate reduction and metals sulfide precipitation are accomplished in separated vessels. Sulfide produced by SRB is transferred from the bioreactor to the precipitator by recycle of either liquid or gas, or with both. The produced sludge can be retained in the precipitation vessel (e.g. by a filter) or it might be separated from the effluent with a clarifier. This treatment arrangement allows independent control of environmental conditions in the precipitator (pH and sulfide level) and the sulfate-reducing bioreactor. Metals are selectively precipitated by installing precipitators and clarifiers in series, controlling the pH and sulfide level in each precipitator unit[82].

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A flow sheet in which the liquid circuits for precipitation and sulfate reduction are completely separated can also be implemented. H_2S is stripped from the bioreactor with an oxygen-free carrier gas and fed to the precipitator. This strategy prevents the co-precipitation of metals phosphates and carbonates. Also, there is no direct contact between bacteria and potentially toxic compounds present in metals-bearing wastewaters[82]. This process is currently in operation at Kovohute Pribram (Czech Republic) to treat wastewater containing sulfate, Pb, Zn, Sn, As and Sb from a slag dump leachate[87].

Recovery in bioelectrochemical processes

Bioelectrochemical systems (BESs) are based on the capacity of microorganisms to respire on solid electron acceptors (i.e., electrodes) to harvest electrons from waste organic matter to generate electricity, remediate contamination, and produce valued chemicals while treating wastewaters[88]. BESs constitute an emerging technology for recovering metals from wastes, process streams, wastewaters, and leachate solutions. Electrons derived from the oxidation of organic matter at the anode are channeled to the cathode to reduce metal(loid)s. The redox potential of the half-cell reaction at the cathode is often higher than the potential generated at the anode, such that metal reduction proceeds at the cathode with a net positive cell potential and power generation. Supply of voltage is required to drive the reduction of certain metals whose half-cell reaction potentials are lower than the anode potential. The efficiency of metals recovery in BESs depends on anode potential, redox potential of half-cell reaction, metallic ions concentration, solution conductivity, fate of reduced species, presence of co-contaminants, pH, BESs design, and the material used at both cathode and anode[68].

Recovery of metals in BESs is mainly focused on the production of insoluble metallic species on the cathode via reductive precipitation. Nevertheless, reduction of some metal ions will generate soluble species with a lower oxidation state [*e.g.*, Cr(VI) $\rightarrow$ Cr(III); V(V) $\rightarrow$ V(IV)], which can in turn be recovered by chemical precipitation. Recovery of several base metals (*e.g.* Cu, Ni, Cd) as well as of a few precious and scarce metal(loid)s (*e.g.* Ag. Au, Co, Se) has been demonstrated in BESs[68]. Table 4 summarizes cases studies reporting the recovery of precious metals from wastewaters using BESs.

Microbial production of nanoparticles from waste streams containing ionic precious metals

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The vast majority of studies have been focused on the recovery of precious metals from synthetic wastewater under controlled conditions either with pure or mixed cultures. However, a few reports have explored real wastewaters for these purposes. For instance, there are reports on Pd recovery from metal refining[90] and catalytic converter production[75] waste streams by reductive precipitation by *Desulfovibrio* and *Cupriavidus* strains. Even though low volumes are released from these effluents, the economic benefit of this recovery strategy becomes interesting, representing a profit of \$25 L^{-1} and \$5 L^{-1} for refining and converter cases, respectively[71]. Reductive precipitation of Rh has also been achieved from wastewater by a sulfate-reducing consortium[91]. Furthermore, Ru recovery from a plating industry wastewater was described using selective adsorption on *Rhodopseudomonas palustris* strains[92]. Ru could also be recovered from acetic acid waste solution by adsorption on bacterial biomass/chitosan[93]. Additionally, complete recovery of Te was accomplished from acid leachate by reduction by *Pseudomonas mendocina*[94].

Therefore, there certainly is a great potential to recover precious metals (as NPs) from waste streams by microbial processes. Nevertheless, several challenges should be overcome when dealing with real wastewaters for this purpose. Waste streams may contain high concentrations of toxic metals, which may affect the metabolic capacity of microorganisms applied for precious metals recovery. Extreme acidity prevailing in most industrial effluents containing valued metals is also challenging and will require pH control or the application of acidophilic bacteria to overcome this limitation. Furthermore, produced NPs tend to agglomerate with biomass; thus, strategies to separate NPs from cells will also be required. One strategic option could be the application of redox mediators to promote the extracellular production of NPs[18-19,60], which may facilitate the separation of the NPs from the biomass.

ENVIRONMENTAL APPLICATIONS OF MICROBIALLY SYNTHESIZED METALLIC NPs

Biogenic metallic NPs have been employed in several environmental applications. For instance, microbially produced Pd(0) NPs (bio-Pd), supported on *Desulfovibrio desulfuricans* and *Bacillus sphaericus*, were applied as catalyst in the hydrogenation of organic molecules[95–97]. The application of bio-Pd in green chemistry has also been expanded to catalyze the Suzuki-Miyaura and Mizoroki-Heck coupling reactions[90,98]. Furthermore, several metallic NPs have also been applied in bio-catalysis to enhance the biodegradation of an array of recalcitrant contaminants. Hennebel et al. (2009)[99] described the use of bio-Pd for dechlorination of

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trichloroethylene (TCE). Bio-Pd particles were deposited on *Shewanella oneidensis*, which dechlorinated TCE with a rate up to 2,515 mg TCE day^{-1} g^{-1} Pd using hydrogen as an electron donor. Also, dehalogenation of TCE and diatrizoate using bio-Pd in microbial electrolysis cell (MEC) was carry out by Hennebel et al. (2011)[100]. TCE dehalogenation using bio-Pd (5 mg g^{-1} graphite) to coat cathode granules, reached a removal rate of 151 g TCE m^{-3} total cathode compartment (TCC) day^{-1}; and using bio-Pd free MCE the rate was 120 g TCE m^{-3} TCC day^{-1}, applying a power of -0.8 V. In addition, reduction efficiencies of diatrizoate were ~48% and ~93% for the treatments without and with bio-Pd, respectively[100]. Application of biologically produced metals was also conducted by by Forrez et al. (2011)[101]. These authors tested bio-Pd in lab-scale membrane bioreactor, and they found that iomeprol, iopromide and iohexol were removed by >97%, and diatrizoate by 90%. Moreover, with biogenic manganese oxides (bio-MnOx), 14 of 29 substances (pharmaceutical and personal care products) detected in the secondary effluents of sewage treatment plants were removed; achieving different values of removal for each substance, ranging from 52% to 95%.

Another application of metallic NPs in biological processes was conducted by Ansari et al. (2009)[102]. These authors decorated *Rhodococcus erythropolis* with NPs of Fe_3O_4 for the degradation of dibenzothiophene (DBT). Unlike of the biologically obtained metals described before, Fe_3O_4 NPs were chemically synthesized. Nevertheless, important results were obtained when the NPs were adsorbed on the bacterial surface, achieving 56% higher of DBT desulfurization compared with the control lacking NPs.

More recently, it has been proposed the recovery of Pd and other precious catalytic metals from wastewaters by anaerobic granular sludge for their subsequent application as biocatalysts in the biodegradation of recalcitrant pollutants in bioreactors with biomass enriched with NPs [103,104]. Suja et al. (2014)[105] first reported the enrichment of granular biomass with bio-Pd, whose catalytic activity was tested in the microbial reduction of *p*-nitrophenol and Cr(VI). Reductive transformation of *p*-nitrophenol by bio-Pd was ~20 times higher in comparison to microbial granules lacking bio-Pd in batch incubations. Also, complete reduction of up to 0.25 mM of Cr(VI) by bio-Pd was achieved in 24 h. *In situ* formation and immobilization of biogenic nano-Pd in anaerobic granular sludge was also accomplished to enhance the reductive decolorization of azo dyes[106]. Decolorization kinetics performed with Congo Red, Evans Blue and Orange II showed up to 10-fold increase on the rate of decolorization as compared to sludge control lacking bio-Pd in batch incubations. Moreover, continuous reduction of Pd(II) for its subsequent immobilization as bio-Pd in an up-flow anaerobic sludge bed

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(UASB) reactor was achieved[107]. Immobilized Pd(0) NPs were then tested as a biocatalyst for the continuous degradation of iopromide, a contrast X-ray medium, as well as 3-chloro-nitrobenzene (3-CNB) in UASB reactors. Enhanced conversion of 3-CNB, involving nitro-reduction and dehalogenation, occurred in the UASB reactor enriched with Pd(0), while only nitro reduction occurred in the control UASB reactor operated in the absence of bio-Pd. Furthermore, higher efficiency and extent of biotransformation of iopromide was accomplished in Pd(0)-enriched UASB reactor as compared to the control lacking the biocatalyst[107]. *In situ* production and immobilization of bio-Pd in anaerobic granular sludge is easy to achieved, economically feasible and more sustainable than alternative immobilizing strategies, such as encapsulation in alginate beads, coating on zeolites or retention by membranes (discussed in De Corte et al. 2012[108]). Therefore, recovery of ionic palladium and other catalytic elements from waste streams by granular biomass for their application as biocatalyst for the biodegradation of recalcitrant pollutants in bioreactors is an attractive, sustainable approach.

CONCLUDING REMARKS AND FUTURE PERSPECTIVES

Microbial synthesis of metallic NPs has become a competitive alternative to chemical synthesis not only because of its advantages and green approach, but also due to recent advances and dynamic research on this field. Synthesis parameters and mechanisms of biological NPs production are being established and understood facilitating the implementation and also the scale-up of these processes. An example is the case of the production of nanoscale biomagnetite particles by the Fe(III)-reducing bacterium, *Geobacter sulfurreducens*, which was successfully scaled up from laboratory- to pilot plant-scale production, while maintaining the surface reactivity and magnetic properties, which make this material well suited for commercial exploitation[109].

Once NPs are produced, and according to their composition, they can be applied for different purposes, such as medicine, electronics, catalysis, and remarkable environmental applications. Many nanomaterials, such as nano zero valent iron, TiO_2, Pd(0), etc., have been applied for contaminants removal with high efficiencies. More interesting, some approaches consider a global vision from the recovery of metals from metal-rich effluents to metallic NPs production and their application for the removal of target contaminants. Hence, wastewater treatment has a maximized additional value when this objective is pursued. Different effluents

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have the potential to be used as sources of metal recovery-NPs production: industrial wastewater, metallurgical effluents, hospitals wastewater and even abandoned mining sites. The challenges to get a successful NPs production process are the chemical and biotechnological aspects, including metal concentration and speciation (presence of more than one metal at important concentration), bacterial strain (metabolic requirements), synthesis conditions (pH, temperature, time, cell concentration), all of them set at lab conditions by testing.

Other important aspect to highlight is that even when pure cultures are demonstrated to be effective to NPs production, consortia have also been used successfully for some types of metallic NPs, therefore the process can be developed for scaling and practical applications. As it was reviewed in this paper, there are crucial aspects to consider and with more understanding on the mechanisms, better results can be obtained from biological processes producing metallic NPs.

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Table 1. List of microorganisms used for metallic nanoparticle synthesis and their relevant characteristics

	Microorganism	Characteristics	Nanoparticle	Size (nm)	Shape	NP Properties/Relevant information	Reference
AEROBES	*Actinobacter spp.*	Gram (-) Isolated from an air-exposed aqueous solution of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$	Fe_3O_4 γ-Fe_2O_3	10-40 (Fe_3O_4) 50-150 (γ-Fe_2O_3)	Quasi-spherical Cubic	Extracellular Superparamagnetic Shape was reaction time-dependent	11
			Fe_3S_4	Average size ≈19			12
	Bacillus megatrium	Gram (+)	Fe_3O_4	40-60	Cubic	NPs exhibit antibacterial properties	13
	Bacillus amyloliquefaciens	Gram (+) Isolated from dairy industry wastewater	TiO_2	15.23–87.6		Extracellular Tested for photocatalytic degradation of Reactive Red 31.	49
	Bacillus mycoides	Gram (+)	TiO_2	40–60	Spherical	Extracellular Biosynthesized nanoparticles were evaluated in Quantum Dot Sensitized Solar Cells (QDSSCs) and compared	50

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						with chemically produced TiO_2 nanoparticles.	
	Aeromonas hydrophila	Gram (-)	TiO_2	40-50	Spherical and uneven nanoparticles	Extracellular Antibacterial and inhibitory activity	51
	Acidithiobacillus thiooxidans	Gram (-) Sulfur oxidizing acidophilic	CdS	6.9-10		Intra- and extracellular	53
	Bacillus subtilis	Gram (+)	Se^0	50–150	Spherical	Size was time-dependent NPs have been used as enhancing and settled materials for building HRP (H_2O_2) biosensor.	44
			TiO_2	66–77	Spherical, oval	Individual as well as a few aggregates	45
	Acinetobacter sp. SW 30	Gram (-) Isolated from fresh activated sewage sludge	Au^0	19	Spherical	Monodispersed at lowest cell density and HAuCl4 salt concentration. Increase in cell number resulted in formation of polyhedral AuNP-39 nm	30
			Se^0			Intracellular Amorphous nanospheres of size 78 nm at	31

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						1.5 mM and crystalline nanorods at 2.0 mM Na_2SeO_3 concentration onward. SeNPs were selective against breast cancer cells.	
	Acidocella aromatica PFBCT	Gram (-) Acidophilic Fe(III)-reducing	Pd^0	18–19		Extra- and intracellular	40
	Acidiphilium cryptum SJH	Gram (-) Acidophilic Fe(III)-reducing	Pd^0			Extracellular	
	Rhodococcus aetherivorans BCP1	Gram (+) hydrocarbon- and chlorinated solvent degrader	Se^0	Variable	Nanorods	Synthesized SeNPs and nanorods (SeNRs) Unconditioned BCP1 cells: NPs average size of 71 ± 24 nm and 78 ± 42 nm. SeNRs average lengths 555 ± 308 nm and 494 ± 261 nm. Conditioned cells: average sizes of 53 ± 20 nm and 97 ± 21 nm. SeNRs average	41

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						lengths of 474 ± 279 nm and 444 ± 253 nm.	
			Te^0	Variable	Rod-shaped TeNRs	Intracellular Rod-shaped TeNRs (0.4 mM) of 295±61 nm (unconditioned) and 295±22 nm (conditioned). TeNRs (2 mM) 342 nm (unconditioned and conditioned).	42
	Geobacillus sp. strain ID17	Aerobe Gram (+) Thermophilic Isolated from Antarctica	Au^0	5–50	Quasihexagonal	Intracellular	32
	Deinococcus radiodurans	Aerobe Stain Gram (+) Radiation-resistant organism	Ag^0	4-50, average particle size, 16.82	Spherical	Extracellular Broad-spectrum antimicrobial and anti-biofouling activity. Effective anticancer activity against human breast cancer cell line (MCF-7).	34
ANAL ROBES	*Strain LS4* *96% similarity*	Gram (-)	Fe_2O_3			Extracellular NPs present toxicity towards fish	14

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	with Desulfovibrio dsulfurican aestuarii	Hypersaline Dissimilatory sulfate-reducer		19		embryo	
	Enriched SRB Clostridiaceae sp.	Gram (+)	Bi_2S_3	Dose-depending	Nanorods Nanobundles	Extracellular High dose, nanorods with diameter of 100 nm and length 1 µm Low dose, nanobundles with tip diameter 10–20 nm and length 5.0–10.0 lm.	52
	Geobacter sulfurreducens	Gram (-) Dissimilatory metal- and sulfur-reducing microorganism	α-FeOOH Fe_3O_4 $FeCO_3$	10-50		Extracellular. Narrow size distribution NPs composition and size were strongly dependent upon the rate of Fe(III) reduction, total concentration and cells concentration. Application to Cr(VI) remediation	15
			Au^0	10-90 Average size 20.	Spherical	Extracellular (some intracellular) Excessive time of incubation (16h) leads to aggregation of AuNPs because of uncontrolled growth.	16

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			Ag^0	30 diameter	Deposits	Extracellular Maximum rate of reduction=7.26 µmol of Ag (I)/(mg protein [dry weight]*h)	17
			Pd^0	5-15 14-25		Extracellular Increase of CDW:Pd ratio resulted in the decrease of nanoparticle size. AQDS enhance reduction and extracellular NPs. Tested on chromate (Cr(VI)) reduction.	18–20
	Bacillus cereus SVK1	Facultative anaerobe Gram (+)	Fe_2O_3	15-40	Spherical/hexagonal	Extracellular Evaluated for its possible anticancer activity against HepG2 liver cancer cells	21
	Consortium *Geobacter sp.*	Gram (-) Enrichment cultures (Fe(III)-reducers) from lake sediment	Fe_3O_4	<30		Extracellular Metal cation sorption capacities 30- to 40-fold higher compared to the synthetic magnetite capacity ($Zn^{2+} > Ni^{2+} \approx Co^{2+} > Mn^{2+}$)	22
	Consortium	Enriched mixed	Au	10-60	Spherical	Extracellular	23

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	K. pneumoniae, *L. amylotrophicious* and *S. enterica*	culture from swine manure	Ag	5-50	Spherical	Extracellular	
	Shewanella oneidensis MR-1	Facultative anaerobe Gram (-)	FeS	≈ 30		Extracellular/Intracellular This study demonstrates that the released Fe^{2+} from naphtol green B reduction and the generated H_2S from thiosulfate reduction by *S. oneidensis* MR-1 can be utilized in-situ to synthesize FeS nanoparticles in one single system.	24
			Au^0	2–50, with an average of 12 ± 5	Spherical	Extracellular Homogeneous, spherically shaped	25
			Ag^0	~2 to 11	Spheres	Extracellular Biogenic-Ag NPs had a greater bactericidal activity than did chemically synthesized colloidal-Ag.	26
			Pd^0			Extracellular and periplasm The bioPd(0) NPs reductively	27

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						dehalogenate polychlorinated biphenyl (PCB) congeners in aqueous and sediment matrices.	
	Shewanella putrefaciens	Facultative anaerobe Gram (-)	Au^0	7.42 ± 0.16		Intracellular Reported sorption capacity of 1346 mg Au/g and significant evidence of zero valent gold nanoparticles (AuNPs) deposited within the bacterial cell wall.	28
	Thermus scotoductus SA-01	Facultative anaerobe Gram (+) Unique to South Africa Thermophilic	Au^0			Extracellular Physico-chemical parameters have a definite influence on particle size (lower pH+higher temperatures=larger particles; higher pH+lower temperatures=smaller particles).	29
	Cupriavidus metallidurans CH34	Facultative anaerobe Gram (-) Metallophilic	Au^0	100		Intra- and extracellular Colloidal Au^0	33

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	Enterococcus faecalis	Facultative Anaerobe Gram (+) Fermentative	Pd^0	10		Extra- and intracellular Pd^0-NPs were effective to reduce Cr^{6+}	36
	Desulfovibrio desulfuricans	Anaerobe Gram (-) Sulfate-reducer	Pd^0	114-117		Extracellular/periplasmic space Hypophosphite test revealed superior chemical catalyst properties Pd recovery from Industrial waste solution	37
			ZnS	5–12	Triangular	mono-dispersed nanocrystals Variety of morphologies, mainly triangular	38
	Alishewanella sp. WH16-1	Facultative anaerobe Gram (-) Isolated from the soil of a copper and iron mine	Se^0	100-220	Spherical	Intracellular	43
			Cr(III)	100-220	Spherical	Intracellular	

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		Metal-reducer					
	Bacillus selenitireducens	Anaerobe Gram (+) Isolated from the anoxic muds of Mono Lake, California, an alkaline, hypersaline, arsenic-rich water body.	Te^0	10-nm diameter by 200-nm length	Nanorods	Intra- and extracellular Capable of growth via dissimilatory reduction of Te oxyanions.	46
			Se^0	200-400	Nanospheres	Intra- and extracellular	47
	Sulfurospirillum barnesii	Anaerobe Gram (-) Isolated from a selenium-contaminated freshwater marsh	Te^0	<50	Nanospheres	Intra- and extracellular Capable of growth via dissimilatory reduction of Te oxyanions.	46
			Se^0	200-400	Nanospheres	Intra- and extracellular	47
	Rhodobacter capsulatus	Facultative anaerobe	Te^0	200 up to 600–700		Extracellular Growing cultures with daily additions of	48

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		Gram (-) Non-sulfur photosynthetic				1 mM tellurite led to the accumulation of TeNPs	
	Pantoea agglomerans	Anaerobe Gram (-) Selenite-reducing bacteria	Cu_2Se	100	Nanospheres	Extracellular	54
	Serratia Sp.	Anaerobe Gram (-)	CuO Cu_2O Cu_4O_3	10-30		Intracellular Polydispersed	55
	Shewanella loihica PV-4	Facultative anaerobe Gram (-)	Cu^0	10-16		Intra- but mainly extracellular High antibacterial activities of Cu-NPs	56

Table 2. Mechanisms reported for metallic nanoparticle synthesis by microorganisms under different experimental conditions

Microorganism	Precursor (metal salt and concentration)	NP	Synthesis Parameters* (1)Cells growth used, (2)reaction medium,	Mechanism reported	Reference

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			(3)pH; temperature; (4)reaction time, (5)oxygen condition, (6)cells concentration		
Actinobacter spp.	$K_3Fe(CN)_6/K_4Fe(CN)_6$ 2:1	Fe_3O_4 γ-Fe_2O_3	(1)24h cells growth (2)LB (3)6.4; (-) ºC (4)24 h (5)aerobic (6) -	Different from that observed in magnetotactic and iron-reducing bacteria. Induction of two proteins with molecular weights of ca. 120 and 70 kDa are responsible to hydrolyze iron precursors to form iron oxide nanoparticles predominantly in the magnetite phase at room temperature.	11
	1 mM $FeCl_3$	γ-Fe_2O_3	(1)48 h cells growth (2)LB (3) -, 35ºC (4)48-72 h (5)aerobic (6) -	Reduction of Fe^{3+} into Fe^{2+} involves the enzyme iron reductase which has a siderophore activity as it reduces Fe^{3+} extracellularly. Precursor dependent synthesis of iron oxide and iron sulfide is governed by different enzymatic pathways.	12
	Mixture $FeCl_3$-$FeSO_4$ 2:1	Fe_3S_4			

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Strain LS4	$FeCl_3$-$FeSO_4$ 3:2 M (5 mL)	Fe_2O_3	(1) - (2)Hatchikian's media (3) 7.8, 30ºC (4)35 days (5)anaerobic (6) 20 ml of 10^6 cells/mL	LS4 might be releasing various enzymes in the media for governing the bioreduction process to synthesize Fe_2O_3 nanoparticles. Presence of excess iron in the media might have induced excretion of specific reductase enzymes to reduce ionic iron or convert iron sulfides in to Fe_2O_3 nanoparticles	14
Geobacter sulfurreducens	Fe(III)-Oxyhydroxide 50 mM	α-FeOOH Fe_3O_4 $FeCO_3$	(1)Late log-phase cultures (2)modified freshwater medium (3) 7, 30º C (4)1 week (5)anaerobic (6) - *Addition of electron shuttle (AQDS)	The mechanism underpinning iron biomineral formation is strongly dependent upon the rate of Fe(III)-reduction. The presence of AQDS enhance the rate of iron reduction.	15

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Geobacter sulfurreducens	$HAuCl_4$ 250 µM Au^{3+}	Au^0	(1)8 days biofilm on electrode (2)fumarate-free growth medium (3) 6.8, 30 ºC (4)8 hours (5)anaerobic (6) -	Extracellular substances from *G. sulfurreducens* biofilms were found to reduce Au^{3+} to AuNPs. FTIR spectra analysis suggested that reduced sugars were involved in the bioreduction and synthesis of AuNPs and that amine groups acted as the major biomolecules involved in binding.	16
Bacillus cereus SVK1	$FeCl_3$ 1 mM	Fe_2O_3	(1)Culture supernatant (2) nutrient agar (3) - , 35° C (4)3 weeks (5)aerobic (6) 1:1	Proteins/enzymes were suggested to be responsible for the reduction of metal ions according to FT-IR spectrum. The presence of metabolites in culture broth could be responsible for the reduction of metal ions and formation of the metal nanoparticles.	21
SRB + natural air oxidation	FeSO4 (0.5 g/L)	Fe_3O_4	(1)1 week cultivation (2) nutrient agar (3)7.2, 28° culture (80°	Sulfate-reducing bacterium(SRB) was used to reduce ferric sulfate to produce ferric sulfide, then ferric sulfide was oxidized to iron protoxide and ferroferric	59

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			and 500° drying) (4)3 weeks (5)aerobic (6) 1:1	oxide in the end under natural air oxidation condition	
Enrichment culture	Fe_2O_3 200 mM Fe(III)	Fe_3O_4	(1)enrichment culture (2) Growth medium (3) 7.1-7.8, 35 ºC (4)7 days (5)anaerobic (6) -	The sequence (196 bp) was 100% identical with the corresponding positions of sequences from *Geobacter sp.* which are known to be dissimilatory Fe(III) reducers.	22
Shewanella oneidensis MR-1	Naphtol Green B (NGB) 100 mg/L $C_{30}H_{15}FeN_3Na_3O_{15}S_3$	FeS	(1)late stationary phase (2) Defined medium (3) 7.0, 30° C (4)5 days (5)anaerobic (6) $4–6\times10^6$ CFU/ml	FeS NPs synthesis occurred sequentially in a coupled process: released Fe^{2+} from NGB reduction and the generated H_2S from thiosulfate reduction by *S. oneidensis MR-1* Extra- and intracellularly FeS NPS are attributed to the transport of a fraction of Fe^{2+} into the periplasmic and cytoplasmic spaces as well as a free diffusion of H_2S cross the cell	24

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				membranes.	
Geobacter sulfurreducens	$HAuCl_4$ 250 µM Au^{3+}	Au^0	(1)8 days biofilm on electrode (2)Fumarate-free growth medium (3) 6.8, 30 ºC (4)8 hours (5)anaerobic (6) -	Extracellular substances from *G. sulfurreducens* biofilms were found to reduce Au^{3+} to AuNPs. FTIR spectra analysis suggested that reduced sugars were involved in the bioreduction and synthesis of AuNPs and that amine groups acted as the major biomolecules involved in binding.	16
Anaerobic enriched mixed bacteria	$HAuCl_4$ 1 mM	Au^0	(1) - (2) Defined medium (3) 7.0, 35° (4)1 hour (5)anaerobic (6) -	From FTIR analysis it was conclude that AgNPs and AuNPs could bind to free amino or carboxylate groups in the protein; suggesting that these groups may be responsible for the reduction and stabilization of nanoparticles. Step 1. The uptake of Ag+ /Au3+ and formation of complex formation with the anaerobic enriched mixed bacteria.	23
	$AgNO_3$ 0.04 mM	Ag	(1)- (2) Defined medium		

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			(3) 7.0, 35° (4)2-3 hours (5)anaerobic (6) -	Step 2. The NADH-dependent reductase is responsible for the bio-reduction of Ag+ /Au3+ into Ag and AuNPs, respectively	
Shewanella oneidensis MR-1	$HAuCl_4$ 1 mM	Au^0	(1) overnight culture (2) Aqueous solution (3) -, 30° (4)48 hours (5) - (6) -	Involvement of proteins present in the bacterial cell membrane for the biofabrication of nanoparticles.	25
Shewanella putrefaciens	$HAuCl_4$ <300 mg/L	Au^0	(1)stationary growth phase (2) Aqueous solution (3) 3.0, 25° (4)24 hours (5)anoxic (6) 0.005 L of $1x10^{10}$	Step 1: Film diffusion – Transport of $AuCl_4^-$ from the bulk solution to bacterial cell wall. Step 2: Pore diffusion – Transport of the ion to protein enzyme metal recognition peptide motifs sorption and nucleation sites. Step 3: $AuCl_4^-$reduction – Electron transfer to metal ions by cytochromes or hydrogenase	28

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			cells/L	Step 4: AuNP nucleation	
Thermus scotoductus SA-01	Au(III) 2 mM	Au^0	(1) late exponential-early stationary growth phase (2) acetate buffer (3) 3.0, 25° (4) 8 hours (5)anoxic (6) 0.005 L of $1x10^{10}$ cells/L	It was purified an ABC transporter, peptide-binding protein of T. scotoductus SA-01, able to reduce Au(III) through an electron shuttle mechanism involving a cysteine disulfide bridge.	29
Acinetobacter sp. SW 30	$HAuCl_4$ 0.1 mM Different conc.	Au^0	(1)24h growth (2) Aqueous solution (3) -, 30° (4)72 hours (5) - (6) < $0.3x10^9$ cfu/ml Different cell conc.	Amino acids are involved in reduction of gold salt while amide groups may help in stabilization of AuNP.	30

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Geobacillus sp. strain ID17	$HAuCl_4$ 1 mM	Au^0	(1)24h growth (2)20 mM potassium phosphate buffer (3) -, 65° (4)16 hours (5) - (6)OD 0.5 suspended in 10 mL	Results strongly suggest that the biosynthesis of gold nanoparticles by ID17 is mediated by enzymes and NADH as a cofactor for this biological transformation.	32
Cupriavidus metallidurans CH34	$HAuCl_4$ 50 µM	Au^0	(1)Growth cells (2) PME medium (3) 5-8, 30°C (4)16 hours (5) - (6) 2.5 mL growth medium with 5.5 x 10^4 cells/mL	Cellular Au accumulation is coupled to the formation of Au(I)-S complexes. This process promotes Au toxicity and *C. metallidurans* reacts by inducing oxidative stress and metal resistances gene clusters (Au-specific operon) to promote cellular defense. Au detoxification is mediated by a combination of efflux, reduction, and possibly methylation of Au-complexes.	33

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Deinococcus radiodurans	$AgNO_3$ 2.5 mM	Ag^0	(1)Midlog phase culture 2 h-adapted to $AgNO_3$ (2) Tryptone glucose yeast broth (3) 6.8, 32° (4)24 hours (5) aerobic (6) -	Interaction of the proteins/peptides with synthesized nanoparticles.	34
Geobacter sulfurreducens	$AgNO_3$ 2 mM Ag(I)	Ag^0	(1)Late-exponential-phase cultures (2) Growth medium acetate-fumarate (3) -, 30° (4) 10 minutes (5) anaerobic (6) -	Ag(I) (as insoluble AgCl or Ag+ ions), is reduced on the surface of the cell, with c-type cytochromes traversing the periplasm and outer membrane implicated in electron transfer to the metal.	17

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Shewanella oneidensis	$AgNO_3$ 1 mM	Ag^0	(1)Overnight culture (2) Aqueous solution (3) -, 30° (4)48 hours (5) aerobic (6) 3-5 g of wet bacterial biomass	The possible synthesis mechanism may involve reduction of silver ions to convert toxic Ag^+ to stable Ag^0 and subsequent stabilization of particles using capping proteins/peptides secreted by the bacteria under metal stress.	26
Enterococcus faecalis	Na_2PdCl_4 50-250 mg/L	Pd^0	(1) Log-phase (2) Aqueous solution (3) Different pH and T° (4)48 hours (5) aerobic (6) biomass dry weight 0.6 to 3.6 g/L	The results showed that the mechanism of Pd^{2+} reduction mainly occurred by the chemical reaction of ion-exchange process and electron donor was supplied by sodium formate.	36
Shewanella oneidensis	Na_2PdCl_4 50 mg Pd(II)/L	Pd^0	(1) Overnight culture (2) M9 medium	Involvement of a periplasmic hydrogenases with cytochrome c3 activity as proposed (by Lloyd et al.	27

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			[3] 7.1, 28° [4]24 hours [5] anaerobic [6]OD_{610} of 2.0 ± 0.2	1998, for *D. desulfuricans*). Biosorption and subsequent bioreduction. Different electron donors were tested.	
Desulfovibrio desulfuricans	Na_2PdCl_4 $Pd(NH_3)_4Cl_2$ 2 mM	Pd^0	[1] 2-days growth [2] Buffer [3] 2-7, 30° C [4]40 minutes [5] anaerobic [6] ≈ 0.25 mg/L dry weight	The target ions form the crystal nuclei, interacting initially with localized surface bonding sites, and reduction, probably occurs via H+ using the reducing power focused by hydrogenase activity. Pd(II) crosses the outer membrane and reduction probably occurs via periplasmic hydrogenase.	37
Geobacter sulfurreducens	Na_2PdCl_4 25-100 mg Pd/L	Pd^0	[1]Late-logarithmic phase [2] Buffer, minimum medium [3] 7, 30° C [4] 2 hours [5] anaerobic [6] 800 mg cell dry	*Geobacter sulfurreducens* can reduce both soluble and insoluble species of Pd(II) by means of two mechanisms: (i) direct contact typically involving reduction by outer membrane c-type cytochromes; and (ii) indirectly by using AQDS as an electron shuttle. Steps involved in the reduction mechanism are: (i) electrostatic interaction, (ii) ligand substitution	18,60

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			weight/L	(amide, phosphoryl groups), (iii) reduction and nucleation. (electron transport, cytochromes)	
Shewanella sp. CNZ-1	Na_2PdCl_4 0.14-1.41 mM Pd(II)	Pd^0	(1) Overnight culture (2)Mineral salt medium (3) different pH, 30°C (4)24 hours (5) anaerobic (6) 0.5 g/L	Involved enzymes for Pd(II) reduction in CNZ-1 and MR-1 were different. Chemical groups of the extracellular secretion on CNZ-1 cell surface contributed to the Pd(II) reduction process. Functional amine groups were also involved in Pd(II) adsorption and reduction.	39
Acidocella aromatica PFBCT Acidiphilium cryptum SJH		Pd^0	(1) Late-exponential phase (2)Heterotrophic basal salts (HBS) medium (3) - , 30°C (4)120 hours (5)anaerobic conditions (6) 1.0×10^9 cells/ mL	Monosaccharide (or intracellular NADH)-dependent reactions lead to visualization of intra/extra-cellular enzymatic Pd(0) nucleation. Formic acid-dependent reactions proceeded via the first slow Pd(0) nucleation phase and the following autocatalytic Pd(II) reduction phase regardless of the presence or viability of the cells.	40
Rhodococcus aetherivorans	Na_2SeO_3 0-500 mM	Se^0	(1)5 days conditioned and unconditioned	Explained by the LaMer mechanism of nanoparticle formation, upon SeO_3^{2-} bioconversion into Se^0, the	41

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BCP1			cultures (2) LB medium (3) - , 30°C (4)24 hours (5)aerobic conditions (6) inoculum 1% v/v	Se atoms as generated organize themselves into Se-nucleation seeds, turning into NPs through a ripening process. It is reported cells growth.	
Acinetobacter sp. *SW 30*	Na_2SeO_3 1.5-3 mM	Se^0	(1)18 h grown culture (2)aqueous solution (3) from 2-10, 37°C (optimum) (4)6-48 hours (5)aerobic (6) 2.7×109 cfu/mL	FTIR studies have confirmed that proteins are the essential molecules for the reduction and coating of SeNPs. Synthesis of Se rods could be due to the Ostwald ripening process at higher concentration of Na_2SeO_3.	31
Alishewanella sp. *WH16-1*	Na_2SeO_3 0.5 mM K_2CrO_4 0.5 mM	Se^0 Cr (III)	(1)OD_{600}=0.8-1.0 (2)LB medium (3)-,37°C (4)- (5)aerobic (6) -	The Se(IV)/Cr(VI) reduction and SeNPs/CrNPs assemble mechanisms within strain WH16-1 are somehow similar. CsrF, selenite reductase catalyzes the reduction of Se(IV) and Cr(VI) using NAD(P)H as cofactors with optimal condition of pH 7.0 and temperature of 30–	43

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				37◦C. Flavoenzymes, such asChrR, FerB and ArsH, may also be able to act as Se(IV) reductases.	
Bacillus subtilis	Na_2SeO_3 4 mM	Se^0	[(1)]12 h bacterial growth [(2)]Enrichment medium [(3)]-,35°C [(4)]48 h [(5)]aerobic [(6)] 1 mL culture	Reduction of the SeO_3^{2-} ions and stabilization of monoclinic-Se were believed to occur by the participation of protein and other biomolecules excreted from *B. subtilis*.	44
Rhodococcus aetherivorans BCP1	K_2TeO_3 0.4 – 2 mM	Te^0	[(1)]5 days conditioned and unconditioned cultures [(2)]LB medium [(3)]7, 30°C [(4)]48 h [(5)]aerobic [(6)] inoculum 1% v/v	Grow in the presence of high amounts of tellurite. Isolated TeNRs were embedded into a slightly electron-dense surrounding material, corresponding to carbon, oxygen, nitrogen and sulfur as detected by EDX spectroscopy. Negative surface potential of Te NPs associated to carboxylic groups of l-cysteine ligands in solution. suggest that the nanorod formation may be mediated by the biosurfactant co-produced by the BCP1 strain.	42

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Rhodobacter capsulatus	K_2TeO_3 1mM Redox mediator lawsone	Te^0	(1)Growth cultures (2)Growth medium (3)6.8, - °C (4)24,120-240 h (5)anaerobic (6) inoculum 1:10	Pyruvate and lactate resulted to be the best electron donors for Te^0 NPs as they compete with tellurite for the use of the ActP2 permease to entry into cells, these two monocarboxylic acids not only act as substrates but also preserve the cells from tellurite toxicity by limiting the oxyanion entry into cytosol.	48
Bacillus amyloliquefaciens	$TiOSO_4$ 25 mM	TiO_2	(1)72 h growth (2)diluted growth medium (3)-, 37°C (4)24 h (5)aerobic (6) -	Activity of amylase in bacterial supernatant revealed involvement of enzyme in biosynthesis of NPs.	49
Bacillus mycoides	$TiO(OH)_2$ 5 mM	TiO_2	(1)12h growth (2)LB medium (3)-, 37°C (4)24 h (5)aerobic (6) 0.1% v/v	Peptides or carbohydrates can provide support for the nucleation of the nanoparticles, and/or be involved in the biosynthesis process acting as stabilizing and capping agents. The organic coating protects bacteria from the phototoxic damage by interacting with UV-produced radicals.	50

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Aeromonas hydrophila	$TiO(OH)_2$ 1 mM	TiO_2	(1)24h growth (2)distilled water+nutrients (3)-, 30°C (4)24 h (5)aerobic (6) 0.33 mLcells/mL	The major secondary metabolite was glycyl-L-proline was identified and may be responsible for the synthesis of the TiO_2 NPs. The FTIR spectrum of the synthesized TiO_2 NPs indicated that alcohols, phenols, primary amines, lactones and aliphatic amines may have been participated in the process of nanoparticle synthesis.	51
Bacillus subtilis	$TiO(OH)_2$ 5 mM	TiO_2	(1)24h growth (2)distilled water+nutrients (3) -,60°C (10-20min) (4)12-48 h (5)aerobic (6) 0.33 mLcells/mL	The synthesis of n-TiO_2 might have resulted due to pH-sensitive membrane bound oxidoreductases and carbon source dependent rH2 in the culture solution. Composition of nutrient media plays a pivotal role in biosynthesis of metallic and/or oxide nanoparticles.	45
Desulfovibrio desulfuricans	$ZnCl_2$	ZnS	(1)Mid-exponential phase (2)Modified metal toxicity medium (3) -,30°C	Complexation and stabilization effects of the bacterial metabolites. Acetate produced affected the availability of free Zn^{2+}resulting in a slow-down of the ZnS nucleation. Bacterial metabolites are also involved in the	38

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			[4]- h [5]anaerobic [6] 0.33 mLcells/mL	crystallization of ZnS via other mechanisms.	
Enriched SRB *Clostridiaceae sp.*	$Bi_2(SO_4)_3$ 0.1 mM	Bi_2S_3	[1]20-day old SRB culture [2]CCl_4+growth media [3] 7,30°C [4]- h [5]anaerobic [6] 25 mL inoculum (OD≈0.6)	The water–oil two-phase system successfully eliminated hydrolysis of Bi^{3+} and efficiently prepared the Bi_2S_3 crystal with high purity. Couple reaction of biological reduction and chemical precipitation process. It was speculated that the morphology and size were related to the generation speed of S^{2-}.	52
Acidithiobacillus sp. *A. ferrooxidans* *A. thiooxidans* *A. caldus*	$CdSO_4$ 0.33–5 mM	CdS	[1] Stationary phase [2]Phosphate buffer [3] 3,5,7, 28° (*A. ferrooxidans y A. thiooxidans*) y 40°C (*A. caldus*) [4]24 h [5]aerobic	Sulfide generation enhances CdS QDs biosynthesis, probably by acting as sulfur donor for CdS nanoparticle core formation. Other unidentified cellular moieties (different from H_2S) like proteins, thiols or small biomolecules, must be involved in NPs formation and acid tolerance in *Acidithiobacillus*.	53

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			(6)OD_{620}=1.3 (approx.1×10^{11}cells/mL)		
Pantoea agglomerans	Na_2SeO_3 3.8 g/L EDTA-Cu 10 mM	Cu_2Se	(1) - (2)Biosynthesis medium (3) -,32°C (4)2 weeks (5)aerobic (6) 50 mL inoculum	Three steps: (1) Chemical reduction reaction, free Cu^{2+} ions are reduced into Cu^{+} ions by $NaBH_4$, and biological reduction reaction, SeO_3^{2-} is reduced into Se NPs by *P. agglomerans*. (2) Catalytic reaction, Cu^{+} ions catalyzed the Se NPs into Se^{2-} and SeO_3^{2-} recycled by the reduction of *P. agglomerans*. (3) Chemical precipitation, Cu^{+} ions and Se^{2-} ions combine to generate Cu_2Se.	61
Serratia sp.	$CuSO_4$ 1-10 mM	CuO Cu_2O Cu_4O_3	(1)Stationary phase (2)Distilled water (3) -,37°C (4)48 h (5)aerobic (6) -	Cells experience an oxidative and osmotic stress. When they are exposed to the salt, the stress is increased further. The salt is internalized into the cells and then the Cu^{2+} ions are reduced by specific biomolecules to copper in its metallic form, which is less toxic than the ionic forms.	55
Shewanella loihica PV-4	$CuCl_2\cdot2H_2O$ Cu(II)-1 mM	Cu^0	(1)Overnight culture (2)Simulated groundwater	Series of enzymatic reactions, extracellular reduction could be mainly responsible for biosynthesis of Cu-NPs since this strain possessed cytochrome c genes	56

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			[3] -,30 ± 2◦C [4]120 h [5]Anaerobic [6] OD_{600}= 2	in the metal reductase-containing locus.	

*In most of the cases when pH value is not specified we can assume that it was neutral condition.

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Table 3. Potential sources of precious metals from different wastes

Metals present	Concentration/Flux	Source	Reference
Cr, Ni	48 mg Cr L^{-1}, 30 mg Ni L^{-1}	Metallurgic effluent	69
Co, Cu, Zn, Ni	16 Ton Cu yr^{-1}, 14 Ton Zn yr^{-1}, 6.3 Ton Ni yr^{-1}, 4.2 Ton Co yr^{-1}	Abandoned mining sites	70
Pt, Gd	Considering an average flow of 500 m^3 day^{-1} from a hospital: 13.7 Kg Pt yr^{-1}, 182.5 Kg Gd yr^{-1}	Hospital wastewater	71
Eu, Nd	~225 mg Nd L^{-1}, ~300 mg Eu L^{-1}	Geothermal fluids	72
Zn, Cu, Mo, Ni, V and many others	Ranging from 1.5×10^4 to 1.5×10^5 μg metal (Kg dry solids)$^{-1}$	Purged sludge from WWTPs	67
Zn	~3000 Ton Zn yr^{-1}	Zinc refinery site	73
Au, Pt, Pd and others	4.2-5.8 mg Au L^{-1}, 12.9-15.3 mg Pt L^{-1}, 131-137 mg Pd L^{-1}	Metallurgic effluent	74
Pt, Pd, Rh, Cu, Zn	81 mg Pt L^{-1}, 29 mg Pd L^{-1}, 7 mg Rh L^{-1}, 24 mg Cu L^{-1}, 102 mg Zn L^{-1}	Industrial waste processing leachate	75
Au, Ag, Cu, Ni	16 mg Au L^{-1}, 250 mg Ag L^{-1}, 14200 mg Cu L^{-1}, 22500 mg Ni L^{-1}	Industrial waste from Shchelkovo plant	76
Cu, Zn, Ni, Cr	1527 mg Cu L^{-1}, 689 mg Zn L^{-1}, 462 mg Ni L^{-1}, 264 mg Cr L^{-1}	Electroplating wastewater	77
Li, Cs, Rb	Maximum values: 219 mg Li L^{-1}, 39 mg Cs L^{-1}, 170 mg Rb L^{-1}	Geothermal fluid	78

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Table 4. Examples of recovery of precious metals from wastewater by BES (Adapted from Jadhav et al. 2017)[89]

Metal	Concentration ($mg\ L^{-1}$)	Removal (%)	Power density	Remarks
V	250-1000	26.1	0.97 $W\ m^{-2}$	Pollutant removal
Ag	50-200	99.9	4.25 $W\ m^{-2}$	Wastewater with Ag ions
Cu	1000	97.8	0.536 $W\ m^{-3}$	$CuSO_4$ catholyte
Se	200	98	12.8 $W\ m^{-2}$	Constructed wetland MFC
Cd	200 mM	90	3.6 $W\ m^{-2}$	Single chamber membrane-less MFC
Hg	25-100	90-99	0.93 $W\ m^{-3}$	$HgCl_2$
Ni	50-1000	99	-	Abiotic cathode with external voltage

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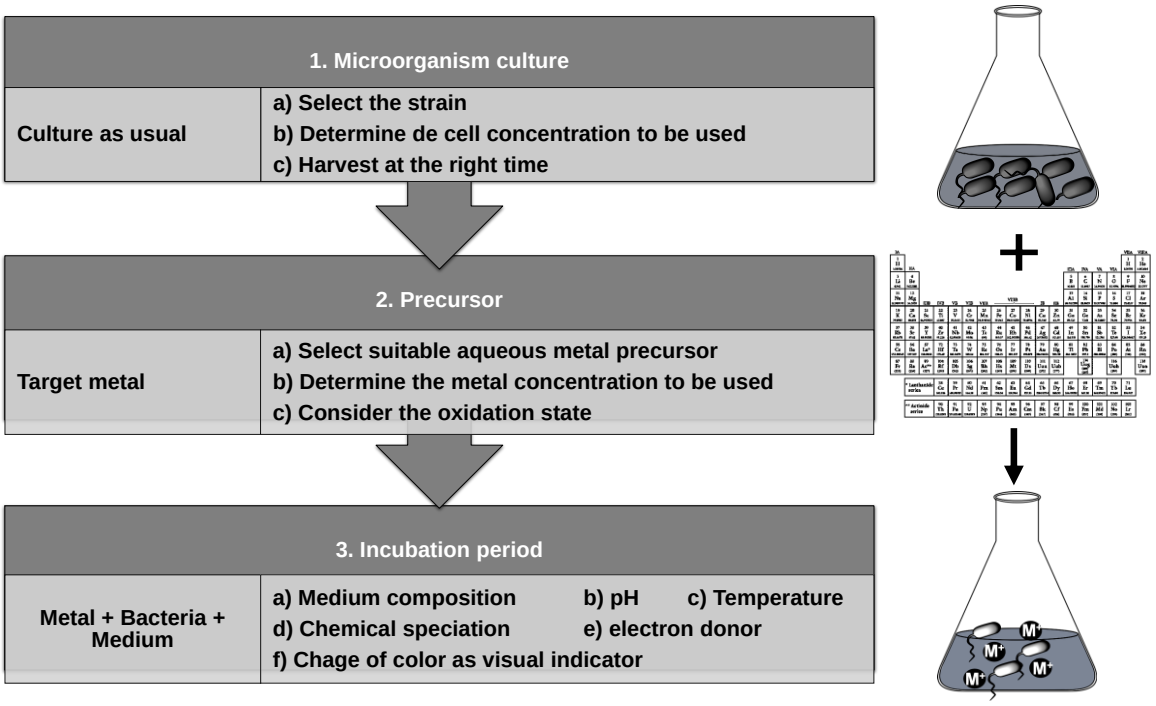

Figure 1. Main elements to consider in a typical methodology for the synthesis of metallic NPs by bacteria.

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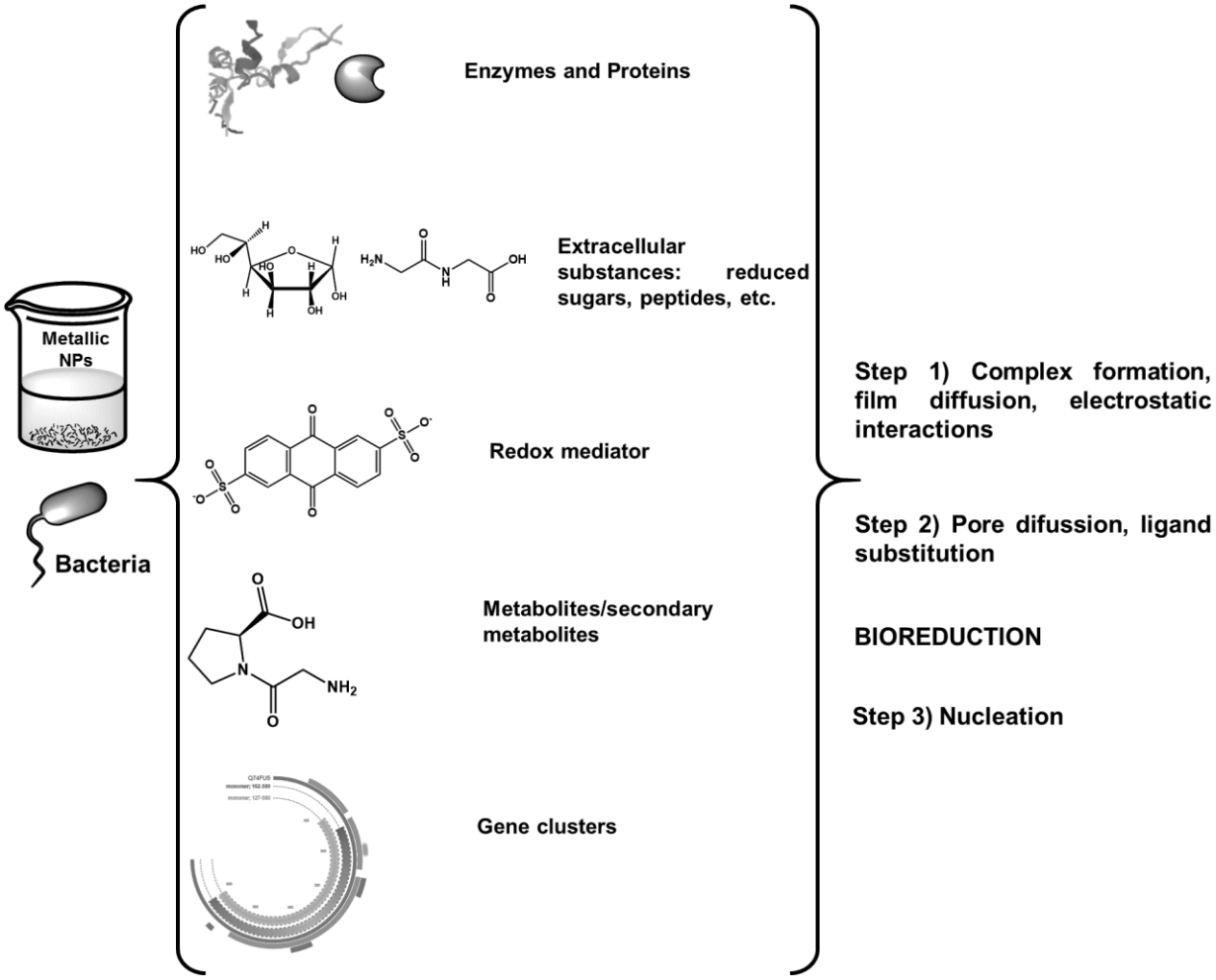

Figure 2. Illustration of the different mechanisms involved in the synthesis of metallic NPs by microorganisms.

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