Green Synthesis of Transition metal & Transitions metal oxides of Nanoparticles and their Antimicrobial Activity

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ABSTRACT

It has been know that nanoparticles and its compounds have strong inhibitory and microbial activities for bacteria, virus, and fungi. In today's world due to the outbreak of infectious diseases coused by different pathogenic bacteria and development of antibiotic resistance the pharmaceutical companies and the researchers are searching for new antimicrobial agent. The synthesis, characterization and application of biologically synthesized nanoparticles have now become an important factor of nanotechnology. Nanoparticles are manufactured worldwide in large quantities for use in a wide range of application. The green synthesis of metal and semiconductor nanoparticles in an expanding research area due to the potential applications for the development of novel technologies.More recent advancement in researches on metal nanoparticles. A nanoparticle has lot of scope for health care products such as burn dressings, antimicrobial applications, medical devices and scaffolds. Various type of method used to synthesis of nanoparticles with including chemical reduction, photochemical reactions, electrochemical techniques and green chemistry route. In this paper we repot highlighted about the various plants, fungi, bacteris and actinomycetes used in this process, synthesizing methodology; nanoparticles shape, size and their application as antimicrobials in elatorate manner. We also highlighted the basic mechanism by which nanoparticles interact with microbes.

KEYWORDS: Green Synthesis of Nanoparticles, Transition metal Nanoparticles, Antimicrobial Activity.

1. INTRODUCTION

Over the last decade, novel synthesis approaches/methods for nanomaterials (such as metal nanoparticles, quantum dots (QDs), carbon nanotubes (CNTs), graphene, and their composites) have been an interesting area in nanoscience and technology [1–9]. To obtain nanomaterials of desired sizes, shape, and functionalities, two different fundamental principles of synthesis (i.e., top down and bottom up methods) have been investigated in the existing literature Fig. 1.

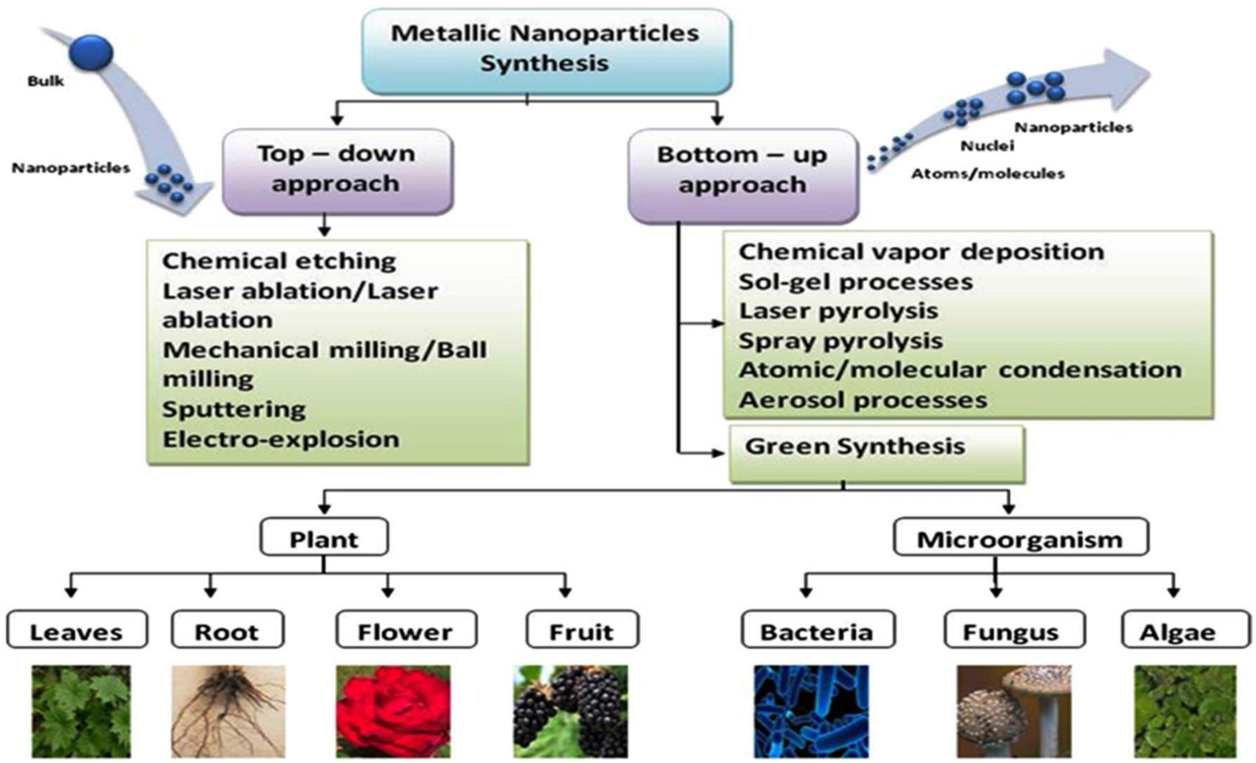

Fig. 1 Different synthesis approaches available for the preparation of metal nanoparticles

In the former, nanomaterials/ nanoparticles are prepared through diverse range of synthesis approaches like lithographic techniques, ball milling, etching, and sputtering [10]. The use of a bottom up approach (in which nanoparticles are grown from simpler molecules) also includes many methods like chemical vapor deposition, sol–gel processes, spray pyrolysis, laser pyrolysis, and atomic/molecular condensation.

Interestingly, the morphological parameters of nanoparticles (e.g., size and shape) can be modulated by varying the concentrations of chemicals and reaction conditions (e.g., temperature

and pH). Nevertheless, if these synthesized nanomaterials are subject to the actual/ specific applications, then they can suffer from the following limitation or challenges: (i) stability in hostile environment, (ii) lack of understanding in fundamental mechanism and modeling factors, (iii) bioaccumulation/ toxicity features, (iv) expansive analysis requirements,
(v) need for skilled operators, (vi) problem in devices assembling and structures, and (vii) recycle/reuse/regeneration.

In true world, it is desirable that the properties, behavior, and types of nanomaterials should be improved to meet the aforementioned points. On the other hand, these limitations are opening new and great opportunities in this emerging field of research.

To counter those limitations, a new era of 'green synthesis' approaches/methods is gaining great attention in current research and development on materials science and technology. Basically, green synthesis of materials/ nanomaterials, produced through regulation, control,
clean up, and remediation process, will directly help uplift their environmental friendliness. Some basic principles of "green synthesis" can thus be explained by several components like prevention/minimization of waste, reduction of derivatives/pollution, and the use of safer (or non-toxic) solvent/auxiliaries as well as renewable feedstock.

'Green synthesis' are required to avoid the production of unwanted or harmful by-products through the build-up of reliable, sustainable, and eco-friendly synthesis procedures. The use of ideal solvent systems and natural resources (such as organic systems) is essential to achieve this goal. Green synthesis of metallic nanoparticles has been adopted to accommodate various biological materials (e.g., bacteria, fungi, algae, and plant extracts). Among the available green methods of synthesis for metal/metal oxide nanoparticles, utilization of plant extracts is a rather simple and easy process to produce nanoparticles at large scale relative to bacteria and/or fungi mediated synthesis. These products are known collectively as biogenic nanoparticles Fig. 2.

Green synthesis methodologies based on biological precursors depend on various reaction parameters such as solvent, temperature, pressure, and pH conditions (acidic, basic, or neutral). For the synthesis of metal/metal oxide nanoparticles, plant biodiversity has been broadly considered due to the availability of effective phytochemicals in various plant extracts, especially in leaves such as ketones, aldehydes, flavones, amides, terpenoids, carboxylic acids, phenols, and ascorbic acids. These components are capable of reducing metal salts into metal nanoparticles [11]. The basic features of such nanomaterials have been investigated for use in biomedical diagnostics, antimicrobials, catalysis, molecular sensing, optical imaging, and labelling of biological systems [12].

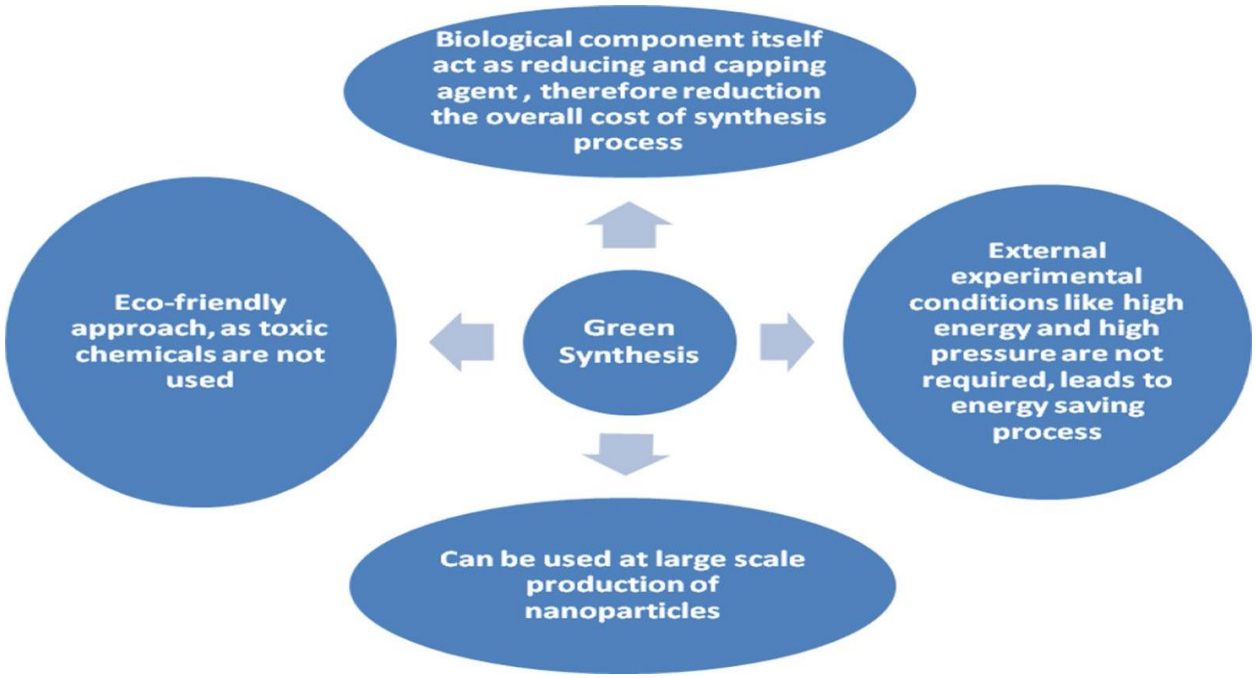

Fig. 2 Key merits of green synthesis methods

Here, we summarized the current state of research on the green synthesis of metal/metal oxide nanoparticles with their advantages over chemical synthesis methods. In addition, we also discussed the role of solvent systems (synthetic materials), various biological (natural extracts) components (like bacteria, algae, fungi, and plant extracts) with their advantages over other conventional components/solvents. The main aim of this literature study is to provide detailed mechanisms for green synthesis and their real world environmental remediation applications. Overall, our goal is to systematically describe "green" synthesis procedures and their related components that will benefit researchers involved in this emerging field while serving as a useful guide for readers with a general interest in this topic.

CLASSIFICATION OF NPs

NPs can be classified into two groups as organic NPs which includes carbon NPs (Fullerenes) and Inorganic NPs includes Magnetic NPs, Noble metal NPs (Gold and Silver), and semiconductor NPs (zinc oxide [ZnO] and Titanium oxide). Noble metal NPs such as gold and silver provide superior material properties with functional versatility. Metallic NPs considered as the most promising as they contain remarkable biomedical agents. Silver, aluminum, gold, carbon, iron, titanium, copper, palladium, and fullerenes are routinely used as NPs.[13] Green synthesis of NPs from plant extracts and microbes has attracted the attention of researchers in recent years. Biosynthesis of NPs is considered better than chemical synthesis due to formation of toxic chemical species which gets adsorbed on the particle surface after chemical synthesis. This makes the NPs improper for medical applications. Moreover, they are cost effective and environmental-friendly in nature due to a biological process, which makes them superior than chemical and physical process of synthesis.[15]

GREEN SYNTHESIS

The "green" environment-friendly processes in chemistry and chemical technologies are becoming increasingly popular and necessary as a result of worldwide problems associated with environmental concerns.[16] Biological methods of NPs synthesis and plant or plant extract have been suggested as possible eco-friendly alternatives to chemical and physical processes.[17] It is significant that the NP production using plants described in the present review displays essential advantages over other biological systems.[18] Use of biological organisms such as bacteria, fungi, yeast, plant extract or plant biomass, and algae extract, could be an alternative to these methods for the synthesis of NPs in an eco-friendly manner, less time consuming, high yielding, low-cost technology, and non-toxic to vertebrate animals. Green synthesis methods reduce hazardous waste in the context of global efforts.[14] This review focuses on the green synthesis of silver, zinc, copper, and gold NPs using various plants and microbial sources.

BIOLOGICAL COMPONENTS FOR "GREEN" SYNTHESIS

Innumerable physical and chemical synthesis approaches require high radiation, highly toxic reductants, and stabilizing agents, which can cause pernicious effects to both humans and marine life. In contrast, green synthesis of metallic nanoparticles is a one pot or single step eco-friendly bio-reduction method that requires relatively low energy to initiate the reaction. This reduction method is also cost efficient [19–25].

BACTERIAL MEDIATED NANOPARTICLE SYNTHESIS.

Bacterial species have been widely utilized for commercial biotechnological applications such as bioremediation, genetic engineering, and bioleaching [26]. Bacteria possess the ability to reduce metal ions and are momentous candidates in nanoparticles preparation [27]. For the preparation of metallic and other novel nanoparticles, a variety of bacterial species are utilized. Prokaryotic bacteria and actinomycetes have been broadly employed for synthesizing metal/metal oxide nanoparticles.

The bacterial synthesis of nanoparticles has been adopted due to the relative ease of manipulating the bacteria [28]. Some examples of bacterial strains that have been extensively exploited for the synthesis of bioreduced silver nanoparticles with distinct size/shape morphologies include: *Escherichia coli*, *Lactobacillus casei*, *Bacillus cereus*, *Aeromonas* sp. SH10 *Phaeocystis antarctica*, *Pseudomonas proteolytica*, *Bacillus amyloliquefaciens*, *Bacillus indicus*, *Bacillus cecembensis*, *Enterobacter cloacae*, *Geobacter* spp., *Arthrobacter gangotriensis*, *Corynebacterium* sp. SH09, and *Shewanella oneidensis*. Likewise, for the preparation of gold nanoparticles, several bacterial species (such as *Bacillus megaterium* D01, *Desulfovibrio desulfuricans*, *E. coli* DH5a, *Bacillus subtilis* 168, *Shewanella alga*, *Rhodopseudomonas capsulate*, and *Plectonema boryanum* UTEX 485) have been extensively used. Information on the size, morphology, and applications of various nanoparticles is summarized in Table 1.

Table 1 Examples of metallic nanoparticles prepared in ILs by a chemical reduction method

S. No	Metal NPs	Metal salt	Reducing agent	Ionic liquid	Size (nm)	Ref.
1	Ag	$AgBF_4$	H_2, 85 °C, 4 atm BIm as scavenger	$[BMIm][BF_4]$, $[BMIm][PF_6]$	0.8–2.8 1.3–4.4	[29]
2	Ag	$AgBF_4$	H_2	$[BMIm][BF_4]$, [BMpy][TfO]	~ 9 (DLS) ~ 11 (DLS)	[30]
3	Ag	$AgBF_4$	$[BMIm][BH_4]$	$[BMIm][BF_4]$ purified and H_2O	0.8–4.4 4.0, 0.9–4.5	[31]
4	Ag	$AgNO_3$	Tween 85	$[BMIm][PF_6]$	3–10	[32]
5	Au	$HAuCl_4$	Ascorbic acid	[BMIm] [$C_{12}H_{25}OSO_3$] (lauryl sulfate)	20-50	[33]
6	Au	$HAuCl_4$	$NaBH_4$	[ShexMIm][Cl]	5	[34]
7	Au	$HAuCl_4$	$NaBH_4$	$[BMIm][BF_4]$ in a microfluidic reactor	0-5-4	[35]

8	Au	$HAuCl_4$- $3H_2O$	Glycerol	[EMIm][TfO], [EMIm][$MeSO_3$]	5–7 low temp. 5–7 aggregate at higher temp.	[36]
9	HAuBr 4		Me_2NCHO (DMF)	[Me2NH2][Me_2NCO_2] with small amounts of DMF	2-4	[37]
10	Cu	$Cu(OAc)_2$- H_2O	H_2NNH_2-H_2O (hydrazine hydrate)	[BMIm][BF_4]	80-130	[38]

FUGAL MEDIATED NANOPARTICLE SYNTHESIS

Fungi-mediated biosynthesis of metal/metal oxide nanoparticles is also a very efficient process for the generation of monodispersed nanoparticles with well-defined morphologies. They act as better biological agents for the preparation of metal and metal oxide nanoparticles, due to the presence of a variety of intracellular enzyme [39]. Competent fungi can synthesize larger amounts of nanoparticles compared to bacteria [40]. Moreover, fungi have many merits over other organisms due to the presence of enzymes/proteins/reducing components on their cell surfaces [41]. The probable mechanism for the formation of the metallic nanoparticles is enzymatic reduction (reductase) in the cell wall or inside the fungal cell. Many fungal species are used to synthesize metal/metal oxide nanoparticles like silver, gold, titanium dioxide and zinc oxide, as discussed in Table 1.

VIRAL AND YEAST MEDIATED NANOPARTICLE SYNTHESIS.

The studies with bacteria and fungi have yielded the synthesis of nanoparticles that are mostly metal based or in some very specialized conditions, the metal oxide nanoparticles

Table 2.

Table 2: Major viral species for nanoparticle synthesis.

Sr.No.	Microorganism	Nanoparticle	Location/Morphology	Ref.
1	Tobacco mosaic virus (TMV)	SiO_2, CdS, PbS, and Fe_2O_3	Nanotubes on surface	[42]
2	M13 bacteriophage	ZnS and CdS	Quantum dots, nanowires	[43,44]

However, fungus may lead to heterogeneous nanoparticle synthesis but such studies with bacteria are far less in number Table 3. When we talk about the application of nanoparticles, a significant focus is seen to be highlighted over the electronic aspects, the way they improve semiconducting applications.Themechanisms by which they lead to phenomena such as those of cathodoluminescence and surface plasmon resonance really present some intriguing aspects. Such applications require the synthesis of the nanoparticles that are made up of inorganic materials such as those of cadmium selenide, cadmium sulphide, iron oxide, and lead sulphide. Viruses, though almost impossible to culture *in vivo*, can be unique assets.

Table 3: Major yeast strains involved in nanoparticle synthesis.

Sr.No.	Microorganism	Nanoparticle	Size, shape	Location	Ref.
1	*S. cerevisiae*	Sb2O3	3–10 nm, spherical	Intracellular	[45]
2	*C. glabrata*	CdS	20A, spherical	Intracellular	[46]
3	*S. pombe*	CdS	1–1.5 nm, hexagonal	Intracellular	[47]
4	*Torulopsis* sp.	PbS	2–5 nm, spherical	Intracellular	[48]
5	Yeast strain MKY3	Ag	2–5 nm, hexagonal	Extracellular	[49]

NANOPARTICLES AS MICROBICIDES:

The field of biology such as antimicrobial agent and DNA sequencing. A nanoparticle has been known to exihibit strong toxicity to wide range of microorganism. Antimicrobial property of nanoparticles against *Staphylococcus aureus, Pseudomonas aeruginosa* and *E.coli* has been investigated[50]. Nanoparticles were found to be cytotoxic to *E.coli*. That the antimicrobial activity of nanoparticles was size dependent. Silver nanoparticles mainly in the range of 1-10nm attached to the surface of cell membrane and drastically disturb its proper function like respiration and permeability[51]. The fluorescent bacteria were used to investigate the antimicrobial properties of nanoparticles. The green fluorescent proteins were adapted to these studies. The general understanding is that nanoparticles get attached to sulphur containing proteins of bacterial cell causes the death of bacteria the full area cent measurement of the cell free supernatant reflected the effect of nanoparticles on recombination of bacteria[52].Various form of investigated silver ions and silver nanoparticles for their antifungal potency against two plant pathogenic fungi, *Bipolarissoro kiniana* and *Magnaporthegrisea* important pathogens on grasses. *In vitro* studies indicated that silver ions and silver nanoparticles had a significant effect on the colony formation by 50% were higher *Bipolarissoro kiniana* than for *Magnaporthe grisea* [53].The inhibitory effect on colony formation significantly diminished after silver cations were neutralized with chloride ions. Growth chamber inoculation assays further conformed that both ionic and nanoparticles silver significantly reduced two fungal diseases. Synthesized colloidal silver nanoparticles by reducing silver nitrate solution with glucose, in the presence of gelatin as capping agent[54].Govindaraju *et al.,* studies the antimicrobial activity of *Solanum torvum* mediated silver nanoparticles against pathogenic bacteria and fungi of silkworm *Bombyxmori* such as *Pseudomonas aeruginosa, Staphylococcus aureus, Aspergillusflavus* and *Aspergillusniger* using agar well diffusion method.

SYNTHESIS OF NANOPARTICLE FROM PLANTS

The most interesting biochemical and yield specific source for synthesis of nanoparticles is the plant biodiversity. Plants with highly rich genetic variability possess a number of interesting biomolecules in the form of coenzyme, vitamin based intermediates, and so many others which can reduce metal ions to nanoparticles in a single step. Moreover, these methods can be easily conducted at room temperature and pressure, without any hard and fast technical requirements.

Furthermore, plant based nanoparticle synthesis approaches are easy to scaleupandare traditionally also favouredbecause of their environment friendliness. Plant metabolite materials serve as excellent reducing agents, which include phenolic compounds, alkaloids, and sterols. Additional advantage is that it is a green synthesis method and, along with the use of plant extracts, live plants can also be used for nanoparticle synthesis. Till date, most of the studies have focused on the use of plant material for silver and gold nanoparticles.Thethrust behind plantmediated nanoparticle synthesis attracting significant boost is due to the fact that this route of nanoparticle synthesis enables the products which can be exploited for multiple applications such as those of nanomedicine based innovations. One significant advantage of plant mediated nanoparticle synthesis getting more favorability and reliable application potentials has been the fact that plant modified materials are easy and inexpensive to be cultured as compared to those of microorganisms.

Another significant factor is the ease of procedural and result based advantages coupled with relatively quicker applicational administrations which make plants better and more favoured destinations. Studies have been reported in the literature which has involved the use of whole plant based material as extracts for the synthesis of nanoparticles [48, 49]. In comparison to usingwhole plant tissue as extracts, studies with plant extract materials as inputs for making nanoparticles have reported much better control and also significantly better results. With advancements and increasing requirements of nanoparticles, the plant extract based nanoparticle synthesis has receivedmuch needed boost in the recent years [57–73]. Plant extracts are believed to act as reducing agents and stabilizing agents in the nanoparticle synthesis. The nature of plant extract affects the kind of nanoparticles synthesized in a highly criticalmannerwith the source of plant extract being the most vital factor affecting the morphology of synthesized nanoparticles [74]. Interestingly, this is so because different plant extracts contain different concentrations of biochemical reducing agents [75].

In the production of nanoparticles from the plant extracts, the plant extract is simply mixed with a solution of metal salt at room temperatures. The reaction is completed within few minutes and, as a result of biochemical reduction, the metals are converted from their mono or divalent oxidation states to zero-valent states. This marks the formation of nanoparticles, which is physically indicated through the colour change observed in the culture medium vessel. Synthesis of gold, silver, and a number of other metal based nanoparticles have been reported in this manner [76].

These plant based biochemical reductions are so versatile in nature that silver nanoparticles have been produced from extremely common plants such as those of *Azadirachta indica* (neem) and *Ocimum tenuiflorum* (tulsi), which are familiar in almost every household. Fig. 3 highlights some of the most frequently employed plant varieties for nanoparticle synthesis. Every new plant species has some excellent biomolecule in its genome through which it brings about the biochemical reduction. For instance, during the synthesis of silver nanoparticles from geranium leaf extract, the synthesized particles formed quite rapidly and a size limit of 16–40 nanometers was obtained [77]. In another nice modification, a study reported the synthesis of silver nanoparticles from geraniol, a natural alcoholic substance found in some plants. This compound reduced silver ions from its monovalent state from the silver nitrate salt to its zero-valent state, which was gathered together with a size range of 1–10 nm [78]. Subsequent studies with these synthesized nanoparticles revealed their anticancer potentials when they were used at a concentration of 5 micrograms per mL with a potency of almost 60% [78, 79]. Similarly, synthesis of silver nanoparticles was reported using the extract of plant *Desmodium* triflorum.

These were attributed to the bioreducing abilities of hydroxyl ions, NAD+, and ascorbic acid in the extract [80]. Similarly, excellent nanoparticles, in terms of size and morphology, were

Aloe vera *Ocimum tenuiflorum* (tulsi) *Azadirachta indica* (neem)

Geranium species *Camellia sinensis* (tea) *Datura metel*

Fig. 3: Some plant species used to make nanoparticles.

obtained from the leaf extract of *Datura metel* by Kesharwani and coworkers. The product in this study had excellent stability and size limit was also highly appropriate within the range of 16–40 nanometers. The most interesting aspect revealed in this study was the presence of several bioactive compounds in the concerned leaf extracts, ranging from alkaloids, amino acids, alcoholic compounds, and several other chelating proteins, which were collectively considered responsible for the reduction of silver ions in the nanoparticle form. Further analysis found that alcoholic intermediates such as those of quinol and chlorophyll pigments were responsible for reduction of silver ions to the zero-valent forms and their excellent stabilization as product formation [58]. Table 4 provides us a detailed picture regarding the major plant species used for nanoparticle synthesis. An interesting aspect of plant mediated nanoparticle synthesis is the fact that the bioconversions are undermuch better control as compared to other biological methods employed for nanoparticle synthesis. Many useful plant species such as those of *Jatropha*, *Geranium*, and common lotus plant (listed in Table 6), have been viciously used for nanoparticle

Table 4: Major plant species employed for nanoparticle synthesis.

Sr.No.	Plant involved	Type of nanoparticle	Morphology and size	Ref.
1	*Acalypha indica*	Ag	20–30 nm, spherical	[81]
2	*Aloe vera*	Au and Ag	50–350nm,spherical, triangular	[57]
3	*Azadirachta indica* (neem)	Ag/Au bimetallic	50–100 nm	[82]
4	*Cinnamomum camphora*	Au and Pd	3.2–20 nm, cubic hexagonal crystalline	[83]
5	*Datura metel*	Ag	16–40 nm, quasilinear superstructures	[58]
6	*Geranium* leaf	Au	16–40 nm	[77]
7	*Jatropha curcas* L. latex	Pb	10–12.5nm	[84]
8	*Nelumbo nucifera* (lotus)	Ag	25–80 nm, spherical and triangular	[85]
9	*Rhododedendron dauricam*	Ag	25–40 nm, spherical	[86]

synthesis. A significant observation drawn out from Table 4 clearly shows that most of the plants have been used for the synthesis of gold and silver nanoparticles. Another interesting aspect of concern is the fact that these plants give these products only when specifically cultured under a particular set of variable conditions that include temperature, pH, and characteristic salt concentrations administered. The only thing that makes the plant derived nanoparticle synthesis route, less popular, is the fact that plant cell culture is relatively difficult when compared to microbial cultures. Moreover, in some cases, the callus development is essential which imparts more complicacy to the process. Fig. 4 presents the summary of plant mediated nanoparticle synthesis which tells us what the possible configurations for nanoparticle synthesis through the biochemically rich plant species can be. Plant extract material is rich in compounds of different nature such as those of flavonoids, terpenoids, and many other phenolic intermediates which brings about the bioreduction of metal salt solutions administered during the culture. Fig. 4

further explains how plant driven nanoparticle synthesis can be directed towards highly selective and specific nanoparticle formation which

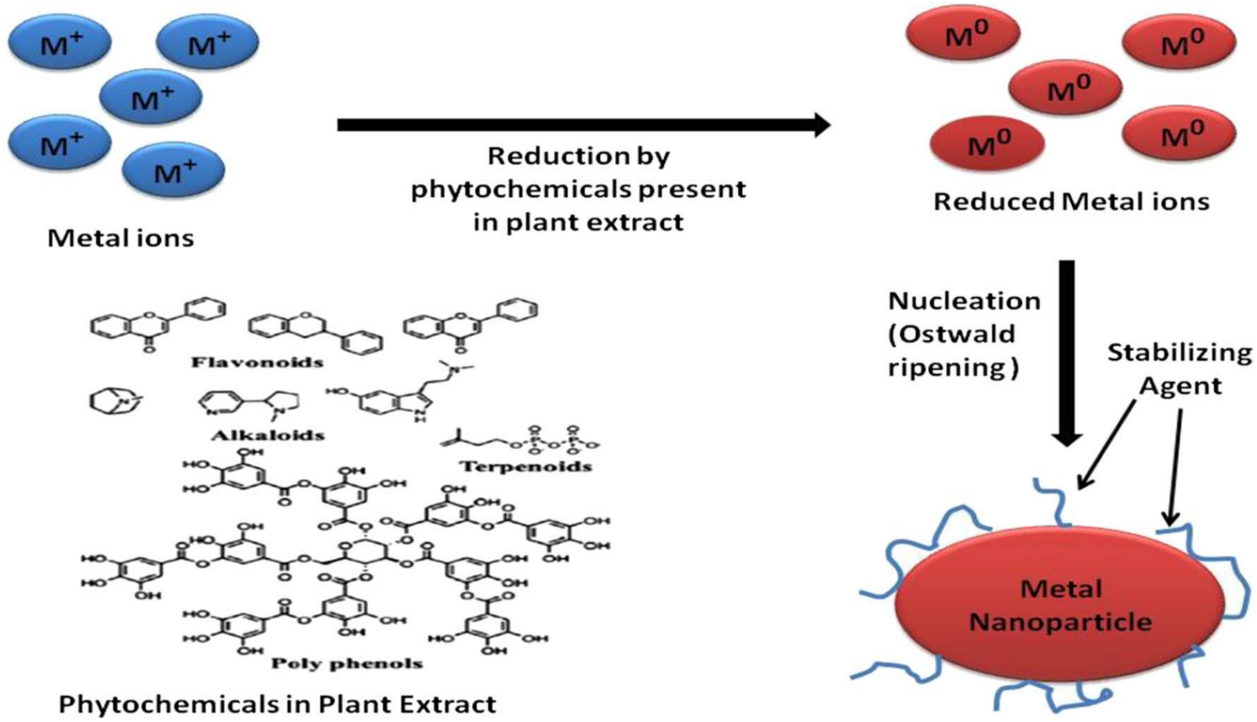

Fig. 4 Mechanism of nanoparticle formation by plant leaf extract

can be either in the form of dictated aggregation mediated through self-assembly or the nanoparticle stabilization by their synthesis within controlled structures that can hold them without altering their stabilities. This particular ability can be very useful for applications of integrated nanostructure assembly. Fig. 4 explains that nanoparticles are not only synthesized by plants but they can also be formed if the surrounding environment presents with stabilizing environment to mediate the redox status required for their critical formation.This is further helpful for the optimization of these nanoparticles with respect to their properties. First step explains the formation of zero-valent nanoparticles which lead to the growth of these particles upon their aggregations mediated via noncovalent interactions.The second step shows thematrix stabilization of a particular type of nanoparticles which can be in a resinmatrix or in some other hybrid form. The formation of phenolic resins composed of nanoparticles of a particular kind is one such application of this kind. Plants can therefore serve as readily available and faster biochemically rich sources for nanoparticle synthesis.

ANTIMICROBIAL ACTIVITY

Various studies have been carried out to ameliorate antimicrobial functions because of the growing microbial resistance towards common antiseptic and antibiotics. According to in vitro antimicrobial studies, the metallic nanoparticles effectively obstruct the several microbial species [87]. The antimicrobial effectiveness of the metallic nanoparticles depends upon two important parameters: (a) material employed for the synthesis of the nanoparticles and (b) their particle size. Over the time, microbial resistance to antimicrobial drugs has become gradually raised and is therefore a considerable threat to public health. For instance, antimicrobial drug resistant bacteria contain methicillin-resistant, sulfonamide-resistant, penicillin-resistant, and vancomycin- resistant properties [88]. Antibiotics face many current challenges such as combatting multidrug-resistant mutants and biofilms. The effectiveness of antibiotic is likely to decrease rapidly because of the drug resistance capabilities of microbes. Hence, even when bacteria are treated with large doses of antibiotics, diseases will persist in living beings. Biofilms are also an important way of providing multidrug resistance against heavy doses of antibiotics. Drug resistance occurs mainly in infectious diseases such as lung infection and gingivitis [89]. The most promising approach for abating or avoiding microbial drug resistance is the utilization of nanoparticles. Due to various mechanisms, metallic nanoparticles can preclude or overwhelm the multidrug-resistance and biofilm formation, as described in Figs. 5 and 6.

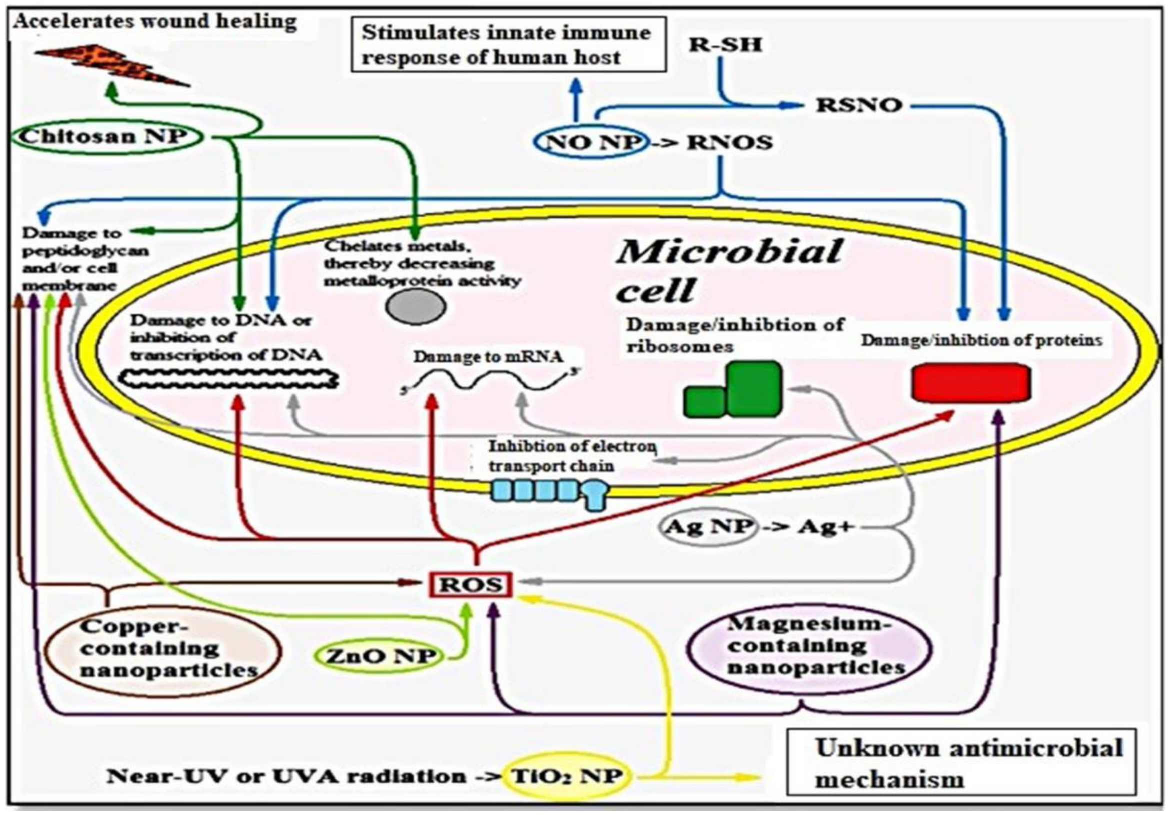

Fig. 5 Schematic for the multiple antimicrobial mechanisms in different metal nanoparticles against microbial cells.

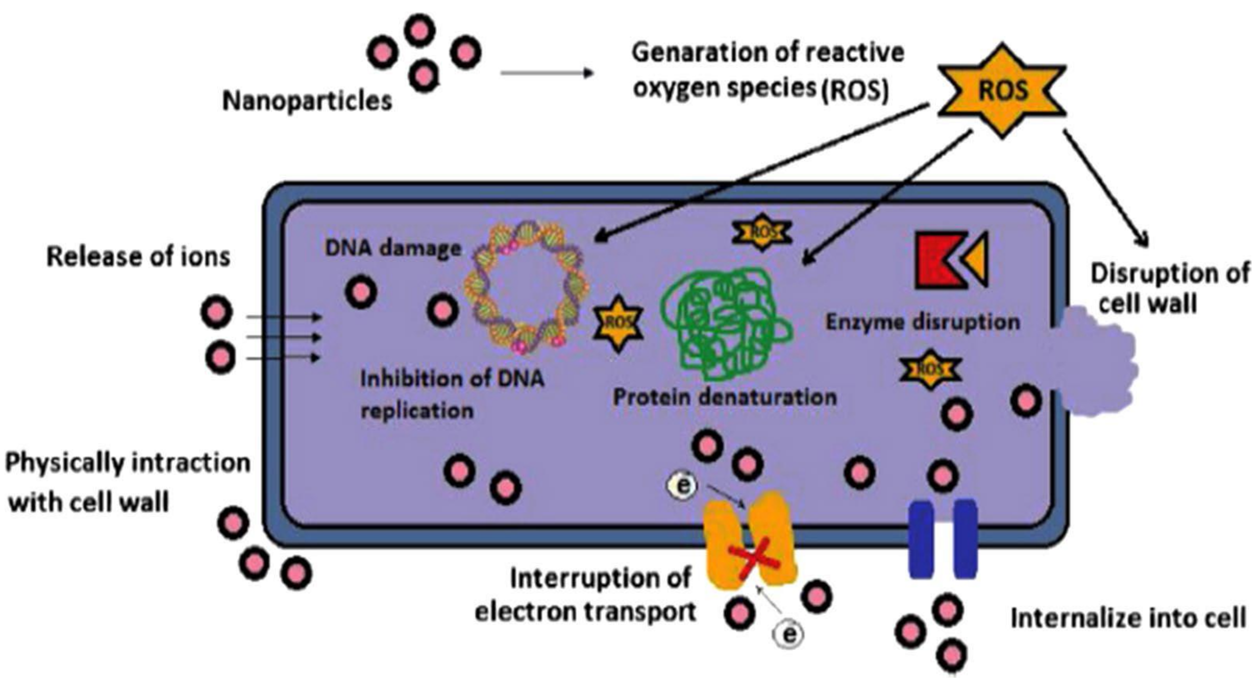

Fig. 6 Various mechanisms of antimicrobial activity of metal nanoparticles.

Various nanoparticles employ multiple mechanisms concurrently to fight microbes [e.g., metal-containing nanoparticles, NO-releasing nanoparticles (NO NPs), and chitosan-containing nanoparticles (chitosan NPs)]. Nanoparticles can fight drug resistance because they operate using multiple mechanisms. Therefore, microbes must simultaneously have multiple gene mutations in their cell to overcome the nanoparticle mechanisms. However, simultaneous multiple biological gene mutations in the same cell are unlikely [90]. Multiple mechanisms observed in nanoparticles are discussed in Table 4. Silver nanoparticles are the most admired inorganic nanoparticles, and they are utilized as efficient antimicrobial, antifungal, antiviral, and anti-inflammatory agents [91]. According to a literature survey, the antimicrobial potential of silver nanoparticles can be described in the following ways: (1) denaturation of the bacterial outer membrane [92], (2) generation of pits/gaps in the bacterial cell membrane leading to fragmentation of the cell membrane [93, 94], and (3) interactions between Ag NPs and disulfide or sulfhydryl groups of enzymes disrupt metabolic processes; this step leads to cell death [95]. The shape-dependent antimicrobial activity was also examined. According to Pal et al. [96], truncated triangular nanoparticles are highly reactive in nature because their high-atom-density surfaces have enhanced antimicrobial activity.

The synthesis of Au nanoparticles is highly useful in the advancement of effective antibacterial agents because of their non-toxic nature, queer ability to be functionalized, polyvalent effects, and photo-thermal activity [97–99]. However, the antimicrobial action of gold nanoparticles is not associated with the production of any reactive oxygen species-related process [100]. To investigate the antibacterial potential of the Au nanoparticles, researchers attempted to attach nanoparticles to the bacterial membrane followed by modifying the membrane potential, which lowered the ATP level. This attachment also inhibited tRNA binding with the ribosome [100]. Azam et al. [101] examined the antimicrobial potential of zinc oxide (ZnO), copper oxide (CuO), and iron oxide (Fe_2O_3) nanoparticles toward gram-negative bacteria (*Escherichia coli*, *Pseudomonas aeruginosa*) and gram-positive bacteria (*Staphylococcus Aureus* and *Bacillus subtilis*). Accordingly, the most intense antibacterial activity was reported for the ZnO nanoparticles. In contrast, Fe_2O_3 nanoparticles exhibited the weakest antibacterial effects. The order of antibacterial activities of nanoparticles was found to

be as ZnO (19.89 ± 1.43 nm), CuO (29.11 ± 1.61 nm), and Fe_2O_3 (35.16 ± 1.47 nm). These results clearly depicts that the size of the nanoparticles also play a momentous role in the antibacterial potential of each sample [101]. The anticipated mechanism of antimicrobial action of ZnO nanoparticles is: (1) ROS generation, (2) zinc ion release on the surface, (3) membrane dysfunction, and (4) entry into the cell. Also, the antimicrobial potential of ZnO

nanoparticles is concentration and surface area dependent [102]. Mahapatra et al. [103] determined the antimicrobial action of copper oxide nanoparticles towards several bacterial species such as *Klebsiella pneumoniae*, *P. aeruginosa*, *Shigella Salmonella paratyphi* s. They found that CuO nanoparticles exhibited suitable antibacterial activity against those bacteria. It was assumed that nanoparticles should cross the bacterial cell membrane to damage the crucial enzymes of bacteria, which further induce cell death. For instance, green synthesized nanoparticles show enhanced antimicrobial activity compared to chemically synthesized or commercial nanoparticle This is because the plants [such as *Ocimum sanctum* (Tulsi) and *Azadirachta indica* (neem)] employe for synthesis of nanoparticles have medicinal properties [104, 105]. For example, green synthesized silver nanoparticles showed an efficient and large zone of clearance against various bacterial strains compared to commercial silver nanoparticles (Fig. 7) [106].

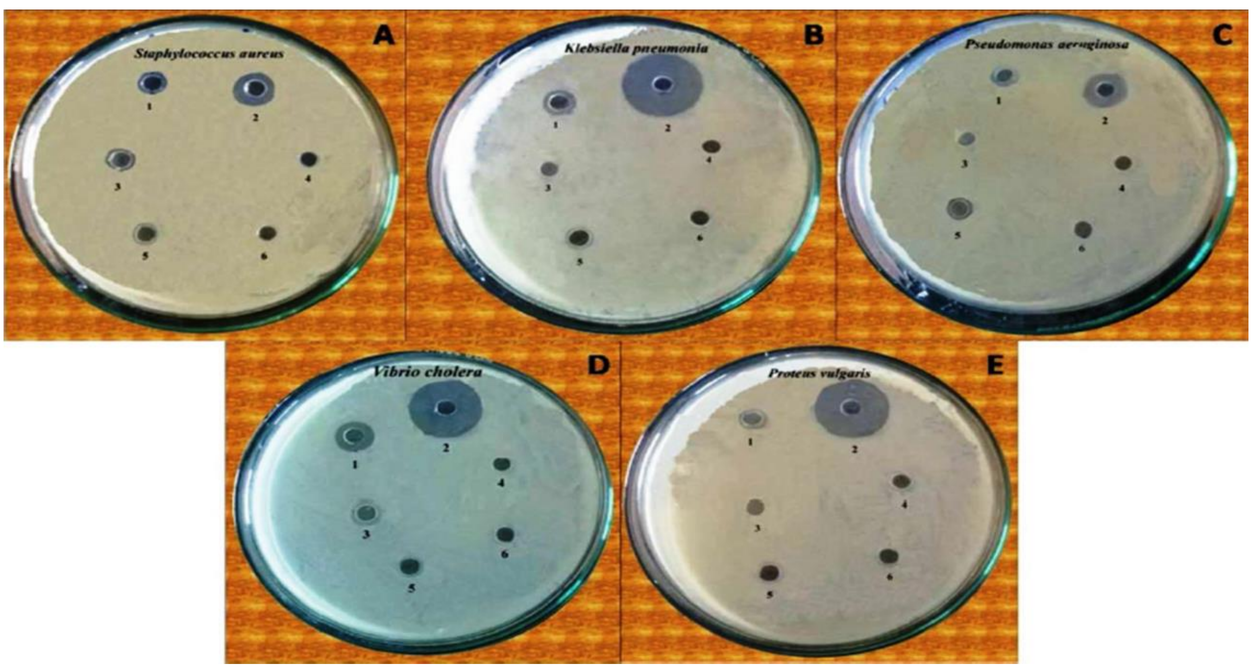

Fig. 7 Schematic for the antimicrobial activity for the five bacterial strains: a *Staphylococcus aureus*, b *Klebsiella pneumonia*, c *Pseudomonas aeruginosa*, d *Vibrio cholera*, and e *Proteus vulgaris*. Numbers of 1 through 6 inside each strain denote: (1) nickel chloride, (2) control ciprofloxacin, (3) *Desmodium gangeticum* root extract, (4) negative

control, (5) nickel NPs prepared by a green method, and (6) nickel NPs prepared by a chemical method.

CATALYTIC ACTIVITY

4-Nitrophenol and its derivatives are used to manufacture herbicides, insecticides, and synthetic dyestuffs, and they can significantly damage the ecosystem as common organic pollutants of wastewater. Due to its toxic and inhibitory nature, 4-nitrophenol is a great environmental concern. Therefore, the reduction of these pollutants is crucial. The 4-nitrophenol reduction product, 4-aminophenol, has been applied in diverse fields as an intermediate for paracetamol, sulfur dyes, rubber antioxidants, preparation of black/white film developers, corrosion inhibitors, and precursors in antipyretic and analgesic drugs [107, 108]. The simplest and most effective way to reduce 4-nitrophenol is to introduce NaBH4 as a reductant and a metal catalyst such as Au NPs [109], Ag NPs [110], CuO NPs [111], and Pd NPs [112]. Metal NPs exhibit admirable catalytic potential because of the high rate of surface adsorption ability and high surface area to volume ratio. Nevertheless, the viability of the reaction declines as a consequence of the substantial potential difference between donor (H_3BO_3/NaBH4) and acceptor molecules (nitrophenolate ion), which accounts for the higher activation energy barrier.
Metallic NPs can promote the rate of reaction by increasing the adsorption of reactants on their surface, thereby diminishing activation energy barriers [113, 114] (Fig. 8).

The UV–visible spectrum of 4-nitrophenol was characterized by a sharp band at 400 nm as a nitrophenolate ion was produced in the presence of NaOH. The addition of Ag NPs (synthesized by *Chenopodium aristatum* L. stem extract) to the reaction medium led to a fast decay in the absorption intensity at 400 nm, which was concurrently accompanied by the appearance of a comparatively wide band at 313 nm, demonstrating the formation of 4-aminophenol [115] (Fig. 9).

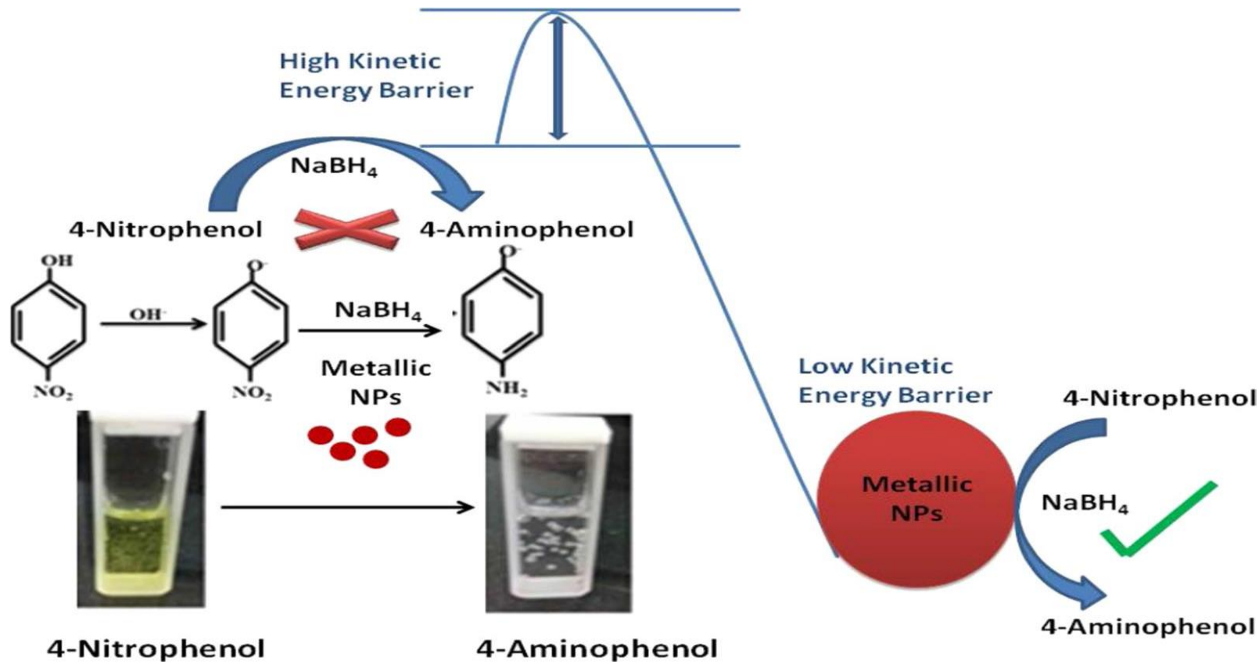

Fig. 8 Schematic of the metallic NP-mediated catalytic reduction of 4-nitrophenol to 4-aminophenol.

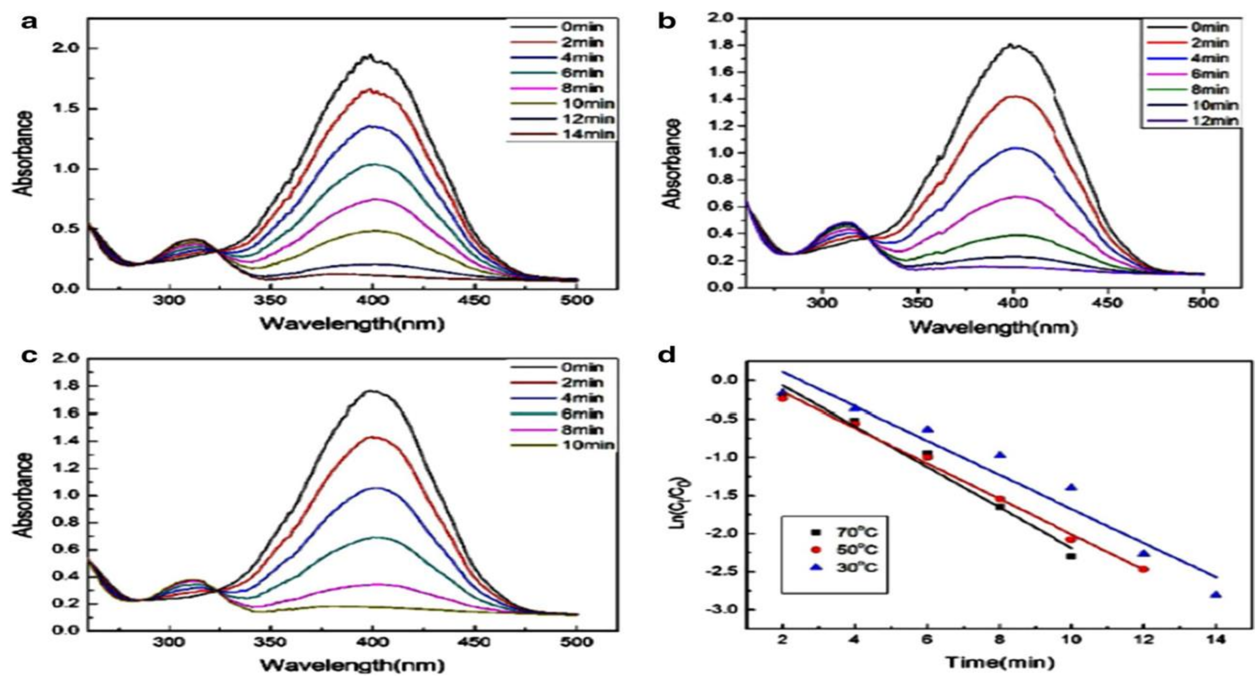

Fig. 9 UV-visible spectra illustrating *Chenopodium aristatum* L. stem extract synthesized Ag NP-mediated catalytic reduction of 4-NP to 4-AP at three different temperatures a 30 °C, b 50 °C, and c 70 °C. Reduction in the absorption intensity of the characteristic

nitrophenolate band at 400 nm accompanied by concomitant appearance of a wider absorption band at 313 nm indicates the formation of 4-AP

CONCLUSION

'Green' synthesis of metal and metal oxide nanoparticles has been a highly attractive research area over the last decade. Numerous kinds of natural extracts (i.e., biocomponents like plant, bacteria, fungi, yeast, and plant extract) have been employed as efficient resources for the synthesis and/or fabrication of materials. Among them, plant extract has been proven to possess high efficiency as stabilizing and reducing agents for the synthesis of controlled materials (i.e., controlled shapes, sizes, structures, and other specific features). This research article was organized to encompass the 'state of the art' research on the 'green' synthesis of metal/metal oxide nanoparticles and their antimicrobial activity.

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