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Review

Revisiting the mechanistic pathways for bacterial mediated synthesis of noble metal nanoparticles

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ABSTRACT

Synthesis and application of reliable nanoscale materials is a progressive domain and the limelight of modern nanotechnology. Conventional physicochemical approaches for the synthesis of metal nanoparticles have become obsolete owing to costly and hazardous materials. There is a need to explore alternative, cost-effective and eco-friendly strategies for fabrication of nanoparticle (NPs). Green synthesis of noble metal nanoparticles has emerged as a promising approach in the last decade. Elucidation of the molecular mechanism is highly essential in the biological synthesis of noble metal nanoparticles (NPs) for the controlled size, shape, and monodispersity. Moreover, mechanistic insights will help to scale up the facile synthesis protocols and will enable biotransformation of toxic heavy metals hence also providing the detoxification effects. Therefore, the current review article has primarily targeted the mechanisms involved in the green synthesis of metal NPs, which have been reported during the last few years. Detailed mechanistic pathways have highlighted nitrate reductase as a principle reducing agent in the bacterial mediated synthesis and stabilization of NPs. Furthermore, we have highlighted the potential implications of these mechanisms in bioremediation and biomineralization processes, which can play a critical role in biogeochemical cycling and environmental impacts of heavy metals. We anticipate that this review article will help researchers to address the challenges of bioremediation and modern nanotechnology.

1. Introduction

Nanotechnology has emerged as a progressive and interdisciplinary science during the last few decades. The prefix "nano" indicates one billionth or 10^{-9} units. It is widely known that nanoparticles (NPs) range in size from 1 to 100 nm (Jafar Ali and Ali, 2015). Nanomaterials usually display unique biological, physical and chemical properties compared to their bulk matter (Ahmad et al., 2013; Wang et al., 2018a, 2018b). Synthesis of noble metal NPs has drawn the much attention due to potential applications in electronics, photonics, catalysis, nanomedicine, biofuel cells, biomedical engineering and biological recovery of metals (Daraee et al., 2016; Park and Na, 2015; Rana et al., 2017; Wang et al., 2015). Remarkably, silver nanoparticles (AgNPs) possess inhibitory and bactericidal effects. Antibacterial characteristics of AgNPs have enabled to minimize the antibiotic resistance, which has emerged as a major health problem in recent years (Jain et al., 2009; Musarrat et al., 2010; Prabhu and Poulose, 2012). Recently there has been an upsurge of interest in the microbial reduction of metallic ions to metal nanoparticles (NPs). Significant applications of the nanomaterials are usually size dependent, thus controlled size synthesis of nanomaterials is highly desired (Jiang et al., 2008; Narayanan and Sakthivel, 2010; Wang et al., 2017).

Various physical and chemical strategies could be employed to synthesize well-defined nanomaterials (Daraee et al., 2016; Shah et al., 2019). But these conventional synthesis protocols are not preferred due to high cost and involvement of hazardous materials (Jha et al., 2009;

Abbreviations: AgNPs, Silver Nanoparticles; GNPs, Gold Nanoparticles; PdNPs, Palladium Nanoparticles; NPs, Nanoparticles; BacMP, Bacterial magnetite particle; PtNPs, Platinum Nanoparticles; KDa, kilo Dalton

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Narayanan and Sakthivel, 2010; Starowicz et al., 2006). Moreover, the large scale synthesis also face many issues such as low stability and less monodispersity (Manoj et al., 2018). Henceforth there is a growing demand for the employment of environmentally benign processes for the synthesis of stable NPs (Fayaz et al., 2010). In this regard elucidation of molecular mechanisms may play a critical role in the green synthesis of noble metal NPs with controlled dimensions and high monodispersity (Ali et al., 2016). Various mechanistic theories about bio-synthesis of NPs have been presented in literature (Ali et al., 2017; Ali et al., 2016). Majority of studies have speculated the nitrate reductase as a principle reducing agent along with its stabilizing feature. However, a plausible bio-synthesis mechanism may involve more than one cellular components. Pathways involved in the green synthesis of nanomaterials are of prime importance for commercialization of nanotechnology and also for environmental sustainability.

Synthesis mechanisms will also improve the bioremediation and biomineralization processes for environmental contaminants. Biomineralization is the utmost process of controlling the ultimate fate in biogeochemical cycling and ecological impacts of heavy metals (Diaz et al., 2015). A better understanding of microbial transformation pathway at the genetic level may lead to develop new genetic tools for accelerating the bioremediation strategies (Kang et al., 2017; Wu et al., 2016). Assumingly, biological transformation pathways of heavy metals can be explored further. An escalating number of publications about nanomaterials during the last decade illustrates the potential of this active domain. A thorough and comprehensive review of literature is needed to provide facts about the green synthesis. The fundamental insight of enzyme-metal interaction is elaborated here which, will enable the biotransformation of toxic heavy metals hence providing the detoxification effect (Liu et al., 2016; Venkatachalam et al., 2017).

Although several detailed reviews about the synthesis and applications as antimicrobial agents have been published (Davis and Shin, 2008), but very few studies have focused on mechanistic pathways involved in the green synthesis of NPs (Zhao et al., 2013). We have tried to summarize the mechanisms for green synthesis of NPs which have been reported during the last few years. Moreover, we have highlighted various biomolecules involved in the reduction of metals into their NPs. We have also described the potential remedial prospects based on these mechanisms. It is anticipated that the current study will improvise the understandings of molecular routes involved in biochemical processes at complex interfaces.

2. Mechanisms for the synthesis of noble metal nanoparticle

The specific mechanisms of NPs formation varies from organism to organism. However, the synthesis of NPs follows a generalized scheme wherein; metal ions are either entrapped into the microbial cells or on the microbial surface in the presence of an enzyme, metal ions get reduced to NPs (Yin et al., 2016). Initially, algal biomass of *Verticillium* sp. formulated the intracellular NPs of gold and silver, the exact pathway was not identified but NPs synthesis on the mycelial surface have demonstrated that electrostatic forces of attraction are responsible for the entrapment of metal ions on the fungal cell wall, mainly due to negative charge of carboxylate group of enzymes. Next reduction of metal ions by the enzymes to form nuclei of noble metals, which later on grow through further accumulation and reduction (Fig. 1) (Mukherjee et al., 2002).

2.1. Mechanisms of silver nanoparticle synthesis

Among all the noble metals silver has been studied comprehensively, for biological synthesis of metal nanoparticles due to enormous applications. In this regard, Kalishwaralal et al., (Kalimuthu et al., 2008; Kalishwaralal et al., 2010) investigated the participation of the nitrate reductase enzyme in the synthesis of AgNPs by *Bacillus licheniformis*. Authors proposed that nitrate ions may help for the induction of enzyme, which reduces the Ag^+ to Ag^0. The probable mechanistic pathway assisting the reduction of metallic ions is the enzymatic reduction process by electron shuttle (Fig. 2). Cofactors like NADH in NADH-dependent nitrate reductases enzymes are required for generating metal NPs. *B. licheniformis* releases cofactors NADH and NADH-dependent enzymes, along with some other factors especially nitrate reductase the possible reason toward the bio reduction of Ag^+ to Ag^0 (Durán et al., 2011; Li et al., 2011a, 2011b). Sintubin and colleagues hypothesized another mechanism of AgNPs synthesis by *Lactobacilli,* (Sintubin et al., 2009) according to which pH upsurge is directly correlated with competition for the negatively charged binding site between metal ion and protons (Sintubin et al., 2009). Lin and coworkers (Li et al., 2011a, 2011b) further investigated that biosorption of silver ions on the culture of *Lactobacillus* A09 with the sudden fall in pH due to the interaction of between metal ions and protons. The ring structure of monosaccharides was catalyzed by high pH and reducing power is provided by aldehydes. In the presence of metal ions, the aldehyde got oxidized into respective carboxylic acid, and metal ions get reduced. However, which cellular component is mainly involved in biosorption and reduction is still needs further evaluation. *Lactobacillus* mediated synthesis of AgNPs from probiotic tablets and yoghurt has also been reported. Lactate from NADH depending lactate dehydrogenase and pyruvate generated two protons involved in the synthesis process alongside thioredoxin systems and glutathione. Conclusively, all components work in coordination to facilitate the synthesis of AgNPs (Nangia et al., 2009). Effect of visible light on the production of AgNPs was studied, especially when the culture of *Klebsiella* and silver nitrate was exposed to visible light resulted in variable synthesis rate (Mokhtari et al., 2009).

Klaus et al., (Klaus et al., 1999) proposed that silver accumulation outside the cellular membrane of bacteria was associated to reacting potential with H_2S gas turning it non-toxic to itself in case of Pseudomonas. The bio-reduction of the ionic silver into AgNPs was due to the cofactor and nitrate reductase enzyme secreted by *Bacillus licheniformis*. Optimization in activity and production reconfirmed the hypothesis that there is involvement of catalytic proteins in reduction and synthesis. (Vaidyanathan et al., 2010). However, bacterial interaction with different metals is not yet completely understood. A protein assay was performed to confirm the involvement of catalytic proteins in AgNPs synthesis by *Fusarium oxysporum*. Authors identified that protein was NADH-dependent reductase responsible for reducing the silver nitrate solution and subsequent formulation of AgNPs. It was also observed that the NADH-dependent reductase enzyme was not present in all fungi, because *Fusarium moniliforme* was unable to synthesize intracellular and extracellular NPs (Ahmad et al., 2003). In another study, extracellular synthesis of AgNPs was carried out using the *Fusarium oxysporum*, in this work a mechanistic approach was taken into account. The verification of reduction (metal ions) through extracellular shuttle quinone and nitrate-dependent reductase was done by fluorescence spectra, Uv-vis and especially by enzyme activity.

Synthesized AgNPs from *F. oxysporum* were stabilized by proteins (Durán et al., 2011). The additional evidence to the Duran et al., (Durán et al., 2011) findings was provided by Ingle et al., (Ingle et al., 2009). Through a comparative study of nitrate reductase from the fungal filtrate and commercially available nitrate reductase discs. Along with the synthesis of NPs authors also pointed out that there was a close association in the synthesis process and reductase enzyme. *F. moniliforme* has the nitrate reductase but unable to perform the synthesis process due to lack of anthraquinone. These findings clarified the understanding of synthesis mechanism that not only nitrate reductase was essential, but an electron shuttle is also required for reduction of metals. Similarly, Durán et al. (Durán et al., 2011) results were confirmed by Kumar et al., (Kumar et al., 2007) wherein, in vitro synthesis of AgNPs was carried out by a purified enzyme nitrate reductase and a cofactor (NADPH). The stabilizing agent was provided externally in the form of, 4-hydroxyquinoline and phytochelatin. In the absence of enzyme and

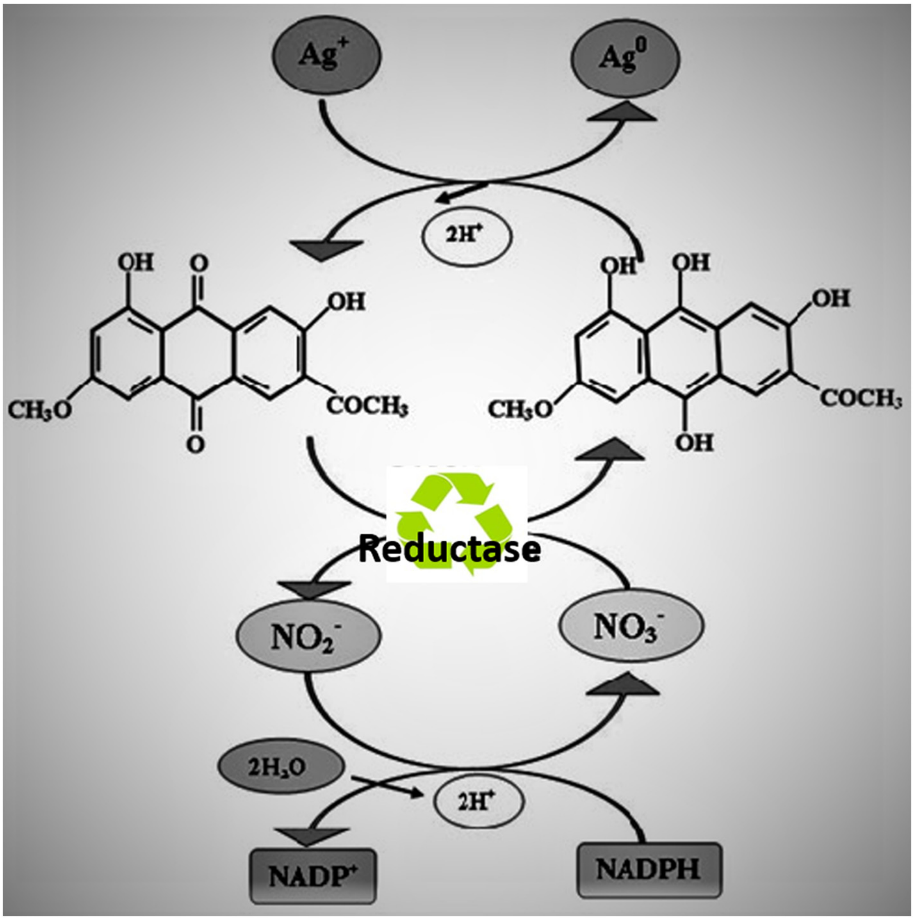

Fig. 1. Extracellular reduction of silver ions and the transfer of electrons.

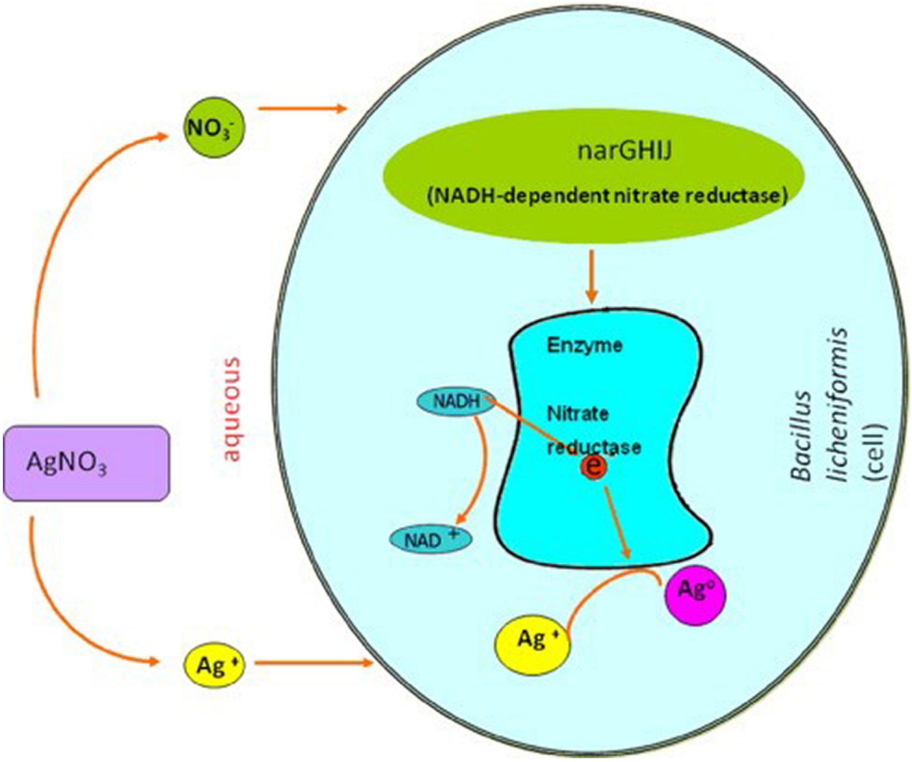

Fig. 2. Enzymatic reduction of silver in the presence of coenzyme by *Bacillus lichniformis* adopted from(Kalimuthu et al., 2008) with permission.

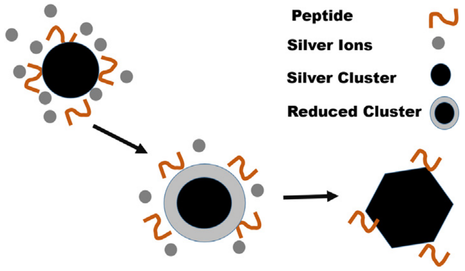

Fig. 3. Model presenting the silver crystal formation by silver-binding peptides. Adopted from (Naik et al., 2002) with permission.

cofactor, synthesis of AgNPs was entirely inhibited hence confirming the participation of nitrate reductase enzyme in the synthesis of AgNPs. Naik et al. (Naik et al., 2002) established the synthesis process of AgNPs using peptides attached to the surface of AgNPs. According to his findings reduction of silver ions was accelerated when peptide adhered to the nanoclusters or nuclei.

A mechanistic model was proposed that explained how peptides were added to the solution of silver ions, and they reacted with preformed metal ions nuclei and created a reducing vicinity around the metal nanocluster (Fig. 3). Due to this interaction reduction process was catalyzed and distribution of shape, size (60–150 nm) was observed. Peptides with special amino acid like cysteine, methionine, arginine, and lysine may attach on the surfaces of nuclei and can be used in the production of AgNPs (Selvakannan et al., 2013). In this way, the silver and peptide interaction was examined in detail (Balachandran et al., 2013; Naik et al., 2002). Tyrosine amino acid under alkaline conditions acts as a reducing agent. Indeed it is the phenolic group of tyrosine that can reduce silver and later on modifying itself into a semi-quinone structure. Tyrosine-based synthesis was preferable because newly synthesized NPs were easily achievable through centrifugation (Dubey et al., 2015; Selvakannan et al., 2004). Furthermore, they also observed that tyrosine has also the potential for reducing gold. Free N terminus of peptides with metal surface provides the stabilization. A tripeptide containing tyrosine residue at C terminus to reduce the gold ions and free N terminus to stabilize and attach with GNPs (Bhattacharya and Gupta, 2005; Shankar et al., 2015).While the oligopeptide holding tyrosine can also be used in a gel-network structure for reducing metals and synthesizing GNPs and AgNPs (Daima et al., 2014; Jones et al., 2008). It was also demonstrated that the peptides lacking the specific tyrosine residue were failed to perform reducing activity. These findings were in accordance with idea that tyrosine plays a key role for in situ reduction. At alkaline pH, tryptophan can also be used to formulate the metal NPs.

Another mechanism was proposed by Si and Mandal, (Si and Mandal, 2007) describing the reductive properties of tryptophan moieties. This study demonstrated that initially tryptophan is changed into tryptophol radical which can donate electrons to the metal ions and subsequently forming metal NPs. Because this radical can act as a fluorescent agent (ditryptophan), in the kynurenine form, hence attachment of peptide can be analyzed by fluorescence spectroscopies and UV–vis techniques (Si and Mandal, 2007). In ambient light aspartic acid and glutamic acid can produce AgNPs in the presence of carboxylic groups of short peptides of yeast can support the synthesis process. Recently a study has reported the eco-friendly fabrication of AgNPs using the supernatant of *Pseudomonas aeruginosa* JP1 culture which was isolated from a metal contaminated soil. Authors have linked the nitrate reductase with AgNPs synthesis through retreating the nitrate reductase with purified protein (Fig. 4) (Ali et al., 2017). However, another study has also reported that superoxide dismutase is responsible for the extracellular synthesis of AgNPs by Fusarium *oxysporum* (Yin et al., 2016). Broadly, the enzymes involved in the synthesis of metal NPs are nitrate reductases for which NADH act as a coenzyme.

Mostly, assimilatory type of nitrate reductases is metalloproteins having the molybdenum ions as cofactor and catalyzes the several reactions in nitrogen, carbon and sulfur cycle. Through different mechanistic approaches, it can be concluded that enzymes may play a critical role in the reduction of metal salts subsequently formulating the metal NPs. Thus the optimization of different parameters for its maximum activity and production can enhance the AgNPs synthesis process. Moreover, by controlling the mechanistic steps monodispersity and uniformity are attainable. Different types of enzymes involving NPs synthesis with their sizes are mentioned in Table 1.

2.2. *Mechanism of gold nanoparticle synthesis*

Discussion about the bacteriogenic synthesis mechanism of gold nanoparticle (GNPs) was started when a closely resembled mechanistic process was elaborated for the extracellular synthesis of GNPs by using the culture of *Rhodopseudomonas capsulate* (He et al., 2007). Different cofactors like NADH or NADH-dependent enzymes are also released extracellularly. In the reduction process, the initial step is the transfer of an electron from NADH through an electron carrier (NADH-dependent reductase), while in next step electrons are transferred to gold ions (Au^{3+}) and got reduced to elemental gold (Au^0) or GNPs. The mechanism of GNPs synthesis by a bacterium *Stenotrophomonas maltophilia* was proposed by Nangia et al., (Nangia et al., 2009). Authors have suggested the involvement of NADPH-dependent reductase enzyme in the reduction of Au^{3+} to Au^0 and stabilization via capping molecules. Das et al. (Das and Marsili, 2010) have reported GNPs were synthesized extracellularly using *Rhizopus oryzae*. The FTIR spectrum of the reaction mixture containing AuCl$_4$$^-$ showed the presence of different amides like amide I (primary), II (secondary) and amide III and vanishing carboxylic group, indicating the involvement peptides or proteins in the reduction of gold ions. The involvement of the phosphate bond was revealed by the peak shifting from 1034 cm^{-1} to 1025 cm^{-1}. Thus it was concluded that GNPs could be synthesized by surface bounded molecules which also act as stabilizing agent (Singaravelu et al., 2007).

2.3. *Mechanism of palladium nanoparticle synthesis*

Palladium is another precious metal commonly used in electrochemical catalysts and refining industries as well as an important catalytic converter in automobiles to lower the emission of dangerous pollutants. The high consumption rates of Palladium have outperformed the production rates during the last few years. Although, some chemical practices are being employed for the bulk recovery of palladium from the waste streams, there is a need to develop sustainable and more efficient strategies. Microbial reduction of soluble Pd(II) to Pd(0) to recycle precious metals and synthesize catalytic nanoparticles has proven as an effective, sustainable method (Ahmed et al., 2018). Several studies have reported the palladium reduction to palladium nanoparticles (PdNPs) through bacteria along with diverse applications. Extracellular reduction of palladium to PdNPs by *Geobacter sulfurreducens* was reported as a sustainable method to recover precious metal catalysts (Yates et al., 2013). Another recent investigation pointed out the selective electrocatalysis of biofuel molecular oxidation using palladium nanoparticles generated on *Shewanella oneidensis* MR-1 (Wu et al., 2018).

2.4. *Mechanism of platinum nanoparticle synthesis*

Earliest microbial mediated synthesis of platinum nanoparticles was achieved by the reduction of Pt (IV) via hydrogenase enzyme extracted from sulphate-reducing bacteria (SRB) (Fig. 5) (Martins et al., 2017). Since then a diverse range of microbes has served as nanofactories for platinum nanoparticles (PtNPs). Although fungal based synthesis is reported in most of the studies, *Desulfovibrio vulgaris opted a bioreduction mechanism to formulate the spherical PtNPs in periplasmic spaces. However,*

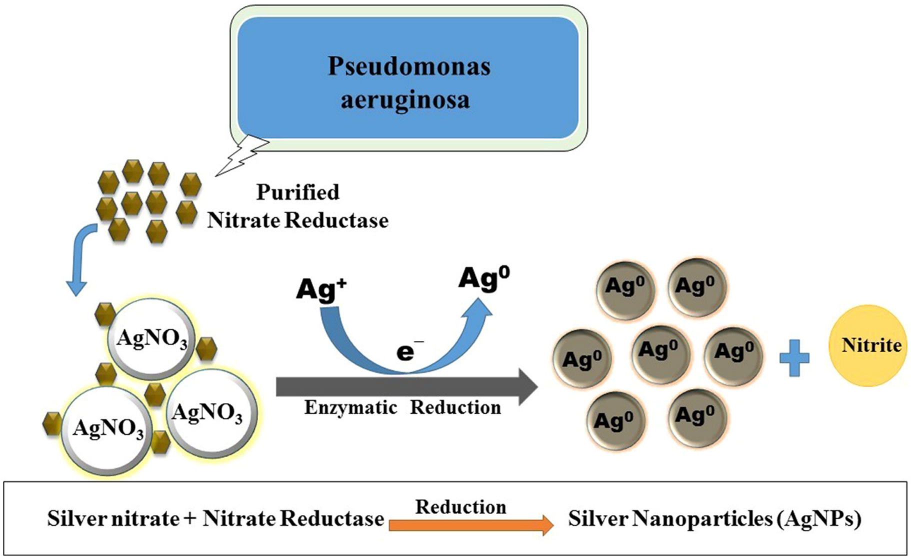

Fig. 4. Extracellular and nitrate reductase-mediated synthesis of AgNPs *by Pseudomonas aeruginosa* JP1.adopted from(Ali et al., 2017) permission.

Table 1
Different sizes of enzymes or biomolecules involved in metal nanoparticles synthesis.

Serial #	Microorganism	Nanoparticle type	Biomolecules/enzyme involved	Molecular size	Reference
1.	*Enterobacter cloacae*	AgNPs	Nitrate reductase	–	(Shahverdi et al., 2007)
2.	*Pseudomonas aerogenosa* JP2	AgNPs	Nitrate reductase	66 kDa	(Ali et al., 2017)
3.	*Pseudomonas aerogenosa* JP1	AgNPs	Nitrate reductase	65 kDa	(Ali et al., 2016)
4.	*E. coli*	AgNPs	Nitrate reductase	–	(Huang et al., 2015)
5.	*Bacillus subtilis*	AgNPs	proteins	66–116 kDa	(Reddy et al., 2010)
6.	*Verticillium sp.*	Magnetite	Protein	55- and 13-kDa	(Bharde et al., 2006)
7.	*Shewanella oneidensis*	AgNPs	C-type cytochromes	–	(Law et al., 2008)
8.	*S. maltophilia*	AgNPs	Chromium reductase	–	(Oves et al., 2013)
9.	*Tetrathiobacter*	SeNPs	–	90-kDa protein	(Hunter and Manter, 2008)
10.	*Sclerotium rolfsii*	AuNPs	NADPH-dependent enzyme	28.7&19.5	(Narayanan and Sakthivel, 2011)
11.	*D.desulfuriacans* ATCC 29577	PdNPs	Hydrogenase and cytochrome C$_3$	–	(Mabbett et al., 2004)
12.	*M. psychrotolerans53*	Ag-nanoplates	Ag-reductases	–	(Ramanathan et al., 2010)
13.	*Aspergillus flavus*NJP08.	AgNPs	Protein fragment	32 & 32 kDa	(Jain et al., 2011)
14.	*Penicillium fellutanum*	AgNPs	–	70 KDa protein	(Kathiresan et al., 2009)
15.	*F. oxysporum*	AgNPs	α-NADPH-dependent nitrate reductase and phytochelatin	(44 kDa)	(Kumar et al., 2007)
16.	*Fusarium oxysporum*	AuNPs	protein	66- and 10-kDa	(Mukherjee et al., 2002)

– no information found.

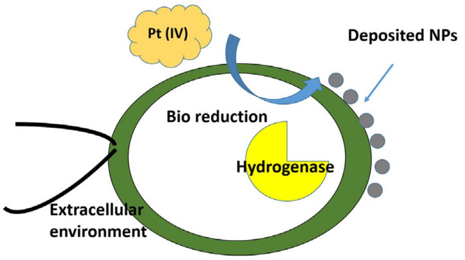

Fig. 5. Extracellular synthesis mechanism of platinum nanoparticles.

an enzymatic reduction was also reported for the intracellular synthesis of monodispersed cuboidal PtNPs (5 nm) by Acinetobacter calcoaceticus (Gaidhani et al., 2014). Similarly, a reductive decomposition channel was used by Shewanella strain to synthesize the intracellular PtNPs which were located inside the periplasmic membranes (Martins et al., 2017).

2.5. Mechanisms of non-noble metal nanoparticle synthesis

Metal NPs formulation can be linked with the fact that metallophilic microbes evolve genetic and proteomic reaction in response to toxic environments (Casals et al., 2012). Heavy metal ions such as Hg^{2+}, Ni^{2+}, CrO4 $^{2+}$, Ag^{+}, Co^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}and Pb^{2+} can hinder the growth of organisms. In order to alleviate the toxicity and regulate the metal homeostasis microorganisms have developed proteomic and genetic responses (Sinha et al., 2014). Numerous metal resistance genes or gene clusters can reside in microorganisms which enables them to detoxify metals through a series of mechanisms such as efflux, complexation, or reductive precipitation efflux. In this way, metallophilic bacteria flourish in environments harboring ions of heavy metals, like efflux streams of metal processing plants, mine waste rock piles and naturally mineralized zones (Reith et al., 2013). Another study revealed the active and passive mechanisms used for the magnetite synthesis from *Shewanella oneidensis* (Perez-Gonzalez et al., 2013). When ferrihydrite is utilized as a final electron acceptor by bacteria, the pH around the cell raised which results in active production of Fe^{2+} ions. Later on, localized concentrated ions of Fe$_2$$^+$ and Fe$_3$$^+$ at cell wall increase in supersaturation state of the cell through the passive mechanism. Biomineralization of bacterial magnetite particle (BacMP) is speculated to be a multistep process. The invagination of the cytoplasmic membrane is the first step, and newly organized vesicles act as precursor BacMP membrane. It is believed that vesicle formation in magnetotactic bacteria resembles with GTPase mediated study in eukaryotes. Then vesicles are joined in chains along with cytoskeletal filaments. The assemblage of Fe^{+2} inside the vesicles by siderophores molecules (iron transporters), is the next step of BacMP biomineralization. Oxidation-reduction firmly control the internal iron. Finally, proteins attached to BacMP initiate nucleation an also regulate the morphology of magnetite crystals. Several proteins attached to the BacMP membrane play an important role for the generation of magnetite (Arakaki et al., 2008).

Sangha et al., (Sanghi and Verma, 2009) have also investigated the synthesis of cadmium sulfide NPs. They proposed disulfide bonds of cysteine are involved in NPs formation which can be assigned to breakage of S—H bond and creation of new bonds, which is Cd-thiolate (Cd–S–CH_2COOH) complex on the surface of NPs. The carboxylic group (COOH) of the cadmium-thiolate complexes interacts with hydrogen bond instead of reacting with the amino group of proteins. Therefore, the hydrogen bond is responsible for amino group binding with capped CdS. Beveridge et al., (Beveridge et al., 1997) have explained the mechanisms that were under consideration for the biosynthesis of nanomaterials including alteration of toxicity and solubility, bioaccumulation, oxidation, reduction, biosorption, efflux systems precipitation and extracellular complexation of metals. Cell wall has a significant influence on the intracellular synthesis of NPs. The positively charged metallic ions electrostatically attached toward the negatively charged wall. Small diffused NPs are obtained as a result of reduction through the enzymes present in the cell wall (Jager et al., 2018).

Mukherjee et al., (Mukherjee et al., 2002) described the intracellular synthesis of NPs takes place through a step-by-step mechanism in case of *Verticillium* species. The mechanism contains two stipulating steps mainly, bioreduction and synthesis. A similar mechanism was also found in fungus for the synthesis of NPs. Moreover, Nair and Pradeep (Nair and Pradeep, 2002) observed that firstly metal ions nucleate; thus nanoclusters formation is the result of electrostatic interaction between the bacterial cell and metal clusters. Subsequently, the small nanoclusters get diffused through the bacterial cell wall. The same mechanism was witnessed in the case of Actinomycete (Sastry et al., 2003). Extracellular bacterial synthesis of NPs has been presented through nitrate- reductases reducing metal ions into nanocomposites (Ali et al., 2016; Jain et al., 2011).

3. Conclusion

Green synthesis of metal NPs has resulted in efficient, cost-effective and eco-friendly fabrication methodologies. Applications of nanomaterials are highly size dependent. Exploring the underlying molecular mechanism of NPs formation is very necessary for controlled size synthesis and enhanced applications. Although several studies have presented the underlying mechanisms of NPs formulation, generally nitrate reductase is considered as principle reducing agent. Role of catalytic proteins and stabilizing agents will undoubtedly provide sufficient information to control the morphology and crystallinity of nanomaterials. Moreover, Pathways involved in the green synthesis of nanomaterials are not only of prime importance for commercialization but also for environmental sustainability. Synthesis mechanisms will also improve the bioremediation and biomineralization processes for environmental contaminants. Future research on the microbial mediated biological synthesis of nanoparticles with unique optoelectronics, physicochemical and electronic properties are of great importance for applications in the areas of chemistry, electronics, medicine, and agriculture.

4. Future prospects

Nanotechnology has emerged as a promising domain of modern science. Enzymatic pathways are mainly contributing to the biosynthesis of metal NPs. Mechanistic insights will accelerate the synthesis processes of controlled morphology, stabilized nanomaterials for enhanced applications. Biological synthesis of metal NPs has also contributed to remediate the environment contaminants (Prabhu and Poulose, 2012). Heavy metals contamination has become a significant concern due to non-biodegradable nature and hazardous environmental impacts (Pejman et al., 2015). Bioremediation is preferred over chemical remedies (electrochemical treatment and chemical precipitation) due to economic reasons, simple nature and high efficiency (Masood and Malik, 2013). Combination of microbial physiology, metabolic and genetic engineering tools can offer innovative bio-based clean-up processes. Interestingly, microbes have evolved the serval mechanisms for metal resistance (Wu et al., 2016). Metal-reducing microbes act as geochemical agent and promote the transformations, precipitations, and dissolutions of minerals (Diaz et al., 2015). Enzymatic reduction mechanism has provided a new platform to explore biomineralization activity in detail. Biomineralization is the utmost process of controlling the ultimate fate in biogeochemical cycling and environmental impacts of heavy metals (Engel, 2017).

The fundamental insight of enzyme-metal interaction is elaborated here which will enable the biotransformation of toxic heavy metals hence providing the detoxification effect (Liu et al., 2016). Nitrate reductase producing microbes can potentially enhance the efficiency of bioremediation strategies. Nitrate reductase and other enzymes have been investigated for improving the remediation of heavy metals and toxic contaminants (Noor Afifah et al., 2016; Wang et al., 2018a, 2018b). Metal microbe interaction and role of secreted enzymes still needs further annotation (Neumann et al., 2017). A better understanding of microbial transformation pathway at the genetic level will lead to develop new genetic tools for accelerating the bioremediation (Kang et al., 2017). Whereas, these mechanisms may also assist in elucidating the antibiotic resistance phenomena (Engel, 2017; Waseem et al., 2019). The worldwide upsurge in antibiotic resistance has become a severe concern for modern medicine (Goossens et al., 2005; Neu, 1992; Yelin and Kishony, 2018). One of the promising approaches for overcoming bacterial resistance is the use of metallic nanoparticles in combination with antibiotics (Ghosh et al., 2012). However, recently co-occurrence of metal resistance genes and antibiotics resistance genes have been reported (Jang et al., 2018). Therefore metal transforming microbes may have a critical role in the production of superbugs (Lindsay and Holden, 2004). Moreover, the metal reducing microbes and extracellular electron transfer mechanism may have implications in electro-microbiological applications for renewable energy (Ali et al., 2018; Jackson and Mantsch, 1995).

Conflict of interest

Authors declare the no conflict of interest.

Acknowledgments

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References

Ahmad, A., Senapati, S., Khan, M.I., Kumar, R., Ramani, R., Srinivas, V., Sastry, M., 2003. Intracellular synthesis of gold nanoparticles by a novel alkalotolerant actinomycete, Rhodococcus species. Nanotechnology. 14, 824.

Ahmad, T., Wani, I.A., Manzoor, N., Ahmed, J., Asiri, A.M., 2013. Biosynthesis, structural characterization and antimicrobial activity of gold and silver nanoparticles. Colloids Surf. B: Biointerfaces 107, 227–234.

Ahmed, E., Kalathil, S., Shi, L., Alharbi, O., Wang, P., 2018. Synthesis of ultra-small platinum, palladium and gold nanoparticles by Shewanella loihica PV-4 electrochemically active biofilms and their enhanced catalytic activities. J. Saudi Chem. Soc. 22, 919–929.

Ali, J., Hameed, A., Ahmed, S., Ali, M.I., Zainab, S., Ali, N., 2016. Role of catalytic protein and stabilizing agents in transformation of Ag ions to nanoparticles by Pseudomonas aeruginosa. IET Nanobiotechnol. 10 (5), 295–300.

Ali, J., Ali, N., Jamil, S.U.U., Waseem, H., Khan, K., Pan, G., 2017. Insight into eco-friendly fabrication of silver nanoparticles by Pseudomonas aeruginosa and its potential impacts. J. Environ. Chem. Eng. 5, 3266–3272.

Ali, J., Sohail, A., Wang, L., Rizwan Haider, M., Mulk, S., Pan, G., 2018. Electro-microbiology as a promising approach towards renewable energy and environmental sustainability. Energies 11, 1822.

Arakaki, A., Nakazawa, H., Nemoto, M., Mori, T., Matsunaga, T., 2008. Formation of magnetite by bacteria and its application. J. R. Soc. Interface 5, 977–999.

Balachandran, Y.L., Girija, S., Selvakumar, R., Tongpim, S., Gutleb, A.C., Suriyanarayanan, S., 2013. Differently environment stable bio-silver nanoparticles: study on their optical enhancing and antibacterial properties. PLoS One 8, e77043.

Beveridge, T.J., Makin, S.A., Kadurugamuwa, J.L., Li, Z., 1997. Interactions between biofilms and the environment. FEMS Microbiol. Rev. 20, 291–303.

Bharde, A., Rautaray, D., Bansal, V., Ahmad, A., Sarkar, I., Yusuf, S.M., Sanyal, M., Sastry, M., 2006. Extracellular biosynthesis of magnetite using fungi. Small 2, 135–141.

Bhattacharya, D., Gupta, R.K., 2005. Nanotechnology and potential of microorganisms. Crit. Rev. Biotechnol. 25, 199–204.

Casals, E., Gonzalez, E., Puntes, V., 2012. Reactivity of inorganic nanoparticles in biological environments: insights into nanotoxicity mechanisms. J. Phys. D. Appl. Phys. 45, 443001.

Daima, H.K., Selvakannan, P., Kandjani, A.E., Shukla, R., Bhargava, S.K., Bansal, V., 2014. Synergistic influence of polyoxometalate surface corona towards enhancing the antibacterial performance of tyrosine-capped Ag nanoparticles. Nanoscale 6, 758–765.

Daraee, H., Eatemadi, A., Abbasi, E., Fekri Aval, S., Kouhi, M., Akbarzadeh, A., 2016. Application of gold nanoparticles in biomedical and drug delivery. Artif. Cells Nanomed. Biotechnol. 44, 410–422.

Das, S.K., Marsili, E., 2010. A green chemical approach for the synthesis of gold nanoparticles: characterization and mechanistic aspect. Rev. Environ. Sci. Biotechnol. 9, 199–204.

Davis, M.E., Shin, D.M., 2008. Nanoparticle therapeutics: an emerging treatment modality for cancer. Nat. Rev. Drug Discov. 7, 771.

Diaz, M.R., Swart, P.K., Eberli, G.P., Oehlert, A.M., Devlin, Q., Saeid, A., Altabet, M.A., 2015. Geochemical evidence of microbial activity within ooids. Sedimentology 62, 2090–2112.

Dubey, K., Anand, B.G., Badhwar, R., Bagler, G., Navya, P., Daima, H.K., Kar, K., 2015. Tyrosine-and tryptophan-coated gold nanoparticles inhibit amyloid aggregation of insulin. Amino Acids 47, 2551–2560.

Durán, N., Marcato, P.D., Durán, M., Yadav, A., Gade, A., Rai, M., 2011. Mechanistic aspects in the biogenic synthesis of extracellular metal nanoparticles by peptides, bacteria, fungi, and plants. Appl. Microbiol. Biotechnol. 90, 1609–1624.

Engel, J., 2017. Biominerals and Their Function in Different Organisms, A Critical Survey of Biomineralization. Springer, pp. 7–11.

Fayaz, A.M., Balaji, K., Girilal, M., Yadav, R., Kalaichelvan, P.T., Venketesan, R., 2010. Biogenic synthesis of silver nanoparticles and their synergistic effect with antibiotics: a study against gram-positive and gram-negative bacteria. Nanomedicine 6, 103–109.

Gaidhani, S.V., Yeshvekar, R.K., Shedbalkar, U.U., Bellare, J.H., Chopade, B.A., 2014. Bio-reduction of hexachloroplatinic acid to platinum nanoparticles employing Acinetobacter calcoaceticus. Process Biochem. 49, 2313–2319.

Ghosh, S., Patil, S., Ahire, M., Kitture, R., Kale, S., Pardesi, K., Cameotra, S.S., Bellare, J., Dhavale, D.D., Jabgunde, A., 2012. Synthesis of silver nanoparticles using Dioscorea bulbifera tuber extract and evaluation of its synergistic potential in combination with antimicrobial agents. Int. J. Nanomedicine 7, 483.

Goossens, H., Ferech, M., Vander Stichele, R., Elseviers, M., Group, E.P, 2005. Outpatient antibiotic use in Europe and association with resistance: a cross-national database study. Lancet 365, 579–587.

He, S., Guo, Z., Zhang, Y., Zhang, S., Wang, J., Gu, N., 2007. Biosynthesis of gold nanoparticles using the bacteria Rhodopseudomonas capsulata. Mater. Lett. 61, 3984–3987.

Huang, J., Lin, L., Sun, D., Chen, H., Yang, D., Li, Q., 2015. Bio-inspired synthesis of metal nanomaterials and applications. Chem. Soc. Rev. 44, 6330–6374.

Hunter, W.J., Manter, D.K., 2008. Bio-reduction of selenite to elemental red selenium by Tetrathiobacter kashmirensis. Curr. Microbiol. 57, 83–88.

Ingle, A., Rai, M., Gade, A., Bawaskar, M., 2009. Fusarium solani: a novel biological agent for the extracellular synthesis of silver nanoparticles. J. Nanopart. Res. 11, 2079.

Jackson, M., Mantsch, H.H., 1995. The use and misuse of FTIR spectroscopy in the determination of protein structure. Crit. Rev. Biochem. Mol. Biol. 30, 95–120.

Jafar Ali, S.Z., Ali, N., 2015. Green Synthesis of Metal Nanoparticles by Microorganisms; A Current Prospective.

Jager, A., Jäger, E.z., Syrova, Z., Mazel, T., Kováčik, L.r., Raška, I., Höcherl, A., Kučka, J., Konefal, R., Humajova, J., 2018. Poly (ethylene oxide monomethyl ether)-block-poly (propylene succinate) nanoparticles: synthesis and characterization, enzymatic and cellular degradation, micellar solubilization of paclitaxel, and in vitro and in vivo evaluation. Biomacromolecules 19, 2443–2458.

Jain, D., Daima, H.K., Kachhwaha, S., Kothari, S., 2009. Synthesis of plant-mediated silver nanoparticles using papaya fruit extract and evaluation of their anti microbial activities. Digest J. Nanomater. Biostruct. 4, 557–563.

Jain, N., Bhargava, A., Majumdar, S., Tarafdar, J., Panwar, J., 2011. Extracellular biosynthesis and characterization of silver nanoparticles using Aspergillus flavus NJP08: a mechanism perspective. Nanoscale 3, 635–641.

Jang, H.M., Lee, J., Kim, Y.B., Jeon, J.H., Shin, J., Park, M.-R., Kim, Y.M., 2018. Fate of antibiotic resistance genes and metal resistance genes during thermophilic aerobic digestion of sewage sludge. Bioresour. Technol. 249, 635–643.

Jha, A.K., Prasad, K., Prasad, K., 2009. Biosynthesis of Sb2O3 nanoparticles: a low-cost green approach. Biotechnol. J. 4, 1582–1585.

Jiang, W., Kim, B.Y., Rutka, J.T., Chan, W.C., 2008. Nanoparticle-mediated cellular response is size-dependent. Nat. Nanotechnol. 3, 145.

Jones, N., Ray, B., Ranjit, K.T., Manna, A.C., 2008. Antibacterial activity of ZnO nanoparticle suspensions on a broad spectrum of microorganisms. FEMS Microbiol. Lett. 279, 71–76.

Kalimuthu, K., Babu, R.S., Venkataraman, D., Bilal, M., Gurunathan, S., 2008. Biosynthesis of silver nanocrystals by Bacillus licheniformis. Colloids Surf. B: Biointerfaces 65, 150–153.

Kalishwaralal, K., Deepak, V., Pandian, S.R.K., Kottaisamy, M., BarathManiKanth, S., Kartikeyan, B., Gurunathan, S., 2010. Biosynthesis of silver and gold nanoparticles using Brevibacterium casei. Colloids Surf. B: Biointerfaces 77, 257–262.

Kang, F., Qu, X., Alvarez, P.J., Zhu, D., 2017. Extracellular saccharide-mediated reduction of Au3+ to gold nanoparticles: new insights for heavy metals biomineralization on microbial surfaces. Environ. Sci. Technol. 51 (5), 2776–2785.

Kathiresan, K., Manivannan, S., Nabeel, M., Dhivya, B., 2009. Studies on silver nanoparticles synthesized by a marine fungus, Penicillium fellutanum isolated from coastal mangrove sediment. Colloids Surf. B 71, 133–137.

Klaus, T., Joerger, R., Olsson, E., Granqvist, C.-G., 1999. Silver-based crystalline nanoparticles, microbially fabricated. Proc. Natl. Acad. Sci. 96, 13611–13614.

Kumar, S.A., Abyaneh, M.K., Gosavi, S., Kulkarni, S.K., Pasricha, R., Ahmad, A., Khan, M., 2007. Nitrate reductase-mediated synthesis of silver nanoparticles from AgNO3. Biotechnol. Lett. 29, 439–445.

Law, N., Ansari, S., Livens, F.R., Renshaw, J.C., Lloyd, J.R., 2008. Formation of nanoscale elemental silver particles via enzymatic reduction by Geobacter sulfurreducens. Appl. Environ. Microbiol. 74, 7090–7093.

Li, L., Hu, Q., Zeng, J., Qi, H., Zhuang, G., 2011a. Resistance and biosorption mechanism of silver ions by Bacillus cereus biomass. J. Environ. Sci. 23, 108–111.

Li, X., Xu, H., Chen, Z.-S., Chen, G., 2011b. Biosynthesis of nanoparticles by microorganisms and their applications. J. Nanomater. 2011.

Lindsay, J.A., Holden, M.T., 2004. Staphylococcus aureus: superbug, super genome? Trends Microbiol. 12, 378–385.

Liu, S.-H., Zeng, G.-M., Niu, Q.-Y., Liu, Y., Zhou, L., Jiang, L.-H., Tan, X.-F., Xu, P., Zhang, C., Cheng, M., 2016. Bioremediation mechanisms of combined pollution of PAHs and heavy metals by bacteria and fungi: a mini review. Bioresour. Technol. 224, 25–33.

Mabbett, A.N., Yong, P., Farr, J.P.G., Macaskie, L.E., 2004. Reduction of Cr (VI) by "palladized" biomass of Desulfovibrio desulfuricans ATCC 29577. Biotechnol. Bioeng. 87, 104–109.

Manoj, D., Saravanan, R., Santhanalakshmi, J., Agarwal, S., Gupta, V.K., Boukherroub, R., 2018. Towards green synthesis of monodisperse Cu nanoparticles: An efficient and high sensitive electrochemical nitrite sensor. Sens. Actuat. B 266, 873–882.

Martins, M., Mourato, C., Sanches, S., Noronha, J.P., Crespo, M.B., Pereira, I.A., 2017. Biogenic platinum and palladium nanoparticles as new catalysts for the removal of pharmaceutical compounds. Water Res. 108, 160–168.

Masood, F., Malik, A., 2013. Current Aspects of Metal Resistant Bacteria in Bioremediation: From Genes to Ecosystem, Management of Microbial Resources in the Environment. Springer, pp. 289–311.

Mokhtari, N., Daneshpajouh, S., Seyedbagheri, S., Atashdehghan, R., Abdi, K., Sarkar, S., Minaian, S., Shahverdi, H.R., Shahverdi, A.R., 2009. Biological synthesis of very small silver nanoparticles by culture supernatant of Klebsiella pneumonia: the effects of visible-light irradiation and the liquid mixing process. Mater. Res. Bull. 44, 1415–1421.

Mukherjee, P., Senapati, S., Mandal, D., Ahmad, A., Khan, M.I., Kumar, R., Sastry, M., 2002. Extracellular synthesis of gold nanoparticles by the fungus Fusarium oxysporum. ChemBioChem 3, 461–463.

Musarrat, J., Dwivedi, S., Singh, B.R., Al-Khedhairy, A.A., Azam, A., Naqvi, A., 2010. Production of antimicrobial silver nanoparticles in water extracts of the fungus Amylomyces rouxii strain KSU-09. Bioresour. Technol. 101, 8772–8776.

Naik, R.R., Stringer, S.J., Agarwal, G., Jones, S.E., Stone, M.O., 2002. Biomimetic synthesis and patterning of silver nanoparticles. Nat. Mater. 1, 169.

Nair, B., Pradeep, T., 2002. Coalescence of nanoclusters and formation of submicron crystallites assisted by Lactobacillus strains. Cryst. Growth Des. 2, 293–298.

Nangia, Y., Wangoo, N., Goyal, N., Shekhawat, G., Suri, C.R., 2009. A novel bacterial isolate Stenotrophomonas maltophilia as living factory for synthesis of gold nanoparticles. Microb. Cell Factories 8, 39.

Narayanan, K.B., Sakthivel, N., 2010. Biological synthesis of metal nanoparticles by microbes. Adv. Colloid Interf. Sci. 156, 1–13.

Narayanan, K.B., Sakthivel, N., 2011. Facile green synthesis of gold nanostructures by NADPH-dependent enzyme from the extract of Sclerotium rolfsii. Colloids Surf. Physicochem. Eng. Aspects. 380, 156–161.

Neu, H.C., 1992. The crisis in antibiotic resistance. Science. 257, 1064–1073.

Neumann, W., Gulati, A., Nolan, E.M., 2017. Metal homeostasis in infectious disease: recent advances in bacterial metallophores and the human metal-withholding response. Curr. Opin. Chem. Biol. 37, 10–18.

Noor Afifah, F., Hajar, S., Rasdi, M., Essam, A.M., Hasbi, M., Rahim, A., 2016. Bioremediation of disposed X-Ray film for enzymes production. Global J. Adv. Res. 3, 101–106.

Oves, M., Khan, M.S., Zaidi, A., Ahmed, A.S., Ahmed, F., Ahmad, E., Sherwani, A., Owais, M., Azam, A., 2013. Antibacterial and cytotoxic efficacy of extracellular silver nanoparticles biofabricated from chromium reducing novel OS4 strain of Stenotrophomonas maltophilia. PLoS One 8, e59140.

Park, W., Na, K., 2015. Advances in the synthesis and application of nanoparticles for drug delivery. Wiley Interdiscip. Rev. 7, 494–508.

Pejman, A., Bidhendi, G.N., Ardestani, M., Saeedi, M., Baghvand, A., 2015. A new index for assessing heavy metals contamination in sediments: a case study. Ecol. Indic. 58, 365–373.

Perez-Gonzalez, T., Valverde-Tercedor, C., Yebra-Rodriguez, A., Prozorov, T., Gonzalez-Muñoz, M.T., Arias-Peñalver, J.M., Jimenez-Lopez, C., 2013. Chemical purity of Shewanella oneidensis-induced magnetites. Geomicrobiol J. 30, 731–748.

Prabhu, S., Poulose, E.K., 2012. Silver nanoparticles: mechanism of antimicrobial action, synthesis, medical applications, and toxicity effects. Int. Nano Lett. 2, 1–10.

Ramanathan, R., O'Mullane, A.P., Parikh, R.Y., Smooker, P.M., Bhargava, S.K., Bansal, V., 2010. Bacterial kinetics-controlled shape-directed biosynthesis of silver nanoplates using Morganella psychrotolerans. Langmuir 27, 714–719.

Rana, S., Nazar, U., Ali, J., Ali, Q.U.A., Ahmad, N.M., Sarwar, F., Waseem, H., Jamil, S.U.U., 2017. Improved antifouling potential of polyether sulfone polymeric membrane containing silver nanoparticles: self-cleaning membranes. Environ. Technol. 1-9.

Reddy, A.S., Chen, C.-Y., Chen, C.-C., Jean, J.-S., Chen, H.-R., Tseng, M.-J., Fan, C.-W., Wang, J.-C., 2010. Biological synthesis of gold and silver nanoparticles mediated by the bacteria Bacillus subtilis. J. Nanosci. Nanotechnol. 10, 6567–6574.

Reith, F., Brugger, J., Zammit, C.M., Nies, D.H., Southam, G., 2013. Geobiological cycling of gold: from fundamental process understanding to exploration solutions. Minerals 3, 367–394.

Sanghi, R., Verma, P., 2009. A facile green extracellular biosynthesis of CdS nanoparticles by immobilized fungus. Chem. Eng. J. 155, 886–891.

Sastry, M., Ahmad, A., Khan, M.I., Kumar, R., 2003. Biosynthesis of metal nanoparticles using fungi and actinomycete. Curr. Sci. 85, 162–170.

Selvakannan, P., Swami, A., Srisathiyanarayanan, D., Shirude, P.S., Pasricha, R., Mandale, A.B., Sastry, M., 2004. Synthesis of aqueous Au core− Ag shell nanoparticles using tyrosine as a pH-dependent reducing agent and assembling phase-transferred silver nanoparticles at the air− water interface. Langmuir. 20, 7825–7836.

Selvakannan, P., Ramanathan, R., Plowman, B.J., Sabri, Y.M., Daima, H.K., O'Mullane, A.P., Bansal, V., Bhargava, S.K., 2013. Probing the effect of charge transfer enhancement in off resonance mode SERS via conjugation of the probe dye between silver nanoparticles and metal substrates. Phys. Chem. Chem. Phys. 15, 12920–12929.

Shah, J.H., Fiaz, M., Athar, M., Ali, J., Rubab, M., Mehmood, R., Jamil, S.U.U., Djellabi, R., 2019. Facile synthesis of N/B double-doped Mn2O3 and WO3 nanoparticles for dye degradation under visible light. Environ. Technol. 1–20.

Shahverdi, A.R., Minaeian, S., Shahverdi, H.R., Jamalifar, H., Nohi, A.-A., 2007. Rapid synthesis of silver nanoparticles using culture supernatants of Enterobacteria: a novel biological approach. Process Biochem. 42, 919–923.

Shankar, S., Soni, S.K., Daima, H.K., Selvakannan, P., Khire, J.M., Bhargava, S.K., Bansal, V., 2015. Charge-switchable gold nanoparticles for enhanced enzymatic thermostability. Phys. Chem. Chem. Phys. 17, 21517–21524.

Si, S., Mandal, T.K., 2007. Tryptophan-based peptides to synthesize gold and silver nanoparticles: a mechanistic and kinetic study. Chem Eur J 13, 3160–3168.

Singaravelu, G., Arockiamary, J., Kumar, V.G., Govindaraju, K., 2007. A novel extracellular synthesis of monodisperse gold nanoparticles using marine alga, *Sargassum wightii* Greville. Colloid Surf. B 57, 97–101.

Sinha, A., Sinha, R., Khare, S.K., 2014. Heavy Metal Bioremediation and Nanoparticle Synthesis by Metallophiles, Geomicrobiology and Biogeochemistry. Springer, pp. 101–118.

Sintubin, L., De Windt, W., Dick, J., Mast, J., van der Ha, D., Verstraete, W., Boon, N., 2009. Lactic acid bacteria as reducing and capping agent for the fast and efficient production of silver nanoparticles. Appl. Microbiol. Biotechnol. 84, 741–749.

Starowicz, M., Stypuła, B., Banaś, J., 2006. Electrochemical synthesis of silver nanoparticles. Electrochem. Commun. 8, 227–230.

Vaidyanathan, R., Gopalram, S., Kalishwaralal, K., Deepak, V., Pandian, S.R.K., Gurunathan, S., 2010. Enhanced silver nanoparticle synthesis by optimization of nitrate reductase activity. Colloids Surf. B: Biointerfaces 75, 335–341.

Venkatachalam, P., Jayaraj, M., Manikandan, R., Geetha, N., Rene, E.R., Sharma, N., Sahi, S., 2017. Zinc oxide nanoparticles (ZnONPs) alleviate heavy metal-induced toxicity in Leucaena leucocephala seedlings: a physiochemical analysis. Plant Physiol. Biochem. 110, 59–69.

Wang, H., Thorling, C.A., Liang, X., Bridle, K.R., Grice, J.E., Zhu, Y., Crawford, D.H., Xu, Z.P., Liu, X., Roberts, M.S., 2015. Diagnostic imaging and therapeutic application of nanoparticles targeting the liver. J. Mater. Chem. B 3, 939–958.

Wang, L., Ali, J., Zhang, C., Mailhot, G., Pan, G., 2017. Simultaneously enhanced photocatalytic and antibacterial activities of TiO 2/Ag composite nanofibers for wastewater purification. J. Environ. Chem. Eng. https://doi.org/10.1016/j.jece.2017.12.057.

Wang, L., Miao, X., Ali, J., Lyu, T., Pan, G., 2018a. Quantification of oxygen Nanobubbles in particulate matters and potential applications in remediation of anaerobic environment. ACS Omega 3, 10624–10630.

Wang, L., Zhang, C., Cheng, R., Ali, J., Wang, Z., Mailhot, G., Pan, G., 2018b. Microcystis aeruginosa synergistically facilitate the photocatalytic degradation of tetracycline hydrochloride and Cr (VI) on PAN/TiO2/Ag nanofiber mats. Catalysts 8, 628.

Waseem, H., Jameel, S., Ali, J., Saleem Ur Rehman, H., Tauseef, I., Farooq, U., Jamal, A., Ali, M., 2019. Contributions and challenges of high throughput qPCR for determining antimicrobial resistance in the environment: a critical review. Molecules 24, 163.

Wu, W., Huang, H., Ling, Z., Yu, Z., Jiang, Y., Liu, P., Li, X., 2016. Genome sequencing reveals mechanisms for heavy metal resistance and polycyclic aromatic hydrocarbon degradation in Delftia lacustris strain LZ-C. Ecotoxicology 25, 234–247.

Wu, R., Tian, X., Xiao, Y., Ulstrup, J., Christensen, H.E.M., Zhao, F., Zhang, J., 2018. Selective electrocatalysis of biofuel molecular oxidation using palladium nanoparticles generated on Shewanella oneidensis MR-1. J. Mater. Chem. A 6, 10655–10662.

Yates, M.D., Cusick, R.D., Logan, B.E., 2013. Extracellular palladium nanoparticle production using Geobacter sulfurreducens. ACS Sustain. Chem. Eng. 1, 1165–1171.

Yelin, I., Kishony, R., 2018. Antibiotic resistance. Cell 172, 1136 (e1131).

Yin, Y., Yang, X., Hu, L., Tan, Z., Zhao, L., Zhang, Z., Liu, J., Jiang, G., 2016. Superoxide-mediated extracellular biosynthesis of silver nanoparticles by the fungus Fusarium oxysporum. Environ. Sci. Technol. Lett. 3, 160–165.

Zhao, P., Li, N., Astruc, D., 2013. State of the art in gold nanoparticle synthesis. Coord. Chem. Rev. 257, 638–665.