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T. Bastin Baskar and C Elizabeth Rani

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# Green Synthesis Mechanism and Environmental Applications of Metals and their Oxide Nanoparticles: A Review

T. Bastin Baskar\*<sup>1</sup> and C Elizabeth Rani<sup>2</sup>

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## ABSTRACT

Nanoparticles have arisen as perhaps the most sought-after materials discovering application in different areas. Synthesis of green nanoparticles has attracted in broad interest worldwide because of its biocompatibility and tremendous potential for usage as catalysts, antimicrobial agents, in energy harvesting, cancer/gene therapy, sensing etc. Inherent properties of nano-materials like specific size, shape, composition, greater surface area to volume ratio and purity of individual constituents makes it an entrancing multifunctional material. Different groups of living organisms (prokaryotes and eukaryotes) and biomolecules are progressively being utilized as bio-template for designing nanoscale materials. Characterization tools, for example, SEM, TEM, AFM, FTIR, XRD, NMR help in disentangling their unique properties. In this review, we summarized the fundamental processes and components of "green" synthesis approaches, particularly for metal and metal oxide [e.g., gold (Au), silver (Ag), copper oxide (CuO), and zinc oxide (ZnO)] nanoparticles utilizing normal concentrates. Critically, we investigated the role of biological components, essential phytochemicals (e.g., flavonoids, alkaloids, terpenoids, amides, and aldehydes) as reducing agents and solvent systems. The stability/toxicity of nanoparticles and the related surface designing procedures for accomplishing biocompatibility are likewise examined. At long last, we covered utilizations of such integrated items to ecological remediation as far as antimicrobial activity, catalytic activity, removal of pollutants dyes, and heavy metal ion sensing.

**Key words:** Silver, Phytochemicals, Catalysts, Antimicrobial agents

In science and technology, one among the quickly creating ideas in the most recent years is nanotechnology, which has brought tremendous development. The nanomaterial which includes particular physicochemical properties has the potential to develop new systems, structures, devices, and nanoplatfroms with impending bids in extensive variety of disciplines [1-2]. Nanomaterials are particles that are in nanoscale size, and they are very small particles with improved thermal conductivity, catalytic reactivity, nonlinear optical performance, and chemical stability due to their large surface area-to-volume ratio [3] is quality has drawn in numerous scientists to find novel procedures for their synthesis. However regular procedures (physical and compound techniques) utilize less an ideal opportunity to synthesize bulk amount of nanoparticles, they require toxic chemicals like protective agents to maintain stability, which leads to toxicity in the environment. Remembering this, green innovation by utilizing plants is ascending as an eco-friendly, nontoxic, and safe option, since plant extract-mediated biosynthesis of nanoparticles is

economically advantageous and offers natural capping agents in the form of proteins [4]. To direct compound harmfulness in the climate, natural combination of different metal oxide and metal nanoparticles through plant extraction is utilized, which is a marginal technique for regulating chemical synthesis, and it allows a particular shape and size of nanoparticles with a meticulous synthesis [5].

Based on the origin of nanomaterial, it is classified into natural nanomaterial and artificial nanomaterial [6]. On considering the components of nanomaterial, it is ordered as zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3-D) nanomaterials. i.e., zero-dimensional nanomaterials have nano dimensions at all three directions; one-dimensional nanomaterials have just a single nano dimension which is outside to the nanometer reach; and two-dimensional nanomaterials have two nano dimensions outside to the nanometer range, while three-dimensional nanomaterials have all the nano dimensions outside to the nanometer range. These comprise bulk materials developed with individual blocks that are in the nanometer scale (1–100 nm) [7].

As per the primary setup and morphology, nanomaterials have been separated into amalgamated materials and nano dispersions. Amazingly extended macromolecules are dendrimers with the measurements in the nanometer scale. In the metal-based materials, the chief component for these

\* T. Bastin Baskar

✉ bastinbaskar@gmail.com

<sup>1-2</sup> Department of Biotechnology, Hindustan College of Arts and Science, Chennai - 600 020, Tamil Nadu, India

particles is metal, where the nanomaterials included nano silver, nanogold, metal oxides like titanium dioxide, finally closely packed semiconductors such as quantum dots. The morphology of carbon-based nanomaterials is tubes, hollow spheres, or ellipsoids. i.e., carbon nanomaterials that are spherical and ellipsoidal are referred as fullerenes and cylindrical ones are called as nanotubes [8].

Curiously, 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 evident world, it is beneficial that the properties, behavior, and types of nanomaterials ought to be improved to meet the previously mentioned focuses. 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. Essentially, green synthesis of materials/nanomaterials, delivered through regulation, control, clean up, and remediation process, will directly help uplift their environmental friendliness. Some basic principles of "green synthesis" would thus be able to be clarified by a few parts 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 syntheses are needed to keep away from the creation of undesirable or unsafe results through the build-up of reliable, sustainable, and eco-friendly synthesis procedures. The utilization of ideal solvent systems and natural resources (such as organic systems) is fundamental to accomplish this objective. Green synthesis of metallic nanoparticles has been various biological materials (e.g., bacteria, fungi, algae, and plant extracts). Among the accessible green methods of synthesis for metal/metal oxide nanoparticles, use of plant separates is a somewhat straightforward and simple interaction to create nanoparticles everywhere scale comparative with microorganisms or potentially organisms interceded union. These items are referred to aggregately as biogenic nanoparticles.

Green synthesis procedures 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 comprehensively viewed as because of the accessibility of successful phytochemicals in various plant extracts, especially in leaves such as ketones, aldehydes, flavones, amides, terpenoids, carboxylic acids, phenols, and ascorbic acids. These segments are capable of reducing metal salts into metal nanoparticles [9]. 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 [10].

Here, we summarized the current advances of research on the green synthesis of metal/metal oxide nanoparticles with their advantages over chemical synthesis methods. The main aim of this literature study is to provide detailed mechanisms

for green synthesis and their real-world environmental remediation applications. By and large, we will likely methodically portray "green" amalgamation systems 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.

#### Plants for "green" synthesis

Plants can possibly amass certain amounts of heavy metals in their diverse parts. Thus, biosynthesis procedures utilizing plant extracts have gained increased consideration as a simple, efficient, cost effective and feasible methods as well as an excellent alternative means to conventional preparation methods for nanoparticle production. There are different plants that can be used to diminish and balance out the metallic nanoparticles in "one-pot" synthesis process. Numerous analysts have utilized green synthesis process for preparation of metal/metal oxide nanoparticles via plant leaf extracts to further investigate their different applications.

Plants have biomolecules (like carbohydrates, proteins, and coenzyme) with excellent potential to reduce metal salt into nanoparticles. Like other biosynthesis processes, gold and silver metal nanoparticles were first investigated in plant extract-assisted synthesis. Different plants [including aloe vera (*Aloe barbadensis* Miller), Oat (*Avena sativa*), alfalfa (*Medicago sativa*), Tulsi (*Osimum sanctum*), Lemon (*Citrus limon*), Neem (*Azadirachta indica*), Coriander (*Coriandrum sativum*), Mustard (*Brassica juncea*) and lemon grass (*Cymbopogon flexuosus*)] have been used to combine silver nanoparticles and gold nanoparticles, as recorded in (Table 1). The significant piece of this kind of exploration has investigated the ex vivo synthesis of nanoparticles, while metallic nanoparticles can be formed in living plants (in vivo) by reducing metal salt ions absorbed as soluble salts. The in vivo synthesis of nanoparticles like zinc, nickel, cobalt, and copper was also observed in mustard (*Brassica juncea*), alfalfa (*Medicago sativa*), and sunflower (*Helianthus annuus*) [11]. Also, ZnO nanoparticles have been prepared with a great variety of plant leaf extracts such as coriander (*Coriandrum sativum*) [12], crown flower (*Calotropis gigantean*) [13], copper leaf (*Acalypha indica*) [14], China rose (*Hibiscus rosa-sinensis*) [15], Green Tea (*Camellia sinensis*) [16], and aloe leaf broth extract (*Aloe barbadensis* Miller) [17]. Perusers can refer to the work of Iravani [18] for a comprehensive overview of plant materials utilized for the biosynthesis of nanoparticles.

#### Characterization of ZnO NPs

The blended nanoparticles are described by using various methods: FTIR (Fourier change infrared spectroscopy), EDAX (energy scattering investigation of X-beam), AFM (nuclear power microscopy), XPS (X-beam photoelectron microscopy), ATR (lessened absolute reflection), UV-DRS (UV-noticeable diffuse reflectance spectroscopy), XRD (X-beam diffractometer), TEM (transmission electron microscopy), TG-DTA (thermogravimetric-differential warm examination), DLS (dynamic light dissipating), FE-SEM (field discharge checking electron microscopy), PL (photoluminescence examination), Raman spectroscopy, and SEM (filtering electron microscopy) [19-21]. Plants are being inspected widely especially that have a place with Lamiaceae family, for example, Vitex negundo [22], Plectranthus amboinicus [23], and Anisochilus carnosus [24] which had the development of NP with various shapes, for example, hexagonal, bar formed with agglomerates, quasispherical, and round, and further different sizes are likewise seen. From the result, it is plainly recognized that the size of combined NPs is

diminished on expanding the grouping of a plant extricate [25–26].

From the outcomes, the size range is being noticed and looked at utilizing different strategies, for example, TEM, XRD, and FE-SEM which had a nearer scope of qualities [27], though SEM and EDAX had a comparable outcome assorted from XRD results. Through Debye–Scherrer equation, synthesis of NPs from both *Vitex negundo* flower and leaf had a similar size of 38.17 nm, which was confirmed through XRD analysis. For the synthesizing ZnO NPs, leaves of *Azadirachta indica* from Meliaceae family are generally being used [28–29]. A comparative size scope of NPs was distinguished in each trial, which was affirmed through the examination of TEM and XRD with nanobuds, hexagonal plate shape, and circular shape. From the investigations, it is uncovered that the development of NPs is through the inclusion of amine, carboxylic corrosive, carbonate moieties, liquor, alkane, and amide, which was additionally affirmed by FTIR contemplates. Aloe vera's leaf strip and new leaf separate have a place with Liliaceae family [30–31]. Agglomerate formation was found in the NP synthesis, which was extracted from *Moringa oleifera*, *Calotropis gigantea*, *Plectranthus amboinicus*, *Agathosma betulina*, *Nephelium lappaceum*, and *Pongamia pinnata*. To affirm the synthesis of NPs, UV-Vis spectrophotometry is employed, and the crystal NPs are obtained through centrifugation of mixture and drying the pellet in a hot air oven [32].

#### Plant extract-based mechanism

For nanoparticle synthesis mediated by plant leaf extract, the extract is blended in with metal precursor solutions at various reaction conditions [33]. The parameters determining the conditions of the plant leaf extract (such as types of phytochemicals, phytochemical concentration, metal salt concentration, pH, and temperature) are conceded to control the rate of nanoparticle formation as well as their yield and stability [34]. The phytochemicals present in plant leaf extracts can possibly diminish metal particles in a much shorter time as compared to fungi and bacteria, which demands the longer incubation time [35]. Accordingly, plant leaf extracts are considered as a brilliant and considerate hotspot for metal just as metal oxide nanoparticle synthesis. Also, plant leaf extract plays a dual role by acting as both reducing and stabilizing agents in nanoparticles synthesis process to facilitate nanoparticles synthesis [36]. The arrangement of the plant leaf separate is likewise a significant factor in nanoparticle synthesis, for instance various plants include changing concentration levels of phytochemicals [37]. The primary phytochemicals present in plants are flavones, terpenoids, sugars, ketones, aldehydes, carboxylic acids, and amides, which are responsible for bioreduction of nanoparticles [38].

Flavonoids contain different functional groups, which have an improved capacity to reduce metal ions. The reactive hydrogen atom is released due to tautomeric transformations in flavonoids by which enol- form is converted into the keto-form. This cycle is acknowledged by the decrease of metal particles into metal nanoparticles. In sweet basil (*Ocimum basilicum*) extricates, enol-to keto-change is the critical factor in the blend of biogenic silver nanoparticles [39]. Sugars, for example, glucose and fructose exist in plant extracts can also be responsible for the formation of metallic nanoparticles. Note that glucose was capable of participating in the formation of metallic nanoparticles with different size and shapes, whereas fructose-mediated gold and silver nanoparticles are monodispersed in nature [40].

A FTIR analysis of green synthesized nanoparticles by means of plant extracts confirmed that nascent nanoparticles

were repeatedly found to be associated with proteins the metal ions. Gruen *et al.* [41] observed that amino acids (viz cysteine, arginine, lysine, and methionine are capable in binding with silver ions. Tan *et al.* [42] tried the entirety of the 20 normal  $\alpha$ -amino acids to establish their efficient potential behavior towards the reduction of Au<sup>0</sup> metal ions. Plant extracts are comprised of carbohydrates and proteins biomolecules, which act as a reducing agent to promote the formation of metallic nanoparticles. Likewise, the proteins with functionalized amino groups ( $-\text{NH}_2$ ) accessible in plant extracts can effectively partake in the decrease of metal particles [43]. The functional groups (such as  $-\text{C}-\text{O}-\text{C}-$ ,  $-\text{C}-\text{O}-$ ,  $-\text{C}=\text{C}-$ , and  $-\text{C}=\text{O}-$ ) present in phytochemicals such as flavones, alkaloids, phenols, and anthracenes can help to generate metallic nanoparticles.

As indicated by Huang *et al.* [44], the absorption peaks of FTIR spectra at (1) 1042 and 1077, (2) 1606 and 1622, and (3) 1700–1800  $\text{cm}^{-1}$  imply the stretching of (1)  $-\text{C}-\text{O}-\text{C}-$  or  $-\text{C}-\text{O}-$ , (2)  $-\text{C}=\text{C}-$  and (3)  $-\text{C}=\text{O}$ , individually. In view of FTIR examination, they affirmed that utilitarian gatherings like  $-\text{C}-\text{O}-\text{C}-$ ,  $-\text{C}-\text{O}-$ ,  $-\text{C}=\text{C}-$ , and  $-\text{C}=\text{O}$ , are the covering ligands of the nanoparticles [45]. The fundamental job of the covering ligands is to balance out the nanoparticles to forestall further development and agglomeration. Kesharwani *et al.* [46] covered photographic movies utilizing an emulsion of silver bromide. At the point when light hit the film, the silver bromide was sharpened; this uncovered film was put into a solution of hydroquinone, which was additionally oxidized to quinone by the activity of sensitized silver ion. The silver ion was reduced to silver metal, which stayed in the emulsion. Based on the chemistry of photography, we accepted that hydroquinone or plastoquinone or quinol (alcoholic compound) fill in as a main reducing agent for the reduction of silver ions to silver nanoparticles through non-cyclic photophosphorylation. Hence, this examination demonstrates that the biomolecules and heterocyclic compounds exist in plant extract were responsible for the extracellular synthesis of metallic nanoparticles by plants. It has effectively been established that various plant phytochemicals including alkaloids, terpenoids, phenolic acids, sugars, polyphenols, and proteins play a significant role in the bioreduction of metal salt into metallic nanoparticles. For instance, Shanakr *et al.* [47] affirmed that the terpenoids present in geranium leaf extract actively take part in the conversion of silver ions into nanoparticles. Eugenol is a primary terpenoid part of *Cinnamomum zeylanisum* (cinnamon) extracts, and it assumes a pivotal part for the bioreduction of  $\text{HAuCl}_4$  and  $\text{AgNO}_3$  metal salts into their respective metal nanoparticles. FTIR information showed that  $-\text{OH}$  groups originating from eugenol disappear during the formation of Au and Ag nanoparticles. After the formation of Au nanoparticles, carbonyl, alkenes, and chloride functional groups showed up. A few different gatherings [e.g.,  $\text{R}-\text{CH}$  and  $-\text{OH}$  (aqueous)] were additionally found both prior and then afterward the creation of Au nanoparticles [48]. Regardless, the specific key component for metal oxide nanoparticle arrangement by means of plant separates is as yet not completely inferred. As a rule, there are three periods of metallic nanoparticle synthesis from plant extracts: (1) the activation phase (bioreduction of metal ions/salts and nucleation process of the reduced metal ions), (2) the growth phase (spontaneous combination of tiny particles with greater ones) via a process acknowledged as Ostwald ripening, and (3) the last one is termination phase (defining the final shape of the nanoparticles) [49–50]. The process of nanoparticle formation by plant extract is depicted in (Fig 1) [51].

#### Environmental applications



*Antimicrobial activity*

Different examinations have been completed to improve antimicrobial functions as a result of the developing microbial resistance towards common antiseptic and antibiotics. As indicated by in vitro antimicrobial investigations, the metallic nanoparticles viably obstruct the several microbial species [52]. The antimicrobial viability of the metallic nanoparticles depends upon two significant parameters: (a) material employed for the synthesis of the nanoparticles and (b) their particle size. Throughout the time, microbial resistance to antimicrobial drugs has become gradually raised and is in this way an extensive danger to general wellbeing. For instance, antimicrobial drug resistant bacteria contain methicillin-resistant, sulfonamide-resistant, penicillin-resistant, and vancomycin-resistant properties [53]. Antibiotics face numerous current difficulties, for example, combatting multidrug-resistant mutants and biofilms. The viability of antibiotic is likely to decrease rapidly because of the drug resistance capabilities of microbes. Consequently, in any event, when bacteria are treated with enormous doses of antibiotics, diseases will continue living creatures. Biofilms are additionally a significant method of giving multidrug resistance against heavy doses of antibiotics. Drug resistance happens mostly in infectious diseases such as lung infection and gingivitis [54]. The most encouraging methodology for abating or avoiding microbial drug resistance is the use of nanoparticles. Because of different systems, metallic

nanoparticles can preclude or overwhelm the multidrug-resistance and biofilm formation.

Different nanoparticles utilize numerous components simultaneously to fight microbes [e.g., metal-containing nanoparticles, NO-releasing nanoparticles (NO NPs), and chitosan-containing nanoparticles (chitosan NPs)]. Nanoparticles can fight drug resistance since they work utilizing various components. Thusly, 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 [55].

Silver nanoparticles are the most appreciated inorganic nanoparticles, and they are used as effective antimicrobial, antifungal, antiviral, and anti-inflammatory agents [56]. According to a literature survey, the antimicrobial potential of silver nanoparticles can be portrayed in the following ways: (1) denaturation of the bacterial outer membrane [57], (2) generation of pits/gaps in the bacterial cell membrane leading to fragmentation of the cell membrane [58–59], and (3) interactions between Ag NPs and disulfide or sulfhydryl groups of enzymes disrupt metabolic processes; this step leads to cell death [60]. The shape-dependent antimicrobial activity was also examined. According to Pal *et al.* [61], shortened triangular nanoparticles are highly reactive in nature in light of the fact that their high-atom-density surfaces have enhanced antimicrobial activity.

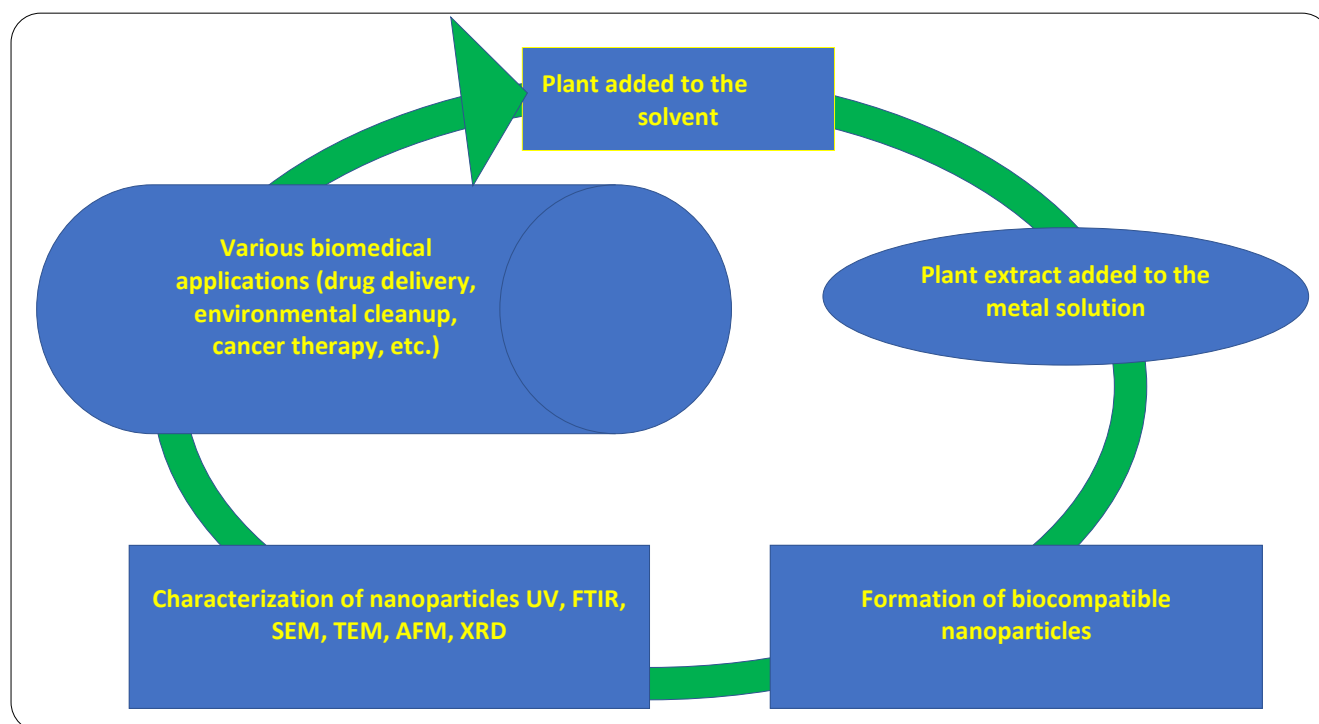


Fig 1 Nanoparticle formation by plant extract

The synthesis of Au nanoparticles is profoundly 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 [62–64]. Be that as it may, the antimicrobial activity of gold nanoparticles isn't related with the creation of any reactive oxygen species-related process [65]. To examine the antibacterial potential of the Au nanoparticles, specialists endeavored 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 [66]. Azam *et al.* [67] examined the antimicrobial potential of zinc oxide (ZnO),

copper oxide (CuO), and iron oxide ( $\text{Fe}_2\text{O}_3$ ) nanoparticles toward gram-negative bacteria (*Escherichia coli*, *Pseudomonas aeruginosa*) and gram-positive bacteria (*Staphylococcus Aureus* and *Bacillus subtilis*). In like manner, the most exceptional antibacterial activity was reported for the ZnO nanoparticles. Conversely,  $\text{Fe}_2\text{O}_3$  nanoparticles exhibited the weakest antibacterial effects. The order of antibacterial activities of nanoparticles was found to be as ZnO ( $19.89 \pm 1.43$  nm), CuO ( $29.11 \pm 1.61$  nm), and  $\text{Fe}_2\text{O}_3$  ( $35.16 \pm 1.47$  nm). These results clearly depicts that the size of the nanoparticles also play a momentous role in the antibacterial potential of each sample.

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 [68]. Mahapatra *et al.* [69] not really settled the antimicrobial activity of copper oxide nanoparticles towards a few bacterial species such as *Klebsiella pneumoniae*, *P. aeruginosa*, *Shigella* *Salmonella paratyphi* s. They found that CuO nanoparticles showed reasonable antibacterial activity against those bacteria. It was expected 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 nanoparticles. This is because the plants [such as *Ocimum sanctum* (Tulsi) and *Azadirachta indica* (neem)] utilized for synthesis of nanoparticles have medicinal properties [70-71]. For instance, green synthesized silver nanoparticles showed a efficient and large zone of clearance against various bacterial strains compared to commercial silver nanoparticles [72].

#### Catalytic activity

4-Nitrophenol and its subordinates are utilized to produce herbicides, insecticides, and synthetic dyestuffs, and they can essentially harm the biological system as common organic pollutants of wastewater. Because of its poisonous and inhibitory nature, 4-nitrophenol is an extraordinary ecological concern. In this way, the decrease of these pollutants is crucial. The 4-nitrophenol reduction product, 4-aminophenol, has been applied in different fields as a transitional for paracetamol, sulfur dyes, rubber antioxidants, preparation of black/white film developers, corrosion inhibitors, and precursors in antipyretic and analgesic drugs [73-74]. The least complex and best approach to lessen 4-nitrophenol is to present NaBH<sub>4</sub> as a reductant and a metal impetus, for example, Au NPs [75], Ag NPs [76], CuO NPs [77], and Pd NPs [78]. 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<sub>3</sub>BO<sub>3</sub>/NaBH<sub>4</sub>) and acceptor molecules (nitrophenolate ion), which accounts for the higher activation energy barrier.

Metallic NPs can advance the pace of response by expanding the adsorption of reactants on their surface, in this way lessening actuation energy obstructions [79-80] (Fig 8). The UV-apparent range of 4-nitrophenol was portrayed by a sharp band at 400 nm as a nitrophenolate particle was delivered within the sight of NaOH. The expansion of Ag NPs (orchestrated by *Chenopodium aristatum* L. stem remove) to the response medium prompted a quick rot in the ingestion force at 400 nm, which was simultaneously joined by the presence of a similarly wide band at 313 nm, exhibiting the development of 4-aminophenol [81] (Fig 9).

#### Removal of pollutant dyes

Cationic and anionic dyes are a principle class of organic pollutants utilized in different applications [82]. Organic dyes assume an extremely basic part because of their massive interest in paper mills, textiles, plastic, leather, food, printing, and pharmaceuticals industries. In textile industries, about 60% of dyes are consumed in the manufacturing process of pigmentation for many fabrics [83]. After the fabric process, almost 15% of dyes are wasted and are discharged into the hydrosphere, and they represent a significant source of pollution due to their recalcitrance nature [84]. The pollutants

from these manufacturing units are the main important sources of ecological pollution. They produce undesirable turbidity in the water, which will reduce sunlight penetration, and this prompts the opposition of photochemical union and natural assaults to amphibian and marine life [85-87]. Therefore, the management of effluents containing dyes is one of the daunting challenges in the field of environmental chemistry [88].

The requirement for hygienic and safe drinking water is expanding day by day. Thinking about this reality, the utilization of metal and metal oxide semiconductor nanomaterials for oxidizing harmful contaminations has happened to extraordinary interest in late material exploration fields [89-91]. In the nano system, semiconductor nanomaterials have better photocatalytic movement relative to the bulk materials. Metal oxide semiconductor nanoparticles (like ZnO, TiO<sub>2</sub>, SnO<sub>2</sub>, WO<sub>3</sub>, and CuO) have been applied preferentially for the photocatalytic activity of synthetic dyes [92-94]. The benefits of these nano photocatalysts (e.g., ZnO and TiO<sub>2</sub> nanoparticles) are ascribable to their high surface region to mass ratio to enhance the adsorption of organic pollutants. The surface energy of the nanoparticles increases due to the large number of surface reactive sites available on the nanoparticle surfaces. This leads to an increase in rate of contaminant removal at low concentrations. Consequently, a lower quantity of nanocatalyst will be required to treat polluted water relative to the bulk material [95-98]. Like metal oxide nanoparticles, metal nanoparticles likewise show improved photocatalytic degradation of various pollutant dyes; for example, silver nanoparticles synthesized from *Z. armatum* leaf extract were utilized for the degradation of various pollutant dyes.

#### Heavy metal ion sensing

Hefty metals (like Ni, Cu, Fe, Cr, Zn, Co, Cd, Pb, Cr, Hg, and Mn) are notable for being pollutants in air, soil, and water. There are innumerable sources of heavy metal pollution such as mining waste, vehicle emissions, natural gas, paper, plastic, coal, and dye industries [99]. Some metals (like lead, copper, cadmium, and mercury ions) show improved toxicity potential even at follow ppm levels [100, 101]. Therefore, the distinguishing proof of toxic metals in the biological and aquatic environment has become a vital need for proper remedial processes [102-104]. Customary procedures dependent on instrumental frameworks by and large offer astounding affectability in multi-component investigation. In any case, trials set ups to perform such examination are exceptionally expensive, time-consuming, skill-dependent, and non-portable.

Because of the tunable size and distance-dependent optical properties of metallic nanoparticles, they have been ideally utilized for the detection of heavy metal ions in polluted water systems [105-106]. The benefits of utilizing metal NPs as colorimetric sensors for heavy metal ions in environmental systems/samples include simplicity, cost effectiveness, and high sensitivity at sub ppm levels. Karthiga *et al.* [98] blended AgNPs utilizing different plant separates utilized as colorimetric sensors for substantial metal particles like cadmium, chromium, mercury, calcium, and zinc (Cd<sup>2+</sup>, Cr<sup>3+</sup>, Hg<sup>2+</sup>, Ca<sup>2+</sup>, and Zn<sup>2+</sup>) in water. Their as-synthesized Ag nanoparticles showed colorimetric sensing of zinc and mercury ions (Zn<sup>2+</sup> and Hg<sup>2+</sup>). Likewise, AgNPs synthesized using mango fresh leaves and dried leaves (fresh, MF-AgNPs and sun-dried, MD-AgNPs) exhibited selective sensing for mercury and lead ions (Hg<sup>2+</sup> and Pb<sup>2+</sup>). Also, AgNPs prepared from pepper seed extract and green tea extract (GT-AgNPs) showed selective sensing properties for Hg<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup> ions.

Table 1 Green synthesis of metallic NPs from various plant extracts

Plant origin	Nanoparticle	Size (nm)	Morphology	Applications	Reference
<i>Aloe barbadensis</i> Miller (Aloe vera)	Gold and silver	10–30	Spherical, triangular	Cancer hyperthermia, optical coatings	[107]
<i>Aloe barbadensis</i> Miller (Aloe vera)	Indium oxide	5–50	Spherical	Solar cells, gas sensors	[108]
<i>Acalypha indica</i>	Silver	20–30	Spherical	Antibacterial activity against water borne pathogens	[109]
Apiin extracted from henna leaves	Silver and gold	39	Spherical, triangular, and quasi-spherical	Hyperthermia of cancer cells and IR-absorbing optical coatings	[110]
<i>Avena sativa</i> (Oat)	Gold	5–20 (pH 3 and 4)	Rod-shaped		[111]
<i>Azadirachta indica</i> (Neem)	Gold, silver and silvergold alloys	5–35 and 50–100	Spherical, triangular, hexagonal	Remediation of toxic metals	[112]
<i>Camellia sinensis</i> (Black tea leaf extracts)	Gold and silver	20	Spherical, prism	Catalysts, sensors	[113]
<i>Brassica juncea</i> (Mustard)	Silver	2–35	Spherical		[114]
<i>Cinnamomum camphora</i> (Camphor tree)	Gold and silver	55–80	Triangular, spherical (Au), and quasi-spherical (Ag)		[115]
<i>Carica papaya</i> (Papaya)	Silver	60–80	Spherical		[116]
<i>Citrus limon</i> (Lemon)	Silver	< 50	Spherical, spheroidal		[117]
<i>Coriandrum sativum</i> (Coriander)	Gold	6.75–57.91	Spherical, triangular, truncated triangular, decahedral	Drug delivery, tissue/tumor imaging, photothermal therapy	[118]
<i>Cymbopogon flexuosus</i> (Lemongrass)	Gold	200–500	Spherical, triangular	Infrared-absorbing optical coatings	[119]
<i>Cycas</i> sp. (Cycas)	Silver	2–6	Spherical		[120]
<i>Diospyros kaki</i> (Persimmon)	bimetallic gold/silver	50–500	Cubic		[121]
<i>Emblia officinalis</i> (Indian gooseberry)	Gold and silver	(10–20) and (15–25)			[122]
<i>Eucalyptus citriodora</i> (Neelagiri)	Silver	20	Spherical	Antibacterial	[123]
<i>Eucalyptus hybrida</i> (Safeda)	Silver	50–150	Crystalline, spherical		[124]
<i>Garcinia mangostana</i> (Mangosteen)	Silver	35	Spherical	Antimicrobial activity against <i>E. coli</i> and <i>S. aureus</i>	[125]
<i>Gardenia jasminoides</i> Ellis (Gardenia)	Palladium	3–5	-	Nanocatalysts for <i>p</i> -nitrotoluene hydrogenation	[126]
Pear fruit extract	Gold	200–500	Triangular, hexagonal	Catalysis, biosensing	[127]
<i>Pelargonium roseum</i> (Rose geranium)	Gold	2.5–27.5	Crystalline	-	[128]
<i>Psidium guajava</i> (Guava)	Gold	25–30	Mostly spherical		[129]
<i>Sedum alfredii</i> Hance	Zinc oxide	53.7	Hexagonal wurtzite and pseudo-spherical	Nanoelectronics	[130]
<i>Tanacetum vulgare</i> (Tansy fruit)	Gold and silver	11, 16	Triangular, spherical	Antibacterial, sensors	[131]

## CONCLUSION

‘Green’ synthesis of metal and metal oxide nanoparticles has been an exceptionally attractive research area over the last decade. Various sorts of normal concentrates (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 review article was coordinated to include the ‘state of the art’ research on the ‘green’ synthesis of metal/metal oxide nanoparticles and their use in environmental remediation applications. Detailed synthesis mechanisms and an updated literature study on the role of solvents in synthesis have been explored completely dependent on the writing accessible to assist with experiencing the current issues in ‘green’ synthesis. In synopsis, future innovative work of imminent ‘green’ materials/nanoparticle synthesis ought to be guided toward stretching out research facility-based work to a mechanical scale by considering conventional/present issues, particularly

wellbeing and ecological impacts. All things considered, 'green' material/nanoparticle blend dependent on biocomponent-determined materials/nanoparticles is probably going to be applied broadly both in the field of ecological remediation and in other significant regions like pharmaceutical, food, and

cosmetic industries. Biosynthesis of metals and their oxide materials/nanoparticles using marine algae and marine plants is an area that remains largely unexplored. Accordingly, ample possibilities remain for the exploration of new green preparatory strategies based on biogenic synthesis.

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