

Review Article

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Bioinorganic metal nanoparticles and their potential applications as antimicrobial, antioxidant and catalytic agents: a review

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Abstract: This review article covers the biogenic synthesis of metal nanoparticles (MNPs) having definite shape and size while using extract obtained from different biological sources such as bacteria, fungi, algae and plants. These biological materials are composed of chloroplast, thylakoid, different types of enzymes extracted from different biogenic sources, different phytochemicals such as phenols, flavonoids, and citric acid having functional groups such as sulfate, carboxyl, amino, amide and hydroxyl groups. These functional groups and enzymes act as efficient reductants to convert metal ions into metal atoms and alternatively metal atoms combine to form MNPs while long hydrocarbon chains present in these bio-macromolecules act as cage to stabilize them for prolong time. Effect of nature of source extract, different reaction conditions such as extract amount, salt amount and solvent used during MNPs preparation process have been critically discussed here in detail. Use of synthesized bioinorganic NPs in various areas including their effectiveness in fighting against bacteria, viruses, fungi, cancer, inflammation, and their potential role in catalytic reduction of environmental harmful substances into friendly products has also been

described in a clear and concise manner along with their future consideration.

Keywords: algae; bacteria; plant; nanoparticles; catalysis; remediation

Abbreviations

4-AP	4-Aminophenol
4-NP	4-Nitro phenol
ABTS	2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid)
Ag NP	Silver nanoparticle
AgNO ₃	Silver nitrate
Au NP	Gold nanoparticle
AuHCl ₄	Chloroauric acid
BSA	Bovine serum albumin
DNA	Deoxyribonucleic acid
DPPH	2,2-diphenyl-1-picrylhydrazyl
EDX	Energy dispersive X-ray spectroscopy
FESEM	Field emission scanning electron microscope
FETEM	Field emission transmission electron microscopy
FTIR	Fourier transform infrared spectroscopy
GA	Glutamic acid
GO-Ag-NPs	Graphene oxide silver nanoparticles
HIV	Human immunodeficiency viruses
HRTEM	High-resolution transmission electron microscopy
KC ₄ H ₅ O ₆	Potassium bitartrate
MB	Methylene blue
MNPs	Metal nanoparticles
MOF	Metal organic framework
MPEG	Methoxypolyethylene glycol
NCDs	Native cyclodextrins
PAA	Poly acrylic acid
PRRSV	Porcine reproductive and respiratory syndrome virus
PVP	Polyvinyl pyrrolidone
ROS	Reactive oxygen species
SAED	Selected area electron diffraction
SDBS	Sodium dodecyl benzyl sulfate
SEM	Scanning electron microscope
TEM	Transmission electron microscopy
UV-vis	UV-visible
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ROS	Reactive oxygen species
RhB	Rhodamine B

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1 Introduction

In modern era, nanoparticles have attained much attention due to their wide range of applications in different fields such as catalysis [1], optics [2], biomedical sciences and agriculture [3] etc. Wide range applications of metal nanoparticles (MNPs) are based on their nano-size and high surface to volume ratio [4, 5]. MNPs can be prepared by chemical [6] or biological methods [7]. Biological synthesis of MNPs is a preferable method due to low cost, non-toxicity and easily availability of biological products. These biological synthesized MNPs have been utilized in different biomedical applications such as antimicrobial [8], anti-cancer [9], anti-inflammation [10], photo thermal therapy, photo-imaging against cancer cell [11], drug delivery [12], bio-sensing [13] and cosmetics [14]. Yet, MNPs exhibit drawback of rapid aggregation due to high surface energy and result in lost surface properties.

Aggregation of NPs is irreversible inter-particles adherence process, leads to the formation of large and irregularly shaped clusters and result in lost surface properties [15]. Different polymeric materials such as poly(ethylene glycol) (PEG), poly(vinyl pyrrolidone), poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) and poly(N-isopropyl acrylamide) (PNIPA) [16, 17], inorganic materials such as silica [18] and graphene oxide (GO) [19], and different organic materials [20–22] have been reported by different researchers to stabilize the MNPs synthesized by chemical or biological reduction method. Stabilizing materials do the successful stabilization of NPs, prolong their life time by increasing their inter-particle distance and preventing their agglomeration. But these methods require toxic chemicals like reducing agents, organic solvents or non-biodegradable stabilizing agents [23, 24]. Use of chemicals during the preparation and stabilization of MNPs limits their applicability to larger scale because of environmental concerns. Additionally, these methodologies also require the use of some other hazardous chemicals such as sodium dodecyl benzyl sulfate or polyvinyl pyrrolidone as anti-agglomerating agent. Sometimes, the chemically synthesized NPs also possess chemical contamination so these nanoparticles are not considered suitable for biological applications [25]. On the other hand, biological materials mediated synthesis of NPs is preferred method due to the simple synthetic methodology, less toxicity, being economical, easy availability of biological materials and environment friendliness. Different researchers reported the use of bacteria, algae, fungi, polypeptides and plant extracts as reducing and stabilizing agent for the successful fabrication of MNPs via simple methods [26–28].

Gul et al. [29] and Thatikayala et al. [30] reported the green synthesis of Ag NPs by using *Poa annua* (meadow

grass) extract and husk, pulp and seed of *Theobroma cacao*, respectively as reducing and stabilizing agent. They used these bioinorganic NPs in the biomedical field as antioxidant, antifungal and antibacterial agent along with investigated catalytic potential against toxic dyes. Joseph and Mathew [31] also designed the biogenic strategy for the preparation of Ag NPs under microwave irradiation by using *Aerva lanata* leaf extract. Microwave irradiation was performed to get enough number of MNPs. They also evaluated their efficiency against the catalytic reduction of 4-NP.

Many researchers reported the preparation of biogenic MNPs while using different biological materials as source of phenols, flavonoids and alkaloids [32]. Yet, no one reported the comparative analysis of algae, fungi, bacteria and plant extract induced potential efficiency for MNPs fabrication. So, due to keeping in mind the potential advantages of green synthesized NPs, we critically analyzed the effect of extract nature on the properties of fabricated MNP. A brief overview about the importance of biogenically synthesized metal nanoparticles as compared to the chemically synthesized MNPs are given in Section 1. Different methods based on the used biological sources for MNPs fabrication are explained in detail in Section 2. A brief overview of purification of bioorganic NPs are given in Section 3. Applications of bioorganic NPs as catalyst and biomedical agents are described in Section 4. Conclusion and future directions are given in Section 5.

2 Biological sources for the preparation of metal nanoparticles

Different biological materials such as bacteria, algae, fungi, polypeptides and plant extracts are mostly reported for the successful green fabrication of MNPs [33]. Different routes for the biogenic synthesis of MNPs are described diagrammatically in Figure 1.

2.1 Synthesis of metal nanoparticles by fungal extract

Fungi serves as a valuable biogenic source of secondary metabolites and active biomolecules that play a significant role in the fabrication of MNPs. They consist of bio-components like melanin with redox properties, various active proteins in the form of reductive enzymes such as cytochromes and reductases, various secondary metabolites such as phenolic groups and flavonoids. These components

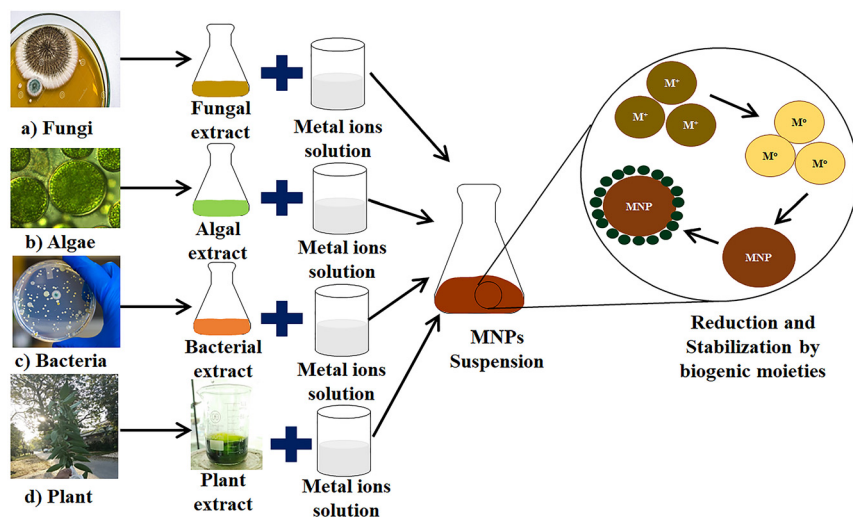


Figure 1: Schematic representation of biogenic preparation of metal nanoparticles by (a) fungi, (b) algae, (c) bacteria and (d) plant extract.

have capabilities to reduce metal ions into metal atoms. Some fungal species also consist of ligands such as siderophores that can entrap large contents of metal ions and effectively facilitates their reduction process by hydroxyl groups. Thus fungi assisted synthesis of metal nanoparticles has gained significant attention mainly due to several advantages such the ease of scaling up the production process, downstream handling processes, economic feasibility, and more importantly the presence of mycelia that provides an extensive surface area for the formation/fabrication of NPs [34]. MNPs synthesized through fungi are fastidious to grow, easy to control their size and easy to fabricate [35].

Additionally, their remarkable tolerance towards metals and their capacity for bioaccumulation made them a suitable candidate for the fabrication of NPs. Fungi are easy to use, require simple nutrients to grow, high wall binding capacity to immobilize and capacity of intracellular metal uptake. MNPs can be fabricated either by using fungal extract prepared in water medium or isolation of endophytic fungus, grown their culture in the media and used that culture for MNPs fabrication from metal salts. So, they are assumed as potential candidates for growth of MNPs.

Certain fungal species such as *Fusarium oxysporum* possess the ability to secrete proteins having functional moieties such as nitrate reductase and nicotiamide adenine dinucleotide hydride-dependent reductase [36], different types of polymers and variety of NADH-dependent enzymes present in the extracellular matrix [37]. Some other species have extracellular amino acid residues. These biological components having functional groups act as reductant for metal ions and long polymer chains acts as cadge to stabilize MNPs [34]. For instance, surface of the yeast contains amino acids like glutamic acid and aspartic acid which are responsible for the photo-reduction of silver ions into silver atoms

resulting in the formation of Ag NPs [38]. Some other variety of yeast such as *Candida guilliermondii* produces citric acid that has the ability to reduce silver and gold ions into their atoms that coalesce to form NPs [39]. It has also been reported that by increasing the amount of fungal extract in the reaction mixture, large number of metal ions are reduced to metal atoms that coagulate to form large sized MNPs [40]. Some other fungus species such as *Streptomyces hygroscopicus* are important source of antibiotics, anti-parasitic agents and enzymes that act as active reagent to reduce metal ions into atoms to form multidimensional MNPs such as spheres, triangles and hexagonal [41]. These factors contribute to the growing interest in exploring the potential of fungi extract for NP synthesis. Different researchers reported the successful fabrication of wide variety of MNPs such as Au, Ag, Pt, TiO₂, Zn, Cu, CeO, Fe₂O₃ and Se NPs while utilizing the reduction and stabilizing potential of fungal extracts [42–50]. Schematic preparation of MNPs while using fungal extract and metal salt is shown in Figure 1a.

Ballottin and coworkers [51] reported the use of *Aspergillus tubingensis*, an isolated endophytic fungus from *Rizophora mangle* for the synthesis of Ag NPs. They utilized extracellular fungal protein as reducing/stabilizing agent and investigated the supramolecular interaction between Ag NPs and protein functional groups. For preparation purpose, colonies of endophytic fungi *A. Tubingenis* were transferred to 5 mL saline solution (9 % NaCl), stirred for 72 h at 150 rpm and filtered with the help of polypropylene. Then, AgNO₃ solution (0.1 M) was added in this filtrate and kept at 25 °C in dark for 96 h to prepared Ag NPs. Diameter of Ag NPs determined by TEM was 35 nm while hydrodynamic diameter measured by DLS was found as 264 nm. They also observed a peak at 280 nm in SPR spectra attributed to the electronic excitations within tryptophan, tyrosine, and

phenylalanine residues found in fungal proteins. This confirmed the successful fabrication of Ag NPs. These fungal proteins were covalently attached to the AgNPs surface primarily through sulfur-silver (S–Ag) bonds originating from cysteine residues (HS–) and a few nitrogen-silver (N–Ag) bonds from amino groups (H₂N–). Furthermore, supramolecular interactions including electrostatic and other protein-protein interactions were also observed which strongly indicated the involvement of proteins in surface capping of Ag NPs.

Fayaz et al. [52] used the *Trichoderma viride* fungus to yield highly stable extracellular synthesized Ag NPs from AgNO₃ solution. Progress of reaction was monitored by UV–vis spectroscopy and it was seen that peak at 423 nm was increased in intensity with increase of time. Good quantity of NPs was obtained in 24 h with high absorbance values. Disk diffusion method was used to evaluate the bactericidal activities against bacterial test strains. They reported that these Ag NPs exhibit high antibacterial activity against both the gram-positive and gram-negative bacteria. They also investigated that antibacterial activity of several antibiotics such as ampicillin, kanamycin, erythromycin, and chloramphenicol were increased due to the presence of Ag NPs. High percentage increased activity was observed in case of ampicillin drug.

Many other researchers reported the synthesis of different MNPs while using fungal strains as source of reducing and capping agents [36, 37, 53]. Fungal strains induced descriptive methods adopted for the synthesis of metal nanoparticles with various shapes/sizes, their characterization and use in different fields are given in Table 1.

2.2 Synthesis of metal nanoparticles by algal extract

Algae are eukaryotic aquatic photoautotrophs which are capable of accumulating heavy metals [117]. Single cell green alga *Chlorella vulgaris*, when dried, exhibits a strong binding ability towards metal salts resulting in the formation of algal-bound metal ions which are subsequently reduced to metal atoms. It is reported that approximately 88 % of the algal-bound metal ions are reduced to metal atoms, and metal crystals with size in nano range are accumulated in the inner and outer parts of the algae in the form of different shapes such as tetrahedral, decahedral, and icosahedral [23].

Algal extracts are the major natural source of bioactive molecules and functional groups like –OH, carboxylic and amide which are mainly responsible for the synthesis and stability of MNPs. Amide and amino groups have also been reported mostly as reductants for the conversion of Ag⁺ ions to Ag⁰ atoms or may also involve the formation of phenolic

products at intermediate stage along with stabilizing the nanoparticles [60]. Therefore, algal extracts have exhibited an excellent potential for the preparation of nanoparticles of required particles size at large-scale. Biomolecules present in algal extracts perform dual functions like reduction of metal ions into metal atom and stabilizing them by acting as surface capping agent [118]. Reducing potential of different algal species is mainly due to their cellular activity as well as due to the presence of reducing enzymes in them [119]. Synthesis of metal nanoparticles involves a significant contribution from cellular components, such as fucoxanthin extracted from diatom *Amphora* which has been found to serve as a reducing agent for the reduction of silver ions into Ag⁰ and yield spherical nanoparticles. Some polysaccharides present in algal extract have also been observed to be involved in the stabilization of gold nanoparticles. Thus, use of algae for nanoparticle synthesis also offers several advantages, including ease of handling, low-temperature processes, low toxicity, and reduced environmental risk.

Thus, like other microbes, algal extracts of different species have also been reported for the synthesis of different types of metal nanoparticles such as Au, Ag, Pt, Ti, ZnO, CeO, FeO₂ and Se NPs etc. [120–126]. Algal carotenoids also play a crucial role in metal NPs synthesis owing to their electron-donating ability which also confers their antioxidant properties. Presence of water and hydrophilic conditions further enhance their electron-donating power. Therefore, the use of a water based medium facilitates the electrons transfer to metal ions for their reduction into metal atoms that ultimately resulting in the formation of metal nanoparticles with different shapes and sizes depending upon the used amount of salt and extract [63].

Tetraselmis kochinensis algal species have huge importance among biomedical species due to the production intracellular gold nanoparticles in the aqueous solution from AuCl₄[–] ions. The alga causes reduction of AuCl₄[–] into gold atoms that leads to the formation of gold nanoparticles and are found to be more concentrated upon the cell wall than on the cytoplasmic membrane [127]. Thus, biogenic synthesis of NPs by using algal species is beneficial as it makes the nanoparticles easily accessible and aids in various catalysis, coating, electronic and drug delivery applications.

Gopu et al. [59] prepared Ag NPs by using red algae, *Amphiroa rigida* extract as reducing and stabilizing agent. They mixed 10 mL algal extract with 90 mL of 1.0 mM aqueous solution of AgNO₃. Successful fabrication of Ag NPs was indicated by the appearance of reddish-brown coloring of the suspension. Ag NPs were separated out by centrifuging at 9000 rpm for 15 min at 4 °C. They observed that Ag NPs were successfully fabricated with 25 nm in size and spherical in shape as investigated by UV–vis and TEM analysis. Upon

Table 1: Different biogenic extract induced green synthesis of various noble metal nanoparticles, site of synthesis, their size, shape, characterization and applications in numerous fields.

Biogenic source	NPs	Site of formation	Size (nm)	Shape/nature	Characterization	Applications	Reference
<i>Cladosporium cladosporioides</i>	Au NPs	Extracellular	30–60	Face-centered cubic	UV–vis spectroscopy, FTIR, XRD, FESEM, DLS, AFM,	Antibacterial activity against <i>E. coli</i> , <i>Staphylococcus aureus</i> , <i>Bacillus subtilis</i> , and <i>Aspergillus niger</i> , antioxidant activity by DPPH radical scavenging	[54]
<i>Fusarium oxysporum</i>	Ag NPs	Extracellular	10–50	Spherical	UV–vis spectroscopy, FTIR, XRD, SEM, AFM,	Antimicrobial potential against <i>E. coli</i> , <i>Klebsiella pneumoniae</i> , <i>Salmonella typhi</i> , <i>Staphylococcus aureus</i> and <i>Pseudomonas aeruginosa</i> .	[53]
<i>Magnusiomyces ingens LH-F1</i>	Au NPs	Intracellular	10–80	Spherical	UV–vis spectroscopy, FTIR, XRD, SEM, TEM	Catalytic reduction of 4-NP	[55]
<i>Meyerozyma guilliermondii KX008616</i>	Ag NPs	Intracellular	2.5–30	Crystalline	UV–vis spectroscopy, FTIR, XRD, SEM, TEM	–	[56]
<i>Tinospora cordifolia</i>	Ag NPs	Extracellular	~11.6	Crystalline	UV–vis spectroscopy, FTIR, XRD, TEM	Anti-inflammatory, antioxidant activity, antibacterial activity against <i>E. coli</i> , <i>Klebsiella pneumoniae</i> , <i>P. aeruginosa</i> and <i>Staphylococcus aureus</i>	[57]
<i>Penicillium italicum</i>	Au NPs	Extracellular	33–46	Cluster	UV–vis spectroscopy, SEM	Antimicrobial activity against <i>Staphylococcus aureus</i> , <i>Vibrio parahaemolyticus</i> , <i>E. coli</i> , <i>S. putrefaciens</i> and fungal pathogen <i>Candida albicans</i>	[41]
<i>Trichoderma viride</i>	Ag NPs	Extracellular	5–40	Spherical	UV–vis spectroscopy, FTIR, EDS, XPS, TEM	Antimicrobial activity against <i>E. coli</i> , <i>S. typhi</i> , <i>S. aureus</i> , and <i>M. luteus</i>	[52]
<i>Acutodesmus dimorphus</i>	Ag NPs	Extracellular	2–20	Spherical, poly dispersed	UV–vis spectroscopy, FTIR, AFM, SEM, TEM,	Antioxidant activity by DPPH and ABTS assays	[58]
<i>Amphiroa rigida</i>	Ag NPs	Extracellular	~25	Spherical	UV–vis spectroscopy, XRD, FTIR, TEM, SEM, EDX	Anti-larval activity against <i>A. aegypti</i> Cytotoxic activity against breast cancer cells	[59]
<i>Amphora-46</i>	Ag NPs	Extracellular	20–25	Polycrystalline spherical	UV–vis spectroscopy, FTIR, SAED, EDAX, TEM	Antimicrobial activity against <i>E. coli</i> , <i>B. steartothermophilus</i> , <i>S. mutans</i>	[25]
<i>Chlorella pyrenoidosa</i>	Ag NPs	Extracellular	5–20	Crystalline	UV–vis spectroscopy, FTIR, XRD, EDX, TEM	Antibacterial activity against <i>Klebsiella pneumoniae</i> , <i>A. hydrophila</i> , <i>Acinetobacter</i> and <i>S. aureus</i> Photocatalytic reduction of MB	[60]
<i>Chlorella vulgaris</i>	Au NPs	Intracellular	40–60	Spheroid, polyhedral	UV–vis spectroscopy, FTIR, XRD, SEM, TEM	For the large-scale synthesis of Pd, Ru and Rh nanoparticles using <i>C. vulgaris</i> cells	[61]
<i>Chlorococcum humicola</i>	Ag NPs	Intracellular and extracellular	4–16	Crystalline	UV–vis spectroscopy, FTIR, XRD, SEM, TEM	Antibacterial activity against <i>E. Coli</i>	[62]
<i>Chlorococcum infusionum</i>	Ag NPs	Extracellular	2–7	Spherical	UV–vis spectroscopy, FTIR, XRD, SEM, TEM	–	[63]
<i>Chondrus crispus</i>	Au NPs	Extracellular	30–50	Spherical	UV–vis spectroscopy, FTIR, EDS, SEM, TEM	–	[23]
<i>Ecklonia cava</i>	Ag NPs	Extracellular	~43	Spherical	UV–vis spectroscopy, FTIR, TGA, XRD, TEM	Antibacterial activity Antioxidant activity Anticancer cancer	[64]
<i>Enteromorpha compressa</i>	Ag NPs	Extracellular	4–24	Spherical	UV–vis spectroscopy, XRD, FTIR, HRTEM, SAED pattern EDX.	Antifungal potential against <i>A. flavus</i> , <i>A. niger</i> , <i>A. ochraceus</i> , <i>A. terreus</i> , <i>F. moniliforme</i> Antibacterial activity against <i>E. coli</i> , <i>S. aureus</i> , <i>K. pneumoniae</i> , <i>Pseudomonas</i> , <i>S. paratyphi</i>	[65, 66]

Table 1: (continued)

Biogenic source	NPs	Site of formation	Size (nm)	Shape/nature	Characterization	Applications	Reference
<i>Cladophora glomerata</i>	Ag NPs	Extracellular	8–11	Spherical	XRD, FTIR, TEM, UV–vis spectroscopy	Anticancer activity against colon cancer cells	[67]
<i>Galaxaura elongate</i>	Au NPs	Extracellular	8–77.1	Mostly spherical	FTIR, TEM, UV vis spectroscopy,	Antimicrobial activity against <i>S. aureus</i> , <i>E. coli</i> , <i>K. pneumonia</i> , <i>P. aeruginosa</i>	[68]
<i>Gelidiella acerosa</i>	Ag NPs	Extracellular	~22	Spherical	UV–vis spectroscopy, XRD, SEM, TEM	Antifungal activity against <i>Humicola insolens</i> , <i>Fusarium dimerum</i> , <i>Mucor indicus</i> , <i>Trichoderma reesei</i>	[69]
<i>Halymenia dilate</i>	Au NPs	Extracellular	~16	Triangular, spherical	UV–vis spectroscopy, XRD, FTIR, EDAX, FESEM	Antioxidant activity Antibacterial activity Anticancer activity Cytotoxicity potential	[70]
<i>Laurencia catarinensis</i>	Ag NPs	Extracellular	39.4–77.7	Spherical, triangular, rectangular, polyhedral, hexagonal	UV–vis spectroscopy, FTIR, DLS, TEM	–	[71]
<i>Nannochloropsis species</i>	Ag NPs	Extracellular	38–137	Crystalline	FTIR, DLS, TEM, EDX, GCMS	Antibacterial activity against <i>P. aeruginosa</i> , <i>E. coli</i> , <i>S. aureus</i> and <i>B. subtilis</i> Cytotoxic potential Antioxidant activity	[72]
<i>Padina pavonia</i>	Ag NPs	Extracellular	49.5–86.3	Spherical, triangular, rectangular	FTIR, DLS, TEM, UV–vis spectroscopy	–	[73]
<i>Saccharina cichorioides</i>	Ag NPs	Extracellular	~54	Spherical	FTIR, XRD, TEM, UV–vis spectroscopy	Antibacterial activity against <i>Escherichia coli</i> and <i>Agrobacterium tumefaciens</i>	[74]
<i>Sargassum tenerrimum</i>	Au NPs	Extracellular	27–35	Spherical	FTIR, DLS, TEM, UV–vis spectroscopy	Catalytic reduction of 4-NP, Rh B, Sulforhodamine	[75]
<i>Scenedesmus abundans</i>	Ag NPs	Extracellular	59–66	Polydisperse	DLS, UV–vis spectroscopy, SEM	Antibacterial activity against <i>E. coli</i> , <i>K. pneumoniae</i> , <i>A. hydrophila</i>	[76]
<i>Spirulina platensis</i>	Au NPs	Intracellular	15–60	Spherical	TEM, SEM, FTIR, XRD, UV–vis spectroscopy, EDAX	–	[77]
<i>Synechococcus elongates</i>	Ag NPs	Intracellular	7–12	Cubic	TEM, XRD, FTIR, UV–vis spectroscopy	Bactericidal and algicidal studies against <i>A. hydrophila</i> , <i>V. parahaemolyticus</i> , <i>E. tarda</i>	[78]
<i>Turbinaria conoides</i>	Au NPs	Extracellular	27–35	Spherical	FTIR, TEM, UV–vis spectroscopy, DLS	Catalytic reduction of 4-NP, Rh B, sulforhodamine	[75]
<i>Anabaena doliolum</i>	Ag NPs	Extracellular	10–50	Spherical	XRD, TEM, UV–vis spectroscopy, FTIR	Antibacterial activity against <i>K. pneumoniae</i> , <i>E. coli</i> , <i>S. aureus</i> Antioxidant activity	[79]
<i>Anabaena sphaerica</i>	Ag NPs	Intracellular	2–7	Spherical	XRD, TEM, UV–vis spectroscopy, FTIR	–	[63]
<i>Cyanobacterial species</i>	Ag NPs	Extracellular	13–31	Irregular	SEM, TEM, UV–vis spectroscopy, EDS	Antibacterial activity against specie of <i>Anabaena</i> , <i>Lyngbya</i> , <i>Synechococcus</i> , <i>Synechocystis</i> , <i>Cylindrospermopsis</i>	[80]
<i>Enterobacter aerogenes</i>	Ag NPs	Extracellular	25–35	Spherical	EDX, TEM, UV–vis spectroscopy, SEM	–	[81]
<i>Escherichia coli</i>	Au NPs	Extracellular	~50	Spherical	XRD, TEM, UV–vis spectroscopy, AFM, FTIR,	Catalytic reduction of 4-NP	[82]
<i>Klebsiella pneumonia</i>	Ag NPs	Extracellular	15–37	Spherical	XRD, TEM, UV–vis spectroscopy, FTIR	Bactericidal activity against <i>S. enterica</i> , <i>E. coli</i> , <i>S. pyogenes</i> .	[83]

Table 1: (continued)

Biogenic source	NPs	Site of formation	Size (nm)	Shape/nature	Characterization	Applications	Reference
<i>Leptolyngbya WUC 59</i>	Ag NPs	Extracellular	20–35	Spherical	XRD, TEM, UV–vis spectroscopy, FTIR, EDS	Antibacterial activity against <i>B. subtilis</i> , <i>E. coli</i> Impact on seed germination and early seed growth	[20–22]
<i>Nostoc commune</i>	Ag NPs	Extracellular	15–54	Mostly spherical	TEM, FTIR, UV–vis spectroscopy,	Antibacterial properties against <i>E. coli</i> Excellent sterilizing agent against fungi Effect on seed germination	[84]
<i>Oscillatoria limnetica</i>	Ag NPs	Extracellular	3.3–17.9	Quasi-spherical	SEM, TEM, UV–vis spectroscopy, FTIR	Antibacterial activity against <i>Escherichia coli</i> and <i>Bacillus cereus</i> cytotoxic effects against human breast (MCF-7) cell and colon cancer cell	[85]
<i>Pseudomonas aeruginosa</i>	Ag NPs	Intracellular	5–25	Quasi-spherical	XRD, TEM, UV–vis spectroscopy, FTIR	–	[86]
<i>Pseudomonas aeruginosa</i>	Ag NPs	Extracellular	45–100	Spherical	XRD, TEM, UV–vis spectroscopy, FTIR, SEM, EDX	Algicidal effect against <i>Chlorella vulgaris</i> and <i>Chlorella pyrenoidosa</i>	[87]
<i>Rhodobacter sphaeroides</i>	Ag NPs	Extracellular	9.2–9.8	Spherical	SAED, XRD, TEM, UV–vis spectroscopy	–	[88]
<i>Acalypha indica</i>	Ag NPs	Extracellular	20–30	Crystalline	XRD, SEM, UV–vis spectroscopy, EDS, FTIR	Antimicrobial activity against <i>Escherichia coli</i> and <i>Vibrio cholerae</i> .	[89]
<i>Acorus calamus</i>	Au NPs	Extracellular	~10	Spherical	XRD, TEM, UV–vis spectroscopy, FTIR, SEM, EDAX	Antibacterial activity against <i>Staphylococcus aureus</i> and <i>Escherichia coli</i>	[90]
<i>Aerva lanata</i>	Ag NPs	Extracellular	10–34	Crystalline	XRD, TEM, UV–vis spectroscopy, FTIR	Chemical reduction of 4-NP	[31]
<i>Aerva lanata</i>	Au NPs	Extracellular	10–30	Polycrystalline	XRD, TEM, UV–vis spectroscopy, FTIR	Chemical reduction of 4-NP	[31]
<i>Allium cepa</i>	Ag NPs	Extracellular	~33.67	Spherical	DLS TEM, UV–vis spectroscopy,	Antibacterial activity against <i>E. coli</i> and <i>Salmonella typhimurium</i>	[91]
<i>Allium sativum</i>	Ag NPs	Extracellular	2.9–11.7	Spherical	XRD, TEM, UV–vis spectroscopy, FTIR	Antibacterial activity against <i>S. aureus</i> and <i>P. aeruginosa</i>	[92]
<i>Alpinia nigra</i>	Au NPs	Extracellular	20–60	Hexagonal	XRD, TEM, UV–vis spectroscopy, FTIR	Photochemical reduction of MO and RhB Antibacterial potential against <i>Bacillus subtilis</i> , <i>E. coli</i> and <i>Candida albicans</i>	[93]
<i>Andrographis echinoides</i>	Ag NPs	Extracellular	~48.6	Spherical, cubic	XRD, TEM, UV–vis spectroscopy, FTIR, EDX, AFM, SEM	Anticancer activity against adenocarcinoma cancer cell Antibacterial activity against <i>Escherichia coli</i> and <i>Staphylococcus aureus</i>	[94]
<i>Andrographis paniculata</i>	Ag NPs	Extracellular	35–55	Spherical	XRD, TEM, UV–vis spectroscopy, SEM	The antiparasitic activity against <i>Plasmodium falciparum</i>	[95]
<i>Annona muricata</i>	Ag NPs	Extracellular	20–53	Spherical	XRD, TEM, UV–vis spectroscopy, FTIR, SEM, EDX	Larvicidal activity against <i>Aedes aegypti</i> , <i>Anopheles stephensi</i> , and <i>Culex quinquefasciatus</i>	[96]
<i>Argemone mexicana</i>	Ag NPs	Extracellular	25–50	Cubic	XRD, TEM, UV–vis spectroscopy, FTIR	Antifungal activity against <i>Aspergillus flavus</i> Antibacterial activity against <i>Escherichia coli</i> and <i>Pseudomonas aeruginosa</i>	[97]

Table 1: (continued)

Biogenic source	NPs	Site of formation	Size (nm)	Shape/nature	Characterization	Applications	Reference
<i>Artemisia nilagirica</i>	Ag NPs	Extracellular	70–90	Crystalline	XRD, TEM, SEM, EDX, FTIR, UV–vis spectroscopy	Antimicrobial activity against <i>Staphylococcus aureus</i> , <i>Bacillus subtilis</i> , <i>Escherichia coli</i> , and <i>Proteus subtilis</i>	[98]
<i>Artocarpus heterophyllus</i>	Ag NPs	Extracellular	3–25	Irregular shape	SAED, EDAX, XRD, TEM, UV–vis spectroscopy, FTIR	Antibacterial activity against <i>Bacillus cereus</i> , <i>Bacillus subtilis</i> , <i>Staphylococcus aureus</i> , <i>Pseudomonas aeruginosa</i>	[99]
<i>Averrhoa carambola</i>	Ag NPs	Extracellular	~14	Spherical	DLS, XRD, TEM, UV–vis spectroscopy, FTIR	–	[100]
<i>Boswellia ovalifoliolata</i>	Ag NPs	Extracellular	30–40	Spherical	EDAX, SEM, UV–vis spectroscopy	–	[101]
<i>Boswellia serrata</i>	Ag NPs	Extracellular	3.7–11.3	Quasi spherical	XRD, TEM, UV–vis spectroscopy, FTIR	Antibacterial activity against <i>Staphylococcus aureus</i> , and <i>Escherichia coli</i> and <i>Pseudomonas aeruginosa</i>	[102]
<i>Butea monosperma</i>	Ag NPs	Extracellular	18–50	Spherical	SAED, DLS, XRD, TEM, UV–vis spectroscopy, FTIR	Cytotoxic effect on human myeloid leukemia cell line Antibacterial activity against <i>Bacillus subtilis</i> , <i>Escherichia coli</i>	[103]
<i>Calotropis gigantean</i>	Ag NPs	Extracellular	5–30	Spherical	EDAX, SEM, XRD, TEM, UV–vis spectroscopy, FTIR	Antimicrobial potential against <i>B. cereus</i> , <i>Enterococci</i> , <i>Shigella</i> , <i>P. aeruginosa</i> , <i>K. pneumonia</i> , <i>S. aureus</i> and <i>E. coli</i> Cytotoxicity against Hela cells.	[104]
<i>Camellia sinensis</i>	Ag NPs	Extracellular	2.3–5.5	Spherical	TGA, AFM, XPS, XRD, TEM, UV–vis spectroscopy, FTIR	Antibacterial activity against <i>S. aureus</i> , <i>P. aeruginosa</i> , <i>K. pneumoniae</i> , <i>E. coli</i> , <i>S. enterica</i> ,	[105]
<i>Catharanthus roseus</i>	Ag NPs	Extracellular	48–67	Spherical	XRD, TEM, UV–vis spectroscopy, FTIR	Antibacterial activity against <i>B. cereus</i> , <i>S. aureus</i> , <i>E. coli</i> , <i>K. pneumoniae</i> , <i>P. aeruginosa</i>	[106]
<i>Cissus quadrangularis</i>	Ag NPs	Extracellular	15–23	Spherical	XRD, TEM, UV–vis spectroscopy, FTIR	Antibacterial activity against <i>S. pyogenes</i> , <i>S. aureus</i> , <i>E. coli</i> , <i>P. vulgaris</i>	[107]
<i>Cola nitida</i>	Ag NPs	Extracellular	12–80	Spherical	XRD, TEM, UV–vis spectroscopy, FTIR	Antioxidant activity Antimicrobial activity against <i>S. aureus</i> , <i>K. granulomatis</i> , <i>P. aeruginosa</i> , <i>E. coli</i> , <i>Aspergillus niger</i> , <i>A. flavus</i> , <i>A. fumigatus</i>	[108]
<i>Cola nitida</i>	Ag NPs	Extracellular	8–50	Spherical	SAED, EDX, XRD, TEM, UV–vis spectroscopy, FTIR	Antimicrobial activity against <i>K. granulomatis</i> , <i>P. aeruginosa</i> , <i>E. coli</i>	[109, 110]
<i>Cucurbita pepo</i>	Au NPs	Extracellular	1–100	Polydisperse	SEM, EDS, XRD, TEM, UV–vis spectroscopy, FTIR	Antibacterial activity against <i>Escherichia coli</i> and <i>Listeria monocytogenes</i>	[111]
<i>Gongronema latifolium</i>	Ag NPs	Extracellular	14–20	Spherical	SEM, EDX, XRD, TEM, UV–vis spectroscopy, FTIR	Antibacterial activity against <i>E. coli</i> , <i>S. aureus</i> , <i>coliform</i>	[4, 5]
<i>Helicteres isora</i>	Ag NPs	Extracellular	16–95	Spherical	XRD, TEM, UV–vis spectroscopy, FTIR, DLS, SAED	Antioxidant activity Antibacterial activity against <i>S. typhi</i> and <i>P. aeruginosa</i> , <i>B. subtilis</i> and <i>M. luteus</i>	[112]
<i>Indoneesiella echioides</i>	Ag NPs	Extracellular	~29	Spherical	XRD, TEM, UV–vis spectroscopy, FTIR	Antioxidant activity Cytotoxicity against lung adenocarcinoma cancer cells	[113]

Table 1: (continued)

Biogenic source	NPs	Site of formation	Size (nm)	Shape/nature	Characterization	Applications	Reference
<i>Moringa oleifera</i>	Ag NPs	Extracellular	11–14.3	Rod shaped	XRD, TEM, UV–vis spectroscopy, FTIR	Antimicrobial activity against <i>Coliform</i> , <i>Staphylococcus aureus</i> , <i>Escherichia coli</i>	[4, 5]
<i>Phyllanthus emblica</i>	Ag NPs	Extracellular	19.8–92.8	Spherical	EDS, XRD, TEM, UV–vis spectroscopy, FTIR	Antibacterial activity against <i>Acidovorax oryzae</i>	[114]
<i>Stevia rebaudiana</i>	Ag NPs	Extracellular	80–200	Rod shaped	XRD, EDX, SEM, UV–vis spectroscopy, FTIR	–	[115]
<i>Terminalia arjuna</i>	Au NPs	Extracellular	20–50	Spherical triangular cubic crystal	SEM, DLS, EDX, XRD, TEM, UV–vis spectroscopy, FTIR	Antioxidant activity Cytotoxic potential	[116]
<i>Theobroma cacao</i>	Ag NPs	Extracellular	6–18	Spherical	XRD, TEM, UV–vis spectroscopy, FTIR	Photochemical reduction of MB Antibacterial activity against <i>E. coli</i> and <i>B. subtilis</i>	[30]

analyzing the biomolecules responsible for the reducing properties, they also observed that the present polysaccharides are responsible for reducing the Ag^+ ions to silver atoms and further formation of the stabilized Ag NPs. Moreover, they also examined the antibacterial activity of Ag NPs against different bacterial pathogens such as *Staphylococcus aureus* (21 ± 0.2 mm) and *Pseudomonas aeruginosa* (15 ± 0.2 mm) and found them effective candidates for the treatment of different pathogens.

Many other researchers also reported the synthesis of AuNPs by using algal extract as reducing/stabilizing agent and evaluated their role as antioxidant, anti-cancer and anti-bacterial activities [70, 121, 125]. Diagrammatic representation of preparation of MNPs by using algal extract as reducing/stabilizing source is shown in Figure 1b.

2.3 Bacterial extract mediated synthesis of metal nanoparticles

Utilization of bacteria for NPs synthesis is highly favored over other microbes due to the favorable conditions they require, the ease of purification, and their ability to yield high quantities of NPs [128]. Bacteria are one of the extensively investigated microorganism for the biogenic synthesis of NPs. For this reason, they are often referred as the “nanomaterial factories” [129]. Bacteria possess great ability to reduce heavy metal ions into metal atoms [130]. Different types of bacteria have been reported as reducing and stabilizing agent for the preparation of different MNPs such as Au, Ag, Pt, TiO_2 , ZnO and Fe_2O_3 NPs etc. [65, 66, 131–134]. MNPs can be synthesized by using bacterial intracellular (using biomass) and extracellular (using cell extracts) matrix [135]. Synthesis of MNPs via bacteria by two mechanisms

such as extracellular and intracellular approaches are shown in Figure 2. Extracellular synthesis offers several advantages over the intracellular approach. It is less time-consuming as it eliminates the need for downstream processes for the collection of NPs from the bacteria. Additionally, extracellular synthesis also facilitates the easier scalability, higher purity of the NPs, enhanced stability, and lower potential cytotoxicity [20–22]. These advantages make the extracellular method a favorable and practical choice for the preparation of bacteria-assisted nanoparticles with versatile properties.

Bacteria possess the nitrate dependent reductase enzymes which induces the reduction of metal ions into metal atoms that coagulate to form MNPs. When AgNO_3 salt is added in cyanobacteria as a source of Ag^+ ions, the functional groups like amino, carboxyl group or sulfate groups present in the bacterial protein are used to reduce silver ions into silver atoms. These reduced atoms then coagulate to produce Ag NPs which are then stabilized by the similar functional moieties of amino acids [136].

Bio-reduction of silver ions into silver atoms by *P. aeruginosa* extract due to metabolite pyoverdine was found a time-dependent process and gained maximum speed after 24 h as reported by Kumari et al. [87]. The pyoverdine is a green pigment that possess carboxylic and amide free groups for the reduction of metal ions into metal atoms.

Shivaji and coworkers [137] used five varieties of psychrophilic bacteria such as *Pseudomonas antarctica*, *Pseudomonas proteolytica*, *Pseudomonas meridiana*, *Arthrobacter kerguelensis* and two varieties of mesophilic bacteria such as *Bacillus indicus* and *Bacillus cecembensis* for the synthesis of Ag NPs. They found that Ag NPs were stable in dark for 8 months with the size found in range of 6–13 nm. However, when these NPs were stored in the presence of light, their life

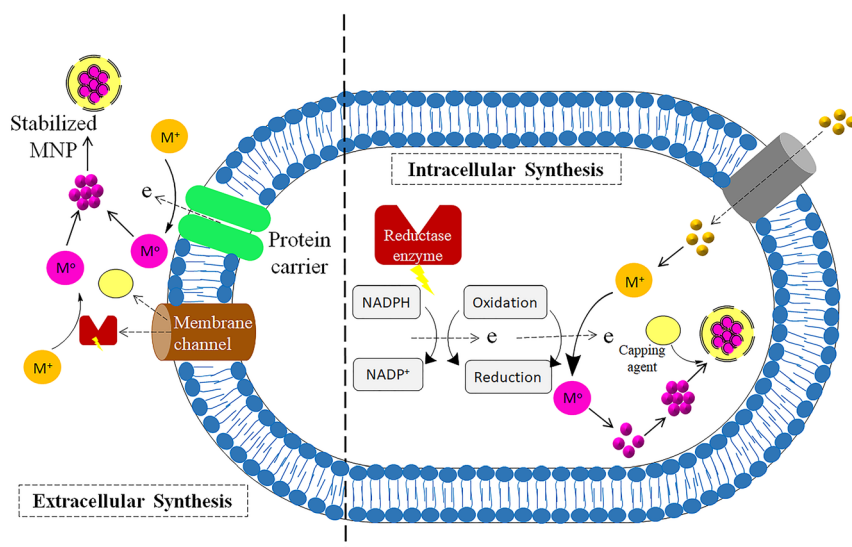


Figure 2: Mechanism of intracellular and extracellular synthesis of nanoparticles by bacteria.

span was decreased. It was also investigated that Ag NPs synthesized by using culture medium were found relatively less stable irrespective of either prepared by incubation in the light or in the dark. Marine bacterial strain of *Marinobacter pelagius* for the rapid synthesis of Ag NPs with a smaller size around 2–6 nm has also been reported by Sharma et al. [138]. *Escherichia coli* extract is reported for the reduction of Au^{2+} ions into Au^0 from the $HAuCl_4$ solution resulting in the formation of Au NPs by Srivastava et al. [82]. These Au NPs were found very effective for the complete reduction of 4-nitrophenol (4-NP) into 4-aminophenol (4-AP) in the presence $NaBH_4$. These heterogeneous catalysts are proved to be efficient for the complete reduction of nitro-aromatic compounds present in polluted wastewater into less toxic substances.

Growth of AuNPs in presence of variety of bacteria has also been reported by different researchers [109, 110, 139]. Diagrammatic representation of MNPs fabrication by using bacterial extract is shown in Figure 1c.

2.4 Plant extracts mediated synthesis of metal nanoparticles

Plants are the source of different natural reducing and capping agents such as phytochemicals with different functional groups such as hydroxyl, amine and carboxyl groups [89]. These groups act as reducing agent and convert metal ions into metal atoms that coagulate to form MNPs [96]. Researchers reported the use of extract of different plants as reducing and stabilizing source for the biogenic synthesis of different types of MNPs [114, 116, 140]. Extract of different parts of plants such as stem, root, fruit, seed, peel, leaves, bulb, gum, husk, pod, rhizomes, cloves, bark and flowers

have been reported to be used as a potential reducing and stabilizing agent [93, 99, 101, 114]. It has also been investigated that MNPs were fabricated in both extracellular and intracellular environment, especially within the epidermal cell walls, xylem cell walls, cell membrane and vacuoles during the biogenic synthesis while using plant extract as source of reducing and stabilizing agent [4, 5, 105, 141]. However, vacuoles were found to be less efficient stabilizing agent as compared to the other reported components and leads to the aggregation of NPs and lost their surface properties [142]. On contrary to that, different cell organelles such as extracted chloroplast [106], extracted thylakoids [63], and phytochemicals like phenols [95, 104] and flavonoids [93] were found significantly responsible for anti-agglomeration of MNPs. It was also investigated that phenolic functional groups act as a cage and prevent the aggregation of NPs to prolong their life span [93]. Bhakya et al. [112] reported *Helicteres isora* extract mediated synthesis of Ag NPs and depicted the plausible reduction mechanism of Ag^+ ions into Ag NPs. The primary bioactive constituent within the biogenic extract responsible for this reduction was identified as sapogenin, categorized as a triterpene compound. The hydroxyl and carboxyl groups of sapogenin entrapped the Ag^+ ions resulting in the formation of intermediate complex. The carboxyl or hydroxyl group then reduces to COOH form ultimately resulting in the reduction of Ag^+ ions into Ag NPs.

Microbe-interceded synthesis of metal nanoparticles require maintenance of sterile conditions and highly complex reaction [115]. Yet, plant extract supported synthesis of metal nanoparticles is usually carried out at normal and easily attainable reaction conditions [90, 99, 143]. The utilization of plants for the synthesis of NPs has also proved to be more effective in terms of achieving higher yield as

compared to microbes induced synthesis of MNPs, easy availability different parts of variety of plants [92, 100, 144]. Furthermore, plant-assisted synthesis of NPs surpasses the microorganism-based synthesis in several aspects such as easy scalability, reduced biohazards, economic feasibility, readily available plant sources, and simplified process of maintaining cell cultures [97, 98, 103]. All these factors contribute to the overall superiority of plants mediated NP synthesis making it a preferred choice in various applications [4, 5, 101, 145]. Conclusively, plant extracts induced NPs preparation have got a lot of attention.

Raj et al. [146] reported the synthesis of Ag NPs by using *Terminalia arjuna* leaf extract. They mixed 1.0 mM aqueous solution of AgNO_3 with 1% w/v solution of the leaf extract. Continuous stirring turned the solution reddish-brown which highlighted the successful synthesis of Ag NPs. TEM and FE-SEM analysis showed that these synthesized Ag NPs were spherical in shape and diameter was found in range of 10–50 nm. These biogenic synthesized Ag NPs were employed as nano-catalyst for the reduction of hazardous dye methylene blue (MB) into environmentally friendly products. Different other researchers also reported the plant extract reinforced synthesis of Ag and AuNPs and investigated their use in the field of catalysis and biomedical applications [93, 147]. Diagrammatic representation for the synthesis of Ag NPs while using *Azadirachta indica* plant extract as source of reducing and stabilizing agent is shown in Figure 3.

3 Purification of biogenic nanoparticles

Purification of metal nanoparticles is very important step before their use in various applications. Their potential activity can be effected/reduced due to the presence of

impurities in form of un-utilized metal ions and plant's contents. In this regard, centrifugation and dialysis can be performed [148–150]. Centrifugation has been adopted as a commonly used method for MNP purification as short period of time required for purification purpose, ease of operation and effective purification [151]. Thus, separation and purification of biologically produced NPs are achieved through repetitive washing and high-speed centrifugation. Thus, centrifugation can effectively eliminate any unreacted bioactive molecules, enhances the purity and quality of the NPs to ensure their optimal performance as well as to get similar size particles and alternatively to attain more efficiency. However, this method has certain limitations such as potential agglomeration of nanoparticles during the centrifugation process that lead to the formation of larger clusters having decreased efficiency in different applications [20–22].

Additionally, centrifugation can also cause destabilization of nanoparticles by detaching the surface capping agents involved in the stabilizing the nanoparticles. This detachment can further reduce the intrinsic properties and behavior of the nanoparticles. Hence, an alternative method is required to overcome these limitations and ensures the integrity of the synthesized nanoparticles. An alternative and relatively simple method of nanoparticle purification is dialysis which involves the use of a selectively permeable membrane with an appropriate size selected according to the size of the purified sample particles. This method allows the small organic molecules present in the biogenic extract as well as un-reacted metal ions to pass through the dialysis membrane while retaining the organic molecules that are conjugated with NPs and serving as surface capping agents. However, it is important to note that this purification method is time-consuming requiring more than 24 h or more time for complete purification [20–22]. On the other hand, diafiltration is not a commonly utilized technique for the purification of bio-fabricated nanoparticles because biogenic MNPs often exhibit a wide range of sizes and shapes. Contrary to this, diafiltration involves the use of a membrane of definite pore size which may not effectively separate particles based on their size and shape. Moreover, NPs may interact with the membrane and get adsorb on membrane surface resulting in decreased efficiency of purification process due to loss of NPs [152]. In the case of magnetic nanoparticles such as Fe_2O_3 and Fe_3O_4 , they can easily be separated by applying an external magnetic force [26, 153]. Alternatively, centrifugation, ultrafiltration, and density gradient centrifugation are usually preferred methods for the purification of biogenic metal nanoparticles because they offer selective separation based on size and shape, less interaction of NPs with membranes, and can be more easily scaled up for large-scale production [154]. Nevertheless, the effective removal of tightly bound

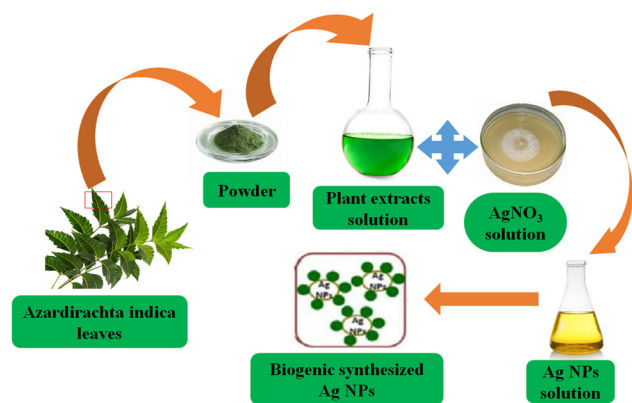


Figure 3: Biogenic synthesis of Ag NPs from *Azadirachta indica* leaves extract.

biomolecules from the surface of nanoparticles is still a challenge in the purification process.

4 Applications

4.1 Antibacterial activity

The emergence of bacterial resistance toward conventional antibiotics has raised the significant concerns in the treatment of bacterial infections [155]. Misuse and overuse of antibiotics is one among the major factors that has accelerated the development of antibiotic resistance in bacterial strains. Consequently, there is an urgent need for the development of novel and potent bactericidal agents. In modern era of nanotechnology, MNPs have emerged as a promising alternative to the antibiotics and have exhibited excellent antibacterial activity against a wide variety of bacterial species [156]. These NPs interact with the vital cellular organelles and biomolecules such as DNA, enzymes, ribosomes, and lysosomes and affect the cell membrane permeability, oxidative stress, gene expression, protein activation, and enzyme activity [157]. Due to their multi-targeted approach, it becomes difficult for bacteria to develop resistance against MNPs [158]. Interestingly, MNPs have shown antibacterial activity against both type of bacteria like gram positive and gram-negative bacteria. It was also investigated that Ag NPs demonstrated higher antibacterial activity against gram-negative bacteria including *Klebsiella* species and *Pseudomonas* species as well as gram-positive bacteria including *Staphylococcus* and *Bacillus* species when compared with the activity of Au NPs and Pt NPs [159]. High antibacterial activity of Ag NPs against gram-negative bacteria is mainly due to the presence of thin layer of peptidoglycan in their cell wall which is more easily ruptured by the NPs as compared to the gram-positive bacteria [81]. Ag NPs have also been utilized in a wide range of antibacterial applications such as wound treatment

[160], against clinical isolation [161], nosocomial pathogens [162], and food pathogens [163]. Although the mechanisms underlying the antibacterial activity of MNPs have not been fully interpreted but several hypothetical mechanisms have been proposed [164]. Few of them are following

- (i) One proposed mechanism is that MNPs are absorbed by bacterial cells causing disruption to ATP and DNA replication leading to bacterial cell death.
- (ii) Another hypothetical mechanism is the generation of reactive oxygen species (ROS) by metal nanoparticles and metal ions which leads to the oxidative destruction of cellular structures and ultimately bacterial cell death.
- (iii) A third proposed mechanism is the accumulation of MNPs in the bacterial membrane leading to changes in membrane penetration and release of lipopolysaccharides, membrane proteins, and intracellular factors eventually resulting in bacterial cell death [165].

The proposed mechanism of bacterial cell death induced by Ag NPs involves the generation and attack of ROS. Molecular oxygen captures electrons to produce superoxide anions, which react with H_2O_2 to generate hydroxyl radicals ($\cdot OH$). Electrons are then absorbed from water and hydroxyl ions to cause mineralization of the bacterial cell. ROS production is a critical and dominant factor in inducing cell death as it leads to oxidative stress resulting in the rupture of cell membranes, protein deactivation or denaturation, disrupted electron transport chains, DNA and mitochondrial damage, and ultimately cell death [166] as shown in Figure 4. Moreover, the interaction of metal NPs with thiol groups leads to the accumulation of ROS that inhibits the activity of respiratory enzymes and ultimately results in the death of the cell.

Sometimes, silver ions seep into the extracellular matrix from the surface of MNPs and interact with the peptidoglycan present in the cell wall and plasma membrane. It

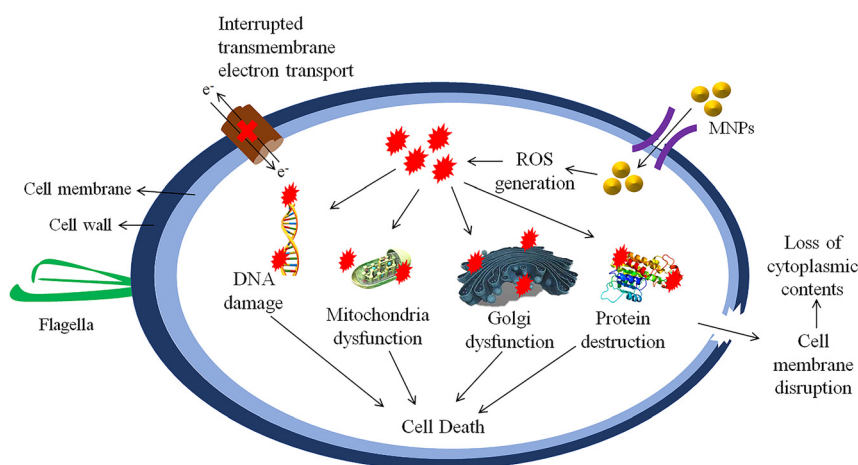


Figure 4: Proposed mechanism of bacterial cell lysis by metal nanoparticles.

induces the disruption in the cell wall structure, leads to malfunctioning and alternative death of the cell [167]. It also interacts with sulfhydryl groups present in the protein and induces the prevention of bacterial DNA replication [168].

Antibacterial activity of MNPs also depends upon their morphology, shape and stability. It also depends upon the dosage of particles, methodology used for treatment purpose and treatment time [169]. Thus, by tuning the size, shape and morphology of MNPs, their antibacterial potential can also be tuned. Despite of high antibacterial potential of MNPs, their toxicity has been a significant concern among researchers in their use in biomedical field [170]. Therefore, agglomerated particles having size larger than 100 nm are considered to have fewer side effects. These concerns highlight the significance to address the potential toxicity of MNPs when considering their use in the biomedical field. In our opinion, biogenically synthesized MNPs are necessary evil as they are prepared for the remediation of toxic substances yet their usage comes with the toxicity issues as well.

Nayak et al. [171] prepared Ag NPs by using *Jatropha curcas* seed cake extract as biogenic reductant and stabilizer. Appearance of brown color in the suspension indicated the successful fabrication of Ag NPs which were further characterized by UV-vis, SEM, XRD, and FTIR analysis. Successful fabrication of NPs was confirmed by appearance of SPR peak at 437 nm in UV-vis spectra as well as change of color of suspension from light yellow to brown. SEM analysis predicted that NPs were monodispersed with size found in range of 80–95 nm. XRD analysis confirmed the crystalline nature of Ag NPs. They illustrated that FTIR analysis showed the reduction in intensity value of band associated with primary amine in case of fabricated NPs as compared to the extract. It also represents that amine groups are involved in reduction of metal ions into metal atoms. The antibacterial activity of these NPs was assessed against gram-negative bacteria such as *E. coli* and *P. aeruginosa* and gram-positive bacteria such as *Bacillus subtilis*. It was observed that in an aqueous solution Ag NPs released silver ions (Ag^+). When, these Ag^+ ions come in contact with the outer membrane of both gram-negative and gram-positive bacteria, they lead to the formation of pores in the membrane and enters the bacterial cell. Subsequently, the presence of these Ag^+ ions inside the bacterial cell resulted in growth inhibition and bactericidal activity against the targeted bacteria. It was also observed that gram-negative bacteria were more adversely affected as compared to gram-positive bacteria under similar conditions due to thick layered cell wall.

Bose and Chatterjee [172] reported the preparation of Ag NPs utilizing the *Psidium guajava* (guava) leaf extract as reducing and stabilizing agent. Guava was selected due to its medicinal properties and easy availability in all seasons. The change in the color of the suspension from light yellow to

reddish brown color indicated the fabrication of Ag NPs. They also observed that Ag NPs exhibited significant antibacterial activity against *P. aeruginosa* which is a known human pathogen. The Ag NPs synthesized through agar biogenic methods demonstrated great efficiency in inhibiting the growth of the bacteria as evident by an average zone of inhibition (ZoI) ranging from 2.26 to 2.40 cm.

Different other researchers reported the preparation of biogenic nanoparticles of different metals and discovered their antibacterial properties against different bacterial strains [173–178].

4.2 Anticancer activity

Cancer is the major cause of mortality in the world among the noninfectious diseases [179]. MNPs have shown potential in cancer diagnosis and treatment due to their unique physical and chemical properties [157]. These particles can be functionalized with targeting ligands to selectively accumulate in cancer cells and tissues, enabling early detection and imaging. However, the biocompatibility and toxicity of MNPs need to be carefully evaluated to ensure their safe use in cancer therapy [180].

In cancer treatment, alkylating agents and antimetabolites are commonly used which have many side effects [181]. Therefore, they are known as systemic toxicities. Hence, non-toxic or less toxic agents are essential for cancer treatment [182]. MNPs have unique physiochemical properties that are known as intrinsic antitumor effects. These unique properties of NPs can facilitate their anti-cancer activity either through their intrinsic properties such as antioxidant action or through external stimuli such as infrared rays or magnetic fields. The external stimuli can generate ROS that induces cancer cell death. Additionally, NPs can interfere with the development of tumor masses by interacting with the tumor microenvironment such as blood vessels or stroma [183]. It has also been reported that biogenic synthesized ZnO NPs are used *in situ* production of ROS. ROS is a nonpolar molecule and can easily diffuse into the cancer cell. Alternatively, intracellular materials are slowly oxidized due to the presence of ROS in the cell. Upon increasing the concentration of ZnO NPs in the intracellular environment of cancerous cells, a significant increase in oxidative stress is observed which leads to the permanent damage of cellular components such as lipids, proteins, and nucleic acids. Specifically, lipid peroxidation and protein denaturation occur causing membrane damage. Consequently, this membrane damage leads to DNA damage within the cell. These damages cumulatively result in the programmed cell death mechanism called apoptosis [184–186].

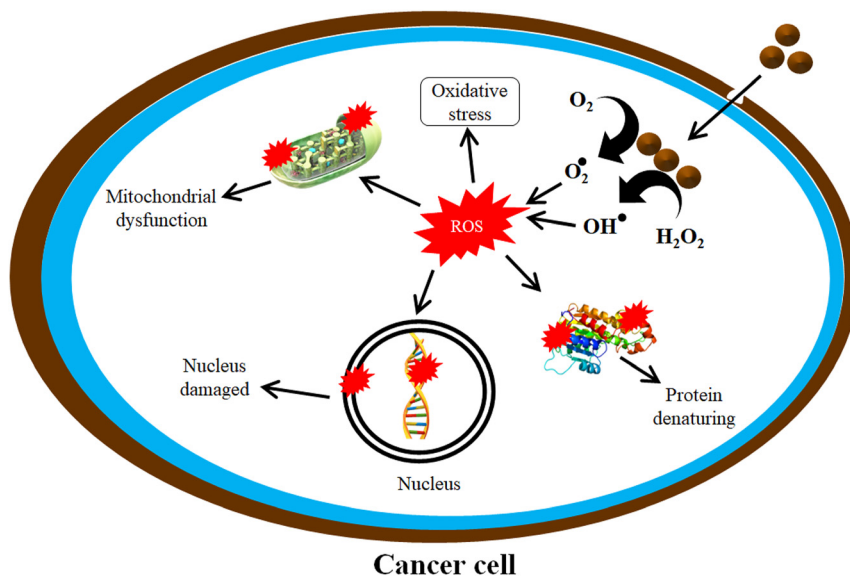


Figure 5: The cytotoxic effect of NPs against cancer cell.

MNPs have been observed to induce mutations in cellular permeability, inhibit enzymatic actions, and cause morphological changes in cells resulting in cell death as illustrated in Figure 5. These effects are attributed to the interaction of nanoparticles with the cellular environment [187–189]. Biogenic synthesized metal nanoparticles have ability to inhibit the growth of cancer cells. Ag NPs synthesized from *Cleome viscosa* are used against the treatment of the lung and ovarian cancer which shows 50 % inhibitory concentration at 28 and 30 $\mu\text{g/mL}$, respectively [190].

Mittal et al. [191] reported the use of *Potentilla fulgens* extract for the synthesis of silver nanoparticles and evaluated their anti-cancer activity against MCF-7 (breast) and U-87 (glioblastoma) cells at concentration of 4.91 and 8.23 $\mu\text{g/mL}$, respectively. Bethu et al. [192] prepared Ag NPs by using *Rhynchosia suaveolens* leaf extract as reducing and stabilizing agent. They mixed 5 mL of *R. suaveolens* leaf extract with 95 mL of 1.0 mM AgNO_3 into amber colored bottle and incubated for 3–24 h in dark with continuous stirring at 45 °C. Successful fabrication of Ag NPs was confirmed by UV–vis, XRD, SEM, TEM, EDX, TGA, DLS and FTIR analysis. Anti-cancer activity of Ag NPs was determined by the MTT assay which was measured in term of percentage of cell viability and IC_{50} valued as calculated for each cell line. It was seen that Ag NPs exhibited highest potential against SKOV3 cell with an IC_{50} value found as 4.2 $\mu\text{g/mL}$ among DV14, PC-3 and A549. Balasubramanian et al. [193] prepared Au NPs by using *Jasminum auriculatum* leaf extract. They mixed 10 mL plant extract with 90 mL of 1.0 mM HAuCl_4 solution in beaker. After successful synthesis, they evaluated the anticancer activity of these Au NPs by using MTT assay method. They supported the dose and time dependent anticancer activity against Hela cancer cells. They observed that the cytotoxic

effect of the Au NPs was most pronounced in Hela cell lines. This cytotoxicity was attributed to the generation of ROS by the Au NPs. The ROS caused damage to the cancer cells leading to their death.

Various other researchers reported the preparation of biogenic nanoparticles and evaluated their anticancer activities to get their wide range practical applications [140, 194, 195].

4.3 Anti-inflammatory activity

Inflammation is a somatic response in the body that protects the body from injury, infection, and stress by a multiple mechanism [196]. Tumor progression is the final stage of tumor development and can be facilitated by an inflammatory response which is triggered by oxidative stress. This stress increases the risk of several disorders such as atherosclerosis, coronary heart disease, Alzheimer's disease, insulin resistance, and diabetes [197, 198]. In diseases that are primarily caused by inflammatory responses, treatment using anti-inflammatory agents can be effective. Steroidal or non-steroidal anti-inflammatory drugs (NSAIDs) are commonly used for this purpose, but they can have severe side effects. Therefore, there is a need for an alternative option that can resolve inflammation in a homeostatic, modulatory, efficient, and well-tolerated manner [199]. Au NPs can inhibit the effect of inflammation which are shown by the interposed of 21 nm sized Au NPs into the mice during the reduction in $\text{TNF-}\alpha$ and IL-6 mRNA levels as reported by Chen et al. [200]. Purposeful anti-inflammatory activity has also been reported by Moldovan et al. [201] which might be due to the enhanced permeability and retention effect of the Ag NPs in the edema region. They investigated that garlic clove

mediated Ag NPs showed greater inhibition of 1 % bovine serum albumin (BSA) (0.45 mL) while pH was maintained at 6.3 by using 1.0 N HCl solution. Percentage inhibition was calculated by using Equation (1) [202].

$$\text{Percentage inhibition (\%)} = \frac{\text{Absorbance}_{(\text{control})} - \text{Absorbance}_{(\text{sample})}}{\text{Absorbance}_{(\text{control})}} \quad (1)$$

By increasing the number of incorporated NPs, an increase in the percentage inhibition was seen. Maximum inhibition of about 85 % was observed for BSA when 250 μM dose of NPs was used. It was also observed that Ag NPs used in low dose as 10 μM is good enough to potentially inhibit the denaturation of BSA protein [203]. Shah et al. [204] prepared Ag NPs by using *Silybum marianum* seed extract while mixing seed extract and 1.0 mM AgNO_3 at ratio of 1:5 to synthesize Ag NPs. Prepared Ag NPs were characterized by UV-vis, XRD, TEM and FTIR analysis. These Ag NPs tested *in vitro* assay against COX-2, COX-1, sPLA2 and 15-LOX. They recorded the highest anti-inflammatory activity against COX-1 (38.56 ± 1.29 mm).

Rajput et al. [205] prepared Ag NPs by using *Atropa acuminata* leaf extract as reducing and stabilizing agent and investigated their anti-inflammatory effects. They found that denatured proteins were responsible for severe inflammation in individuals with rheumatoid disease. They evaluated the inhibitory effect of Ag NPs on denatured albumin comparing it to the standard drug Diclofenac sodium salt and discovered that Ag NPs exhibited a stronger inhibitory effect on denatured albumin. Various phytochemicals particularly flavonoids were found to possess anti-inflammatory properties by reducing metal ions into metal atoms and stabilizing the MNPs. These phytochemicals interacted with different enzymes involved in the inflammation process. Furthermore, the compounds atropine and scopolamine derived from *A. acuminata* exhibited significant anti-inflammatory activity alliance with the effects of Ag NPs.

Different other researchers also synthesized nanoparticles of different metals by using biogenic source as reducing/capping agent and depicted their anti-inflammatory activities [206–208].

4.4 Antiviral activity

Use of NPs and nanoparticle complexes for antiviral therapy has been extensively reported for several decades [38]. Studies have focused on two main directions for application of NPs in antiviral activities. First direction involves the use of modified nanoparticles that are functionalized with specific functional groups. These functionalized nanoparticles can affect viruses by forming chemical bonds with the receptors

on the virus's surface [209, 210]. In second direction, pure and non-functionalized nanoparticles are employed against viral diseases [117]. Different researchers reported the antiviral action of various nanoparticles such as Ag NPs and Au NPs against different viruses such as influenza virus H1N1, hepatitis B virus, herpes simplex virus, HIV-1 and foot and mouth disease virus [211–215].

They reported that antiviral action of Ag NPs is greater than Ag^+ ions due to the greater tendency of adsorption of NPs on the surface of the virus as compared to the silver ions [213]. However, drastic decrease in the antiviral activity of Ag NPs was seen which was due to the entangling of naked Ag NPs due to their reactivity [216]. To avoid this, the surface of Ag NPs is modified by using a different types of organic/inorganic substances or bio-macromolecules present in biogenic extract that act as stabilizer [217, 218]. A single-stranded positive-sense RNA virus which is known as a porcine reproductive and respiratory syndrome virus (PRRSV) were exposed in a pig meat industry and causes considerable financial loss to the global livestock industry [219]. It was analyzed that biogenically synthesized Ag NPs can invade the host cell as well as have the capability to inhibit the viral replication and multiplication of PRRSV due to the activating antiviral natural responses [220].

El-Sheekh et al. [221] prepared $\text{Ag}_2\text{O}/\text{AgO}$ -NPs and Au-NPs by using *Spirulina platensis* extract and found that these MNPs showed antiviral activity against Herpes simplex (HSV-1) virus.

They also observed antiviral activity by used different concentration of MNPs. Both $\text{Ag}_2\text{O}/\text{AgO}$ -NPs and Au-NPs inhibited the replication of HSV-1. They concluded that $\text{Ag}_2\text{O}/\text{AgO}$ -NPs were most effective inhibitor of HSV-1 and showed high reduction rate of 49.23 % as compared to Au-NPs which showed 42.75 % reduction rate. Different other researchers also reported the use of biogenic synthesized NPs against viral infection and found NPs effective in their potential antiviral activity [222–224]. General mechanism of functioning of NPs as antiviral agents has been illustrated in Figure 6.

4.5 Antioxidant activity

Overproduction of ROS can significantly enhances the chances of various disorders like Alzheimer's, atherosclerosis, arthritis, diabetes, neurodegenerative disease, cancer and aging process [225]. MNPs have gained attention in recent years for their antioxidant activity and are proved to be effective scavengers of free radicals and ROS. MNPs have been shown to exhibit antioxidant activity in various *in vitro* and *in vivo* studies including reducing oxidative stress and

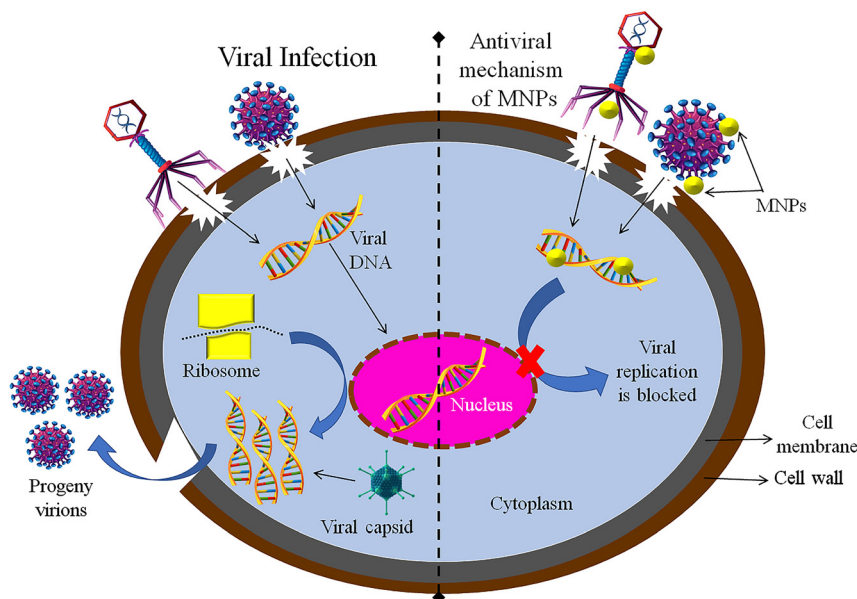


Figure 6: Mechanism of antiviral activity of MNPs.

inflammation [27]. Exact mechanisms responsible for the antioxidant activity of MNPs are not completely understood and needed to be address in future. However, it has been investigated that MNPs with natural antioxidants can reduce the overproduction of ROS while protects the proteins and lipids in the cells from being attacked by ROS, thus counteract the adverse reactions [201]. Free radicals can cause harm to the human body by damaging and mutating cells. Antioxidants are important in preventing this damage by neutralizing these harmful free radicals. Antioxidant activity can be determine by a (2,2-diphenyl-1-picrylhydrazyl) DPPH method due to its potential to reduce free radicals [112]. Antioxidant activity of the solution is measured by a DPPH radical scavenging assay and ABTS⁺ (2,2'-azinobis (3-ethylbenzothiazoline-6-sulfonic acid)) radical scavenging assay methods. Value of radical scavenging ability (RSA) can be calculated from Equation (2) [226].

$$\text{RSA (\%)} = \frac{(A_0 - A)}{A_0} \times 100 \quad (2)$$

where “A₀” express the control or standard absorbance and “A” is the sample absorbance.

Bhakya et al. [112] prepared Ag NPs by using the root extract of *H. isora* and investigated that the stability of NPs was due to the presence of oxidized polyphenols and carboxyl proteins. They also tested the antioxidant potential of these Ag NPs against DPPH, H₂O₂, nitric oxide and reducing powder as shown in Figure 7. DPPH is well known free radical based on their ability to reduce hydrogen or electron taken from donor. Antioxidant activity of Ag NPs in DPPH assay is observed in form of color change that is not observed in case of control. They also found that DPPH

scavenging assay showed effective inhibition activity of Ag NPs as compared to butylated hydroxytoluene (BHT) and ascorbic Acid (AA) that are used as standard in most of the studies. The Ag NPs exhibited more inhibition with 90 % scavenging activity of DPPH. The scavenging of atom to stable DPPH molecule, which showed absorbance at 517 nm.

Many other researchers also prepared biogenic MNPs and evaluated their antioxidant activities to find their wide range applications [58, 116, 126].

4.6 Catalytic activity

Metal NPs are commonly used in heterogeneous catalysis because they possess a high surface area and surface-to-volume ratio allowing for fast rate of reactions. MNPs have demonstrated efficacy in various reactions including dehalogenation [227] and hydrogenation [228]. Some reports are also proved that smaller sized ultrafine MNPs generally manifested noticeable catalytic activity [229]. Crucial factors for assessing the practical applications of a heterogeneous catalyst are their ability to remain stable and reusable. Biogenic synthesized MNPs have been reported as catalyst for the reduction of different toxic dyes and nitro-aromatic compounds and were found effective and recyclable as shown in Figure 8.

Unique properties of MNPs, such as their high specific surface area, resistance to metal leaching and self-poisoning have made them highly desirable for use in catalytic research. Different researchers reported the applications of biogenic nanoparticles as catalyst for various organic reaction and in the treatment of wastewater pollutants.

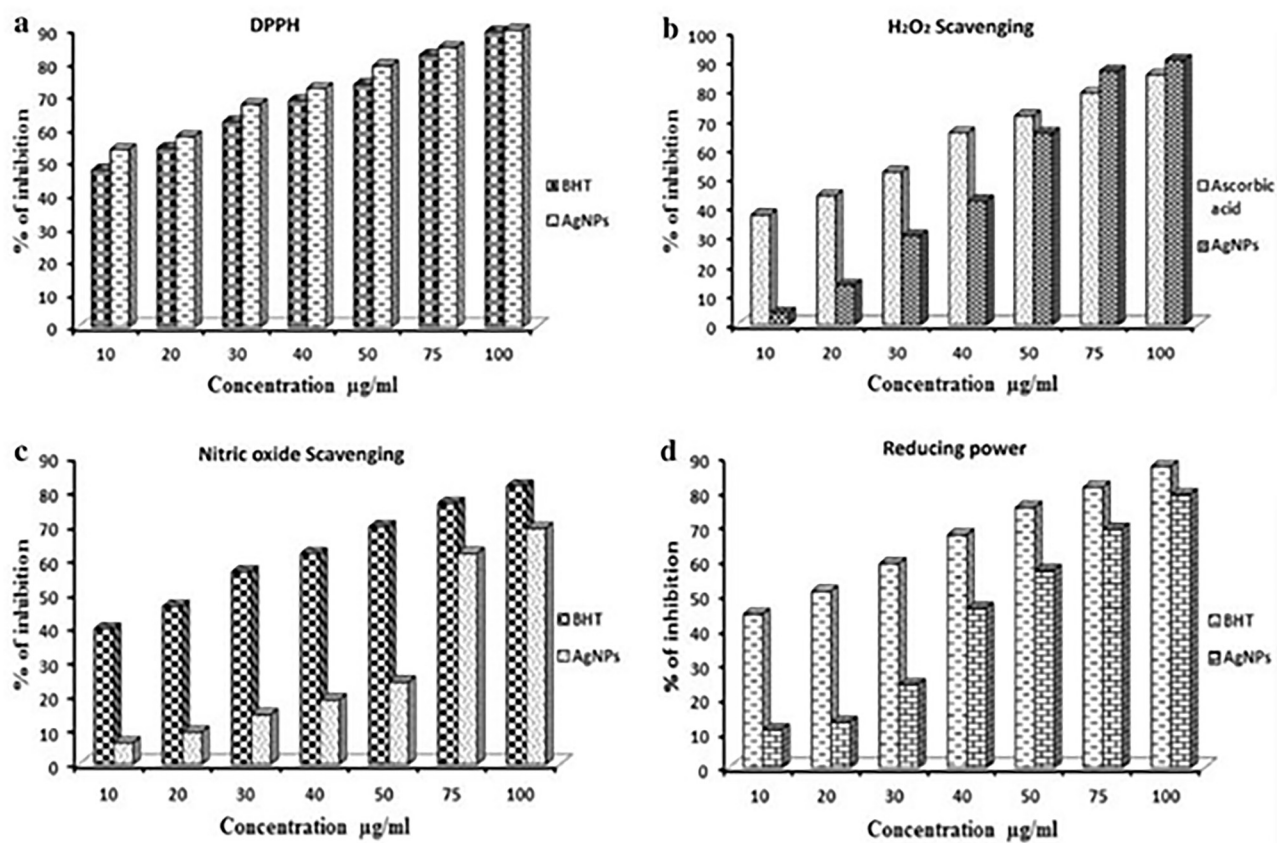


Figure 7: Antioxidant activities of *Helicteres isora* root extract induced Ag NPs [112] [Springer Nature, copy right-2015].

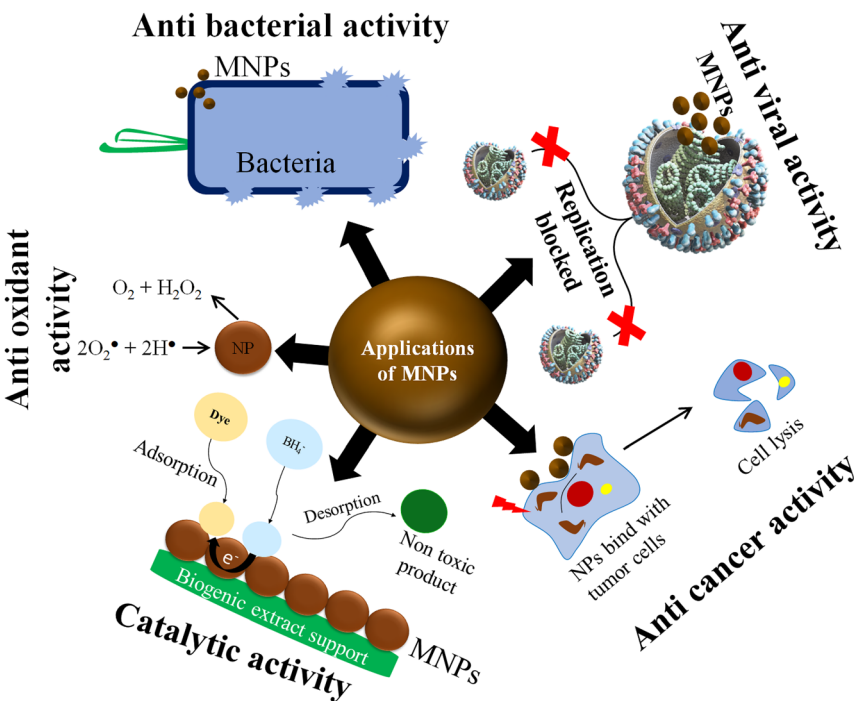


Figure 8: Diagrammatic representation of different applications of biogenic stabilized MNPs.

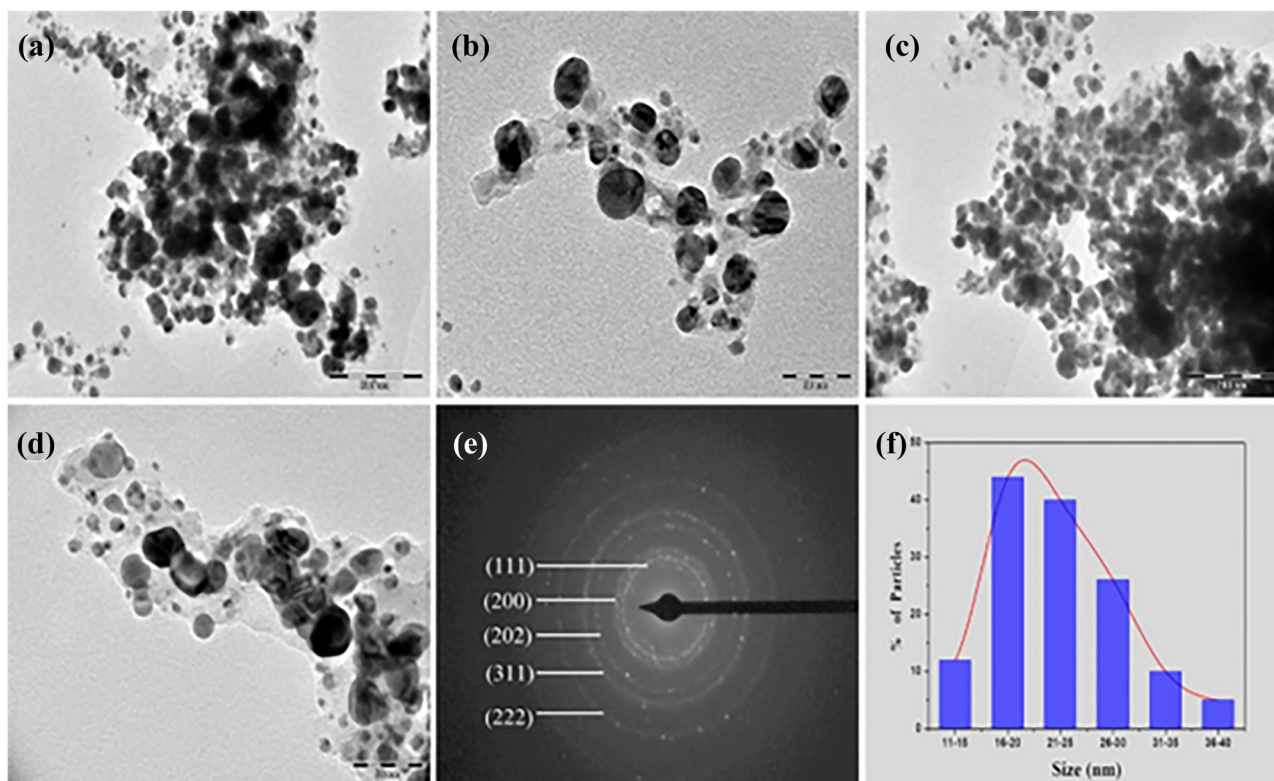


Figure 9: TEM micrograph of biosynthesized Ag NPs with different magnification (a–d), SAED pattern (e) and size distribution histogram of Ag NPs (f) [146]. [Reprinted with the permission from Scientific Reports, copyright-2020].

Raj and coworkers [146] prepared Ag NPs using *T. arjuna* leaf extract as biogenic reductant as well as stabilizer and characterized the prepared particles by UV–Vis, TEM, FESEM, XRD, EDS, selected area electron diffraction (SAED) and FTIR analysis. TEM micrographs of Ag NPs are displayed in Figure 9(a–d) which indicated that nanoparticles are spherical in shape and smaller groups of NPs were also observed which were due to the agglomeration during initial stages of sample preparation. Figure 9e displays the SAED pattern of the Ag NPs which indicates the lattice reflection from inner to outer surface of the ring of NPs. Highest percentage of particles showed the size range between 16 and 20 nm as displayed in size distribution histogram as shown in Figure 9f.

EDS analysis confirmed the presence of Ag, O and Cl in prepared biogenic NPs samples. They used these particles as heterogeneous catalyst for the treatment of toxic dyes such as methylene blue (MB) Congo red (CR), methyl orange (MO) and 4-nitrophenol (4-NP). They observed that reduction of toxic dyes was completed in feasible time in presence of NaBH_4 and Ag NPs. Value of reaction completion time, rate constant (k_{app}), and percentage reduction are given in Figure 10. Pseudo second order kinetic equation was used to find the value of k_{app} . During degradation process, NaBH_4 was

dissociated into BH_4^{-1} ions that act as electrons donor while dyes acted as electrons acceptor while attached at the surface of NPs. NPs worked as electron relay centered and speed up the transfer of electrons from BH_4^{-1} ions to dye molecule and degraded them completely. Turning the colored mixture to colorless indicates the completion of reaction.

Sherin et al. [230] utilized *Terminalia bellerica* kernel extract as both the reductant and stabilizer for the biogenic synthesis of Ag NPs. They studied the morphological features

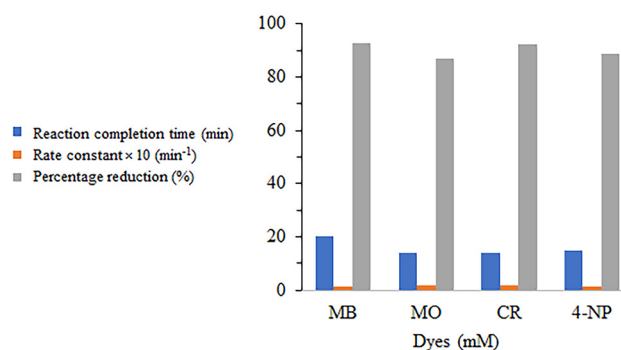


Figure 10: Catalytic degradation of toxic dyes into environmental benign products in presence of catalyst.

of these NPs by different techniques such as FESEM, EDS, XRD and FTIR. FESEM analysis confirmed the spherical shape of NPs while a strong peak at 3.2 KeV in EDX spectra confirmed the successful fabrication of crystalline Ag NPs. Peaks of oxygen and carbon highlighted the presence of phytochemicals from kernel extract as potential surface capping agent. Particle size was assessed by XRD and found as 32 nm. Furthermore, FTIR results signified the involvement of -NH_2 and -OH groups from kernel extract as reducing and stabilizing agent. They further investigated the catalytic potential of these NPs against 4-NP, eosin Y (EY), methyl orange (MO) and MB in aqueous dispersions.

Ag NPs exhibited good potential for degradation of 4-NP as compared to other pollutants. They also investigated the impact of altering the catalyst dosage on the reduction reactions while keeping all other parameters constant. The aim was to determine the amount of catalyst that would result in the highest rate of reduction and reduction percentage. For this objective, they varied the catalyst dosage within the range of 0.0–0.5 mg/mL while maintaining the other reaction parameters at a constant level including 0.2 mL of dye (1.0 mM) and 0.2 mL of NaBH_4 solution (0.5 M). Initially, at zero concentration of catalyst less than 1.5 % reduction rate of dyes was observed. As the concentration of catalyst was increased further, an increase in the value of k_{app} was observed which was due to the availability of large number of reaction sites resulting from the higher catalyst concentration. This effect attributed the higher reduction rate because of simultaneous adsorption and reduction of toxic reactants into environmentally benign products. Similar trend was observed in case of all three dyes when they were subjected to reduction under similar conditions as shown in Figure 11a.

Highest reduction of 4-NP (87 %) was achieved utilizing the catalyst dosage of 0.4 mg/mL, while for MB and EY, percentage reduction value was found as 76.9 and 71 % at catalyst dosage of 0.5, 0.4 mg/mL, respectively. This study revealed that the catalytic efficiency of NPs was dependent on the dose of the catalyst up to a limit. After which further increasing the dose of catalyst does not significantly increase the rate of reaction. They also studied the effect of temperature on the value of k_{app} for the reduction of 4-NP as shown in Figure 11b. It was concluded that value of k_{app} was increased with increase of temperature of the medium. Value of activation energy (E_a) was found as 30.12 kJ/mol for the reduction of 4-NP.

Reddy et al. [231] utilized bark extract of *Cochlospermum gossypium* (Gum kondagogu) as a dual-function material for the green synthesis of Au NPs serving as both a reducing and stabilizing agent. They treated this extract with the HAuCl_4 solution which resulted in the synthesis of red colored Au NPs. Synthesized Au NPs were characterized using various

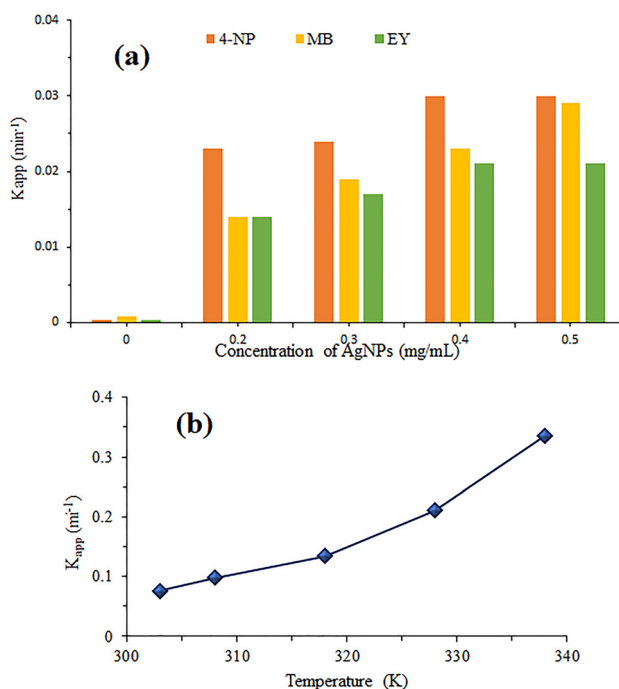


Figure 11: Relation between the value of apparent rate constant and (a) concentration of AgNPs for reduction of different dyes [230], (b) temperature of the medium for the reduction of 4-NP by AuNPs [231].

techniques and evaluated their potential catalytic applications in the reduction of 4-NP to 4-AP. Excellent reduction potential was displayed by these NPs. They also studied the impact of temperature on the rate of reduction reaction. For this study, they varied the temperature from 303 to 338 K by keeping all other parameters of the reaction constant such as 1.7 mL of 0.2 mM 4-NP and 1.0 mL of 0.015 M NaBH_4 .

An observed correlation was found between an increase in temperature and notable improvement in the reaction rate along with a decrease in the time for the reaction completion as shown in Figure 11b. The increase in temperature leads to an elevation in the reduction rate of 4-NP due to enhanced collisions and greater kinetic energy of the reactant molecules. This results in higher frequency of successful collision leading to a more rapid and efficient reduction process.

Eisa et al. [28] prepared Ag NPs by using *Zingiber officinale* as biogenic reductant and stabilizer for the reduction of silver ions into silver atoms giving NPs and subsequent stabilization of Ag NPs to prevent agglomeration. They employed these NPs in the catalytic reduction of 4-NP and MB, and studied the impact of varying the pH of the reaction mixture on the value of rate constant as shown in Figure 12.

They opted to carry out both reduction reactions in alkaline medium because it is crucial to provide the basic

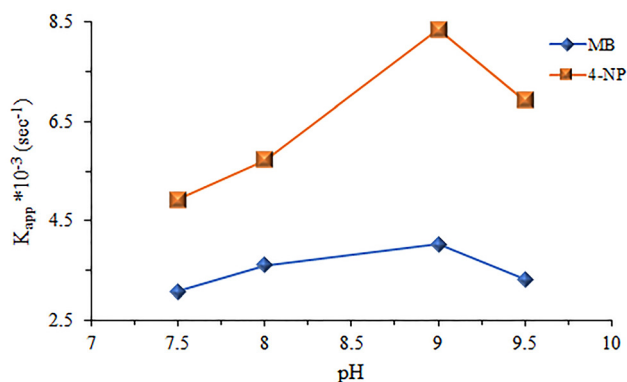


Figure 12: Effect of pH on the rate constant for the reduction of 4-NP and MB by biogenically synthesized Ag NPs [28].

medium to enable the formation of 4-nitrophenolate ions which exhibit a characteristic absorption peak at 400 nm. Due to which exploring the pH effect in an acidic medium is not relevant for this particular reaction. While in case of MB which is a cationic dye, an acidic medium is undesired

because surface of Ag NPs may acquire a positive charge leading to the repulsion of cationic dye molecules and hindering their adsorption onto the catalyst surface [232]. Considering these factors, pH was varied from 7.5 to 9.5 while keeping other parameters constant at 0.08 mM 4-NP, 0.03 mM MB and 7 mM NaBH_4 . Similar trend was observed in case of both dyes. Rate constant values exhibited an increase as the pH value was increased from 7.5 to 9 because at higher pH, large number of OH^- ions facilitated the deprotonation of 4-NP yielding 4-nitrophenolate ions hence reaction speeds up. However, further increase in pH up to 9.5 results in subsequent decrease in rate constant due to the high stability (low decomposition) of NaBH_4 at pH values exceeding 9 [233]. Synthesis of different MNPs from various biological sources used as extract preparation along with their characterization and use as catalyst is given in Table 2.

The proposed mechanism for the catalytic reduction of toxic dyes into environmental benign products is illustrated in Figure 13. According to the researchers, toxic dye molecules along with borohydride ion get adsorb over the surface

Table 2: Preparation of biogenic metal nanoparticle from various extract sources and their use as catalyst for treatment of toxic dyes.

Extract source	MNPs	Characterization	Dyes	Reaction completion time (min)	Rate constant (min ⁻¹)	References
Fungal extract						
<i>Magnusiomyces ingens</i>	Au NPs	UV-vis, TEM, SEM, FTIR	NP, 3-NP and 2-NP	3	0.0005	[55]
<i>Penicillium oxalicum</i>	Ag NPs	UV-vis, FTIR, XRD, EDX, SAED, TEM	MB	30	–	[234]
<i>Saccharomyces cerevisiae</i>	Ag NPs	UV-vis, TEM, XRD, FTIR	MB	3600	–	[235]
<i>Monascus ruber</i>	Ag NPs	UV-vis, FTIR, XRD, EDX, TEM	MB, MO, CR	14, 7, 14	0.0799, 0.2466, 0.1180	[236]
<i>Aspergillus</i> specie NJP02	ZnO NPs	UV-vis, FTIR, XRD, EDX, TEM	MB	30	0.00005	[237]
Algal extract						
<i>Chlorella pyrenoidosa</i>	Ag NPs	UV-vis, TEM, SEM, XRD, EDX, FTIR	MB	150	–	[60]
<i>Turbinaria conoides</i>	Au NPs	UV-vis, FTIR, TEM, DLS,	RhB	0.3	0.0018	[75]
	Au NPs		Sulforhodamine	1.5	0.0003	
<i>Sargassum coreanum</i>	Ag NPs	UV-vis, TEM, SEM, XRD, EDX, FTIR	MB	20	0.106	[238]
<i>Chlorella ellipsoidea</i>	Ag NPs	UV-vis, XRD, TEM, SEM, FTIR	MB, MO	30, 30	0.0324, 0.0472	[239]
<i>Padina tetrastromatica</i>	Au NPs	UV-vis, FTIR, EDX, SEM, TEM, SAED	EY, CR	7, 4	0.4392	[240]
					0.4419	
Bacterial extract						
<i>Streptomyces griseoruber</i>	Au NPs	UV-vis, XRD, FTIR, TEM	MB	5	40	[241]
<i>Microchaete</i> specie NCCU-342	Ag NPs	UV-vis, TEM, DLS	MR	120	–	[165]
<i>Streptomyces griseoruber</i>	Au NPs	UV-vis, XRD, TEM, SEM, FTIR	MB	5	–	[241]

Table 2: (continued)

Extract source	MNPs	Characterization	Dyes	Reaction completion time (min)	Rate constant (min^{-1})	References
<i>Escherichia coli</i>	Au NPs	UV-vis, XRD, TEM, AFM,	4-NP	5	0.0012	[82]
<i>Staphylococcus epidermidis</i>	Au NPs	UV-vis, TEM, FTIR	MB	0.05	–	[242]
Plant extract						
<i>Stemona tuberosa</i> Lour	Ag NPs, Au NPs	EDX, XRD, FTIR, SEM and TEM	4-NP, MB, MO, MR	–	–	[243]
<i>Sargassum myriocystum</i>	Ag NPs	XRD, EDX, FTIR, SAED, DLS	MB	60	–	[120]
<i>Jasminum auriculatum</i>	Au NPs	UV-vis, XRD, FTIR, SEM, TEM, EDX, DLS	4-NP	45	0.0390	[193]
<i>Alpinia nigra</i>	Au NPs	UV-vis, XRD, TEM, SEM, EDX	MO, RhB	120	0.0144 0.0149	[93]
<i>Carica papaya</i>	Fe_2O_3 NPs	FTIR, XRD, FESEM, EDX, TGA	Remazol yellow RR	250	19.800	[176]

of MNPs. Borohydride ions dissociate and release hydrogen gas. During this process electrons are transferred to the dye molecules and reduce them into environmental benign products. Multidimensional applications of bioinorganic metal nanoparticles in different fields have been shown

diagrammatically in Figure 13. Thus, preference of biogenic synthesized NPs over chemical synthesis MNPs protects the environment from exposure of toxic chemicals along with decreased cost of synthesis of MNPs and avoid the use of harsh reaction conditions for preparation process.

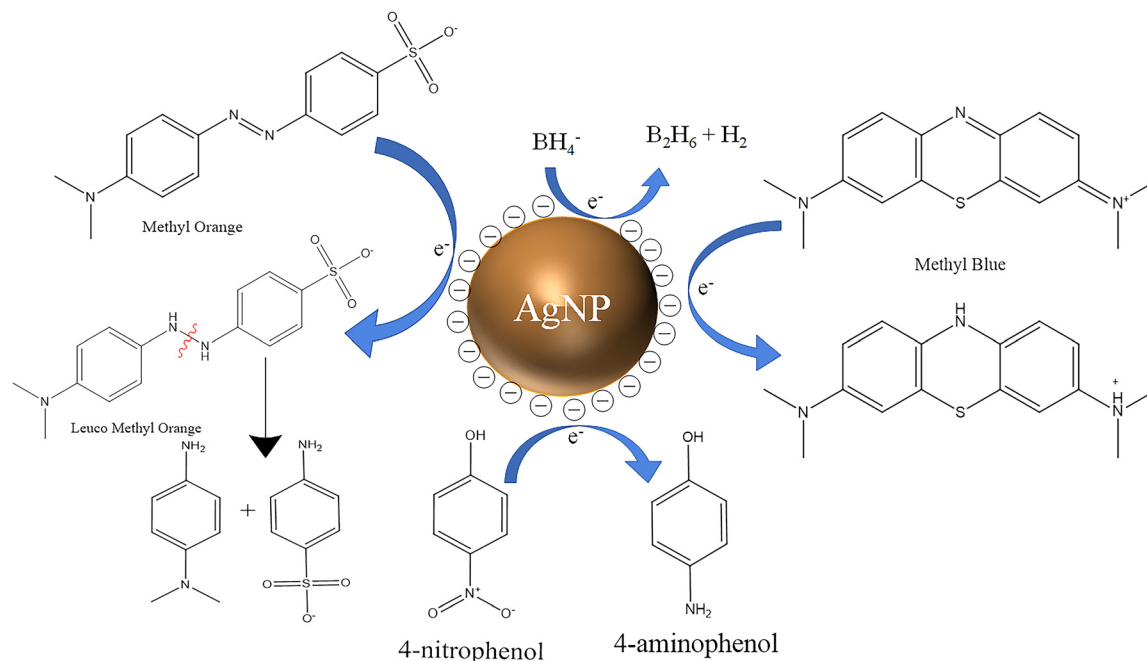


Figure 13: Mechanistic insight of catalytic reduction of MO, MB and 4-NP into ecofriendly products by Ag NPs in the presence of NaBH_4 .

5 Conclusions

This study provides a comprehensive review of various biogenic methods for the synthesis of metal nanoparticles using plant, bacterial, fungal, and algal extracts as reducing and stabilizing agents. Among these methods, plant-mediated synthesis has emerged as an environmentally-friendly and cost-effective approach for the synthesis of metal nanoparticles. In particular, plant-mediated methods are characterized by easy scalability, low biohazard risks, straightforward maintenance of cell cultures, and less complex reaction conditions, as compared to microbe-mediated methods. These advantages make plant-mediated methods attractive for large-scale production of metal nanoparticles with potential applications in various fields. Furthermore, it has been reported by several researchers that the plant-mediated method also offers advantages such as shorter incubation periods and lower risk of contamination compared to microbe-mediated methods, making it a preferred approach for the synthesis of silver and gold nanoparticles. MNPs have high energy content, which allows them to produce ROS. ROS can cause damage to the DNA and proteins of microorganisms, leading to their death. As a result, MNPs have found extensive use in antibacterial, anticancer, anti-inflammatory, and antiviral applications against various types of microorganisms. They have also been reported for the antioxidant activity and catalytic reduction of various toxic dyes like MB, MO, RhB, and 4-NP.

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Research ethics: Not applicable.

Author contributions: Dr. Khalida Naseem contributed as a main supervisor. Asad Aziz contributed to the designing of Figures and tables. Muhammad Ehtisham Khan did the formal analysis. Shahzaib Ali contributed to the writing of the draft. Awais Khalid also did the formal analysis. Thus all authors accepted the responsibility for the entire content of this manuscript and approved its submission.

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