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Contents

Plant Synthesized Nanoparticles for Dye Degradation

Varimadugu Aruna, Nainika Chada, Medagam Tejaswini Reddy, Vadakavila Geethikalal, Kiranmai Dornala, and C. Nagendranatha Reddy

Abstract Dyes are mostly used in many industries such as textile, food, leather, cosmetics, pharmaceuticals, paper industry, etc. Industrial dyes when released spoil the ecosystem, they are hazardous to aquatic life, animals, and mankind. So there is a need to degrade the dyes to reduce the toxicity present in them. Among various methods available for the degradation of dyes the best method is to use nanoparticles synthesized from plants because it is promising, eco-friendly, and nontoxic. Plant sources act as reducing agents for nanoparticles synthesis which will replace the toxic chemicals. And how effective they are in the degradation of dye and the mechanism of action of the degradation of dye that will reduce the toxicity is discussed. It also provides information about how this dye degradation helps in reducing pollution.

Keywords Dye degradation · Nanoparticles · Environment · Pollution · Toxicity

1 Introduction

Dyes, defined as natural or synthetic substances, that result in color (at least temporarily) when applied to a substrate. The substrate can be colored or uncolored (Mohamed et al. 2017; Roy and Bharadvaja 2019; Garg and Roy 2022). This process of converting colored/non-colored substances into colored substances is called Dyeing. According to their source, these dyes are categorized as Natural (organic) and Synthetic (chemical) Dyes (Roy et al. 2021a, b; Mitall and Roy 2021). Natural dyes are derived from natural/organic resources such as plant parts (such as fruits, flowers, leaves, twigs, stems, bark), animals (insects), minerals, and microbial origins. The first synthetic dye was synthesized in the year 1956 (Sujata et al. 2014). Synthetic dyes are commonly derived from two sources: coal tar and petroleum-based intermediates (Gita et al. 2017). These dyes are used as integral parts in several commercials such as cosmetics, food, paper printing, textile, leather, and

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Fig. 1 Classification of synthetic dyes

pharmaceuticals. Generally, chemical industries manufacture these synthetic dyes (Mohamed et al. 2017) and markets in the form of granules, powders, liquid dispersions, and pastes (Gita et al. 2017). Yearly, 80,000 tons of dye are produced worldwide (Mohamed et al. 2017). Globally, around 40% of dyes using dyes contain chlorinated organic compounds which are carcinogenic. These dyes cause diseases in flora and fauna (Lellis et al. 2019) (Fig. 1).

2 Impact of Dyes on the Environment

2.1 Textile Industry

More than 10,000 varieties of dyes have been part of textile industries so far, out of which a percentage of 70 are synthetic (Mohamed et al. 2017). These synthetic chemical compounds have aromatic structures and their xenobiotic nature is against biodegradation (Gita et al. 2017). A major amount of color is released into the surroundings due to partial consumption of dyes onto fiber by process of the liquid dyeing procedure. The necessity to diminish the quantity of residual dye in fabric effluent has to turn out to be a chief assignment to address in current years (Mohamed et al. 2017).

2.1.1 Effect on Humans

As of now, no proof is suggesting that most of the dyes which are used in the coloration and finishing of fabrics are dangerous to human health (Mohamed et al. 2017).

Respiratory System

An accidental or long-term occupational exposure can upset a person's immunity and respiratory system,which results in respiratory sensitization i.e., in extreme cases, when the affected person subsequently smells the dye, their body cannot tolerate and react extraordinarily because these synthetic dyes contain ammonia, acetic acid, formaldehyde-based resins, some optical whiteners, soda ash, caustic soda, bleach, some shrink-resist chemicals. Symptoms include watery eyes, sneezing, itching, and asthma symptoms such as wheezing and coughing (Mohamed et al. 2017).

Skin

Investigations were done to check whether there is any link between skin allergies and textile used. Literature research and information from industries through questionnaires showed that some of the other textile auxiliaries, textile finish resins, and textile dyes may be the cause of Allergic Contact Dermatitis (ACD). ACD is triggered by a substance (or group of related substances). The substance or group that triggers the reaction is called an allergen. If a person has a weak immune system, ACD will appear from 24 to 96 h after being exposed to the allergen. The response begins at the site of contact. The boundaries of the lesions may be well distinguished visually. The borders of the lesions may be easily distinguished visually. In some cases, it may also spread to distant, unrelated sites such as the face and hands by exposure to dyed textiles and/or contact with cross-reactive substances, such as hair dyes. The study conducted by Hatch in 200,378 indicates that only 3 colors (namely Direct Black 38, Vat Green 1, and Direct Orange 34) of the thousands of colors analyzed within these application classes were identified as ACD allergens. In addition, reactive, vat, and disperse dyes are also sensitizers, disperse dyes have irritative properties too (De Wolf et al. 2013).

2.1.2 Effect on Water

Out of all, textile industries consume a huge amount of water and produce liquid wastes in bulk (Lellis et al. 2019). These effluents of textile industries contains compounds of both organic and inorganic (Mohamed et al. 2017). Due to the existence of, nitrates, naphthol, soaps, sulfur, acetic acid, vat dyes, enzymes chromium compounds, and heavy metals such as mercury, arsenic, copper, nickel, cobalt lead and cadmium and certain auxiliary chemicals all collectively result in the toxicity of textile effluent (Manzoor et al. 2020). During the process of dyeing, several ranges of dyes are added to the fabrics in large amounts (Mohamed et al. 2017). Out of which, 10–15% synthetic dyes are washed away and this makes textile effluents (Mohamed et al. 2017) toxic and the main cause for environmental pollution (Gita et al. 2017). The direct discharge of untreated effluent is the main reason for waterpollution (Gita et al. 2017). These effluents are highly rich in color, contain toxic chemicals some of which are cancer-causing agents and non-biodegradable (Manzoor et al. 2020). These chemicals contain hydro sulfides and block the entry of sunlight into the water which is essential for water bodies and aquatic animals. This blocking in turn leads to a decrease in oxygen concentration in water. These dyes even affect the aquatic flora and fauna due to the reduction of penetration of sunlight which is a very important element to flora for photosynthesis and fauna for energy in aquatic systems (Gita et al. 2017).

Nowadays, the number of textile industries has been increasing in developing countries such as India, which is leading to water and air pollution. In South Asia, one of the major contributors to textile wastewater in India. In India, raw materials required for textile industries are available in Maharashtra and Gujarat so these states account for 90% of dyestuff production so textile industries are dominated in these two states (Gita et al. 2017).

3 Synthesis of Plant-Derived Nanoparticle

3.1 Synthesis of Iron Nanoparticles (NPs)

Synthesis of iron NPs in the plants can be done by treating the plant leaf extracts with Ferric chloride ($FeCl_3$) in *Mangifera indica* (Mona et al. 2021), *Chlorophytum comosum* (Leili et al. 2021), *Euphorbia neriifolia* L. (Nayak et al. 2021). The synthesis of iron NPs from leaves of the following plants using ferrous sulfate ($FeSO_4$) is *Camellia sinensis* and *Punica granatum* (Ozkan et al. 2018), *Shorea robusta* (Aditya et al. 2020). So the concentrations of the compound used depends on the type of plant used.

3.2 Synthesis of Silver NPs

The silver NPs synthesis can be done by leaf extract of the following plants using silver nitrate *Mussaenda glabrate* (Sijo et al. 2017), *Cryptocarya alba* (Gonzalo et al. 2019), *Cichorium intybus* (Agnieszka et al. 2021). This extraction can also be done from the flowers, *Cicer arietinum* (Geeta et al. 2017), *Carica papaya* (Jain et al. 2020), *Morinda tinctoria* (Vanaja et al. 2014). The extraction can be done from roots in *Saussurea costus* (Abeer et al. 2021). The extraction can be done by plant extract in *Kyllinga brevifolia* (Isa et al. 2019), *Petroselinum crispum* (Khan et al. 2020). The extraction can be done using seed in *Citrus limon* (Mahmood et al. 2021).

3.3 Synthesis of ZnO NPs

The synthesis of ZnO NPs can be done by leaf extract of the following plant *Cannabis sativa* (Ankush et al. 2020). The compound used for the synthesis of NPs is zinc acetate. It can also be formed from lemon (Davar et al. 2015) pulp or juice using zinc acetate. They can also be formed from *Abelmoschus esculentus* (Prasad et al. 2019) mucilage. The NPs can be prepared from the date pulp waste of the *Phoenix dactylifera* (Rambabu et al. 2021) plant using zinc nitrate. They are also prepared from the leaves of *Solanum lycopersicum* (Preethi et al. 2020) using zinc sulfate.

3.4 Synthesis from Different Metallic NPs

The formation of gold NPs was reported from the leaves of the *Mussaenda glabrata* (Sijo et al. 2017) plant using $HAuCI_4$. Synthesis of CeO_2 NPs was done by ammonium ceric sulfatedihydrate from seeds of *Cassia angustifolia* (Dhivya et al. 2020). The carbon dots NPs can be formed from clean and dry leaves of *Elettaria cardamomum* (Vikrant et al. 2018; Maria et al. 2020). Palladium NPs can be formed from the leaves of *Pimpinella tirupatiensis* (Narasaiah et al. 2017) using Palladium chloride. It is also reported from the leaves of *Catharanthus roseus* (Kalaiselvi et al. 2015) using Palladium acetate. Nickel Oxide NPs were synthesized from the plant extracts of *Tribulus terrestris*L. (Khan et al. 2021) using Nickel chloride. Cadmium sulphide (CdS) NPs were formed by the reaction of CdS from a plant extract of *Dicliptera roxburghiana* (Ullah et al. 2021).

4 Characterization of Plant-Derived Nanoparticles

The following are different methods of characterization UV Visible Spectrophotometer, Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Thermo Gravimetric Analysis, X-Ray Photoelectron Spectroscopy (XPS) (Roy and Bharadvaja 2017; Raina et al. 2020; Roy 2021; Nagore et al. 2021; Pandit et al. 2022).

4.1 UV Visible Spectrophotometer

With a UV Visible Spectrophotometer, the absorbance of the mixture of synthesized particles can be measured; the absorption peak indicates the presence of NPs (Javed et al. 2020; Roy et al. 2022). It helps in qualitative analysis. The range of the spectrophotometer depends on the NPs. The spectrum will show absorption maxima at respective wavelengths due to surface plasmon resonance (SPR) (Geeta et al. 2017). SPR is a property caused by the electron resonances with electromagnetic radiation frequencies (Mulvaney et al. 1996). In this analysis of *Mussaenda glabrata* extract, the SPR band is formed for gold NPs at 555 nm and silver NPs at 427 nm (Sijo et al. 2017). The SPR absorption wavelength for *Cryptocarya alba* silver nanoparticles is between 350 and 550 nm. The range of wavelengths used for this is 300–800 nm (Gonzalo et al. 2019). The silver NPs synthesized from *Cichorium intybus* show the peaks at 250–350 nm gives us the confirmation of various polyphenolic compounds in the plant extract (Agnieszka et al. 2021). The spectrum was observed in silver NPs of *Cicerarietinum* between 300 and 700 nm. The SPR band was observed between 400 and 440 nm (Geeta et al. 2017). Cesium oxide NPs in *Cassia angustifolia* exhibit strong absorption peaks at 365, 368, 378, and 367 nm (Dhivya et al. 2020). For the characterization of *Saussurea costus* silver NPs, a wavelength between 200 and 1000 nm is used (Abeereta et al. 2021). Palladium NPs spectra were measured in the range of 200–800 nm in *Pimpinella tirupatiensis* (Narasaiah et al. 2017). The absorption of *Citrus limon* in silver NPs was observed at 426 nm (Mahmood et al. 2021).

Tribulus terrestris L. NPs SPR appeared at 425 nm in Nickel Oxide NPs (Khan et al. 2021). An absorption band at 364 nm was observed in *Citrus limon* zinc oxide NPs (Davar et al. 2015). A surface plasmon resonance was observed in *Catharanthus roseus* Palladium NPs between 350 and 400 nm in size (Kalaiselvi et al. 2015). Nickel Oxide NP absorb SPR at 425 nm in *Tribulus terrestris* L. (Khan et al. 2020). *Phoenix dactylifera* shows absorption at 381 nm in zinc oxide nanoparticles (Rambabu et al. 2021). The zinc oxide NPs in *Solanum lycopersicum* reach their highest absorbance at 360 nm (Preethi et al. 2020). Silver NPs synthesized from a plant extract of *Carica papaya* exhibited a peak at 468 nm (Jain et al. 2020). Whereas in the case of *Dicliptera roxburghiana,* the absorbance is at 332 nm in CdS NPs (Ullah et al. 2021).

NPs made from *Morinda tinctoria* have a peak of 320–350 nm silver (Vanaja et al. 2014). 370 nm is the maximum absorption wavelength for *Euphorbia neriifolia* L. iron NPs (Nayak et al. 2021).

4.2 Fourier Transform Infrared Spectroscopy

The high potency of these plant-derived NPs is to perform reduction bank on the chemical properties of the aqueous solution. The functional groups of molecules are identified by this technique. It tells about the stretching of bonds and about the double bonds, amine groups, etc., and how these all help in the stabilization of NPs (Sijo et al. 2017; Roy et al. 2021a, b; Mittal and Roy 2021). It helps in the observation of the vibrational modes present on the surface of NPs prepared (Agnieszka et al. 2021). FTIR spectra of silver and gold NPs coincide with *Mussaenda glabrata* extract and this proves the stability of NPs formed (Sijo et al. 2017). The peaks at 1151 and 1095 cm^{-1} in *Chlorophytum comosum* indicate the formation of the C–O and C=C aromatic rings with a stretched H–O bond. The formation of sulfate and amides C=O is observed at a region of 3357 and 1095 cm^{-1}(Leili et al. 2021). Fe–O was detected at 516.9 cm^{-1} in this spectrum of NPs. The peaks at 3200 cm^{-1} of iron NPs show the O–H bond and different peaks at 2911 and 2863 cm^{-1}show the C–H bond of organic compounds, these mainly tell us about the iron NPs functioning with compounds (Wang et al. 2014; Weng et al. 2013). *Cichorium intybus* silver NPs were analyzed in a range of 650–4000 cm^{-1} using KBr pellets. Various groups such as OH, amides, alcohols, phenols are found in the extract (Agnieszka et al. 2021). The peaks are formed due to the presence of C–O, C=C, C–H and it is also mentioned that the formation of alcohol and polyphenol acts as reducing agents (Aditya et al. 2020). Using this analysis, we can identify alkyl halides, aliphatic amines, and aromatic amines in *Cicer arietinum* silver NPs (Ankush et al. 2020). Various bonds have been identified in *Cassia angustifolia* such as H–O, C–O, C=C, etc., and also Ceric oxide (CeO_2) NP bonds (Dhivya et al. 2020). The results showed that a variety of bonds are formed in *Elettaria cardamomum* carbon dots (Vikrant et al. 2018; Maria et al. 2020). These findings reveal that the metal palladium is coated with multifunctional groups in *Pimpinella tirupatiensis* (Narasaiah et al. 2017). The presence of COOH, C=O, –C–N, –C–O–C, etc. are observed in *Citrus limon* silver NPs (Mahmood et al. 2021). The FTIR peaks in *Tribulus terrestris* L. appeared at 3645, 3495, 1639, 1227, 1017, 791, 262, 543, and 464 cm^{-1} (Khan et al. 2021). The result of *Citrus limon* showed the presence of organic residue in citric acid and sucrose in the zinc oxide sample (Davar et al. 2015). The peaks in *Catharanthus roseus*, are due to the presence of –OH and C=O groups (Kalaiselvi et al. 2015). The silver NPs of *Petroselinum crispum* indicate the presence of C–O–C and C–OH groups (Khan et al. 2020). The *Abelmoschus esculentus* zinc oxide NPs showed a sharp band at 470 cm^{-1} indicated the presence of zinc oxide vibrational mode (Prasad et al. 2019). *Phoenix dactylifera* synthesized zinc oxide NPs which showed the presence of C=O, C=N, N=C=S, etc. (Rambabu et al. 2021). It showed the presence of –OH, C–H, N–H, etc. in *Solanum* *lycopersicum* (Preethi et al. 2020). *Dicliptera roxburghiana* containing CdS NPs consist of C=C and C=O (Ullah et al. 2021). *Morinda tinctoria* silver NPs contain –C–O (Vanaja et al. 2014). Iron NPs in *Euphorbia neriifolia*L. show the presence of C=C, C=O, –OH, etc. (Nayak et al. 2021).

4.3 X-Ray Diffraction

It is used in the crystallographic study of NPs. It helps in the identification of the crystalline plane of the NPs, it also tells about the angles in the crystalline plane (Agnieszka et al. 2021). It is a non-destructive and high-tech technique for analyzation of many materials such as NPs, plastics, fluids, etc. This method helps in the identification of detects of any crystal structure, size, and degree of crystallinity, its resistance to stress, its texture, etc. (Bunaciu et al.2015). The result of *Mussaenda glabrata* gold NPs shows the crystalline structure with face-centered cubic lattice and the silver particles show the face-centered cubic lattice. This result revealed the orientation of the crystal is (111) plane (Kora et al. 2012; Sujitha and Kannan 2013). From the leaves of *Cryptocarya alba* in this method different peaks were observed at 38.28°, 44.40°, 64.57°, 77.48°, and 82.32°, this corresponds to (111), (200), (220), (311), (222) plane of cubic silver NPs. From this, we can tell that the extract is crystalline (Gonzalo et al. 2019). This technique demonstrated different diffraction peaks which shows the amorphous nature of iron NPs in different leaf extracts (Njagi et al. 2011). Silver nanoparticles in *Cichorium intybus* contain planes that are at an angle of 28°, 38°, 46°, 55°, 57° (Agnieszkaet al. 2021). *Cicer arietinum* silver NPs exhibited the presence of peaks of hexagonal wurtzite structure (Ankush et al. 2020). *Cassia angustifolia* Cesium oxide NPs, the structure formed is a cubic fluorite structure based on observed peaks (Dhivya et al. 2020). This analysis of *Elettaria cardamomum* carbon dots NPs indicates the presence of C–C, C=C, N–O, C–H, N=C=O, etc. can be found (Vikrant et al. 2018; Maria et al. 2020). *Kyllinga brevifolia* silver NPs show the peaks at 38.081°, 44.162°, 64.400°, and 76.853° corresponding to (111), (200), (220), and (311) planes, respectively, this shows the formation of face-centered cubic structure (Isa et al. 2019). *Pimpinella tirupatiensis* forms Palladium NPs which show the diffraction peaks at 39.550, 46.220, 67.570 which corresponds to the (111), (200), (220) plants of the face-centered cubic crystal (Narasaiah et al. 2017). *Citrus limon* plant silver NPs, contains the peaks that are observed at 38.53, 46.50, 66.81, and, 79.50 corresponding to (111), (200), (220) and, (311) planes. They have face-centered cubic geometry (Mahmood et al. 2021). *Citrus limon* zinc oxide NPs have high-intensity peaks and suggest that the NPs synthesized are highly crystalline (Davar et al. 2015). *Petroselinum crispum* silver NPs tell us about the structure which is face-centered cubic (Khan et al. 2020). The angles obtained for *Phoenix dactylifera* zinc oxide NPs are 31.7, 34.3, 36.2, 47.5, 56.5, 62.8, 67.9 (Rambabu et al. 2021). *Solanum lycopersicum* zinc oxide NPs contain a hexagonal phase (Preethi et al. 2020). *Dicliptera roxburghiana* CdS NPs: the peaks are of 8.15, 11.85, 15.55, 26.45, 37.65, 44.01,1.15, 58.08, and 78.85 (Ullah et al. 2021). *Morinda tinctoria* silver NPs are made of face-centered cubic structure (Vanaja et al. 2014). *Euphorbia neriifolia*L.'s iron NPs: the values of angles are 20.2°, 34.5°, 37.2°, 40.91°, 48.8°, 56.3°, and 64.21°, 70.21° (Nayak et al. 2021).

4.4 Transmission Electron Microscopy

The shape and size of the NPs can be observed using the transmission electron microscope (Sijo et al. 2017). It says the particle size distribution (Ankush et al. 2020). It is a technique in which electron beams transmitting from the specimen forms the image. The fluorescent screen produces the image. TEM samples should be made on a TEM grid and placed in the specialized chamber of the microscope (Tizro et al. 2019). The mean diameters of both gold and silver NPs of *Mussaenda glabrata* are 10.59 nm, 51.32 nm, respectively (Sijo et al. 2017). The TEM analysis of *Cryptocarya alba* silver NPs shows that the average diameter is between 16.9 and 15.7 nm in different concentrations. The size and shape of NPs formed were determined by this analysis (Gonzalo et al 2019). The average size of *Shorea robusta* derived iron NPs is found by using this method and it ranges from 54 to 80 nm (Aditya et al. 2020). *Cannabis sativa* zinc oxide NPs size distribution is known. The NP size is between 34 and 38 nm (Ankush et al. 2020). The average size of *Cassia angustifolia* Cesium oxide NPs ranges from 9 to 11 nm (Dhivya et al. 2020). Silver NPs formed from *Saussurea costus* particle size ranges from 5 to 25 nm (Abeer et al. 2021). This analysis says that the size of *Kyllinga brevifolia* silver NPs is between 5 and 30 nm (Isa et al. 2019). The size of *Pimpinella tirupatiensis* Palladium NPs is given using this technique, the average size of NPs is 12.25 nm (Narasaiah et al. 2017). The size of *Citrus limon* silver NPs prepared is 7.4 nm (Mahmood et al. 2021). The size and shape of *Tribulus terrestris* L. Nickel oxide NPs are 60–90 nm and spherical, respectively (Khan et al. 2021). The size of *Catharanthus roseus* Palladium NPs is 38 nm (Kalaiselvi et al. 2015). *Petroselinum crispum* silver NPs size is between 25 and 90 nm (Khan et al. 2020). The size of zinc oxide NPs formed from *Abelmoschus esculentus* is 29 nm (Prasad et al. 2019). *Phoenix dactylifera* Zinc oxide NPs have an average size of 31.6 nm (Rambabu et al. 2021). *Solanum lycopersicum* Zincoxide NPs size is between 25 and 70 nm (Preethi et al. 2020). *Carica papaya*s size of silver NPs is 10–60 nm (Jain et al. 2020). *Dicliptera roxburghiana* contains CdS NPs of size 2.5–8 nm (Ullah et al. 2021).

4.5 Atomic Force Microscopy

It gives the topographic information of NPs. It gives the 2-dimensional and 3-dimensional structure of nanoparticles (Sijo et al. 2017). It is mostly used for the characterization of nanoparticles with surface roughness and nanomechanical data acquisition being the less common (Smith et al. 2018). The images showed nonuniform morphology in both well separated and agglomerated silver and gold NPs (Jayaseelan et al. 2013; Sijo et al. 2017).

4.6 Scanning Electron Microscopy

The surface morphology is investigated through SEM (Ankush et al. 2020). In this method, electrons are collected and counted by the microscope, and the surface and composition of the sample are the focus (Fischer et al. 2012). *Cichorium intybus* silver nanoparticles analysis shows the spherical structure of the nanoparticles formed and the size is between 30 and 50 nm, the formation of nanowires is also visible (Agnieszka et al. 2021). The surface morphology is found using this technique. The purely formed zinc oxide nanoparticles from *Cannabis sativa* are is homogenous. The 3-dimensional structure can also be known and agglomeration due to densification can also be known (Ankush et al 2020). *Tribulus terrestris L.* Nickel oxide nanoparticles analysis of the porous structure is seen (Khan et al. 2021). *Citrus Limon* Zinc oxide nanoparticle size is observed which is more than 50 nm (Davar et al. 2015). *Dicliptera roxburghiana* has the CdS nanoparticles that are distanced from each other (Ullah et al. 2021). *Morinda tinctoria* contains silver nanoparticles that have a size between 79 and 96 nm (Vanaja et al. 2014). The size of *Euphorbia neriifolia*L. iron nanoparticles is 40–50 nm (Nayak et al. 2021).

4.7 Thermo Gravimetric Analysis

It tells about the loss of different atoms and molecules such as carbon and water molecules etc. and weight loss (Agnieszka et al. 2021). It also tells about the thermal stability of the compounds (Kumar et al. 2020). In *Cichorium intybus* plant-based silver nanoparticles the mass loss can be observed due to the loss of carbon atoms and the oxygen. The formation of CO and CO_2 was facilitated with the increase in temperature, the loss of water can also be observed, carbon loss is at 300–400 °C and the structural differences were observed at 600–800 °C. The major weight loss in the sample was observed at 150 °C, this was because of carbon loss (Agnieszka et al. 2021).

4.8 X-Ray Photoelectron Spectroscopy

Determining the chemical bonding state of elements, the spectra identify the presence of atoms (Ankush et al. 2020). The XPS analysis for *Cryptocarya alba* spectra shows that carbon, silver, gold, oxygen are identified and this supports the formation of silver nanoparticles (Gonzalo et al. 2019). The chemical bonding states of *Cannabis sativa* zinc oxide nanoparticles are analyzed. This method showed the existence of zinc, oxygen, carbon, silver in the sample. The binding energy can also be found (Ankush et al. 2020). *Tribulus terrestris*L. Nickel oxide nanoparticles in XPS spectra are associated with the –C–O bonding excitation of O1s, which is near 531 eV (Khan et al. 2021). *Phoenix dactylifera* Zinc oxide nanoparticles analysis showed the appearance of zinc and oxygen alone in the sample (Rambabu et al. 2021) (Table 1).

5 Mechanism of Dye Degradation

5.1 Catalytic Degradation by Metal Nanoparticles with the Aid of Reducing Agent

In the company of reducing agents such as Lithium aluminum hydride, hydrogen peroxide, or sodium borohydride, an alternate technique for reduction of dye uses the e^- donating property of nanoparticles such as Au, Pd, Ni, Fe, Ag, and Pt. Because of their distinctive qualities, such as large dispersibility, extremely small dimensions, ability to transfer e^- between the donor and acceptor system of electron and, large surface to bulk ratio, the efficiency of catalytic activities in silver nanoparticles is high (Tarasankar et al. 1998; Sujit et al. 2002). Biogenic silver nanocatalysts are now commonly employed to remove dye pollutants effectively (Fig. 2).

5.1.1 Degradation by Silver Nanoparticles Using Reducing Agents

The electron transfer mechanism can be used to explain the process for degradation of dye by plant synthesized Ag nanoparticles in the presence of sodium borohydride. The catalytic process happens on the metals nanoparticle surface region during degradation; therefore, a significant increase in surface area availability was observed, improving the catalyst's efficiency (Grogger et al. 2004). The dye molecules and reductant are most probably adsorbed on the surface of the Ag NPs, which has little effect on their activity. Because $NaBH_4$ is a strong nucleophile, its reductive potential reduces as it is adsorbed on the nanoparticles. When molecules of dye are adsorbed on nanoparticles, their potential for reduction increases because molecules of dye are electrophilic. As a result, when two species are adsorbed on nanoparticles, the $NaBH_4$ molecules become negative and the dye molecules become positive. The biogenic Ag nanoparticles help with "e^-shuttling" from the donor to the acceptor molecules, and so serve as an efficient electron relay substrate (Pradhan et al. 2002). BH_4^- ions are adsorbed on the metal nanoparticles surface simultaneously during the electron transfer reaction, and electron transfer from BH_4^- ions to the dye occurs through the nanoparticles, resulting in the destruction of the dye chromophore structure and the

Table 1 Plants and nanoparticles derived from them

Nanoparticles	Plant	Part	Chemicals used	Size	References
Gold/Silver	*Mussaenda glabrata*	Leaves	$HAuCl_4.3H_2O/AgNO_3$	10.59 nm gold/51.32 nm silver	Sijo et al. (2017)
Silver	*Cichorium intybus*	Leaves and flowers	Silver nitrate	20–30 nm	Agnieszka et al. (2021)
Silver	*Cryptocarya alba*	Leaves	Silver nitrate	15.7–16.9 diameter	Gonzalo et al. (2019)
Silver	*Cicer arietinum*	Leaves	Silver nitrate	10 nm	Geeta et al. (2017)
Silver	*Saussurea costus*	Roots	Silver nitrate	5–25 nm	Abeer et al. (2021)
Silver	*Citrus limon*	Seed	Silver nitrate	diameter 7.4	Mahmood et al. (2021)
Silver	*Petroselinum crispum*	Plant extract	Silver nitrate	25–90 nm	Khan et al. (2020)
Silver	*Carica papaya*	Leaves	Silver nitrate	10–60 nm	Jain et al. (2020)
Silver	*Morinda tinctoria*	Leaves	Silver nitrate	79–96 nm	Vanaja et al. (2014)
Silver	*Kyllinga brevifolia*	Plant extract	Silver nitrate	5–30 nm	Isa et al. (2019)
Iron	*Mangifera indica*	Leaves	Ferric chloride	200–400 nm	Mona et al. (2021)
Iron	*Camellia sinensis and Punica granatum*	Leaves	Ferrous sulfate	43.8,10.1	Ozkan et al. (2018)
Iron	*Chlorophytum comosum*	Leaves	Ferric chloride	246 nm	Leili et al. (2021)
Iron	*Euphorbia neriifolia L*	Latex powder	Ferric chloride	40–50 nm	Nayak et al. (2021)
Iron	*Shorea robusta*	Leaves	Ferrous sulfate	54–82 nm	Aditya et al. (2020)
Zinc oxide	*Citrus limon*	Pulp/juice	Zinc acetate	more than 50 nm	Davar et al. (2015)
Zinc oxide	*Cannabis sativa*	Leaves	Zinc acetate	34–38 nm	Ankush et al. (2020)

(continued)

Table 1 (continued)

Nanoparticles	Plant	Part	Chemicals used	Size	References
Zinc oxide	*Abelmoschus esculentus*	mucilage	Zinc acetate	29 nm	Prasad et al. (2019)
Zinc oxide	*Phoenix dactylifera*	date pulp waste	Zinc nitrate hexahydrate	31.6 nm	Rambabu et al. (2021)
Zinc oxide	*Solanum lycopersicum*	Leaves	Zinc sulfate	21–47 nm	Preethi et al. (2020)
Pd nanoparticles	*Catharanthus roseus*	Leaves	Palladium acetate	38 nm	Kalaiselvi et al. (2015)
Pd nanoparticles	*Pimpinella tirupatiensis*	Leaves	Palladium chloride	12.25 nm	Narasaiah et al. (2017)
Ceric oxide (CeO_2)	*Cassia angustifolia*	Seed	Ammonium ceric sulfate dihydrate	10–12 nm	Dhivya et al. (2020)
Carbon dots	*Elettaria cardamomum*	Leaves	Clean and dry the leaf		Maria et al. (2020)
Nickel Oxide	*Tribulusterrestris L*	Plant extract	Nickel chloride	60–90 nm	Khan et al. (2021)
Cadmium sulphide (CdS)	*Dicliptera Roxburghiana*	plant extract	Cds (helps in reduction)	2.5–8 nm	Ullah et al. (2021)

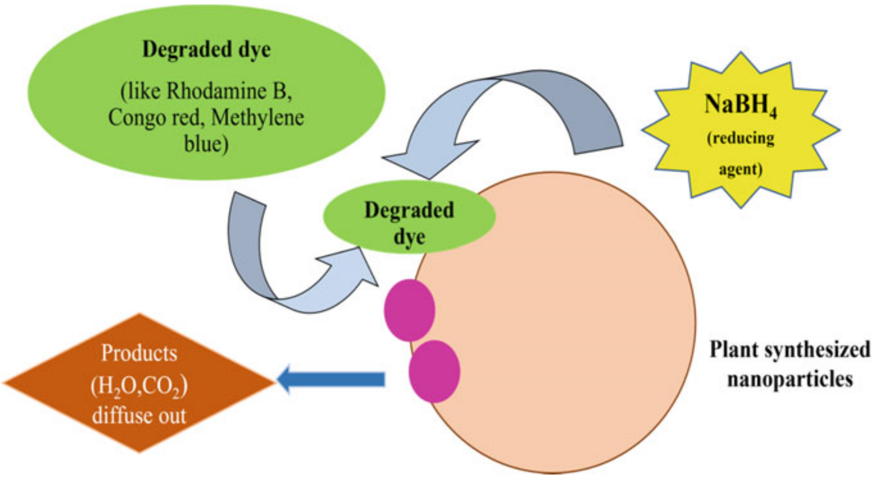

Fig. 2 Schematic diagram for the mechanism of reduction of dyes in presence of plant synthesized nanoparticles using $NaBH_4$ as a reducing agent

formation of species such as acetamide, CO_2, and H_2O, which are comparatively less harmful than the organic pollutant (Mallick et al. 2006).

5.1.2 Degradation of Congo Red

At room temperature, Congo red was catalytically degraded using $NaBH_4$ (sodium borohydride). The absorbance of the aqueous Congo red solution was measured in a cuvette with 2 ml of diluted Congo red solution, and the Congo red absorption peak was observed at $\lambda_{max} = 492$ nm. The catalytic reaction was carried out in all experiments under optimum reaction conditions, which included the concentration of catalyst, the reaction mixture pH, the Congo red concentration, to maximize the Congo red dye degradation rate and, the concentration of $NaBH_4$. To investigate the catalytic impact of the plant synthesized silver nanoparticles, a freshly made sodium borohydride solution (10^{-3} mol dm^{-3}) was mixed with the Congo red solution (10^{-5} mol dm^{-3}), followed by plant synthesized Ag NPs (10^{-9} mol dm^{-3}), and the pH was adjusted for the reaction mixture. The total volume of the reaction mixture was maintained at 5 ml for all degradation experiments. To achieve pseudo-first-order reaction kinetics, the concentration of $NaBH_4$ was kept higher than the Congo red concentration. At various time intervals, the wavelength range was of 250–800 nm, the solution absorbance was determined spectrophotometrically. The decolorization process was noticed as a reduction in the solution's absorbance intensity (λ_{max}) (Albeladi et al. 2020).

5.1.3 Degradation of Rhodamine B

Rhodamine B, a metal-chelating reagent is used in the pharmaceutical, cosmetic, and paper industries as a dye. Rhodamine B is a pollutant that influences the eyes and skin of humans. The removal of these polluting pigments from wastewater is insufficient for aquatic life to thrive (Wilhelm et al. 2007). The elimination of rhodamine B by $NaBH_4$ is too slow in the absence of a catalyst (Joseph et al. 2015). By 5 and 9 min AgNP-*M. glabrata* (0.02 mg/mL) and, AuNP-*M. glabrata* (5 μg/mL) had initiated the total removal of rhodamine B. Ultraviolet and visible absorption spectra were used to assess the deteriorating reaction regularly. The kinetic analysis was carried out by recording the absorbance at 553 nm (Francis et al. 2017). The reactions were discovered to follow a pseudo-first-order behavior regarding concentration of rhodamine B, as evidenced by the graph created by graphing ln[A] versus time (Jeyapragasam and Kannan 2016). Au and Ag nanoparticles had catalytic rate constants of 0.7250 and 0.4464 min^{-1}. The dye was eliminated by the e^- shuttling between $BH_4{}^-$and the moiety of dye at the surface of Au and Ag nanoparticles, resulting in the reduction of rhodamine B to leucorhodamine B. (Paul et al. 2016). Following a Langmuir Hinshelwood mechanism, the surface of nanoparticles is served as a heterogeneous catalyst (Bastús et al. 2014; Bhargava et al. 2016).

5.1.4 Degradation of Methyl Orange

Methyl orange is a hazardous dye that has a horrifying effect on the aquatic world. Because of the N=N functional group, methyl orange dye displays an absorption maxima of 464 nm in the ultraviolet and visible absorption spectroscopy. The reducing agent $NaBH_4$ was ineffective in degrading methyl orange on its own (Vidhu and Philip 2014). The Au and Agnano colloids reduced glabrata eliminated methyl orange in just 4 and 7 min, respectively, in a catalytic pathway. The elimination of methyl orange in the aqueous phase is indicated by the peak disappearance at 464 nm or the peak appearance at 256 nm due to the formation of hydrazine as the product (Francis et al. 2017). Methyl orange degradation occurs when an electron is transferred from a donor to an acceptor via the nanocatalysts surface (Varadavenkatesan et al. 2016). This can be helpful for government missions to prevent water contamination.

5.2 Photocatalytic Degradation by Silver Nanoparticles

The mechanism is composed of two parts: photo and catalysis. Absorption of photon, charge carrier creation, and dynamics were described in the first portion. The second section is concerned with the formation of surface radicals and the reactivity of O_2, H_2O, and organic molecules at the surface (Sinha et al. 2015). When silver nanoparticles absorb photons, energy is gained by $e^-$and moves from the valence band (VB) to the conduction band (CB), leaving a positively charged hole in the valence band ($h^+{}_{VB}$). The reactive species OH• radicals are formed when the valence band holes react with the chemisorbed water molecules. An electron in the nanoparticles' conduction band ($e^-{}_{CB}$) combines with dissolved oxygen molecules in the reacting medium to form oxygen anion radicals. On protonation of superoxide radical anions O_2, (Da Silva et al. 2003) $HO_2^{\bullet}$ radicals were formed. The hole–electron pair recombination process is prevented by the molecular oxygen deposited on the surface of the photocatalyst (Suvith et al. 2014). The rate of photocatalytic degradation is decreased by recombination of the hole–electron pair. The hydroxyl radicals ($OH^{\bullet}$) and superoxide radical anions ($O_2^{\bullet -}$) are powerful oxidizing agents that may attack molecules of dye and dye degradation into non-toxic molecules like carbon dioxide, ammonia, and water.

The degradation mechanism is as follows:

1. Photon absorption by plant synthesized nanoparticles

$$\text{Plant synthesized nanoparticles} + \text{hg} \rightarrow h^+_{VB} + e^-_{CB}$$

2. Production of OH radicals

$$OH^- + h^+_{VB} \rightarrow OH^{\bullet}$$

$$H_2O + h^+_{VB} \rightarrow OH^\bullet + H+$$

3. The organic pollutants are oxidized by the $OH^\bullet$ radicals in a series of attacks (Fig. 3).

$$dye + OH \rightarrow dye^\bullet(intermediates) + H_2O$$
$$dye + h^+_{VB} \rightarrow dye + \bullet \rightarrow \text{Degradation products } NH_4^+, SO_4^{2-}, CO_2$$

4. Oxygen reduction

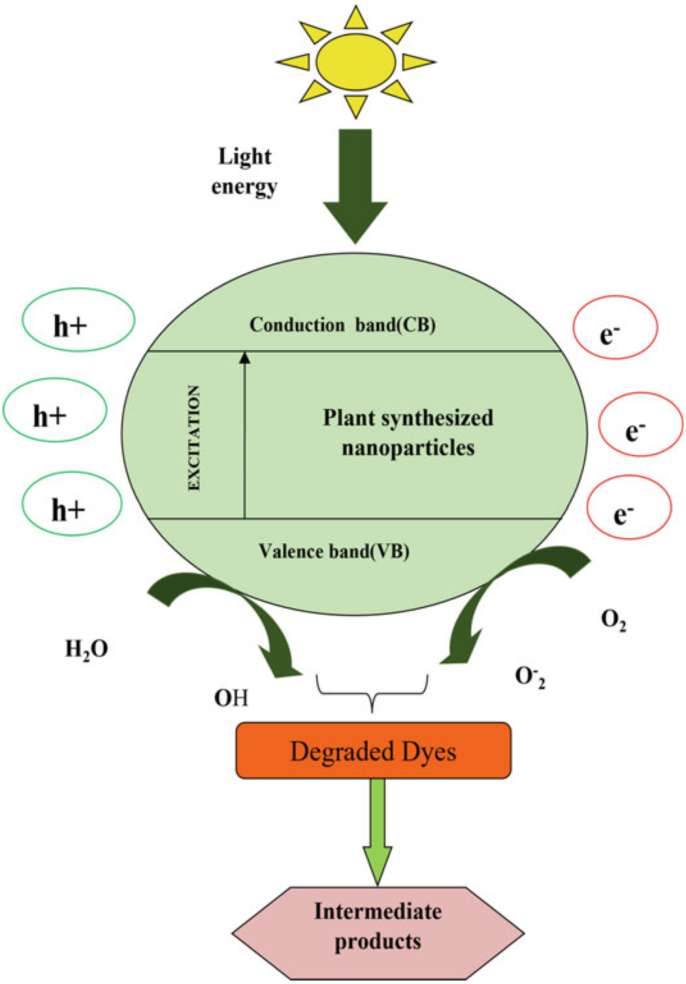

Fig. 3 Mechanism of photocatalytic degradation of dye

$$O_2 + e^-_{CB} \rightarrow O_2^{\bullet}$$

5.2.1 Degradation of Methylene Blue

For a stock solution, add 10 mg methylene blue dye to 1000 ml double-distilled water. In 100 ml of water, 10 mg plant synthesized silver nanoparticles have been added. Without the addition of silver nanoparticles, control was also maintained. The reaction suspension was magnetically agitated for 30 min before being exposed to irradiation to ensure that the working solution was properly mixed. After that, the dispersion was exposed to sunlight and monitored for a period. 2–3 ml aliquots of suspension were filtered and utilized to analyze the photocatalytic degradation of dye at specific time intervals. An ultraviolet and visible spectrum was used to measure the absorbance spectrum of the supernatant at different wavelengths. The absorbance value at 660 nm was used to calculate the concentration of dye during degradation (Vanaja et al. 2014).

By the following formula we can estimate the percentage of dye degradation:

$$\%\,\text{Decolorization} = 100 \times (C_0 - C)/C_0, \tag{1}$$

where C_0 is the concentration of dye solution initially and C is the concentration of dye solution after photocatalytic degradation.

Under solar light, biosynthesized silver nanoparticles were used to photo catalyze the degradation of methylene blue. Color changes were used to detect the initial dye degradation. After 1 h of incubation while exposed to solar light with silver nanoparticles, the dye's deep blue color transformed to a light blue. Following that, light blue became light green. Finally, after 72 h (about 3 days), the degradation process was complete, as evidenced by the color changes in the reaction mixture to colorless.

5.2.2 Degradation of Brilliant Green and Congo Red by Iron Nanoparticle

The irradiation effect on degradation ability was investigated using photocatalysis followed by adsorptive dye degradation of brilliant green and Congo red. The effect of photocatalysis by nanoparticles and powdered biomass on adsorptive reduction of dye was investigated in a CEL-WLAX visible light photochemical system at 228–288 nm light (Liu et al. 2017), in which the adsorption medium was exposed to visible light at a specific wavelength range (228–288 nm), in aqueous solution which promotes adsorption–desorption property.

The dye solution volume was completely mixed with the necessary catalyst dosage in each degrading reaction medium of Congo red and Brilliant green (0.1 g). After a specific contact period, samples were filtered through a 0.45 m PTFE filter to remove the adsorbent from the dye solution. To examine the adsorption mechanism utilizing ferrous nanoparticles and biomass powder from *Mangiferaindica*, different parameters are opted: dye concentration initially, time for shaking, pH, adsorbent mass, and temperature. An ultraviolet and visible spectrophotometer was used to detect the absorbance of both the Congo red and Brilliant green dyes at 497 and 623 nm, respectively.

The mechanism of dye photo adsorption on the adsorbent surface is complex because various elements interact to cause adsorbent–adsorbate interactivity (Pal and Deb 2014). The properties of the adsorbent surface, as well as the structure and functional groups existing in dyes and adsorbents, determine the interaction (positive or negative) and attachment of dye molecules to the surface. Bandgap energies, which correspond to the production of conduction band and valence bands when light falls on a photo-adsorptive media, can predict the photo-adsorption phenomena of dye reduction. The holes in the VB operates as an oxidizing agent, causing dyes to undergo oxidative reduction, whereas the e^-in the CB acts as a reducing agent, reducing adsorbent surface oxygen and inducing congo red and brilliant green dye degradation (Zulfikar et al. 2021).

5.2.3 Degradation of Malachite Green by CeO_2 and Mn-Decorated CeO_2Nanoparticles

Transferring the required amount of CeO_2 and Mn-decorated CeO_2 nanopowders into a 50 ml beaker containing 30 ml of dye solution was used to conduct the photodegradation test. The studies were directed for 60 min in a ultraviolet and visible light source, effectively changing concentration of dye (10–50 ppm), photocatalyst dosage (0.005–0.025 g), and dye solution pH (4–12) to examine photocatalytic activity. To achieve the whole adsorption equilibrium of the organic dyes by the catalyst, the mixture of catalyst and solutions of dye was agitated in the dark for 30 min. After centrifuging the blend solution to remove the catalyst, 5 mL aliquots were exposed to light for 10 min at a time. After irradiation, the transfer of solution to the cuvette was done, and the efficiency of decolorization was calculated using a spectrophotometer and a wavelength of 617 nm as a filter. The amount of photocatalyst, dye concentration, and pH of the solution were all tuned to anticipate dye removal with great efficiency. Due to its condensed bandgap compared to CeO_2, the efficient malachite green dye removal has resulted in the Mn-decorated CeO_2, the generation of carriers charge by the UV light source was simplified (Antony and Yadav 2021).

The decoloration mechanism is done using plant synthesized CeO_2 and Mn-decorated CeO_2 nanoparticles from Cassia seeds. Photocatalysis works based on a redox reaction that is initiated by the drift charge carrier interaction formed on the photocatalyst surface with dye molecules to adsorb them (Tachikawa et al. 2007).

5.2.4 Degradation of Nitro Compounds

Nanoparticles derived from plants are effective at degrading nitro compounds. The absorption peaks of o–nitro anilines are 283 nm and 412 nm, respectively. Degradation was quite slow in the presence of sodium borohydride. The o–nitro aniline reduction to 1, 2 benzene diamines was achieved using *Indigoferatinctoria*-mediated nanoparticles in the presence of the reducing agent. The p–nitroaniline intensity characteristic peak at 380 nm decreased, and a new peak at 240 nm formed, indicating the conversion of p–nitroaniline to phenediamine. Both reductions have high correlation coefficients and follow pseudo-first-order-order kinetics. Sodium borohydride effectively reduced 4–nitrophenol, o–nitro aniline, and p–nitro aniline in *Elephantopusscaber* mediated silver nanoparticles. The 4–nitrophenol aqueous solution is pale yellow color and its ultraviolet and visible spectrum due to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, the absorption spectrum showed peaks at 317 nm and 227 nm, respectively. Most organic pollutants, such as nitrophenol and its derivatives, are produced in the manufacturing of pesticides, insecticides, herbicides, and synthetic dyes (Gangula et al. 2011). The color of the 4–nitrophenol solution rapidly changed to greenish-yellow in the presence of sodium borohydride reducing agent, and the absorption maxima at 317 nm were red-shifted to 400 nm due to 4–nitrophenolate ions production caused by the addition of sodium borohydride in the alkaline condition (Kundu et al. 2004). Alkaline tapioca starch (Kalantari et al. 2019) and *Lawsoniainermis* (Ajitha et al. 2016) capped silver NPs was used to convert 4–nitrophenol to 4–amino phenol using $NaBH_4$. The peak at 400 nm vanished in the presence of a catalyst, due to decoloration of the bright yellow color of 4–nitro phenolate ions, and a new peak at 298 nm emerged due to the formation of 4–amino phenol (Joseph and Mathew 2015). Even though the reduction of 4–nitrophenol to 4–amino phenol by aqueous sodium borohydride is thermodynamically favorable, the presence of a kinetic barrier due to a potential difference between the donor and acceptor molecules made this reaction less feasible significant (Naraginti and Li 2017). The metal NPs promoted this reaction by allowing e^- relay from the donor BH_4 to 4–nitrophenol acceptor kinetic barrier can be overcome, resulting in the synthesis of 4– aminophenol and the new absorption peak appearingat 298 nm (Manjari et al. 2017). On the catalytic surface, both BH_4^- and 4–nitrophenolate ions are adsorbed. The reduction was accomplished by lowering the activation energy, and nanoparticles thus served as effective catalysts (Ajitha et al. 2016). The reduction of 4–nitrophenol was effective with *Chenopodiumaristatum L.* capped silver nanoparticles. In the presence of Ag nanocatalyst, plotting ln (C_t/Co) with time for degradation gave a linear relationship that followed Langmuir and Hinshelwood model kinetics (Yuan et al. 2017). The concentration of $NaBH_4$ remained constant throughout the reaction because the amount of reducing agent utilized for reduction is beyond that of 4–nitrophenol (Joseph and Mathew 2015). In terms of 4–nitrophenol concentration, the degradation followed pseudo-first-order kinetics. Silver nanoparticles mediated by *Hyphaenethebaica*, (Bello et al. 2017) *Dilleniaindica,* (Mohanty and Jena 2017) *Actinidiadeliciosa* (Naraginti and Li 2017) could enhance e^- transfer from the BH_4^- ion to the 4–nitrophenol, resulting in the formation of 4–aminophenol. In the presence of a catalyst, fast electron transfer occurred, resulting in a rapid reaction (Mohanty and Jena 2017).

5.3 Application of Plant-Derived Nanoparticles for Dye Degradation

Nanoparticles derived from plants have great potential to be upgraded to innovative methods that achieve higher efficiency in successfully degrading dyes. The urbanization and increased industrialization of the world are causing environmental pollution, in particular, water pollution in the textiles and dyes industries. Chemical wastes and heavy metals are the main recalcitrants in dye effluents. So the removal of these dyes is of high priority in the current situation keeping all the stringent rules and regulations regarding the removal of dyes from industrial effluents posed by the government legislation. In terms of effluents and dyes, Azo dyes account for about 50% of the annual production. To degrade these Azo dyes and Nitro amines effectively, Silver NPs were synthesized using the leaf extract of *Cicerarietinum* (Geeta et al. 2017). Silver particles synthesized from *Mussaendaglabrata*, *Cichoriumintybus*, *Cryptocarya alba*, *Petroselinumcrispum*, *Saussureacostus*, *Kyllingabrevifolia*, *Citrus limon* are used in water treatment, in neutralizing hazardous substances in the house, in the reduction of organic dyes, in various pharmaceutical industries, etc., in environmental remediation to remove Methylene Blue, Azo dye, Safranin dyes, Brilliant green Gold nanoparticles obtained from *Mussaendaglabrata* extracts can degrade Rhodamine B. Iron nanoparticles from *Camellia sinensis*, *Punicagranatum*, *Chlorophytumcomosum*, *Shorearobusta*, and *PimpinellaTirupatiensis* can degrade Methyl orange, Congo Red and other textile dyes. There are other plant-derived nanoparticles used in environmental remediation such as Palladium, Zinc oxide, Carbon dots, Nickel oxide, and Zinc oxide that are used for dye degradation in water. Here is a table that summarizes the types of nanoparticles that are derived from plants and their applications (Table 2).

6 Future Prospectives and Conclusions

Currently, the biological removal of dyes is a trending area in research. Though there is enough research going on, there is the existence of gaps that can be identified to address their applications in technology, and also the chemical process of degrading and detoxifying dye effluents cannot be effectively applied on a commercial scale because there is no appealing biological method available to date. Efforts still need to be made to establish an effective protocol for biological decolorization and degradation. Synthetic dyes add intense color to the water effluents from textiles, food,

Table 2 Degradation of various dyes by plant-derived NPs and their applications

Name of the plant/plant extract	Nanoparticle	Organic effluent/dye degraded	Applications of plant-derived nanoparticle	References
Mussaendaglabrata	Gold	Rhodamine B (organic coloring pigment)	Mainly used in water treatment reducing environmental pollution, and in the environmental remediation process the zero-valent metals in the nanoscale play a major role	Li et al. (2016), Joseph and Mathew (2014), Sijo et al. (2017), Lim et al. (2016)
	Silver	Methyl Orange (organic coloring pigments)	These silver nanoparticles are being exploited as a part of the water pollution government mission and also in different perspectives of dye degradation these nanometals function as beneficial heterogeneous catalysts	
Cichoriumintybus	Organometallic silver nanostructures (OMAgNs)	Brilliant Blue R	Using these green synthesized organometallic silver nanostructures we can neutralize all of the hazardous substances in the house, in addition to this, the method proves economical	Agnieszka et al. (2021)

(continued)

Table 2 (continued)

Name of the plant/plant extract	Nanoparticle	Organic effluent/dye degraded	Applications of plant-derived nanoparticle	References
Cryptocarya alba	Silver	Methylene blue	These plant-derived silver nanoparticles showed high antimicrobial activity, and also act as an excellent catalytic agent for reducing a variety of organic dyes in water, have applications commercially in industries where they can be easily recovered and reused Aids in removing persistent dyes from water Along with the Peumoextract, these nanoparticles act as an efficient catalyst by reducing the organic dyes in water as Methylene Blue	Vidhu and Philip (2014), Francis et al. (2017), Khodadadi et al. (2017), Gonzalo et al. (2019), Saha et al. (2017)
Cicerarietinum	Silver	Anthropogenic pollutants like nitro-amines and azo dyes	The Silver NPs synthesized from the leaf extract of *Cicerarietinum* showed high catalytic activity resulting in the degradation of pollutants, providing an eco-friendlier approach that is both economic and effective	Geeta et al. 2017

(continued)

Table 2 (continued)

Name of the plant/plant extract	Nanoparticle	Organic effluent/dye degraded	Applications of plant-derived nanoparticle	References
Petroselinumcrispum	Silver	Brilliant green	Helps in sequestering the dyes from contaminated water Pharmaceutical science, the food industry, textiles, and environmental remediation can all benefit from these protein-derived nanoparticles	Khan et al. (2020)
Phoenix dactylifera L.	Ag/Ag_2O Azo Dye	Azo Dye	Reducing exposure to chemicals that are harmful to human health and the environment The prepared photocatalyst Ag/Ag_2O help in treating wastewater in cosmetics, textiles, paints, etc	Laouini et al. (2021)
Saussureacostus	Silver	Safranin dye	Economical and reliable for medicinal, pharmaceutical, and industrial applications	Abeer et al. (2021)
Kyllingabrevifolia (*weed*)	Silver	Methylene blue dye	Environment remediation	Isa et al. (2019)
Citrus limon	Silver	Brilliant green	Are exploited for remediation of different organic effluents from industrial wastewaters	Mahmood et al. (2021)

(continued)

Table 2 (continued)

Name of the plant/plant extract	Nanoparticle	Organic effluent/dye degraded	Applications of plant-derived nanoparticle	References
Mangiferaindica	Iron	Congo red (azo-dye) and Brilliant green	These plant-derived iron NPs along with the powdered biomass are economical, efficient,eco-friendlier, act as reusable adsorbents for photodegradationof Congo red and Brilliant green in wastewater treatment	Mona et al. (2021)
Camellia sinensis and Punicagranatum	Iron	Textile dyes	Color removal from a textile industry wastewater	Ozkan et al. (2018)
Chlorophytumcomosum	Iron	Methyl orange	The biosynthesized FeNPs were successfully used for the decolorization of Methyl Orange and have been exploited for their antibacterial properties These are eco-friendly NPs and they serve as an important candidate in scientific studies especially in organic dye degradation and bacterial destruction	Leili et al. (2021)

(continued)

Table 2 (continued)

Name of the plant/plant extract	Nanoparticle	Organic effluent/dye degraded	Applications of plant-derived nanoparticle	References
Shorearobusta	Iron	Congo Red	These nanoparticles have the potential to degrade other dyes and organic waste as well *Shorea robusta* leaf extract can be used in the synthesis of various NPs and this Sal extract acts as a capping and reducing agent by successfully degrading the Congo Red	Aditya et al. (2020)
PimpinellaTirupatiensis	Iron	Congo red	To degrade common organic pollutants in industrial and agriculture wastewater and also to treat the effluents of textile dyeing	Narasaiah et al. (2017)
Catharanthusroseus	Palladium	Phenol red	Acts as a catalyst for dehalogenation of wastewater, and in soil remediation Are used to design an effective approach in textile effluent remediation	Kalaiselvi et al. (2015)
Cannabis sativa	Ag-doped Zinc Oxide; pure zinc oxide	Congo red and Methyl Orange	There are potential applications of these green nanoparticles in biology and environmental science	Ankush et al. (2020)
Cassia angustifolia	green nano pure CeO_2 and Mn-decorated	Malachite green	Degradation of universal water pollutant Malachite green	Dhivya et al. (2020)

(continued)

Table 2 (continued)

Name of the plant/plant extract	Nanoparticle	Organic effluent/dye degraded	Applications of plant-derived nanoparticle	References
Elettariacardamomum	Carbon Dots	Congo red and Methylene blue	Diverse methods can be utilized to degrade all dyes, thereby reducing water pollution	Vikrant et al. (2018), Maria et al. (2020)
Tribulusterrestris L.	Nickel Oxide	Congo red	Helps in the removal of hazardous environmentally contaminations in water	Khan et al. 2021
Citrus limon	Zinc oxide	Methylene blue; Methyl orange; Methyl red	Synthesized ZnNPs were used in processing and treatment of reactive blue 21 textile dyes (decolorization) In the photodegradation of organic pollutants in water and air, ZnO is one of the most commonly used photocatalysts	Davar et al. (2015)

other industries when released untreated leading to environmental, aesthetic problems. Particularly textile and dye manufacturing industries face greater challenges in treating large amounts of dye effluent and recycling it, which results in higher costs. As a result, using plant-derived nanoparticles can be one of the alternatives for dye treatment.

We summarized the significance of the green synthesis of nanoparticles and their application to dye effluent treatment in this chapter. The mechanisms of action of nanoparticles for treating dye effluents like photocatalytic degradation were discussed along with the synthesis and characterization techniques. Therefore, natural and environmentally friendly reducing agents are effective for both the synthesis of nanoparticles and the removal of dyes from wastewater.

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Plant-Mediated Green Synthesis of Nanoparticles for Photocatalytic Dye Degradation

Vikram R. Jadhav, Jayraj S. Aher, Arun M. Bhagare, Akshay C. Dhaygude, and Dnyaneshwar D. Lokhande

Abstract Due to advancements in industrialization, water pollution has become a major critical issue since it directly affects the quality of global water resources, human beings, organisms, plants, and animals. The main reason for the water pollution is unscientific management of industrial waste and population explosion. Water contamination and treatment technologies are two major topics of interest; water treatment technologies are also being developed in several ways. However, developing an economically feasible and highly efficient water treatment approach for all chemical water pollutants is ongoing. Photodegradation of this effluent is one of the best and simplest ways to convert or degrade contaminants or pollutants into a less harmful or non-toxic substance. Therefore, developing environmentally benign photocatalysts with remarkable stability and recyclability by a cost-effective and green method is becoming a prime requirement. Metal oxide nanomaterials are widely used as efficient photocatalysts due to their outstanding and unique optical properties. Metal oxides can be synthesized by various methods such as electrochemical, Sono-chemical, sol-gel, hydrothermal, polyol, and coprecipitation. However, the plant-mediated route is environmentally benign and straightforward. Hence, in this chapter, we have reviewed plant-mediated metal and metal oxide (M/MO) photocatalyst to dyes degradation. The chapter also focuses on the plausible mechanistic explanation of the photodegradation process. Lastly, we have explained the need for further developments to achieve a highly efficient and stable photocatalyst.

Keywords Green method · Plant-mediated synthesis · Metal oxide · Photocatalysis · Photodegradation

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1 Introduction

Technological advancements in large-scale industrial sectors have resulted in severe environmental issues worldwide (Roy et al. 2021a, b, c). Water pollution is a significant problem that affects people everywhere, and it is mainly caused by several tons of residual dyes which have been produced from various sectors such as pharmaceuticals (pesticides and insecticides) (Roy and Bharadvaja 2021), rubber, paper, and bleaching industries. Synthetic dyes have been widely utilized in various areas, particularly in the textile industry. Azo dyes, which make up many synthetic dyes, have been discovered as possible genotoxic and carcinogenic agents (Roy and Bharadvaja 2019).

Dyes are used as a colorant in various industries (Roy et al. 2021a, b, c). Conventional wastewater treatment techniques fail to break down dyes because of their heterocyclic and non-heterocyclic aromatic structures, hydrophilicity, and resistance to a wide range of chemicals and physical factors. When dyes are discharged into wastewater without being adequately treated, it causes significant environmental damage (Mittal and Roy 2021). Direct contact with the color can result in serious health problems such as eye injury, skin cancer, mental illness, and poisoning. Precipitation, coagulation, filtration, adsorption, and reverse osmosis are physical and chemical techniques used to remove dyes. Dye removal or degradation from wastewater to decrease the environmental effect has been widely researched (Ahmed et al. 2019). Various methods have been developed to remove and degrade these hazardous dyes, with photocatalysis being one of the most sophisticated oxidation processes, including physical, chemical, and biological techniques. However, these processes are neither cost-effective nor ecologically acceptable (Soni et al. 2018; Garg and Roy 2022).

Recent research has been utilized in developing plant-mediated M/MO nanoparticles as photocatalysts for the effective dye degradation process (Roy and Bhardavaja 2019; Raina et al. 2020; Roy et al. 2022). Photocatalysts are chemical molecules that may disintegrate or break down dye materials using light as a co-catalyst. Chemical and physical methods can be used to make nanoparticles; however, green nanoparticle synthesis has gained popularity since it is environmentally benign and less harmful. For nanoparticle production, several plant components or wastes have been used. These materials are inexpensive and widely available. In recent years, the term "green synthesis" has been applied to the plant-mediated synthesis of nanoparticles due to their several compelling advantages (Fig. 1). Several plants and their parts such as leaves, stem, and flowers, as well as a wide range of metabolic products or compounds, have been identified as having tremendous potential for this objective and are being successfully used for an efficient and rapid green synthesis of M/MO NPs in non-hazardous ways, owing to their rich biodiversity. Several variables determine the quality of synthesized nanoparticles for future applications (Roy and Bhardavaja 2019). The procedures employed, plant extract content, type of reduction agents, pH of the reaction mixture, duration, temperature, concentration, and

Fig. 1 Green synthesis method advantages

light intensity, all influence the shape and size of metal or metal oxide nanoparticles produced in plant synthesis.

Several nanoparticles like ZnO (Vinayagam et al. 2019), CuO (Sankar et al. 2014), CaO (Anantharaman et al. 2016), TiO_2 (Kaur et al. 2021), Au (Baruah et al. 2018), and Ag (Rafique et al. 2019), have been utilized for dye degradation. The study briefly elaborates on the green synthesis of M/MO nanoparticles and their role in photocatalytic dye degradation.

2 Need for Dye Degradation

2.1 Dyes

Because of the different colors or color composites all around us, the world looks beautiful. These might be natural or synthetic organic dyes. The colored materials of dyes form a chemical connection when applied to the reactant molecules. It is different in terms of pigments in that they do not attach chemically to the substance

Table 1 Relationship between the wavelength of color observed and color absorbed

Wavelength absorbed (nm)	Color observed	Color absorbed
400–435	Yellow-Green	Violet
435–480	Yellow	Blue
480–490	Orange	Green-Blue
490–500	Red	Blue-Green
500–560	Purple	Green
560–580	Violet	Yellow-Green
580–595	Blue	Yellow
595–605	Green-Blue	Orange
605–700	Blue-Green	Red

they color (Gurr 2012). Dyes are organic molecules that contain at least one chromophore group, and a conjugated system can absorb visible light (400–700 nm) and appear resonance electrons, giving spectral color as shown in Table 1. The dye is applied in an aqueous solution, and a mordant may be required to improve the dye's fastness on the fiber. Since the dawn of the industrial revolution, industries have worked to improve the aesthetics of the manufactured goods surrounding us. Dyes are the primary component that colors our surroundings.

The dyes largely determine the color of the garments and the materials we wear. Dyes are chemical substances that may adhere to a cloth. While dye quality varies by manufacturer, dyes that color the fabric quickly and are chemically stable are preferred. When dyeing a cloth, the dye molecules and the material establish solid chemical connections; it is durable, temperature and time show the durability and stability of dyes (https://www.meghmaniglobal.com).

2.2 Classification of Dyes

More than ten thousand dyes are available worldwide in different structures and molecular compositions. Many dyes used today are organic synthetic molecules, although many more natural dyes and inorganic pigments are based on minerals. Many researchers use these manufactured and natural dyes' application techniques, chemical structures, and verities to categorize them. Like other industrial chemicals like solvents, pesticides, insecticides, and medicines, a dyestuff can have a variety of names, codes and trade names, the common chemical names of dyes that have been based on the International Union of Pure and Applied Chemistry (IUPAC). The Society of Dyers and Colorists and the American Association of Textile Chemists and Colorists collaborate to maintain Color Index International, a reference database. Over twenty-seven thousand different items are presently classified under thirteen thousand Color Index Generic Names, it was initially printed in 1925, but it is

Table 2 Some of the standard dyes, their C.I. generic name, and C.I. number

Common name	C.I. generic name	C.I. number
Alizarin	Mordant red 11	58,000
Congo red	Direct red 28	22,120
Crystal violet	Basic violet 3	42,555
Fuchsin acid	Acid violet 19	42,685
Janus green	Basic dye	11,050
Methyl red	Acid red 2	13,020
Rose Bengal	Acid red 94	45,440
Sudan II	Solvent orange 7	12,140

currently only available on the Internet (http://colour-index.com/cicn-groups-sub-groups). The index is used by both producers and customers, such as artists and decorators, as a standard reference database for produced color goods. Colorants (including dyes and pigments) are classified based on a two-part system that consists of the Color Index Generic Name (first identifier) and the Color Index Constitution Numbers. In all nations, prefixes in C.I., e.g., C.I. 15510. Due to the typeface used to show the information, this abbreviation is sometimes referred to as CL. Each Color Index reference includes a thorough list of items currently available on the market. Color Index International consists of the manufacturer, physical form, and primary applications for each product name, along with manufacturer remarks to help prospective buyers. Using the CI code, various dyes and serial numbers for dyes consisting of the different classes have been made, such as acid dye, base dye, direct dye, disperse, vat, and reactive dyes, some examples are shown in Table 2; further information about the classification of dyes, their generic code, serial number, and names are mentioned on the website (https://colour-index.com).

2.3 Natural Dyes

Natural dyes derived from plants, animals, and biological sources like bacteria, fungi, and minerals are sustainable biomass energy products and have little influence on the environment. It is a sustainable supply of colorants. Though natural dyes are environmentally benign, skin-friendly, and eye-pleasing, they have weak interaction with synthetic textile fiber, necessitating preprocessing with metallic mordants, which are not always environmentally friendly, to fix natural colors on textile fibers. As a result, natural color dominance has waned, and the demand for more study into the use of natural dyes on various natural fibers to create eco-friendly fabrics. Throughout history, they've been used to color fabrics, food substrates, medicinal, handcrafted goods, crude protein fibers like wool, silk, etc., and leather, along with food components and beautification. Natural dyes are also used in dye-sensitized solar cells, histology labeling, pH indicators, and other applications. Natural dye treatments have gotten much attention in recent decades, although there has been a lot of study and research in this field worldwide.

2.4 Synthetic Dyes

Synthetic dyes are made from molecules derived from organic or inorganic compounds, and their classification is shown in Fig. 2 based on water solubility. Dye substances derived from coal tar have been referred to as coal tar dyes because they are made from substances derived from coal tar. Natural dye batches were never identical in hue and intensity, but synthetic dyestuffs can be used and created consistently (Gurr 2012). Color is consistent from part to part with the usage of computers and electronic color matching. The use of synthetic dyes in textiles, paint, and printing is widespread even though they are hazardous to humans and the environment.

Azo dyes are arguably the most well-known synthetic dye category, accounting for around 66 percent of all colorants. Azo dyes (Fig. 3) have a chemical structure that contains an N=N bond. Anthraquinone dyes (Fig. 3) are another prominent dye family (Routoula and Patwardhan 2020). There are various noteworthy natural chemicals in this chemical category, such as alizarin, purpurin, and others. Phthalocyanines (Fig. 3) are four Isoindoles linked together by metal atoms. The most common phthalocyanine dyes are copper phthalocyanides.

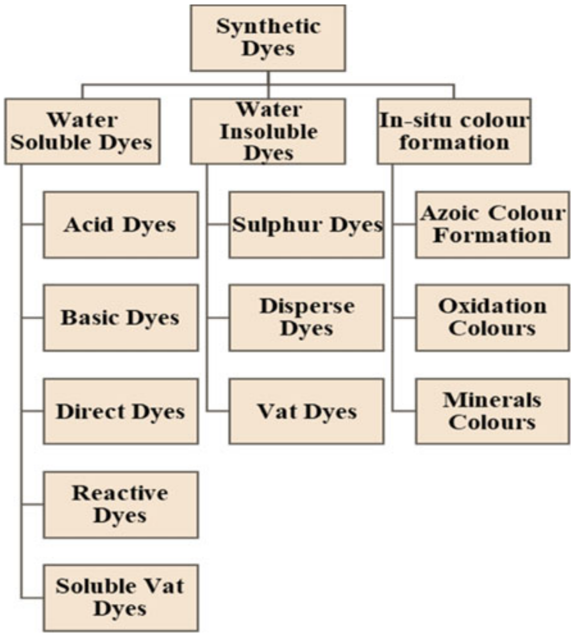


Fig. 2 Classification of synthetic dyes based on water solubility

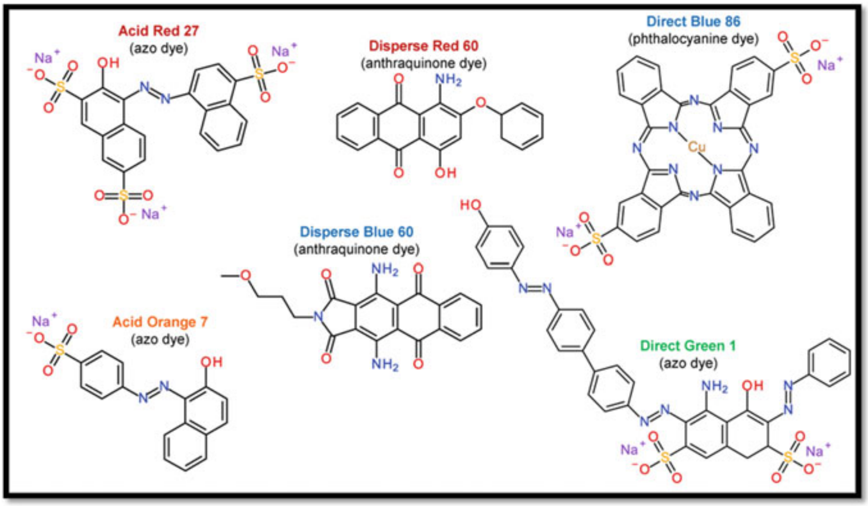


Fig. 3 Azo, Anthraquinone, and phthalocyanine dyes (*Textiles and dyes ut. ee*))

Some common examples of synthetic dyes are acid, basic, reactive, direct, sulfur, and disperse dye, as shown in Fig. 4.

2.5 Dyes Impact Living Things, and the Environment

In both developed and developing countries, environmental pollution is, without doubt, one of the main problems. It results from several factors, such as overuse of natural resources, synthesized organic products, inadequate legislation, and a lack of environmental awareness. Several scientific studies are being used as an essential tool to develop new treatment technologies and to implement environmentally friendly practices in recent years. As a result of various inputs such as raw materials, water, and energy, industrial processes can produce products, by-products, and waste. It is a variation among the types and volumes of dyes waste produced at all stages of human activity based on consumption patterns and production methods. Those worried about the consequences are concerned about human health and the environment (Vasantharaj et al. 2019). It is particularly worrying that the industry's hazardous waste dyes are mainly generated since improperly managed dangerous dyes waste poses a serious threat to human beings, Environment, Plants, and aquatic animals (Fig. 5). It remains a challenge to overcome human contamination by examining new alternatives for treating different types of industrial effluent.

The dyeing and printing process used about 10,000 chemicals. Organic dyes have been identified as a source of pollution in the environment. According to research, over 90 % of the synthetic dye remained on the cloth during the dying process. The

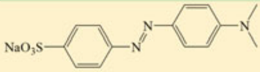
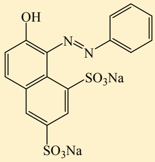
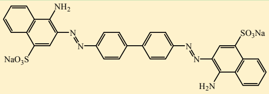
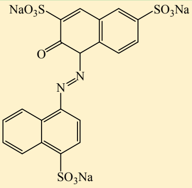
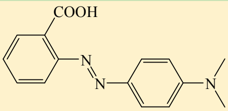
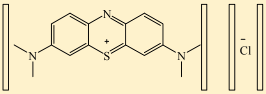
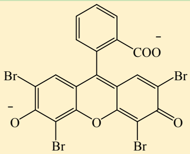
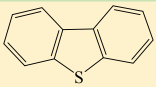
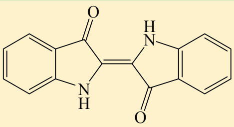
Methyl orange azo dye		Gurr, E. (2012)
Orange G. Dye		National Center for Biotechnology Information (2021).
Congo red Dye		Gurr, E. (2012)
Amaranth dye		Arêas, J. A. G., et al, (2016)
Methyl red Dye		Marczenko, Zygmunt (2000)
Methylene blue Dye		Gurr, E. (2012)
Eosin Y dye		Gurr, E. (2012)
Dibenzothiophene dye		Gurr, E. (2012)
Indigo dye		Gurr, E. (2012)

Fig. 4 Synthetic dyes examples

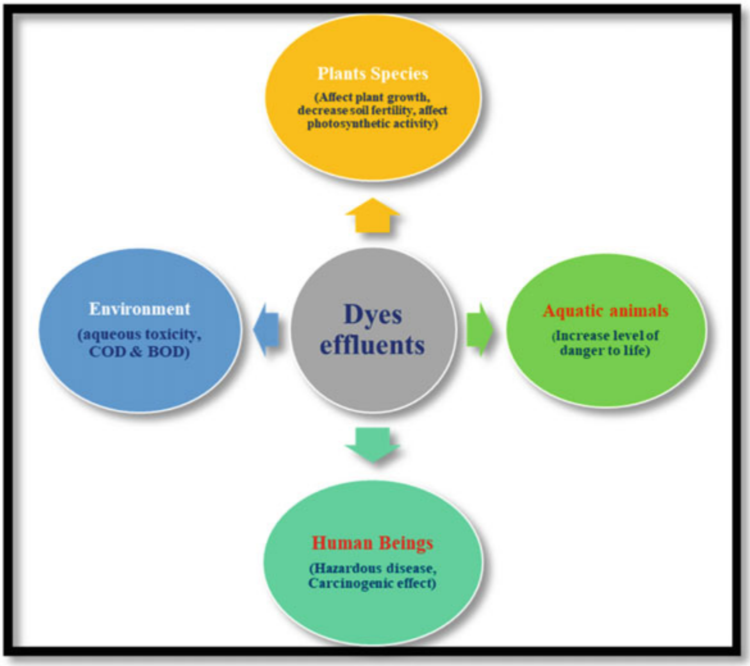


Fig. 5 Effect of dyes effluents

rest would be flushed down the toilet, with potentially disastrous effects due to their hazardous nature. For example, methyl orange (MO) is an orange powder dye used in the textile, leather, and paper printing industries, among other things. However, the incorrect use and disposal process of MO might have negative consequences, particularly concerning human health and the environment. MB is a simple synthetic dye frequently used for medical purposes.

3 The Superiority of Plant-Mediated Routes Over Other Routes

Plants can collect heavy metals in many regions of their bodies (Verma et al. 2020). As a result, plant extracts' biosynthesis approaches indicate a simple, efficient, cost-effective, easy availability, and practical way for nanoparticle (NPs) production and an ideal alternative to traditional preparation methods. In a "one-pot" synthesis procedure, various plants may decrease and stabilize metallic nanoparticles (Gnanasangeetha et al. 2013). Several researchers have used a green manufacturing approach to investigate various uses of M/MO nanoparticles produced using leaf extracts of plants (Parveen et al. 2016). Living things, which represent the kingdom of the biological system, can be used in the green synthesis NPs. It is required not just for nutrition and dietary needs but also for synthesis and characterization. Because of the quantity of biomass in many plants, scientists choose to employ plants to carry out the green synthesis of M/MO NPs because of their molecular ammunition and plenty of biomass. Plants have proteins and carbohydrates, i.e., Biomolecules, that convert metal ions to metal NPs. Ag, Au and other metal nanoparticles were initially explored in plant extract-assisted synthesis; as with other biosynthesis methods, these have been synthesized using plenty of plants (Nair and Jadhav 2020). While metallic nanoparticles may be created in living plants (in vivo) by reducing metal ions absorbed as soluble salts, most of this type of research has concentrated on in vitro nanoparticle formation (Jebril et al. 2020). The primary and secondary metabolites of plants influence the resultant reaction to stress factors and survival agents in plants, and these tactics will make plants the principal bioreactors and molecule suppliers for green synthesis (Rambabu et al. 2021). Primary plant phytochemical compounds such as flavonoids, terpenoids, heterocyclic and nonheterocyclic compounds, tannins, amino acids, citric acid, enzymes, peptides, polysaccharides, ascorbic acids, and saponins are responsible for metal ion reduction due to the presence of metallic counterparts and the stabilizing and capping agent of the surface of the NPs (Tahir et al. 2017). Several methods have been used to synthesize M/MO nanoparticles (Fig. 6). For the green synthesis of M/MO nanoparticles, their precursor and making different concentrations such as a molar and normal solutions (Jadhav 2019), and whole different parts of plants are used. They may produce nanoparticles with various unique properties, so we treat each part of the plant separately for its different concentrations of phytochemical characterization.

3.1 Comparative Study of Metal and Metal Oxide Nanomaterials

According to the literature survey, the comparative study in the following table has given some plant-mediated M/MO nanoparticles (size and morphology) and applications (dye degradation) (Table 3).

4 Possible Mechanism of Degradation

The following is the essential steps for dye degradation (Fig. 7) (Samar 2015),

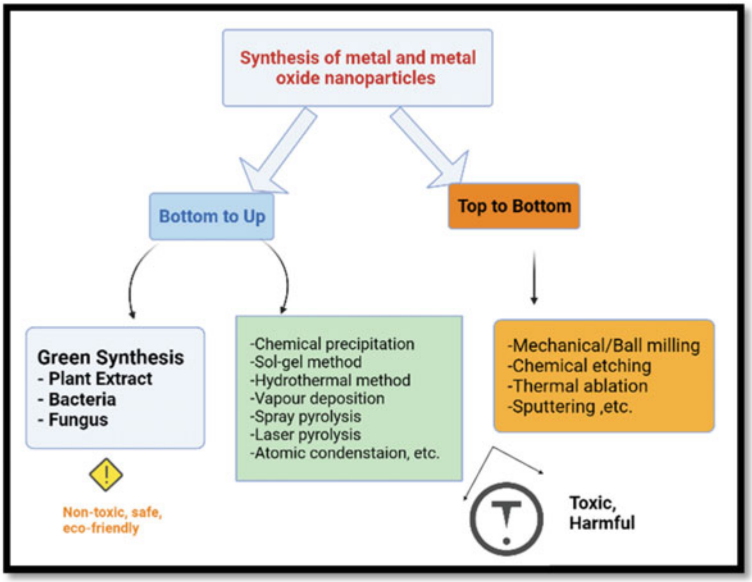


Fig. 6 Synthesis of M/MO nanoparticles

4.1 Charge Carriers' Formation/Generation

An electron (e^-) is stimulated from the valence band (VB) to the conduction band (CB) when a semiconductor (metal oxide nanoparticles) is exposed to UV light with $E \geq$ Bandgap. When a metal oxide nanoparticle is bombarded with enough light energy, it generates electron-hole ($h^+ + e^-$) pairs,

$$\text{MO} + \text{hv(UV)} ------------------\rightarrow \text{MO}\left(h^+ + e^-\right)$$

The electron-hole pair is formed when the excitation leaves an $\boldsymbol{h^+}$ in the VB.

4.2 Charge Carriers Trapping

Electron and hole scavengers capture the ($h^+ + e^-$) pair, preventing recombination. The h^+ is an oxidant directly oxidized to dyes or combined with water, and an electron donor such O_2, OH^- to create the HO• radical (oxidant)

$$H_2O + h^+ -----------\rightarrow OH^{\cdot} + H^+$$
$$h^+ + OH^- -------------\rightarrow OH^{\cdot}$$

Table 3 Comparative study of some plant-mediated M/MO NPs

Sr. No.	Plants	NPs	Size (nm)/morphology	Application (Dye degradation)	References
1	*Calliandra haematocephala (Red powderpuff)*	ZnO	19.45 nm (Nanoflowers)	Methylene blue (88%)	Vinayagam et al. (2019)
2	*Punica granatum (pomegranate) peels extract*	ZnO	50 nm (500 °C) 40–70 nm (600 & 700 °C) (Spherical)	Malachite green (99%, 40 min.)	Sukri et al. (2020)
3	*Moringa oleifera leaves extract*	ZnO	52 nm (Spherical)	Titan yellow (96 %)	Pal et al. (2018)
4	*Ferulago angulata (schlecht) Boiss*	ZnO	32–36 nm (Spherical)	Rhodamine B (RhB) 93%, 2.5 h	Mehr et al. (2018)
5	*Panos extract*	ZnO	480 nm (Leafy flower)	Methylene blue (15 mg/l, >99%, 80 min)	Kaliraj et al. (2019)
6	*Panos extract*	ZnO	480 nm (Leafy flower)	Eosin Y (15 mg/l, >99%, 90 min.)	Kaliraj et al. (2019)
7	*Panos extract*	ZnO	480 nm (Leafy flower)	Malachite green (15 mg/l, > 99%, 110 min.)	Kaliraj et al. (2019)
8	*Jackfruit leaf (Artocarpus heterophyllus)*	ZnO	15–25 nm (Sponge-like)	Rose Bengal dye (>80%, 0.24 g/L, 1h)	Vidya et al. (2016)
9	*Vitex trifolia L.*	ZnO	28 nm (Spherical)	Methylene blue (1 mg/l, 92.13 %, 90 min)	Elumalai et al. (2015)
10	*Syzygium cumini plant L.*	ZnO	16 nm (Spherical)	Rhodamine B (RhB) (98%, 80 °C, 100 min)	Rafique et al. (2020)
11	*Carica papaya leaves*	CuO	140 nm (rod)	Coomassie brilliant blue R-250 dye (10 mg/l)	Sankar et al. (2014)
12	*Calotropis gigantea L.*	CuO	~20 nm (Spherical)	Dye-sensitized solar cell	Sharma et al. (2015)
13	*Aloe-vera leaf extract*	CuO	5–20 nm	Methyl Orange (96%, 24 min)	Sharma and Kumar 2020)

(continued)

Table 3 (continued)

Sr. No.	Plants	NPs	Size (nm)/morphology	Application (Dye degradation)	References
14	*Banana peel extract*	CuO	60 nm (Spherical)	Congo red (CR) dye (10 mg/l, 90%, 60 min)	Aminuzzaman et al. (2017)
15	*Drypetes sepiaria leaf extract*	CuO	18.17 nm (Spherical)	Congo red dye 0.1 mg/l, 14 min)	Narasaiah et al. (2017)
16	*Abutilon indicum leaf extract*	CuO	16.78 nm (Spherical)	Acid Black 210 (AB) dye (13 mM, 1 h)	Ijaz et al. (2017)
17	*Psidium guajava leaf extract*	CuO	153 nm (Spherical)	Congo red (CR) (30 mg/l, 81%, 150 min) Methylene blue (MB) (30 mg/l, 89%, 150min)	Sathiyavimal et al. (2021)
18	*Oak fruit hull (Jaft)*	CuO	34 nm (Quasi-spherical)	Basic violet-3 dye (100 ppm, 86%, 2.30 hrs)	Sorbiun et al. (2018)
19	*Punica granatum leaf extract*	CuO	20–30 nm (Irregular)	Safranin-O dye	Vidovix et al. (2021)
20	*Centella asiatica (L.)*	CuO	2–5 µm (Irregular)	Methyl orange dye (1 mg/l)	Devi et al. (2014)
21	*Green tea leaves*	CaO	23 nm (Agglomeration)	Congo red (CR) dye (25 ppm, 3 h)	Anantharaman et al. (2016)
22	*Benign papaya leaf extract*	CaO	24 nm (Agglomeration)	Congo red (CR) dye. (25 ppm, 3 h)	Anantharaman et al. (2016)
23	*Crataegus pontica C. Koch extract*	CaO	~100 nm (Spherical)	Methylene blue dye (10 mg/l, 98.99%)	Meshkatalsadat et al. (2021)
24	*broccoli extract*	CaO	29–38 nm (spherical)	Bromocrescol green dye (20 mg/l, 60%, 180 min)	Osuntokun et al. (2018)

(continued)

Table 3 (continued)

Sr. No.	Plants	NPs	Size (nm)/morphology	Application (Dye degradation)	References
25	*Papaya leaf*	CaO	NA	Reactive Red 3BS dye (1000 mg/l, 83.64%)	Mukhlish et al. (2016)
26	*Lagenaria siceraria leaf extract*	TiO_2	8.2 nm (Aggregates)	Reactive green (RG-19) azo dye (6.7 mM, 98.88%, 60 min)	Kaur et al. (2021)
27	*Citrus limetta extract*	TiO_2	80–100 nm (Spherical)	Rodhamine B (RhB) (10 mg/l, 90%, 80 min)	Nabi et al. (2021)
28	*Malva parviflora plant extract*	TiO_2	20.3 nm (Aggregates)	Methyl orange (20 mg/l, 240 min, 100%)	Helmy et al. (2021)
29	*Phyllanthus emblica (Amla) leaves extract*	TiO_2	20–30 nm (Aggregates)	Coralline red dye (50 mg/l, ~ 93%, 140 min)	Singh et al. (2020a, b)
30	*Glycyrrhiza glabra plant extract*	TiO_2	60–70 nm (Nanosphere)	Methylene blue, acid red 88, & coumarin 30 (20 mg/l)	Madadi et al. (2020)
31	*Syzygium cumini extract*	TiO_2	10 nm (Aggregates)	Removal of lead (82. 53%)	Sethy et al. (2020)
32	*Glycosmis cochinchinensis leaf extract*	TiO_2	35–45 nm (Spherical)	Photocatalytic evaluation	Rosi and Kalyanasundaram (2018)
33	*Jatropha curcas L.*	TiO_2	13 nm (Spherical)	Cr removal efficiency 76.48%	Goutam et al. (2018)
34	*Ulva lactuca (seaweed)*	Ag	48.49 nm (Spherical)	Methyl orange dye	Kumar et al. (2013)
35	*Albizia procera leaf extract*	Ag	6.18 nm (Spherical)	Methylene blue (10 mg/l, 93.65 %, 30 °C)	Rafique et al. (2019)
36	*Mussaenda erythrophylla leaf*	Ag	~ 88 nm (Spherical)	Methyl orange	Varadavenkatesan et al. (2016)
37	*The coconut tree (Cocos nucifera (L))* *Rubia cardifolia (L)* *Syzgium cumini (L)*	Ag	NA	Azo dye degradation *Cocos nucifera (L) > Rubia cardifolia (L)> Syzgium cumini (L) (2 h, 0.1 % Azo dye)*	Mariselvam et al. (2019)

(continued)

Table 3 (continued)

Sr. No.	Plants	NPs	Size (nm)/morphology	Application (Dye degradation)	References
38	*Plumbago Zeylanica*	Ag	55 nm (Spherical)	Eosin Y > Methylene Blue> Methyl Red > Phenol Red > Methyl Orange. (1 mM)	Roy and Bharadvaja (2019)
39	*Centella asiatica*	Ag	30–50 nm (Spherical)	Eosin Y (93.88%) >Phenol Red> Methyl Orange > Methyl Red (1 mM, 3 h)	Raina et al. (2020)
40	*Vishanika or Indian screw tree*	Ag	25–46 nm (Cubic)	Methylene violet Eosin methylene blue Safarnin Methylene orange (50 mg/l)	Bhakya et al. (2015)
41	*Gmelina arborea fruit extract*	Ag	8–32 nm (Spherical)	Methylene Blue dye (10 mM, 100%, 10 min)	Saha et al. (2017)
42	*Zanthoxylum armatum leaves*	Ag	15–50 nm (Spherical)	Safranine O, Methyl red, Methyl orange, Methylene blue (10mg/l, 24 h)	Jyoti and Singh (2016)
43	*Viburnum opulus L fruit extract*	Ag	16 nm (Spherical)	Tartrazine < Carmoisine < brilliant blue FCF dyes (0.1 mg/mL)	David and Moldovan (2020)
44	*Alpinia nigra leaves extract*	Au	21.52 nm (Spherical)	Methyl Orange (83.25%) Rhodamine B (87.64%) (200 mg/l, 120 min)	Baruah et al. (2018)
45	*Salmalia malabarica gum*	Au	12 ± 2 nm (Spherical)	Methylene blue, Congo red (1 mM)	Ganapuram et al. (2015)

(continued)

Table 3 (continued)

Sr. No.	Plants	NPs	Size (nm)/morphology	Application (Dye degradation)	References
46	*Sterculia acuminata extract*	Au	26.5 nm (Spherical)	4-nitrophenol (4-NP) (1 mg/l, 36 min) methylene blue (MB) (0.1 mg/l, 12 min) methyl orange (MO) (0.1 mg/l, 12 min) direct blue 24 (DB24) (0.1 mg/l, 12 min)	Bogireddy et al. (2015)
47	*Ginkgo biloba Leaf aqueous extract*	Au	18.95 ± 5.95 nm (Spherical)	Azo dye (30 mg/l, 30 min)	Liu et al. (2020)
48	*Sargassum Spp. extracts*	Au	15–30 nm (Spherical)	Methylene blue (99.6%) Methyl orange (98.2%) Methyl red (94.9%) (5 µg/mL)	López-Miranda et al. (2021)
49	*Dalbergia coromandeliana roots*	Au	~10.5 nm (Spherical)	Congo red (1×10^{-5} M) Methyl orange (1×10^{-4} M)	Umamaheswari et al. (2018)
50	*Taro (Colocasia esculenta) plant rhizome powder (TP)*	Au	(68 ± 12) nm (Spherical)	Methyl Orange (MO) Congo Red (CR) Methyl Red (MR) Rhodamine B (RhB) (1 mM, 10 min, 100%)	Ismail et al. (2018)
51	*Cassytha filiformis plant extract*	Au	8–20 nm (Spherical)	Methylene blue (MB) (20 mg/l, 87%, 20 min)	Singh et al. (2020a, b)
52	*Piper longum fruit extract*	Au	56 nm (Spherical)	Methyl blue (65%) Methyl red (28%) Crystal violet (39%) Acridine orange (34%) (28 h)	Nakkala Jayachandra Reddy et al. (2016)

(continued)

Table 3 (continued)

Sr. No.	Plants	NPs	Size (nm)/morphology	Application (Dye degradation)	References
53	*Sansevieria roxburghiana leaf extract*	Au	17.48 nm (Spherical)	Congo red (93.09%), acridine orange (40.44%), methylene blue (49.62%), phenol red (85.88%), bromothymol blue (88.16%) (1 mM, 60 min)	Kumar et al. (2019)

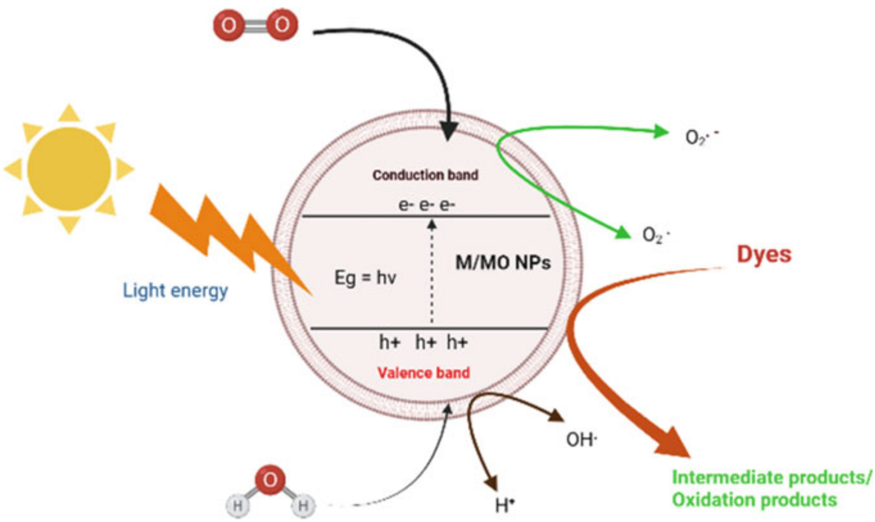


Fig. 7 Mechanism of photocatalytic degradation of dyes compounds utilizing plant-mediated M/MO NPs semiconductor as photocatalyst.

The electron in the conduction band (CB), on the other hand, must be scavenged by an *e* acceptor to prevent recombination with the trapped hole. Reactive ($O_2{\cdot}^-$) radical anions are formed when O_2 is reduced with an e. Due to this reaction, other oxidizing species such as $HO_2^{\cdot}$ & H_2O_2 is generated. The reactions that create extra OH· radicals are as follows:

$$O_2 + e^- - - - - - \rightarrow 2O_2^- + 2H^+ - - - - - \rightarrow HO_2$$
$$H_2O_2 + e^- \rightarrow OH + OH^-$$
$$H_2O_2 + O_2 \rightarrow OH + OH^- + O_2$$

4.3 Charge Carriers' Recombination

(e^- h^+) pair and trapped carrier recombination may occur in the charge transfer process during this process of heat liberation,

$$MO(e^- + h^+) - - - - - - - - - \rightarrow MO + heat$$

4.4 Photocatalytic Degradation of Dyes

The principal photoreactions show that (e^- + h^+) pairs play a crucial role in photocatalytic dye degradation. OH·⁻, O_2·, and HO_2· Radicals and photogenerated holes (h^+) are highly reactive intermediates that react continuously on the neighboring species, eventually resulting in total degradation of the dyes compounds the oxidative, reductive role of the species, i.e., OH·, h^+, and e^- in the dye degradation process.

$$OH^-/OH^{\cdot} + Dye - - - - - - - - - - - - - - \rightarrow Degrade + Product$$
$$H^+/OH^{\cdot} + Dye - - - - - - - - - - - - - - \rightarrow Degrade + Product$$
$$O_2^{-\cdot}/O_2^{\cdot} + Dye - - - - - - - - - - - - - - \rightarrow Degrade + Product$$

A common mechanism of photocatalytic degradation of dyes using plant-mediated M/MO NPs is shown in Fig. 7.

5 Photocatalysts

The heterogeneous photocatalysis process used different plant-mediated photocatalysts such as ZnO, CuO, CaO, TiO_2, Ag, and Au have established their effectiveness in complete dyes degradation. Compared to other M/MO NPs photocatalysts, they are preferred because of their low bandgap (Table 4), high specific activity, simple synthesis methods, high chemical stability, non-toxicity, low cost, and low-cost environmentally friendly.

Below is a review of some research articles on plant-mediated ZnO, CuO, CaO, TiO_2, Ag, and Au nanoparticles.

5.1 ZnO NPs

Sukri et al. (2020), worked under Ultraviolet (UV) light irradiation, ZnO-NPs were tested for their photocatalytic activity. *Punica granatum* fruit peels extract was

Table 4 M/MO NPs and their bandgap

Nanoparticles	Band gap (eV)	References
ZnO	3.2	Khan et al. (2019)
CuO	1.2	Bhattacharjee and Ahmaruzzaman (2015)
CaO	3.44 (Direct)	Anantharaman et al. (2016)
TiO_2	3.22–3.5	Nabi et al. (2021)
Ag	2.51 (Direct)	Aziz et al. (2018)
Au	3.9–3.95	Boruah et al. (2021)

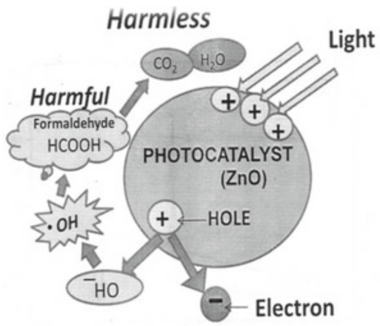


Fig. 8 Mechanism of dye degradation using ZnO NPs (*Image adopted:* Soni et al. 2018)

used as a stabilizing agent to synthesize ZnO. To obtain pure NPs with spherical morphology (40–60 nm) with high photocatalytic properties, the sol-gel method was used and calcination at 700 °C. The degradation studies were conducted with ZnO-NPs degrading Malachite Green dye (10 ppm), ZnO-NPs were calcined for 40 min at 700 °C to achieve 99% removal efficiency. Using biosynthesized ZnO-NPS as a photocatalyst for wastewater treatment proves that photocatalysis can degrade textile dyes rapidly (Fig. 8).

Davar et al. (2015) were synthesized novel ZnO NPs utilizing a green technique using lemon juice and zinc acetate as precursors. According to the results, the obtained products with the mixture of lemon juice (30 mL) and sucrose exhibited a spherical shape (average particle size around 21.5 nm). This sample's photocatalytic activity investigated the degradation of methyl orange, methyl red, and methylene blue solutions. The results also demonstrated that these three organic dyes had photocatalytic activity for degradation.

5.2 *CuO NPs*

Aminuzzaman et al. (2017) presented a green and straightforward approach for biosynthesizing CuO NPs using Banana peel extract acts as a reducing and stabilizing agent. Various techniques were used to characterize biosynthesized CuO NPs. The degradation of Congo red (CR) dye under sun irradiation was used to test the photocatalytic activity of CuO NPs. A UV-visible spectrophotometer is used to measure the degree of CR dye degradation by CuO NPs. The results show that the CuO NPs made from banana peel extract have high purity and an average particle size of 60 nm. The biosynthesized CuO NPs have exceptional photocatalytic activity due to their tiny size and high purity.

Narasaiah et al. (2017) worked on a cost-effective and straightforward method to synthesize CuO NPs using *drypetes sepiaria* leaf extract. The plant extract has different functional groups. The nanoparticles show a larger surface area provides more active sites for reactant molecules to interact, resulting in much catalytic performance. Plant leaf extract might be utilized as a reducing and stabilizing agent in the synthesis of NPs. Using $NaBH_4$ as a reducing agent, the synthesized CuO NPs demonstrated high catalytic activity in degrading Congo red dye. The breakdown of Congo-red dye (10^{-4}M) was used in the degradation process, followed by 300 mL of $NaBH_4$ (0.05M) and 150 mL (1 mg/mL) of the produced catalyst. The dye's color faded quickly, totally gone in 14 min without any by-products. Compared to high $NaBH_4$ concentrations, the degradation rate was good results.

Sharma et al. (2015) worked on the leaves extract of the *C. gigantea* plant that was used to synthesize CuO NPs in an aqueous medium, and they were used as fabrication of counter electrodes in the dye-sensitized solar cell (DSSC) in electrocatalytic materials. The crystalline nature of the produced CuO NPs confirmed by characteristics techniques. The CuO NPs-based counter electrode had an excellent surface for electrocatalytic activity, evidenced by the excellent reduction current. The cyclo-voltammetry measurement demonstrated that the NPs-based thin film had a good surface for reducing I_3^- ions in redox electrolyte, implying that it had electrocatalytic solid activity toward I^- ions. Reasonably high solar to the electrical energy conversion efficiency of 3.4% was reported in the DSSC made using synthesized CuO NPs as the counter electrode, along with a high short circuit current density of 8.13 mA/cm^2 and a fill factor (FF) of 0.62.

5.3 CaO NPs

Meshkatalsadat et al. (2021) worked on calcium oxide (CaO) nanoparticles (NPs) that have been produced in a green, eco-friendly, and cost-effective way. A species of *Crataegus pontica C. Koch* leaves extract as a green, reducing and stabilizing agent made CaO NPs ranging from 40 to 100 nm in size. With 98.99% degradation efficiency under sunlight, the NPs were effectively evaluated for photocatalytic degradation of Methylene blue dye. Under optimal reaction conditions, the CaO photocatalyst was both recoverable and reusable.

Mechanism of Dye Degradation

Excited electrons can be created by moving electrons from the VB to the CB of nanoparticles in the presence of light irradiation. Free radicals such as $HO^{\cdot}$, $O_2^{\cdot-}$ are formed when excited electrons react with oxygen molecules in solution. The active spices will then target dye molecules, causing these chemical compounds to disintegrate.

$$\mathrm{Cao} + \mathrm{hv} \rightarrow \mathrm{e}^{-*}$$
$$\mathrm{e}^{-*} + \mathrm{O_2} \rightarrow \mathrm{O_2^-}$$
$$2^*\mathrm{O_2^-} + 2\mathrm{H_2O} \rightarrow \mathrm{H_2O_2} + 2\mathrm{OH^-} + \mathrm{O_2}$$
$$\mathrm{e}^{-*} + \mathrm{H_2O_2} \rightarrow \mathrm{OH^-} + \mathrm{OH}$$
$$\mathrm{OH/O_2^-} + \mathrm{dye} \rightarrow \text{Dye degradiation}$$

Osuntokun et al. (2018) were synthesized CaO NPs by utilizing calcium chloride ($CaCl_2$) as a precursor and aqueous broccoli extract utilized as a reducing and capping agent. Calcium hydroxide (Ca $(OH)_2$) was formed during the chemical process, and then calcination yielded CaO NPs. CaO NPs characterized by XRD (Crystalline size, 29–38 nm), TEM (morphology-spherical), and FTIR were used to investigate the surface composition of Ca $(OH)_2$. The key functional groups in the capping material responsible for calcium metal salt reduction and surface passivation of Ca $(OH)_2$ have been discovered. Synthesized CaO NPs were utilized as a catalyst for UV irradiation with ultraviolet light to degrade bromocresol green, and the result indicated a 60.1% degradation efficiency.

5.4 TiO_2 NPs

Nabi et al. (2021) were worked on synthesizing TiO_2 NPs using *Citrus limetta* extract utilized. The extracts served as a reducing and capping agent for nanoparticles, resulting in pure TiO_2 nanoparticles. The produced nanoparticles are spherical in size (around 80–100 nm) and almost uniformly distributed throughout the sample. The bandgap of nanoparticles was predicted to be 3.22 eV, confirming the development of anatase phase TiO_2 nanoparticles. RhB was used as a model dye, and its improved photocatalytic activity was investigated about time and catalyst concentration. Within 80 min, about 90% of the dye had decomposed, demonstrating its photocatalytic properties. Nanoparticles with a larger surface ratio may have more active adsorbent sites, improving photocatalytic activity. The high photocatalytic activity of the produced TiO_2 nanoparticles demonstrates that the photocatalyst is environmentally safe and has potential uses in water purification (Fig. 9).

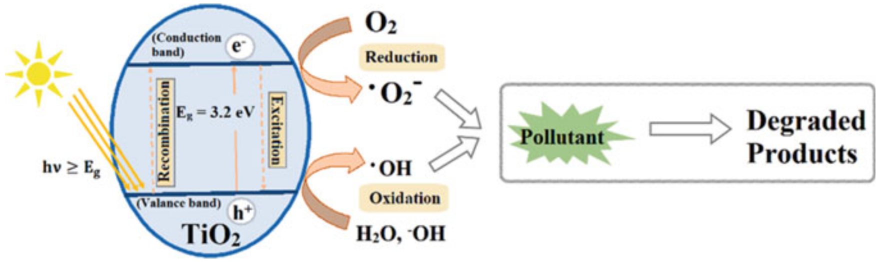


Fig. 9 Photocatalytic mechanism of TiO_2 (*Image adopted:* Nabi et al. 2021)

5.5 Ag NPs

Saha et al. (2017) were synthesized Ag NPs using *Gmelina arborea* fruit extract. TEM, SAED, and ED-X-ray spectrum were used to characterize the AgNPs. The synthesized NPs were spherical and crystalline, with particle sizes (8–32 nm, diameter; 17.0 ± 1.6 nm). The catalytic performance of the NPs in terms of degradation of Methylene Blue (MB) dye was completed in less than 10 min, indicating that silver nanoparticles had outstanding catalytic capabilities in reducing MB.

Jyoti and Singh (2016) were used the application of green-synthesized Ag NPs in the degradation of hazardous dyes such as Safranine O, Methyl red, Methyl orange, and Methylene blue. *Zanthoxylum armatum* leaves extract was utilized as a reducing agent to make AgNPs; The NPs were found to be crystalline, with sizes ranging from 15 to 50 nm, as determined by DLS, TEM, SAED, & XRD. According to the paper, AgNPs are a suitable catalyst for reducing dangerous dyes, and the degradation efficiency is improved in the presence of a larger surface area of NPs and a faster migration rate of electrons/holes to the surface. Degrading efficiency improves with various time intervals, and the process is finished in less than 24 h.

5.6 Au NPs

Baruah et al. (2018) provide a green synthesis of Au NPs using *Alpinia nigra* leaves extract and their photocatalytic activity. The plant's aqueous extract is high in flavonoids contents (491 mg RE/g) which is confirmed by HPLC analysis. As revealed by TEM micrographs, the ANL-AuNPs were spherical (average size: 21.52 nm), and FTIR spectrum analysis was used to identify the polyphenolics and functional groups in the plant leaf extract that shows reducing and capping agents in the production of NPs. The anthropogenic pollutant dyes as Methyl Orange and Rhodamine B were catalyzed by the NPs in the presence of sunlight, with degradation of 83.25% and 87.64%, respectively.

Kumar et al. (2019) were synthesized AuNPs using a simple, straightforward, green, one-pot synthesis approach employing *S. roxburghiana* leaf extract. XRD shows that the produced gold nanoparticles have an FCC crystalline phase. The synthesized nanomaterials' morphology was spherical, triangular, hexagonal, and rod-shaped. The average size of synthesized nanoparticles obtained was 17.48 nm, with a range of 5–31.11 nm. The presence of proteins and polyphenols was confirmed with the help of FTIR and HPLC in plant leaf extract, indicating the reduction of Au^{3+} ions to Au NPs and their catalytic activity of degradation of pollutants like 4-nitrophenol, acridine orange, and bromothymol blue.

6 Future Scope of the Chapter

Developing a green method for the synthesis of plant-mediated M/MO nanoparticles for the degradation/decolorization of synthetic dyes and other hazardous chemicals and the purification of wastewaters is currently in progress. Many laboratories in India and elsewhere are currently working on the same project, and in future years, plant-mediated metal or metal oxide nanoparticles will be a superior alternative for dye degradation. The use of plants in environmental technology, including leaves, blossoms, and stems, is currently being investigated for effective implementation. Remember that a plant component has been demonstrated to operate in vitro doesn't imply it will work in vivo or vice versa. More research is essential into the effects of metal or metal oxide in promoting plant degradation capacity via nanoparticles mediated by plants.

7 Conclusions

Hazardous dyes can be degraded using three different methods: physical, chemical, and biological. Synthetic dyes may stain utilizing plant-mediated metal oxide/metal nanoparticles, a safe, cost-effective, and environmentally beneficial process. For degradation, a wide range of plant-mediated nanoparticles can be employed. Hazardous dye degradation is well-known, and it is now being used as a superior option for degradation. Metal oxide nanoparticles are commercially significant and can degrade a wide range of contaminants. These break down various hazardous organic substances, such as synthetic dyes.

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Plant-Derived Nanoparticles for Heavy Metal Remediation

V. Andal, Karthik Kannan, V. Selvaraj, and K. Suba

Abstract In the domain of material science, a wide range of materials, such as nanomaterials, hybrid materials, and bio-inspired materials, are synthesized extensively using biological molecules derived from plants to form a truly reliable, sustainable, and environmentally friendly protocol. Plant-based nanoparticle synthesis is considered to be effective because of the diversity of plant nature and easy availability. The impact of toxic metal ions in water is a serious global problem because of their human and environmental toxicity. Removal of heavy metal ions in water is a complex process. Adsorption is popular with existing methods because of its economic feasibility. The production of nanomaterials from plants, including carbon, zero-valent metals, metal oxides, and nanocomposites, as well as their applications to remove heavy metal ions from wastewater, were systematically reviewed. We compared, discussed the efficiency, limitations, and benefits of plant-based nanoparticles for heavy metals removal. In addition, there was discussion about the perspective of heavy metals removal by plant-based nanomaterials and potential guidance for future work.

Keywords Green synthesis · Heavy metal remediation · Plant-derived nanoparticles · Adsorption

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1 Introduction

Nanotechnology has been one of the most significant technological and scientific developments in the recent decade. New and unique properties appear to have numerous advantages while preparing nanoparticles (Roy 2021). The interest for nanoparticles with controllable morphologies and unique properties is high. For the synthesis of nanoparticles with varying morphologies and sizes, many synthetic approaches have been used (Ahmed et al. 2021). Although numerous chemical and physical processes for the preparation of nanoparticles are available, they possess a number of drawbacks, such as the use of harmful compounds, the generation of large amounts of waste, and the use of energy (Bhardwaj et al. 2020). Biocompatibility, toxicity, and stability concerns have also hindered the clinical application of nanomaterials generated by chemical techniques. These factors increase the demand for environmentally sustainable, cost-effective, and biocompatible nanomaterial manufacturing technologies. Greener routes for NPs production offer cost-effective, environmentally friendly, and nontoxic alternatives to traditional physical and chemical processes (Roy et al. 2022). Environmentally friendly behavior, low toxicity, cheap cost, increased biocompatibility, and superior size control qualities have pushed greener nanomaterial manufacturing approaches ahead of physiochemical processes. Toxic chemicals employed in nanoparticle production make the nanoparticles generated inappropriate for medical, cosmetic, or food applications. The biocompatibility of nanoparticles is critical since they are widely used in medicinal items, illness detection, and cosmetics (Augustine 2020). Numerous environmentally friendly methodologies for the preparation of NPs systems from plants have been proposed in the literature due to their cost effectiveness, potent, and biocompatibility. Green nanoparticles were made using a variety of plant species and plant-derived components. Biologically active substances found in plants include alkaloids, phenols, flavonoids, ascorbic acid, citric acid, polyphenolic, terpenes, and reductase, which serve as metal reductants. During the synthesis of nanoparticles, both internal and extracellular mechanisms can occur. Enzymes, flavonoids, antioxidants, and alkaloids are some of biomacromolecules found in plants that regulate particle size and improve nanomaterial properties. Plant-derived nanoparticles have been proposed for use in agriculture, the environment, cosmetics, biomedicine, and industry.

Contamination of water, particularly with heavy metal pollution within it, has evolved as a major environmental threat. Mining, electroplating, metallurgy, chemical plants, agriculture, and domestic effluent are all potential causes of heavy metallic elements in water. Pb, Zn, Cu, Hg, and other heavy metals can accumulate physiologically in the food chain, posing a serious threat to human health (Cheraghi 2009). Heavy metals can harm the ecosystem and other ecological receptors because they are not destroyed by microbes once introduced into the environment; instead, they accumulate along the food chain. Heavy metals are extremely hazardous, with the majority of them being carcinogenic. As a result, heavy metal removal from water is critical and has gotten a lot of attention. Chemical precipitation, ion exchange,

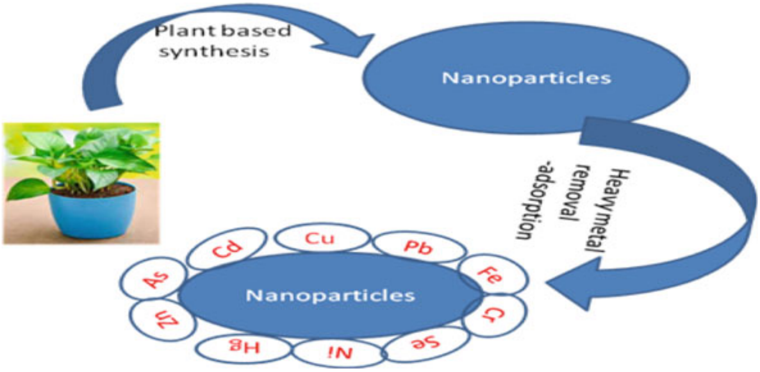

Fig. 1 Summary of plant-derived nanoparticles for heavy metal remediation in a graphical representation

adsorption, membrane filtration, electrochemical treatment, and other approaches have all been explored to overcome this problem. Adsorption is one of the most often used strategies among the approaches listed above, owing to its low cost and ease of application. Nanomaterials have unique features that allow them to have high adsorption capacity and reactivity, both of which are beneficial for removing heavy metal ions. Nanomaterials have been the subject of extensive research into their uses in heavy metal water treatment, and they have shown significant promise as a viable alternative to sequestering heavy metals from wastewater. The synthesis of metallic nanoparticles, metal oxide nanoparticles, and carbon dots using plant-derived materials is the subject of this review. This review also, provides an overview on the plant-derived nanomaterials for heavy metal remediation and its future prospects. Figure 1 shows the graphical depiction of the review.

2 Plant-Derived Synthesis of Nanomaterials

2.1 Plant-Derived Synthesis of Metal Nanoparticles

Physiochemical, and natural processes can all be used to synthesize metal nanoparticles. Physical and chemical approaches are generally thought to be the most effective for producing uniformly sized nanoparticles that are stable over time. However, these methods are costly and result in the release of hazardous compounds into the surroundings. Toxic chemicals utilized in chemical processes for nanoparticle synthesis render the nanoparticles produced unsuitable for medicinal, cosmetic, or food purposes. For the creation of green nanoparticles, a number of plant species and plant-derived components have been identified and exploited. Alkaloids, phenols, flavonoids, ascorbic acid, citric acid, polyphenolic acid, terpenes, and reductase

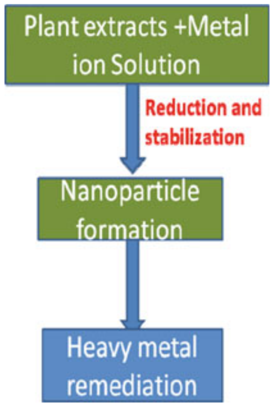

Fig. 2 General flow chart for the manufacture of metal nanoparticles using plant extract

are all physiologically active chemicals that operate as metal salt reduction agents. Because of the presence of phytochemicals in their extract, some parts of plants such as leaves, fruits, roots, stems, and seeds have been employed to synthesize different metal nanoparticles. The stability, shape, and size of metal nanoparticles can be improved by regulating the temperature, pH, amount of plant extract, and metal salt solution, as well as the incubation time. Nanoparticles synthesis with plant extract has advantages over other natural synthesis methods, such as microorganisms, because it may be accomplished through complex operations such as keeping microbial cultures. Plant-assisted nanoparticle synthesis has the benefit of being substantially faster than other biosynthetic strategies that are comparable to chemical nanoparticle production in terms of kinetics. Figure 2 shows a general flowchart for the manufacture of metal nanoparticles using plant extract.

The methodology in Fig. 2 has been used to create nanoparticles of Ag, Au, Cu, and many other metals. The pace of synthesis of nanoparticles, their quantity, and other features are known to be influenced by the nature of the plant extract, its concentration, the concentration of the metal salt, pH, temperature, and contact time.

2.2 Plant-Derived Synthesis of Nano Metal Oxides

Metal oxide nanoparticles have stimulated the interest of research groups in the last 4–5 years due to its wide variety of uses. Heavy metals are removed efficiently and selectively by nanometal oxides. They are crucial in the elimination of heavy metal ions. Generally speaking nanometal oxides include, ZnO, CuO, Fe_2O_3, CaO, CeO_2 etc.

The low cost, safe, and simple manufacturing of ZnO nanoparticles has grabbed researchers' curiosity. The exciton binding energy of these nanoparticles is 60 meV, with a 3.37 eV band gap and as an outcome, they possess broad range of semiconducting properties, such as high catalytic activity, wound healing, anti-inflammation and UV filtering properties, and are widely used in cosmetics such as sunscreen. Several studies on ZnO production using plants have been published so far, few are listed below. The leaves of *Azadirachta indica* are used to produce ZnO. The flower and leaf of the *Vitex negundo* plant were also employed to make ZnO nanoparticles (Bhuyan 2015). Similarly, plant extracts such as *Prosposis juliflora, Acalypha fruticosa, Calotropis gigantean, Urtica dioica*, and others are used to make ZnO nanoparticles (Mydeen 2020; Vijayakumar 2020; Kumar 2020; Bayrami et al. 2020). CuO nanoparticles have recently been produced utilizing *Pimenta dioica* leaf extract as a reducing and stabilizing agent. Various plant parts have been used for synthesizing CuO nanoparticles such as *Tecoma castanifolia* leaf extract, Eucalyptus leaf extract, *Rosa canina* fruit extract, *Punica granatum* peels extract, *Verbascum thapsus* leaves (Kulkarni 2015; Hemmati et al. 2018; Siddiqui 2021; Weldegebrieal 2020). Similarly, different plant component extracts are used to make Fe_2O_3 nanoparticles. In the production of nano Fe_2O_3, plant extracts function as both a reducing and stabilizing agent.

2.3 Plant-Derived Carbon Dots Synthesis

Carbon dots are spherical particles with a size less than 10 nm that have exceptional fluorescence properties. Plant-based carbon dot synthesis has various advantages, including low cost, waste minimization, source renewability, and plentiful source availability. Non-toxic solvents and plant matter are used in the production of carbon dots. Carbon dots have been synthesized from plant materials such as root, stem, leaf, flower, fruit, and seed. Plant parts are widely available, ecologically friendly, renewable, and long-lasting. Green carbon dots are made using a variety of processes, including hydrothermal (Vandarkuzhali 2017), microwave (Bandi et al. 2016), carbonization (Bandi et al. 2018), pyrolysis (Bhatt et al. 2018), and so on. By using a hydrothermal process, various sections of the plant were employed to make carbon dots. Plant products such as banana pseudo stems (Vandarkuzhali 2017), onion waste (Bandi et al. 2016), Lantana camara berries (Bandi et al. 2018), Tulsi leaves (Bhatt et al. 2018), and others have been utilized to synthesize carbon dots by hydrothermal method. Recently, Tian and his colleagues have created water soluble luminous carbon dots from mulberry leaves using a hydrothermal method (Shao et al. 2020). Table 1 lists the numerous plant sources as well as the methods utilized to make carbon dots. Chemical doping is a solid-state modification approach that has been applied to carbon dots. According to reported literatures nitrogen doped carbon dots are very sensitive to cations in aqueous solutions (Bandi et al. 2018).

Table 1 Various plant sources and the methods employed for carbon dot synthesis

S. No.	Plant sources	Methods	References
1	**Leaves** *Azadirachta indica* Mulberry *Lawsonia inermis* Guava Coriander Celery Mint Gingko	Hydrothermal Hydrothermal Carbonization Hydrothermal Hydrothermal Hydrothermal Hydrothermal Pyrolysis Hydrothermal	Kumar et al. Shao et al. (2020) Alex (2020) Ram et al. (2020) Sachdev (2015) Qu et al. (2019) Shahid (2020) Li (2017)
2	***Peels*** Orange Lemon Banana	Hydrothermal Hydrothermal Hydrothermal	Prasannan (2013) Tyagi (2016) Atchudan et al. (2021)
3	***Roots*** Ginger	Hydrothermal	Li et al. (2014)
4	***Seeds*** Fennel Sesame *Nigella Sativa* seeds Mustard	Pyrolysis Microwave Hydrothermal Pyrolysis	Dager (2019) Roshni Yun (2020) Roshni
5	***Fruit juice and fruit pulp*** Orange juice Lemon juice Tomato juice	Hydrothermal Hydrothermal Hydrothermal	Swagatika Hoan (2019) Khaledian et al.
6	***Outer covering of grains*** Wheat straw	Hydrothermal	Ming et al.

3 Heavy Metal Remediation

3.1 Plant Derived Metal Nanoparticles for Heavy Metal Remediation

Heavy metals such as mercury (Hg), lead (Pb), cadmium (Cd), and arsenic (As) are highly toxic and constitute a major hazard to human and environmental health even at low quantities in water. Metal nanoparticles such as Au, Ag, and nano-zero-valent iron nanoparticles are employed to eliminate heavy metals. In recent years, metal nanoparticles have demonstrated their utility in water treatment and heavy metal removal. In terms of heavy metal ions remediation, zero-valent iron has received the greatest attention and is the subject of this section. In addition, some more nano-sized noble metals were discussed.

Nanoscale zero-valent iron nanoparticles were made utilizing a green process that used *Mentha piperita* leaf extract as reductant by microwave treatment. The synthesized nanoparticles with a large surface activity were used for the removal of lead ions from water samples of Worcester and Birmingham canal. Within 24 h, it has removed 79.33% of the lead in the river (Salma et al. 2020). Likewise, Madhavi et al. (2013) used the Eucalyptus globules leaf extract for the production of zero-valent iron nanoparticles at room temperature. The phytogenic Fe nanoparticles were also used for Cr (VI) metal adsorption. Batch studies were used to investigate adsorption parameters such as adsorbent dose (ZVNI), initial Cr (VI) concentration, and kinetics. Fe nanoparticles had the maximum adsorption efficiency of 98.1% at a reaction time of 30 min and a dosage of 0.8 g/L.

Based on their reduction potential, black tea leaves (*Camellia sinensis*), oak tree leaves (*Quercus virginiana*), green tea leaves (*C. sinensis*), pomegranate leaves (*Punica granatum*), and eucalyptus leaves (*Eucalyptus globulus*) were chosen for the production of iron nanoparticles. The removal of arsenic metal ions was studied utilizing the produced iron nanoparticles. Oak leaves produced iron nanoparticles have a higher adsorption ability for arsenic removal than other iron nanoparticles (Vaibhav 2020). The schematic picture representing the synthesis and adsorption studies of iron nanoparticles is shown in Fig. 3

Fresh *Ficus Benjamina* leaves were used to make zero valent silver nanoparticles (AgNPs) to remove Cd (II) from aqueous solutions. Similarly, *Moringa stenopetala* leaf extract was employed to make zero-valent Ag nanoparticles. The Cr (VI) ions were removed using silver nanoparticles that had been produced (Wendimagegn 2021).

Arsenic (V) was removed from mine effluent using Fe/Ni nanoparticles produced from eucalyptus leaf extract. The effectiveness of As (V) removal in mine effluent

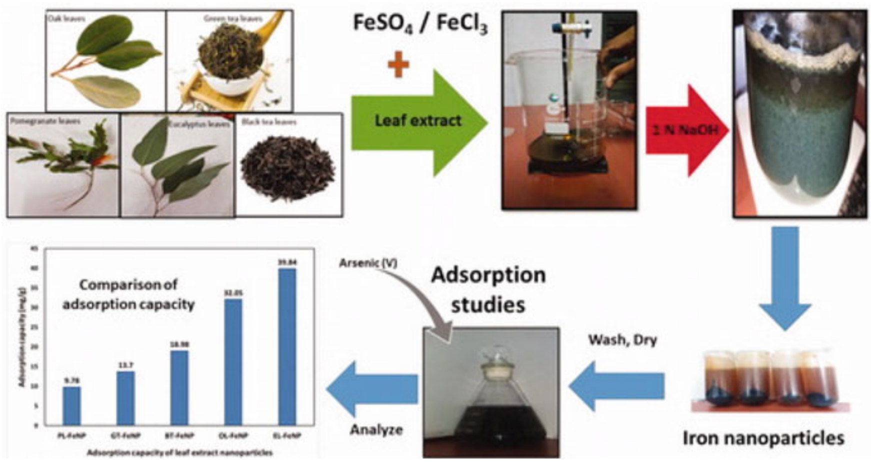

Fig. 3 Arsenic adsorption and the formation of iron nanoparticles utilizing five leaves (Vaibhav 2020)

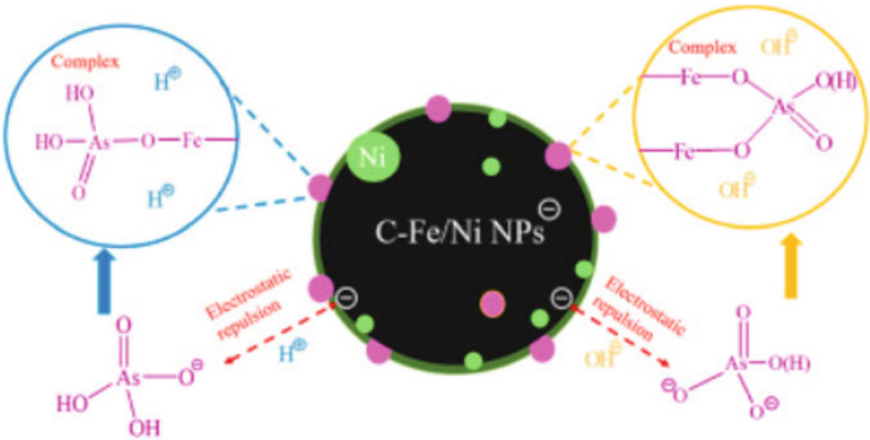

Fig. 4 Arsenic removal mechanism by Bimetallic Fe/Ni nanoparticles

was 82.6%. The As (V) removal mechanism involved only adsorption. Figure 4 depicts the adsorption mechanism.

3.2 *Plant Derived Metaloxide Nanoparticles for Heavy Metal Remediation*

Heavy metals were routinely removed from water and wastewater using a variety of minerals, clays, and waste products (Engates 2011). It was recently highlighted that metal oxide nanoparticles sorbents can be employed as a cost-effective and simple option to traditional adsorbents. Since no centrifugation, filtering, or secondary wastes are formed, magnetic metal oxide nanoparticles have demonstrated to be promising for the elimination of heavy metal ions from aqueous solutions. Especially, Fe_3O_4 has prompted a lot of interest in environmental remediation. Cadmium is commonly found as a minimal ion in both ground and surface water. Iron oxide nanoparticles were created as an adsorbent for the removal of cadmium ions from a contaminated solution in the presence of tangerine peel extract. Because cadmium ions are normally soluble at acidic pH, the highest cadmium removal by green synthesized iron oxide nanoparticles was achieved at pH 4, indicating that these nanoparticles could be a useful adsorbent for cadmium removal from wastewater (Ehrampoush 2015). EDTA@Fe_3O_4/SC nanocomposites and Fe_3O_4 nanoparticles integrated sawdust carbon (Fe_3O_4/SC) composites were synthesized employing a biogenic green synthesis technique. In batch mode, the performance of Fe_3O_4/SC and EDTA@Fe_3O_4/SC ncs for Cd (II) removal from water was compared. For Cd (II) adsorption, the regeneration and reusability efficiency of EDTA@Fe_3O_4/SC nanocomposites were also investigated. In comparison to unmodified Fe_3O_4/SC ncs, the capability for Cd (II) adsorption is increased after EDTA treatment. The results show that Cd (II) adsorption is mediated by carboxyl groups on the surface of EDTA@Fe_3O_4/SC ncs (Kataria 2018).

Using *Punica Granatum* rind (fruit waste), a researcher successfully green synthesized Fe_3O_4 1D magnetic nanorods. Synthesized magnetic nanorods were utilized for the adsorption of Pb (II) from aqueous solution. At various pHs, Fe_3O_4 MNRs play an important role in removing Pb (II) ions by forming a strong electrostatic attraction. Paul Das employed *Trigonella foenum-graecum* leaf extract in a simple way for production of iron oxide nanoparticles (Fe_3O_4-NPs) for potential lead adsorption from aqueous solution and wastewater. The greatest removal of lead (II) ions was reported to be 93 $\pm$ 0.13% at pH 6.0 using 0.4 g of these nanoparticles with 60 min of contact time. These regenerable iron oxide nanoparticles can be used as a nano-adsorbent for removing heavy metal ions from environmental waste because of their strong metal absorption capability (Das and Jeyanthi Rebecca 2018). Many researchers in this field have been drawn to iron-based NPS, particularly magnetite nanoparticles (MNPs), due to the strong affinity of arsenic for iron and the great stability of the arsenic-iron bond. The synthesis of magnetite (Fe_3O_4) nanoparticles (MNPs) is carried out utilizing a simple green synthesis approach including the co-precipitation of $FeCl_36H_2O$ and $FeSO_47H_2O$ in a molar concentration of 2:1 using *Azadirachta indica* leaves extract in an inert atmosphere. The As (V) is removed from water using the synthesized magnetite nanoparticles at optimal pH 2, as (V) has a maximum absorbance of 62.89 mg/g (Parajuli 2020).

Because copper is abundant, green synthesis of CuO and its wide range of uses in environmental remediation have progressed. CuO NPs have recently been made from mint and orange peel extracts. Toxic metal ions such as Pb (II), Ni (II), and Cd (II) are examined for removal from water using the CuO NPs produced. Mint leaves derived CuO (MLCu) was compared to orange peel produced CuO NPs (OPCu) in terms of removal efficiency. When utilizing MLCu and OPCu, the removal percentages of Cd (II), Ni (II), and Pb (II) were 18%, 52.5%, 84%, and 11%, 48%, 80.5%, respectively. The types of extracts utilized have an impact on the percent of heavy metals removed. The selectivity of adsorption of metallic ions follows this trend $Pb^{2+} > Ni^{2+} > Cd^{2+}$. The maximum adsorption was achieved by CuO Nps (MLCu) (Mahmoud et al. 2021). Likewise, another researcher used *Astragalus* (*Astragalus membranaceus*), rosemary (*Salvia rosmarinus*), and mallow leaf extracts (*Malva sylvestris*) to make CuO nanoparticles. The three CuO nanoparticles produced were utilized to investigate the removal of lead ions from polluted water. The copper oxide nanoparticles produced from astragalus, rosemary, and mallow leaf extract had removal efficiencies of 88.4, 84.9, and 69.6%, respectively. Cassava starch and aloe vera are used to make ZnO nanoparticles in an environmentally friendly manner. Copper adsorption was examined in the produced ZnO nanoparticles. According to the findings, the copper removal effectiveness of the ZnO nanoparticles generated by Aloe vera is greater (Julia et al. 2020).

The green synthesis approach was utilized to successfully produce SnO_2 nanoparticles (NPs) by employing the fruit extract of *Vitex agnus-castus*. SnO_2 NPs were also employed as an adsorbent to remove heavy metal ions Co^{+2} from aqueous solutions.

After 60 min at 298 K, the removal effectiveness was found to be 94% (Ebrahimian 2020).

Copper ferrite nanoparticles are magnetic mixed oxide particles that remove heavy metal ions from water. In comparison to simple oxides, the spinel structure is extremely flexible. It is easily detachable from the reaction mixture and can be reused. For the manufacture of copper ferrite nanoparticles, *Simarouba glauca* leaf extract was utilized both as a reductant and stabilizing agent. The magnetic spinels developed are capable of eliminating Pb (II) ions from water. $CuFe_2O_4$ was easily extracted from the reactant solution and can be reusable three times without losing its efficiency. $CuFe_2O_4$'s applicability as an adsorbent is boosted by its low cost of preparation, lack of toxicity, simplicity of separation, and capacity to be reused and recycled. Other heavy metal ions could be removed from water using $CuFe_2O_4$ (Sreekala 2020).

3.3 Plant Derived Carbon Dots for Heavy Metal Remediation

Tunable surface functional groups on carbon dots generated from plant products improve sensitivity and selectivity for heavy metals. Carbon dots are utilized to detect metal ions because when they interact with heavy metal ions, the fluorescence nature of the CDs changes, resulting in a signal. Sensing or detection is also required for heavy metal removal. Ginkgo leaf was employed as a green precursor by Xu et al. (2018) for producing CDs. With a detection limit of 55 pM, the CDs were employed for ultrasensitive, highly selective Pb^{2+} detection. Similarly, by using hydrothermal technique, nitrogen doped carbon dots are made using *lantana canara* berries, a low-cost green precursor. The fluorescence of nitrogen doped carbon dots is particularly selective for Pb^{2+} since carbon dots have polar groups on their surfaces that can detect Pb^{2+} in real water samples. Nitrogen doped carbon dots quenched fluorescence among the various metal ions, and so it is employed as a Pb^{2+} detection cut off sensor (Bandi 2018).

Ferric ion (Fe^{3+}) is an efficient transition metal ion that does a vital role in both environmental and biological systems. Excess or insufficiency of Fe^{3+} ions can cause a variety of ailments and diseases, with excess Fe^{3+} ions causing cancer and deteriorating organ functions such as the heart, lungs, and pancreas, while shortage causes anaemia in the body. As a result, detecting Fe^{3+} in the environment and human health is critical. As an outcome, few researchers have created carbon quantum dots (CQDs) from different parts of the plants and used them to detect Fe^{3+} ions as an interesting alternative to fluorescence probes. Hydrothermal carbonization is used to create carbon nanodots from *Babassu* coconut mesocarp. The synthesized carbon dot is used for sensing heavy metal ions such as Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, and Cd^{2+}. The fluorescence decay of all metal ions was visible. However, when compared to Fe, the ions Co, Ni, and Cu had less interaction with carbon dot. The suppressing activities of Zn and Cd ions are comparable but discrete. The sensing mechanism is based on metallic ions co-ordinating with surface oxygenated groups in C-dots, which enable non-radioactive recombination of the electron–hole pair through an efficient process of transferring electrons or energy, as shown in Fig. 5. Another research group employed pear juice to make carbon dots using the hydrothermal carbonization method. The Fe^{3+} ion was detected using a produced carbon dot, which displayed quenching in the PL emission peak centred at 472 nm without altering the peak position. The attachment of Fe (III) to surface functional groups on the carbon dots causes the quenching mechanism. Various metal ions are used to test selectivity and sensitivity. Figure 6 depicts the synthesis and sensing mechanism as well as selectivity. Gopinath and Abhay used coriander leaves to make carbon dots by hydrothermal method and investigated their fluorescence quenching properties against a variety of metal ions. The Fe^{3+} ion quenched selectively. The detection limit was found to be 0.4M (Sachdev 2015). Similarly, the hydrothermal technique is utilized to manufacture carbon dots from papaya fruit. The Fe^{3+} ion was detected using water soluble carbon dots (Wang 2016). Recently, Mexican Mint leaves were utilized to make carbon dot using the microwave process. For the Fe^{3+} ion, the manufactured carbon dot acts as an effective turn off fluorescence sensor.

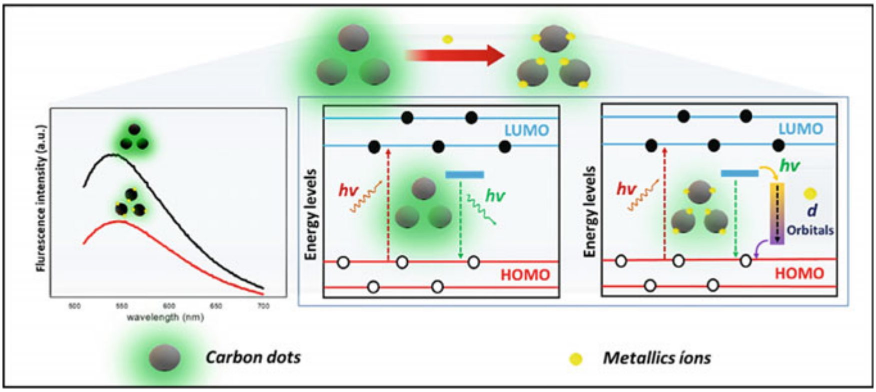

Fig. 5 Fluorescence mechanism and suppression when interaction with metal ions

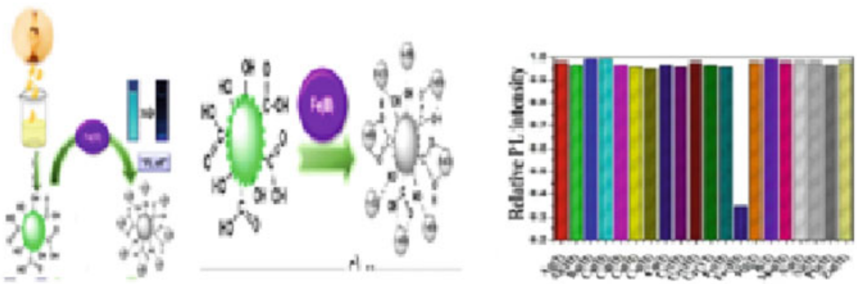

Fig. 6 Synthesis, sensing mechanism and selectivity of Fe^{3+}ions

The researcher uses N@CDs made from P. betel leaves to achieve a simple, quick, and selective detection of Eu^{3+} ion. The numerous functional groups like OH, COOH, NH_2, and O_2 linked to the surface of the N@CDs provide the N@CDs a good ability to detect metal ions. These functional groups can create a coordination bond with a variety of metal ions, making it easier to detect them. The fluorescence intensity of CDs was reduced owing to the development of a linkage between the metal ion and the functional groups on the N@CD surface. Even at 100M, Eu^{3+} was the most effective quenching agent among the various lanthanide metal ions examined. Eu^{3+} sensitively quenched the fluorescence of the N@CDs based on the fluorescence intensity of the N@CDs at 440 nm. The strong chelating interaction between the Eu^{3+} and the carboxylic and amine groups on the N@CD surface resulted in highly effective suppression of the N@CDs fluorescence by Eu^{3+}.

Mercury is another hazardous contaminant that harms humans in a variety of ways. As a result, it is necessary to analyze and identify the Hg^{2+} ion specifically. Lu and his colleagues employed pomelo peel as a carbon source for hydrothermally synthesizing water soluble carbon dots. The Hg^{2+} was detected using the carbon dot that was produced. It is possible to detect a concentration as low as 0.23 nm. They were also successful in analysing a lake water sample (Lu et al. 2012). Another study group used yam and a hydrothermal technique to create luminous nitrogen doped carbon dot. By quenching the fluorescence, the produced carbon dot can be used to detect mercury selectively (Li 2015). A one pot hydrothermal method of cucumber extract yields water-soluble, nitrogen-, sulfur-, and phosphorus-co-doped carbon dots (N/S/P-CDs), which may be used to make water-soluble, nitrogen-, sulfur-, and phosphorus-co-doped carbon dots (N/S/P-CDs). In addition, the N/S/P-CDs can be used as a fluorescent probe to detect Hg^{2+} ions (Wang 2014). Precise and selective detection of Cr^{6+} in aqueous systems is critical for both human and environmental health concerns. A simple and cost-effective hydrothermal technique was used to make water soluble carbon quantum dots (wsCQDs) from lemon peel waste. Ws CQDs were also employed to create a cost-effective, green, and highly sensitive fluorescent probe for detecting Cr^{6+} ions with a detection limit of 73 nm (Tyagi 2016).

Other metal ions which are also detected using carbon dots are listed in Table 2

In recent years, researchers have been concentrating on the creation of heteroatom doped-CQDs. N-doping has also been shown to improve the performance of CQDs in a variety of applications. Carbon dots were created using rice husk as a source. As

Table 2 Other metal ions

S. No.	Plant source	Synthesis method	Heavy metal remediation	References
1	Potato	Hydrothermal	Detecting Fe^{3+}	Xu (2014)
2	Sweet potato	Hydrothermal	Detecting Fe^{3+}	Shen (2017)
3	Bamboo leaves	Hydrothermal	Detecting Cu^{2+}	Liu
4	Pipe tobacco	Hydrothermal	Detecting Cu^{2}	Sha et al. (2013)
5	Mangosteen pulp	Calcination	Detecting Fe^{3+}	Yang

a result, only a few studies employed rice husk to make carbon dot and applied it to heavy metal removal. For example, in under 20 min, Zainal Abidin et al. produced amino functionalized carbon quantum dots from rice husks for cadmium removal, with a removal percentage of over 70% (Hafizah 2020). Similarly, Cu removal from aqueous solution was evaluated using Nitrogen and Bismuth doped carbon dot produced from rice husk. Both have a high level of efficiency. A simple hydrothermal approach was used to make nitrogen-doped carbon quantum dots (N-CQD) from a low-cost green material grass. Adsorption of Cd^{2+} and Pb^{2+} from water was used to test the product's surface activity, and the obtained values conveys that carbon dots have the ability to remove efficiently with 37% (Cd^{2+}) and 75% (Pb^{2+}), respectively (Sabet 2018). Sulfur- and nitrogen-co doped carbon nanospheres (CNs) were also synthesized using a direct hydrothermal approach from *Hibiscus sabdariffa* L. extract. Finally, due to the high surface area of sulfur-carbon nanospheres (CNs), they were employed as an adsorbent to remove Pb^{+2} ions from aqueous solutions (Hussain 2020).

Cu ion sensing and removal was studied using carbon dot synthesized from palm kernel by microwave irradiation method (Lun et al. 2020). The hydrothermal technique is used to syntheszse carbon dot from *Ginkgo biloba* leaves. Without any surface changes, the synthesized carbon dot was employed to selectively sense and remove Pb (II) ions. It showed removal efficiency when it was doped on agarose hydrogel (Xu et al. 2018).

For heavy metal removal, a magnetic nanometal oxide with carbon quantum dots (Fe_3O_4-PPCQDs) from Pomegranate peel (PP) was produced and used. It eliminates lead and cadmium ions from waste water selectively. Cadmium and lead absorption capacities of Fe_3O_4-PPCQDs were 17.92 and 23.75 mg g^{-1}, respectively (Asadollahzadeh et al. 2021).

4 Conclusion

Various parts of plant extracts are affordable, easily scaled up, and environmentally friendly for generating metal, metal oxide, and carbon dot nanoparticles. Toxic pollutants are not present in the synthesis methodology. When compared to conventional ways of nanoparticle preparation, this green process has various advantages, including high reactivity, ease of manufacture, and low cost. Environmental contamination is addressed by green synthesized nanomaterials, according to research. Heavy metal ions have been eliminated, successfully with a very high adsorption capacity. Although green nano adsorbents show excellent potential in environmental remediation, there are several major obstacles that must be overcome before their full potential can be realized. Stable nanomaterials that are selective to certain pollutants, easy to manufacture (in an environmentally responsible manner), and separate from the solution are expected to be produced in the future. They will also be able to perform other vital activities.

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Biomedical Applications of Phytonanotechnology

Satya Lakshmi Siragam

Abstract Phytonanotechnology is an emerging area of agricultural biotechnology that should consider different physicochemical and biological processes for the formulation of nanoparticles to load the extracts derived from innumerable plant parts. Methods exploited for the synthesis of the plant-based nanoparticles have some potential advantages like simple and fast techniques, cost-effectiveness, eco-friendly, stable for a prolonged time, convenient, and reproducible. Apart from these advantages, the phytonanoparticles have tremendous applications in operations related to catalysis, optoelectronics, diagnostic agents, in making of biosensing devices, antimicrobials, therapeutics, etc. It also allows the controlled release of fertilizers, pesticides, herbicides and is involved in the targeted delivery of biomolecules such as nucleotides, proteins, and activators. This chapter summarizes the past, present scenarios of phytonanotechnology in medicinal and pharmaceutical applications. The different classes of nanoformulations using plant extracts with their advantages have been emphasized. The commercial applications of phytonanoparticles in different sectors have been discussed. The use of plant-derived nanoformulations as antimicrobial, wound healing, anticancer agents, diagnostic agents, and targeted drug and gene delivery was discussed. Finally, the future scope of phytonanotechnology was covered in this chapter.

Keywords Phytonanoparticles · Biomedicine · Anti-cancer agent · Gene delivery · Drug targeting

1 Introduction

In past decades, herbal active principles and natural remedies are being used to cure diseases. The employed herbal active principles are alkaloidic, phenolic, flavonoidic, and polyphenolic in nature. Vitamin C, citric acid, and other phytonutrients present in plant-derived products work jointly to fight against a specific disease (Mahesh et al.

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2021a, b). Herbal therapeutic agents need a scientific approach to modify the active principle to change the delivery pattern that suits sustained and target release. This approach helps to increase patient compliance and avoids frequent dosing. As per the reports published by so many researchers, nanotechnology is the best alternative to overcome the toxicity and bioavailability problems associated with conventional dosage forms (Mitchell et al. 2021). The global market assumes the faster growth of the nanotechnology market from $5.2 billion in 2021 to $23.6 billion by 2026 with a 35.5% of growth rate (Dublin-Business Wire 2021).

Extensive research in the field of phytonanoformulations can improve the volume of innovative products, with lesser side effects than existing synthetic and conventional herbal formulations. Researchers investigated various herbal drug delivery techniques to suit the diversified structures of natural compounds, at the same time without loss of any physicochemical and biological properties. World Health Organization (WHO) has provided the suitable technical aid to expand a methodological analysis of plant-derived drugs for safety and quality aspects.

Among the Indian population, approximately 65% of people show interest to use traditional medicines. People of developed countries also demand herbal drugs as well. There is a steady demand for traditional medicines in developed countries. India is in second place, behind China in the herbal market. The AYUSH system of India presently covers 8000 herbal remedies with a domestic market worth of $5 billion. Annually over half a billion dollars revenue is generated through Ayurveda, Siddha, and Unani. The global market expects a profit of 111 billion dollars through plant-based medicines by 2023. Still, the phyto-pharma sector is in a nascent stage in India and in so many developed countries. The advancements in nanotechnology and advantages of nanoformulations over conventional products may increase the demand for phytopharmaceuticals, thereby offering an excellent opportunity for phytonanoformulations shortly.

The new research approaches in novel drug delivery systems can allow pharmaceutical companies to explore phytonanopharmaceuticals more constructively (Business World 2021).

The combined knowledge of science and technology directs the synthesis of nanoparticles to develop various nanotherapeutics and diagnostic agents in 1–100 nm size range.

Nanoparticles offer the following advantages over conventional formulations (Pandit et al. 2022).

1. Improved solubility thereby enhancing the bioavailability
2. Increased resident time in the body
3. Promotes targeted drug delivery
4. High carrier capacity with high stability
5. Maintenance of balance between efficacy and toxicity of a therapeutic compound.

1.1 *Different Approaches to Synthesize Phytonanoparticles*

Currently, various approaches are available to incorporate the herbal active principles into nano delivery vesicles to reach the target thereby being involved in the enhancement of therapeutic activity. Figure 1 outlined various approaches in the synthesis of phytonanoformulations (Roy et al. 2022).

Phytonanoparticles have wide applications in various sectors like agriculture, medicine, and industry. Figure 2 briefly depicts the applications of phytonanoparticles in various fields (Ahmed et al. 2021).

The smaller size and greater surface capacity of a drug containing nanoparticles may establish the rise in solubility and facilitate the bioavailability, in addition, overcome the barrier limitations in various routes of administration. Undoubtedly, people who are taking the conventional herbal formulations for various conditions may shift to the biogenic phytonanoformulations because of their added advantages. The advancements in nano-drug formulations and their delivery can occupy a significant market place and motivate various manufacturers involved in herbal formulations in the coming future (Abhijeet et al. 2021). Figure 3 describes the schematic depiction of phytonanoformulation synthesis and its uses.

The following section highlights the biomedical applications of herbal nanoformulations that were fabricated with various phytoactive principles.

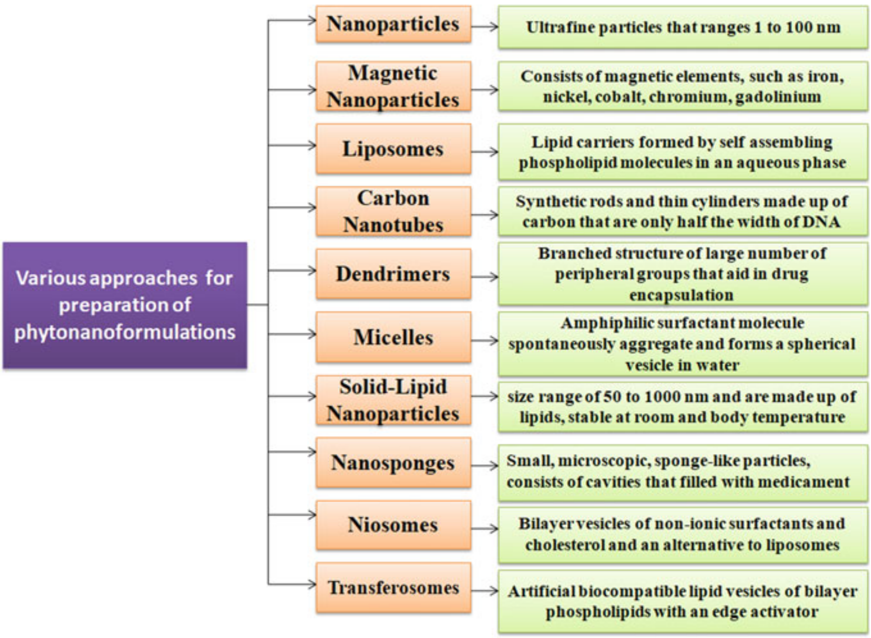

Fig. 1 Various approaches in the synthesis of phytonanoformulations

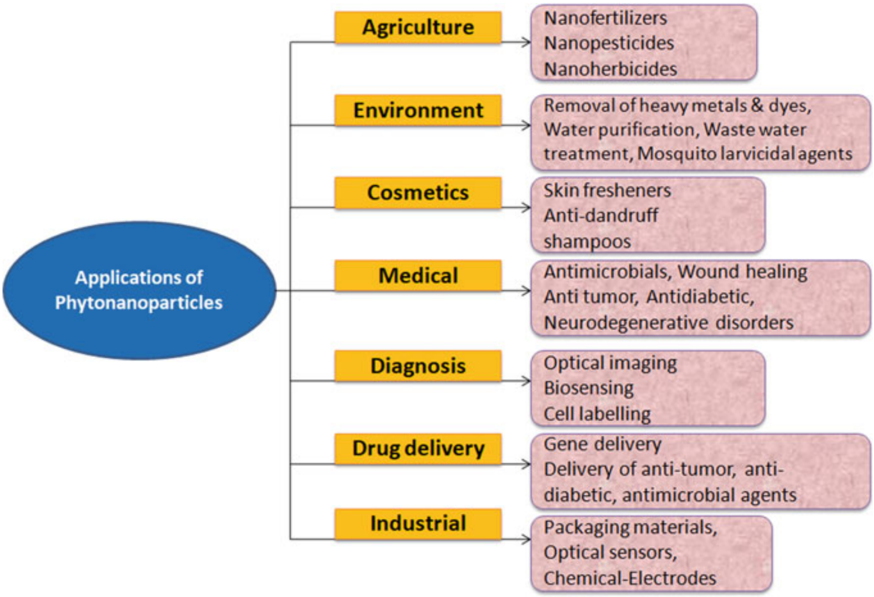

Fig. 2 Thrust areas of phytonanoformulations

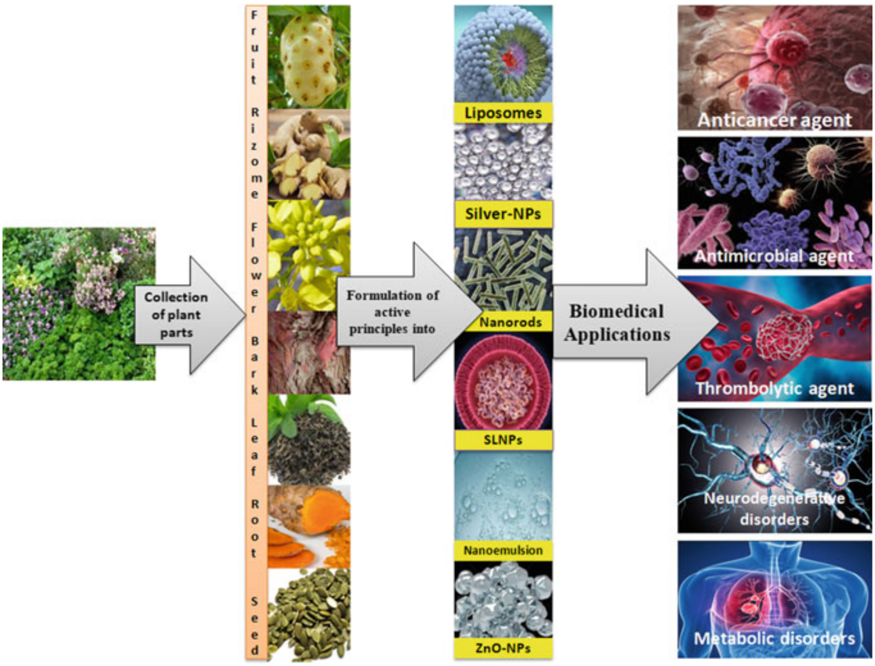

Fig. 3 Schematic depiction of phytonanoformulation synthesis and their potential uses

2 Phytonanoformulations and their Diversified Therapeutic Applications

2.1 As an Anticancer Agent

Targeted drug delivery of nanoformulations overcomes the insolubility and toxicity problems associated with conventional chemotherapeutic agents against cancer. The anticancer activity containing bioactive molecules is isolated from abundant plant parts like fruits, flowers, grains, etc. Plant-derived phyto-medicines are comparatively harmless and well compatible in healthy cells even in high doses than synthetic chemotherapeutic agents. Numerous examples of phytonanoparticles that are currently utilizing for cancer treatment are summarized here.

Extracts of various parts of *Moringa oleifera* reported anti-cancer activity (Charlette et al. 2018). Gold nanoparticles (AuNPs) were synthesized by flower parts of this plant (Anand et al. 2015). Niazimicin is the active principle found in *M. oleifera* that ascribes to anticancer activity. The flowers are fabricated to AuNPs that are cytotoxic to lung cancer cells (A549). The anticancer potentiality also exhibited against MCF7 (Michigan Cancer Foundation-7), HCT116 (human colorectal carcinoma)/Caco2 (human colorectal adenocarcinoma cells), and HepG2 (Human hepatoma cell line) cells with the nanoformulations of leaves and roots of the plant (Abd-Rabou et al. 2017).

Syzygium cumini fruit (Malabar plum) extract was used for formulation of AgNPs and exhibited significant anti-neoplastic and antioxidant potential on Dalton lymphoma cell lines (Mittal et al. 2014).

AgNPs derived from *Origanum vulgare* (Oregano) plant extract have high amounts of monoterpenoid phenols, exhibited increased anti-neoplastic activity on lung carcinoma culture (A549) with increased concentration (Sankar et al. 2013).

Compared to other chemotherapeutic drugs, AgNPs synthesized by green technology using *Morinda citrifolia* (MC) (Noni fruit) exhibited a higher cytotoxic effect against HeLa (cervical carcinoma cells of Henrietta Lacks) cell lines (Suman et al. 2013).

Zinc oxide nanoparticles (ZONPs) of *Salvadora persica* (toothbrush tree) extract were synthesized under optimum conditions (Miri and Sarani 2019).

Apigenin is a familiar class of flavanoid obtained from parsley, chamomile, celery, vine-spinach, artichokes, and oregano. Apigenin exhibits anticancer activity by the following mechanisms such as apoptosis of cells and autophagy, regulating cell cycle, hampering the cell migration, invasion, and initiating the immune responses (Yan et al. 2017). Different nanoformulations of apigenin and its anticancer potential were shown in Table 1.

Resveratrol is a phytoestrogen obtained from grapes, peanuts, cocoa, and berries of *Vaccinium* species. Because of its significant and multi-activity against many cancers, it has drawn so many researcher's attention (Jiang et al. 2017). The nanoformulations developed using resveratrol improved the solubility, bioavailability, and reversed the drug resistance acquired in transformed cell lines (Mondal and Bennett 2016). Some

Table 1 Phytonanoformulation as anticancer agents (Abd-Rabou et al. 2017; Mahesh et al. 2021a, b; Yongvongsoontorn et al. 2019; Wang et al. 2018a, b; Manatunga et al. 2017; Minaei et al. 2016; Zhang et al. 2018; Zhu et al. 2017; Hu et al. 2018; Wang et al. 2015)

Phytochemical	Source	Nanoformulation	Type of cancer cell lines
Niazimicin	*Moringa oleifera*	AuNPs	A549 lung cancer cells MCF7, HCT116/CaCo$_2$ and HepG2cells
γ-sitosterol and Kaempferol 7-Omethylether	*Syzygium cumini*	AgNPs	Dalton lymphoma cell lines
Monoterpenoidic phenols	*Origanum vulgare*	AgNPs	Lung carcinoma
Trisaccharide fatty acid ester (polysaccharides)	*Morinda citrifolia*	AgNPs	HeLa cell lines
Benzyl isothiocyanate	*Salvadora persica*	ZONPs	Oral cancer
Apigenin	*Petroselinum crispum, Matricaria recutita, Apium graveolens, Basella alba, Cynara cardunculus, Origanum vulgare*	PLGA-NPs (Poly(lactic-co-glycolide acid) Phospholipid phytosome	Mouse skin cancer Liver carcinoma
Resveratrol	*Vitis vinifera, Arachis hypogaea, Theobroma cacao, Vaccinium subg. Oxycoccus, Vaccinium sect. Cyanococcus*	Gelatin Liposomes PLGA AgNPs	Lung cancer Glioblastoma Prostate cancer Hepatoma
Curcumin	*Curcuma longa*	Carbon nano-tubes PLGA	Lung glandular cancer Pancreatic tumors
EGCG (epigallocatechin-3-gallate)	*Camellia sinensis*	PLA–PEG-NPs Chitosan NP PEG–EGCG with Sunitinib	22Rν1 prostate carcinoma cell Mel 928 Human melanoma Human renal cell cancer-allografted mice
6-Gingerol	*Zingiber officinale*	Nanosized proliposome Lipid nanocapsules PEGylated nanoniosome Magnetic hydroxyapatite	Liver cancer Liver cancer Breast cancer Breast and liver cancer
6-Gingerol and curcumin	*Zingiber officinale* *Curcuma longa*	Hydroxyapatite bilayered iron oxide NP composite	Breast tumor

(continued)

Table 1 (continued)

Phytochemical	Source	Nanoformulation	Type of cancer cell lines
Quercetin Quercetin–Doxorubicin Quercetin–Vincristine Quercetin–Cisplatin	*Allium cepa*, *Malus domestica*, *Vitis vinifera*	Lecithin Au nanocages Lipid-polymeric Lipid calcium phosphate	Breast cancer Breast cancer Lymphoma Bladder carcinoma
Vincristine sulfate and verapamil hydrochloride	*Catharanthus rosea*	Poly(lactic-coupled-glycolic acid) NPs	Breast tumor
Paclitaxel and etoposide	*Taxus brevifolia*	PLGA-NPs	Bone cancer cell lines

of the resveratrol nanoformulations and their potential uses were described in Table 1.

Curcumin, the bioactive principle isolated from the *Curcuma longa* roots. Curcumin is the familiar traditional herbal component employed in various applications like heart burn, ulcerative colitis, antiseptic, and antimalarial agent (Wilken et al. 2011). A list of the curcumin nanoformulation was shown in Table 1 with their potential uses.

Green tea contains a profuse amount of polyphenolic catechins which shows its impact on cancer cells proliferation, growth, and metastasis. Because of its less stability and low solubility, results in poor bioavailability. Table 1 describes the EGCG nanoformulations with their advantages compared to the conventional formulation.

Ginger is the most common spice used abundantly for the treatment of various ailments. The isolated herbal active principle, 6-Gingerol, was formulated into nano-composites to conquer the obstructions associated with traditional formulation thereby to enhance the medicinal activity. Gingerol nanoformulations were listed with their biological activity in Table 1.

Various fruit and vegetables such as apples, onions, and red grapes contain a profuse amount of quercetin (QUR), which is a pentahydroxyflavone, evidenced to exhibit diversified pharmacological benefits (Kulisic et al. 2012). Verma et al. (2013), delivered formulated core–shell structure of magnetic NPs of QUR through nebulisation and studied the cytotoxic capability of QUR against cancer carcinoma cells. Anticancer activities of quercetin in combination with other chemotherapeutic agents were shown in Table 1.

In addition to the examples covered under Table 1, some other researchers had investigated multiple nanoformulations loaded with phytoactive principles for anticancer activity (Amer et al. 2021).

2.2 As Antimicrobial Agents

Plant and plant derivatives of nanoformulations are extensively used in chronic wound gauzes, tissue grafts, drips, and blood transfusion sacks because of their germicidal activity. The potential antimicrobial activity of various phytonanoformulations has been studied collectively on bacterial pathogens, fungal, and viral microorganisms (Roy and Bharadvaja 2019). Because of the added advantages, all the phytonanoformulations exhibit better antimicrobial activities than the traditional herbal formulations.

The active principles of plant parts can enhance the native germicidal activity of AgNPs (Elani et al. 2018). The AgNPs fabricated with phytochemicals altered permeability property of membrane and lead to destruction of *Candida* sp. and allow the intracellular components to burst out from fungi (Logeswari et al. 2013).

Shyam et al. (2016), studied the formulation of AgNPs using *Saraca indica* leaf extract. This was utilized to determine the antibacterial capability on *Escherichia coli*, *Staphylococcus aureus*, and *Micrococcus luteus*, exhibited potential antibacterial activity with round-shaped AgNPs of herbal extract.

Homogenous root extract of *S. persica* utilized in formulation of AgNPs and was examined its activity on two bacterial pathogens (Arshad et al. 2021).

Ag and AuNPs synthesized from rhizome extract of *C. longa* exhibited significant activity on commonly occurring contaminants (Sharma et al. 2020). The freely soluble extract of *Angelica pubescens* Maxim was broadly used to make AgNPs to control pathogenic bacteria (Markus et al. 2017).

Leaf extract of *Garcinia mangostana*-based AgNPs were expressed activity on various drug-resistant pathogens. *Artemisia nilagirica* (Asteraceae)-based AgNPs also displayed superior action on numerous organisms. AgNPs of marine seaweed *Sargassum wightii* showed effective antibacterial activity against *S. aureus*, *Klebsiella pneumoniae*, and *Salmonella typhi*. Silver NPs of *Ocimum sanctum* leaf extract, *Origanum vulgare* (Oregano), Coptidis rhizome, *Carissa carandas* (Karonda) berry water extract, and *Salicornia bigelovii* displayed competent antibacterial activity on common microbes that comparable with generic antibiotics.

Plant-based AgNPs also exhibited antifungal activity against various fungal pathogens. The most commonly occurring fungal infections are due to *Candida* species (Wilson 2019). Recent studies showed the inhibition of opportunistic human fungal pathogens with Tulsi (*O. sanctum*)-mediated AgNPs (Rout 2012). Synthesized AgNPs with extracts of *Shoreatum buggaia*, *Boswellia ovalifoliolata*, and *Svensonia hyderobadensis* showed inhibitory activity against different species of *Aspergillus niger*, *Aspergillus flavus*, *Curvularia* sp., *Fusarium* sp., and *Rhizopus* sp. (Savithramma et al. 2011). *Svensonia hyderobadensis* showed higher anti-fungal activity with other nanoformulations compared to synthesized AgNPs.

Plant-based AgNPs were reported to contain bioactive principles isolated from various plants and exhibited antiviral activity against feline coronavirus (FCoV), Influenza virus, HIV, Adenovirus, Herpes simplex virus, Dengue virus, Chikungunya virus (Sharma et al. 2019), and Norovirus. The intrinsic antiviral activity of

Table 2 Phytonanoformulation as antiviral agents

Source	Nanoformulation	Type of virus	References
Phyllanthus niruri, *Andrographis paniculata*, and *Tinospora cordifolia*	AgNPs	Chikungunya virus	Sharma et al. (2019)
Centroceras clavulatum	AgNPs	Dengue fever virus	Murugan et al. (2016)
M. oleifera seed extract	AgNPs	Dengue serotype DEN-2	Sujitha et al. (2015)
Curcuma longa	AgNPs	Respiratory syncytial virus infection	Yang et al. (2016)

AgNPs is demonstrated by different mechanisms by inhibiting viral reproduction or by denaturing viral protein (gp120) that can block the entrance into host cells. A list of the phytonanoformulations with antiviral activity were shown in Table 2.

2.3 As Wound Healing Agents

Wounds are if unprotected, susceptible to microbial attack and pathogenesis. Wound dressings loaded with phytonanoparticles provide certain advantages such as reduction in healing time, inhibiting a variety of bacterial organisms, and exhibiting more antibacterial activity than AgNPs. Wound dressings encapsulated with phytonanoparticles are used in the control of burns, chronic ulcers, and diabetic foot ulcers (Cavanagh et al. 2010). Table 3 described some examples of wound dressings loaded with phytonanoparticles.

Table 3 Phytonanoformulations as wound dressings

Source	Nanoformulation	Material for dressing	Activity against	References
Piper nigrum leaf extract	AgNPs	Electrospun PCL (polycaprolactone) membrane	*S. aureus* and *E. Coli*	Augustine et al. (2016a, b)
Biophytum sensitivum	AgNPs	Nano-micro dual-porous calcium pectinate scaffolds	Human pathogens	Augustine et al. (2016a, b)
Mimosa pudica	AgNPs	PVA membranes	Human pathogens	Sundaramoorthi et al. (2009)

2.4 As Drug and Gene Delivery Agents

The main objective of nanoformulation is the site-specific release of entrapped drug formulations. A green approach to nanoparticle synthesis is finding a way to overcome the toxic effects associated with synthetic nanoparticles. *Trichoderma viride* AuNPs conjugated with vancomycin are very effective in the suppression of vancomycin-tolerating *S. aureus* at minimum concentration (Mohammed Fayaz et al. 2011). Nps of *Butea monosperma* leaf extract was fabricated and conjugated with anticancer drug doxorubicin showed enhanced anticancer activity by inhibiting cell proliferation. Another study showed the effective delivery of doxorubicin by *Peltophorum pterocarpum* mediated green-synthesized AuNPs (Patra et al. 2015).

2.5 In Neurodegenerative Disorders

Functional and structural damage of nerves leads to neurodegenerative disorders (NDs). The changes in the nervous system may result in retardation in thinking, motion, perception, and recollection. Alzheimer's disease (AD) and other types of dementia, Parkinson's disease (PD), and PD-related other disorders are most common NDs; multiple sclerosis (MS), Huntington's disease (HD), and Amyotrophic lateral sclerosis (ALS) are the most frequent types. Worldwide, for every four members, one person is going to suffer from NDs (Hodjat et al. 2017). Researchers have been reported the therapeutic benefits of herbal active principles in NDs patients. Phytochemicals such as polyphenols (Davatgaran-Taghipour et al. 2017), alkaloids (Wang et al. 2018a, b), and terpenoids (Khazdair 2015) from a variety of plants were extensively studied and reported. Nanoformulation-based phytochemicals are superior than the conventional dosage forms for curing neurodegenerative disorders-targeting delivery to brain, break down naturally, low toxicity to peripheral organs, modulation of inflammatory events, neuronal tissue restoration, inhibit neural apoptosis or toxicity, and regulate other functions (Seyed et al. 2020). Table 4 describes the phytonanoformulations with their uses in neurodegenerative disorders.

2.6 As an Anti-Diabetic Agent

Phytonanoformulations are studied extensively in the treatment of diabetes mellitus. Nanotechnology-based phytoformulations are recommended for improved therapeutic efficacy against diabetes mellitus (Kesharwani et al. 2018). Nanophytoformulations offer all the advantages of nanoformulations such as delivery of drugs precisely to the target, allowing the various routes of administration, enhanced systemic availability, improved stability of drugs, and reduced risk of toxicity. Table 5 highlighted the plant-based nanoformulations against diabetes. The researchers have

Table 4 Phytonanoformulations in neurodegenerative disorders (Seyed et al. 2020)

Type of nanoformulation	Benefits
Curcumin	
Lactoferrin NPs	Protect SKN-SH neuroblastoma cell line of dopaminergic cells
Lipid-polyethyleneglycolpolylactide nanoparticles	↓ the Aβ (amyloid-beta) aggregation
Plain liposomes and anti-transferrin antibody tagged liposomes	↑ the brain permeation of drug in AD patients
PLGA associated Cur NPs coupled with Tet-1 peptide	AD
Zwitterionic polymer-NPs	Block the fibrillation of Aβ42 fibrils
Solid lipid NPs (SLNPs)	↑ 3-nitro1-propionic acid (3-NP)-enhanced HD in rats
Selenium-conjugated PLGA nanospheres	AD
Drug-loaded lipid-based nanoformulation	PD
Entraped PEG-PLA	Significant increase in memory cue
Cur-loaded lipid core nanocapsules	AD
Quercetin	
Nano lipidic carriers	Elevated drug concentration in plasma and target specific delivery
Nanocrystals	PD
SLNPs	Retention of memory in animal models
Liposomes	Reduced degradation and degradation of cholinergic neurons
Liposome	Dispensing via nasal cavity resulted decreased oxidative damage
PLGA nanocapsule	Higher brain intake and enhanced bioavailability
Resveratrol	
PS80-layered poly(lactide) NPs	↓neuronal damage properties
Lipid-core NPs	Aβ-provoked neuroinflammation was regulated
Mesoporous nano-selenium	Accumulation of Aβ was blocked, decreases oxidative stress, and improves memory
Polymeric micelles	Repression of the Aβ-induced damages via reducing oxidative stress and apoptosis
Nanoemulsion loaded with Vitamin E	Positive effects in PD
SLNPs conjugated with apolipoprotein E	Bioavailability and concentration get enhanced thereby permeation of the drug in the brain improved
Chitosan-over-layered PLGA NPs	Reduced concentration of inflammatory cytokines, enhance the neuroprotective IL-10 concentration

(continued)

Table 4 (continued)

Type of nanoformulation	Benefits
Piperine	
Tween-modified monoolein cubosomes	Higher potency over conventional drugs and ability to re-establish the perception function
Intranasal chitosan NPs	Showed more efficacy in AD model
Gallic Acid	
GA-entrapped chitosan NPs (GANP)	Scopolamine-intensified amnesia in vivo
Ferulic Acid	
SLNPs	Repressed Aβ-promoted cell death, reduced ROS (Reactive oxygen species) production, and inhibit the apoptosis pathway
SLNPs	Induced phosphoinositide 3-kinases (PI3Ks) pathway in ischemic neural injuries mode

investigated the pharmacological effects and enhanced biopharmaceutical properties with various phytoactive principles containing nanoformulations such as rosmarinic acid, berberine, Stevia glycosides, Asiatic acid Glycyrrhizin, α-Eleostearic acid, Scutellarin, Silybum Flavonolignans, Gallic acid, Catechins, Pelargonidin, Thymoquinone, and Ferulic Acid.

2.7 In the Treatment of Metabolic Disorders

Metabolic disorder or the syndrome is a group of medical conditions that leads to an unhealthy condition in humans. Metabolic syndromes increase the risk of cardiovascular disorders such as atherosclerosis, obesity, resistance to insulin, hypertension, cerebrovascular accident, and atherogenic dyslipidemia (McCracken et al. 2018).

Several phytopharmaceuticals are fabricated into nanoformulations that induce molecular mechanisms against diverse pharmacological targets. Table 6 described the list of phytoactive principles and nanosizing methods employed with their improved pharmacological activities.

2.8 As Thrombolytic Agents

To overcome the limitations associated with currently available thrombolytic agents, researchers have investigated various plant-derived products for thrombolytic activity (Ali et al. 2021). Akinola et al. (2020) reported the phytosynthesized TiO2 NPs of

Table 5 Phytonanoformulations as anti-diabetic agents (Dewanjee et al. 2020)

Type of nanoformulation	Benefits
Curcumin	
NPs	Fall in fasting blood glucose and improved production of insulin hormone and insulin receptor (IR) mRNAs get expressed in diabetic rats
ZnO–NPs	Decreased blood glucose levels, improved insulin serum concentration, and GLUT2 and glucokinase genes expression in pancreas
PLGA-NPs	Plasma levels of CUR were improved and increased biological half-life
PLGA-PVA-NPs	Delayed cataract formation in diabetic rats
Polylactic acid (PLA) and polyethylene glycol (PEG) conjugated polymeric NPs	Effective in rendering hyperglycaemia, hypoinsulinemia, and diabetes-induced hepatotoxicity
Resveratrol	
Nanocochleates	Effective in the regulation of insulin-resistant diabetes
Casein NPs	pH tolerance, rapid permeation, and support sustained drug release
SLNPs	Increased therapeutic efficacy
PLGA NPs	Improved drug entrapment efficiency and increased dissolution thereby enhance the plasma level of drug concentration
Naringenin	
Nanoemulsion using PVP	Increased solubility results enhanced gastrointestinal absorption, dissolution, and oral bioavailability
Soluthin-maltodextrin nanocarrier	Enhanced oral bioavailability (116 fold) and reduced toxicity
Liposomal nanoformulation	Increased solubility and oral bioavailability
Chitosan core-shell loaded NPs	Enhanced drug loading capacity (> 90%)
Quercetin	
PLGA-NPs	Increased the oral bioavailability of QUR (> five-fold)
Nanorods	Inhibition of hyperglycaemia condition, regulates glucose-metabolizing enzymes, and oxidative stress
PEG-block nanocarrier	Regulation of diabetes and associated nephropathy via enhancing the serum content of QUR in rats

(continued)

Table 5 (continued)

Type of nanoformulation	Benefits
QUR-succinylated chitosan-alginate core-shell-corona structured NPs	Increased oral hypoglycemic effect of QUR in diabetes-induced rats this effect was contrast to native oral QUR
Soluplus micelles	Increased drug plasma level (> 16%) of QUR and sustain the drug release for prolonged time
Apigenin	
Microwave-synthesized -pluronic F127 NPs	Enhanced dissolution rate and oral absorption
Nanomixed micelles system consisting Soluplus and pluronic F127 polymers	Prolonged release pattern, and improved absorption through GIT
Carbon nano powder-based solid dispersion	Improved stability and bioavailability
Nanoliposomes	Repress apoptosis of myocardial cells in diabetic cardiomyopathy rats
Myricitrin	
SLNPs	Recompensate hyperglycaemia, counteract the insulin activity, ruination of glucose uptake by myotubes
Baicalin	
Nanoliposome	Improved pharmacokinetic parameters
Pluronic P123 and sodium taurocholate conjugated Nanomicelles	Improved absorption and resident time in blood
Nanostructured lipid carriers	Change in release pattern of baicalin and elevated anti-diabetic activity
Luteolin	
SLNPs	Enhance solubility, biological half-life, and bioavailability
Mangiferin	
Nanomicelles fabricated with self-assembled phospholipids	Enhanced biopharmaceutical attributes
Nanomixed micelles	Intestinal penetration and enhanced oral bioavailability
β-lactoglobulin NPs	Improved specificity toward target, counteract pepsin activity, safeguarding the probiotic strains in the gut region
Gymnemic Acid	
Nanocrystals	Increased oral bioavailability
Nanocrystals-loaded tablets	Anti-hyperglycemic activity
Reduced gold nanoparticles	Glucose uptake capacity of 3T3-L1 adipocytes was enhanced via the insulin-dependent/independent pathway

(continued)

Table 5 (continued)

Type of nanoformulation	Benefits
Chitosan NPs	Sustain the release pattern of gymnemic acid for 1 day
Emodin	
Nanoemulsion	Enhanced plasma levels of emodin, increased excretion time interval

Table 6 Phytonanoformulations in the treatment of metabolic disorders

Type of nanoformulation	Benefits	References
Curcumin		
PBLG-PEG-PBLG	↑CaSR (calcium-sensing receptor protein), ↑CSE (Cystathionine-γ-lyase), ↑CaM (complementary and alternative medicine) to suppress diabetic cardiomyopathy	Tong et al. (2018)
SNEDDS	↓TNF-α ↓IL-6 in diabetic neuropathy	Joshi et al. (2013)
PLGA-PVA NPs	↓VEGF (vascular endothelial growth factor) ↑cellular uptake, bioavailability to treat diabetic cataract	Grama et al. (2013)
Pluronic nanomicelles	↑Pdx-1 and NKx6.1 in STZ (streptozotocin)-induced diabetes	El-Far et al. (2017)
PLGA-based NPs with Q10	↓CRP (C-reactive protein), IL-6, total cholesterol, ↓plasma triglycerides ↑HDL in diabetes complications	Devadasu et al. (2011)
Nanoemulsion	Inhibition of HMGR (HMG-CoA reductase) along with ACE to control hypertension and hypercholesterolemia	Rachmawati et al. (2016)
Capsicum oleoresin		
Nanoemulsion	↓Adipogenic gene expression ↑PPAR-α (peroxisome proliferator-stimulated receptor), UCP2 (uncoupling protein) and CPT-1α (Carnitine palmitoyltransferase 1) in treating obesity	Kim et al. (2014)

(continued)

Table 6 (continued)

Type of nanoformulation	Benefits	References
Alginate double layer nanoemulsion	↓mRNA expression for PPAR-γ ↓fatty acid binding protein adipocyte protein-2 hormone-sensitive lipase ↑carnitine ↑palmitoyl transferase-1α ↑HSL(hormone-sensitive lipase) and CPT-1α genes ↓PPAR-γ and aP2 to reduce obesity	Lee et al. (2017)
Berberine		
Solid lipid nanoparticles (SLNs)	↓Body mass, ↓fasting blood glucose, HOMA-IR (homeostasis model assessment of insulin resistance) Increased impairment in glucose tolerance	Xue et al. (2013)
PLGA-PEG-PLGA block copolymers	Regulation of PCSK-9 (proprotein convertase subtilisin/kexin type 9) mRNA expression in high LDL cholesterol	Ochin and Garelnabi (2018)
Naringenin		
Alginate-coated chitosan core-shell	No toxicity, better therapeutic effect in diabetes	Shi et al. (2016)
Quercetin		
PLGA NPs	↑CAT (catalase) and SOD (superoxide dismutases) levels ↓drug doses in diabetes	Chitkara et al. (2012)
Emodin		
Transferosome	Upregulation of ATGL (adipose triglyceride lipase) protein expression, suppression of GOS2 protein expression, body weight, and adipocyte size in obesity	Lu et al. (2014)
Gymnemic acid		
Nanosuspension	↓Blood glucose levels in diabetes	Ravichandran (2014)

(continued)

Table 6 (continued)

Type of nanoformulation	Benefits	References
Baicalin		
Nanostructured lipid carriers	↓FBG, HbA1c (Hemoglobin A1c), and TG levels in diabetes	Shi et al. (2016)
Resveratrol		
Nanoliposomes	↑ROS-inactivating enzymes including GSH-Px and SOD in diabetes	Yucel et al. (2018)
Nanocapsule	Blood pressure regulation	Shahraki et al. (2017)
Silybin		
PLGA polymers	↑antioxidant characteristics, rejuvenating activity on β cells' membrane permeability	Das et al. (2014)
Myricitrin		
SLNs	Improvement of SOD level, ↑muscle and myotube glycogen content, regulation of Glut4 gene in skeletal muscle and C2C12 cells, Bcl-2 gene expression, Bax to Bcl-2 ratio of myotubes	Ahangarpour et al. (2018)

distinct *Cola nitida* plant parts and investigated for thrombolytic activity. Phytosynthesized AgNPs incorporated with leaf and seed extracts of *Synsepalum dulcificum* were reported for thrombolytic activity (Lateef et al. 2016).

3 Conclusions and Future Prospective

Synthesis of nanoformulations using phytoactive principles is an efficient and eco-friendly method to deliver the therapeutic agent to a specific target. Products extracted from plants have numerous bioactive principles of both reducing and stability properties to with stand the reaction conditions while synthesizing phytonanoformulations. The derived phytonanoformulations offer advantages like improved solubility, thereby enhancing the bioavailability, maintenance of parity between efficacy and toxicity of a therapeutic compound. The synthesized nanoformulations find agricultural, environmental, cosmetic, medical, diagnostic, drug delivery, and industrial applications. The tremendous growth of nanotechnology supports the fabrication of bioactive principles of plant into phytonanoformulations. Because of less toxicity, the natural plant formulations are might be good competitors to the synthetic nanoformulations in the coming future. It is necessary to describe the biomolecular interaction of NPs and the regulation of gene expression. Further investigation is needed for the molecular and submolecular level functions of nanophytoformulations.

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Application of Nanotechnology in Plant Secondary Metabolites Production

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Abstract After decades of research, the crucial role of primary metabolites as necessary compounds for the basic life functions and secondary metabolites as essential compounds for the survival and adapting to the environment during abiotic and biotic stresses conditions were deduced. Various secondary metabolites like alkaloids, flavonoids, phenolic acids, steroids, glycosides, tannins, resins, terpenoids, etc., are extensively studied for their commercial applications in cosmetics, pharmaceuticals, nutraceuticals, and food industries. Currently, there is a vast scope in enhancing plant secondary metabolite production to obtain high yields appropriate for commercial use. Different elicitation methods like biotic (rhizobacteria and fungus) and abiotic (light, salt, metals, temperatures, and drought) elicitors are used to increase secondary metabolite production. Lately, phytonanotechnology has been gaining more attention in plant biotechnology to develop efficient methods to increase plant growth and enhance the production of plant secondary metabolites. The framework of this chapter summarizes the impact of nanomaterials in promoting the production of secondary plant metabolites and their applications. Based on available scientific reports, the knowledge of nanomaterial–plant interactions, mechanism, factors governing these cross-talks, and their biological significance are explored here. Additionally, to improve the influence of nanoparticles on the production of valuable pant secondary metabolites, future directions and strategies for developing formulations are discussed.

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1 Introduction

Nanotechnology is a science which works on a scale of one billionth-a-meter (10^{-9}), and it is also a case of deception in the atom and the ratio of cells. The nanoparticles are very crucial elements in the formation of nanostructure and are much smaller than the regular commodities of every day use as defined by Newton's law of motion, but quite larger than atoms or a mere appearing molecules controlled by quantum-mechanics (Roy and Bharadvaja 2017). The nanoparticles are in different size range, shape, morphology character, and of different crystallinities. They may have smaller aspect ratio having either round or cube kind of morphology, or with larger aspect ratio of tubular or whisker form (Iravani 2017; Roy and Bharadvaja 2017).

The uniqueness of nanoparticles compared to their large counterparts of similar composition is due to quantum and surface effects (Roy and Bharadvaja 2019). Nanoparticle represents unique physiochemical and mechanical properties compared to its objects in bulk form. As the size of nanoparticle decreases, the ratios among the atoms on the surface are higher in contrast to ones at its interiors, preceding smooth scaling of the physiochemical properties. Consequently, the nanoparticles are with greater surface-to-volume ratio, higher chemical reactivity, and decreased melting points. Since the size of nanoparticles is way smaller, their electrons emerge as constrained and have quantized energy spectrum, ensuing in quantum-size effects (Roy 2021; Roy et al. 2022). One instance of a quantum-size influence is the overall form of magnetic moments. Such as, nanoparticles with non-magnetic composition in bulk but, when in nanoform, establish magnetic moments (Iravani 2017; Roy et al. 2021a, b). Some of these nanoparticles are platinum, gold, and palladium-nanoparticles (Pacheco and Buzea 2018).

Nanotechnology has pervaded substantially in all sciences, including physics, chemistry, material/medical sciences, and biotechnology (Raina et al. 2020; Nagore et al. 2021; Roy et al. 2021a, b). The nanoparticles are beforehand in our daily appliances such as textile engineering, cosmetology, and food processing. Copious studies were performed to examine the prospective usage of nanoparticles inside the human body, along with delivery of drugs, cancer therapy, gene therapy, tissue engineering, and medication of contagious and genetic-diseases (Pandit et al. 2022).

Because of their nano size, the nanoparticles can be absorbed by the plant, animal, and human systems. In addition, the nanoparticles can get inside the cellular and sub-cellular organs and affect cellular processes. The nanoparticles of specific configurations have beneficial outcomes in particular plant systems (Pacheco and Buzea 2018; Mittal and Roy 2021).

Abiotic and biotic stress can persistently limit the crop's yield and quality of agricultural production. To overcome this stress in agriculture, we need technology or method to improve agriculture production. In its current status, nanotechnology has proven to increase agriculture production by increasing the competence of nutrient delivery and precise management of fertilizers, pesticides, and herbicides (Shang et al. 2019).

Albeit, nanotechnology or specifically the nanoparticles have been helpful to address most of the agricultural issues along with notable improvisation in plant growth, proper nutrient uptake, mitigation of plant diseases in contrast to the ordinary methods (Pacheco and Buzea 2018). For instance, the regulated release of the nano-fertilizers has revamped the crop growth, yield rate, and productiveness. The crops are notably improvised due to the nano-target-delivery perspective (gene-transfer). The application of nano pesticides can protect against various plant diseases. The nanoparticles may also enhance stress tolerance and soil improvement. Nano-sensors and computed techniques have a greater endowment in precision farming. To date, most of the research has been done to eliminate the benefitting or toxic properties of nanoparticles on growth, developmental stage, photosynthetic rates, and metabolism of plants (Kumar et al. 2019).

2 Importance of Nanoparticles Under Stress Conditions

The primary concern for agriculture production is the drastic changes in the climatic factors such as water shortage, extreme temperature, alkalinity, salinity, and toxic metals in soils and affected the physiological and developmental plant processes, which eventually impacts the agriculture crop quality and yield (Calleja-Cabrera et al. 2020). Hence, it is essential to improve agriculture crop tolerance against biotic and abiotic stresses to deal with adverse climatic changes. Various research has been carried out using different methods like cultural methodologies, conventional techniques, and genetics and genomics strategies (genetic engineering and genome editing) to improve the plants adaptation to the fluctuating environment (Raza et al. 2019). Various researchers also developed many stress management strategies that often do not consider environmental factors. The fertilizers and continuous irrigation increase the rising cost of agriculture production every year (Taran et al. 2017). In this regard, nanotechnology may provide promising strategies to improve crop productivity under abiotic and biotic stress conditions.

2.1 Abiotic Stress

Abiotic stress is associated with water stress, extreme temperatures, high salinity, and heavy metals toxicity. These stresses lead to increase in reactive oxygen species, decreasing the efficiency of photosynthesis, increasing membrane and cell wall damage (Kumar et al. 2021). These will affect the overall physiological and molecular processes in plants, leading to a significant loss in crop yield and seed quality worldwide (Rajput et al. 2021). Many strategies have been developed to prevail over these abiotic stressors, including applying different nanoparticles.

2.2 Drought Stress and Nanoparticles

Drought stress is associated with high temperature, leading to water evaporation from the soil. Drought stress is reported to reduce growth, create plant hormones imbalance and oxidative stress, which eventually leads to the underdeveloped growth of plants and loss of agricultural yield (Kumari et al. 2018).

The usage of nanoparticles in drought-affected plants is shown to prevent cell membrane damage, improve photosynthesis, increase secondary metabolite production, and antioxidant enzyme activities to overcome the adverse drought stress. Silicon, titanium, zinc, selenium, and copper nanoparticles application demonstrated the positive influence under drought stress by improving the physiological parameters and the plant performance to improve the crop yield (Seleiman et al. 2021).

The application of selenium and selenium dioxide nanoparticles to the drought-stressed *Fragaria ananassa* improved chlorophyll content and antioxidant enzymes activities (Zahedi et al. 2020). Whereas, titanium dioxide and nanoparticles application on *Dracocephalum moldavicum* increased the production of secondary metabolites such as apigenin-7-O-glucoside, rosmarinic acid, and chlorogenic acid. In addition, applying copper nanoparticles to *Zea mays* against drought stress increased the chlorophyll, anthocyanin, and carotenoids and imparted tolerance to the plants. The exogenous application of zinc and copper nanoparticles under drought conditions stabilized the photosynthetic pigments and improved water retention in *Oryza sativa* seedlings (Taran et al. 2017).

2.3 Salinity Stress and Nanoparticles

Osmotic stress in plants is caused by the build-up of high dosages of sodium and chlorine content of the soil, which results in decreased turgor pressure and soil water potential (Singh et al. 2021). It also generates the cell's ROS content due to its imbalances in ion homeostasis. This osmatic stress causes detrimental effects on biochemical, physiological, and molecular levels associated with productivity of the crops and plant growth (Arif et al. 2020).

Currently, more focus is shifted to the use of nanoparticles to improve growth rate and development during salinity stress (Etesami et al. 2021). The various nanoparticles are reported to regulate salinity tolerance by regulating phytohormone levels, increasing activities of antioxidant enzymes, preserving ion homeostasis, and gene expression of stress-associated metabolites (Zulfiqar and Ashraf 2021). Foliar application and seed priming with zinc oxide nanoparticles to rapeseed and *Lupinus termis* have proven to be very effective in overcoming salinity's detrimental effect by osmoregulation in plants under salinity stress (Hezaveh et al. 2019). In addition, the seed priming with silver nanoparticles on *Triticum aestivum* was also shown to improve salinity stress management (Hezaveh et al. 2019). The exogenous application of copper nanoparticles to the *Solanum lycopersicum* leaves in salt stress conditions has enhanced the growth and content of polyphenols, glutathione, and vitamin C, thereby increasing plant stress tolerance (Huerta-García et al. 2014). Thus, the utilization of nanoparticles will result in increased plant growth and plays a vital part in enhancing the productivity of the plants.

2.4 Metal Toxicity and Nanoparticles

Worldwide, metal toxicity is increasing exponentially due to anthropogenic causes. The soil toxicity with metals is an important factor that affects crop productivity and alters the food chain, affecting the ecosystem and human health. The development of eco-friendly and effective nanoparticles for the application in controlling toxicity of heavy metals (Cd(II), Cr(VI), Cu(II), Pb(II), and Hg(II)) has received much attention in the field. The researcher has developed various methods to deal with metal toxicity, such as physiochemical and biological methods (Yu et al. 2021). However, most of these strategies have significant disadvantages, like secondary pollution and higher expenditures. Therefore, it is imperative to develop technologies that eliminate metal toxicity from contaminated soil. The application of nanoparticles to the plants has decreased metal absorption and increased the synthesis of defense-related enzymes, proline, and glutathione content.

The usage of copper nanoparticles reduced the translocation of cadmium from the soil and improved nutrient uptake and biomass in *T. aestivum* (Noman et al. 2020). Similarly, the usage of silicon nanoparticles in *Glycine max* improved total chlorophyll content and decreased metal uptake under mercury toxicity (Li et al. 2020). In addition, titanium dioxide nanoparticles were successfully applied to alter the movement and toxicity of heavy metals present in water and soil (Yu et al. 2021). Chitosan bound with titanium dioxide nanoparticles removed Cu (II) and Cd (II) from wastewater (Gebru and Das 2017). Numerous investigations are carried out to reduce the toxicity of heavy metals to improve plant growth and development.

2.5 Biotic Stress

Biotic stresses are triggered by organisms such as bacteria, viruses, fungi, parasites, and insects to crops, leading to various diseases and leading to a decrease in crop production. Annually the biotic stress leads to approximately 20–40% of loss in crop loss by multiple pests and pathogens (Khan et al. 2021a, b). The current management of biotic stress largely depend on toxic chemicals that are used indiscriminately and excessively, further aggravating global warming and causing hostile consequences such as increased resistance in pathogens and their expansion, adverse conditions for favorable microbes and pose a risk for the ecosystem and human health (Cavicchioli et al. 2019). The development of nanotechnology promises an alternate way of eco-friendly and cost-effective management of biotic stress in crops.

Many studies have reported that metallic nanoparticles such as copper, silver, and gold exhibit strong antimicrobial activity against various microorganisms in plants. According to Phu et al., the nanoparticles exhibit anti-bacterial and antifungal activity against different plant pathogens among other crops (Phu et al. 2010).

3 Antifungal Properties of Nanoparticles

Among various pathogens, fungi cause numerous disorders in agriculture plants. Phytopathogenic fungi have the flexibility in adapting and colonizing in any extreme environmental conditions. They can potentially infect plants at different development stages from slow growth and production, which are reflected in yield and cause economic and ecological problems worldwide (Pariona et al. 2019). Fungi belong to the Fusarium group infest many crops and forest species, causing many economic and ecological damages. These fungi initially invade plant vascular tissues, and they inhibit the xylem water transport mechanism by blocking the vessel leading to wilting in infected plants (Pariona et al. 2019). To control, there is a need to develop potent fungicides. Nanoparticles have proven to be an excellent antifungal activity, and it is a huge potential for replacing chemical fungicides to control fungal infections in plants. Metal nanoparticles like copper, selenium, nickel, manganese, and iron have been synthesized and demonstrated significant antifungal properties against a wide variety of fungi when applied to field plants (Cruz-Luna et al. 2021).

Silver nanoparticles have been widely investigated to overcome phytopathogenic fungal infections. The size, shape, and structure are crucial and play important part in its activity. The nanoparticles between 10 and 20 nm size are shown to have greater antifungal activity (Cruz-Luna et al. 2021). These metal nanoparticles release various ions, and generated ions bind to the membrane protein and affect the cell membrane permeability. Once they enter inside, they affect the potential of the mitochondrial membrane by up-regulating the expression of genes responsible for oxidative stress. The generated reactive oxygen species cause damage to the membrane and other important macromolecules and affect the nutrient absorption, finally leading to cell death (Cruz-Luna et al. 2021; Mussin et al. 2019).

4 Anti-bacterial Properties of Nanoparticles

One of the major agricultural damage will be caused by the microbial contamination of the crops and their products on the farm, resulting in financial loss to the farmers

(Karimi 2019). At present, various investigations have revealed that the nanoparticles of metal and metal oxide exhibit strong antimicrobial activity (Teow et al. 2018).

Zinc oxide, silver, titanium oxide, and cupper are being proved to demonstrate antimicrobial activity. All these nanoparticles can attach to the bacterial membrane promoting the production of reactive oxygen species and impair cellular elements like lipids, proteins, and nucleic acids (Cai et al. 2018). Manganese oxide nanoparticles persuaded systemic resistance to oppress *Ralstonia solanacearum* infection by activating the ethylene, salicylic acid, and jasmonic acid pathways in *S. lycopersicum* (Imada et al. 2016).

In addition, the green synthesis of copper nanoparticles showed anti-bacterial activity by inhibiting the augmentation of gram-positive and negative bacteria, like *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Klebsiella pneumoniae*, *Shigella flexneri*, and *Proteus vulgaris* (Kasana et al. 2016). This shows the prospect of nanoparticles application to replace chemical pesticides in the agriculture field.

5 Interaction of Nanoparticles in Plants

5.1 Nanoparticle's Uptake

The nanoparticles and plant interactions are a relatively new field of study that has vast potential and helps understand the mechanism of nanoparticles' action mechanisms. Nanoparticle uptake is not clearly defined in the plant system and is subject to much speculation (Pacheco and Buzea 2018; Taylor et al. 2014). Metal nanoparticles may be imported as such, or in oxidized form, dissolved in soil water, or imported in ionic form in plants (Rico et al. 2011). However, a consensus is influenced by numerous factors like, the nature of nanoparticles (size and shape), environmental conditions, and the plant species (Tripathi et al. 2017), affecting the nanoparticles uptake. Size of the nanoparticle is the main limitations for entering into plant tissues. Reports show that 0.5–50 nm dimension nanoparticles can move and amass inside the plant cells (Rico et al. 2011). In addition, different plants showed species variation in response to nanoparticle treatments (Taylor et al. 2014). For example, crops belonging to other families exposed to magnetic carbon-coated gold and titanium nanoparticles showed accumulation and absorption patterns inside the plants (Pacheco and Buzea 2018).

The method or application modes are critical in determining the efficiency of nanomaterials to internalize the plant cells. Roots are intended for absorbing water and nutrients, whereas exchange of gases takes place by leaves, which exhibit a cuticle that inhibits the diffusion of substances. Coating nanomaterial surfaces with different agents can influence its absorption properties in plants (Barua and Mitragotri 2014). However, few studies show particles can also enter through stomatal openings at the lower surface of leaves (Barua and Mitragotri 2014).

There are a few ways nanoparticles can penetrate the plant cells, and it mainly depends on the method/mode of nanomaterials application. Nanoparticles are also shown to interact with several components present in the environment, affecting their uptake from the soil. For example, the existence of organic matter improves the bioavailability of nanoparticles. In addition, microorganisms in soil improve the plant uptake of nanoparticles if they are involved in symbiosis (Wang et al. 2016).

The roots are shown to uptake smaller sized nanoparticles of 0.5–20 nm by apoplastic route (root pores within epidermal cells), and the larger than 20 nm causes a physical barrier for nanoparticles to enter through root pores and into the cells (Deng et al. 2014; Taylor et al. 2014). The internalized nanoparticles are confronted by capillary and osmotic force of the cells, and finally, they will diffuse via the apoplast to enter the endodermis.

Another mode of nanoparticle absorption is by means of symplastic pathway thorough the inward flank of the plasma membrane of a plant cell. In general, nanoparticles are complexed with protein carriers like aquaporins and ion channels to enter into cells (Tripathi et al. 2017).

The exogenous nanoparticles can also internalize via stomatal pores present on the exterior surface of leaves. Nanoparticles, that entered through leaves can translocate to different parts like stems, flowers, fruits, and roots (Hong et al. 2014). Nanoparticles can also transit to neighboring cells via plasmodesmata present between cells (Deng et al. 2014). Additionally, we can identify and utilize nanomaterials that fail to penetrate the plant cell, however can penetrate microorganisms (bacteria and fungi) to treat crop infections and diseases (Rispail et al. 2014).

5.2 Nanoparticle–Plant Interactions

The nanoparticle–plant interaction ranges from subtle to distinguished plant variations at biochemistry, physiology, and molecular levels (Deng et al. 2014). The treatment with nanoparticles will trigger various plant morphological changes like elongation of roots, germination rate, biomass, etc. (Deng et al. 2014). Many nanoparticles are also reported to have negative effect like phytotoxic, inhibiting plant growth and development (Yadav et al. 2014).

The in-depth analysis of nanoparticles studies revealed that these nanoparticles interact with different plant metabolism in regulating, taking up micronutrients, genes expression, interfering with other oxidative enzymes involved in an oxidative burst (Rastogi et al. 2017). Exposure of nanoparticles in some plants shows a positive effect, whereas others are negatively affected by the same nanoparticles. Therefore, it is crucial to screen different nanoparticle types to positively impact plant growth and development.

Many different metal and metal oxide nanomaterials are proven to enhance the secondary metabolites (phenolics, terpenoids, alkaloids, etc.). It has been demonstrated to be one of the plant's best abiotic and biotic stress alleviation methods. For example, the silver nanoparticles enhanced growth of plants and development by augmenting the polyamines biosynthesis and the content of *O. sativa* seedling (Gupta et al. 2018).

Nanoparticles are more effective with expression of genes and cellular mechanisms; it affects plant growth and development via transitions in the expression of multiple genes involved in the various biosynthesis pathways (Etesami et al. 2021). Nanoparticles are also accounted to increase the microRNA (miR408 and miR398) expression that are responsible for controlling seed germination, the development of roots in seedlings of *Arabidopsis thaliana* (Etesami et al. 2021).

The application of zinc oxide nanoparticles increased the expression of serotonin N-acetyltransferase, caffeic acid O-methyltransferase, and N-acetyl serotonin O-methyltransferase, genes involved in melatonin biosynthesis and antioxidative enzymes like catalase, ascorbate peroxidase, and superoxide dismutase to influence drought resistance in *Zea mays* (Sun et al. 2020). Similarly, foliar application of selenium nanoparticles increased phenolic content, pigments, antioxidant enzyme activities, and induced adaptation responses in the drought-stressed *Punica granatum* (Gupta et al. 2018).

Various nanomaterials have been demonstrated to generate oxidative stress in plants. The three main factors involved in nanoparticles induced reactive oxygen species to include (1) presence of prooxidant active groups on the nanoparticles reactive surface; (2) active redox cycling on the surface of nanoparticles due to the transition of metal-based nanoparticles; and (3) particle-cell interactions.

Various researches have demonstrated that both metal (silver) and metal oxide (zinc and titanium oxide) nanomaterials can generate excess reactive oxygen species (ROS) or scavenging of free radicals in plants. However, there is still uncertainty about the mechanism of ROS generation in plants (Li et al. 2008; Rico et al. 2015).

5.3 Role of Nanoparticles in Plant Secondary Metabolites

The vast array of nutraceuticals and pharmacological effects of all the known medicinal plants are based on phytochemical components (Bhattacharya 2019). These components are categorized into primary and secondary metabolites depending on their metabolic functions.

The primary metabolites are engaged in basic life functions directly associated with normal growth, development, and reproduction. In contrast, secondary plant metabolites are the organic molecules synthesized by plants that are less required for growth, development, and reproduction (Hussein and El-Anssary 2018). Classification of secondary plant metabolites is based on their chemical structures. It is classified into four main categories: alkaloids, phenolic compounds, sulfur-containing compounds, and terpenoids. Secondary metabolites are known to hold numerous biological activities, providing the scientific evidence for the practice of medicinal plants in conventional medicines (Teow et al. 2018). These secondary plant metabolites are essential for adaptation of plants during a hostile environment. They are also used in pharmaceutical, cosmetics, and agricultural and food products. Owing to their vast biological importance, secondary metabolite production has attracted attention for developing new approaches to enhance their production.

Recently, an increase in plant secondary metabolites by external application of nanoparticles has gained ground. The beneficial effects, such as increased accumulation of phenolics, flavonoids, and lipids, are reported along with a positive impact on pathogen resistance and stress tolerance (Ahmed et al. 2021; Batool et al. 2021). The nanoparticles used are broadly metal nanoparticles, and some reports are available on engineered nanoparticles where secondary metabolites are usually converted into nano-formulations for effective agents for inducing secondary metabolite production and accumulation in the plants. To prove this statement, the various nanoparticles used for eliciting the secondary metabolites are given in Table 1 and Fig. 1.

6 Impact of Metal Nanoparticles

6.1 Silver

The most used metal nanoparticle for achieving secondary metabolite production in plants is silver and is known to enhance the plant stress tolerance as well higher flowering rate and seed production (Batool et al. 2021). Use of silver nanoparticle (AgNPs) increased the production of diosgenin, a valuable secondary metabolite with broad medicinal properties, in fenugreek plants (Jasim et al. 2017). The report also points that the effect included higher growth rate of the plants with higher biomass accumulation, pertaining to better seed setting.

AgNPs are also enhanced the biochemical profile of *Calendula officinalis* where significant enhancement saponin content was observed (Ghanati and Bakhtiarian 2014). A broad-spectrum enhancement of phenolic and phytoalexin compounds were observed in *Arabidopsis thaliana* upon AgNPs' application. The authors presume that AgNPs can rescue plants from both abiotic and biotic stress as these compounds are well-known molecules of stress tolerance in brassicaceae family. The findings in this model plant pave way for further studies oriented toward the usefulness of AgNPs in commercially important food crops for value addition. In suspension cultures of capsicum, AgNPs is shown to induce higher accumulation of capsaicin (Bhat and Bhat 2016).

In another report, AgNPs improved drought tolerance and enhanced the yield in wheat plants (Ahmed et al. 2021), one of the most consumed cereals in the world. The authors imparted the positive influence of AgNPs through its role in higher chlorophyll production during drought conditions. It can be assumed that the AgNPs are inducing the production of carotenoid moieties in the plants.

Table 1 Effect of nanoparticles on secondary metabolites production in various plant species

Nanoparticles	Metabolites	Plant species	Reference
Silver	Diosgenin	*Trigonella foenum-graecum*	(Jasim et al., 2017)
Silver	Saponin	*Calendula officinalis*	Ghanati and Bakhtiarian, (2014)
Silver	Phenolics and phytoalexin	*Arabidopsis thaliana*	Kruszka et al. (2020)
Silver	Capsaicin	*Capsicum annum*	Bhat and Bhat (2016)
Silver	Carotenoid	*Triticum aestivum*	Ahmed et al. (2021)
Silver	Quercetin	*Ocimum sanctum*	Jain and Mehata (2017)
Silver	Eugenols, linalool, terpenes	*Ocimum sanctum*	Ramteke et al. (2012)
Gold	Phenolics and flavonoids	*Prunella vulgaris*	Fazal et al. (2016)
Gold	Flavone sulfates	*Zostera noltii*	Zarzuela et al. (2018)
Gold	Saponin	*Trianthema decandra*	R. & D.v.l. (2013)
Gold	Hydrolyzable tannins	*Terminalia arjuna*	Gopinath et al. (2014)
Copper	Polyphenols	*Cymbopogon citratus*	Brumbaugh et al. (2014)
Copper	Flavonoids, alkaloids, polyphenols	*Punica granatum*	Nazar et al. (2018)
Palladium	Hydroxyflavones, phenolics	*Euphorbia granulate*	Nasrollahzadeh and Mohammad Sajadi (2016)
Zinc	Stevioside	*Stevia rebaudiana*	Desai et al. (2015)
Iron oxide	Phenolics and flavonoids	*Dracocephalum kotschyi*	Nourozi et al. (2019)
Iron oxide	Hypericin	*Hypericum perforatum*	Sharafi et al. (2013)
Zinc oxide	Phenolics, flavonoids and anthocyanin	*Lilium ledebourii*	Chamani et al. (2015)
Zinc oxide	Glycyrrhizin, phenolics, flavonoids, and anthocyanins	*Glycyrrhiza glabra*	Oloumi et al. (2015)
Zinc oxide	Hypericin and hyperforin	*Hypericum perforatum*	Sharafi et al. (2013)
Titanium dioxide	Monoterpenes, phenolics and flavonoids	*Salvia officinalis*	Ghorbanpour (2015)
Copper oxide	Glucosinolates	*Brassica oleracea*	Chung et al. (2018)
SWCNTs	Parthenolide	*Tanscetum parthenium*	Ahmadi et al. (2018)

(continued)

Table 1 (continued)

Nanoparticles	Metabolites	Plant species	Reference
SWCNTs	Phenolic, tannin and flavonoid	*Simmondsia chinensis*	Gaafar et al. (2018)
MWCNTs	Cucurbitacin, lycopene, and charantin	*Momordica charantia*	Kole et al. (2013)
MWCNTs	Rosmarinic acid	*Setaria verticillata*	Ghorbanpour and Hadian (2015)

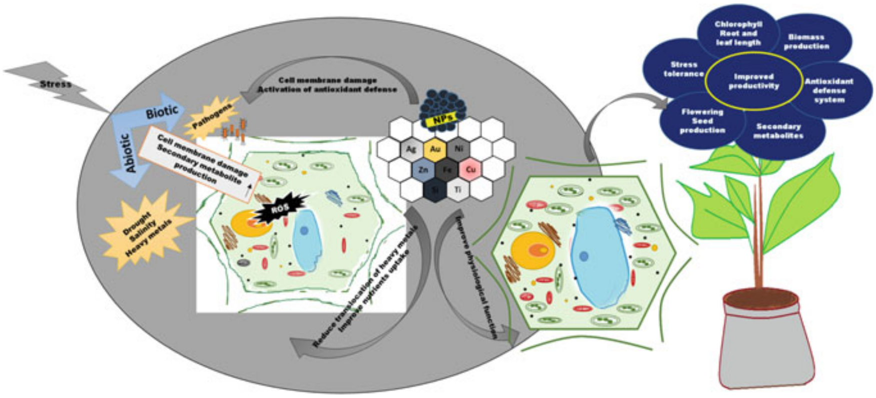

Fig. 1 An overview of nanomaterials induced plant secondary metabolite production

6.2 Gold

Gold nanoparticles (AuNPs) are known to impart higher antioxidant activity and stress tolerance in the plants through the induction of plant secondary metabolite production. In callus cultures of *Prunella vulgaris*, AuNPs augmented the production of phenolics and flavonoids and promoted the growth rate of the callus, resulting in higher biomass accumulation (Fazal et al. 2016). AuNPs treatment caused higher seed yield and biomass accumulation in *Brassica juncea* (Arora et al. 2012). The application also resulted in better redox status in the plants that can be attributed to the antioxidant action of accumulated secondary metabolites.

6.3 Zinc

Zinc nanoparticles (ZnNPs) are also known to increase plant secondary metabolite production. In stevia, the use of ZnNPs increased the production of stevioside (Desai et al. 2015).

7 Impact of Metal Oxide Nanoparticles

Limited reports are available on the use of metal oxide nanoparticles for enhancing the production of secondary metabolites in plants.

7.1 Iron Oxide

Treatment with iron oxide nanoparticles resulted in the accumulation of flavonoid and phenolic compounds in the *Dracocephalum kotschyi* hairy-root cultures. The treatment was beneficial as it increased biomass production, and the secondary metabolite production was achieved by upregulating the biosynthetic genes entailed in the pathway, mainly the rosmarinic acid synthase and phenylalanine ammonia-lyase (Nourozi et al. 2019). Reports indicate that iron oxide nanoparticle protects the *Dracocephalum moldavica* plants from salinity condition (Moradbeygi et al. 2020). Authors pointed out that stress tolerance was accomplished by the accumulation of secondary metabolites like phenolic, flavonoid, and anthocyanin, along with the increased antioxidant enzyme activities (glutathione reductase, ascorbate and guaiacol peroxidises and catalase). Iron nanoparticles application in butterhead lettuce and pepper seedlings resulted in the enhancement of various flavonoid and phenolic compounds and imparted better internal antioxidant activity (Kalisz et al. 2021). In cell suspension, cultures of *Hypericum perforatum* treatment with iron oxide showed substantial increase in hypericin and hyperforin production (Sharafi et al. 2013).

7.2 Zinc Oxide

Zinc oxide nanoparticles (ZnONPs) are also reported to increase secondary metabolite production in plants and provide higher stress tolerance and higher growth vigor. In *Lilium ledebourii*, the ZnONPs treatment enriched phenolic, flavonoid, and anthocyanin content. The treatment also resulted in higher chlorophyll production with better root and leaf length (Chamani et al. 2015). The ZnONPs treated as external agents on *Glycyrrhiza glabra* seedlings enhanced glycyrrhizin, anthocyanins, total phenolic compounds, flavonoids, and proline content of the plants (Oloumi et al. 2015). Treatment with zinc oxide showed enhancement in hyperforin and hypericin in in vitro cultures of *H. perforatum* (Sharafi et al. 2013).

7.3 *Titanium Dioxide*

Another nanoparticle known to effect the production of secondary metabolites in the plants is the titanium dioxide nanoparticles (TiO_2NPs). The application of TiO_2NPs in *Salvia officinalis* leads to an increase in essential oils and the phenolic and flavonoid content. The interesting observation has wide application potential as TiO_2NPs treatment resulted in the augmentation and accumulation of important essential oils such as monoterpenes, including Camphene, p-Cymene, 1,8-Cineol, Cis-Thujene, and Camphor (Ghorbanpour 2015). In one of the studies, TiO2 was combined with silver to produce Ag-TiO_2 nanoparticles and was provided to the plants, *Lactuca sativa*, *Coriandrum sativum*, and *Capsicum annuum* through irrigation. These Ag-TiO_2NPs were highly effective in providing stress tolerance to the plants, where the authors observed an increase in phenolic and flavonoid accumulation inside the plants (Cordoba et al. 2021). Transcriptomic data analysis conducted in the model plant, *Arabidopsis thaliana*, revealed TiO_2NPs upregulate an array of genes involved in secondary metabolite production (Tumburu et al. 2017). The report indicates that secondary metabolite pathways related to abiotic and biotic stress, pathogen infection, and related hormone stimulation were all upregulated, showing that the broad response TiO_2NPs can induce in the plant system (Tumburu et al. 2015, 2017).

7.4 *Copper Oxide*

Similar to copper nanoparticles, the nanoparticles of copper oxides (CuONPs) also increased the production of plants secondary metabolites. Treatment with CuONPs as a hydrogel formulation in *Lactuca sativa* increased its resistance toward *Fusarium oxysporum* infection (Shang et al. 2021). The authors attributed the resistance gained by the plant to various secondary metabolites that can be induced by an upregulation of the signaling molecules such as salicyclic acid induced by the CuONPs. In hairy root cultures of napa cabbage, CuONPs increased the secondary metabolite production with elevated content in glucosinolates (gluconasturtiin, glucobrassicin, 4-methoxyglucobrassicin, neoglucobrassicin, 4-hydroxyglucobrassicin, glucoallysin, glucobrassicanapin, sinigrin, progoitrin, and gluconapin), total phenolic, and total flavonoid was observed. The authors found that the treatment increased gene expression of Phenylalanine ammonia-lyase, Chalcone isomerase, and Flavonol synthase, the key genes involved in the secondary metabolites biosynthetic (Chung et al. 2018). The study conducted in *G. glabra* has shown an increase in glycyrrhizin, flavonoids, total phenolics, anthocyanins, and proline (Oloumi et al. 2015).

Researchers have reported other nanoparticles based on metals and metal oxides, such as cerium oxide, and have observed an upregulation in plant secondary metabolic pathways and higher secondary metabolite augmentation in the plants (Kalisz et al. 2021; Tumburu et al. 2017).

7.5 Engineered Nanoparticles

Unlike other nanomaterials, engineered nanoparticles have unique physicochemical properties that offer various pharmaceutical and biotechnology applications. Their high surface reactivity and ultrafine size enable them to penetrate cells and influence activity of various intracellular molecules and alter metabolic pathways, affecting cellular physiology by varied mechanisms. These nanoparticles influence photosynthesis process, photo-chemical fluorescence and quantum yield, photosynthetic pigments, and metabolites such as primary (proteins and carbohydrates) and secondary (phenols, flavonoids, and alkaloids) in plants. Based on their size, morphology, and composition, engineered nanoparticles are grouped as carbon-based, composites-based, and organic nanomaterials (Hatami et al. 2016; Sohail et al. 2019).

Carbon-based nanomaterials that are commonly used as elicitors include single and multi-walled carbon nanotubes (SWCNTs and MWCNTs), chitosan nanoparticles, and fullerenes. These nanomaterials can alter the expression levels of genes responsible for plant metabolism, thus eliciting secondary metabolite production. The influence of different concentrations of SWCNTs (125–250 mg L^{-1}) was evaluated on the plant *Tanscetum parthenium*, where parthenolide content accumulation was detected (Ahmadi et al. 2018). In a different study, SWCNTs were shown to enhance phenolic, tannin, and flavonoid contents in shoot cultures of *Simmondsia chinensis* (Gaafar et al. 2018). Similarly, different concentrations of MWCNTs (0–500 μg L-1) elicited *Satureja khuzestanica* callus culture showed callus growth with biomass accumulation and increased secondary metabolite content. MWCNTs were also shown to enhance the total phenolic and flavonoid content, antioxidants, rosmarinic acid, and activity of phenylalanine aminolyase in *Thymus daenensis* and *Salvia verticillata*. Foliar exposure of *S. verticillata* leaves with MWCNTs, induced the oxidative stress responses and enhanced rosmarinic acid content in a concentration-dependent mode (Khan et al. 2021a; b; Rahmani et al. 2020). Fullerenes positively influenced bitter melon seed germination growth rate and increased accumulation of compounds such as cucurbitacin-B, lycopene, insulin, and charantin (Kole et al. 2013). Due to non-toxic and biodegradable properties, chitosan nanoparticles are widely exploited in the agriculture and medical disciplines. Chitosan nanoparticles elicited plants such as tea (camellia sinensis) showed increased gallic acid, epigallocatechin, epicatechin, and caffeine accumulation (Chandra et al. 2015).

8 Conclusion and Future Directions

In the prospect of modulating specific metabolic pathways for secondary metabolites production and improving plant performance, a methodology such as nanotechnology provides a practical and potential platform. Developing nano-formulations that serve as specific and productive elicitors for the production of secondary metabolites will transform traditional practices to precision agriculture, ensuring the environment and food security. Based on available scientific reports, this review recapitulates the influence of nanomaterials on production of secondary metabolites in plants and their applications in nanobiotechnology. The overall analysis of reported data on nanomaterials augmenting the elicitation of secondary metabolites in plants showed that the metal and metal oxide nanoparticles are productive, specific, and efficient elicitors. For developing successful and effective nano-elicitors, it is obligatory to consider their physiological effects as well as biochemical interactions with plants. Studies performed using nanomaterials of different types have verified that the elicitation mechanism is complex phenomena and relies on physicochemical properties of nanomaterials such as concentration, morphology, size, exposure time, plant species considered, and growth conditions resulting in different physiological effects.

Although substantial reports on nanomaterials as elicitors of secondary metabolites are available, the knowledge gap of different factors affecting the elicitation mechanism remains obscure. Certain aspects such as biocompatibility of nanomaterials, surface coating and incorporation of biochemicals, mechanism of interaction, and multidisciplinary approaches need to be considered while engineering nanoparticles. Furthermore, available techniques and paradigms of nanotechnology and plant physiology need to be collectively used in experimental systems. Future studies should include the synergistic or antagonistic effects of nanomaterials' combinatorial application and abiotic/biotic elicitors on specialized metabolism. Comprehensive understanding of biomolecular coronas and omics-based analysis such as genomics, transcriptomics, proteomics, and metabolomics must be precisely considered while delineating the molecular mechanisms of elicitation secondary metabolites using nanomaterials. Additionally, a comprehensive picture of the mechanism of action can be accomplished by distinguishing between direct and indirect effects of nano-formulations and plants interactions in physiologically relevant environments.

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Applications of Nanotechnology in Preservation and Development of the Plants: A Look Back

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Abstract In this era of global warming, agrarian strategies across the world are plagued with a slew of issues. Improved nano-engineering is a useful technique for increasing agricultural output and ensuring long-term sustainability in the pursuit of rural livelihoods. Nanotechnology aids in the improvement of agricultural output by boosting input efficiency and reducing relevant losses. Fertilisers and insecticides have a smaller specific surface area than nanomaterials. Nanoparticles also enable regulated, forum nutrition delivery with increased crop protection as distinctive drivers of industrial chemicals. Whilst nanotechnology's rapid advancement in biomedical sciences has transformed therapeutic and diagnostic techniques in recent years, understanding nanoparticle–plant interactions, such as absorption, mobility, and accumulation, is still in its infancy. Because of their direct and intentional use in the specific administration and management of efforts, nanotools, such as nanobiosensors, enable the growth of high-tech farming (fertilisers, pesticides, herbicides). Nonosensors that combine biology and nanotechnology have substantially enhanced their ability to perceive and recognise environmental circumstances or impairments, with the ultimate goal of improving plant defence and/or enhancing photosynthetic activity, as well as farming methods. Humans also feel that multidisciplinary collaboration approaches will be crucial in narrowing the research gaps in plant nanotechnology and increasing the practice of NMs in farming and plant science research a broad sense.

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1 Introduction

The agricultural industry has made significant technological breakthroughs and developments in past few years to address the growing concerns about sustainable production and food security (Liu et al. 2019). Making use of both natural and manmade resources, such continual agricultural advances are critical to meeting the rising food demand of the world's exploding population. Nanotechnology, in specifically, has the opportunity to deliver practical solutions to a variety of agricultural issues. Because nanoparticles cross the gap between bulk materials and nanoscale structures, they are useful in a variety of applications, they are of high relevance. A substantial amount of research has been done on nanotechnology in the previous two decades, with a focus on its various uses in the agriculture industry (Zheng et al. 2005). Fertiliser application is critical for enhancing agricultural productivity; nevertheless, excessive fertiliser use permanently alters the chemical ecology of soil, lowering the amount of land accessible for crop cultivation (Lv et al. 2019). To protect the environment and prevent many invasive species from annihilation, sustainable agriculture involves the use of the fewest agrochemicals feasible. Nanomaterials, for example, promote crop output by increasing farm inputs' effectiveness, allowing for dietary optimisation on a site-by-site basis delivery with little agri-input use. The use of nanotechnology in plant protection products has risen dramatically in recent years, possibly leading to increased agricultural output (Malerba and Cerana 2018). Furthermore, a key challenge in agricultural production is allowing plants to adapt more quickly to progressive climate change elements including severe temperatures, water scarcity, salt, alkalinity, and toxic metal pollution without endangering existing delicate ecosystems. However apart from that, the emergence and use of nanosensors in smart agriculture to quantify agricultural production, growing conditions, diseases (Milewska-Hendel et al. 2017), agrochemical use and infiltration, and the level of pollutants has decreased soil biological nutrition are under human influence, guarantee of quality, and ensured security, all of which have contributed significantly to organic farming and ecological elements. Nanomaterial engineering is a branching research path that improves the benefits of new agricultural fields by offering a bigger contact angle, which is crucial for the long-term sustainability of agriculture systems (Modlitbová et al. 2018; Milewska-Hendel et al. 2017). As a result, nanotechnology might be utilised to not only minimise uncertainty but also to coordinate agricultural production management plans, perhaps replacing earlier technologies. Agro-nanotech breakthroughs often give speedy solutions to problems that beset current industrial agriculture. The current analysis covers nanotechnology's uses in agriculture, which may help to ensure agriculture's and the environment's long-term viability (Moon et al. 2016).

2 Agriculture's Next Frontier: Nano-Farming

Nanoparticle engineering is a recent technical advancement that demonstrates distinct targeted properties as well as increased strength. Norio Taniguichi, a professor at Tokyo University of Science, created the word "nanotechnology" in 1974 (Neamtu et al. 2017). Although the word "nanotechnology" has been used in a variety of fields for a long time, the concept that nanoparticles (NPs) may be useful in farmland progress is a relatively new technical invention that is currently being developed (Neamtu et al. 2017; Zheng et al. 2007; Ahmed et al. 2021). Nanomaterials of various shapes and dimensions, have a multitude of uses in medical, conservation biology, farming, and food processing, due to recent advancements in their synthesis. Agricultural improvements have always benefited agriculture throughout history (Pagano et al. 2016). Furthermore, whilst agriculture confronts a slew of difficulties, including decreasing crop output due to biotic and biotic stresses such as nutrient scarcity and deterioration, nanotechnology's growth has opened up new possibilities for precision agriculture (Palocci et al. 2017). In recent years, the phrase "precision agriculture" or "farming" has become popular, referring to the use of wireless networking and sensor downsizing for monitoring, analysing, and regulating agricultural activities (Pakrashi et al. 2014). It has to do with site-specific crop management in the pre- and post-production phases of farming, horticulture plants to farm commodities are all included in this category. Recent scientific developments include tissue engineering and CRISPR/Cas (CRISPR-associated protein) mRNA and sgRNA controlled delivery using tailored nanomaterials for crop genetic manipulation (GM) (Pérez-de-Luque 2017). Nanotechnology also offers good answers to a growing variety of environmental issues. Nanosensors, for example, have a lot of potential for monitoring environmental stress and improving plants' disease-fighting abilities. As a result, continual advancements in nanotechnology, with a focus on identifying challenges and developing collaborative ways for long-term agricultural growth, have a great deal of potential to help a wide range of people (Pokhrel and Dubey 2013).

Nanomaterials have biological capabilities and may be employed in a number of ways to functionalise proteins. Furthermore, several NMs have been revealed to respond to external stimuli, viscoelastic or hybrid NMs, as well as gold and gravitational nanotubes, allowing macromolecules to be released in a limited environment (Rad et al. 2012). Fabricated nanoparticles have been effectively explored and employed in medicine and pharmacology for the past two decades, primarily for diagnostic and therapeutic applications (Perrault et al. 2009; Roy 2021; Roy et al. 2021; Pandit et al. 2022). The application of nanomaterials (NMs) as agrochemical or biomolecule transporters in plants, as well as the possibility for increased agricultural yields, has piqued attention in plant science recently (Majumdar et al. 2015).

It is logical to say that the prospects and advantages of adopting NMs in plant sciences are viable and farming are currently underutilised due to a variety of hurdles that may be summarised as follows: I believe there is a need to I create and synthesise safe NMs that do not harm the evolution of plants (Lee et al. 2017); (ii) understand the exact processes of NMs uptake and mobilisation in plants (Lau et al. 2017); and (iii) lack of interdisciplinary methods required for the monitoring and assessment of nanocomposite materials in vegetation (Lau et al. 2017).

3 Nanomaterials in Plant Science

Nanomaterials (NMs) are natural or manmade materials with a diameter of 1 to 100 nm, according to ASTM standards (Astm E2456-06, 2012). NMs have a small size and a significant proportion of surface to volume compared to their bulk counterparts, providing them exceptional chemical and physical capabilities (Laware and Raskar 2014; Roy and Bharadvaja 2019; Roy et al. 2022). Because of their distinct and varied physicochemical properties, NMs may be employed in a range of industries, including geotechnical engineering, biological science, and computing (Lattanzio and Nivarlet 2017). Because of the necessity to construct miniaturised methods that are productive to increase seed germination, development, and plant defence against challenges that are both environmental and biological, nanotechnology has recently gotten a lot of interest in plant research (Jeevanandam et al. 2018).

Metallic nanoparticles (NPs) including gold (Au) and silver (Ag) NPs have long been employed in conservation biology for a range of submissions. Their chemical production is highly expensive, and it necessitates the employment of potentially toxic substances (Islam et al. 2017; Jahan et al. 2018). Plant extracts and ionising granular nuclear technology have been used to generate more environmentally friendly approaches (Ivanov et al. 2016). Because of their optimisation of energy, biochemical, and radiation hydrophilic nature, oxidised NMs as an example MgO, CaO, ZnO, and TiO_2 NMs have also been frequently advocated (Jahan et al. 2018). Because of their biological properties, minimal manufacture, and ability to respond to environmental inducements, polymeric nanoparticles have gotten a lot of interest in recent years (Glass et al. 2018). Core/Shell NPs may be formed from a variety of resources, as well as abiotic, biologically inert, organometallics, biodynamic, and sustainably sourced. The way NPs are applied and used has a significant influence on their shell. Polymeric shells, for instance, have been considered as a way to improve NP biocompatibility (García-Gómez et al. 2018). Nanostructured NPs have also been created, including nanocrystals, which are made up of with a material characterisation large functionalised surface area (Geisler-Lee et al. 2013).

Nanogels (NGs) are a relatively new form of NM that is gaining traction in the world of nanotechnology. These provide good thermodynamic features, aqueous consistency, a lot of bioconjugation capability, and shock tolerance (pH, temperature, etc.). NGs are ionic and non-ionic hydrogels that are built up of chemically or mechanically cross-linked synthetic or natural polymer chains (Gopinath et al. 2014; Neamtu et al. 2017). NGs have a lot of water (70–90% of the overall assembly), as well as a surface morphology with a high fatigue strength. Chitosan, alginate, poly(vinyl alcohol), poly (ethylene oxide), poly(ethyleneimine), poly(vinylpyrrolidone), and poly(vinylpyrrolidone) are the most frequent NGs (N-isopropylacrylamide). Hybrid architectures consisting of polyamide or components that are not viscoelastic can be used to create NGs (Neamtu et al. 2017). The classifications for hybrid NGs are as follows: Polymeric nodes, nanocomposites, and basic fragments are used in nanostructured materials compounds, and interpenetrated networks (IPNs), copolymers, and essence elements are used in polymer–nanogel composites. IPNs and copolymer NGs respond to stimuli, but core-shell NGs have extra potential peptides embedding and delivering drugs.

4 Nanofertilisers Are a Cost-Effective Way to Provide Optimum Crop Nutrition

To boost crop output and soil fertility, vital nutrient supplementation (element fertilisation) is necessary in general (Goncalves et al. 2017). However, one of the most significant factors for long-term agricultural performance is proper fertiliser management (González-Melendi et al. 2008). Food, on the other hand, is a basic human right. All around the world, global food security is under jeopardy. Food security is jeopardised in part owing to a scarcity of natural resources. The present world population (seven billion) is expected to grow through time, reaching roughly nine billion by 2050. About 60–100% more food will be required to feed the growing population (Etxeberria et al. 2019). To address the growing demand for nutrition, strenuous cropping is used, which unswervingly contributes to soil fertility exhaustion and a loss of agricultural productivity. Almost 40% of the globe's farmlands has been seriously contaminated, resulting in significant soil fertility loss as a result of such intensive farming activities. As a result, massive amounts of fertilisers are utilised to boost soil fertility and agricultural yields (Cunningham et al. 2018; Avellan et al. 2017). It's also been proven that fertilisers account for one-third of crop productivity, with the remainder relying on the efficiency of other agricultural inputs. Conventional fertilisers, on the other hand, have nutrient usage efficiencies of just 30–40% (Chichiriccò and Poma 2015). Throughout the past couple of decades, the nutrient utilisation proficiency of traditional fertilisers, for example nitrogen (N) 30–35%, phosphorous (P) 18–20%, and potassium (K) 35–40%, has been consistent (Bagal-Kestwal et al. 2015). Furthermore, the efficacy of conventional fertilisers sprayed on leaves or applied directly to the soil is largely determined by the fertiliser's final concentration reaching the target regions (Giraldo et al. 2014). A very little quantity, due to chemical weathering, a concentration much below the minimum permissible intensity reaches the target place, dispersion, precipitation, disintegration, condensation, thermolysis, or despite bacterial decomposition (Raliya et al. 2016). As a result, the frequent application of excessive fertilisers has a negative impact on the soil's natural nutrient balance. Aside from that, aquatic habitats have been severely damaged as a result of harmful chemicals seeping into rivers and water reservoirs, contaminating drinking water as well (Chichiriccò and Poma 2015). In early 1970, to generate a tonne of grain, just 27 kg NPK ha^{-1} was needed, but in 2008, 109 kilogramme NPK ha1 was essential to achieve the same level of output. Worldwide fertiliser usage has been steadily growing, in accordance with International Fertilizer Industry Association (IFIA), with global demand expected to reach 192.8 Mt by 2016–2017 (Rastogi et al. 2019). Chemicals from these large volumes of conventional fertilisers stay in the soil or may infiltrate other conservational cubicles, producing major pollution and affecting normal flora and fauna growth.

In terms of agriculture's long-term viability, the practice of engineered nanomaterials has revealed a fundamentally new approach to food production that may overcome agricultural sector unpredictability with limited earnings (Rai, Acharya and Dey 2012). Green nanotechnology has transformed the agriculture's worldwide ecosystem, and nanomaterials like microbial inoculants have showed promise in fulfilling global food demand forecasts and maintaining agribusiness that is both sustainable and profitable. Nanofertilisers may be the greatest option for alleviating macro- and micronutrient deficiencies through improved nutrient usage efficiency and overcoming the persistent problem of eutrophication (Verma et al. 2018). Nanofertilisers, they are designed to manage the delivery of nutrients in response to crop demands whilst reducing mortality due to inequality, offer enormous potential. For example, traditional nitrogen fertilisers lose up to 50–70% of their nitrogen content in the soil owing to runoff, dispersion, or decomposition, lowering fertiliser effectiveness and raising production costs (Verma et al. 2018; Sabo-Attwood et al. 2012). Nanoformulations of nitrogenous fertilisers, on the other hand, coordinate fertiliser-N release with crop uptake need. As a result, nanoformulations limit unwanted nutrient losses by direct internalisation by plants, avoiding interactions between nutrients and soils, water, air, and microbes (Saharan et al. 2016). Porous nanomaterials like sorbents, bentonite, and alginate, for example, can drastically reduce nitrogen losses by limiting market release and increasing plant absorption. Phosphate mineral solubility can be improved by ammonium-charged zeolites, leading in increased phosphorus accessibility and crop uptake (Schwab et al. 2016). The carbon-based nanomaterial graphene oxide sheets can delay potassium nitrate release, extending the life of the system and reducing nullification (Tarafdar et al. 2014). Sharma et al. (2012) have made a praiseworthy effort to demonstrate the use of nanomaterials in agricultural output as a substitute for conventional fertilisers. They discovered that mixing nanocalcite ($CaCO_3$-40%) with nano SiO_2 (4%), MgO (1%), and Fe_2O_3 (1%), not only enhanced Ca, Mg, and Fe absorption, but also dramatically improved P uptake with micronutrients Zn and Mn. Nanofertilisers are available in a wide range of forms and sizes. Nanofertilisers are characterised as control or delayed release fertilisers, lack of control fertilisers, magnetic fertilisers, or nanocomposite fertilisers based on their activities as a combined nanodevice that distributes a broad series of macro- and micronutrients with desirable features (Servin and White 2016). The most frequent way of making nanofertilisers is to encapsulate nutrients with nanostructures. For cationic nutrients (NH^{4+}, K^+, Ca^{2+}, Mg^{2+}), the elements are encased in nano adsorbents or wrapped with thin polymer films, whereas electrophilic nutrients (NO^{3+}, PO^{4+}, SO_4) are delivered as nanoscale particles or dispersions, or after chemical treatment (Tarafdar et al. 2014).

Fertiliser treatment, watering, and the use of high-quality seeds are all things that may be improved upon agricultural productivity may be boosted by 35–40%. The usage of nanoformulated fertilisers has been discovered to offer a significant potential for enhancing agricultural productivity (Verma et al. 2018). Carbon nanoparticles mixed with fertiliser, for example, can increase grain output by 10.29% in rice, 10.93% in spring maize, 16.74% in soybeans, 28.81% in winter wheat, and 12.34–19.76% in vegetables (Valetta et al. 2014). When compared to control yield factors, Abdel-Aziz et al. (2016) revealed that employing chitosan-NPK fertiliser considerably boosts the harvest index, crop index, and the wheat productivity parameters' activation factor. Perennial root and leaf interfaces are critical nutritional gateways for plants, and they are very permeable at the nanoscale, nanomaterials stimulate several important characteristics of plant biology (Torney et al. 2007; Vidyalakshmi et al. 2017). As an outcome, applying nanofertilisers to plants may aid in the absorption of additional nutrients through these pores, or the method may boost strong interaction with biochemical carriers or organic residues by building new pores or utilising endocytosis (Shi et al. 2013). Furthermore, a significant collection of research papers has decisively established that nanomaterial size reduction promotes an increase in particle surface mass ratio, resulting in a large number of nutritional ions being adsorbed and desorbed for a long period (Alawadhi et al. 2018). As a result, fertiliser nanoformulations enable balanced crop feeding during the entire growing period, resulting in increased agricultural yield. It's worth mentioning that the enhanced farmers may be inspired to utilise a product more efficiently if it is productive (Almutairi and Alharbi 2015).

Nanotechnology has sparked interest in agriculture as a possible multidisciplinary research subject. Micronutrients such as manganese, boron, copper, iron, chlorine, molybdenum, and zinc, in addition to macronutrients, have a substantial influence on agricultural output. However, when intensive farming is practised, a number of elements, such as soil pH (alkalinity or acidity), have a role in agricultural output shortages (Chaudhry et al. 2018). Due to the intake of micronutrient-deficient meals, micronutrient insufficiency reduces agricultural productivity and has a detrimental influence on human health. Anemia, developmental delay, procreative strength issues, and even a drop in physically and psychologically effectiveness are all symptoms of iron deficiency in humans. Plant absorption, crop growth and production, and soil health will all benefit from supplementing with nano tailored or phytonutrients encased in nanoparticles that deliver nutrients gradually or in a regulated manner (Etxeberria et al. 2019). In comparison to control, treatment with a modest dosage of nano zinc oxide improves growth and physiological responses in a variety of plant species in zinc-deficient soil, elongation of the shoots and roots, pure dry mass, and oxygenation (Faisal et al. 2013). Fathi et al. (2017) saw that consolidating zinc oxide nanoparticles with different composts in zinc insufficient soil works on supplement usage whilst additionally helping grain yield by 91% over control, yet common mass $ZnSO4$ just lifts usefulness by 31% (Torney et al. 2007; Vidyalakshmi et al. 2017).

Scientific progress is aimed at enhancing human well-being. Plant scientists also strive to enhance fertiliser-saving technologies without jeopardising agricultural productivity or the environment's sustainability (Garcia-Gomez et al. 2018).

In agriculture with long-term sustainability, a particular term is being used: "control loss fertiliser". When these fertilisers come into touch with water in the soil, they self-assemble into a nano network, preventing non-point contamination of agricultural inputs (Ivanov et al. 2016). By hydrogen holding, surface pressure, atomic power, or thick power, captured manure supplements enter the dirt organisation. Accordingly, their spatial scale reaches out to where they are handily hindered by soil filtration and stays fixed in the dirt close to trim roots, permitting plants to assimilate supplements to satisfy need all through the development cycle. For instance, a unique technique has been effectively used to lessen nitrogen move into the environment (Wang et al. 1995). In relation to conventional fertilisers, Verma et al. (2018) discovered that using a control loss fertiliser diminutions nitrogen overflow and filtering misfortune by 21.6% and 24.5%, respectively, whilst also increasing soil residual mineral nitrogen by 9.8% and wheat output by 5.5%. Despite the fact that a number of study papers have been published on the subject, there seems to be a paucity of data and research on the article's wider aspects. As a result, further study should be conducted to identify unique and promising techniques for controlling the migration of other macro- and micronutrients as contaminants into the environmental matrix on a micro-scale (Ranjan et al. 2017).

5 Plant Nanoparticle Accumulation, Remobilisation, and Biological Effects

Nanotechnology techniques in plants essential a thorough assessment of nanoparticle–plant relations, as well as a conception of nanoparticle absorption, translocation, accumulation mechanisms, and also a determination of any potential adverse consequences on plant development and advancement (Zhao et al. 2017). Plant take-up of NPs is hard to foresee because of an assortment of variables including the nanoparticle itself (size, substance structure, interface polymerisation, and surface energy), lessons on enrollment, communications with ecological parts (soil surface, water accessibility, microbiota), the biochemistry and various life systems of distinct plant species, as well as the restrictions imposed by the existence of a substratum. Prior investigations have mostly relied on the ingestion of little metal and metal oxide NPs because of their broad use in industry and the effortlessness with which they can be spotted and followed utilising microscopy strategies (González-Melendi et al. 2008). Only a few comprehensive comparison studies have been suggested to determine the role of hydrodynamic properties of NPs (e.g., structure, energy, surfaces, etc.) in symbioses (Zhu et al. 2012; Moon et al. 2016; Vidyalakshmi et al. 2017; Garca-Gómez et al. 2018).

6 Nanoparticles' Contribution to Photosynthesis

Photosynthesis is a basic strategy for changing over light energy into compound energy in plants on Earth, as we probably are aware. Just 2–4% of the accessible energy in radiation is moved to newly established development by plants (Shi et al. 2013). Researchers are effectively exploring different avenues regarding methodologies and quality modifications to improve the shortcoming of vascular plants. Scientists are working with Rubisco, a critical photosynthesis enzyme that catalyses the integration of carbon dioxide into biological components, to speed up plant photosynthesis and boost agricultural yields. They likewise demonstrated that extra examination is required to increase the influence of CNTs on the final results of photosynthesis, like sugars and glucose. Shi et al. (2013) also reported that a nano microcapsules accumulate (SBA) constrained with photosystem II (PSII) and induced sustainable advancement of a photochemical anion response, demonstrating light-dependent electronic conductivity from water to the dihydroxy granules, and that the PSII-SBA form may have properties to produce for photosensors and counterfeit photosynthetic frameworks, and that the PSII-SBA form may have properties to produce, and they recommended that the PSII-SBA conjugate SiO_2NPs increment photosynthetic rate through upgrading carbonic anhydrase action and the union of photosynthetic shades (Sun et al. 2014). Carbonic anhydrase gives CO2 to the Rubisco, which might help photosynthesis (Zhu et al. 2012). They asserted that utilising nanobionics to make plants will take into account new and upgraded practical elements in photosynthetic organelles. They additionally expressed that more examination is expected to decide the effect of CNTs on the finished results of photosynthesis, like sugars and glucose. Zhu et al. (2012) discovered that a nano microcapsules components constrained with photosystem II (PSII) and induced consistent response of a photorespiration o2 reactions, illustrating light-dependent charge separation from water to the quinone atoms, and that the PSII-SBA form may have properties that could be used to make photosensors and counterfeit photosynthesising paradigms. SiO_2NPs support photosynthetic rate through expanding carbonic anhydrase movement and photosynthetic shade creation (Simonin et al. 2016; Zhu et al. 2012). Carbonic anhydrase helps photosynthesis by providing CO_2 to the Rubisco (Simonin et al. 2016). Light assimilation, energy change from light to electrical and compound energy, and carbon dioxide take-up are completely improved by the photocatalysed normal for nano-anatase TiO_2. Under long-term light, TiO_2NPs shield chloroplasts from maturing (Yao et al. 2009). In continuing Rubisco (a mix of Rubisco and Rubisco activase), nano-anatase TiO_2 further develops carbon fixation in photosynthetic organisms, advancing Rubisco carboxylation, and subsequently supporting plant advancement (Gao et al. 2006). As per Ma et al. (2008), higher Rubisco activase protein activity and exercises, just as expanded Rubisco activase mRNA, influenced by better Rubisco carboxylation and a high pace of photosynthetic carbon response. Exogenous TiO_2NP treatment worked on net photosynthetic rate, water conductance, and emergence frequency in plants (Marchesano et al. 2013). Under both apparent and bright light, nano-anatase expanded entire chain electron transport, photoreduction movement of photosystem II, O_2-developing, and photophosphorylation action of chlorophyll, as per Ma et al. (2008). Metal nanoparticles, as per Majumdar et al. (2015), can expand the effectiveness of compound energy age in photosynthetic frameworks. Because of electromagnetic dispersion and a quick acceptors division, the chlorophyll in the photosynthetic response community interfaces with the AuNPs and Ag nanocrystals, establishing a unique mixing platform capable of producing many times more supercharged particles. The improving procedures might help illumination devices.

7 Plant Surface Delivery Methods and Primary Interactions

Engineered nanoparticles can be applied to a plant's roots or vegetative region, with the leaves proving to be the most effective. Bark thickness, cellular membranes, retransmission, and marginalisation are examples of natural plant apertures with nano or micro-scale segregation sizes that can passively take up NPs at the shooting surface (Eichert et al. 2008; Kurepa et al. 2010). In order to have a good knowledge of how NP-plant relations work, other plant anatomical and physiological characteristics must be explored. Biomaterials (e.g., cutin, cutan) and similar hydrocarbons are commonly applied to shoot surfaces as a solubilised membrane to safeguard the primary components of above-ground plants whilst only permitting natural openings for access (Khan et al. 2017). Although it has been demonstrated that nano-TiO_2 may create holes in the cuticle, nothing is known about NP dynamics at the cuticle level. Right now, this hindrance seems, by all accounts, to be a practically invulnerable covering to nanoparticles (Laware and Raskar 2014; Pagano et al. 2016). Trichomes on plant organs can impact plant surface elements by catching NP on a superficial level and thusly expanding the time outer materials stay on tissues. Plant gashes and lesions in the airborne and hypogeal areas might be plausible pathways for NP disguise (Al-Salim et al. 2011). The effectiveness of plant NP absorption appears to be influenced by distribution strategies. As previously established, aerosol treatment generates higher internalisation rates of various nanoparticles than NP drop cast in watermelon (Abdel et al. 2016). Furthermore, as established carbon based with a single-wall (Giraldo et al. 2014), influx of the leaf lamina techniques may improve NM diffusion in plant tissues, resulting in functional distribution of genomes. The Rhizodermis' stem elongation attachments may allow NMs to reach the root level with ease, especially at the root tip, because of the presence of suberin, whereas the higher sections are impermeable (Chichiricco and Poma 2015). The permeation mechanics of NP in soil appeared to be more difficult than those in plants' aerial component. NP availability may be influenced by a variety of variables, counting the presence of adhesive and exudates, advantageous organic entities, and humus. For example, root mucilage and exudates have a dual role in the root system: they may either increase NP adherence to the root surface, increasing NP internalisation rate, or they can cause NP entrapment and accumulation (Fathi et al. 2017; Goncalves et al. 2017). As per late discoveries utilising X-beam processed nanotomography and upgraded dull field microscopy joined with hyperspectral imaging, basic state line cells and related celluloses endeavour to catch gold NPs paying little heed to molecule power, though contrarily charged NPs are not confiscated by *Arabidopsis thaliana* root cap adhesive and move straightforwardly into root tissue (Islam et al. 2017). Besides, the occurrence of cooperative microorganisms and parasite in the dirt has been displayed to have an inconvenient effect; they increment the testimony of different weighty metal NPs in evident grasses, whilst they repress the assimilation of nano-Ag and nano-FeO in beats (Lee et al. 2017; Laware and Raskar 2014).

8 Plant Nanoparticle Aggregation

After gaining access to the plant's exterior coating materials, NMs can mobilise in one of two ways, depending on whether they were exposed aerially or hypogeally: apoplastic and symplastic (Simonin et al. 2016). Water and solutes are transported between cytoplasms of neighbouring organisms via plasmodesmata and sieve plate cavities, symplastic movements are the transfer of molecules and dissolved substances between cytoplasms of adjoining cellular membranes via plasmodesmata and sieve plate cavities, whereas extracellular environment transport happens exterior to the cytoplasmic membrane via the cell wall and extracellular spaces. Lau et al. (2017) have shown that basolateral membrane movement boosts NMs' circumferential mobility, which may carry NPs to the root's core cylinder and extracellular matrix, as well as their upward migration in the aerial region. For claims that need systemic NP transport, this technique of NP administration is perfect. The Casparian strip, a laterally aligned overlay of lignin-like substances, stops the root endodermis from completing this radial movement (Lv et al. 2019). The shift from paracellular to simplastic is made by water and another component or channel to get past this natural barrier. Several types of NPs have exhibited comparable abilities to overcome the barrier in the Casparian strip, according to Moon et al (2016). This is more likely to happen in regions where the Casparian strip hasn't fully grown, for example, root tips and root sidelong intersections (Lv et al. 2019).

NPs should pervade the cells sooner or later due to their symplastic carriage. Plant cells have a thick cell divider that makes an actual boundary to cell passage, making intracellular NP conveyance altogether more troublesome than in animal cells. The cell divider is a diverse design included generally of cellulose/hemicellulose microfibrils and platform proteins, bringing about a permeable climate with a mean distance across of 10 nm and up to 20 nm in specific circumstances, which goes about as a restricted particular channel. In fact, this essential element may be the most impediment to the course of events and organisation of bioengineering approaches in plants. Notwithstanding, a few plant animal categories have shown that nanoparticles with a mean breadth of 3 to 50 nm, just as carbon nanotubes, may effectively go through the cell divider (Etxeberria et al. 2019).

Although different cell entrance methods have been discovered in cells (Perrault et al. 2009; Rad et al. 2012) and invertebrate models (Zhao et al. 2017), endocytosis may be the favoured means of future cell internalisation (Valletta et al. 2014; Vidyalakshmi et al. 2017).

Because plasmodesmata, membrane-lined intracellular barriers with a variable width (20–50 nm) that retain membrane and morphological endurance between cells in connective tissue of plants, NPs can migrate from cell to cell once they've reached the cytoplasm. The plasmodesmata of Arabidopsis, rice, and poplar have all been discovered to transport NPs of various sizes (Zhu et al. 2012).

Fine molecules can enter the xylem and phloem capillaries and go to various areas of the body via the symplastic and apoplastic routes. Organs such as flowers, fruits, and seeds, for example, show a remarkable ability to ingress liquids from the phloem and accumulate NMs (sink activity). The presence of NPs in specialised organs raises serious questions about their safety in both human and animal applications (Pérez-de-Luque 2017). Metal-NPs have been found to infiltrate seeds and transfer into seedlings in a variety of crops, including maize, spinach, and cabbage, without adversely impacting vegetative growth, reproduction rate, or shoot development. These findings show that functional NPs might be used for seed priming and plant growth improvement in a range of situations (Rastogi et al. 2019).

9 Toxicology of Nanomaterials

Despite the fact that our insight into NM poisonousness in farming plants is as yet creating, it is pivotal for the making of new agro-nanotech items and hardware (Servin and White 2016). Existing plant NP research has looked into impractical settings as well as increased and quick shutter, often in typical environments and plant species, with mixed outcomes (Marchesano et al. 2013). As per most examinations, adequate metal-based NPs cause a genotoxic oxidative burst in developed species (e.g., tomato, wheat, onion, and zucchini). Meddling with the respiratory chain is one way to do so and hindering the responsive oxygen species (ROS) detoxifying hardware (Pagano et al. 2016; González-Melendi et al. 2008). Supplementary biochemistry, insulin sensitivity, and plant proliferation are frequently harmed as a result. Current transcriptome analyses in *A. thaliana* have revealed that knowing about diverse forms of NPs (e.g., zinc oxide, fullerene soot, or titanium dioxide) inhibits a high number of phosphate malnutrition-related genes, viral infection, and psychosocial factors, potentially affecting plant root development and protective factors (Islam et al. 2017). Metal NMs cause a wide pressure reaction with a high predominance of oxidative pressure parts, as per a new frameworks science concentrate on that included omics information from tobacco, rice, rocket salad, wheat, and kidney beans (Jahan et al. 2018). These discoveries show that, in spite of the impression of negative harmfulness, extra investigation into the hereditary and metabolic reactions created by NP ingestion is expected to give light on an assortment of parts of NP phytotoxicity in crops (Majumdar et al. 2015). In context of this research, apparently customisable

NMs with a grounded security profile in creature frameworks, like delicate polymeric NPs, may be utilised in plants later on.

10 Relevant Plant Science Implications

Whilst nanotechnology is quickly spreading across a number of branches of biology, user relations in plant and horticultural exploration are as yet in their early stages (Fathi et al. 2017).

10.1 Biosensors

In the agricultural biotechnology, agriculture, and food sectors, NMs have been employed to make biosensors or as "sensing materials" (Fathi et al. 2017; Chaudhry et al. 2018). Amongst other nanosensor types, plants have been utilised to test plasmonic nanosensors, FRET-based nanosensors, carbon-based electrochemical nanosensors, nanowire nanosensors, and neutraliser nanosensors. Despite the fact that nanoparticles are used in plants is as yet in its beginning phases (Rai et al. 2012), stimulating papers have suggested utilising NMs to distinguish and quantify plant metabolic transition, pesticide build-ups in food, and bacterial, viral, and contagious diseases. In light of the assembling of invertase-nanogold groups entrenched in plant films, a fluorometric optical onion layer-based sensor for sucrose recognition was as of late made (Raliya et al. 2016). Single-walled carbon nanotubes (SWNTs) have likewise been utilised to screen nitric oxide in *A. thaliana* through close infrared fluorescence checking (Giraldo et al. 2014). To gauge and recognise phytoalexins, FRET tests coupled to polystyrene NPs were used.

NMs-based biosensors, as recently demonstrated, are especially encouraging since they empower for the speedy recognition and careful evaluation of growth, microorganisms, and infections in plants (Goncalves et al. 2017). *Xanthomonas axonopodis* pv. *vesicatoria*, which produces fungal blotch sickness in Solanaceae plants, was recognised utilising fluorescent silica NPs and immune response, for instance (Yao et al. 2009), utilising differential heartbeat voltammetry (DPV) on dispensable screen-printed carbon cathodes, Lau et al. (2017) as of late proposed Au NPs as DNA biochemical markers for distinguishing Pseudomonas syringae in *A. thaliana.* Utilising fluorescently labelled DNA oligonucleotides coupled to Au NPs, the phytoplasma connected to grapevine flavescence dorée sickness was likewise distinguished. At long last, modern nanosensors can identify mycotoxin deposits in corn, wheat, oat, and grain. The 4mycosensor, for instance, is a market-prepared counter acting agent-based test for distinguishing ZEA, T-2/HT-2, DON, and FB1/FB2 mycotoxin build-ups in maize, wheat, oat, and grain (Neamtu et al. 2017).

10.2 Controlled Release of Agrochemicals and Nutrients

NMs can be used as nanostructured fertilisers (nanofertilisers, such as Fe, Mn, Zn, Cu, Mo NPs) or as improved transfer techniques to boost the absorption and uptake of orthodox fertilisers (nutrients and phosphates) (Majumdar et al. 2015). Regardless of whether nanofertilisers and NM-improved fertilisers are incredibly auspicious for farming, nanotechnology is used in fertiliser manufacture in a limited way (Verma et al. 2018). Phosphorous nanofertilisers consisting of hydroxyapatite nanoparticles improve soybean growth rate and seed yield by 33 and 20%, correspondingly, when related to a standard P fertiliser (Majumdar et al. 2015). Nanofertilisers can likewise be showered at more slow rates, which can assist with keeping up with soil richness by limiting the progression of supplements into overflow or ground water, as well as the danger of contamination and other negative consequences from over-application (Majumdar et al. 2015).

By irrigation or foliar treatments, magnetic nanoparticles based on iron oxide, zinc oxide, titanium dioxide, and copper have been used as soil nanofertilisers in plants such as mung bean, cucumber, and rapeseed (Tarafdar et al. 2014; Saharan et al. 2016; Verma et al. 2018). Tomato plants produced twice as many flowers and fruits after MWNTs were added to the soil, almost possibly due to the phenomenon of genetic traits being stimulated involved in the evolution of plants (Shi et al. 2013). Considering all of the findings, nanofertilisers are still controversial. Soil microbial communities, which include tiny invertebrates, bacteria, and fungus, may be threatened by deposition in treated soils (Majumdar et al. 2015; Goncalves et al. 2017). Due to their negative impacts on the agro-ecosystem, metallic nanoparticles are frequently avoided in agriculture.

Foliar assimilation of a characteristic polymer, for example, chitosan NPs, has as of late been utilised to control nitrogen, phosphorus, and potassium discharge in wheat (Abdel-Aziz et al. 2016). Inorganic NPs pollute the environment more than organic NPs. However, more evidence is needed to demonstrate their efficacy in terms of nutrient availability when compared to traditional fertilisation methods (Majumdar et al. 2015).

Nanoparticle-conveyed antimicrobials, then again, have a higher compound strength, taking into account a slower rollout and better bug the executives (Duhan et al. 2017). Natural and polymeric NPs as nanospheres or nanocapsules have been utilised to spread herbicides (Waalewijn-Kool et al. 2013). Polymeric NPs, specifically Poly(epsilon-caprolactone), have great biocompatibility and have been utilised to typify the herbicide atrazine on numerous events (Waalewijn-Kool et al. 2013). Another investigation discovered that chitosan nanoparticles containing three triazine herbicides had a lower natural effect and genotoxic impacts on *Allium cepa* (Simonin et al. 2016).

11 Plant Genetic Engineering Using Nanocomposites

Plant cell cultures have been utilised in the majority of spearheading endeavours for nanomaterial-based plant hereditary designing. Silicon Carbide-Mediated Transformation, for instance, has been depicted as a powerful strategy for conveying DNA in various harvests (tobacco, maize, rice, soybean, and cotton) (Wang et al. 1995; Lau et al. 2017). New plant investigations reveal that NMs can break through the epithelial wall in mature plants, reducing the constraints of classic transgenic delivery methods whilst still falling short of what has been accomplished in animal systems.

Several plant viruses' dsRNA may be encumbered on non-toxic, biodegradable incrusted double hydroxide (LDH) clay nanosheets, generally known as BioClay, according to a key finding. dsRNAs and/or their RNA toxic metabolites block the Cauliflower Mosaic Virus (CMV) in sprayed tobacco leaves, but they also provide systemic protection to newly emerging, unsprayed leaves 20 days after a single spray treatment on highly contagious challenge in tobacco leaves (Wang et al. 2016). This is real evidence for the non-transgenic transfer of lifeforms and inactive genetic code into plant cells, which might be beneficial in a variety of plant biotechnologies.

The use of magnetic nanoparticles resulted in an effective and durable genetic manipulation of cotton plants. The -glucuronidase (GUS) reporter gene-MNP complex was permeated into cotton pollen grains using magnetic force without having any negative consequences nodulation. By pollinating with magnetofected propagules, cotton plantlets were effectively generated, and inclusion of foreign DNA into the genome was effective, efficiently transcribed, and consistently transmitted in self-infected progeny (Zhao et al. 2017). Carbon nanotube scaffolds were employed to transfer linear and plasmid DNA, as well as siRNA, to *Nicotiana benthamiana*, *Eruca sativa, Triticum aestivum*, and *Gossypium hirsutum* leaves and protoplasts, resulting in high temporary Green Fluorescent Protein (GFP) production. A same study also argued that siRNA was administered to *N. benthamiana* plants that were generating GFP constantly, resulting in a 95% silence of this gene. MSNs (mesoporous silica nanoparticles) were recently discovered to be the first and most effective technique of genome editing. MSNs were used to transport Cre recombinase to immature *Zea mays* embryos, and loxP sites were inserted into the chromosomal DNA. The loxP gene was correctly recombined following genetic transformation introduction of modified MSNs into plant tissues, leading to more effective genome editing (Valletta et al. 2014).

12 Insights and Prognostications for the Future

In recent years, nanotechnology has achieved major advances in the synthesis of NMs as well as their use in biology for diagnostics and therapeutics. The current use of NMs for plants, on the other hand, is insufficient. According to recent findings and current applications, more research is needed in this area to improve NM synthesis and biofunctionalisation for plant applications, as well as to unravel plant absorption processes and improve agro-ecosystem and human health sustainability. Remarkably, technologies will need to be expanded to include hitherto unknown plant physiology components. Nanobiosensors for real-time detection of secondary metabolites or phytoregulators, for example, might build plant improvement and connections with the climate, particularly in confined growth surroundings.

Presenting exogenous DNA as well as catalysts for genome altering stays a genuine boundary, in spite of critical advances in plant hereditary qualities. New plant hereditary qualities strategies dependent on nanoparticle-interceded bunched consistently sprinkled palindromic rehashes—CRISPR related proteins (CRISPR-Cas9) innovation may be progressive, like those used in other biological systems.

Delicate materials, for example, nanogels and polymeric nanostructures, can be additionally taken advantage of as optimal choices for building up progressive ways for controlled arrival of biomolecules and plant genome altering, in view of combined information revealed in cell and animal models. Polymeric and hydrogel-based NPs provide apparent benefits in drug delivery due to their safe profile, a large carrying capacity, and good cargo preservation against deprivation. This type of NM has also been effectively exploited in cell and animal models to create a regulated (spatial and temporal) release of cargos in response to outside influences (e.g., UV, NIR, sonic waves, etc.). These incredible discoveries reveal that soft nanomaterials' enormous potential in plants has yet to be completely realised. Aside from the effective agrochemical delivery attempts, further research is needed to create methodologies and smart instruments for plant applications based on polymeric or hybrid materials. Of course, before polymeric nanoparticles are extensively employed in agriculture, a thorough research of production scalability and cost-effectiveness is required.

Furthermore, supporting the use of interdisciplinary methods to fusion and development of smart nanomaterials might help plant nanotechnology develop. Joint cooperation efforts including complementary professional skills such as plant biologists, geneticists, chemists, biochemists, and engineers may be able to provide fresh phyto-nanotechnology alternatives in order to attain this goal.

Nanotechnology has been employed in agriculture to increase crop output whilst also enhancing quality through modernising agricultural operations. Due to their uniqueness, engineered nanomaterials and inherent activities in the framework of organic development have fundamentally revolutionised the worldwide agricultural canvass in order to meet predicted global food demand, rapid development, and vastness. Nanomaterials provide better control and conservation of plant inputs, which is a key objective for sustainable agriculture trade. Nanomaterials have the potential to usher in a new green revolution with less dangers for farmers. However, we still have a lot to learn about many nanomaterials' absorption capacity, acceptable limit, and ecotoxicity. As a result, more study is needed to better understand genetically modified agricultural inputs' behaviour and destiny, as well as their interactions with biomacromolecules found in biological systems and ecosystems.

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Environmental Applications of Phytonanotechnology: A Promise to Sustainable Future

Rakhi Chahar and Manishita Das Mukherji

Abstract Plants have been using phytonanotechnology to boost their capacity to deal against adverse environmental conditions in recent years (e.g., nutritional insufficiency, pollution) and other hazardous compounds, as well as to introduce target-specific nanomaterials into the plant, increasing and improving production. This chapter gives an overview of phytonanotechnology, including its features and functions. This chapter will also look at how this technology affects the environment. The goal of this study is to get a fundamental knowledge of plant species and adjust their functions. Using a cross-analysis of papers measured the results are phytonanotechnology is helpful to our environment. By the use of phytonanotechnology was found to play the greatest role in making, environment and plants. This study definitely answers the questions regarding the correlation between proximity to nanotechnology to its applications and how is it beneficial. Improved development of phytonanotechnology may also ultimately result in the emergence of "advanced plants," allowing humans to sense and comprehend individual plants and their environs, so ensuring the planet's long-term viability.

Keywords Nanomaterials · Plants · Pollutants · Removal · Applications

1 Introduction

Nanotechnology is a multifunctional field. Nanotechnology is defined as the study, strategy, construction, and operation of substances at the nanoscale, which is a scale that converts atoms and molecules into macroscopic and bulk materials (Roy and Bharadvaja 2019). Phytonanotechnology is the utilization of nanotechnology toward plant systems (Verma et al. 2020). In recent years, phytotechnology has received a lot of interest as a nanotechnology application in the plant system. The suitable application of nanoscience to plants and crops can provide better outcomes and a search for their bioavailability and noxiousness in the environment. It is important that

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the materials used for the remedy of pollution are not another pollutant themselves after they have been employed. Phytonanotechnology, or the use of nanotechnology to plant systems, has recently gained popularity. Nano composts, nano bug sprays, and nano pesticides, for instance, have filled in acknowledgment in view of the intrinsic advantages of nanoscale length impacts, which allow plants to better absorb nutrients, insecticides, and pesticides (Li and Yan 2020). It is mostly a voluntary inexperienced innovation plan for soil, water, and air remediation. As an implementation of a sustainable option, phytoremediation is described as the usage of flora to do away with or delivery pollution from the environment (Garg and Roy 2022).

The following are the seven key tactics used in this technique:

(i) Phytoremediation, also known as phytosequestration, phytoaccumulation, or phyto absorption, is a process in which plants absorb xenobiotics from the lithospheric system and accumulate the same in its body parts which are harvested later.
(ii) Phyto-degradation, also known as phytotransformation, is the process by which plants degrade contaminants into simpler molecules. The molecules are thus embedded into the tissues of the plant which results in plant growth.
(iii) Phytofiltration, also known as rhizofiltration, is the process of contaminants being absorbed, adsorbing, concentrated, or precipitated by plants or roots.
(iv) Plants are utilized to improve evapotranspiration, hence limiting soil water and pollutant movement; phytohydraulic, that can be utilized to restrict the flow of contaminants with water.
(v) Phytoremediation, also known as phytoimmobilization, is a process in which plants immobilize or prevent pollutants from moving, therefore limiting their mobility and bioavailability in the environment.
(vi) Phytostimulation, also known as phytodegradation, is a process in which plants' roots release compounds that stimulate nutrient uptake in the rhizosphere through rhizospheric linkages between plants and symbiotic soil bacteria.
(vii) Phytovolatilization is a process in which plants use their capacity to absorb, translocate, and then transpire volatile toxins to accelerate the elimination of contaminants into the atmosphere (Roberto et al. 2020).

Most of the other nanotechnological possibilities for agricultural food sustainability include: phytotechnology, which is an enhanced delivery system for disease diagnosis and treatment, new plant pathogen specialist care technologies, molecular mechanisms biology tools, and novel materials (Nair et al. 2010). After reaching a specific concentration within the plant, most nanoparticles have the ability to dramatically lower agricultural production and productivity through changing structural, morphological, microbiological, pharmacological, and genetic structures seen in crops. The main issue is rising food demand, which is constrained by a lack of natural and food resources (soil, water, etc.), fertilizer input, low agricultural output, pesticides, and weedicides, as well as any environmental and health consequences. Another topic to be concerned about is trash management. Through the formulation of nano fertilizers, nano herbicides and pesticides, nutritional enrichment, food storage, and packaging, phytonanotechnology manages for a means to look at these problems using a nanotechnology manner. Phytonanotechnology opens up new possibilities for the environmentally friendly, easy, quick, stable, and cost-effective production of different nanoparticles. Some of the positives include the ease with which NPs may be synthesized using water, as well as biocompatibility and medicinal uses (Karupannan et al. 2020).

2 Phytonanotechnology: A Historical Perspective

Because of its capacity to use natural ingredients to convert metals into nanoparticles, phytonanotechnology is growing rapidly. The fast lowering of ions present in the solution resulted in the formation of nanoparticles after exposing different ions to the leaf extract. Nanotechnology now provides a thorough understanding, description, and programs of biologically produced nanomaterials. Engineered nanoparticles' unique properties and potentials have sparked a revolution in a variety of fields, including medication delivery, diagnostics, tissue engineering, and environmental cleanup. Dangerous decreasing and stabilizing chemicals, like sodium borohydride, N, N-dimethyl formamide, besides harmful solubles are typically used in chemical-based combination methods. Green chemistry is becoming increasingly important in modern research, with efforts focusing on mixes such as glucose, chitosan, soluble starch, a few microbes, and so on. Because of the need to maintain an aseptic environment during the process, nanoparticle manufacturing employing biochemical methods using plant extracts as reducing and stabilizing mediators has gotten a lot of interest (Basavaraja et al. 2008). Plant-mediated nanoparticle production has piqued attention in current nanoscience due to its eco-friendly nature and versatility. As a result, shape and structured-controlled nanoparticle manufacturing is widely employed with well-characterized therapeutically significant medicinal plants. The researchers demonstrated that it is an environmentally benign technology that may be utilized to produce nanoscale inorganic materials as an alternative to conventional technologies (Fig. 1) (Mathew 2020). Because of their unique properties and possibilities, engineered nanoparticles have become a revolution in the areas of medication delivery, tissue engineering, environmental remediation, agriculture, and pollution (Navarro et al. 2008). Mammalian systems are more interested in phytonanotechnology applications like nanotechnology in plant science and plant production than plants since nanoparticles have a limited absorption via cell walls (Rico et al. 2011). The most common elements that govern drug translocation and absorption include nanoparticle size and quality, and the types of plant tissues or cell architectures. Passive administration methods such as protoplast or tissue incubation, or passive absorption from the leaf and leaflets (as cuticles, trichomes, stigma, and stomata) and root are some prominent approaches for introducing chemicals into plant cells. Nanoparticles could enter living plant tissues and float to various areas of the plant vegetation, while it appeared that short-distance movements were favored (Corredor et al. 2009). Nanotechnology's application in agriculture has resulted in the controlled

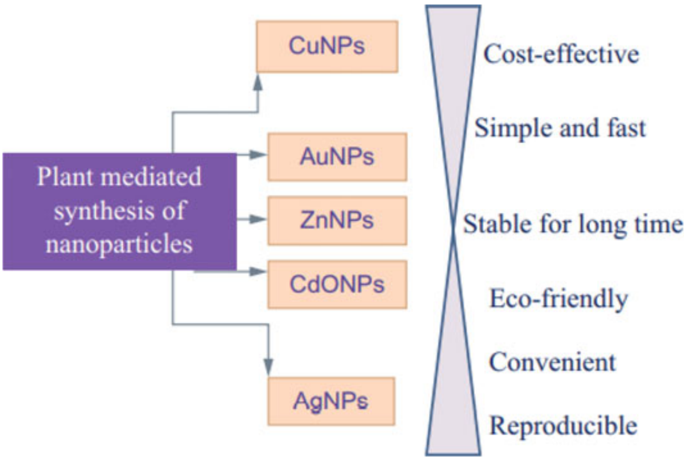

Fig. 1 Representation of characteristics of plant synthesized nanoparticles (Mathew 2020)

appearance of agrochemicals and the site-specific conveyance of various macromolecules to further enhance disease resistance, supplement usage productivity, and enhance plant growth, to name a few outcomes. For the most part, agrochemical loss due to drainage, photolysis, hydrolysis, and microbial debasement is reduced when using agrochemical nanoencapsulation, and therefore there is no need to visit the use of crop protection items to have successful management (Nair et al. 2010). Mesoporous silica nanoparticles (MSNs), single- or multi-walled carbon nanotubes (SWNTs or MWNTs), AuNPs, magnetic virus-like NPs (VNPs), carbon-coated magnetic NPs, quantum dots (QDs), and starch nanoparticles (NPs) have all been utilized as transporter for the transfer of bioactive compounds (such as nucleotides, proteins, and activators) (Wang et al. 2016). Using nanoparticles, nanotechnology brings a different set of instruments for transferring a huge nucleotide sequence as well as substances that activate gene expression into plants (Xia et al. 2009).

3 Nanotechnology and Plants

Phytonanotechnology aids in the development of a “smart” crop. Do not consume time, priority, changeable, self-directed, and multipurpose nanoscale materials are all possible (Nair et al. 2010). ENPs, for particular, may provide chemicals and pesticides (like manures, insecticides, and herbicides) on demand, either to meet nutrient demands or to protect crops from pests and microorganisms. This provides a practical means of avoiding repetitive applications of common agrochemicals while reducing negative impacts to the environment and vegetation Furthermore, nanoparticle designated transport of nucleotides, peptides, and other phytoactive particles has the ability to transport nucleotides, proteins, and other phytoactive particles to affect plant metabolism and guide it. Despite the relative abundance of benefits, the security by-plan guideline should be followed to address local area issues about the potentially detrimental consequences of revolutionary ENPs on environmental frameworks (e.g., the usage of ENPs in consumer items) (Scheringer 2008). Despite the fact that identical concepts may be used to create plant systems, nanotechnology's use in plant sciences including plant manufacturing activities to yet, (phytonanotechnology) has gotten relatively little consideration. We look at phytonanotechnology applications and talk about the uptake, mobility, action, and hazards of using ENPs in this field.

Plant or fruit peelings that are high in the formation of nanoparticles, flavonoids, phenolic compounds, and reducing agents. Furthermore, nanotechnology offers waste treatment that is adaptable solutions for the creation of useful goods (Roy et al. 2021). The green production of organic materials or plant educe are used to make nanomaterials is a fascinating aspect of nanotechnology (Roy and Bharadvaja 2017). This technology is appealing because it allows for a broad range of nanomaterial synthesis, eliminates the need for hazardous synthetic compounds, and is both cost-effective and safe. Due to the obvious origin and the complex materials and reagents, green synthesized nanomaterials are far more bio/ecologically viable than traditionally manufactured materials. Practically According to studies, all plants (trees, shrubs, or spices) include some level of alcohols, flavonoids, smell, proteins, phenols, and latex material that may be used to make metal-based nanoparticles from metal salts (Burris et al. 2012).

Phytonanotechnology technologies that target plants can improve their existing functionality in a variety of ways (Lowry et al. 2019). And from the other hand, in plant species, additional functions for example changing transforming plants into sensor devices might be introduced (Giraldo et al. 2019). Phytonanotechnology applications might help us better understand molecular and genetic analysis of plant species (Li and Yan 2020), at the nanoscale, providing energizing Biomolecules and genetic materials with smart transport potential (Giraldo et al. 2014) closing the knowledge gap in phytonanotechnology and, as a result, offering huge logical and social benefits (Mitter and Hussey 2019).

Engineered nanomaterials had already demonstrated great potential to improve photosynthesis efficacy by easing ecological pressure (Xiong et al. 2018). Engineered nanomaterials can also improve a plant's capacity to endure harsh environments such as drought, flooding, disease, and salt (Mitter and Hussey 2019). According to certain research, nanoparticles can aid in plant development while also preventing the development of plant disease owing to surface features (Elmer and White 2016). Nanomaterials, instead, can boost a capability of plant to eliminate pollutants environmental contaminants like heavy metals and reduce their toxicity (Wang et al. 2015). Furthermore, several nanomaterials have the ability to boost plant development and so produce more agricultural output. When soil was boosted with multiwalled carbon nanotubes, tomato plants generated twice as many flowers and organic compounds as the control group (Khodakovskaya et al. 2013).

4 Applications of Phytonanotechnology

Nanomaterials are used in plants for a variety of purposes, ranging from the creation of nanomaterials from plant fixes to the use of nanomaterials for affecting plant bioactive parts and controlling plant development or disease (Pandit et al. 2022). Despite the enormous potential for nanomaterials in agriculture, variations in nanomaterial elements and their impact on plant species must be assessed rapidly. Similarly, for each application, the negative consequences of nanomaterials in plant structures and devices should be assessed (Dietz and Herth 2011). Because ENPs have a negative impact on plants and the atmosphere, their usage in diverse productions should follow defined rules. Nanotechnology's application in plant sciences is a large topic of research with various unique topics for scientists to investigate (Mohammadi et al. 2019). By targeting precise delivery in a regulated manner, nanotechnology can minimize the need for plant protection chemicals, reduce nutrient loss from fertilizers, and increase yield through better management of nutrients. Engineered nanoparticles can be created as agrochemical-loaded "magic bullets" that transport agrochemicals to specified tissues in a regulated manner. ENPs offer another method of delivering bioactive nanoparticles (including nucleotides, proteins, and activators) (Wang et al. 2016). In comparison to applications of nanotechnology in other fields like materials, electronics, energy, and medical, Agriculture is still in its early stages of development. Application areas and plant-based nanoparticle manufacturing studies demonstrate its development and promise. The use of nanoparticles in agriculture lowers the cost of plant protection, eliminates supplement mistakes in treatment, and boosts yields across the board through improving supplementing (Gogos et al. 2012).

4.1 Fate of Phytonanoparticles in Plants

Nano fertilizer uptake and destiny in plants are becoming more popular in the area of study subjects. The uptake of nanoparticles into the plant's cell wall is determined by the aperture radius of the cell wall, which ranges from 5 to 20 mm (Fleischer et al. 1999). Nanoparticles or nanoparticles thousands with a diameter less than the pore length of the plant mobileular wall can bypass the mobileular wall and reach the plasma membrane without difficulty (Navarro et al. 2008). Functionalized nanoparticles use size of pore expansion or the insertion of a new cell-wall pore to improve nanoparticle uptake. After entering the cell, nanoparticles might transfer apoplastically or symplastically. Plasmodesmata may move them from one cell to the next. There are few studies on the destiny of NPs such mesoporous silica NPs (MSNPs), silica NPs (SNPs), carbon nanotubes (CNTs), fullerene (C70), quantum dots (QDs), Au-NPs, titanium dioxide NPs (TiO_2 NPs), iron (II, III) oxide (Fe_3O_4) NPs, and infectious NPs (VNPs). The future existence of nanoparticles in the plants is mostly unknown (Rico et al. 2011).

4.2 Removal of Recalcitrant Pollutants

Green science norms have been validated by nanotechnology by demonstrating nature's ability to address climate-related challenges. Phytonanotechnology was produced recently, and it works by using a natural blend of phytochemicals from microbes and plant extricates to lessen and settle experts (Ahmad et al. 2019). Magnetically absorbent materials are attracting a growing amount of interest from dye manufacturers (Roy et al. 2021). A few solutions for removing colors from material effluent have been developed, although natural techniques are not damaging to the ecology. Scientists separated the protein peroxidase and immobilized it in attractive Fe_3O_4 nano particulates that glutaraldehyde co-precipitation was used to create and modify the samples. Because the chemical was immobilized, they were able to employ it in a second bioreactor to treat the material company's wastewater (Darwesh et al. 2019).

4.3 Environmental Pollution Detection

Environmental pollution is becoming a more serious a danger to people's and the environment's health on a daily basis, necessitating the development of effective and reliable detection technologies (Roy et al. 2022). These must be centered on the identification and emergence of new environmental and trace contaminants. Actinomycetes, microbes, yeasts, parasites, and plants, for example, can manage the combination of natural and inorganic nanomaterials based on physiological boundaries and development circumstances such as supplement pH, temperature, culture time, soil quality, soil wetness, and concentration of pollutant are all factors to consider. The organization of nanomaterials by mass natural or inorganic materials collaborating with diverse living forms is interrupted by a few intracellular and extracellular cycles. Various wild species are now being for environmental remediation, it's employed for the inside the cell and outside the cell union of nanoparticles. Accompanying economic growth and as the world's population grows, so does pollution. An inevitably huge global issue even when contaminants are present at extremely low amounts, as the world's population grows, so does pollution. As a result, the improvement of delicate scientific methodologies is critical for the detection of trace and ultra-trace environmental contaminations. As a result, it is critical to promote the comparison of explicit and sensitive scientific methodologies. Along these lines, traditional scientific tactics have steadily improved their identification capabilities, resulting in state-of-the-art innovations for differentiating ecological poisons that have the highest affectability, simpler chores, in situ inspection, and transportability. One of the most feasible approaches for identifying environmental contaminants is surface-upgraded Raman dissipating (SERS) among these advancements (Song et al. 2019). Due to its unique mark data, ultrahigh affectability, and quickness, SERS is an incredibly insightful process for detecting environmental contaminations, which might be seen as noteworthy benefits when compared to comparable and contemporary innovations.

4.4 Current Challenges and Prospects in Phytonanoparticle Synthesis

Nanoparticles may quickly permeate plants and affect morphological, biochemical, and physiological features, and gene expression due to their small size (Tripathi et al. 2017). The silver nanoparticles which were created and evaluated the increased antibacterial effects of unique silver nanoparticles have greater antimicrobial properties than those disclosed in previous papers (Shrivastava et al. 2007). Gram-negative organisms had more unique traits than Gram-positive species. The use of marijuana is also an innovative method. Silver nanoparticle synthesis from *Desmodium triflorum*, for example (Belloni 2003). Belloni (2003) discovered. In all abstracts, *D. triflorum*, a traditional medicine, contains a lot of polyphenols, flavonoids, sterols, triterpenes, and reducing sugars. Desmodium plants, which function as both reducing and capping agents in the process, are also promising candidates for the production of silver nanoparticles (Ahmad et al. 2009). Phytonanoparticles given from different plants to *Coriandrum sativum* have been used in a variety of ways, according to several sources. The utilization of natural plant conditions has been the subject of recent studies potential prospects for the generation of silver nanoparticles include xerophytes, mesophytes, and hydrophytes (Jha et al. 2009). The bio-enhanced manufacture of very stable *Ocimum tenuiflorum* was used to make silver nanoparticles. leaf extract, and research into their antibacterial properties. In their review, they found that the size of the colloidal silver solution demonstrated strong antibacterial activity against three distinct bacteria strains: *Escherichia coli* (Gram-negative), *Corney bacterium* (Gram-positive), and *Bacillus subtilis* (Gram-positive) with nanoparticles in the range of 25–40 nm (spore shaping) (Patil et al. 2012). Recent research has focused on modulating the antibacterial activities of extracts from numerous medicinal plants against a variety of bacteria, particularly Gram-negative bacteria (Akinnibosun et al. 2008). To fully realize the potential of phytonanotechnology, a number of challenges must be solved (Li and Yan 2020). The following are the primary agricultural concerns that nanotechnology will address:

- Food security for the increasing population
- Reduction in yield of crop fields
- Reduced agriculture productivity
- Farm management that is unsustainable
- In agricultural regions, there has been a reduction.
- Losses incurred after harvest (processing and packaging).

Nanomaterials can solve environmental issues while still ensuring continued agricultural production due to target specificity, coordinated and gradual distribution, and low toxicity. As a result, it is obvious that they can address the nutritional security, food security, and a good standard of living are all challenges that need to be addressed production while being environmentally conscious (Nuruzzaman et al. 2016). The lack of sufficient specialized knowledge on the toxicological component of nanoparticles, on the other hand, allows both proponents and opponents of nanotechnology to draw inconsistent, conclusions on the safety of nanoparticles are unscientific and clear. This feeling of uncertainty is the feature of nanotechnology that pessimists are most concerned about (Colvin 2003).

4.5 *Different Properties of Phytonanoparticles*

Nanoparticles have appealing traits such as well as excellent stability and capacity to alter their external properties quickly (Tom et al. 2004). The topic of synthesis of nanoparticles using plants is a subject of research that is continually growing and full of opportunities intriguing predictions Medicines, agricultural, human well-being, and agroindustry are all affected, and other fields. Agriculture is an example of this, developing novel genetic disease therapy and weed management tools, and boosting plant nutrient assimilation capability is not damaging to the environment. Nano fertilizer manufacture is the notion of a smart delivery system is tremendously advantageous to crop development. It may time the delivery of nutrients to coincide with crop absorption, avoiding nutrient losses and lowering the danger of pollution of groundwater (Mathew 2020). The growing importance of green science in modern research concentrates on efforts using substances like glucose, chitosan, soluble starch, a few microbes, and so on. Nanoparticle manufacturing via biochemical pathways plant extracts has been used as reducing and capping agents gained a lot of attention, thanks to the ability to maintain an aseptic environment during the interaction (Basavaraja et al. 2008). Nanoparticles of silver are important components that have been widely explored in plants to aid in the development of nanoparticles. A few physical, material, and natural strategies can be used to include them (Sharma et al. 2009).

Antimicrobial characteristics of nanoparticles of silver make them important materials. The antibacterial activity was shown by TEM design (Nabikhan et al. 2010). As a result of the fact that only nanoparticles having a direct interface with microscopic organisms have diameters of roughly 1–10 nm, the silver nanoparticles have antibacterial properties that are size-dependent (Morones et al. 2005). Recently, much emphasis has been placed on utilizing the antibacterial characteristics of several therapeutic plant extracts against a few pathogens, notably Gram-negative bacteria (Akinnibosun et al. 2008). In situ extracellular production nanoparticles made of metal were achieved utilization of extracts from plants like *Azadirachta indica* (Neem) and *Zingiber officinale* (Ginger). A comprehensive research of nanoparticle antibacterial activity and synergetic adequacy with commonly used antibiotics with a restricted range of action has been successfully developed conducted (Nazeruddin et al. 2014).

Antioxidant capabilities are also seen in silver nanoparticles. Soare et al. and his colleagues discovered that extracts of *Hyacinthus orientalis* flowers have antibacterial antioxidants and activities characteristics similar to other therapeutic plants (Soare et al. 2012). The antioxidant activity of phytosynthesized *Elephantopus scaber* leaf extract was shown to contain nanoparticles, indicating the fact that this plant extraction might be employed as a possible scavenger of free radicals (Kharat and Mendhulkar 2016). Biosynthesized AgNPs made from *Lawsonia inermis* extract of a leaf appears to have significant antimicrobial and antifungal properties effects, as well as better antioxidant and DNA-defensive characteristics. Finally, our research demonstrated the potential for *Lawsonia inermis* to be used as a unique hotspot for AgNP union as well as the articulated materiality of AgNPs in the biological area (Ajitha et al. 2016). In chloroaurate solution, Sesbania seedlings framed plant cells with gold nanomaterials. The gold nanoparticle's reactant capacity has a biomatrix with the ability to easily decrease a harmful substance contaminant, 4-nitrophenol (4-NP), which has a top wavelength of 317 nm in the UV–visible spectral range. With the strengthening of the shadow of the arrangement, the expansion of sodium borohydride to 4-NP exhibited the top to 400 nm. In addition, the production of 4-aminophenol (4-AP) confirmed the gold nanoparticles' reactant migration in a watery arrangement of Sesbania seedlings (Sharma et al. 2009).

4.6 Applications of Agriculture Use Nano Fertilizers and Insecticides.

The production of effective detailing of nanoparticles, insecticides, or fertilizers is known as nanoencapsulation (Karupannan et al. 2020). Fertilizers that are often used are frequently given to the plants via transmitting or spraying. Because of chemical leaching drift, runoff, microbial and photolytic destruction, hydrolysis by soil moisture, and evaporation are all factors that must be considered before reaching the objective, only a little quantity of fertilizer makes it to the plants, causing maintainable and monetary losses while also influencing the soil's nourishing balancing (Ombódi and Saigusa 2000). Nano fertilizers are devices with a nanoscale size that provide nutrients to crops. Nanotechnology in agribusiness is useful for supplying crops with micro and macronutrients. A nanostructure acts as a nutrient transporter, allowing for the regulated secretion of nutrients with a little setback. This also creates new opportunities to improve fertilizer use productivity in order to reduce costs and pollution (DeRosa et al. 2010). There are many studies have found that transmitted nanoparticles boost plant development and output (Gao et al. 2006). Using nano herbicides, nanotechnology has the potential to eliminate weeds in an environmentally acceptable manner deprived of discharging any dangerous compounds in the soil or environment (Pérez and Rubiales 2009).

A smart delivery system for herbicides is one that uses nanoparticles as transporters. Weeds can be completely eradicated by encapsulating herbicides and delivering them in a controlled manner. Validamycin (pesticide) packed on permeable hollow silica nanoparticles (PHSNs) is an effective pesticide delivery system that is water-soluble architecture through regulated manufacturing. Nano silica stands ingested by insects over their epidermal lipids, resulting in physical death (Ulrichs et al. 2005). The regulated distribution of pesticides in PHSNs makes them a reliable transporter in agriculture, particularly for pesticides that require quick and expanded delivery for plants (Rai and Ingle 2012). The term agro-nanobiotechnology refers to a combination of bioengineering, nanoscale technology, and agronomy. Agro-nanobiotechnology is a field in which nanotechnology is used to agriculture-based devices are created and used for the analysis of agricultural and agricultural issues and organic specialties (Fernández et al. 2018). In this way, nanoparticle-based details, also known as nano fertilizers, may be termed as nanomaterials or nanoparticles that provide crucial or advantageous supplements to plants at the nanoscale to aid plant development and further progress creation. In comparison to traditional fertilizers, nano fertilizers appear to be able to deliver wholesome components in a planned manner (gradually or rapidly) in reaction to various natural vacillations soil salinity, moisture, and temperatures, allowing them to improve plant development even more effectively (Roberto et al. 2020).

Carbon nanotubes (CNTs), Cu, Ag, Mn, Mo, Zn, Fe, Si, Ti, and nanoformulations of classic rural information sources such as phosphate, urea, sulfur, validamycin, tebuconazole, and azadirachtin take all transformed into nano pesticides as well as nano fertilizers (Fernández et al. 2014). Nano fertilizers are classified into three groups depending on their chemical composition plant supplement necessities: (a) macro-nanofertilizers (N, P, K, Mg, Ca, and S), (b) micro-nanofertilizers (Fe, B, Cl, Zn, Mg, Cu, Ni, and Mo), and (c) nanomaterials acting as supplement transporters (Kah et al. 2018). Micro-nutrients are added to N, P, and K manures in lesser amounts as dissolvable salinities to aid crop absorbed (Liu and Lal 2015). However, there are other nanoparticles, like Ce, Ti, and CNT structures, that are not comprised in the basic plant supplements but have been demonstrated to have beneficial impacts on plants (Oloumi et al. 2018). Other Nanoparticles aren't covered, such as Ce, Ti, and CNT structures in the standard plant supplements yet have been demonstrated to have beneficial effects on plants. Liu and Lal (2015) have studied the widespread usage of nano fertilizers in Urea-coated zeolite chips and urea-altered hydroxyapatite nanoparticles have been developed in agriculture created by way of a source of nitrogen and have demonstrated their ability to produce N in a gradual and regulated manner over an extended length of time (Kottegoda et al. 2011). The pesticide industry's particle space is quite popular. Nanoencapsulation of pesticides is beneficial in controlling and slowing the appearance of vibrant fixing by controlling the exterior case of the nanocapsule, which allows for the release of a low dose over a long period of period and decreases pesticide runoff (Agrawal and Rathore 2014). Nanomaterials have a larger surface strain than slow-release compound manures. Additionally, compost nanomaterial coatings may be able to completely retain these synthetic compounds (Solanki et al. 2015).

Slow-release sulfur nanocoated composts (100 nm) and zeolite-based nano fertilizers sulfur-deficient soils benefit from these plants, as they increase the amount of sulfur in the soil supplement accessibility during the vegetative and regenerative phases of the plant's life cycle. This can help to reduce denitrification, leaching, volatilization, and chemical buildup in the soil. The penetrating capability of nanoparticles with greater surface areas, which results in the effective nutrient uptake by plants is a key component accompanying delayed delivery (El-Ghamry et al. 2018). Nanopesticides are "either tiny elements of an insecticide dynamic fixing (ai) or other lesser tailored constructs through beneficial pesticide capabilities," according to the FDA (Kookana et al. 2014). Nano encapsulated pesticides not only reduce the number of synthetic substances in the environment, but they also improve the efficacy of composting. Organic specialists such as plants, green growth, parasites, actinomycetes, yeast, microbes, and diseases are used in nanoparticle production (Chokriwal et al. 2014). Silver nanoparticles or nanomaterials have excellent antibacterial (bacteriostatic and bactericidal) action, enhanced strength and dissolved, and, most prominently, a regulated slow-release characteristic due to their physicochemical features (Bhattacharyya et al. 2016).

Regardless of the fact that the use of substance manures might improve yield usefulness, their broad use is everything but a sensible decision in the long term. Furthermore, the available nutrient provided in typical manure's chemical forms in bulk is not totally open to plants. Furthermore, because the bulk of macronutrients reverts to an insoluble state in soil, their consumption is quite low (Solanki et al. 2015). Any nano fertilizer should be made in such a manner that it has all of the ideal features, such as high solvency, security, viability, time-controlled distribution, enhanced focused action with compelling fixation, and reduced eco-poisonousness with protected, simple transfer and removal methods (Torney et al. 2007). In biological systems, nanoparticles have the capacity to carry nutrients to particular target locations. Nutrient nanoparticle loading is typically accomplished through (a) Nanoparticles absorb energy, (b) ligand-mediated nanoparticle attachment, (c) encapsulated in a polymeric nanoparticulate shell, (d) polymeric nanoparticle ensnarement, and (e) the production of nanoparticles from the nutrient itself. The nanotechnology's application in agriculture is critical since it has a direct impact on humans (Bouwmeester et al. 2009).

Nano fertilizers, made possible by nanotechnology, has become yet another milestone in the history of harvest creation. There are a lot of issues to be concerned about with the use of traditional chemical fertilizers, but one of the most pressing is poor usage proficiency, which raises production costs while also increasing contamination (Wilson et al. 2008). Nanoparticles because of their nano size, they may overcome this challenge by having a large surface area. These might be employed as nano-coatings, such as sulfur nano-coating (100 nm layer), confirming regulated distribution, and, last, surface protection increasing utilization productivity. Nanoparticles, plants (such nano composts), and microbes (as biofertilizers) might need to be investigated additional. These links might consist of (1) the advantages of using biofertilizers (or horticulturally valued microorganisms) in reducing nanoparticle toxicity; and (2) the beneficial effects of biofertilizers (or horticulturally valuable microorganisms) in decreasing nanoparticle toxicity reactions of plants to nanoparticles or nano fertilizers, (3) Biofertilizers and plants have a tight interaction and plants and microorganisms' roles in the production of bio- and nano fertilizers (El-Ghamry et al. 2018).

4.7 Nanoparticle Uptake and Transport in Plants

It is difficult to focus that how plants create nanoparticles (NPS), as well as how they enter and interact with plant cells. NPS's unique qualities, such as its small size, high surface energy, large explicit external region, and solubility, increase its absorption through plants. Nanotechnology may be used in farming in this way to distribute agrochemicals to different sections with minimal waste. The dimension of the hole in the cell wall regulates the filtering characteristics of plant cells, and big-sized nanoparticles cannot enter because the cell wall works as a barrier. As a consequence, nanoparticles having a diameter lower than the pore diameter of the cell (5–20 nm) can penetrate the plant cell by breaking over the cell wall (Mohammadi et al. 2019). Following their infiltration into the plant, nanoparticles might enter and transfer through apoplastic or symplastic routes, affecting its efficiency and eventual destiny. Nanomaterials can reach the plant's root and aerial portions through the apoplastic channel (Sun et al. 2014). Aquaporin is another type of entrance that is accounted for in the seed coat's nanoparticles portion of the rules (Tripathi et al. 2017). The cycles of NPs uptake are commonly viewed as a working transport system containing a variety of extracellular processes like plasma membrane signaling, recycling, and signaling control (Etxeberria et al. 2009).

The age and species of the plant, development climate, physicochemical properties, function, strength, and manner of nanoparticle conveyance all have a role in nanoparticle absorption, movement, and growth. The absorption of nanoparticles into plant cells has been the subject of several research by constraining transporter proteins via aquaporin, particle channels, or endocytosis (Nair et al. 2010). Nanoparticles can also be introduced into by building compounds with membrane transporters or root exudates, plants are able to survive. These "nano-nano fertilizers" feature a large surface area, a low sorption limit, and a controlled energy discharge to specific locations, making them a smart delivery system. However, being a young expertise, the moral and health concerns surrounding the usage of nanoparticles in plant applications are numerous and should be thoroughly investigated earlier modifying the usage of ostensibly nano fertilizers (Solanki et al. 2015).

Although nanomaterials may infiltrate live plant tissues and build up in the environment and suitability as per dazzling transfer frameworks in living plants raise concerns (Ali et al. 2021). In-plant research, nanomaterials have been offered as a means of boosting agronomic capabilities (Verma et al. 2019). In the soil, NPs go through a collection of bio/transformations that regulate their toxicity and bioavailability. Following your interaction with the plant, establishes, the NPS migrate toward flying bits besides gather in the cell or subcellular organelles. The earliest step of bioaccumulation might be defined as the NPs from the soil are absorbed by plant roots (Nair et al. 2010). Furthermore, the fundamental structure of nanomaterials is critical for determining their influence absorption, translocation, and transport of NPs and collection in plants (Raliya et al. 2016). Small nanoparticles (diameters ranging from 3 to 5 nm) have been shown osmotic pressure and capillary pressures are used to enter plant roots, otherwise direct passage root epidermal cells are responsible for this. The root cell-wall cuticular cells are semipermeable, including minute holes that restrict the massive NPs. A few nanoparticles caused new pores to appear in the cuticular cell wall, which helped it enter (Du et al. 2011). This is accomplished by confining transporter proteins to the endodermal cell membrane via transport, endocytosis, and pore architecture NPS is transferred from a cell to the other via plasmodesmata, which are impacted in the cytoplasm. The NPS that cannot be disguised is entire on the Casparian strip, but the NPS that have reached the xylem are transferred to the shoots and returned to the roots via the phloem (Tripathi et al. 2017).

5 Conclusion

For nanoparticle combinations, several experts have recently turned to natural frameworks. Nanotechnology's advancement has confirmed broad and substantial uses in a variety of industries, including microelectronics, medication, maquillages, materials, nutrition science, energy, and farming. The absorption, location, and activation of nanoparticles produced by plants concentrate might cause havoc in the agricultural region with almost no negative consequences. Plant NPs have larger levels of full phenolic mixes and all-out flavonoids than the plant extract alone. In comparison to plant extract alone or particles, plant NPs demonstrated stronger cancer prevention agents and antimicrobial movement. As a result, the precision of plant-mediated NP synthesis has inspired their anticipated uses in biomedicine, pharmacology, food science, agribusiness, and natural design. Currently, a few organically formed natural or inorganic nanoparticles have contaminated hazardous combinations, mostly by adsorption, change, photocatalysis, and synergist decrease in biochemical mixes mixed by plants, i.e., Ecological remediation with phytonanotechnology. Three main technologies include phytoremediation, nanotechnology, and biotechnology information fields that are coming altogether to provide environmentally beneficial breakthroughs that will help to advance human prosperity, distribute contaminants, and ensure natural and human well-being.

6 Future Outlook

Phytonanotechnology offers a lot of promise in a variety of fields, including agriculture, medicine, natural remediation, and so on. Phytonanotechnology has applications in the creation of devices for the delivery of agrochemicals and bioactive combinations with the goal of managing hereditary data in plants. Environmentally friendly phytomediated nanoparticles benign, more lucrative, takes less time to make and last a long period product security. Future work can assist in debunking the myths in this subject to start changing the innovation bringing new ideas to on-the-field applications and develop advancements to track down its implementation in different areas, as well as there are numerous neglected phytonanotechnology research areas, as well as the absence of research facilities to handle work change. A number of laboratory trials have yielded beneficial results for plant growth and development. Before embarking on a considerable procedure or a field sort, the long-term effects must be calculated under numerous exploratory and natural situations. Because the uptake, mobility, and the majority of NPs' fates are unknown, this poses a slew of moral and security concerns. As a result, it has to be improved for new applications in the sector. The biomolecular partnership of NPs, as well as the quality articulation criteria, must be clarified. The subatomic and sub-molecular level constituents of NMs need to be investigated further (Khan 2013). Drug distribution in animal cells, like the transfer of agrochemicals in plants, can be looked into in the future. The optimal distribution of pharmaceuticals, specified exact delivery, the capability to halt medication delivery inside the creature framework, and the nontoxic obliteration or termination of the transporter nanoparticle are only a few of the areas that phytonanotechnology might investigate more. In any event, the application of phytonanotechnology may expose plants to large amounts of man-made nanoparticles, which might be harmful to plants and their habitats (Tsang et al. 2017). Furthermore, considering the whole a full life cycle of nanomaterials in the environmental security valuation methodology should be developed to address the potential risks of nanomaterial bioabsorption and biotransformation (Fadeel et al. 2018). Because nanomaterials can be tailored to a specific purpose to improve—various plant capacities in addition to adding new capacities toward plants, Phytonanotechnology can potentially be summed up in a larger setting, city planning with phytonanotechnology, for example -empowered plants with self-fluorescence that act as streetlights and plants with smart sensors that can detect movement react toward outer and inner upgrades actuality utilized as alerts before markers aimed at ecological security or natural (Lowry et al. 2019). Nanotechnology is emerging as the most advanced gadget that has the potential to significantly contribute to a more sustainable future.

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Phytonanotechnological Approach for Silver Nanoparticles: Mechanistic Aspect, Properties, and Reliable Heavy Metal Ion Sensing

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Abstract The environmentally benign and reliable methods for the nanoparticles (NPs) synthesis are playing significant role in the area of nanotechnology. The traditional methods of silver nanoparticles (AgNPs) synthesis are costly, hazardous, and non-eco-friendly. The phytonanotechnology is the alternative method to tackle these problems which includes NPs synthesis using natural sources like plants, fungi, bacteria, and biopolymers as presence of various phytochemicals acting as stabilizing along with capping agents. AgNPs are widely used in the sensing field for the detection of toxic heavy metal ions like mercury (Hg^{2+}), lead (Pb^{2+}), zinc (Zn^{2+}), cadmium (Cd^{2+}), arsenic (As^{2+}), copper (Cu^{2+}) etc. with very low detection limits. The present chapter lights on the green and mechanistic approach towards the synthesis of plant-based AgNPs, its properties, and heavy metal ion sensing applications.

Keywords Phytonanotechnology · Silver nanoparticles (AgNPs) · Bio-mediated synthesis · Sensing · Heavy metal ions · Nano-biotechnology

1 Introduction

Phytonanotechnology is a green science used to synthesize NPs from plant or bio resources. It is an unconventional method that attracts an interest from researchers due to its simplicity, expensiveness as well as the usage of benign plant-based phytochemicals as reducing agents to substitute hazardous chemicals. Today's progression of nanotechnology in various fields viz. nanomedicine, optoelectronics, catalysis, and water treatment is the outcome of eco-friendly materials fabricated via plants (Phull

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et al. 2016). Till date, many reports represent the biogenic synthesis of chalcogenides, metal, metal oxide, NPs etc. (Roy et al. 2021).

The fabrication of metal NPs will be done by different ways, including chemical, physical, and biological routes. The chemical synthesis method either directly or indirectly causes a great threat to environment. As a result, researchers focused on the easy, simple, reproducible, and eco-friendly synthesis way for metal NPs. For a long time, phytoextracts from plant leaves, stem, flowers, fruits, seeds, shells, peels, roots, and latex etc. have been used for synthesis of metal NPs because of their consortium role as a reducing and capping or stabilizing agents (Nagore et al. 2021).

Amongst the bio-mediated synthesized metal NPs, the AgNPs have been one of the most investigated materials till date. AgNPs are utilized in wide range of applications including but not limited to catalysis, drug delivery, biomedical, imaging, sensing, photonics, pollution control etc. (Gil-Sánchez et al. 2019). The plant parts contain many functional agents such as phenols, flavonoids, alkaloids, saponins, fatty acids, protein, fibres, sugars, vitamins, minerals, terpenoids, anthraquinone, and tannins. The antioxidant, polyphenols, and phenolic acids are the most important constituents and are responsible for the NPs formation (Al-Dhafri and Ching 2019). The presence of various metabolites by the virtue of which the fabricated material embraces the antioxidant, radical scavenging, antibacterial, and anthelmintic properties useful to exploit them traditionally for treatment various diseases (Ansari and Alzohairy 2018).

The applications of NPs are based on its properties like particle size and its morphology, surface area with crystallinity, aggregation, adsorption potential etc. which must be characterized/verified accurately otherwise the NPs will not be recommended for its further use (Kora et al. 2012). Plant-based AgNPs are produced by reacting silver salt, particularly $AgNO_3$ with aqueous extracts derived from parts of plant below 100 °C. The size and nature of the NPs depends on reduction conditions such as time, pH, temperature, extract, and precursor concentration etc. Prime objective of present chapter is to summarize the AgNPs fabrication methods by various plant parts and to highlight its sensing properties in field of sensing of heavy metal ions in aqueous medium.

2 Synthesis Methods of AgNPs

Top-down and bottom-up routes are main approaches of AgNPs synthesis. The physical method of synthesis was commonly comprised in top-down route, whereas the bottom-up route includes biological and chemical method. Physical method includes milling, spray pyrolysis, etching, grinding, etc. which is used to reduce bulk materials to nanopowder or particles. Physical methods of synthesis render more homogeneous NPs but are less endorsed due to exorbitant synthesis cost (Xu et al. 2020). Chemical method which includes polyol, solvothermal, chemical reduction, coprecipition, and pyrolysis methods etc. is somewhat superior over physical methods except use of hazardous chemicals. The biogenic synthesis method can be understood as typical bottom-up approach of NPs synthesis that includes the use of plants, enzymes, biomolecules, microorganisms like fungi, bacteria, algae, actinomycetes (Li et al. 2011).

Chemical synthesis involves conversion of metal ions using some chemical reducing agents including ascorbic acid, sodium borohydride, citrate, thiosulphate, polyethylene glycol etc. However, polyvinylpyrrolidone, cetyltrimethyl ammonium bromide, and polyvinyl alcohol plays a pivotal role in NP stabilization (Daniel et al. 2004). The synthesis of abundant quantity of nanomaterials within short time span is the advantage of chemical method but may pose risk to the environment as presence of hazardous chemicals. The reduction and stabilization of Ag^+ ions using phytochemicals like terpenoids, flavones, ketones, aldehydes, amides, proteins, tannins, polysaccharides, polyphenols, and vitamins in the plant extracts were extensively studied as an environmentally benign route for synthesis of AgNPs (Roy and Bharadvaja 2019).

The different plant parts (leaf, bark, root, and stem) have been applied by some researchers for the AgNPs synthesis. Following steps are included in the general protocol for AgNP synthesis: collection of the plant parts from the available sites, its washing with distilled water for removal of epiphytes and necrotic plants, and washing with deionized water to remove any debris. Followed by, cleaning and drying of fresh plant sources in the dark for 10–15 days before being powdered. Boiling of ~10 g of powder in 100 mL distilled water to make the plant extract called as hot percolation method. In most cases, the aqueous plant extracts are preferred to obtain reducing agents however, as per some reports the usage of organic solvents (alcohols and acetates) are preferred. The saline or acetone are preferred for pre-treatment of plant parts before preparation of plant extracts (Shaikh et al. 2021). The various approaches for AgNP synthesis including green synthesis and micro-organisms are shown in Fig. 1.

2.1 Green/Bio-mediated Synthesis of AgNPs

In bio-mediated methods, AgNPs are synthesized using various microorganisms and plant parts. Recently, the NPs derived from biological method with tuneable physico-chemical properties have been attracted lot of attention because of extensive application in many fields (Zhang et al. 2016). The bio-mediated synthesis method includes microorganism and plant parts derived phytochemicals which are responsible to reduce the Ag^+ ions to form AgNPs.

2.1.1 Microorganism-Mediated Synthesis of AgNPs

Microbial nanotechnology offers a wide scope towards environmentally benign methodology. The NPs are synthesized using bacteria, fungi, and algae show enormous use in nanobiotechnology field. The AgNPs may be synthesized using either intra or extracellular matrix present in the bacteria. Nanda et al. stated the AgNPs

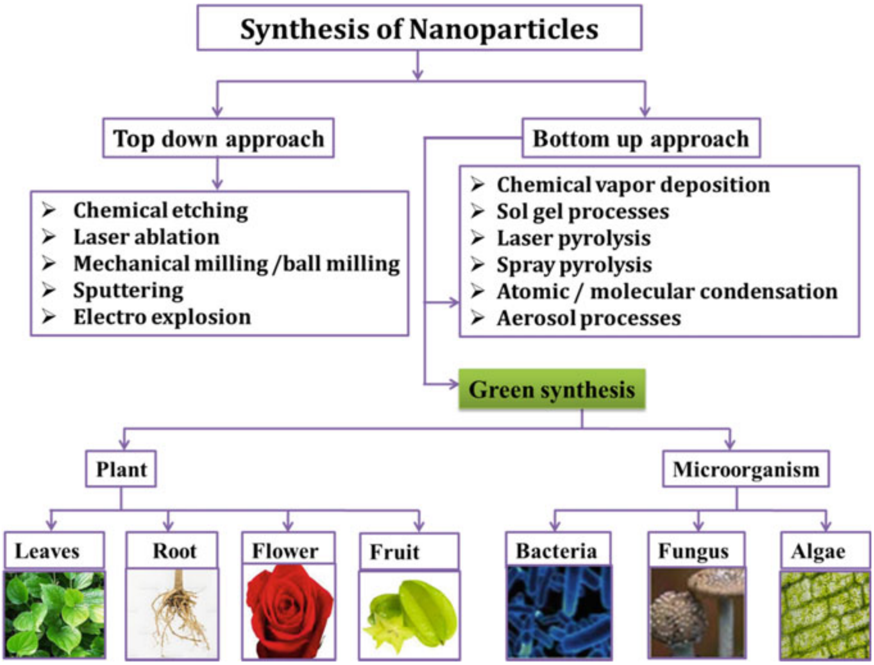

Fig. 1 Approaches for AgNP synthesis including green synthesis

synthesis by using culture supernatants of *Staphylococcus aureus* explored to determine antimicrobial properties (Nanda and Saravanan 2009). The culture supernatant of *Enterobacteria* was used to obtain AgNPs by researchers (Shahverdi et al. 2007). Monowar et al. (2018) used extracellular extract of an endophytic bacterium from *Pantoea ananatis* to fabricate AgNPs which showed the antimicrobial activity against human pathogens. Also, fungi are foremost choice for the AgNPs synthesis owing to their enormous advantages. The metal ion reduction ability of the enzyme and protein secreted by fungi is utilized to synthesize the AgNPs. *Penicillium citrinum* obtained from soil sample applied for the extracellular formation of AgNPs (Honary et al. 2013). The *Fusarium oxysporum* along with optimization of physico-chemical conditions such pH, concentration, biomass volume, temperature etc. plays an important role in production of AgNPs (Birla et al. 2013). Ma et al. (2017) stated the usage of *Penicillium aculeatum* Su1 fungal strain to synthesize AgNPs. Neethu et al. (2018) synthesized the AgNPs using the extracellular biomass of *Penicillium polonium* through the green synthesis approach.

Algae plays a significant role in biologically derived AgNPs. Marine brown alga (*Padina pavonia*) is used as reducing and capping agent for the synthesis of AgNPs effectively (Abdel-Raouf et al. 2019). Deepak et al. (2018) synthesized AgNPs using *Sargassum wightii* and used for biological applications. A variety of microorganism-mediated NPs synthesis are given in Table 1.

Table 1 Summary of microorganisms and their reducing agents for the AgNP synthesis with size, shape etc

No.	Microorganisms	Reducing agent	Conc. of $AgNO_3$ (mm)	Temperature Time	Size (nm), shape and structure	Reference
1	*E. coli*	*E. coli* supernatant	1–10	20 °C–90 °C 24 h	10–90, Sph, Cry	Perni et al. (2014)
2	*E. coli*	*E. coli* cells	1 or 5	30 °C 24 h	5 Sph	Gurunathan et al. (2009)
3	*Staphylococcus aureus*	*Staphylococcus aureus* supernatant	1	5 min	160–80, Sph	Nanda and Saravanan (2009)
4	*Bacillus cereus* PGN1	Isolated and harvested *Bacillus cereus* PGN1 cells	1	37 °C 120 h	4–5, Sph, FCC	Ganesh Babu and Gunasekaran (2009)
5	*Brevibacterium casei*	*Brevi bacterium casei* harvested cells	1	37 °C 24 h	10–50, Sph, FCC	Kalishwaralal et al. (2010)
6	*Streptomyces sp. ERI*-3	Aqueous cell filtrate of *Streptomyces sp. ERI*-3	1	28 °C 48 h	10–100, Sph	Faghri Zonooz and Salouti (2011)
7	*Lactobacillus fermentum* LMG 8900	*Lactobacillus fermentum*.LMG 8900 cells		30 °C 24 h	6, Sph, FCC	Zhang et al. (2014)
8	*Fusarium Semitetum* fungus	Aqueous filtrate	1	27 °C 48 h	10–60, Sph, Cryst	Durán et al. (2005)
9	*Fusarium solani* fungus	Aqueous cell filtrate	1	R.T 10 min	5–35, Sph	Ingle et al. (2008)
10	*Penicillium Brevicompatum* WA 2315	*Penicillium Brevicompatum* WA 2315 fungal aqueous filtrate	1	25 °C 72 h	58.35 ± 17.8, Sph, FCC	Shaligram et al. (2009)

Note R.T-Room Temperature; Sph-Spherical; Cry-Crystalline, FCC-face centred cubic, tri-FCC-Triangular face centred cubic

Amongst the diverse bio-mediated methods, microoraganism-mediated AgNPs synthesis does not possess industrial feasibility as they require aseptic conditions and its overpriced maintenance. Hence, plant parts extract-based phytonanotechnology can be advantageous over other biological methods towards the AgNPs synthesis.

2.1.2 Plant-Mediated Synthesis of AgNPs

Plant associated AgNPs synthesis is more widely used over microorganism-based AgNPs due to less bio-threats, easy availability, simplicity, and does not require cell culture. Most of the plant parts contain biomolecules including but not limited to phenols, alkaloids, polysaccharides, enzymes, terpenoids, vitamins etc. which play important role in formation of AgNPs (Fig. 2) and are beneficial to the environment despite their complex structures. Hence, the reducing reagents are replaced with such plant extract. The synthesis of AgNPs, which is stabilized using flavonoid and terpenoid from leaf broth, whilst the Ag^{+} ions reduction supported by heterocyclic and polyol components (Shaikh et al. 2021).

Leaf broth and leaf extract are the two common constituents used for the synthesis of AgNPs. Also, the fruit pulp and fruit rind aqueous extracts obtained at particular temperature are frequently used in synthesis of NPs (Pechyen et al. 2021). However, usage of fresh plant extract is preferable due to its immediate transformation. Ramasami et al. (2018) have used the fruit rind of *Garcinia mangostana* for synthesis of noble metal NPs, including silver. The result in well-defined spherical shape is the outcome of plant extract-mediated synthesis. The list of plant materials is tabulated (Table 2) and few of them are discussed briefly in the present chapter.

Sathishkumar and his co-workers reported green synthesis of nano-crystalline AgNPs using *Cinnamon zeylanicum* bark extract which showed appreciable antibacterial activity. The size (average) of the NPs obtained between 31 and 40 nm, as

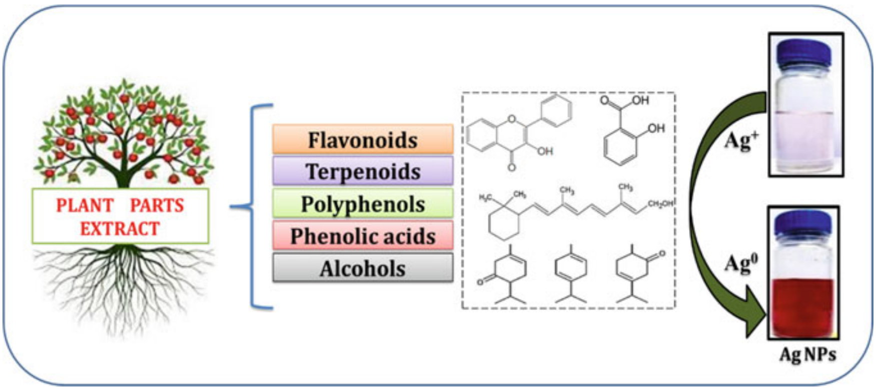

Fig. 2 Schematics showing synthesis of AgNPs using various biomolecules derived from plant part extract

Table 2 Summary of plant parts and their reducing agents used for the synthesis of AgNPs with their size and shape

S. No.	Name of plant part	Reducing agent	Conc. of $AgNO_3$ (mM)	Temperature Time	Size (nm), Shape, and Structure	References
1	*Pistacia atlantica*	Hydromethanolic extract of seed	1	R.T 35 min	10–50, Sph, FCC	Sadeghi et al. (2015)
2	*Ziziphora tenuior*	Hydromethanolic extract of leaf	0.1	R.T 35 min	8–40, Sph, FCC	Sadeghi and Gholamhoseinpoor (2015)
3	*Tephosia purpurea*	Aqueous Leaf extract	1	37 °C 5 min	20, Sph, FCC	Ajitha et al. (2014)
4	*Delphinium denudatum*	Aqueous root extract	1	R.T 2 h	< 85, Sph, FCC	Suresh et al. (2014)
5	*Boerhaavia diffusa*	Aqueous plant extract	0.1	100 °C 24 h	25, Sph., FCC	Vijay Kumar et al. (2014)
6	*Withania somnifera*	Aqueous leaf extract	100	R.T 12 h	5–30, Sph, FCC	Raut et al. (2014)
7	*Parthenium hysterophorous*	Saline washed aqueous root extract	10	R.T 24 h	Sph	Khari and Kumar (2018)
8	*Myrmecodia pendan*	Aqueous plant extract	2.5	R.T	10–20, Sph, FCC	Zuas et al. (2014)
9	*Tinospora cordifolia*	Aqueous stem extract	1	R.T 30 min	60, Sph, Cry	Anuj and Ishnava (2013)
10	*Cocos nucifera*	Aqueous extract of mesocrap	1	60 °C 1 h	24, Sph, FCC	Roopan et al. (2013)
11	*Mangifera indica*	Aqueous extract of peel	0.5–4	25–100 °C 15–90 min	7–27, Sph, FCC	Yang and Li (2013)
12	*Artocarpus heterophyllus*	Aqueous seed extract	2–10	121 °C 5 min	3–25, Sph	Jagtap and Bapat (2013)

(continued)

Table 2 (continued)

S. No.	Name of plant part	Reducing agent	Conc. of $AgNO_3$ (mM)	Temperature Time	Size (nm), Shape, and Structure	References
13	*Olive leaf*	Aqueous leaf extract	1	30–90 °C 2 min	20–25, Sph, FCC	Khalil et al. (2014)
14	*Lxoracoccinea*	Aqueous leaf extract	1	R.T 15 min	13–57, Sph, FCC	Karuppiah and Rajmohan (2013)
15	*Trianthema decendra*	Saponin extracted from *Trianthema decendra*	1	15 min	17.9–59.6, Sph	Geethalakshmi and Sarada (2018)
16	*Rumex hymenosepalus*	Ethanol/aqueous root extract	2.5–15	R.T 24–96 h	2–40, Cubic & hex, FCC	Rodríguez-León et al. (2013)
17	*Cucumis sativus*	Fruit extract	–	R.T	8–10, Sph	Roy et al. (2015)
18	*Chenopodium album*	Leaf extract	–	R.T	10–30, Sph	Dwivedi and Gopal (2010)

evident by TEM. The NPs showed that the pH played a crucial role in the determination of particle size and however it was observed that bark extract is more effective for synthesis of AgNPs than the bark powder (Sathishkumar et al. 2009).

Gade et al. (2010) reported colloidal AgNPs using *Opuntia ficus-indica* for antibacterial activity and explained the mechanism involved in nanomaterial synthesis and confirmed that the AgNPs in amalgamation with commercial antibiotics are better option. The AgNPs showed maximum antibacterial activity than Ampicillin followed by Streptomycin and Vancomycin. The green synthesis of AgNPs was studied by Farooqui et al. (2010) using leaf extract of the medicinal plant *Clerodendrum inerme.* The AgNPs are synthesized from the sun and hot-air oven dried as well as fresh leaves. Where, the fresh leaves were used to obtain the smallest AgNPs. The plant *Clerodendrum inerme* is beneficially used for biosynthesis of AgNPs.

The bio-mediated synthesis of AgNPs using extract of *Cucumis sativus* and its photo catalytic and antibacterial properties was reported by Roy et al. (2015). The biosynthesized AgNPs showed spherical shape with size range between 8 and 10 nm. The photocatalytic study shown, the NPs are efficient in degrading methylene blue under solar radiation (Roy et al. 2015). A quick bio-fabrication of AgNPs from an obnoxious weed *Chenopodium album* was reported by Dwivedi and Gopal (2010). The synthesized metal NPs are of 10–30 nm in size. The TEM image confirms the increased concentration of leaf extract produces the AgNPs with spherical shape (Dwivedi and Gopal 2010).

The fabrications of AgNPs using *Tribulus terrestris* fruit extract with unique morphology were stated by Gopinath et al. (2012). The phytochemical compounds present in plant extracts take active part in reaction and cause reduction of Ag^+. The high antimicrobial activity was shown by silver NPs against human pathogenic bacteria. The presence of polysaccharide and ascorbic acid in fruit extract of *Carambola* fruit play a vital role for the reduction of Ag^+ in to AgNPs (Mane-Gavade et al. 2015).

The manufacturing of complexed molecules between Ag and stem extract of *Callicarpa maingayi* was reported by Shameli et al. (2012). They proposed of the silver ion reduction into AgNPs is due to the –O = C-H group. The various organic groups viz. C=O, C=N, O=C–N–H, are accountable for the stabilization and conversion of ions into respective NPs (Kuppusamy et al. 2016).

The reduction of Ag^+ ions into AgNPs by carboxyl, amine, and phenolic compounds was reported by Vanaja et al. (2014). Singh et al. (2016) used red *ginseng* root extract for the synthesis of Ag and AuNPs. The presence of various potent phytocostituents such as flavanone, flavonoids, alkaloids, polyphenols, terpenoids, tannin, high antioxidant are responsible for reduction of metal ions (Aswathy Aromal and Philip 2012). The presence of Piperine in seeds of *Piper nigrum* plays role of reducing agent in the process of fabrication of AgNPs (Shobana et al. 2018). Therefore, biogenic synthesis using plant extracts is advocated as better replacements to the chemical methods of AgNP synthesis.

3 Application of AgNPs for Heavy Metal Ion Sensing

Depending on the nature or type of analyte, the colorimetric sensing of heavy metal ions by green synthesized AgNPs is discussed below. There is a lot of attention in the progress of colorimetric sensors for the detection of various metal ions has been paid since their simplicity, low cost of operation, and on-site monitoring (Anthony 2012). Due to the extraordinary optical properties in combination with biocompatibility and solubility, AgNPs received an attention for heavy metal ion sensing. Furthermore, Photobleaching resistance and photostability of AgNP-based colorimetric sensors over organic dyes are more reliable.

Biologically synthesized AgNPs were used as a sensor for identifying Hg^{2+} ions. To evaluate the detection capability of AgNPs, alkali (Li^{+}, K^{+} and Na^{+}), alkaline earth (Mg^{2+}, Sr^{2+}, Ca^{2+} and Ba^{2+}), and transition (Ni^{2+}, Hg^{2+}, Mn^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, and Co^{2+})-metal ions were studied by Pourreza et al. (2015). Karthiga and Anthony conveyed the biogenic synthesis of AgNPs using fresh and sun dried leaf extract of neem for detection of Pb^{2+} and Hg^{2+}. The detection of hazardous metal ions was studied by varying pH from 2 to 11. Often the sensors work at specific pH v but in this work sensor system showed performance at different pH range. Similarly, AgNPs obtained from neem bark extract showed selective detection of Zn^{2+} and Hg^{2+} ions. AgNPs obtained from green tea and leaf of fresh and sun dried mango have been reported for sensing of Pb^{2+} and Hg^{2+}ions selectively. Also, the selective sensing of Zn^{2+}, Pb^{2+}, and Hg^{2+}ions was showed by AgNPs derived from seed extract of pepper. The sensing by AgNPs for a different heavy metal ions was showed that SPR absorption intensity slightly changed by addition of metal ions excluding Hg^{2+}whilst Hg^{2+}addition changed the brown AgNPs solution to colourless. The LOD Hg^{2+} ions were determined by adding 10^{-6} mol L^{-1} Hg^{2+} ions with varying concentration (Durairaj and Anthony 2013).

In case of neem dried AgNPs, addition of Hg^{2+} vanished brown yellow colour, however Pb^{2+} ions cause the red shift in SPR peak from 420 to 447 nm accompanied by notable colour change. The change in colour was observed for Pb^{2+} and Hg^{2+}ions by naked eyes. In this case the study depending on concentrations showed, the addition of Hg^{2+} solution (120 mL 10^{-6} molL^{-1}) causes complete decolourization of AgNPs whereas yellow coloured precipitate was observed after addition of Zn^{2+} solution (240 mL of 10^{-6} molL^{-1}) (Durairaj and Anthony 2013).

Ravi et al. (2013) stated the synthesis of AgNPs for selective sensing of Hg^{2+} ions at different pH (3.2–8.5). The synthesized AgNPs selectively detected Hg^{2+} ions at 3.2 pH, further increasing pH causes SPR peak broadening with blue shift. The yellow colour decolourization was observed at lower and higher pH by addition of Hg^{2+} ions to the AgNPs. However, at pH more than 8.5 the colorimetric sensing property diminishes (Ravi et al. 2013). A same kind of study was carried out by Manivel by applying *ficus amplissima* leaf extract. Obtained AgNPs were used for colorimetric detection of Hg^{2+} ions with 1.30×10^{-7} mol L^{-1} LOD (Manivel and Ilanchelian 2017). Also, green synthesis of AgNPs using *Agaricus bispores* was used for electrochemical and optical sensing behaviour for Hg^{2+} ions at pH range

3–6 (Sebastian et al. 2018). The study also shows the use of AgNPs for detection of Hg^{2+} ions selectively by colorimetric sensing (Samari et al. 2018).

The flourometric sensing of Cu^{2+} with limit of 1.0×10^{-6} mol L^{-1} was carried out by AgNPs obtained from *Azadirachta indica* extract where they observed restoration florescence with colour change.. The fabricated AgNPs-based sensor revealed a very high co-relation coefficient (LOD 1.0×10^{-13} mol L^{-1}). The selectivity of green synthesized AgNPs was carried out using different ions with concentration 1.0×10^{-6} mol L^{-1}. AgNPs show effective sensing of Cu^{2+} ions as compared to other ions. The colour change to purple from yellow denotes that the AgNPs are effective for sensing of Cu^{2+} compared with other ions (Kirubaharan et al. 2012).

Annadhasam and co-workers reported green synthesized AGNPs and their mechanism of colorimetric sensing of Hg^{2+} ions. Hg^{2+} (LOD 5.3×10^{-8}) and Mn^{2+} (1.6×10^{-8} mol L^{-1}) ions were shown to be very sensitive to L-tyrosine stabilized AgNPs. After adding other metal ions to AgNPs, the SPR intensity shows slight variation although the colour remains same. However, the yellow AgNPs solution became colourless after addition of Hg^{2+} and changes to brown with Mn^{2+}. The absorption intensity changes after addition of alkali and alkaline metal ions in AgNPs solution as shown in Fig. 3a. Furthermore, hypsochromic shift in SPR peak was observed after addition of Hg^{2+} ions where the shifting amount depends on concentration of Hg^{2+} (Fig. 3b). Colorimetric response of AgNPs for different metal ions shows its capability in the sensing of Mn^{2+} and Hg^{2+}ions (Fig. 3c) (Annadhasan et al. 2014).

Aadil et al. reported the sensing of metal ions including Hg^{2+}, Cd^{2+}, Ni^{2+}, Fe^{2+}, As^{2+} etc. using lignin stabilized AgNPs. The change in SPR properties of AgNPs was recorded by UV–Visible spectrum to understand the interaction with metal ions. The interaction of AgNPs and Hg^{2+} causes a SPR peak strength reduction at low concentration. However, the peak reduction with longer wavelength shift resulted due to Ni^{2+} and Cd^{2+} ions. The blue shift was seen for Fe^{2+} and Pb^{2+} ions, however shift towards red was observed for As^{2+} at higher concentration ($0.1–1.0 \times 10^{-2}$ mol L^{-1}); blue shift at lower concentration ($1.0 \times 10^{-6}–1.0 \times 10^{-9}$ mol L^{-1}). The highest sensing property with concentration 1.0×10^{-9} mol L^{-1} is observed for Fe^{2+} and As^{2+}. The sensing of 1.0×10^{-9} mol L^{-1} Fe^{2+} and As^{2+} was found to be higher detection limit using AgNPs (Aadil et al. 2019). The AgNPs synthesized from *Moringa oleifera* flower extract are used to fabricate Cu^{2+} ions optical sensor. AgNPs solution shows the SPR peak (457 nm) which gradually decreases with the Cu^{2+} ions addition (Bindhu and Umadevi 2014). The sensing application for metal ions using bio fabricated AgNPs is summarized in Table 3.

3.1 Plausible Mechanism of Sensing of Heavy Metal Ion

For sensing application, the metal ion detection can be carried out by observing the SPR band (shape, position, and intensity). The change in SPR band properties and colour of AgNP solution is due to the interaction of heavy metal ion with AgNPs.

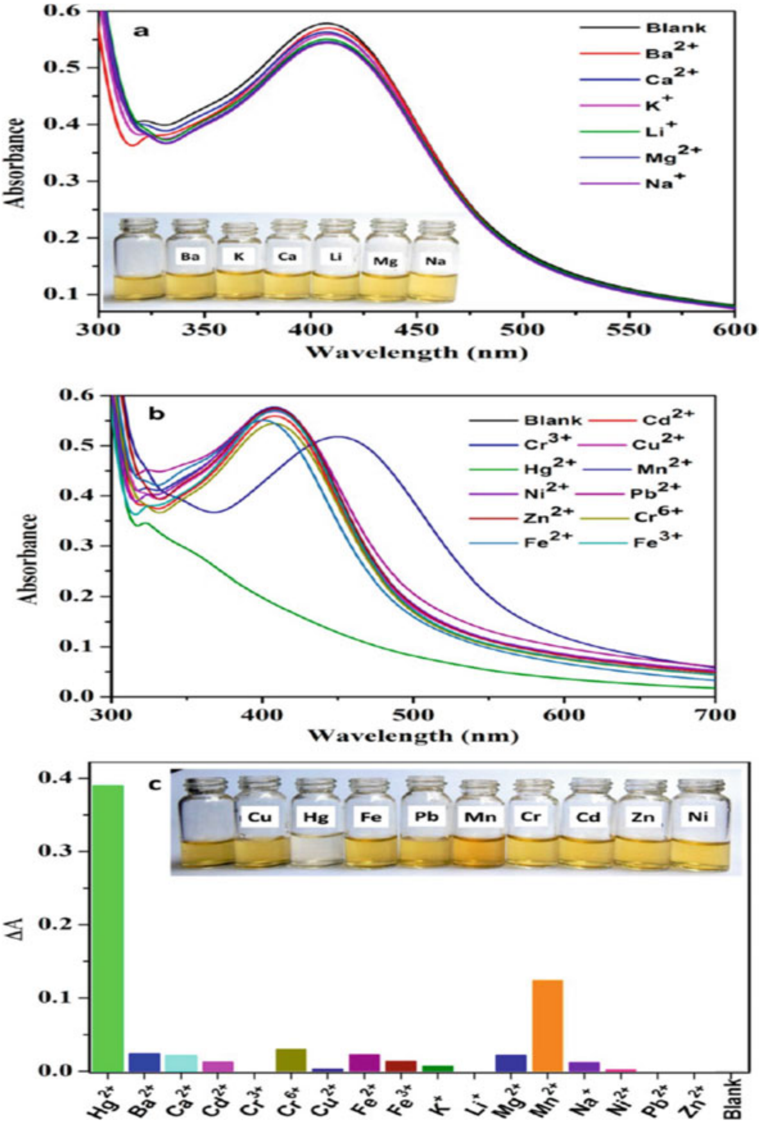

Fig. 3 UV Visible spectra for alkali and alkaline (**a**) and transition metal ions (**b**) with AgNPs stabilized by L-tyrosine; the graph showing metal ions sensing response of AgNPs (Annadhasan et al. 2014). (Permission from ACS)

Table 3 Summary of colorimetric AgNPs-based sensing of heavy metal ions

Plant/fruit	Extract of plant part used	Detection of metal ion	Limit of detection (LOD) mol L^{-1}	Reference
Mango	Leaf	Hg^{2+}	0.5 ppm	Samari et al. (2018)
Pepper	Seed	Hg^{2+} Pb^{2+}	1×10^{-6} 1×10^{-6}	Durairaj and Anthony (2013)
Green tea	Leaf	Hg^{2+} Zn^{2+}	1×10^{-6} 1×10^{-6}	
Neem	Bark	Hg^{2+} Zn^{2+}	1×10^{-6} 1×10^{-6}	
Fresh neem	Leaf	Hg^{2+}	1×10^{-6}	
Sun-dried neem	Leaf	Hg^{2+} Pb^{2+}	1×10^{-6} 1×10^{-6}	
Mango	Leaf	Hg^{2+} Pb^{2+}	1×10^{-6} 1×10^{-6}	
Citrus limon and *Citrus limetta*	Leaf	Hg^{2+}	–	Ravi et al. (2013)
Hibiscus sabdariffa	Leaf/stem	Pb^{2+}, Hg^{2+}, Cd^{2+}	–	Vinod Kumar et al. (2014)
Soap	Root	Hg^{2+}	2.2×10^{-6}	Pourreza et al. (2015)
Azadirachta indica	Leaf extract	Cu^{2+}	$10^{-13\ 1}$	Kirubaharan et al. (2012)
Lycopersicon esculentum	Leaf extract	Cr^{3+}	8.04×10^{-7}	Aravind et al. (2018)
Allium cepa (Onion)	Extract	Hg^{2+}	–	Alzahrani (2020)
Ficus retusa	Extract	Fe^{3+}	4.5×10^{-6}	Zayed et al. (2019)
Ficus benjamina	Leaf extract	Zn^{2+}	1.0×10^{-6}	Puente et al. (2019)
Acacia lignin		Hg^{2+} As^{2+}	1.0×10^{-9} 1×10^{-7}	Aadil et al. (2019)
L-tyrosine	-	Hg^{2+}; Mn^{2+}	1.6×10^{-8}	Annadhasan et al. (2014)
Solanum lycopersicums	Extract	Fe^{3+}	1.24×10^{-5}	Bindhu and Umadevi (2014)
Ficus amplissima	Leaf extract	Hg^{2+}	1.30×10^{-7}	Manivel and Ilanchelian (2017)

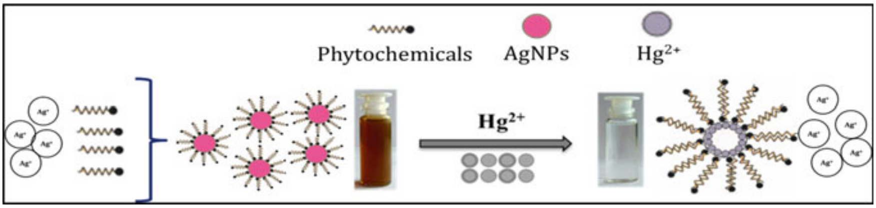

Fig. 4 Showing the formation of AgNPs and its interaction with Hg^{2+} ions for sensing applications

In several cases, the SPR peak shifts to higher wavelength or lower energy along the change in colour of NP solution (Mehta et al. 2016).

AgNPs-based sensing is typically stabilized by polymers, anions or biomolecules that become adsorbent on the surface. However, even minor changes in the medium of AgNPs dispersion, like ionic strength and pH, cause destabilization and aggregation of the AgNPs. As AgNPs aggregate, LSPR red shift is observed with concurrent peak broadening. In these cases, it is supposed that on the surface of AgNPs, the metal ion interacts with the capping agent, resulting in aggregation of colloidal solution (Prosposito et al. 2020). Vinodkumar et al. (2014) noted a colour change from yellowish brown to colourless after addition of Hg^{2+} ions which indicates the strong interaction between AgNPs and Hg^{2+}. The decrease in the SPR intensity through a blue shift is a result of influence of Hg^{2+} ions on AgNPs with or without amalgamation or decrease in size of AgNPs. It is expected that redox reaction occurs between Ag^0 and Hg^{2+} as the redox potential of Ag(I)/Ag(0) (+0.8 V) couple is lower than Hg(II)/Hg(0) (+0.85 V) couple. The Hg atoms and Ag^+ ions are produced due to oxidation of Ag^0 by Hg^{2+}. Thus, Hg^{2+} oxidizes Ag from AgNPs and becomes colourless (Vinod Kumar et al. 2014). The plausible mechanistic approach of Hg^{2+} ion sensing using AgNPs is depicted in Fig. 4.

4 Conclusion

A bio-derived approach towards the synthesis of metal NPs (AgNPs) is the promising and environmental friendly method as it did not include any harmful chemicals (organic solvents as medium and surfactants as stabilizing agents) and additional reducing agents. Thus, biogenically synthesized NPs are biocompatible, which can be used in various fields. The detailed development mechanism of AgNPs synthesis through the phytoextract is discussed in this chapter. The plant-based synthesized method is facile, rapid, energy efficient, and with predictable mechanism. Green synthesized AgNPs without further modification may offer a new sensing approach for heavy metal ions. Therefore, opportunities remain to explore the novel green synthetic strategies on the basis of biogenic method. The determination of exact concentration of reagent is tedious job. To gain control over morphology of AgNPs, it is important to explore the parameters including pH, metal ion, temperature, and concentration of plant extract.

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Plant Material Assisted Magnetic Nanoparticles (MNPs) for the Separation of Inorganic Pollutants

Gedda Gangaraju, Gollavelli Ganesh, Randhi Uma Devi, and Kolli Balakrishna

Abstract Mainly Inorganic pollutants like heavy metals are generated from many industrial processes, agricultural activities and domestic sources. These pollutants enter into water bodies and lead to damage to the entire ecosystem. Consequently, it affects the living organisms, including human health. Therefore, it is essential to develop an effective method for removing heavy metals from water bodies. Recent development in nanotechnology has also directed the progress of novel nanoparticles. Specifically, developing environmentally friendly green methodologies for the synthesis of nanoparticles has been increased to reduce the negative impacts of synthetic strategies, their supplementary chemicals/solvents and derivative materials. Among the various kinds of materials, magnetic nanoparticles (MNPs) based nanosystems gained significant attention because of their rapid adsorption, highly selective and sensitive and effective removal of heavy metals. The modification of nanomaterials on their surface plays a vital role in the selective adsorption of different metal ions. It is due to electrostatic interaction like complex formation, ligand combination and chemical binding, in addition to regular weak forces between metal ion and adsorbent. Here in this book chapter, we discussed the impact of plant materials, viz. leaves, roots, fruit, etc. for the synthesis of MNPs to remove/separate heavy metals from contaminated water.

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1 Introduction

The environment is formed with different variables, such as air, water and land. Science and technical advancements in industrial civilizations have contributed to severe air, soil and water pollution, all of which are considered essential components of human life (Chaudhry & Malik 2017; Khan et al. 2021; Zwolak et al. 2019). Urbanization and industrialization are regarded as serious obstacles to water resource management in both affluent and developing countries (Cohen 2006). Apart from water scarcity, water pollution is a national and worldwide issue. Water pollution occurs when pollutants are released into bodies of water, making them unfit for human consumption and disrupting aquatic ecosystems (Ng et al. 2021). Various substances, such as organic waste, poisonous chemicals, sediments, heat, petroleum, radioactive compounds and even infectious bacteria, damage water bodies (Tang et al. 2021).

Many study reports have proven the presence of heavy metal contamination in several countries, indicating that it is a global issue. Significant quantities of harmful heavy metals such as Cd, As, Cr, Cu, Pb and others have been found in water in several nations (Zaynab et al. 2022). Eight heavy metals, including Lead (Pb), Cadmium (Cd), Copper (Cu), Mercury (Hg), Chromium (Cr), Arsenic (As), Zinc (Zn) and Nickel (Ni), are identified as the most ubiquitous heavy metals in the environment by the United States Environmental Protection Agency (USEPA) (Kaur and Roy 2021; Varagiya et al. 2022). Heavy metals are also classified as class B metals, which are non-essential (very hazardous) trace elements (Gjorgieva Ackova 2018). However, a lack of understanding of effective wastewater treatment and a failure to impose strong regulatory standards have contributed to environmental degradation. Human exposure to heavy metals increases the risk of environmental harm as well as serious health consequences in people, such as cardiovascular disease, developmental anomalies, neurological problems and even cancer (Engwa et al. 2019; Rahman et al. 2022). In general, heavy metal exposure to humans is mostly detected through three distinct routes: oral intake, inhalation and cutaneous exposure (Briffa et al. 2020).

The pollutants cause health-related problems by entering into living species' biological systems either directly or by converting into another form. For example, mercury in water is converted to the water-soluble compound methyl mercury through bacterial activity. Fish accumulate this methyl mercury. People in Japan contracted the Minamata disease in 1953 as a result of eating methyl mercury-contaminated fish captured in Japan's Minamata Bay (Harada 1995). Numbness in body parts and visual and hearing issues and odd mental behaviour have all been reported (Eto et al. 2010). This sickness claimed the lives of 50 people and left more than 700 people permanently crippled. In another case, cadmium metal contamination contaminated rice through the bioaccumulation process, causing the Itai-Itai sickness (Inaba et al. 2005). The bones, pancreas, liver, kidneys, lungs and thyroid were all impacted (Satarug 2018). In another case, arsenic contamination of groundwater in Bangladesh and West Bengal resulted in a variety of deformities (Adeloju et al. 2021; Chowdhury et al. 2000; De et al. 2022). The blue baby syndrome is caused by excess nitrate in drinking water (Gamage et al. 2021; Knobeloch et al. 2000; Panda et al. 2022). High levels of cadmium produce degenerative borne disease, whereas chromium and arsenic are carcinogenic (Ma et al. 2021; Munir et al. 2022). Similarly, a high concentration of lead and mercury in the human body harms the CNS (Central Nervous System) (Bittencourt et al. 2022).

Heavy metals can be removed from the environment using a variety of treatment methods, including physical, chemical and biological (Akhtar et al. 2020; Kumar and Khan 2021). However, they all confront difficulties in terms of cost and in-situ treatment. As a result, integrated processes are gaining popularity since they are reported to efficiently fulfil the goal in a variety of environmental matrices and will overcome a substantial disadvantage of large-scale implementation.

In this scenario, nanomaterials (nanotechnology) show a promising way to solve the issue. (Bhaisare et al. 2016; Gedda et al. 2016; Lu et al. 2016). In a glimpse, nanoparticles (NPs) are materials having in the range of 1–100 nm in size. As the materials become nano-sized, various properties come into picture in comparison to their bulk state. For example, a shiny yellow gold metal can be converted to another colour, i.e. pink. It is possible by converting the bulk gold to a particular nano-sized form (Hammami and Alabdallah 2021). It implies that material properties (physical to others) can be modified to the desired level based on the conversion to particle size. This is the critical step for the development of nanomaterials which created a new technology called nanotechnology (Modi et al. 2022). In particular, for the environmental applications, the NPs should have some characteristics viz. extremely small size, desired shape, high specific surface area and high surface area to volume ratio, high catalytic ability and charge which is opposite to targeted pollutants, strong mechanical force, non-toxic and magnetic in nature (Thakur et al. 2022).

Over time, several nanomaterials based on metals to various types of metal-oxides came in to picture for various applications. Interestingly, the nanomaterials can be replaceable of the currently available electronics to other related market goods by decreasing the price and enhancing the performance with respect to lifetime (Roy et al. 2021a, b).

There is a separate category of NPs like iron oxide (Fe_3O_4), Cobalt ferrite ($FeCoO_4$), chromium dioxide (CrO_2) and so on, having magnetic properties called magnetic nanoparticles (MNPs) (Garanina et al. 2022; Pandit et al. 2022; Issa et al. 2013; Nehra and Singh 2015). These MNPs have several applications in catalysis, biomedicine, bio-electrochemical sensing, absorption and various fields of medicine like diagnosis and even in the development of batteries (Ali et al. 2021; Roy et al. 2022). Out of available MNPs, Fe_3O_4 NPs have been studied extensively with and without further surface modification (Nguyen et al. 2021). Studies revealed that the surface-modified Fe_3O_4 has enhancement in property for a particular application.

Also, the MNPs superparamagnetic property makes the utilization of these materials better for the removal of pollutants from water efficiently (Aragaw et al. 2021).

Broadly, these NPs are synthesized by two approaches viz. top-down and bottom-up (Patil et al. 2022). There are various methods like ball milling and chemical vapour deposition by which one can achieve the desired NPs (Das and Pradhan 2022). In the top-down and bottom-up approach, physical and chemical means of synthesis mode were involved (Fig. 1). In most of these methods, the utilization of synthetic chemicals is common to synthesize NPs. But green chemistry continuously insists the research community regarding usage of natural resources to synthesize materials for the sustainable development (Abdelhafeez et al. 2022).

Nature has given an alternative way to approach the bottom-up method without using harmful synthetic chemicals. In this sense, the biological mode can also be adopted in a bottom-up approach by using naturally available matter like microbes and templates like DNA and plants (Roy and Bharadvaja 2019). In light, out of those, parts of the plants like leaf, root, fruit, etc. have shown a promising corridor for the chemical synthesis of NPs and especially for synthesizing MNPs (Ahmed et al. 2021; Mittal and Roy 2021; Raina et al. 2020; El Shafey 2020). Because plant-related mass has various non-toxic chemicals within it, which conveniently helps for synthesize of MNPs (Ali et al. 2021; Nagore et al. 2021). This one can reduce the consumption of toxic chemicals usage for the synthesis of NPs, especially for MNPs. This approach will fulfil the idea of utilization of environmentally friendly chemicals for the fabrication of NPs, which intern is like non-toxic and less energy-consuming material (Roy et al. 2021a, b). This methodology will be helpful if it comes into

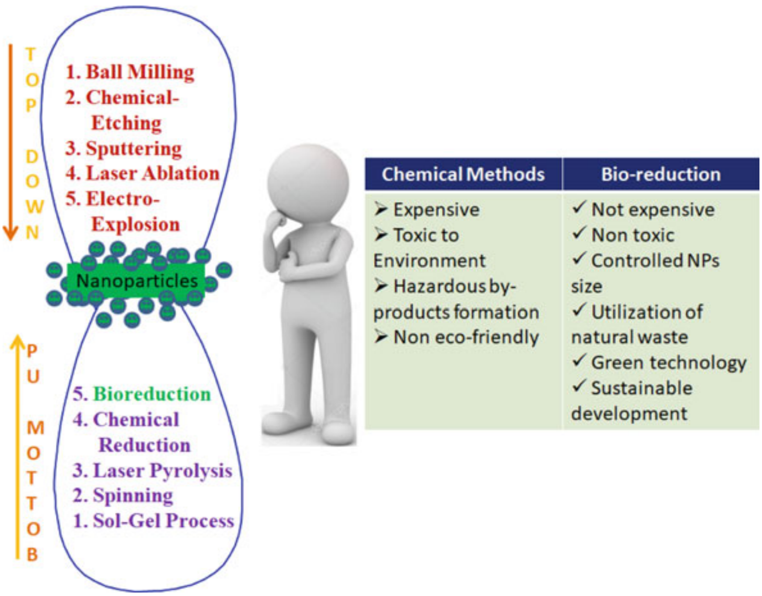

Fig. 1 Synthesis methods of nanomaterials

reality in respect to water purification and the recovery of precious metals from industrial waste. It gives a possibility and hopes to remove different pollutants from wastewater by using plant-based MNPs (PMNPs) economically in comparison to other methods. Here the leading role in removing the pollutants from wastewater is by the biochemicals present in plant materials. As shown in Fig. 2, these biochemicals have different active moieties, like polyphenols, amino acids, aldehyde, proteins, carbonyl, alkaloids, terpenoids and even carboxyl groups in the plant play the lead role in the synthesis of PMNPs (Ali et al. 2017). The biochemical molecules present in a plant species, either in leaf or other parts, help in reducing the metal ions to NPs. The main advantage of using the PMNPs is their easy removable nature after the adsorption of pollutants by using an external magnet easily. Hence it is a convenient as well as a simple method for removing metal ions from wastewater. The current research also focuses on this area in an enthusiastic way to solve the current water body contamination problem.

In this book chapter, we have discussed recently developed PMNPs synthesis by using plant sources and their characterization along with pollutants (Hg(II), Cr(VI), Cd(II) and As(V)) removal efficiency.

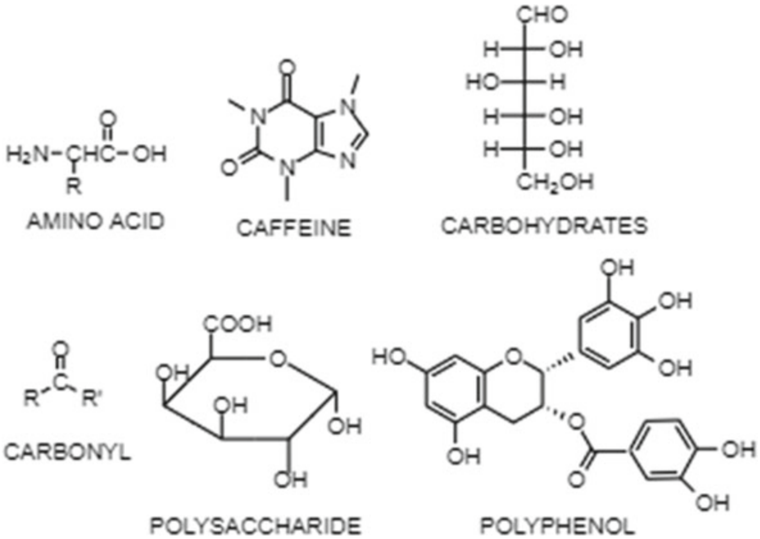

Fig. 2 The structures of the chemicals presented in the plant extract used for the synthesis of phytogenic magnetic nanoparticles (PMNPs)

2 Separation of Heavy Metals Using Plat Mediate Synthesized Nanomaterials

2.1 Removal of Hg(II)

Hg is a heavy metal pollutant commonly known as a quicksilver and exists as Hg(II) and Hg(I) oxidation states (Pratush et al. 2018). Among these oxidation states, Hg(II) is very toxic in nature even in 1–2 ppb (parts per billion) levels of its presence in drinking water and in whole blood; the limit was set by world health organization (WHO) and US EPA (Kinuthia et al. 2020). It is very important to avoid its contamination in the living environment for better health concerns and, nanotechnology could offer a better aid for its eradication effectively. Among the NPs, MNPs offer a greater advantage in adsorption, magnetic separation and recycling efficiency (Cano et al. 2012).

Venkateswarlu and Yoon (2015b) synthesized black-coloured Fe_3O_4 MNPs by using eco-friendly watermelon rind by maintaining 80 °C for two hours. Further, after continuous washing and drying, these MNPs were capped by using 3,4-dihydroxyphenethylcarbamodithioate (DHPCT). This has been done by using the sonication method for 10 h at room temperature. By this process, a better MNP has been achieved at last, DHPCT@Fe_3O_4 XRD analysis revealed no change in the crystalline behaviour of Fe_3O_4 MNPs due to the attachment of DHPCT. Their XPS analysis also revealed the phase purity. The results obtained by TEM analysis regarding the size (13 nm) are also supported by the Scherrer equation-based calculations. FT-IR data reveals that the watermelon extract containing polyphenols acted as reducing and capping agents during these MNPs syntheses. Also, after the attachment of DHPCT to Fe_3O_4, there is a change in the FT-IT pattern and in especially observing a peak at 1073 $cm\text{-}^1$ for C=S confirms the reaction between DHPCT to Fe_3O_4. These MNPs are used get rid of Hg(II) and it was witnessed that the Hg(II) adsorption increased upon increasing the pH from 2 to 7, after this pH decrement was experienced. This is due to the formation of mercury hydroxyl colloidal precipitates. The capped adsorbent, showed excellent Hg(II) adsorption at its concentration of 60 mg/L under pH 7. It was observed that the Fe_3O_4 alone could only absorb Hg(II) pollutants up to 35%. But the capped $Fe_3O_{4,}$ i.e. DHPCT@Fe_3O_4, has shown excellent adsorption over Hg(II) up to a value of 52.1 mg/g with an efficiency of 98% at room temperature and neutral pH. This adsorption was undergone through chemisorption only and which was supported by the data fitting in the pseudo-second-order reaction. Also, the magnetic property of the synthesized MNP was examined by the magnetic hysteresis loops at standard temperature. It was observed that it took only 15 s to remove the MNP from the liquid by using an external magnet. Their recyclable study also most encourages the use of the MNPs to remove Hg(II) pollutants from contaminated water compared to other pollutants.

Marimón-Bolívar et al. (2018) from Colombia has investigated the adsorption tendency of Hg(II) by modifying the iron oxide surface. For the modification, they have used a naturally available Yam peel biomass. These authors initially synthesized the Fe_3O_4 MNPs in a traditional way. But later, they had treated the formed MNPs with Yam peel (YM) extract for 12 h by maintaining 25 °C. The entire process leads to the generation of an adsorbent, MNP-YP. In this study, a 100 ppm mercury chloride solution was prepared under the pH range of 3–9. It was observed that this new adsorbent has a saturation magnetization of 27 emu/g. This low value was due to the reduction of ferrite content compared to other unnatural materials attached to Fe_3O_4 MNPs. Here the effect of pH on adsorption was studied by using MINEQL+ modelling software. It was concluded that the pH condition makes a lot of difference for the binding of Hg(II) to the adsorbent, especially at neutral and basic conditions. The desorption study was performed by using 100 ml of different solutions as eluents, namely hydrochloric acid and sodium chloride. This study helps to understand the recovery of Hg(II) and the reusability of the adsorbent.

Also, Inglezakis et al. (2020), have studied the removal of Hg(II) from an actual water sample by modifying the iron oxide nanoparticles by using Glutathione with a significant enhancement in the results. These Kazakhstan authors synthesized nanocomposites to remove Hg(II) by using silver amalgamation nature with mercury. For the first time, in addition to bare Fe_3O_4, the authors have used Fe_3O_4-AgO nanocomposites to remove the aforesaid pollutant. Here, the bare Fe_3O_4 was synthesized in a traditional chemical method using ferric chloride and sodium acetate in ethylene glycol at a temperature of 200 °C for 8 h. Further, the final Fe_3O_4-AgO nanocomposite has been synthesized by taking naturally available green tea leaves to remove the Hg(II) from the aqueous solution. The SEM analysis reveals that the quasi-spherical Fe_3O_4 particle's surface became rougher due to the anchored Ag nanoparticles. This is also supported by their TEM image as well as XRD and EDX analysis. The EDX analysis specifically revealed that the silver-loaded iron oxide nanocomposite has shown that the Hg(II) adsorption was five times higher compared to bare iron oxide. It is also observed that the chlorine adsorption also takes a higher weight percentage onto the Fe_3O_4-Ag nanocomposite. The Hg(II) adsorption results were more encouraged to scale up the present adsorbent. It was observed that the Fe_3O_4-Ag nanocomposite successfully removed 80% of Hg(II) pollutant from water quickly within an hour. It is an excellent enhancement in Hg(II) adsorption compared to bare Fe_3O_4 alone, which only adsorbed less than 10%. The same has been observed by changing the concentration of Hg(II) solution.

2.2 Removal of Hexavalent Chromium Cr(VI)

Cr available as potassium dichromate, sodium-dichromate, chromium dioxide and chromic acid. It has a versatile applications in various industries as chemical reagents, leather tanning agents, pigments, etc. (Ina 2013). The major sources of its availability in the environment are Cr deposits erosion and poorly treated industrial waste. Cr(VI) is poisonous and mutagenic, whereas Cr(III) is an essential mineral to the human system and these are the stable oxidation states of Cr. The maximum allowed limits of Cr(VI) in drinking water by WHO and US EPA are 50 and 100 ppb (parts per billion) (Gollavelli et al. 2013). Hence it is very important to avoid its environmental contamination. Plethora of NPs has been demonstrated to its abolition including MNPs (Ganesh et al. 2013).

Song et al. (2015) developed a new kind of PMNPs using amine functional groups containing raw corn stalks and used for the effective adsorption of Cr(VI). During the adsorbent synthesis, Fe_3O_4 loaded corn stalk by co-precipitation method in traditional way. Later, by using epichlorohydrin and followed by the addition of Ethylenediamine, the present adsorbent was synthesized. This adsorbent's magnetic property was evaluated using a Vibrating sample magnetometer at room temperature and the results revealed that these MNPs had 6.2 emu/g as saturation magnetization value. This result indicated that the adsorbent could be easily removed from the aqueous solution by using an external magnet in a few seconds. The XRD peak at 35.6^{o} assigned to the (3 1 1) crystal plane indicated that the Fe_3O_4 was loaded. The SEM image revealed the favourable surface formation due to the chemical modification of the surface of Fe_3O_4, which favours the condition for pollutant adsorption. Also, the average particle diameter was observed as 9.8 nm. Hence, this adsorbent has been tested for the Cr(VI) dismissal from water. Studies revealed that the adsorbent dosage also influences the adsorption of the adsorbate. It was apparent that the dosage of 1.0 g/L is optimum for the condition and after that the adsorbent becomes saturated. The pH was also shown a significant effect of the adsorption of Cr(VI). In the present case, the highest uptake of the pollutant, 97.4 mg/g, occurred at pH 3 and then after the adsorption decreased. It was also revealed that the presence of higher charged anions would show interference behaviour during the Cr(VI) adsorption. Interestingly, after regeneration, the adsorbent showed exceptional adsorption of 85.9 mg/g even next to subsequent two cycles. This adsorbent has shown a high surface assimilation capability of 231.1 mg/g at 45 °C. All these results indicated that chemisorption and physisorption also showed their effect on the adsorption, in addition to normal electrostatic attraction, between PMNPs and metal ions.

Srivastava et al. (2017) used Lagerstroemia speciosa bark (LB) for surface modification of MNPs to remove Cr(VI) from contaminated water. The constituents in bark, such as cellulose, hemicelluloses, lignin and structural proteins, contain carboxyl and hydroxyl functional groups acting as a metal scavenger. Hence, these surface functional groups play a crucial role in the interaction with adsorbents. Due to the maintenance of the 2:1 ratio of Fe^{+3} and Fe^{+2}, the formed MNP, i.e. (Fe_3O_4) Magnetite, was in homogeneous composition and in the particles was in narrow size distribution. During the synthesis of these MNP, 1 g of LB was added to achieve the final adsorbent in brownish-black colour. Further, SEM and EDX were used to study surface morphology study and elemental composition of the formed MNP. In especially, the adsorption of Cr(VI) onto the Lagerstroemia speciosa embedded MNP (MNPLB) was confirmed by revealing the formation of a thick layer in their SEM image compared to non-adsorbed one. Also, EDX showed a clear indication regarding Cr(VI) and C, O, S, Fe elements. TEM analysis also revealed that the Cr(VI) has adsorbed onto the adsorbent by increasing the average size of the particle from 8.76 nm to 18.54 nm after the adsorption onto MNP. It was also observed there is no change in the spherical shape due to Cr(VI) adsorption. It is an exciting point concerning the Cr(VI) adsorption as the particles were spherical. Their BET surface analysis also confirmed the larger surface area. The output of this analysis of the MNPLB was as follows: Surface area (52.791 m^2/g), Pore size (5.269 nm) and Total pore volume (0.07 cm^3/g). It was observed that the maximum adsorption found for MNPLB was 434.78 mg/g. This higher value compared to other similar magnetic adsorbents boosts the present new MNP's importance in removing the Cr(VI) from water. The authors have studied the behaviour of recycling the adsorbent and recovery of adsorbate, which is essential, mainly in scaling up the process. It was observed that the MNPLB was shown 93.72% of desorption by using 0.1 mol/L, which is the highest recovery compared to other desorption agents, namely 0.1 mol/L of Na_2CO_3 and $NaHCO_3$ each. Also, the results showed that the adsorbent, MNPLB, showed excellent reusability up to five cycles with minor loss in adsorption capacity.

Currently, several research groups have been focussing on preparing phytogenic-based MNPs (PMNPs). For example, Lingamdinne et al. (2017) prepared PMNPs by the biogenic reduction of $Fe^{2+}$and Fe^{3+} using seed extract of Cnidiummonnieri (L.) Cuss (CLC). The MNPs were synthesized in a round bottom flask containing a 2:1 ratio of ferrous and ferric salts solutions along with the seed extract by maintaining 120 °C for 2 h. Before utilizing the synthesized MNPs for the adsorption study, they were washed multiple times with distilled water and their magnetic behaviour was observed by using a magnet. The magnetic property was also studied by using a SQUID magnetometer in detail. 1H-NMR study reveals that the seed extract contains aromatic olefins, hydroxy and methoxy moieties, which were helpful for the formation of MNPs through the bioreduction process. The same has been observed after their FT-IR analysis. The XRD and AFM analysis revealed that the formed MNPs were around 45.5 nm. The same has matched with the results of TEM. The BET analysis revealed that the MNPs had 122.54 m^2/g of surface analysis which is a significant improvement compared to bulk Fe_3O_4, whose value is 56 m^2/g. Batch adsorption study has been done on specific water pollutants viz. Pb (II) and Cr(III). The adsorption of these pollutants was observed by changing the concentration of the synthesized MNPs. It was clearly observed that upon increasing the dosage of MNPs beginning at0.1 to 0.2 g/L, the Pb (II) and Cr(III) adsorption also increased but became saturated at 0.5 g/L level. Adsorption behaviour of Pb(II) and Cr(III) were changed upon changing the acidic environment. These ions show an increment in adsorption from pH 2–4 range only and become saturated thereon. Under MNPs dosage levels of 0.2 g/L and 0.5 g/L, Cr(III) adsorbed better compared to Pb (II) at pH 4. The study also revealed that the pollutants get adsorbed rapidly within 30 min due to more active cites and reached equilibrium at 100 min for both metals. Interestingly, the MNPs were shown the exact behaviour of adsorption for Pb (II) and Cr(III) up to five regeneration cycles without losing their adsorption capability. Sravan et al. prepared MNPs for Cr(VI) removal with biomass containing with isolates of two fungal species such as Aspergillus niger and Aspergillus and the adsorbent was named as MNP-FB. The adsorption efficacy of this MNP-FB were studied against removal of Cr(VI). The effect of temperature, Ph, adsorbent dosage, time and concentration of Cr(VI) were well investigated with the bio- sorbent and shown to be a highest removal efficiency of 250 emu/g. The Freundlich curves, kinetic and thermodynamic studies reveal that it follows pseudo-first-order reaction and exothermic in nature.

2.3 Eradication of Arsenic (V and III)

As is one of the most potential contaminants and is listed top 10 in the WHO proposed contaminants of drinking water (Fawell and Nieuwenhuijsen 2003). It is available as +III in arsinite (H_3AsO_3) and +V in arsenate (H_3AsO_4). Due to its hazardous nature the permitted levels of As(III) and As(V) are 10 ppb to 0 ppb by both WHO and US EPA (Ning 2002). Here the As(V) is identified more toxic than As(III) and to be a typical carcinogen, affects lungs, kidneys and hearts. The representative sources of its contaminations are poorly treated industrial wastewater, tobacco and As poisoned air. Another distinctive source is groundwater contaminated with As observed in many countries such as Bangladesh in India, Chile, China and USA (Huang et al. 2015). Tian et al. (2011) prepared a variety of PMNPs by loading different compositions of Fe_3O_4 into wheat straw and using it to remove arsenic from water. Here the authors prepared different magnetic wheat straws (MWS) such as, i.e. MWS1, MWS2 and MWS3 by increasing the amount of iron ion and using wheat straw as a template during preparation. They investigated that the adsorption ability order found to be MWS5 > MWS2 > MWS1. It was very clear that the loading of wheat straw can improve the As efficacy than the bare Fe_3O_4 NPs. Hence, here the WS is not only serving as the capping agent to avoid the aggregation of Fe_2O_3 it can also enhance the number of surface functional groups to hold the arsenic.

Venkateswarlu et al. (2016) synthesized different types of PMNPs, i.e. Fe_3O_4@2D-CF. This PMNP was achieved by surface modification of MNPs with onion sheathing-derived 2D-carbon flakes. TEM revealed that the Fe_3O_4 was well settled over the surface of the 2D-CF. This dispersion enhances the surface area and pore volume, which are required for better adsorption. These PMNPs were used to remove As(III) from water and the observed adsorption was found to be 57.47 mg/g at neutral pH. The Fe_3O_4@2D-CF has shown a 98.9% As(III) removing ability within an hour. Especially, these PMNPs were exhibited excellent recoverability in 28 s due to their large saturation magnetization. On the other hand, Martínez-Cabanas et al. (2016) applied Eucalyptus plant extract as a reducing agent to prepare PMNPs for large-scale pollutant adsorption. Further, the surface of the PMNPs was modified with chitosan to develop a new hybrid nanomaterial and was used as an adsorbent in removing As(V) from wastewater. Parajuli et al. (2020) synthesized PMNPs using Azadirachata indica leaves extract to remove As(V) from water. XRD results concluded that these MNPs had an average particle size of 8.4 nm. The SEM images revealed that these PMNPs were spherical and uniform in shape. For checking the efficiency of this adsorbent, authors have considered different parameters: pH effect, amount of adsorbent used, time of contact and concentration of adsorbate as 2–10, 0.025–3 g/L, 10–240 min and 10–100 mg/L, respectively.

Upon increasing the pH, there was a decrease in the adsorption tendency of the adsorbent. This is due to at very low pH, the adsorbent surface possesses positive charge which draws As(V), the negatively charged pollutant on top of PMNPs. This study gives the optimum working condition of the new adsorbent as pH 2, which plays a critical role during the bulk scale of the adsorbent. It has taken almost 90 min to get saturation adsorption onto the adsorbent. The experimentally determined adsorption is close to the value got by the pseudo-second-order model. It was apparent that the pollutant dismissal capability increases up to 99% upon increasing the PMNs dose. Specifically, the adsorption increases up to 1 g/L only and then after the adsorption efficiency decreases.

2.4 Removal of Cd(II)

Cd is similar to the Zn chemically and available in +II oxidation state. Cd majorly uses in pigments, anticorrosive agents, electroplating agent on steel, etc. (Ayyanar and Thatikonda 2020). Its presence superiorly occurs from phosphate ores containing fertilizers and its Cd(II) solubility greatly enhances in acidic environments (Toft et al. 1987). Its long-term and short-term exposure to human causes flue, fever, muscle pain called as 'Cd–blues' and anosmia, animia and kidney failure. Traces of its presence in drinking water cause many more adverse effects and the WHO and EPA allowed levels are 3 and 5 ppb. Henceforth, it is indispensable to avoid its level of contamination alarmingly (Purkayastha et al. 2014; Teng et al. 2020).

Venkateswarlu and Yoon (2015a) have been synthesized a novel nanocomposite DEAMTPP@Fe_3O_4 by peel pulp extract of Ananas comosus. The pineapple peel pulp extract solution serves as the best reducing agent to form Fe_3O_4 nanoparticles from ferric chloride. Further, these nanoparticles were functionalized by using diethyl-4-(4-amino-5-mercapto-4H-1,2,4-triazol-3-yl) phenyl phosphonate (DEAMTPP) to get the final adsorbent, DEAMTPP@Fe_3O_4, for the Cd(II) deletion from water. A clear XRD pattern reveals the phase purity and nanoparticle nature of iron oxide phases. The Scherrer equation shows the average size of the composite as 12 nm. The same has been confirmed by TEM analysis also. The FT-IR spectra provided the data related to the anchoring of Fe_3O_4 to DEAMTPP covalently. This is observed by the shifting in FTIR peak from 1038 to 1014 cm^{-1} of the P-O group. This is also confirmed by the 31P NMR spectra and Raman spectroscopy of the adsorbent. It is observed that there was a significant effect of pH in removing the Cd(II) from the aqueous solution. At lower and higher pH, the Cd(II) removal efficiency of the adsorbent was low. Finally, it was observed that pH 6 was the best condition for removing the pollutant under 60 mg/L concentration of Cd(II). Interestingly, the new composite (adsorbent) was able to remove 96% of the Cd(II), which was remarkably higher in comparison to the 40% efficiency of Fe_3O_4 MNP. This proves the capacity of the present PMNP in removing the Cd(II). Also, it was observed that the adsorbent had its highest adsorption capacity at 0.1 g/L only and beyond this, the adsorption tendency was declined continuously. Hence, the authors studied the adsorption study by recycling the adsorbent multiple times.

Zhou et al. (2018) synthesized good reusable MNPs by using multi-porous structured biomaterial, Cyclosorus. After synthesizing the MNPs by using Cyclosorus, the surface of these MNPs was modified by using 3-triethoxysilylpropylamine (TSA) for getting the final shape of adsorbent (MCIA) as well as to enhance the adsorption capability of Cd(II). The TSA anchoring onto the MNPs' surface was confirmed by their FT-IT, XRD and XPS analysis. This 0.2 mm average-sized novel adsorbent had a saturation magnetization value of 20.4 emu/g. The pH effect study revealed that the adsorption is better at neutral pH compared to lower values. This is due to the charge conflict between protonated amine and the pollutant at lower pH, making the adsorption weak. It was noticed that the Cd(II) adsorption tendency decreased to 72% after increasing the concentration of another industrial pollutant, sodium chloride. Interestingly, MCIA showed an excellent reusable trend, i.e. more than 90%, even after five cycle usage.

Very recently Vázquez-Guerrero et al. (2021) have been demonstrated the iron oxide nanoparticles based on cellulose fibre extract from Moringa (Fe NPs/ NFCs) for the dismissal of Cd and Pb from waste water effectively. The batch adsorption studies reveal that the Cd can remove first competitively than the Pb in the water sample with the adsorption rates of Cd–K_2 = 0.44861/min and Pb–K_2 = 0.01701/min. But the removal efficiency of Cd is >12 mg/g which was lower than the Pb (>80 mg/g) have been noticed from Langmuir fittings and it followed the pseudo-second-order reaction. The greater adsorption of Pb was due to the smaller hydration size which is 0.45 nm than Cd 0.5 nm. Here the positively charged pollutants would bind to the negatively charged Fe–O, –OH, –CHO and –COOH on MNPs. From the experimental demonstration, we can observe that the Moringa extract has served as a green capping and reducing agent for the synthesis of plant-based MNPs for inorganic metal eradication. It is believed that it can also useful to remove other metals like Cr, As, Hg as well. According to Table 1, Yam peel is good for Hg removal than comparing with watermelon rind and green tea leaves. Whereas Cnidiummonnieri (L.) Cuss, Onion sheathing and Ananas comosus peel pulp extract is best for Cr, As and Cd at specified conditions in the table.

3 Conclusions and Future Perspectives

Here in this chapter, we highlight the magnetic bio sorbents prepared by eco-friendly approach for the elimination of hazardous metals like Hg, Cr, As and Cd from water. The heavy metals are highly poisonous in nature when they intake more than the prescription of WHO, USEPA and FDA. Hence it is highly indispensable to find out the better adsorbent which is economical and eco-friendly. The MNPs prepared by biomass which containing phenols, carbonyl, amino acids, glucose, polysaccharide compounds are well discussed by demonstrating the removal efficacy of adsorbent by studying the effect of time, pH, temperature, concentration of pollutant and its

Table 1 Has the listed plant-based magnetic adsorbents for various toxic metal removals and the adsorption efficiencies

S. No.	Name of the plant extract used for MNPs preparation	Size of MNPs in nm	Metal and its concentration (mg/L)	Adsorption pH	Q_{max} (emu/g)
1	Watermelon rind	13	Hg(II) and 60	7	24.7
2	Yam peel	60 ± 20	Hg(II) and ?	7	26.6
3	Green tea leaves	217 ± 76	Hg(II) and 71.3	Without any pH adjustment	–
4	Corn stalk	9.8	Cr(VI) and 97.4	3	6.2
5	Lagerstroemia speciosa bark	8.76	Cr(VI) and 434.78	2.05	–
6	Cnidiummonnieri (L.) Cuss	45.5	Cr(VI) and 0.5	2–4	54.6
7	Wheat straw	–	As(V)	7–9	11.87
8	Onion sheathing	< 10 nm	As(V) and 57.47	7	52.6
9	Eucalyptus plant extract	–	As(V)	6–8	–
10	*Azadirachata india* leaves extract	8.4	As(V)	2	–
11	Ananas comosus peel pulp extract	12	Cd(II) and 60	6	16.9
12	*Cyclosorus*	0.2	Cd(II) and 49.4	7	20.4
13	*Moringa*	–	Cd(II)	5	12.5

kinetics and thermodynamics. As the MNPs have a magnetic property, these sorbents have a great advantage in recycling capability hence we can avoid the minimal adsorbent of maximum number of usages. As a result, we can avoid the sorbent-related eco toxicity, though it is originated from biomass. The hazardous issues related to heavy metals are ever-growing concerns and the adsorption process is economic than compare with other processes, it is urgently important to fabricate economic and eco-friendly high surface area, sorbents with ultra-high adsorption, magnetic susceptibility and less toxicity.

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Environmental Applications of Green Engineered Silver Nanoparticles

Jyothi C. Abbar, G. A. Swetha, Manjunath D. Meti, and Kirthi S. Byadagi

Abstract Nano materials are used in each and every field like energy storage, environmental science, health, transportation and catalysis, because of their improved, unique and stable properties. Among many materials, silver nanoparticles (AgNPs) since decades have attracted many researchers for the usage of these materials in potential areas due its non-toxic nature. These particles are widely known for their inherent and interesting properties like chemical stability, catalytic activity, high conductivity, etc. Known to possess anti-viral, antifungal and antibacterial kind of properties. Physicochemical processes can be used to create such materials. However, in today's world, environmentally friendly synthesis of such elements is getting stronger. Considerable attention is paid by researchers towards the biological and plant-based synthesis protocols due to the low cost, greener, less wastage of resources and employing renewable materials. This book chapter briefly highlights the detailed overview of the AgNPs. It also goes over the various properties of AgNPs, the methods employed towards AgNPs green synthesis with the help of fungi, bacteria and plant extracts as medium. Finally, attention will be given towards the environmental applications of such nanoparticles (NPs) in diverse fields of waste water treatment, its usage as disinfectant, as metal ion detectors, dye removal, etc.

Keywords Nanoparticles · Green synthesis · Silver nanoparticles · Environmental applications · Eco-friendly biological synthesis

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1 Introduction

One of the most emerging fields that have gained phenomenal attention from wide across the world scientists is nanotechnology which is multidisciplinary having enormous applications. Nanomaterials show different but unique and distinctive physical properties and chemical properties which make to be applicable in diverse areas of applications (Roy et al. 2021a, b; Roy et al. 2022). Many scientists have worked and are working in the different areas of nanomaterials applications like agriculture, pharmacy, cosmetics, electronics, catalysis, energy, environment pollution reduction strategies, etc. (Ahmed et al. 2021; Roy et al. 2021a, b). Development of nanomaterials has increased, their applications in different areas have increased, as they are known to fulfil most of the trending demands in various applications (Roy et al. 2021a, b).

Four classes of nanoparticles (NPs) are classified depending upon the chemical composition viz., carbon-based that may include nanofibers of carbon and nanotubes, etc. Ag, Cu, etc. fall under metal and metal oxide, liposomes, micelles, etc. falls under bio-organic and also another type is composite-based (Roy et al. 2021a, b). The nanoparticles may also be divided into organic and inorganic types (Roy et al. 2021a, b). Organic nanoparticles, such as polymeric nanoparticles, liposomes, lipid-based nanocarriers, solid lipid nanoparticles and carbon-based nanoparticles, are biodegradable, whereas inorganic nanoparticles are made of inorganic materials that contain metals, metal oxides by employing silver (Ag) and zinc (Zn), etc. Amidmost of the nanoparticles that are synthesised, silver NPs (AgNPs) can be considered to be the greatest and extensively used NPs due to their supremacy in different customer stuff and the percentage of its use is found to be around 25% (Raina et al. 2020; Roy 2021).

The fact that AgNPs are progressively expended in numerous areas that may include medicinal, foodstuff, healthiness & care, customer products and also in industrialised and manufacturing products. This is all due to the unique properties of physical and chemical like high electrical conductivity, optical, electrical, thermal, as well as biological (Mittal and Roy 2021). Because of such curious properties, they are found to be employed in numerous applications. They are also used in addition to those mentioned above as antibacterial agents because of its biological properties, drug delivery, coating on medical devices, households, optical sensors, in food industry, pharmaceuticals, in orthopaedics, in diagnostics, as anticancer agents-Anticancer medications' tumour-killing effects have been improved as a result of these studies. Freshly, AgNPs also are found to be used in several fabric industries, biomedical devices, wound dressings and even in keyboards (Li et al. 2014).

Actually, nanosised metallic particles because of their unique and peculiar characteristics they can significantly alter their physical, chemical, as well as biological properties. This is as owing to their surface: volume ratio. Hence, NPs are brow beaten for innumerable purposes. Coming to AgNP and its requirements, there are several protocols followed for its synthesis and are adopted widely globally. Physical methods of synthesis are possible and similarly, chemical-based synthesis methods are also possible. But these methods seem to be very harsh and can cause hazardous impact on nature and not only that it seems to be a bit expensive (Mittal and Roy 2021). But there is an alternative for everything, such an interesting method to overcome such difficulties is the green synthesis which is a biological method. Fascinatingly, AgNPs that are synthesised biologically are known to show high stability, high yield and solubility. Green biological methods appear to be simply ingenuous, speedy, non-toxic, reliable and also green methodologies generate well-defined size and morphology at optimal elevated circumstances and conditions for revolutionary research. Thus, in brief, we can say that green chemistry methodology for the AgNPs synthesis is much assuring having great potential about which we are going to study in this chapter.

This chapter furnishes a widespread framework of the green engineered-biological synthesis of metallic AgNPs as well as numerous aspects that influence the preparation process. The use of nanoparticles in environmental applications will be thoroughly deliberated. Current difficulties exposing the harmful effects of NPs, as well as future perspectives, provide us with a comprehensive roadmap for the foreseeable future.

2 Properties of Silver Nanoparticles

Several physical properties and chemical properties like particle surface chemistry, morphology and particle composition, coating of the particle and dissolution rate, capping, agglomeration, ion release efficiency, reactivity of the particle in solution, cell type, shape, size and size distribution, are borne by the silver particles that are in nanosised. And at last, the reducing agents that are being used towards the synthesis of AgNPs become the important factors towards the determination of cytotoxicity (Zhang et al. 2016). As an illustration, if we make use of the biological reducing agents like culture supernatants of several species of *Bacillus*, AgNPs are found to be prepared in versatile shapes, such as rod, spherical, flower-like, triangle, hexagonal, octagonal and many more. Many reported work showed that the smaller size particles can cause much toxicity than larger size particles, which is due to the larger surface area. This shows that the shape becomes equivalently crucial towards detection of lethal and toxicity To see an instance, in the biomedicinal field, several types of nanostructures will be used, that includes nanoplates, nanocubes, spherical, nanorods, flower-like and many more (Wei et al. 2015). Presence of chemical & biological coatings present oversurface of nanoparticle may be reason of toxicity. It should also be mentioned that the surface charge on the surface of the Ag nanoparticle can find the toxicity effect present in the cells. As an instance, the nanoparticles bearing the positive charge on their surface make them more reliable and make them available for much duration in the bloodstream in comparison to nanoparticles that are charged negatively this can be the significant path for the adoption of the anticancer agents (Zhang et al. 2016).

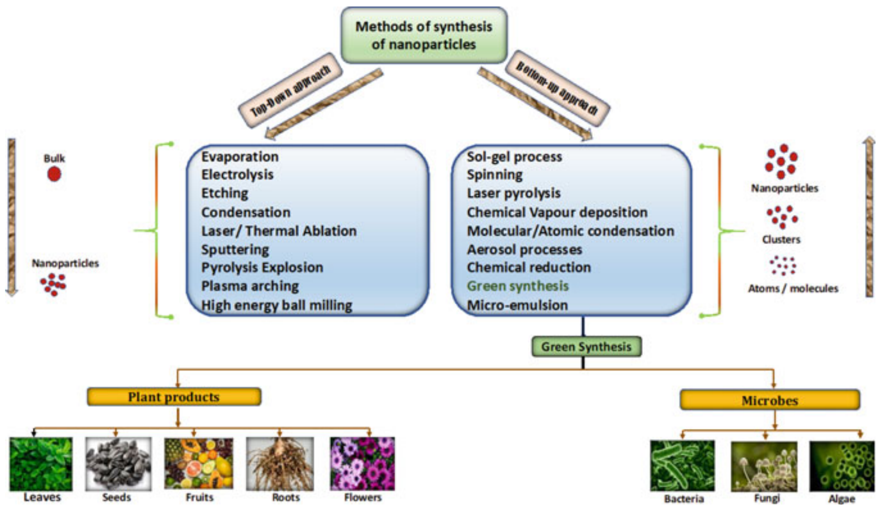
3 Synthesis of Nanoparticles

Nanoparticle synthesis includes two different types of methods or approaches (Wei et al. 2015) viz. (a) top-down methodology and (b) bottom-up methodology.

Later from these approaches, three practices like physical, chemical and green synthetic approaches are implemented for the nanoparticle's synthesis. Scheme 1 shows the schematic representation of different approaches that are followed for the nanoparticles synthesis.

Top-down methodology encompasses breakdown of bigger and bulk-sized particles to the tiny particles that are of nano-size dimensions. Here the miniaturisation of the particles from bulk to the desired size with the retention of the properties is carried. But the major problem with this is the defects or the imperfections that may arise on the surface structure. For the synthesis of NPs, physical approaches follow a top-down strategy, whereas the bottom-up methodology strategy is employed via the chemical route and biological route. NPs synthesis with physical synthesis route includes etching, evaporation, laser ablation, condensation, sputtering, electrolysis, sputter deposition, diffusion, thermal ablation, pyrolysis, explosion, plasma arcing and ball milling with high energy, mechanical methods (Dikshit et al. 2021). Nonetheless, these approaches are constrained by low production rates, costly actions and high energy consumption.

The bottom-up technique, on the other hand, is a substitute way that has potential to create minimal waste and so be additionally inexpensive. In bottom-up strategy assembling of a substance happens atom by atom, then later molecule by molecule or by cluster by cluster. Voluminous processes are in research still or are being used for commercial nanopowder production. The organometallic chemical route, chemical



Scheme 1 Different types of methods adopted for the nanoparticles synthesis

reduction, laser pyrolysis, spinning, revere-micelle route, sol–gel synthesis, chemical vapour deposition method, micro-emulsion, molecular condensation or atomic condensation, colloidal precipitation, electrochemical and thermal decomposition, hydrothermal synthesis, aerosol process, template-assisted sol–gel and electrodeposit are the well-known bottom-up practices testified for manufacture of brilliant AgNPs.

By cause of its ease of operation and low equipment requirements, NPs chemical reduction from their corresponding metal salt precursor's through appropriate addition of reducing agents is widely employed NPs chemical synthesis process. Several reducing agents and stabilising agents were examined during the synthesis, including sodium borohydride ($NaBH_4$), formaldehyde, methoxypolyethylene glycol, potassium bitartrate, dodecyl benzyl sulphate, polyvinyl pyrrolidone, and hydrazine (Dikshit et al. 2021).

Chemical approaches are cost-effective for wide-reaching production, but the practice of poisonous chemicals and creation of damaging by-products that harm environment, restricting their clinical and biological applications (Hua et al.2018). Consequently, with growing demand for metallic NPs like silver nanoparticles, the need of the synthesis procedures that are dependable, non-toxic, high-yielding and environmentally sustainable are needed. The green synthesis method which is a biological method can consequently deliver an attractive substitute to the physicochemical methods for synthesis.

Precise and specific particle characterisation is necessary once the synthesis is done; as the particle's physicochemical qualities show a chief impression on their biological properties. Before application, it is necessary to describe the created nanoparticles in a dynamic manner so as to crack the security issue of using the possible fullest potential of nano material for the health care business, human well-being, nanomedicines, among other things (Lin et al. 2014).

4 Characterisation of Nanoparticles

Before causal checking of the toxicity or biocompatibility step, a detailed characterisation of the NPs with surface area, shape, size, size distribution, form, aggregation, solubility, etc. should be evaluated. Many techniques of analytical field, such as UV–visible spectroscopy, XRD—X-ray diffractometry, XPS—X-ray photoelectron spectroscopy, DLS—dynamic light scattering, SEM-scanning electron microscopy, TEM-transmission electron microscopy, AFM-atomic force microscopy and FT-IR-Fourier transform infrared spectroscopy, have been used to evaluate the synthesised silver nanomaterials (Dikshit et al. 2021).

Chemical concentrations with reaction circumstances, namely temperature, pH, to be adjusted to change the morphological features of NPs, such as size and form. However, when these synthesised nanomaterials are put to use in real-world or specific applications, they may encounter the undermentioned constraints:

(i) stability under extreme hostile environments,
(ii) scarcity of knowledge in basic mechanisms and modelling aspects,
(iii) bioaccumulation/toxicology characteristics,
(iv) extensive investigational needs,
(v) a requirement for trained operators,
(vi) device assembly and structural issues and
(vii) recycling/reuse/regeneration.

The qualities, behaviour and kinds of nanomaterials must be improved in the real world to meet the afore said necessities. So, these constraints, on the contrary, are generating new-fangled and exciting opportunities in this burgeoning field (Singh et al. 2018).

5 Importance of Green Engineered Synthesis of Nanoparticles

To address the limitations described in Sect. 4, green-designed synthesis procedures is attaining utmost traction in contemporary materials science and technology and its research and development. Regulation, cleanup, control and remediation will all help to increase the ecofriendliness of materials/nanomaterials. Few simple principles of 'green synthesis' can thus explain numerous components, viz. waste avoidance, by-products/effluence reduction and harmless solvents/auxiliaries usage, along with renewable feedstock. To evade the formation of unwanted or unsafe by-products, green synthesis procedures are essential via developing dependant, sustainable and environmental-friendly synthesis procedures. For this, an appropriate system of solvent and organic systems as natural resources is obligatory.

The green engineering of metallic nanoparticles has been exploited to acclimatise numerous biological components for example with plant extracts, bacteria, fungi and algae. Plant extracts are a reasonably up-front and cool technique to create NPs on a greater scale in comparison to fungal and/or bacteria-assisted synthesis amid existing green means of metal synthesis and/or synthesis of metal oxide nanoparticles. These products are collectively known as biogenic nanoparticles.

Based on biological precursors, conditions like solvent, pressure, temperature and pH play a critical function in green synthesis (acidic, basic, or neutral). Plant biodiversity has been widely studied towards the metal and metal oxide-based synthesis of nanoparticles. This is due to occurrence of useful phytochemicals in diverse plant extracts, particularly in leaves. The phytochemicals like ketones, flavones, phenols, terpenoids, amides, aldehydes, ascorbic and carboxylic acids are present using which the metal salts can be subjected to reduction into metal nanoparticles (Singh et al. 2018). The fundamental properties of such kind of nanomaterials are being studied for the applications in antimicrobials, optical imaging, catalysis, molecular sensing, biomedical diagnostics and biological system labelling (Singh et al. 2018).

Similarly, the green engineered AgNps synthesis protocols are been reported by using the plant extracts and microorganisms are reported. The details are explained in the next section.

6 Green Synthesis of AgNps

Traditional NP production methods are expensive, toxic and harmful to the environment. Researchers have found the specific green pathways or existing natural sources that are employed in synthesis of NPs. The sources of green blend/synthesis are categorised into three:

(i). Microbes. (here, fungi, yeasts, bacteria and actinomycetes as examples of eukaryotes).
(ii). Plant extracts.
(iii). Membranes, DNA of virus and diatoms.

In the formation of NPs from metal salt precursors in biomaterials, flavonoids, proteins, alkaloids, polyphenols, reducing sugars and few other compounds behave as reducing and agents for capping (Dikshit et al. 2021). Due to specific benefits over other approaches, microbial production of NPs has recently surfaced as a potential field for research. Depending on the kind of microbe, intracellular or extracellular production of NPs is possible. During the microbial manufacturing process, enzymes, sugars, polysaccharides, proteins and other secreted biomolecules oxidise/reduce metallic ions, resulting in the creation of NPs (Dikshit et al. 2021). However, because NP synthesis techniques differ depending on the type of bacterium, a thorough apprehension of microbial NP synthesis remains a mystery. However, because NP synthesis techniques differ depending on the type of bacterium, full knowledge of NP synthesis via microbial ones' remains elusive. Because of the growth media and inoculum, the isolation of the strain and the maintenance of culture medium and operational conditions, the microorganism-based NPs manufacturing technique is exceedingly complex and hard. However, the microorganism-interceded NPs manufacturing technique is incredibly puzzling and troublesome due to the production of inoculum and development media, isolation of strain and support of culture medium and working conditions, such as pH, temperature and agitation. Plant extracts or broths, on the other hand, are simple and convenient to use, as they do not require the sophisticated processes of cell cultivation and preservation. The amount of time necessary to attain total NP reduction using microbes is typically 24–120 h, whereas the time required to reduce NPs using plant extract is substantially less, ranging from a few hours to 48 h (Dikshit et al. 2021). The plant's decrease rate is significantly higher.

6.1 Synthesis of AgNps Using Bacteria

Bacteria are effective in reducing metal ions and are key up-comers in the creation of NPs (Dikshit et al. 2021). An array of bacterial genus is employed in the metallic and other new NPs synthesis. Bacteria are known to create inorganic compounds both within and outside the cell. As a result, prokaryotic microorganisms were first investigated as biofactories and are used as for the production of NPs. Bacterial-based biosynthesis is versatile, affordable and ideal for large-scale production when contrasted with conventional synthetic strategies of blend. The principal inconvenience of involving microscopic organisms as nano factories is the delayed combination rate and confined assortment of the available sizes and shapes. Bacteria are chosen for NP synthesis over other microorganisms because of ease of maintenance, more products and less purification price. Bacterial NP production has been embraced because bacteria are relatively easy to manipulate. Commercial biotechnological applications have all made use of bacterial species (Dikshit et al. 2021).

Metal/metallic oxide NPs have been extensively synthesised using bacteria (prokaryotic) and actinomycetes (Dikshit et al. 2021). Silver is widely known for its biocidal qualities. AgNPs can be made by converting silver ions to silver metal NPs with the help of bacteria species (Koul et al. 2021). Silver is mostly reduced by DNA or proteins (contain sulphur) in bacteria for production of extracellular AgNPs and intracellular AgNPs. Some are silver-resistant bacteria and may collect Ag on their cell walls up to 25% of dry weight biomass, suggesting that they could be used in commercial silver recovery from mining sources. It's worth noting that bacteria continued to multiply after the AgNPs were created. *Pseudomonas stutzeri* AG259 (Ag resistant strains) were cultivated in high concentrations of silver nitrates for the first noble metal NP production. The cells were shown to accumulate substantial amounts of silver, deposited in the type of 200 nm-diameter particles. When bacteria *Proteus mirabilis* PTCC 1710 was employed to make AgNPs, significant results were discovered. Table 1 summarises data on the morphology, size of numerous NPs (Dikshit et al. 2021).

AgNPs have recently been synthesised using a cell-devoid extract of the endophytic bacterium *Pantoea ananatis* (Dikshit et al. 2021). Sphere-shaped NPs antibacterial activity with a size 8.06–91.32 nm was found to be significant against a variety of harmful microorganisms. Researchers found that AgNPs generated with acidophilic actinobacterial strains had the highest antibacterial efficacy against *E. coli*, *S. aureus* and *B. subtilis*. Other bacterial strains employed to make AgNPs are summarised in Table 1.

Varied bacteria species have different rates of NP formation. *Klebsiella pneumoniae Escherichia coli* and *Enterobacter cloacae* are demonstrated for producing AgNPs with incubation of five minutes. *Enterobacter cloacae* having the highest efficacy for NP synthesis. *Bacillus licheniformis*, on the other hand, has been found to produce AgNPs within 24 h of incubation when it contains the nitrate reductase enzyme.

Table 1 Bacterial strains employed to synthesise AgNPs

Bacteria	Size (nm)	Morphology
Pseudomonas stutzeri AG259	200	Triangular
Bacillus indicus	–	–
Bacillus licheniformis	40	–
Proteus mirabilis PTCC 1710	10–20	–
Klebsiella pneumonia, *Escherichia coli,* *Enterobacter cloacae*	28–122	Sphere-shaped
Pseudomonas proteolytica, Bacillus cecembensis	6–13	Sphere-shaped
Bacillus cereus	20–40	Sphere-shaped
Lactobacillus casei	20–50	sphere-shaped
Ochrobactrumanhtropi	38–85	Sphere-shaped
Actinobacter	13.2	Sphere-shaped
Pantoeaananatis	8.06–91.31	Sphere-shaped
Bacillus subtilis	3–20	Sphere-shaped
Marine Bacteria		
Streptomyces rochei MHM13	–	–
Streptacidiphilusdurhamensis	–	–
Streptomyces xinghaiensis OF1	–	–
Streptomyces sp. OSIP1 *Streptomyces sp.* OSNP14	–	–

This emphasises how important microbe selection is in the synthesis process. By varying the metal ion parameters while incubation, such as temperature, reactant concentration, duration of reaction and metallic salt, culture medium, different sizes and forms of AgNPs can be produced (Zhang et al. 2020). *Morganellapsychrotolerans* species at different temperatures were used to demonstrate different sizes and forms of AgNPs. At 25 °C, the authors saw formation of triangular, hexagonal and sphere-shaped NPs. At 20 °C, sphere-shaped NPs with diameters of 2–5 nm were generated, while between 15 and 20 °C, a mixture of sphere-shaped and nanoplates was detected. At 4 °C, sphere-shaped NPs of 70–100 nm diameter were generated. *Arthrobacter sp.* B4 was used to study the impact of pH, concentration and temperature on green production of AgNPs. The authors found face-centred Ag-NPs of size 9–72 nm around 70 °C and a pH = 7–8 using a 1 mM solution of $AgNO_3$. The synthesis time was reduced from 10–2 min by increasing temperature from 70 to 90 °C, while $AgNO_3$ increased concentration to 3 mM ensured creation of AgNPs bunches (Dikshit et al. 2021).

Actinobacteria, a phylum within the bacterial territory that primarily comprises of gram-positive bacteria, sometimes known as sea bacteria, has also been used to make AgNPs. Ag^+ to AgNPs was reduced by NADH-dependent nitrate reductase from sea bacterium *Streptomyces sp.* LK-3 (Dikshit et al. 2021) shows an extracellular manufacture of Ag-NPs employing these types of bacteria. Table 1 lists the few other marine bacteria employed in production of Ag-NPs.

6.2 Synthesis of Ag-Nps via Fungi

In comparison to algae or bacteria, fungal-mediated NP synthesis has significant advantages with regard to biomass management and downstream procedures, besides the huge amounts of protein are secreted, which boosts productivity by many folds. Fungi, like bacteria, have been studied in the biological creation of metallic NPs because of high binding capacity, tolerance, metal bioaccumulation ability and intracellular uptake (Dikshit et al. 2021). Fungi are increasingly used in green synthesis because of their ecofriendliness and easy in handling in contrast to other groups of microbes. Fungi are easier to manage in a laboratory setting than bacteria. Fungi produce NPs in a distinct way; they secrete huge amounts of enzymes in that are utilised to decrease Ag ions, which cause the development of metal NPs (Dikshit et al. 2021).

Enzymatic degradation in cell walls or within fungal cells is utmost plausible mechanism for formation of metallic NPs. Metal/metal oxide NPs are made using a variety of fungal species. In the case of fungi, reduction of silver for the formation of external and intracellular Ag-NPs is made by a nitrate-dependent reductase or a carboxylic group. The extracellular synthesis approach is preferred since the purification stages are simple and straightforward. The intracellular NPs production approach, on the other hand, is difficult and expensive because of the additional separation and purification operations required. Ahmad et al. 2003 published the earliest 1st research on extracellular manufacturing of AgNPs using eukaryotic systems like fungus. The reduction process is mediated by secreted enzymes, according to the researchers (Dikshit et al. 2021). All fungi-based biosynthesis was intracellular prior to this research. Extracellular synthesis is favourable because the NPs produced do not bond to the biomass (Dikshit et al. 2021), making it possible to apply this protocol to the biosynthesis of nanomaterials with a variety of chemical composition, like nitrides, oxides, etc. Due to fungi's high metal accumulation potential, this synthesis is said to be more efficient and less expensive (Dikshit et al. 2021).

Furthermore, external NP synthesis using fungus is simple because it do not require doping, as in the case of intracellular synthesis. It also do not require any additional reagents, like detergents for physical factor modulation, like ultrasound. Metal ions adhere tightly to the fungus cell walls, allowing for high metal concentrations. When compared to bacteria-based NPs, this provides higher yields (Dikshit et al. 2021).

Fungi are also been used to successfully synthesise silver nanoparticles. In the early twentieth century, the first fungus-mediated metal NP synthesis was conducted, with AgNPs utilising the fungus Verticillium. Verticillium-based synthesis pushes the green approach even farther. The reduction of ions and production of AgNPs occurs when fungus is exposed to $AgNO_3$ solution. NPs had a diameter of about

25 nm and had a good monodispersity and spherical shape (Table 2). AgNPs are generated underneath the fungal cells surface, unlike bacteria (Dikshit et al. 2021). This differs from Klaus et al. 1999s findings, which showed that particle shapes generated using bacteria varied from sphere-shaped, hexagonal and triangular.

The production of NP was next investigated by a mechanism, with the major idea being that NPs be produced over the mycelia surface instead of in the solution for fungi-based synthesis. It was therefore proposed that adsorption of silver ions over the surface of fungal cells in the first phase as a result of an electrostatic interaction between positively charged silver ions and carboxylate—negatively charged groups ($RCOO^-$) in enzymes, found in mycelia's cell wall. Finally, enzymes found in cell wall decrease the silver ions, resulting in creation of silver nuclei (Dikshit et al. 2021). Switching from bacteria to fungi as a method of developing natural nano factories has the advantage of making biomass processing and handling easier downstream.

Table 2 List of diverse species of fungi used to synthesise AgNPs

Fungi	Size (nm)	Morphology
Verticillium	21–25	Sphere-shaped
Aspergillus fumigates	5–25	Sphere-shaped
Aspergillus favus	1–8	–
Phanerochaetechrysosporium	50–200	Pyramidal
Fusarium semitectum	10–60	Crystalline Sphere-shaped
Aspergillus niger	20	Sphere-shaped
Penicillium fellutanum	5–25	Sphere-shaped
Phoma glomerata	60–80	Sphere-shaped
Cariolus versicolor	25–75	Sphere-shaped
Fusarium solani	5–35	Sphere-shaped
Cladosporium cladosporioides	10–100	Sphere-shaped
Alternata alternate	20–60	Sphere-shaped
Penicillium brecompactum	23–105	Crystalline Sphere-shaped
Trichoderma viride	5–40	Sphere-shaped
Rhizopus nigricans	35–40	Sphere-shaped
Schizophyllumradiatum	10–40	–
Rhizopus stolonifer	2.86	Sphere-shaped
Candida albicans ATCC 10231	10–20	Sphere-shaped
Candida glabrata	2–15	Sphere-shaped
Aspergillus terreus	7–23	Sphere-shaped
Ganoderma sessiliforme	45	Sphere-shaped
Trichoderma longibrachiatum	10	Sphere-shaped
Fusarium oxysporum	21.3–37	Sphere-shaped
Trametestrogii	5–65	Sphere-shaped

Nonpathogenic fungi such as white-rot fungus, add to the bulk production of AgNPs. The reaction rate is another significant consideration when choosing a synthesis process. The initial research on fast synthesis with fungi was with *Aspergillus fumigatus*, which produced monodispersed AgNPs in less than ten minutes. In addition, when Ag ions came in connection with the cell filtrate, *Aspergillus fumigatus,* moulds the most common, was used to produce AgNPs in minutes. These experiments demonstrated the usefulness and feasibility of using fungus to produce significant amounts of NPs. AgNPs were recently generated utilising *A. Flavus* fungi, coupled with antibiotics for biocidal efficiency for multidrug-resistant bacteria. Antibiotics coupled with Ag-NPs were shown to be effective in this investigation (Dikshit et al. 2021).

The pH effect on the fungi-mediated AgNPs has demonstrated that changing the pH can modify the shape of the NPs. This is because the acidity or basicity of amino acids, which are used in NP formation, is determined by pH fluctuations. *Fusarium oxysporum* 405 fungi were used to create sphere-shaped, rod-shaped, triangular and uneven forms of AgNPs at a pH of 3. Authors also discovered that monodispersed spherical NPs formed at pH 7 and 5, whereas long and sphere-shaped NPs formed at pH 9. Temperature investigations have shown variation in size of AgNPs with temperature for different species of fungi (Dikshit et al. 2021). The diverse species of fungi used in green synthesis AgNPs are listed on Table 2.

6.3 Synthesis of Ag-Nps via Plant Extracts

Plant-mediated NP production can be accomplished in three ways: intracellularly, extracellularly and individually using phytochemicals. As a result, biosynthesis approaches using plant extracts have attracted considerable interest because of its fast development, one-step approach, cost-effective protocol, nonpathogenicity and ecologically benign character. It is an excellent alternative to traditional preparation method and has generated several studies. Green synthesis in plants is quick than in bacteria and fungi.

A variety of plants have been utilised to synthesise a wide spectrum of metallic NPs (Dikshit et al. 2021). Kharissova et al. (2013) have effectively utilised flowers, leaves, seeds, shoots, stems, barks and their derivatives in the production of NPs. Biomolecules like alcoholic compounds, terpenoids, enzymes polysaccharides, flavones, phenolics, proteins, alkaloids, amino acids, are the main substances that influence the capping and reduction of nanoparticles resulting in stable and shape-controlled NPs (Siddiqi et al. 2018; Nadiyah et al. 2021). Chlorophyll and quinol pigments, as well as methyl chavicol, ascorbic acid, caffeine, theophylline, linalool, eugenol and other vitamins () is also documented.

However, throughout the past several years, the mainstream research has concentrated on biosynthesis of NPs employing the inactive component of the plants, either as an extract or in powder form (Siddiqi et al. 2018; Nadiyah et al. 2021). Metallic NPs are synthesised from a variety of plant parts, including flower, leaves, fruit, seed, stem, seed coat, root and latex. Metal salt, concentration of the extract, pH, temperature and the contact time are the primary affecting parameters once plant extract is selected. For a full survey of plant materials used in the biosynthesis of nanoparticles, readers might refer to Iravani's study (Dikshit et al. 2021).

Even though metallic nanoparticles with in vivo technique can be made (in living plants) by reducing metal salt ions absorbed as soluble salts, much of this study has focused on ex vivo generation of NPs. *Alfalfa sprouts*, the earliest report involving biosynthesis of metallic NPs with a living plant system, were the first endeavours to employ plants as metallic NPs sources. Alfalfa roots may absorb silver from agar medium and transmit it to the plant's shoots in the same oxidation state. By joining and creating larger groupings, these silver atoms organise themselves in the shoots to make NPs (Siddiqi et al. 2018; Nadiyah et al. 2021).

For the production of AgNPs, Salih et al. (2020) employed plant extract using leaves of three distinct plants, namely *Ziziphus Spina Christi*, *Piper nigrum* and *Eucalyptus globulus*. The average particle size distribution was 8–35 nm and it reduced with increase in plant extract concentration. Dhar et al. (2021) showed AgNPs production utilising *Phyllanthus emblica* fruit extract in a similar work and the synthesised AgNPs were spherical and measured 60–80 nm in diameter on average. The antioxidant activities of AgNPs generated using *Crassocephalum rubens* leaves extract are similarly influenced by the extraction procedures (Adewale et al. 2020). AgNPs with sizes of 10–15 nm were found to have spherical and hexagonal forms in SEM and TEM pictures.

Using *Geranium leaf* extract AgNPs extracellular synthesis including $AgNO_3$ and quick Ag ion breakdown, results in stable AgNPs with diameters of nm. To make stable and sphere-shaped AgNPs with 10 nm as average particle size, researchers used *Ficus benghalensis* leaf extract. The characteristics of produced NPs were investigated using thermal gravimetric analysis (TGA), XRD, FTIR and SEM and (). *Acorus calamus* extract was employed as a capping agent for AgNPs synthesis to analyse their oxidising, antibacterial activities and anticancer (Siddiqi et al. 2018; Nadiyah et al. 2021). Kumar et al. (2014) investigated the making of AgNPs using a *Boerhaaviadiffusa* extract. The TEM and XRD results revealed a typical size of approximately nm with a spherical shape. *Flavobacterium, Pseudomonas fluorescens* and *Aeromonas hydrophila*have all been tested with these NPs. Krishnaraj et al. (2010), synthesised AgNPs employing a leaf extract from *Acalypha indica.*

Sphere-shaped AgNPs are made from lethal weed *Chenopodium album*, with a size 10–30 nm, according to Dwivedi and Gopal (2010). To make AgNPs, Aldebasi et al. (2015), employed an aqueous combination leaf extract of *Ficus carica.* Awwad et al. (2012) used another approach to synthesise AgNPs using *Olea europaea* extract and characterisation were done by spectroscopic methods. The antibacterial activity of the spherical AgNPs against *E. coli*, *S. typhi*, *B. subtilis*, *S. aureus* and pathogens was examined using *Abutilon indicum* extract (). Shape and size-based regulated AgNPs synthesis from plant extract of *Aloe vera* was described by Logaranjan et al. (2016).

To create dependable and capped AgNPs with a diameter of 5–68 nm, *Syzygiumalternifolium*aqueous fruit extract was utilised. Moldovan et al. (2016) showed green synthesis of sphere-shaped AgNPs with *Sambucus nigra* fruit extract. After an XRD analysis, they were discovered to be crystalline. AgNPs were made from *Artocarpus heterophyllus* seed powder extract (Siddiqi et al. 2018; Nadiyah et al. 2021). The structure and crystal structures of the NPs were having a peculiar form and studied using TEM, EDAX, SEM, SAED and IR spectroscopy.

Kumar et al. (2014) described a biosynthesis of AgNPs using plant extract of *Boerhaavia diffusa* as a capping and reducing agent. In UV–vis spectrum, the Ag-NPs colloidal solution had an absorption limit of 418 nm. TEM and XRD examinations showed a face-centred cubic structure with standard particle dimension of 25 nm. AgNPs were sphere-shaped, face-centred, crystalline measuring 50–70 nm were made from methanolic leaf extract of *Leptadenia reticulate*. Extract of Mulberry leaves was employed to make sphere-shaped and monodispersed AgNPs with a particle size of 20 nm. The characteristics of produced AgNPs were investigated by spectroscopic techniques which showed their potent antibacterial activity against *Shigella spp* and *Staphylococcus aureus* (Siddiqi et al. 2018; Nadiyah et al. 2021). AgNPs are generated by reducing $AgNO_3$ solution with leaf extract of olive plant and has demonstrated to be efficient antibacterial agents against drug-resistant bacteria. The properties of NPs were investigated via spectroscopic techniques, TGA and results showed that those NPs are mainly spherical with 20–25 nm diameters (Siddiqi et al. 2018; Nadiyah et al. 2021). Plant extract of *Alternanthera dentate* was used as a capping agent for AgNPs green synthesis (Kumar et al. 2014). Extract of *Acacialeucophloea* is employed to synthesise AgNPs with 38–72 nm size range. *Chrysanthemum indicum L.* was employed to produce AgNPs with a size of 17–29 nm (Siddiqi et al. 2018; Nadiyah et al. 2021). Kumar et al. (2013) demonstrated AgNPs preparation by combining leaf extracts of *Parthenium hysterophorus* and *Premnaherbacea* with $AgNO_3$ solution. The majority of AgNPs produced through green synthesis are being studied in biomedicine, primarily as antibacterial agents and cancer treatments. According to recent research, AgNPs with diameters 38–72 nm and 17–29 nm range may be madeusing an extract of *Chrysanthemum indicum L.* or *Acacia leucophloea* (Siddiqi et al. 2018; Nadiyah et al. 2021). Samples of AgNPs synthesised from both plants showed exceptional antibacterial properties. *Ganoderma neojaponicum*in the same way, Imazeki was used to synthesise AgNPs as potential cytotoxic agents against cells of breast cancer (Siddiqi et al. 2018; Nadiyah et al. 2021). By adding *Argemone mexicana* leaf extract to an aqueous solution of $AgNO_3$, it acts as a capping and reducing agent in the formation of AgNPs. Roy et al. (2014) synthesised spherical AgNPs with an average 20 nm diameter using the fruit extract of *Malus domestica* as a capping agent. Latex from *Jatropha curcas* was used to reduce $AgNO_3$ solution to synthesie AgNPs. Also, AgNPs were generated employing leaf extract of *Cassia auriculata*as a capping agent (Siddiqi et al. 2018; Nadiyah et al. 2021).

The characteristics of NPs are investigated using a X-ray, UV–Vis spectrometer, nanoparticles tracking analysis (NTA), XRD, SEM, FTIR. TEM micrographs showed sphere-shaped NPs with an average 12 nm as diameter. AgNPs produced using *Ananas comosus* were analysed utilising different spectroscopic techniques. As per Singh et al. (2010), the average size of NPs is 30 nm, as determined by spectral and surface examination. Gavhane et al. (2012) found that lowering the concentration of aqueous $AgNO_3$ solution created AgNPs from *Neem* and *Triphala* extracts. Rout et al. (2012) generated sphere-shaped AgNPs *Ocimum sanctum* leaf extract and obtained particle characteristics with various spectroscopic techniques.

As these green chemistry methods become more widely investigated, scientists are beginning to combine various choices. It was found in recent times that symbiotic biological systems, like *Geranium* leaf mixed with endophytic fungus *Colletotrichum sp.*, can synergise the reaction's result. AgNPs synthesised by means of a variety of plants and plant extracts are listed in Table 3 which is adapted from Siddiqi et al. (2018) and Nadiyah et al. (2021).

6.4 Synthesis of AgNps via Algae

Eukaryotic autotrophs expanded the potential of green synthesis in the same way that shifting from prokaryotes to eukaryotes did. Algae are another unusual bioagents used in the production metal oxide NPs using metals like Au, Ag, Pd, Zn, Fe, etc. Its distinctiveness stems from the presence of secondary metabolites and other bioactive chemicals in its cells, which cap and stabilise the produced NPs. Proteins, lipids, vitamins, carotenoids, polyphenols and polysaccharides are among the bioactive components found in algae and they stand out due to their large proportion in the dry weight of the material and their reducing and stabilising properties. When compared to previous biological approaches, utilising the sea algae *Sargassum wightii* resulted in extremely stable NPs (Singh et al. 2018).

AgCl NPs are one-of-a-kind metal salt NPs created utilising algae. In the production of AgNPs, algae extracts such as *Padina pavonia, Cladophora glomerata (L.) Kütz* and *Ulva compressa* (*L.*) *Kütz* has been employed (Abdel-Raouf et al. 2019). It's important to note that a highly stable biomaterial with a tiny size (from 49.58 to 86.37 nm) and a variety of shapes (sphere-shaped, triangular, rectangular, polyhedral and hexagonal) was created quickly (Abdel-Raouf et al. 2019). Bioflavonoids found in brown algae *Padina pavonia*, such as epigallocatechin, epicatechin, catechin, gallic acid and epigallocatechin gallate, can decrease and stabilise Ag^+ ions for the corresponding AgNPs, according to Abdel-Raouf et al. (2019).

Sargassum plagiophyllum was used to synthesise 21–48 nm AgCl NPs, *Caulerpa racemose*, a marine alga, was used to produce highly stable 25 nm sized AgNPs and *Chlorella vulgaris* was used to synthesise 9.8 nm AgCl NPs. Another study used *Laminaria japonica* for biosynthesis of AgNPs and found that incubation of $AgNO_3$ at 120 °C resulted in a considerable rate of synthesis. The red alga *Portieriahornemannii* was used to make spherical AgNPs (Fatima et al. 2020), whereas the marine macroalgae *Padina sp.* was used to make 25–60 nm sized AgNPs (Bhuyar et al. 2020). SEM, TEM, FTIR and XRD were used to characterise these NPs.

Table 3 List of AgNPs synthesised using a variety of plants and plant extracts

Plant Species	Plant part (extract)	Size (nm)	Morphology
Carica papaya	Fruit	15	Hexagonal and cubic
Allium cepa	Leaf	33.6	Sphere-shaped
Chenopodium album	Leaf	10–30	Sphere-shaped
Hibiscusrosa sinensis	Flower	14	Prism or Sphere-shaped
Citrus limon	Limon	>50	Spheroidal and sphere-shaped
Eclipta prostrate	Leaf	35–60	Hexagons, triangles and pentagons
Psidium guajava	Leaf	26 ± 5	Crystalline and sphere-shaped
Cuminum cyminum	Seeds	12	Smooth surface and sphere-shaped
Tribulus terrestris	Fruit	16–28	Sphere-shaped
Artocarpus heterophyllus	Seeds	10.78	Irregular
Solanum lycopersicum	Fruit	10	Sphere-shaped
Albizia lebbeck	Leaf	–	Sphere-shaped
Brassica rapa	Leaf	16.4	–
Ficus carica	Leaf	13	–
Boerhaaviadiffusa	Whole plants	25	Sphere-shaped
Melia dubia	Leaf	35	Sphere-shaped
Olea europaea	Seed	34	Crystalline
Aegle marmelos	Fruit	22.5	spherical, hexagonal, roughly circular
Calotropis gigantean	Flower	10–50	Sphere-shaped
Eucalyptus globulus	Leaf	1.9–4.3 & 5–25	–
Salacia chinensis	Powdered plant	20–80	Sphere-shaped, rods, triangular, hexagonal
Euphorbia amygdaloides	Plant	7–20	Sphere-shaped
Salvadora persica	Stem	1–6	Sphere-shaped
Syzygiumalternifolium	Fruit	4–48	Sphere-shaped
Tamarindus indica	Seed coat	~12.73	–
Piper nigrum	Seeds	10–60	Rod shaped
Trachyspermumammi	Seeds	36	Cubic
Erigeron bonariensis	Leaves	13	Sphere-shaped
Trigonella foenum-graecum	Seeds	20–50	Sphere-shaped
Ziziphoratenuior	Leaf	8–40	Sphere-shaped

(continued)

Table 3 (continued)

Plant Species	Plant part (extract)	Size (nm)	Morphology
Mangifera indica	Seed	14	Sphere-shaped and hexagonal
Picrasmaquassioides	Bark	17.5–66.5	Sphere-shaped
Solanum tuberosum	Tuber	10–12	Crystalline and Sphere-shaped
Morinda tinctoria	Leaves	80–100	Sphere-shaped
Momordica charantia	Leaves	11	Sphere-shaped
Nigella sativa	Leaves	15	Sphere-shaped
Piper betle	Leaves	48–83	Sphere-shaped
Leptadenia reticulate	Leaves	50–70	Crystalline, face-centred
Parsley (Petroselinum crispum)	Leaves	30–32	Sphere-shaped
Peach gum	Powder	23.56 ± 7.87	–
Acmella oleracea	Flower	2–20	Sphere-shaped
Aloe vera gel	Leaves	5–50	Octahedron
Hydrocotyle asiatica	Leaves	21	Sphere-shaped
Lantana camara	Leaves	33.8	Sphere-shaped
Parkia roxburghii	Leaves	5–25	Poly dispersped, quasi-sphere-shaped
Pedalium murex	Leaves	50	Sphere-shaped
Prunus serotina	Fruit	20–80	Sphere-shaped
Prunus japonica	Leaf	26	Hexagonal and Sphere-shaped
Chelidonium majus	Root	15.42	Sphere-shaped
Cydonia oblonga	Seeds	38	Face-centered cubic
Sterculia acuminata	Fruit	~10	Sphere-shaped
Saraca indica	Leaf	23 ± 2	Sphere-shaped
Sambucus nigra	Fruit	26	Sphere-shaped
Terminalia arjuna	Bark	2–100	Sphere-shaped
Terminalia cuneata	Bark	25–50	Sphere-shaped
Terminalia chebula	Fruit	30	distorted Sphere-shaped
Catharanthus roseus	Leaf	20	Sphere-shaped
Citrullus lanatus	Fruit rind	20	Sphere-shaped
Rubus glaucus	Fruit	12–50	Sphere-shaped
Cannabis sativa	Stem fibre	30	Sphere-shaped
Ficus hispida Linn. f	Leaf	20	Sphere-shaped
Alpinia nigra	Fruit	6	Sphere-shaped

(continued)

Table 3 (continued)

Plant Species	Plant part (extract)	Size (nm)	Morphology
Phyllanthus pinnatus	Stem	<100	Cubicle
Peganum harmala	Leaves	20	Sphere-shaped
Catharanthus roseus	Bark	1–26	Sphere-shaped
Salvadora persica	Root	37.5	Rod-like

6.5 Synthesis of AgNps via Yeast

In eukaryotic cells, yeasts are single-celled microorganisms. There have been 1500 yeast species recognised. Yeasts, like fungi, have been extensively studied for AgNP formation (Apte et al. 2013). Among eukaryotic organisms, yeast has been utilised to synthesise NPs using Au, Ag, Pd, Se and other metals. Like fungus, yeast can tolerate high concentrations of metal ion, enabling for high metal NP accumulation (Shah et al. 2015). Several research groups have reported successful production of NPs/ nanomaterials using yeast.

Extracellular synthesis was first done with the silver tolerant yeast strain MKY3. Due to the ease with which the NPs could be separated by differential thawing (Kowshik et al. 2003), the synthesis result was satisfactory. Several investigations followed, but commercial baker's yeast accessible in grocery shops was never used for synthesis until recently. A yeast strain that is silver tolerant and *Saccharomyces cerevisiae* broth were employed to produce Ag and AuNPs. Table 4 lists a wide variety of yeast species that are used to make variety of metallic NPs.

Apte et al. (2013), employed a pigment (brown) from yeast called melanin from *Yarrowiali polytica* to demonstrate the biosynthesis of AgNPs using yeast. In another study, utilising *Candida utilis* NCIM 3469 yeast, effective extracellular biosynthesis of 20–80 nm sized AgNPs was accomplished (Waghmare et al. 2015). Different study (Eugenio 2016) used a termite gut isolate *Candida lusitaniae* to produce smaller AgNPs (2–10 nm). NPs of uniform size have been created using genetically modified yeasts. The fusion of a metal-resistant gene from *Mucor racemosus* with a *Pichia*

Table 4 List of AgNPs synthesised using a variety of yeast species

Yeast species	Size (nm)	Morphology
MKY3	2–5	Hexagonal
Saccharomyces cerevisae broth	4–15	Sphere-shaped
Cryptococcus laurentii	35–400	–
Saccharomyces cerevisiae	2–20	Sphere-shaped
Rhodotorulaglutinis	15–220	–
Rhodotorula sp. ATL72;	8–21	Sphere-shaped and oval
Rhodotorulaglutinis	15.5	Sphere-shaped

pastoris yeast strain has been reported to create the cytochrome b5 reductase enzyme (Elahian et al. 2017). Stable and uniform-sized AgNPs are synthesised using this enzyme.

Soliman et al. (2018), produced AgNPs from yeast *Rhodotorula sp.* (pink colour), which were sphere-shaped and oval in shape with a varying range of size from 8.8 to 21.4 nm. These green synthesised AgNPs displayed potent antibacterial properties, totally killing a broad range of bacteria and fungi (both Gram-negative and Gram-positive). Similarly, two yeasts *Cryptococcus laurentii* and *Rhodotorulaglutinis* were used to measure the antifungal activity of biosynthesised Ag-NPs against phytopathogenic fungi (Fernández et al. 2016). In this work, AgNPs prepared from *R. glutinis* were found to have stronger antifungal activity than AgNPs prepared from *C. laurentii*.

7 Environment Applications of AgNPs

Biomineralization, bioremediation, bioleaching and biocorrosion have all been used in the past to take advantage of the interaction between metals and microorganisms. Ag-NPs provides a versatile foundation for a wide range of purposes that includes thermal, electrical and antibacterial properties. According to reports, Ag-NPs have no negative effects on the body and serve as an antibacterial agent when used properly (Panyala et al. 2008). Some of the important applications are discussed in this chapter.

7.1 Water Treatment and Wastewater Treatment Process

Antibacterial and anti-pathogen properties of AgNPs are well-known. AgNPs are thought to be a beneficial mechanism in the fight against contagious diseases led by bacteria in the environment because of their durability and antimicrobial activity. AgNPscan avoid bacterial infection due to its significant efficiency against a number of pathogenic microorganisms. Colloidal AgNPs have been shown to have disinfecting properties in the healing of the infections caused by gastrointestinal bacteria according to recent research. The authors discovered in a published study that using AgNP-containing filters can provide 100% bacterial suppression when compared with their counterparts (Mpenyana-Monyatsi et al. 2012).

The release of wastewater into the ecosystem has damaged the aquatic environment due to population development, industry and excessive use of chemicals. Due to the presence of organic, inorganic, biological and radioactive contamination, water from natural resources is unfit for human consumption. For wastewater treatment, a variety of approaches have been used. Currently, nanotechnology offers a new high-efficiency technique for removing toxins from wastewater because of its less cost, ease of process and lack of secondary contaminant production. Adsorption (interfacial surface chemistry) is the most extensively used approach for removing pollutants from water (Punia et al. 2021). They are also explored as adsorbents in the treatment of industrial effluents and in different water sources. Because of their high porosity, tiny size and wide active surface area, nano adsorbents have a better efficiency and faster adsorption rate than traditional adsorbents. These nano adsorbents also have a high level of reactivity and catalytic efficiency. These nano adsorbents remove pollutants from wastewater with remarkable efficiency; however, the process has major flaws (Punia et al. 2021).

Another approach to remove contaminants from water is to filter contaminated water or wastewater using membranes. Metal NPs are frequently used as nano-catalysts in water treatment because of high surface-to-volume ratio and surface catalytic nature. Nanofiltration is effective at removing a wide range of contaminants from wastewater and the effectiveness of removal is mostly determined by the pore size and charge characteristics of the membrane (Wang et al. 2020). The construction and application of a composite membrane for water treatment formed by inserting NPs into polymeric or inorganic membranes have been the subject of several investigations. Furthermore, antimicrobial NPs such as AgNPs incorporated into membrane matrix inhibit bacterial attachment and biofilm development. These nano-catalysts improve quality of water by degrading pesticides, dyes, polychlorinated biphenyls, herbicides and nitro aromatics, among other contaminants (Patanjali et al. 2019). The wastewater treatment process uses a variety of nano-catalysts. Several investigations have shown that green-produced AgNPs have photocatalytic activity in the breakdown of various dyes in water (Patanjali et al. 2019). AgNPs derived from aqueous extract of *S. myriocystum* will be tested for possible suppression of *Aedes aegypti* and *Culex quinquefasciatus* mosquito vectors, anticancer activities and clinical human pathogens in HeLa cells (Balaraman et al. 2020).

Stable Ag-NPs made from *Anacardium occidentale* fresh leaf extract at 80 °C have been developed as a novel probe for sensing chromium ions [Cr(VI)] in tap water. When AgNPs synthesised using *Prosopis juliflora* leaf extract (10 mg) were left with 100 mL of sewage for 6 h, the number of bacteria decreased and grew as the incubation time rose (Kumar et al. 2016).

7.2 Agro Systems with Nanoparticles

Nanotechnology has shown its ability to improve agriculture by overcoming agricultural and environmental concerns, hence enhancing food supply and security. In current years, nanomaterials are been utilised in agriculture in two ways: as.

- Nanofertilisers: to increase agricultural production
- Nanopesticides: to kill pests, illnesses and weeds that obstruct crop plant growth.

In this section, we'll look at how nanofertilisers and nanopesticides are used in modern farming. NPs have been proved to be beneficial agricultural agents in terms of enhancing crop productivity while also reducing pests. Plant cuticles and tissues are easily penetrated by NPs, allowing for a delayed and effective release to the appropriate location. Herbicides, insecticides and fertilisers are only a few applications for NPs.

7.2.1 AgNPs as Nanopesticides

Pests are increasingly posing a threat to agriculture, resulting in reduced crop yields and, as a result, lower product quality. Synthetic insecticides applied on soil or plants also have negative environmental effects. It is a potential approach to incorporate nanotechnology into pest management. Nano silver is a non-toxic, safer, and more effective weapon against pests and the pesticide based on silver nanoparticles provides a large dose of pesticides to the target plants (Wang et al. 2020). In the green technique of generating AgNps, microorganisms or plants can be employed as biologicalmediator. As a result, AgNPs pesticidal action can substantially assist in pest management. AgNPs have also been demonstrated to exhibit antifungal properties, signifying that they might be used to treat plant fungal disease. Sap-lam et al. (2010) demonstrated the efficacy of UV-irradiated AgNPs in mosquito larvae bio controllability.

7.2.2 AgNPs as Nanofertilisers

Commercial fertilisers, such as urea and nitrate, are used in large quantities nowaday, despite the fact that they harm plants and beneficial bacteria. They contaminate the environment as well. Nanomaterials can help here since their high surface area allows for a slower release of agrochemicals than standard materials. AgNPs have a number of distinct properties and as a plant nutrient, they can be used to improve nutrient uptake efficiency. In comparison to bulk silver, nano silver enhances nutrient uptake from the soil. As a result, it's suitable for both crop protection and crop protection. They could be used as nanofertilisers in the future.

The ability of AgNPs to increase seed germination in a range of plants has been described. Nanofertilisers help to distribute nutrients slowly and effectively, decreasing nutrient loss. Plants can take more nutrients from the soil with the help of nanofertilisers (Shao et al. 2018).

7.3 Catalytic Elimination of Contaminant Dyes

Anionic and cationic dyes are two types of organic contaminants that are commonly utilised in different applications. Organic dyes are extremely important in paper, leather, textile, culinary printing, plastic and pharmaceutical industry since they are in such high demand. These manufacturing operations, pollutants are the most significant contributors of environmental contamination. They cause unwanted turbidity in water, that reduces penetration of sunlight, resulting in photochemical synthesis resistance and biological attacks on aquatic and marine species. As a result, one of the most difficult tasks in environmental chemistry is the control of effluents containing colours. The need for clean, germ free and safe drinking water is increasing day by day. Given this, the utilisation of metal and metal oxide NPs for oxidising harmful contaminants has become a hot topic in contemporary material science research (Fowsiya et al. 2016).

Many surface reactive sites on NP surfaces boost the NPs surface energy. As a result, in comparison to bulk material, a smaller amount of nanocatalyst is necessary to clean dirty water. Metal nanoparticles, like metal oxide nanoparticles, demonstrate improved photocatalytic degradation of several contaminant dyes; for example, AgNPs generated from *Z. Armatum* leaf extract were used for contaminant dye degradation. Hatamifard, Nasrollahzadeh and Sajadi (Hatamifard et al. 2016) synthesised an Ag/zeolite nanocomposite from *Euphorbia prolifera* leaf extract and used it to catalytically reduce methylene blue, congo red, rhodamine B and methyl orange. Furthermore, the antibiofilm result shows that biofilm inhibition was considerably high in both *S. epidermidis* and *P. aureginosa* bacteria exposed to AgNPs (Balaraman et al. 2020). Ag-NPs could be considered as an alternative and effective nano-drug for various bacterial infections, anticancer therapy and environmentally friendly insecticides (Balaraman et al. 2020). Furthermore, AgNPs demonstrated the photocatalytic destruction effectiveness of hazardous dyes in aqueous solution.

Heavy metals are well-known soil, air and water contaminants. Automobile emissions, plastic, natural gas, mining waste, coal, dye and paper industries are only a few examples of heavy metal contamination. Even at trace ppm levels, several metals have increased toxicity potential. As an outcome, identifying hazardous metals in the biological and aquatic environments has become critical for effective remediation (Annadhasan et al. 2014). Because of their variable size and distance dependant optical properties, metallic NPs have been used to detect heavy metal ions in polluted water systems. Metal NPs can be used as colorimetric sensors for heavy metal ion detection in environmental samples since they are simple, cost-effective and have an elevated sensitivity at sub-ppm levels. Karthiga and Anthopny (2013) produced AgNPs utilising a variety of plant extracts that may be employed as colorimetric sensors in water for heavy metal ions like Cd, Cr, Hg, Ca and Zn. Similarly, AgNPs made from fresh and dried mango leaves showed selective sensitivity for mercury and lead ions. AgNPs made from green tea extract pepper seed extract and also demonstrated selective sensitivity for Pb^{2+}, Hg^{2+} and Zn^{2+} ions (Karthiga and Anthopny 2013).

7.4 *AgNps as Sensors*

A chemical sensor is a device that measures the presence and/or concentration of analytes. Colorimetric, optical and electrochemical sensors stand out among them because they have been used to analyse environmental samples successfully (de Almeida et al. 2020). Karimi and Samimi 2019 determine Hg^{2+} in mineral and tap water in a wide concentration range using a colorimetric sensor and AgNPs produced from the algae *Chaetomorpha spiral*. The amount of light absorbed, the fluorescent properties of the examined molecules, or a chemical-optical transduction medium are all used to quantify analytes using optical sensors. This type of sensor has been successfully employed to detect Fe^{3+} in water using AgNPs derived from *Solanum lycopersicums* extract. Electrochemical devices, on the other hand, can translate analyte-electrode interactions into electrical signals. The modification of sensors with NPs to get simple and portable devices with low cost, high sensitivity and selectivity (Turunc et al. 2017) is an important application of nanotechnology in electroanalysis. As a result of their outstanding electrocatalytic activity, AgNPs have been successfully used in the modification of sensors for the analytical determination of substances that are readily present in the environment.

8 Challenges and Future Perspectives

In current years, research/study on NPs and their potential applications has advanced at a breakneck pace. Plants, yeast, algae, fungi and bacteria all are expended in the green manufacture of Ag metallic NPs, according to several researches. However, a number of impediments to large-scale fabrication and subsequent application purposes remain. The following are some of the most critical challenges to consider: size controlling and form controlling of the NPs, convincing and sufficient studies on reactants like plant extract, fermentation medium and composition, microbe inoculum optimisation to be focused. And also process parameters like rotational speed, pH, temperature, etc. are necessary and are to be focused. As a result, getting AgNPs to have a constant size and form is still a work in progress. AgNPs with improved physicochemical characteristics for specific applications must also be a research priority. Prioritise the use of green synthesis technologies to scale up AgNP production for commercial reasons. To improve AgNP production and stability while minimising reaction time, several reaction parameters must be optimised. Green synthesis options for large-scale NP production, particularly silver, could become cost-effective and equivalent to traditional processes if these barriers are overcome. Researchers should also focus on separating and purifying NPs from the reaction mixture. A careful toxicological examination of the metallic NPs on animals and plants is also essential to widen the applicability in other sectors including environment.

9 Conclusion

To summarise, numerous efforts have been done in recent years to create green silver nanoparticles (AgNP). A rising understanding of green technology, as well as the usage of green pathways and techniques for various NPs, including AgNPs synthesis, spurred the development of eco-friendly approaches. This chapter covers the most trending developments in the Ag-NPs green synthesis and its eco-friendly employability in water and wastewater treatment, agrosystems using nanoparticles as nanopesticides and nanofertilisers, catalytic removal of pollutant dyes and as sensors.

Focus was on the study of plant-mediated and microbe-mediated synthesis of Ag-NPs. It is noted that plant-mediated synthesis has been widely embraced in comparison to microbe-mediated synthesis. To a great extent, research is done and is going on, on the green synthesis approach for Ag-NPs due toits environmental friendliness, availability easily and less pricy. A careful investigation and strategies for green-mediated large-scale AgNP production, controlling the size and form of NPs, separation and purification, toxicological examination are to be focused which will leave no stone unturned in developing the AgNPs in wide variety of applications.

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Bioremediation of Heavy Metal Contaminated Sites Using Phytogenic Nanoparticles

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Abstract Heavy metals (HMs) accumulate in milieu due to various human activities that persist leading to biomagnification in food chains and cause unpleasant effects on human health and environment. Pollutants such as organic matter and HMs are remediated traditionally by chemical precipitation, electrochemical treatment, adsorption, reverse osmosis, ion exchange, coagulation, and photo-catalyzation, remained ineffective. Use of nanomaterials conjugated with various compounds showed significant reduction in several contaminated sites. However, existing implication of nanotechnology works with nanoparticles (NPs) synthesis majorly involved the use of chemical raw materials and physical methods which are relatively toxic and unstable. Aforesaid difficulties made researchers and entrepreneurs to reconnoitre effective, newer, and novel synthesis approaches for the replacement over older version. During the past decade, to overcome these issues plant-derived NPs are extensively used because of its less cost, efficiency, and eco-friendly in nature. Hence, advanced alternative technology like phytoremediation using nanomaterials with innovative techniques has been a boon for HM remediation. Efficiency of green synthesized NPs is based on redox reactions which makes metals stable facilitated by flavonoids and polyphenols responding to HM-stress. Several metal complexation processes are known to produce phytochelatins or other metal-chelating peptides helping the bioremediation of HMs. Current chapter throws light on adaptive mechanism employed by NPs coupled with plant or microbial extracts in overcoming the HM stress. Furthermore, here we also focus on the possible mechanism and interaction between NPs and HM in minimizing severity of polluted sites with many examples.

Keywords Phytoremediation · Low-cost · Eco-friendly · Flavonoids · Heavy metal stress

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1 Introduction

Human health is being a major concern in today's era due to environmental pollution. Heavy metals (HMs) are elements having a density of more than 5.0 g/cm^3. HMs with less concentration have significant importance in animals and plants with less standard consumption concentration approved by WHO (Coelho et al. 2015). HMs occur naturally on the earth's crust through weathering of sedimentary rocks, volcanic emissions contributing to the addition of a few HMs such as Chromium (Cr), Cadmium (Cd), Zinc (Zn), Lead (Pd), Nickel (Ni), Aluminum (Al), and Mercury (Hg). HMs are also emitted through natural vegetation, forest fires, sea sprays, aerosols, decomposition, and volatilization, leaching of leaves and stems, and oceanic activities (Verma and Bharadvaja 2021). Anthropogenic work is the major source of metal pollution like agricultural, industrial, domestic waste effluents, etc. HM pollution is at an alarming rate in most of the developed and rising countries due to industrialization, modernization, and intensive use of sewage sludge for manuring, pesticides, fungicides for good agricultural yield consisting of various amounts of Cr, Cd, Ni, Pb, Zn, etc. Industrial let HMs are from the activities such as mining, smelting, and recycling of metals. During the process of smelting, metals escape into the atmosphere and combine with water to form aerosols. These aerosols are deposited through wind and get precipitated during rainfall. Household waste mainly detergents and untreated or mechanically treated industrial wastewater, substances escaped from the biological treatment plant consist of HMs, which directly runoff to the water bodies pose serious problems on water organisms and plants (Thakare et al. 2021).

Further, HMs contamination has been a cause of concern worldwide due to its lethal nature and existence in the environmental system (Uchimiya et al. 2020). HMs accumulated in the plant body contaminate the food chain and cause an adverse ill effect on human health. Several research reports have displayed the toxicity and severity of HMs on biological systems (Alengebawy et al. 2021). Several techniques have been introduced in the past few years for the *in-situ* and *ex-situ* HM remediation from the contaminated soils like vitrification, soil flushing, electrokinetic extraction, solidification, surface capping, and bioremediation. However, use of bioremediation has been beneficial using plants and microbes to remediate HMs has certain limitations like initial operational costs, lack of suitable parameters for the growth of microbes etc. (Rahman and Singh 2020). Implementation on commercial scale for bioremediation requires the progress of innovative techniques that are recyclable, less expensive, non-toxic to the environment. The uses of HMs immobilization are one such method that needs to acquire and develop newer technology to develop the decomposable adsorbents. In order to handle such challenges, in current existence the use of Phytonanoremediation with engineered nanoparticles (NPs) has aroused to be another useful remediation method (Shafi et al. 2021) which comes from plant origin. Nanoremediation depends on the unique characteristics of the NPs like small size, shape, large surface area, and their high reaction to get freed from HMs from the ecological system. Newer techniques have put forth themselves in the environment to control pollution, to behave as scavengers of pollutants, in wastewater treatment, and so on. This technique is advantageous as requires minimal time to clean up, protracted duration effectiveness, and decreases certain HMs concentrations to near zero. Many studies have used these NPs in various applications and they have significantly helped in improvising plant growth and development by alleviating the toxicity of HMs (Hussain et al. 2019). Recent studies have conveyed the potential efficacy of the nanoremediation approach by using zero-valent iron NPs in HMs (Cd, Pb and Zn) remediation (Fajardo et al. 2020). Prominent research emphasized phytoremediation as a proposed lot of scope in researchers to further work in the field of nano-sized green chemistry, it has made researchers manifest microbes for synthesizing nanomaterial (NM). The components such as enzymes, exopolysaccharides, peptides, proteins derived from microbes such as bacteria, fungi, microalgae, actinomycetes, and viruses are the main source in synthesizing NPs (Annamalai et al. 2021).

2 Occurrence of Heavy Metal, Toxicity on Health and Environment

Toxicity issues with the environment are growing rapidly in turn affecting the livelihood of the human being. Amongst various toxicity, one of the most common and detrimental situations is contaminations with HMs. This is predominantly due to rapid industrialization and other human activities. The problems with HMs are its long natural half-life contrasted with other xenobiotics and are non-biodegradable, damaging, stable, and get aggregated with candid biological outcomes in the surroundings. Prolonged contact to HMs such as Cd, Cu, Pb, Ni, and Zn has ill effects in humans (Singh et al. 2016). HMs exist naturally through the action of wind during weathering of rocks, volcanic eruptions, and forest fires. The artificial causes of HMs are urbanization, mining, industrialization, smelting, fossil fuel combustion, electronic industrial combustion, vehicle exhaust, etc. (Fig. 1) (Alloway et al. 2013) The development of industries such as petroleum, electroplating, chemical, and dye industries has increased the usage of HMs as raw materials to fulfil the needs of the growing population; (Kabir et al. 2020). The maximum cause of pollutants such as As, Cr, Pb, Hg, Ni, Zn, Cu, and Cd is due to coal combustion, excessive use of pesticides, cement dust, etc. (Archana et al. 2021; Huang et al. 2018).

a. **Lead**
   Pb is released naturally in the environment through volcanic eruptions, aerosols, and anthropogenically through the burning of fossil fuels, mining, and industrial activities. It is used in lead acid batteries, shied x-ray, pipes, and soldering. Pb is a highly toxic HM and its widespread has caused negative impacts on the environment. Even it is used in paints where children playing barefoot are inhaling the lead dust which is toxic to them. Exposure to lead dust and aerosols, taking in lead contaminated food, drinking water leads to lead poisoning in human beings. Absorbing these metals from the soil has a toxic effect on metabolic processes such as electron transport chain, cellular organelles integrity, membrane stability

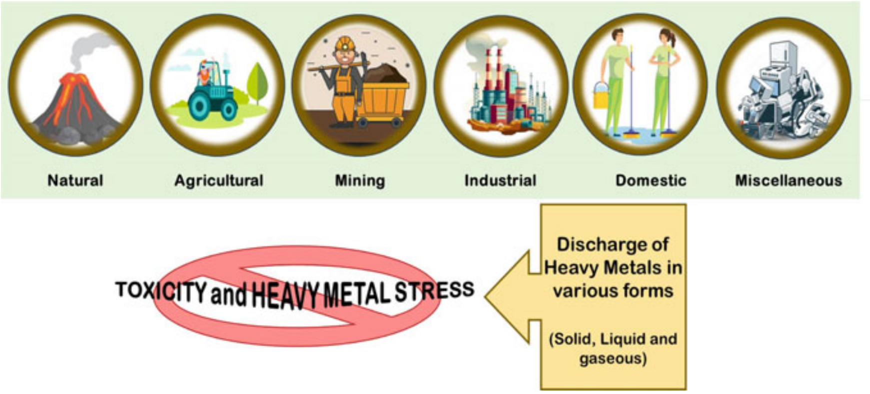

Fig. 1 Illustration of various activities through which heavy metal is released to the environment causing metal toxicity and also challenges the organisms for heavy metal induced stress

index, mineral metabolism, oxygen-evolving complex, and enzymatic activity. Pb toxicity is observed due to its accumulation and exhibiting oxidative stress. Its exposure is more concerned in the case of pregnant women because inhaled lead gets into the fetus directly causing reduced birth weight with preterm delivery and neurodegenerative disorders. The toxicity is exhibited through the biochemical mechanism, where lead mimics the function of calcium and attaches to the sulfhydryl group and amide group of enzymes by changing their conformation interfere with protein. Pb toxicity causes aberrations at the gene and chromosomal level leading to morphological changes observed in rodent cells. Absorption of Pd creates stress at cellular level by causing destruction to lipids, DNA binding proteins, DNA repair mechanisms, and tumor suppressor genes (Fig. 2) (Dipaolo et al. 1978).

b. **Chromium**

Cr is commercially used in pain dye industries, lather tanneries, also used in cooking structures and boilers anticorrosive agent. Cr being the most abundant metal exists in nature as divalent, trivalent, and to hexavalent. Trivalent form of Cr occurs in stable form in ores, next stable form of chromium is hexavalent. Cr enters in to the earth crust naturally and anthropogenically through industrial activities. Largest anthropogenic source is through industries such as stainless steel, chromate producing, tannery industry, and chemical industries. Severity of toxicity is decided by the valence form of Cr present in the atmosphere. Amongst them trivalent Cr (III) and hexavalent Cr (VI) are more dangerous to humans. The salt forms of chromium called chromate are produced through smelting, roasting, and extraction process. Non-occupational humans get exposed through ingestion of Cr containing food. Labourers working extensively in this Cr-based industries are more prone to diseases due to inhalation of Cr (VI) which further gets reduced to its intermediates such as Cr (II), Cr (III), and reactive oxygen species (ROS) like superoxide, peroxides, alpha-oxygen hydroxyl radical and

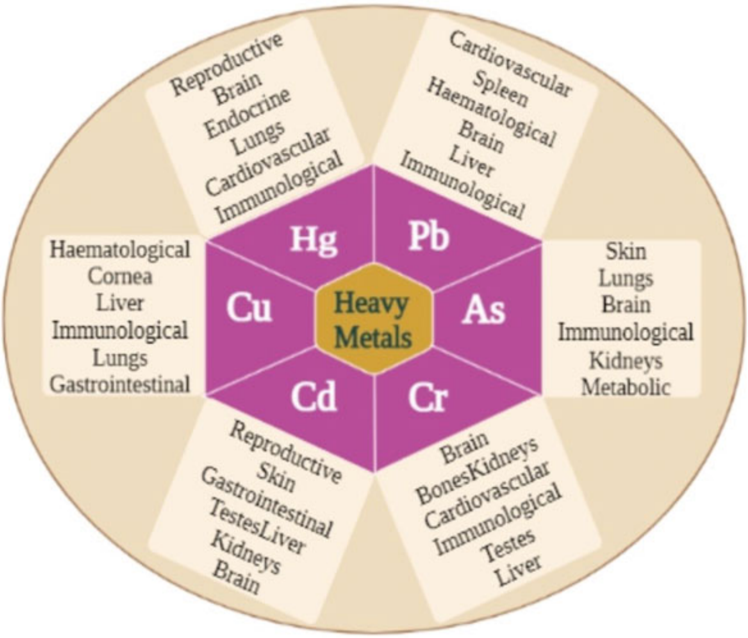

Fig. 2 Ill-effects of heavy metals on the human health and disorders caused at cellular levels in various organs due to over-accumulation of several heavy metals

singlet oxygen which also effects at genetic level. The trivalent form of Cr is also toxic and causes cellular damage. Intense mining and other industrial activities have caused Cr pollution in water that has shown skin damages by absorption in the communities utilizing the same water for domestic activities. Along with these other diseases like lung cancer, skin allergy, and kidney damage are also induced (Fig. 2). Chromite being exposed to the environment due to a lot of mining activities has proven to be a carcinogen and a lot of research has been progressed in this field (Das et al. 2021).

c. **Cadmium**

Cd is present in ores as carbonates, sulfides, and oxides in zinc, lead, and copper (Cu) ores. Cd is toxic and considered to have no known biological significance in humankind. Cd enters through both normal and artificial activities such as smelting, fossil fuel burning, fertilizers, electroplating, paint industries, etc. Cd on accumulation leads to organs like liver, kidney, and testes damage the causing poor filtration of HMs. Cd toxicity is observed to induce dysfunction in spermatogenesis leading to apoptosis of cells and less sperm production. In plants, Cd induces stress on seed germination, photosynthesis, and other physiological activities (Omidifar et al. 2021). Like other HMs Cd toxicity also produces ROS are liberated as free radicles to combat oxidative stress created in the organisms due to metal accumulation. The immune system is adversely affected by persuading inflammatory responses about gene expression and susceptibility to microbial contaminations. Similarly, in humans when get exposed to HMs mainly through food, drinking water also inhaling cigarette smoke which negatively impacts human metabolism and results in high mortality seen worldwide. Hence, exposure to Cd leads to cancers like breast, lung, prostate, pancreas, and kidneys (Fig. 2). Kidney and liver are the two organs severely get affected by Cd contamination by synthesizing metallathionein protein, which binds tightly and prevents the cells from oxidation. Other dysfunctions like arthritis, neurodenerative diseases, atherosclerotic diseases, lung fibrosis, kidney injuries, liver toxicities low level leads to cardiovascular diseases were also documented due to Cd overaccumulation.

d. **Arsenic**

As is the naturally found metal in the soil, water as a process of volcanic eruptions, leaching of rocks, and sediments. The occurrence and toxicity of As in an aqueous system can be identified and quantified based on its presence in different forms. As present in trivalent (arsenate) form is more toxic compared to pentavalent form (arsenate). Several of anthropogenic activities like the usage of herbicide, pesticide, burning of fossil fuel, gold mining, etc., employs the usage of excessive heavy metal which badly gets accumulated in the soil and enters the food chain. The main source of arsenic is arsenite (III) and arsenate (V) enters through food, air, potable water in the inorganic form. Whilst an organic form of arsenic arsenolipids, arsenobetaine, arsenosugars is obtained from marine organisms such as fish, jellyfish, and algae, which are non-toxic as the atoms of As are held up tightly and are not available freely to bind with the proteins (Fayiga et al. 2007). Extensive usage of As contaminated water leads to carcinogenic and non-carcinogenic impacts based on a particular area. High concentration of As found in drinking water is leading to many pathological disorders like cardiovascular diseases, neurological disorders, renal disease, hearing impairment, diabetes, anemia, eosinophilia, in turn, affect all the organ systems (Fig. 2).

e. **Mercury (Hg)**

Hg accumulates naturally through volcanic eruptions, weathering of rocks, and human activities like mining, incineration of waste, burning of coal for domestic usage. Metallic mercury is used in dental fillings, thermometers, bulbs, and batteries. Hg is a predominant metal present in both organic and inorganic forms, which binds to sulfhydryl groups present in protein and inactivates it leading to oxidative stress created by ROS. Several microbes convert Hg to methylmercury and get accumulated in small fish and jellyfish through intake of planktons and it gets biomagnified as predator fish feeds on smaller fish. Both elemental and methyl mercury are toxic, inhalation of this metal leads to neurodegenerative disorders. A neurological and behavioural disorder that leads to insomnia, vomiting, memory loss, headaches, tremors, etc. was observed (Fig. 2). Other than that it also causes digestive and kidney disorder and prolonged exposure to Hg in the form of methyl chloride can induce cancer (Mulware et al. 2013).

3 Synthesis of Green Nanoparticles Over Chemical Nanoparticles

Ever since several decades usage of NPs occupies a prime part in the remediation of HMs. NPs emerged as an outcome that facilitated a widespread application in various industries and in the arena of research because of their nanosize (1–100 nm) (Kaur and Roy 2021) and most importantly their involvement of matter relating to their atomic and molecular balance. NPs are synthesized artificially using chemical and physical approaches which are quite exclusive, and the chemicals utilized are noxious, that put deadly properties on the environment (Roy et al. 2022). To overcome the effects of chemicals, recently, the biological method is used for synthesizing NPs. The living organisms can be employed in this production of NPs such as microorganisms, fungus, and plant cells. Biological extracts have proved to be beneficial as constantly tangled with redox reaction to synthesize safe, eco-friendly, less expensive, and resourceful nano-sized particles via physicochemical method to minimum usage of toxic chemicals (Table 1) (Nagore et al. 2021; Pandit et al. 2022). In contrary, physicochemical methods used in NP synthesis involve the reduction, electro-reduction, photochemical reduction, high-temperature thermolysis, micro-emulsion, pulse plasma mediated, microwave-assisted, sonochemical and others using toxic as well as hazardous substances (Annamalai et al. 2021). The major contributor of green synthesis (GS) of NMs is contributed by plants using its extracts from leaves, seeds, fruits, flowers, peels, etc., and microbes such as algae, fungi, and bacteria. The NPs extracted from such organisms are more suitable for environmental cleaning application in the field of metal remediation, as biosensors, nanomedicine, nanotherapeutics (Pattanayak et al. 2021). They act as anticancer, antioxidant, and also as an ability of ROS scavenging. Most importantly a report shreds of evidence on plant-mediated NPs which have shown the capacity of inhibiting cancer cell proliferation. This however shows the sustainable development of NPs utilizing green technology.

3.1 Microorganisms-Based Synthesis of NPs

Microbe synthesized NPs occur through bioaccumulation, biosorption, biomineralization, and bioprecipitation process by reducing the metal ions to nanometals with the support of cell biomolecules (DNA, proteins, carbohydrates) under two different methods such as intracellular and extracellular methods. The intracellular method involves trapping, bioreduction, and capping in the procedure of synthesizing NPs. The major structure of the microorganisms involved in the uptake of nanoparticles is the the cell wall. The positively charged metal ions interact electrostatically with the negatively charged cell wall and reduce the metal ions into nano-sized in presence of cell wall proteins and diffused out of the cell. In the case of fungi the metal ions are reduced to nano-metals due to the enzymes present on the cell wall. NPs formed

Table 1 Formation of different forms of NPs through metal oxides with their wider applications on various fields of environmental remediation

Nanomaterials	Different types of nanoparticles	Advantages
Metallic NPs (MtNPs)	Copper Iron oxide Zinc oxide Titanium oxide Magnesium oxide	High chemical reactivity High biocompatibility Large surface area High stability Small size
Polymeric NPs	Chitosan Alginate-based NPs	Hydrophilic nature Higher stability Biocompatible Biodegradable Non-toxic
Carbonaceous NPs	Carbon nanotubes Graphene nanosheets Graphene oxide nanosheets	Thermal conductivity Dynamic interactions Light mass density Large surface area Hollow structure High porosity
Nanocomposites	Biochar supported zerovalent iron Alignate-based Silica coated Graphene-based	Electrical and thermal conductivities Toughness Higher stability High surface to volume area Mechanical strength

have different sizes and shape depending upon the microbes, example *Rhodopseudomonas capsulata* shows the ability to synthesize NPs of 10–20 nm at pH 7 but same was altered at pH 4 whilst producing AuNPs. Another study employed *Deinococcus radiodurans* for the GS-AuNPs which was observed in cell wall of extracellular spaces and cytosol confirmed by transmission electron microscopy. Here it revealed that Au^{3+} readily acts together with proteins, carboxyl, phosphorus, and amine group to form Au^0 with the capping groups to stabilize NPs (Li et al. 2016). Along with AuNPs, AgNPs were also synthesized by *D. radiodurans* at varied concentrations of temperature, pH and at different HMs concentrations (Kulkarni et al. 2015). The morphology and cell size both are dependent on the environmental stress during the synthesis of NPs (Chen et al. 2017; Li et al. 2016). The importance of GS-NPs lies with the involved bioactive compounds acting as reducing agent, forming the capping and conjugates with intracellular enzymes, sugar molecules, canonical membrane proteins, NADH, FAD, and their derivatives. A recent study by Zou showed that

Shewanella and *Geobacter spp* featured have good potential in extracellular reduction used to synthesis NP-based nanoconjugates using graphene for extracellular electron transferrin (Zou et al. 2021). In parallel a recent study also demonstrated the Graphene oxide-Nickle oxide nanocomposites performed itself as an excellent adsorbent for the chemisorption of the HM removal from contaminant waste water with less cost (Archana et al. 2021). If this kind of nanocomposites is engineered with plant origin, they may have good bioremedial potential in minimizing the HMs in urbanized population. Another study focusing on NPs formed by endopythic plant *Cuprividus spp.* extracellularly synthesized spherical particles of AgNPs (10–50 nm) through an enzymatic reduction of Ag ions to AgNPs in presence of amides. In addition, *Berberis lyceum* having endophytic bacteria *Bacillus cereus* also exhibited good yield in the production of AgNPs (Mujaddidi et al. 2021) and marine bacteria, *Marinobacter algicola* are a good resource for biosynthesizing AuNPs. Apart from having environmental application these phytoNPs found to be tremendous good in exhibiting antimicrobial activity, anticancer activity, and anti-inflammatory activity. Several genera of fungi involved in fungal mediated GS metal due to occurrence of large amounts vitamins and essential aminoacids in them (Priyadarshini et al. 2021). Few include *Verticillium spp*, *Fusarium oxysporum,* P*ycnoporus sanguineus* are well-known give AuNP and AgNP both extracellularly or intracellularly. Amongst many fungi white rot fungal species are efficient in giving remarkable yield 98.9% AgNP with the diameter of 52.8–103.3 nm. These NPs coupled with proteins extracellularly by mycelial surface are responsible for bioreduction which is confirmed through Fourier transform infrared spectroscopy. *Fusarium solani* filtrate comprising chitosan forms a rich source of cell-free fungal protein is a promising way of synthesizing NPs having the size ranging from 2 to 18 nm act as adsorbents for the removal of HMs like Cu^{2+}, Pb^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+}, and Fe^{2+} (Mohammed and Khedr 2021). It is an important tool in biofabricating NPs with its monodispersity, specific size, and potential applications because the fungal system is considered to possess various characters comprising high wall binding capacity, easy handling of biomass, and culturing.

3.2 Plant-Based Synthesis of NPs and Phytonanotechnology

Plant crude extract is considered as good source of secondary metabolites including alkaloids, tannins, phenolic acid, flavonoids, and terpenoids which have outstanding redox prospective in combining with MtNPs formation. The syntheses are popularized as GS which is booming as a powerful tool in the biotechnological field of research and innovation. These metabolites are constantly involved in the redox reaction to synthesize eco-friendly nano-sized particles. Several ideas are validating the biosynthesizes of NPs known to meritoriously control the play between oxidative stress, genotoxicity, and adaptions. In the biological method, the bioactive agents such as plants and microorganisms are manipulated to synthesize NMs that actively take part in cleaning up the pollutants without driving any negative impact on the environment (Roy et al. 2021).

Since, plant is an excellent model of synthesizing and stabilizing the NPs with the help of plant-derived chemicals such as terpenoids, sugars, aldehydes, ketones, carboxylic acid, proteins, amides, etc. these NPs are helpful in the detoxification of HMs even a small trace of them are toxic to the organisms. Plant leaf extract is an important phytochemical which is required to reduce the metals to metal oxide NPs. The functional groups of the plant exudates have an important function in the reduction of metals to metal oxide. The application of plants over the metal contaminated area converts it to a simpler form by adsorbing it onto the surface, organs, and tissues. The biofabricated NMs derived from plant extracts discover wide applications due to its phenomenon of photo and enzymatic catalysis, electrostatic interaction, surface-active site interactions for detoxification of the pollutants. These bioactive compounds are considered to be taking part as biological entities that act as bionanofactories possessing the capacity to synthesize biochemicals that are involved in NPs synthesis. NMs that are biofabricated with the plant and fungal extract have shown higher potentiality in adsorbing the pollutants. Fungal extract such as protein and enzymes shows reducing activity which can be used as biofabricating materials are with high stability (Gade et al. 2014).

Several plant-derived NPs are known to reduce the salt content in the soil and stabilize it by capping. There are many NPs synthesized utilizing different parts of the plant such as the bark of Cinnamon, lemongrass, neem leaves, tannic acid, and various plant leaves, flowers also Au, Ag, and PdNPs are synthesized by plant extract (Fig. 3) (Agarwal et al. 2017). Any part of the plant is taken and it is crushed and put into the boiling water with continuous stirring and finally, it is filtered and further characterized by via Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, photoluminescence analysis (PL), transmission electron microscopy (TEM), scanning electron microscopy, energy dispersion analysis of X-ray, X-ray diffractometer, atomic force microscopy, X-ray photoelectron microscopy and UV–visible diffuse reflectance spectroscopy.

In the current chapter we are concentrating more on HM bioremediation via the phytonanotechnology as biosorption and any other chemical and physical methods

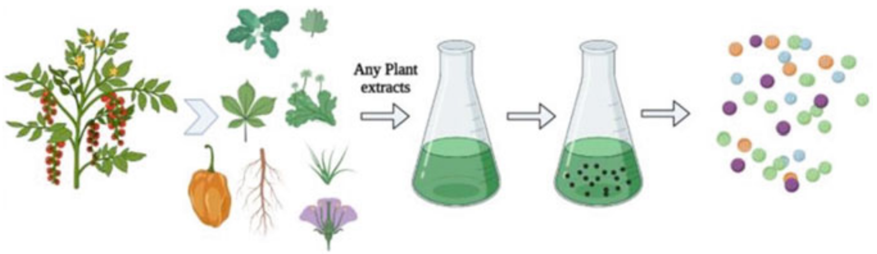

Fig. 3 Plants are loaded with bioactive components which form a necessary ingredient to produce and synthesis nanoparticle to obtain complex structure conjugated with metal ions

are very expensive. Several of the metal oxides conjugated with plant extracts were studied so far and in recent years Fe-based NPs are used as a wider option due to its biocompatible and less expensive nature. Fe-based bioremediation is used for scavenging HM pollutants, nitrates organic dyes, etc. HMs including Cr, Cd, As, and Pb are remediated from the aqueous medium. Therefore, FeNPs supported with porous material such as kaolinite, bentonite, and zeolite (Kapahi and Sachdeva 2019). Neem leaf broth extract consists of terpenoids along with proteins, enzymes, amino acids, phenolics, and other components are important in reducing Ag ions. The functional groups such as the keto, amide group help in capping the metallic substances to MtNPs. Three important components essential in synthesizing AgNP are silver salt, reducing agent, stabilizing or capping agent. In this GS procedure, metal in the solution taken along with the leaf extract that acts as a reducing agent which converts the metal ions into NPs, the biochemical compounds present in the plant extract such as polysaccharides, proteins, enzymes, vitamins, and amino acids act as reducing agents (Fig. 3). The mechanism embroils; first, the Ag metal being trapped by surface proteins and reduced to its secondary structure called silver nuclei. Further, these Ag nuclei grow and settle at nuclei. Not only proteins even aldehydes, amides, and other functional groups help in reducing Ag ions to AgNPs (Chung et al. 2016). Likewise, AgNPs and other NPs are synthesized by utilizing the plant extract which will be more eco-friendly, less expensive accomplishing the greener world. Amongst many other metals, AgNPs have grabbed attention due to their characteristics and application in varied fields like agriculture, sewage water treatment, pharmaceuticals, textile industries, air filtration, and also act as an antibacterial against various bacteria without harming animals (Yadav et al. 2021). The capacity of plants in transforming the huge energy derived from the sunlight to form into biomass shows the ability to fabricate stable NMs in large capacities at less expenditure in minimum time. Based on this, NPs are synthesized industrially through tissue culture and downstream processing techniques for optimization.

Several of GS-NPs are studied for its exceptional remediate properties like reactive surface with hydroxyl groups with modifications it becomes functional by various alterations for surface functionalization and surface modifications seen in various plant extracts like *Capsicum annuum*, leaf extract of Magnolia, *Acalypha indica*, bark extract of *the Cinnamon zeylani and many others* (Ahmad et al. 2020). Nanocellulose derived from cellulose, consists of polymeric fibres which are less than 100 nm in diameter and has large surface area, automated strength, thermal stability, and biocompatibility it is been considered as potent biosorbent used for many environmental bioremediation including HM adsorption (Sharma and Kumar 2021). Chitosan nanolayer formed by the TiO_2NPs is used for HM detoxification in the soil and water is also been synthesized by using a leaf extract. Utilization of microwave technique was employed in this synthesis of TiO_2NPs, which showed powerful adsorbent and removed 88% of chromium from sewage waste water (Yu et al. 2021). Main principle being plants and parts of the plant used are a decent source flavonoid (like flavonols, flavones, flavanols, flavanones, isoflavones, and anthocyanidins), quinones (having the derivatives of aromatic compounds such as benzene or naphthalene) as well as phytosterols (Campesterol, Stigmasterol, β–Sitosterol and Avenasterol) substantiating as commendably reducing and stabilizing agents in synthesizing AuNPs is an ideal approach in recent years. However, metabolism of living plants is utilized in the production of tailored uniform sized NMs that are harvested from plant cells and tissues with the help of enzymes. In the course of synthesizing, many metal ions that are surrounded on the cell wall enable the reduction in presence of several enzymes or metabolites during the extracellular production of GS-MNPs (Fig. 4). Various microbes associated with plants also synthesis intracellular transport systems in which the negative charge of the cell wall plays a key role acting as a driving force to pull the positively charged metal ions in depositing on negatively charged cell walls with the help of electrostatic interactions. Metal ions after being transported into the cell get accumulated in the periplasmic region and cell cytoplasm followed by which sequential metabolic interactions take place with the participation of enzymes such as nitrate reductase and others to decrease the metal ions in the intracellular production of GS-MNPs (Fig. 4) (Tiquia-Arashiro and Rodrigues 2016). Because of their absorption and chelation properties of the resistant plant and microbes in their intracellular and extracellular environment, related proteins dwell in metal-rich surroundings are highly resistant to toxic HMs. Hence, this technology has been exploited as it mimics the natural HM bioremeduation process as promising stratagem for the production of GS-NPs (Yusof et al. 2019). In addition, species of plant like *Salvia officinalis*, *Lippia citriodora*, *Pelargonium graveolens,* and *Punica granatum* contributed towards the GS-NPs helping in phytomining to recover Pd from mine waste materials due to its reducing and stabilizing properties attributed for bioreduction of (Shamsul Harumain 2016). Hence in this regard; in upcoming years NP remediation with the use of plant extract has found to have an immense impact. The different forms of FeONPs are like magnetite (Fe_3O_4), maghemite (γ–Fe_2O_3), and hematite (α–Fe_2O_3) are widely used in the HM remediation due to its less expensiveness, surface mobility, and magnetic properties. This helps in absorption of HM like Cr and Cd at much higher concentration, eventually helping in decontaminating the waste water. Green synthesis of this FeONPs through utilizing phytochemicals having alcoholic group helps in reducing Fe^{3+} ions. And hence GS-FeONPs are successfully proven for bioremediation process (Sebastian et al. 2018).

3.3 Plant and Microbial-Based Synthesis of Phytonanoparticles

Plant microbial association has created a novel idea against phytoremediation like arbuscular mycorrhizal fungi and plant growth-promoting rhizobacteria have an important application in improving soil and plant health by increasing the plant biomass so that it can combat stress conditions. In association with plants and microbes, nanotechnology creates a wide range of applications in the area of agriculture, drug, and remediation. An eco-friendly NPs were used as adsorbents with

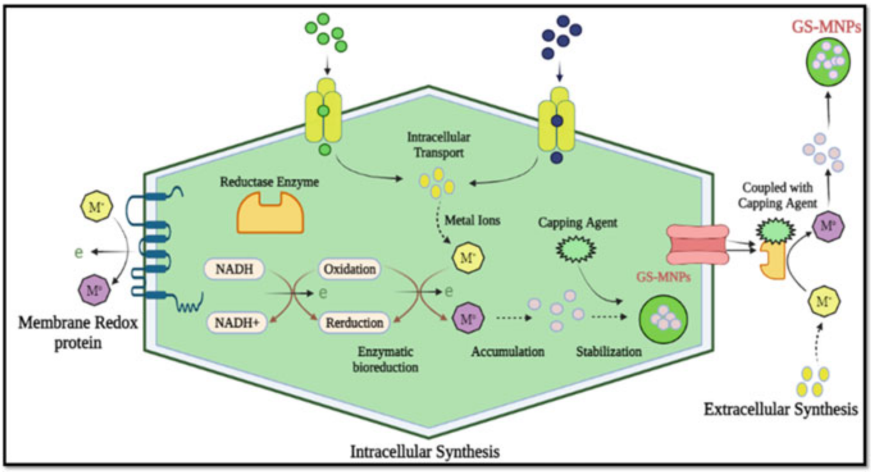

Fig. 4 Extracellular and intracellular biosynthetic pathways of GS-MNPs are depicted schematically. Metal ions are trapped on the cell wall and reduced in the presence of released enzymes or metabolites in the extracellular production of GS-MNPs. After metal ions are transferred into the cell cytoplasm, metabolic interactions involving enzymes such as nitrate reductase decrease the metal ions in the intracellular production of GS-MNPs. (GS: Green synthesis NPs mediated by microorganisms; GS-MNPs: Green Synthesis Metal NPs: M + : Reduced Metal ion in Native Alkali State; Mo: Metal Ion in its oxidized state; NAD: Nicotinamide adenine dinucleotide; NADH: Reduced form of NAD; NAD + : Oxidized form of NAD; e: Electron)

the microbial association which has high impact on the plant growth. In this context, bacteria are very useful to the plants in adsorbing the metal. Phytonanotechnology has revealed the capacity of plants to combat HM stress through NP synthesis. Microbial and plant interaction leads between the microbial cell surface and the exudates produced by the plant roots, and material present in the soil water pores. Zero-valent FeNPs in association with plant microbes help in combating environmental contaminants. It is reported that small doses of iron NPs will have a less toxic impact on the plant with respect to Cd remediation. Glenn et al. (2012) reported on the association between AuNPs and aquatic plant *A. caroliniana*, and *M. simulans*, and its remediation against HM was observed due to the release of the plant exudates into water. The AuNP gets adsorbed into the root and enters into the cell and helps in fighting against HM (Ebrahimbabaie et al. 2020). AgNPs in combination with a salt marsh plant, *Phragmites australis*, have shown the responsibility in phytoremediation of Ag. This salt marsh plant association with microbes shows remediation along with CuONPs. The use of wastewater for irrigating crops is a fashion followed from the past, to combat this rhizosphere in the soil helps plants to fight HM toxicity. In combination with rhizosphere with NPs have a wide application in remediation. NMs from both plant and animal-based possess a significant surface area, no. of active sites, adsorption capacity, and provide solicitation in remediation.

4 Mechanism of Toxicity Caused by Heavy Metals on Cellular Structures

Cellular systems have been exposed to varied concentrations of HMs that have been adsorbed by the cells over the period of time that have led to the acute or chronic effects on them. Most common of these HMs that have been manifesting cell organelles and cellular components such as mitochondria, chloroplast, lysosome, endoplasmic reticulum, nuclei and enzymes include the Hg, As, Cr, Cd, Pb etc. Cell organelles and their components help in metabolism, detoxification, and DNA repair mechanisms that are sometimes affected even at low concentrations of HMs leading to organ damage. In humans, increased toxicity of HMs has severe impact on cardiovascular, respiratory, gastrointestinal, hepatic, renal, hematopoietic, immunological, and dermatologic systems. This will lead to several types of Cancer, Parkinson disease, Alzheimer's disease, atherosclerosis, heart failure and many more (Fig. 5). As reported by Inoue et al. (2013), Hg had an increased toxic level in humans leading to neurological disorder. However, the mechanism and the toxicity shown by each metal depend on its unique physicochemical properties.

Metal ions bind to the essential cellular components causing changes in the cell cycle modulation, carcinogenesis, or apoptosis. Many studies have revealed that the oxidative stress created by HMs synthesizes ROS that gets accumulated leading to cellular damage. During the process, electron transfer chain, proteolytic cleavage, oxidative phosphorylation also creates ROS along with the immune cell signalling

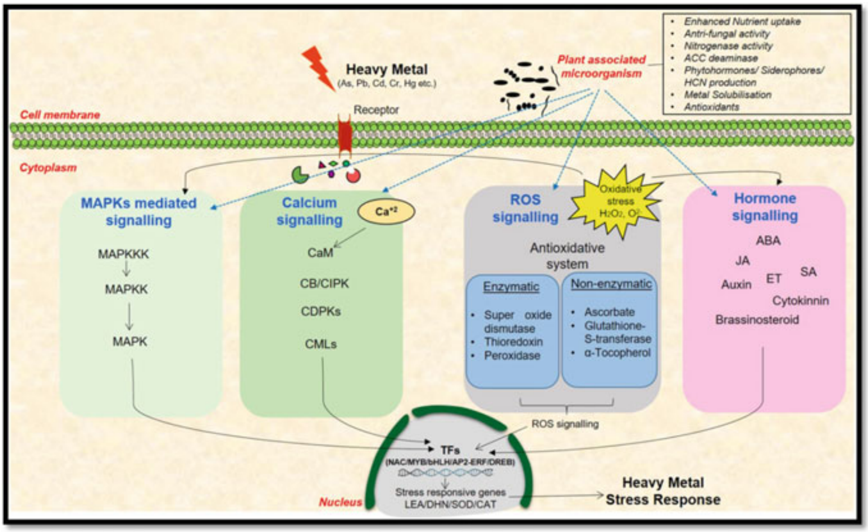

Fig. 5 Representation of various pathways triggered in various organisms when they are exposed to HMs; some adopts itself to the changing environment and other die and kill them by producing several oxidative stress intermediates as combat. Adopted from Tiwari and Lata (2018)

through the NADPH oxidase pathway. These ROS are formed by the action of cellular metabolism of the oxymolecules and through endogenous and exogenous sources. The endogenous sources include super hydroxyl anion, peroxyl radicle, hydroperoxyl radical, hydrogen peroxide, hypochlorous acid whilst, exogenous include ozone exposure, irradiation of ions and HMs. These ROS are beneficial during defence mechanism to kill the pathogens, by engulfing them through the macrophages and utilizing O_2 for generating free radicles (Fig. 5). Further, increased accumulation of free radicals leads to oxidative stress creating an imbalance in the expression of ROS which disrupts the normal cellular signalling. At low concentration it is managed by cellular activities however, higher concentration creates stress to biomolecular components including lipid, proteins, and DNA leading damage to the cells and eventually death. (Sytar et al. 2019).

5 Application of Phytonanotechnology in Heavy Metal Bioremediation

NPs due to their unique characteristics have received immense attention from researchers to use them in different fields of environmental sciences like in bioremediation. The strategy of this technique is to clean up wastes particularly the recalcitrant. Existing methods for remediation of HMs are not effective, hence NPs can be applied for bioremediation that include plants and microbes that are reducing the cost, non-toxic, and eco-friendly (Fig. 6). In recent years nanoremediation has gained its place as a major subject of research for the development of techniques that are potential for cleaning up the contaminated sites and help to protect the environment. Plant-based NPs are compatible in soil to remediate in deeper soils present with HM contaminants (Huang et al. 2016). The major application source of NPs is the nanofertilizer involving biostimulation and bioaugmentation, nanominerals via biostimulation or green synthesized nanooxidizers in the PAH oxidation that can signify as a major source of bioremediation of HMs (Lawal 2017).

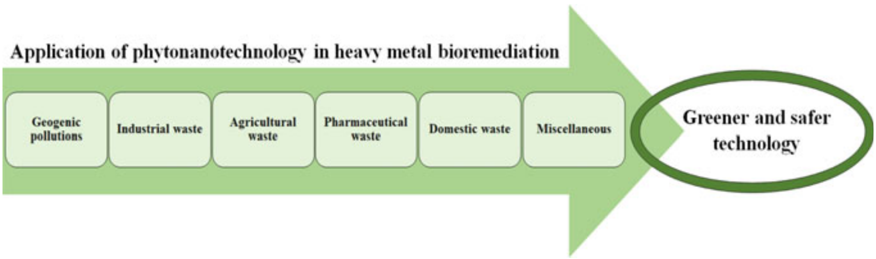

Fig. 6 Application of GS-NPs in various environmental bioremediation

5.1 Geogenic Pollutions

One of the freshwater resources is the groundwater that is used excessively for various purposes like agriculture, drinking, industrial use etc. that has been contaminated. The quality is affected by the topological and climatic approaches like landslide, earthquake, and floods. The geogenic components are As, Fluoride (F), Iodine (I), Uranium (U), Na (Sodium), Cl (Chlorine), SO_4, and trace elements such as Fe, Mn (Manganese), Cr, Selenium (Se), etc. There has been a lot of studies on the As and F in different topographical regions. With the onset of novel Covid-19 pandemic, it has contaminated the surface waters that might be under high-risk contamination that has been due to untreated municipal waste water discharge which hypothetically comprising of the genetic material RNA as in SARS-CoV-2 (Ahmad et al. 2020). With the molecular detection of such novel virus in waste water it certainly restricts the use of surface water and increases the dependency of ground water (Wu et al. 2020). In our surrounding environment that the law of limitation imposes the overuse or exploiting resources that become relevant for groundwater contamination caused by naturally occurring geogenic pollutants involving some key elements As, F–, Antimony (Sb), various phosphate (PO4 3–), Selenium (Se), and others that limit its application in a new geological anthropocene leading to the world water crisis (Kumar 2020).

The most important recorded geogenic contaminant is the As that is a well-known carcinogenic metalloid and toxicity to humans. Also anthropogenically, As and its compounds are been added by means of synthetic fertilizers and pesticides, several of drugs, food, and feed additives along with textile and wood preservatives which can easily get inside the groundwater to increase its bioavailability (Kumar et al. 2019). The effectivity of nanocrystalline TiO_2 has been used in removing different forms of As has been more successful with the combination of photocatalyst. Nanocomposites of TiO_2 NPs have been anchored to that of graphene sheets have been used to lessen Cr (VI)–Cr (III) during daylight and parallelly, Cr was bioremediated using Pd-NPs. Elimination of arsenate As(V) from groundwater was achieved by using bilayer–oleic coated iron–oxide NPs (bilayer–OA@FeO NPs in the contanimated region. High–affinity carboxyl groups are used as a part of functionalized adsorbents in several bioremedial techniques (Raval and Kumar 2021). Also its been documented that iron oxide is used to effective in the removal of As in combination with permeated mesoporous rice-husk nanobiochars (IPMN). This is mainly because of the effectiveness IPMN in adsorbing the As and along with up taking it at greater capacity of >90% with comparison to the native milled rice husk (~20%). NPs based with iron oxide like magnetite, hematite (α–Fe2O3), maghemite(γ–Fe2O3), Goethite (α–FeOOH), and akaganéite (β–FeOOH) are the finest absorbents for the removal of As, since they have easy collecting property with external magnetic response and can be reused multiple times. These plant-based NPs help to reduce the secondary pollution (Chowdhury et al. 2011; Tang and Lo 2013).

5.2 Industrial Waste

One of the major contaminants from the industries is the increased usage of synthetic dyes due to its high demand in paper, cosmetic, textile, leather, and food industries. The structural compounds present of synthetic dyes present in industrial waste water are dangerous to living organisms (Varjani et al. 2020). Cationic and anionic dyes are used in various applications and are the major class of organic pollutants. Nearly 15% of dyes are wasted and discharged into environment by fabric industries producing undesirable water turbidity, reduced sunlight penetration, leading to the resistance of photochemical synthesis, disrupting aquatic and marine life. Thus, these synthetic dyes represent a significant recalcitrant pollutant (Ananda et al. 2022). Therefore, effluent management with dyes is one of the daunting challenges in the treatment options.

MtNPs have been utilized in many applications that include medical, agricultural, and industrial aspects. Green synthesis of NPs using biological extracts specially, plant sources has exhibited superiority over chemical forms. Plant-based cellular molecules endure high controlled assembly for making them most suitable metal NP synthesis. The *Padina tetrastromatica*, leaf extract has been used for biosynthesis of AgNPs that has been efficient in degrading the direct brown 95 and Congo red dye, a technique that is eco-friendly and less expensive method. It has also been used in the water purification and to harness the photo catalytic activity (Varun and Prabhu 2014). A study done by Ananda et al. (2022) revealed that green synthesis of Magnesium oxide by *Phyllanthus emblica* also called as amla juice serves a good source for the degradation of Evans blue which is seen in waste water of tedtile industries. The GS-NPs are favoured by the presence of several of amino acids like aspartic acid, methionine, lysine, glutamic acid, alanine, tryptophan, and proline in the amla juice. Along with this amla juice is a rich source of tannins like emblicanin A and B, gallic acid and ellagic acid. It also contains many oligosaccharides, sucrose, inorganic salts, reducing sugars helping the quick reduction of magnesium nitrate to reduce to magnesium oxide.

Micropollutants gain entry due to improper discharge of untreated wastewater, and disposal of pesticides and insecticides used in farming in the nature due to various human activities that are a threat to health and environment. Nanobiochar has been used for various environmental applications like carbon sequestration, bioremediation specially with plants i.e. waste controlling, pollutant deduction, wastewater effluent treatment etc. A good adsorbent helps in eliminating pollutants like medical, steroid hormones, agrichemical, toxic metals, and personal care products. Nanobiochar and biochar along with nanominerals observed to exhibit exceptional remediation to these various contaminants. For example, Pine wood-derived nanobiochar was able to remove micropollutants and 95% carbamazepine from waste water (Naghdi et al. 2019).

5.3 Agricultural Waste

With increasing population, the demand for agricultural activities has imposed a negative impact on the environment with a serious risk to soil, underground marine, and vegetation that affect human health. The geogenic sources such as As, F, U, Na, Fe, Mn (Manganese), Ni, Cr, Co (Cobalt), Cu contribute HMs to the soil by various factors like chemical fertilzers etc. (Cangemi and Kuo 2019). Rice being the staple food for humans has increased concentration of HMs due to the activities like mining located near water bodies and agricultural fields. It has been observed that Cd, As, Pb, Hg, Co, and Cu concentration affects rice plants by accumulating into the root, shoot, and grains. Humans exposed ingestion of metal-contaminated food led to carcinogenic effects (Archana et al. 2021).

Numerous investigations have asserted on the metal bioremediation through plant-associated NPs. The symbiotic association of plants, microbes, and NPs has shown future promising prospects in the field of agriculture. MtNP is synthesized by physical, chemical, and biological methods. The use of harmful chemicals, luxurious equipment, generation of high heat, utilization of high energy, and less production yield are shortcomings of physical and chemical processes (Gahlawat and Choudhury 2019). Environmental friendly MtNP emphasizes on using biological channels such as microbes, microbial, enzymes plants, polysaccharides, and degradable polymers (Roychoudhury 2020). Microbes have gained a particular place amongst the many biological sources for the green synthesis of MtNPs due to their rapid growth rate, ease of cultivation, and capacity to grow under ambient temperature, pH, and pressure conditions (Ali et al. 2020). Plants and microbes as biofactories for MtNPs synthesis include Ag, Au, Cu, Zn, titanium, palladium (Pd), and Ni accomplished by defined shape, size, composition, and monodispersity (Khan et al. 2020).

Natural biomineralization using NPs based with algae helps to remediate HMs by reducing them to ions; this process could be a promising strategy for the production of NPs (Yusof et al. 2019). Intracellular biosynthesis requires unique transport systems in which negative charge of the cell wall plays a key role: positively charged metal ions get deposited on the negatively charged cell walls via electrostatic interactions. Ions are reduced through metabolic events driven by enzymes like nitrate reductase to create NPs after being transported into the cell. MtNPs are transferred through the cell wall after accumulating in the periplasmic region (Tiquia-Arashiro and Rodrigues 2016). Studies have shown the application of nanobiochar have positive influence on plant biomass and seed germination. Alongside this has also marked its potential in stabilisation of Cd ions by decreasing its availablility in the soil exhibiting bioremediational effect. ZnO/ZnS modified nanobiochar had potential to adsorb Cu (II), Pb (II), and Cr (VI) (Liu et al. 2020). It reduces the metal toxicity (Cd2+) and oxidative stress on rice seedlings and has been used as pesticide remediation (Yue et al. 2019).

Another promising use of NPs-zeolite is the soil improvement by increasing the water and nutrient uptake, fertility, to balance soil salinity, ammonia votalization to help increase the crop products. Further, nano-zeolite has the property of slow progress of degradation and decomposition that increases the availability of nutrients to plants for the required time (Kieta and Owens 2019). However, some metals like Cu when excessive get accumulated in the plants that can hinder the biological activity and act as toxins to plants this process can be prevented by applying CuO NPs to plants like *Halimione portulacoides*, *Phragmites australis* etc. (AndreottiF et al. 2015).

Pharmaceutical waste

Pathogenic microbes have shown resistance to various antimicrobials like methicillin, sulfonamide, penicillin, and vancomycin etc. (Fair and Tor 2014). Antimicrobial effectiveness decreases rapidly due to various resistance factors and biofilms formation provides multidrug resistance to the pathogens (Mayegowda et al. 2022; Jadimurthy et al. 2022). According to an in vitro study done by Dizaj, several MtNPs are effective in blocking the growth of microbes' species which was confirmed by antimicrobial studies (Dizaj et al. 2014). Besides, two important parameters determine the antimicrobial effectiveness is the material employed and particle size for the synthesis of NPs. Many studies proof the strength of AgNPs as an efficient antimicrobial agent, potential antifungal, probable antiviral with rich anti-inflammatory properties which are done by several mechanism like denaturation bacterial outer membrane generate pits/gaps in bacterial cell membrane leading to fragmentation. These NPs interface with disulphide or sulfhydryl groups of amino acids present in numerous enzymes, there by disrupting the metabolic processes leading to the death of microbial cell (Iavicoli et al. 2013). It has been well noted that truncated triangular NPs are highly reactive in nature due to their high-atom-density surfaces that enhance the antimicrobial activity (Tak et al. 2015). Pharmaceutical and medical waste remediation has been carried out by the herbal extracts of plants which have been very effective for degrading the hazardous chemicals. It has been studied that *Azadirachta indica*, neem extract, and tobacco extract can act effectively on HMs and both have greater impacts on biomedical waste (Patil et al. 2019). Neem extracts along with lime have proved to be a promising factor in helping to dissolve teichoic acids and other surface components on bacteria that helps to stop spreading the infection. In future, probably these plants-based can be coupled with NPs so that the efficacy of their antimicrobial activity and bioremediation process can be enhanced to improve the environmental settings.

Domestic waste

The waste generated from operations involving domestic and municipal are treated partially and disposed in the environment that enters into water bodies and soil. The domestic pollutants consist of household garbage and rubbish that has HMs like chemicals, medicines, electronic devices etc. These pollutants further get dissolved and remain suspended in water or get deposited in sediments of soil resulting in water and soil pollution, impacting on the human health. An alternative pathway to remediate is biodegradation that is eco-friendly and reduces the traditional ones like incineration and composting. Advances in the application of plant extracts in biosynthesizing NPs are one of the major steps taken forward in the research to combat HM contamination in wastewater. A few examples of plant-based NPs in the remediation are, TiO2 NPs extracted from the plant leaf extract *Psidium guajava* have shown to play a vital role in wastewater treatment. *Trigonella foenum-graecum* leaf extract used for biosynthesizing FeO-NPs is used for Pb containing wastewater treatment. Due to its adsorbent nature, FeO is widely used in the treatment of HM removal from the environment. Biomolecules present in microalgal employed in the synthesis of NPs showed good result in remediating HM contaminated wastewater. Nanoscale Fluorescent metal chalcogenide quantum dots and carbon dots are more realistic, feasible inexpensive, and more than anything environmentally, hence a safer approach (Omran et al. 2021).

GS-AgNPs produced by *Piliostigma thonningii* plant in the aqueous form obtained from the leaf extract used for the purification of wastewater and showed effective results in cleaning up the contamination (Shittu and Ihebunna 2017). CuONPs biosynthesized by the Madhuca longifolia plant show photoluminescence property depending on NP size and help in the degradation of methylene blue in wastewater treatment (Das et al. 2018). CuO produced by flower extract through alkaline processes and zero-valent iron NPs provides in situ remediation to HMs. In the same way, banana peel extract was used to synthesize nano zero valent iron particles to get GS-FeNPs for treating waste water. Maghemite (γ-Fe2O3) synthesized from leaf extract of tridax plant is useful in the removal of HMs from 20% aqueous solution of fly ash. The leaf extract of *Catharanthus roseus* shows the capacity of synthesizing AgNPs and CuO NPs with the removal ability of Cd and Cr (Verma and Bharadvaja 2021) as polyphenols and caffeine both present in tea extract act as good reducing and capping agents during the preparation of Fe NPs which adsorb the HM into the surface of iron oxide, HM Pb gets adsorbed on to the functional group present and reduces into non-toxic form.

Miscellaneous

Heavy Metal Ion Sensing

HM pollutants in air, soil, and water are supplemented from mining waste, automobile emissions, petroleum, paper, fossil, and fabric industries in the environment. Even at trace ppm levels some metals like Pb, Cd, Hg ions have enhanced toxicity potential hence, their identification in the environment becomes important necessity for appropriate remediation (Mehta et al. 2013). It has been observed that the experimental set ups, to take forward such examination is highly cost effective, laborious, expertise-dependent, and non-transferable. Therefore, the tuneable size and distance-dependent optical properties of metallic NPs are rather employed for identifying HMs in contaminated zones (Maiti et al. 2016). In environmental systems the advantage in the usage of metal NPs as colorimetric radars for HM is considered to be minimalistic, economical, and high sensitivity at sub ppm levels (Karthiga and Anthony 2013).

Anti-Foulants

Formation of biofilm in marine bacteria is more predominant and several strains have shown excellent biofilm formation which includes *Aeromonas hydrophila*, Salmonella spp. And *Serratia Liquefaciens*. However, biopolymers which are formed during this process used for the generating various NPs. A study explains the importance of biosynthesized AuNPs used as anti-biofilm against pathogenic microbes as these biofilms forming microbes used are non-pathogens (Vijayan et al. 2014). Likewise, seaweeds like *Sarconema furcellatum* and *Sargassum wightii* as well as sea grass like *Syringodium isoetifolium* and *Cymodocea serrulate* were also used for the biosynthesis of GS-AuNPs. These algal crude extracts used to get GS-AuNPs which were food to have anti-microfouling activity against the microfoulers. This property seen in GS-NPs is due to occurrence of imperative functional side chain which has aliphatic fatty acid, amide group I and II with NH2 terminal, amino groups, phosphoryl, carbonyl and hydroxyl groups. Trees like *Rhizophora apiculata*, *Rhizophora mucronata*, and *Avicennia* extracts have shown to have greater anti-fouling action against *Bacillus spp* which is very well known as fouling bacteria. GS-NPs made by *Halimeda macroloba*, *Ulva reticulate*, and *Sargassum wightii* seaweeds extract and the sea grass extract of *Halodule pinifolia*, *Cymodocea serrulata*, *Flavobacterium spp*, *Cytophaga spp* also exhibited decent anti-fouling action against *Pseudomonas spp* but less compared to *Bacillus spp.*

6 Future Prospective

Biosynthesis of metal NPs engaging plant and its derivatives are exceptionally considered in the last two decades. Eco-friendly nature of phytometabolites using plant crude extracts and its innumerable purified forms them as novel substrates for environmental bioremediation. In counter, it has been well observed globally due to advancement of industrialization and globalization environment and mankind is facing severe lethal effects due HMs contamination in the environment and it has been a challenging issue to overcome. With the, there has been an increased demand of HMs use in various products like automobile fuels, automobile fuels, explosives, photographic films, storage batteries pigments, aeronautical, as coating materials, and steel industries. NPs have revolutionized with their properties like nanoscale size, large specific surface area, and great reactivity. Even though, NPs have higher efficiency in bioremediating HMs from the environment through the use of plants, the widespread use has raised concerns regarding the ill-effects on the environment and threatening human health through the food chain. Therefore, it becomes a prime importance for the investigators to develop biodegradable and biocompatible NPs to minimize their accumulation in plants and henceforth help in concern with affecting the human health. There still exist crucial restrictions and information gaps on the societal acceptance of this method. Hence, it needs more of trials to necessitate the technique successfully with considering the safety, efficiency, feasibility, and inherent toxicity of these NPs on plants, animals, and the microbial community, combined application of NMs with other treatments such as phytoremediation, long-term efficacy with the need to bioremediate HMs from the contaminated soils using plants have to be targeted. Our future research needs to be emphasized on the optimization and targeted delivery on NPs in plants, low cost and eco-friendly will surely help to overcome the implications of these HMs to be remediated from the environment.

7 Conclusion

NMs are one of the state of arts in bioremediation that not only catalyze the waste and hazardous chemical degradation but also enhance the efficiency of their degradation by plant and microbe-based NPs. In last few years, NPs have been enormously designed and synthesized for their application in various fields such as medical therapy, agriculture, remediation etc. Despite a great improvement of using phyto-nanotechnology specially, NPs in crop breeding and plant genetics still need to be worked on. Evidences show that plant cells can be used as nano-based polymers and nanogels that can be promising to advance the novel approach in editing genome and control plant biomolecules. In agricultural aspects, these NPs need to be carefully designed and used for the treatment of HMs to ensure the crop productivity and quality not being deteriorated. A better understanding with the type and concentration of NPs to be used and their environmental fate needs to be being investigated. However, being sustainable these NPs will definitely have a diverse spectrum of applications like biomedicine, agriculture, and bioremediation. The most important being the process of phytoremediation has an immense application for the removal of HMs contaminated soil and water resources. It can be ascertained as a powerful technique that will surely increase the crop improvement and clean up the environment from hazardous chemicals in the near future.

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Environmental Applications of Green Engineered Copper Nanoparticles

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Abstract Naturally engineered nanomaterials in recent times have myriad potential in different fields. Moreover, green derived nanoparticles (NPs) encourage broader implementation for wider applications. Amongst many metals, copper and its oxide-based nanoparticles (CuONPs) have increased utmost consideration owing to its specific characteristics, abundance, and cost-effectiveness. Major setback of chemical and physical methods of synthesising CuONPs involves high cost along with environmental hazards. Aforementioned challenge compelled researchers to explore green synthesised CuONPs that is much cheaper, efficient, economically beneficial, non-toxic, and eco-friendly. Existing plant-based CuONPs have potential efficiency to enhance the toxic effects against the plant pathogens and combating environmental pollution through bioremediation. Several extracts of plant derivatives have been used for the synthesis of CuONPs such as *Azadirachta indica, Hibiscus rosa-sinensis, Murraya koenigii, Moringa oleifera*, *Tamarindus indica, Eclipta prostrate, Olea europaea,* etc. Microbes as cell factories are more efficiently used as NPs compared to larger plants such as, green algae *Botryococcus braunii,* brown algae *Macrocystis pyrifera*, *Bifurcaria bifurcate* etc. Bio-based CuONPs have been applied in numerous fields such as pharmaceutical, molecular biology, bioremediation, cosmetics, textiles etc. Several of them also employed in dye degradation, water treatment, food preservation, Photovoltaic devices, solar energy conversions, and field emission emitters. However, as in clinical setup due to their efficacy these are exclusively used as anti-cancer, antimicrobial agents. Further, their high antioxidant potential renders them as an invaluable tool for biomedical devices.

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Keywords Green synthesis · Cu nanoparticles · Bioremediation · Anticancer · Dye degradation · Crop management

1 Introduction

Copper (Cu), a metallic element is the 8th abundant available in the Earth's crust. Solubilised copper cannot be either created or destroyed and can control the homeostatic regulations. A transitional metal that has a discrete red–orange colour and a metallic sheen. It has numerous properties that are more fascinating like good ductility, malleability, electrical conduction, high corrosion resistance, high thermal, and low chemical conductivity (Mohajerani et al. 2019). Their unique properties have been helped us to utilise in different essential functionalities for the benefits of the society from centuries. This metal element is one of the key trace essential requirements in humans, plants, and animals for their normal functioning. In humans, the minimal copper requirement is <100 mg/day, with its diverse role in structure, catalysis, and exists in both oxidised and reduced forms in various cell pathways (Al-Fartusie and Mohssan 2017). The reduced form of copper, Cu^{+} attracts towards thiol and thiol-ether groups with that of cysteine and methionine whilst, Cu^{+2} coordinates with imidazole nitrogen or oxygen groups as in aspartic, glutamic acids, and histidine. This interaction with protein structure leads to various biochemical and structural changes like synthesis of neuropeptides, regulating cell signalling pathways, antioxidant defence mechanism, immune cell activation like macrophages, neutrophils, helps T cells to kill the pathogens, helps to maintain the immune system of hair and elastic tissue of skin, bones, and other parts of the body organs (Dey et al. 2020). In plants, copper is present in optimum concentrations of 10^{-14} to 10^{-16} M for Cu^{+} and Cu^{2+} respectively. It plays numerous roles in plants for normal functioning of various important enzymes and proteins like cytochrome-C oxidase, amino oxidase and others, as cofactor for enzymes, structural component of several regulatory proteins, helps to carry out electron chain in photosynthesis, oxidative stress response, mitochondrial respiration, hormonal signalling, iron chelation etc. (Rajput et al. 2020).

Nanotechnology has emerged as an improvised advanced area with its role in medical, pharmaceutical, and textile industries throughout the world (Roy and Bharadvaja 2019; Roy 2021). Currently, this field has gained significant popularity and applied in diverse fields that include, medical diagnostics, as biomarkers, cell labelling antimicrobial agents, in drug delivery and cancer treatment options. It has been an exciting curiosity in the field of metallic nanoparticles (NPs) that have been variously utilised in biomedical sciences and engineering (Pandit et al. 2022). The most effective NPs are of the range 1–200 nm in size and their shape dependent variabilities have gained attractive applications in medicine, biofuel production, catalysis, electronics, and biotechnology (Roy et al. 2021; Nagore et al. 2021).

NPs are synthesised using notable metals in nanotechnology field that are gold (Au), silver (Ag), titanium (Ti), aluminium (Al), zinc (Zn), iron (Fe), cobalt (Co), silica (Si), nickel (Ni), bismuth (Bi), indium (In), tin (Sn) etc. However, most frequently noted metal-oxide NPs include copper oxide (CuO), cuprous oxide (Cu_2O), zinc oxide (ZnO), iron oxide (Fe_2O_3), silicon oxide (SiO_2), nickel oxide (NiO), magnesium oxide (MgO), cerium oxide (CeO_2), titanium oxide (TiO_2), aluminium oxide (Al_2O_3), zirconium oxide (ZrO_2), indium dioxide (In_2O_3), and lanthanum oxide (La_2O_3) (Rajput et al. 2019). These NPs have uniqueness in their properties that they exhibit such as optical, electrical, chemical, area, and surface functional groups. Currently, metallic NPs have been modified with a varied range of desired shapes and sizes that include production by different chemical, physical, and biological techniques (Nikam et al. 2018; Roy et al. 2021).

NPs have contributed towards diverse applications in varied agricultural aspects, industries, and human related medical health care systems too. Nano-enabled products have increased many folds over the past decades with their advancement. Owing to their unique properties, these NPs have been functional in various fields like cosmetics, material science, electronic devices, antimicrobial, optical, textiles, fuel additives, sensors, energy production, catalysis, waste water treatment etc. (Chaudhry et al. 2018; Thota et al. 2017). Metal oxide-NPs have been extensively used in many fields like solar cells, energy storage devices, microelectronics, and as coating material for their varied properties like tensile strength and electrical conductivity. Their nano-specific properties have made them applicable in some of the most important fields of biomimetic sensors, renewable energy process, aerospace and automobile engineering (Han et al. 2018). NPs had enormous role in synthesising materials that included carbon nanotube (CNT), carbon quantum dots, epoxy resin-coated CNTs, polymer-coated Ag, super magnetic iron oxide nanoparticles (SPION), mesoporous silica particles, catalytic metals, metal oxides, quantum dots, dendrimers, nanofilms, nanofibres, and strengthened nanocomposites. Few of the metal oxide NPs are used as conductors and semiconductors, elements in rubber additives, sensors, photovoltaic cells, catalytic converters, biomedical imaging, bioremediation of dyes, cosmetics and plastics (Goswami et al. 2017).

NPs have positively contributed in the agricultural sector for production, crop improvisation, economic stability and help to sustain ecological stability. Agricultural products derived along with NPs like nanopesticides, nanofertilisers are potential in helping to transform the process of crop production as well as its protection (Ahmed et al. 2021). Additionally, food industries have gained more importance with advanced NPs techniques involved in the food processing, packaging, and preservation techniques (Chaudhry et al. 2018). The most important aspect of NPs in food industries is the nanosensors that help to deliver security during production process, food processing, and transportation of the food products through sensors that help to detect the contaminants and pathogens (Prasad et al. 2017).

Copper nanoparticles (CuNPs) are synthesised by chemical, physical methods, and biological methods as in Table 1. CuNPs by green synthesis using plants and microorganisms have expanded more importance because of its distinctive characteristics, cost effective, eco-friendly, non-toxic, suitable, and possibility of scaling up into commercial production and also have potential efficacy (Fig. 1). CuONPs have been distinctively used in various applications like waste water treatment, bioremediation, gas sensors, as food preservatives, high temperature superconductors, synthetic dye remediation, field emission emitters in agricultural fields, solar energy conservations. These NPs have been also used exclusively in biomedical applications like anticancer, antioxidant, and antimicrobial therapy for their efficacy (Roy et al. 2021). Conclusively, this area of nanotechnology as a discipline can be known as one of the most important empowering technologies.

Table 1 CuNPs synthesis using different methods with their advantages and disadvantages

Techniques	Advantages	Disadvantages
Chemical	Increases large-scale production	Generates toxic products Requires high energy for the process. Solvents used as reducers and stabilisers are toxic
Physical	Crystal controlled Shapes and forms NPs are controlled in uniform size Greater purity is achieved	High capital cost investment Requires high energy
Biological	Process is cost effective Non-hazardous chemicals used Eco-friendly Microbes completely degrade and utilise Simple in operation using microbes	Requires aseptic conditions for growth

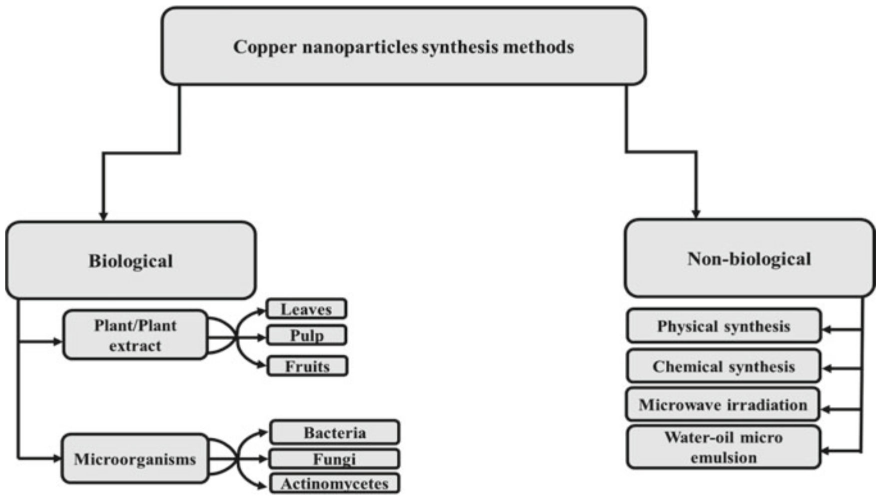

Fig. 1 Different approaches for the synthesis of CuNPs

2 Synthetic Strategies of Green Engineered CuNPs

CuNPs are formed by various techniques characteristically classified as the chemical or bottom-up methods and physical or top-down method. These CuNPs have gained abundant consideration due to its availability, cost effective compared to that of gold and silver and can be variously formed through physical and chemical methods such as microwave irradiation, thermal decomposition, sol–gel, colloidal thermal synthesis, sonochemical, hydrothermal and quick precipitation processes (Jeronsia et al. 2019). However, these techniques for the synthesis of CuNPs are labour intensive, expensive, require high energy, exhaustive processes and utilise hazardous chemicals that are highly toxic. This intensive and detrimental techniques led to develop novel biocompatible methods to help overcome these issues and necessitate the biosynthesis of NPs that are eco-friendly and cost effective.

CuNPs were mechanochemically synthesised using diluted salts that were ball milled enclosing NPs in salt matrix, further washed with distilled water in ultrasonic bath that showed antimicrobial property against *S. aureus* and *E. coli* (Javadhesari et al. 2019). There has been an increase in the shift of NPs synthesis using both the physical and chemical methods to that of biological methods termed as "biosynthesis or green synthesis of NPs". Metal or metal oxide NPs biosynthesis has been focused by the use of various biological cells like bacteria, yeast, fungi, algae, and various plant extracts as reducer/reducing agents that support the biocompatibility and help to synthesis on commercial scale (Roy et al. 2022). Due to its sustainability, cost effectiveness, and simplicity the plants and microbe-based CuNP synthesis has increased consideration. (Mittal and Roy 2021).

3 Green Synthesis of CuNPs

The synthesis of CuNPs is relatively easier compared to the production of other metal NPs. Various methods are utilised to synthesise them such as, water–oil microemulsion, polyol reduction, supercritical CO_2) and through high-temperature decomposition of organometallic precursors. However, large-scale synthesis by physical and chemical techniques is difficult to be carried out and the methods for CuNPs synthesis have numerous limitations such as forming hazardous toxins, high cost of reagents and methods, more tedious techniques involved in the isolation and purification. These problems highlighted an alternative approach for the use of green synthesis by plants and microbes involving simple, cost effective, non-hazardous, eco-friendly in nature, reproducible, and give stable product (Fig. 2).

Green synthesis of NPs has gained importance and are being synthesised by using plants and microorganisms that are considered to be more compatible with environment. Synthesis of NPs by microbes and plants does not need high energy consumption, temperature, pressure or any toxic chemicals (Raina et al. 2020). Bottoms up approach is to use green synthesis similar to that of chemical reduction of NPs,

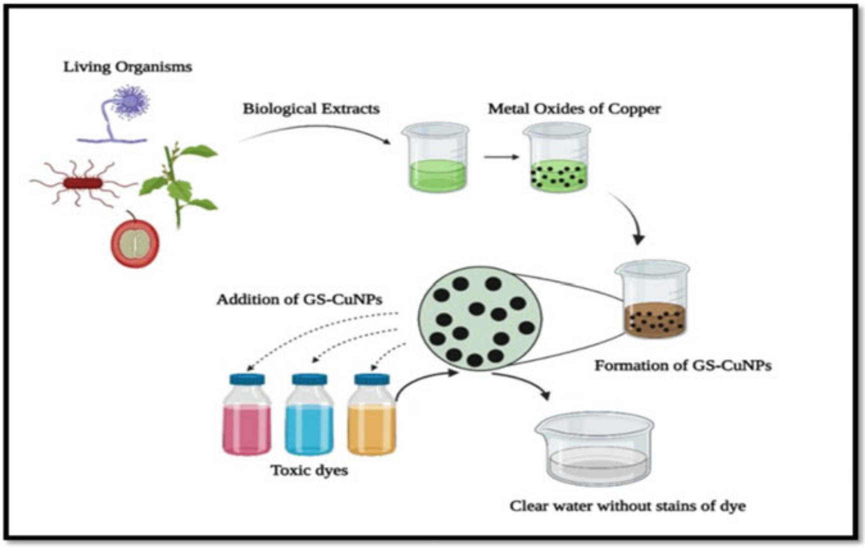

Fig. 2 Biosynthesis of CuNPs using microbes and plants

only the difference is chemical reducing agent will be replaced with the extracts of plants, fruits, flower, and microbes like algae, bacteria (Hussain et al. 2016; Pal et al. 2019). There have been records that the NPs biosynthesis is simple that involves the mixing of metal solution with that of plant extracts. NPs are produced in the medium due to the reduction of metal ions wherein, CuNPs are synthesised by using of most common precursors of Cu-salts like, cupric acetate (monohydrate) ($(CH_3COO)_2Cu{\bullet}H_2O$), copper chloride dihydrate ($CuCl_2{\bullet}2H_2O$), and copper sulphate pentahydrate ($CuSO_4{\bullet}5H_2O$) and used in various applications. However, nature and properties of chemically synthesised CuNPs are predisposed by various factors such as concentration of salts, bio-based extracts, temperature, pH etc.

3.1 Plant-Based Green Engineered CuNPs

Bio-based NPs synthesis encompasses the use of microbes and extracts from different parts of the plants as reducing agents to the metal ions (Roy et al., 2021; Roy 2021). Biomolecules of the plant extracts act as reducers as well as stabilisers for the CuNPs and other metallic NPs biosynthesis (Thapa et al. 2017). These biomolecules of various types that are used as good reducers and stabilisers include the flavonoids, proteins, tannins, phenols, and terpenoids for CuONPs synthesis. It has been well known that plants possess a huge number of biologically active compounds and of them few plants have shown certain metabolites that are antimicrobial, antifungal, anthelmintic, antitumor, and antimutagenic properties. The various plant extracts that are used for the green synthesis of CuNPs are given in Table 2.

Biosynthesis of CuNPs has also been carried out by using the leaf extracts of *Capparis zeylanica* (Saranyaadevi et al. 2014). *Syzygium aromaticum* (Cloves) with a diameter of 5–40 nm has been used for the synthesis of CuNPs (Subhankari and Nayak 2013). Number of plant extracts have been used for copper nanoparticle biosynthesis such as, *Catha edulis, Enicostemma axillare* (Lam), *Juglans regia, Abutilon indicum, Daturameta, Carica papaya, Thymus vulgaris L., Malus domestics, Thymbra spicata, Gingko biloba L., Hagenia abyssinica, Ageratum houstonianum Mill., Jatropha curcas, Camellia sinensis, Uncaria gambir, Eclipta prostrata* etc. (Andualem et al. 2020; Asemani and Anarjan 2019; Chowdhury et al. 2020; Chandraker et al. 2020; Mali et al. 2019; Sankar et al. 2014; Veisi et al. 2017). These particles are synthesised with a range of 1.5 nm–40 nm (Ghosh et al. 2020).

3.2 Microbes-Based Green Engineered CuNPs

Microbial-based NPs are eco-friendly and cost-effective approach along with their important biological activities (Table 3). Various biomolecules are present in these microorganisms and plant extracts that function as both reducing and stabilising agents for the synthesis of CuONPs and other metal NPs (Thapa et al. 2017). CuONPs synthesis is carried out using good reducing and stabilisers such as phenols, tannins, flavonoids, proteins, and terpenoids. These NPs have been successfully biosynthesised by using microbes, algae, fungi, plant extracts derived from angiosperms, and certain phytochemicals like sinapic acid for the biosynthesis of CuONPs (Preeth et al. 2019; Singh et al. 2010).

Several studies have been reported CuNPs synthesis from various microorganisms. *Pseudomonas fluorescens* MAL 2 (metal copper-resistant) bacterial cell culture has been successfully carried out for the biosynthesis of CuNPs with a range of 10–70 nm in size, whilst supernatant culture of *Salmonella typhimurium* produces 40–60 nm (El-Saadony et al. 2020). *Pseudomonas stutzeri, Schewanella oneidensis, Serratia sps,* and *Lactobacillus spp* have also been reported for the CuONPs synthesis by various researchers (Varshney et al. 2010; Kouhkan et al. 2020). Similarly, other microbes that have been reported for the CuNPs include the *Phormidium cyanobacterium, Escherichia coli, Morganella morganii, Serratia spp.* (Ghasemi et al. 2017). Green alga *Botryococcus braunii* has been reported to synthesise CuNP that are 10–70 nm, spherical in shape whilst, a white rot fungus, *Stereum hirsutum* can form 5–20 nm, *Hypocrea lixii* a dead biomass 24.5 nm, *Aspergillus niger* strain STA9 synthesised 398.2 nm of CuNPs (Noor et al. 2020; Rolim et al. 2019).

Table 2 Green synthesis of NPs using different precursors of plants extracts along with their applications

$(CH_3COO)_2Cu$	*Psidium guajava* leaf extract	11.07 nm	Photocatalytic dye degradation	Singh et al. (2019)
$CuSO_4$	*Centella asiatica* leaf extract	20–30 nm	Dye Degradation	Raina et al. (2020)
$CuSO_4$	Punica granatum leaf extract	20.33 nm	Dye Degradation	Vidovix et al. (2019)
$CuSO_4$	*Sida acuta* leaf extract	50 nm	Antibacterial, Textile dye degradation	Sathiyavimal et al. (2018)
$CuCl_2$	*Tinospora cordifolia* leaf extract	50–130 nm	Catalytic textile dye degradation	Sharma et al. (2018)
$(CH_3COO)_2Cu$	*Cissus quadrangularis* leaf extract	30.08 nm	Antifungal activity	Devipriya and Roopan (2017)
$Cu(NO_3)_2.3\ H_2O$	*Tinospora cordifolia* leaf extract	6–8 nm	Photocatalytic, Antioxidant, Antibacterial activity	Nethravathi et al. (2015)
$Cu(NO_3)_2$	*Aloe vera* leaf extract	22 nm	Antibacterial activity against fish pathogens	Kumar et al. (2015)
$CuSO_4$	*Tabernaemontana divaricate* leaf extract	48 nm	Antibacterial activity against urinary tract pathogen	Sivaraj et al. (2014)
$CuSO_4$	*Strawberry* fruit extract (Stabilising Agent-L ascorbic acid)	10–30 nm	Antioxidant, Antifungal, Antibacterial, Anticancer, Activity of healing cutaneous wounds	Hemmati et al. (2020)
$CuSO_4$	*Terminalia bellirica* fruit extract	2–7 nm	Antimicrobial activity	Viswadevarayalu et al. (2016)
$Cu(NO_3)_2.3\ H_2O$	*Cordia sebestena* flower extract	20–35 nm	Dye degradation Antimicrobial activity	Prakash et al. (2018)
$CuSO_4$	*Eichhornia crassipes* leaf extract	28 nm	Antifungal activity against plant fungal pathogen	Asemani and Anarjan 2019

Table 3 Green synthesis of NPs using different precursors of microbes and their applications

Precursor	Reducing/Oxidising agent	Size (nm)	Application	References
$CuSO_4$	*Streptomyces* spp.	78–80	Antimicrobial, Antifungal, Antioxidant activity, Larvicidal activity	Andualem et al. (2020)
$CuCl_2$	*Shewanella loihica PV-4*	10–16	Antimicrobial activity	Lv et al. (2018)
$CuSO_4$	*Bifurcaria bifurcate* brown alga extract	18–34	Antimicrobial activity	Abboud et al. (2013)
CuSO4	*Escherichia coli*	10–40	–	V Singh et al. (2010)
$CuSO_4$	*Pseudomonas stutzeri*	8–15	–	Varshney et al. (2010)
$CuSO_4$	*Pseudomonas stutzeri*	50–150	–	Varshney et al. (2011)
$CuCl_2$	*Fusarium oxysporum*	93–115	–	Majumder (2012)
	Rhodotorula mucilaginosa	10.5	–	Salvadori et al. (2014)

4 Environmental Applications of Green Engineered CuNPs

CuNPs are similar to other NPS in terms of size and synthesis. However, CuNPs have commended advantages of being low cost, eco-friendly, that can be produced on large scale have gained more importance than the other metals and have a plethora of uses in the fields of science and technology. CuONPs are prepared through the process of green engineering technology and are considered as more efficient due to its catalytic and sensor applications as in Fig. 3. They have shown promising application in both engineering and biological systems through their mechanisms involving both catalytic and optical properties. NPs derived from plant-based extracts have added advantage of possessing properties acquired from capping agents present in plant (Hashmi et al. 2021) There have been lot of advancements in the research involving the bioremediation processes in the environment including the waste water treatment and photocatalytic degradation of dyes in effluents using CuNPs. Although NPs are engineered specific to their engineered usage, there are two distinct types of NPs that are essential in order to understand the CuNPs and their engineering process. These two types include the metal and magnetic types NPs. However, the advantage of metal NPs is that they are having a fixed shape, size, and stability, controlled by their polymers such as dendrimers. Usually, these metal NPs range in between 1 and 4 nm in size. They are variedly used in diverse applications for their unique properties like optical, magnetic, and catalytic aspects (Chakraborty and Pradeep 2017) Certain plant extracts like *Syzigium aromaticum* (bud), *Azadirachta indica* (leaves), *Tinospora cordifolia*, *Stachys lavandulifolia*, *Asparagus adscendens* etc. have been able to provide efficient CuNPs using chemical extraction process. These

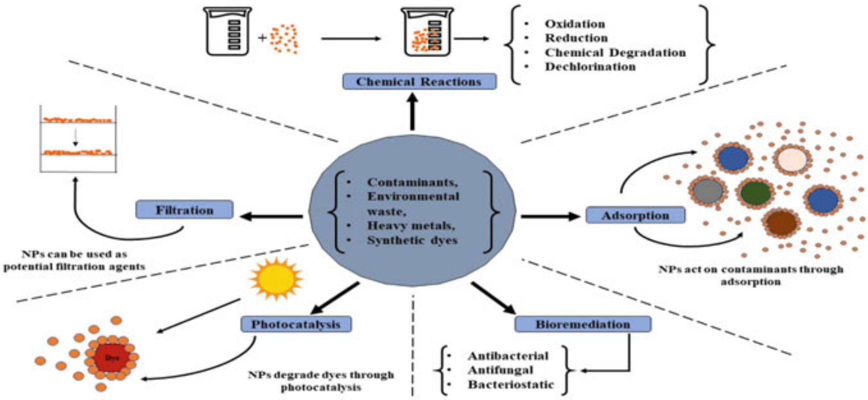

Fig. 3 Role of green engineered CuNPs derivatives using plant extracts and microbes in various environmental applications

synthesised CuNPs from specific areas of the plant extracts have been beneficial in bioremediation activities as green engineered or green derived CuNPs.

Through years of research, it has been seen that various fungal species have been efficient in the synthesis of CuNPs as well as other metal NPs. Comparatively, to bacteria, algae or even plants, fungal cells have highly efficient and are potential synthesisers for the NPs. It can undergo the parameters in the bioreactors such as, flow pressure, agitation, pH, temperature etc. or any other growth chamber in a much higher rate and intensity hence, commercial application with these microbes is easy. Fungi synthesise NPs by primarily two pathways, i.e., the intracellular and extracellular pathway. Synthesis of NPs in fungal species varies with the size, intracellular NPs are smaller with good dispersity as compared to the extracellular synthesis of NPs. Although, this is still under research, fungi hold potential agents for the synthesis of CuNPs and their usage for environmental remediation (Waris et al. 2021).

4.1 Waste Water Treatment

In recent times, waste water treatment has become an important topic of discussion due to acute shortage of potable water sources. With increase in population, industrialisation, and urbanisation it has led to adverse effect with water pollution causing impairment to the milieu and human health. This has made the researchers extremely conscious about implementing different methods for waste water treatment, purifying and reusing it. Whether, it is industrial or municipal waste water contamination remains same that occurs with the quality of water. Of the added wastes include the harmful metal ions that are highly toxic include, Hg (II), Pb (II), Cr (III), Cr (VI), Ni (II), Co (II), Cu (II), Cd (II), Ag (I), As (V), and As (III) that has caused severe damage to the atmosphere and public well-being (Sandhya

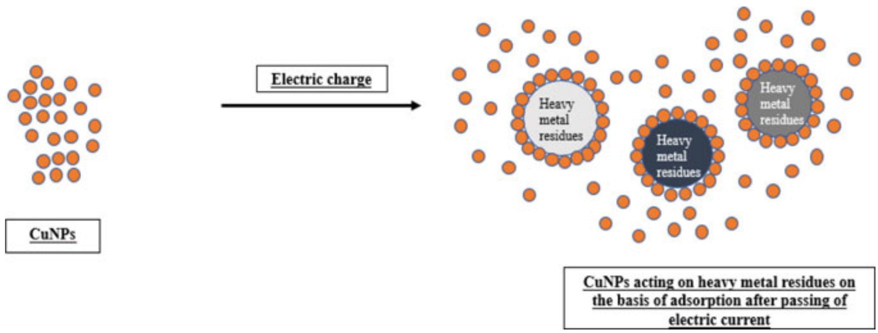

Fig. 4 Representation of action of CuNPs on heavy metal residue using electric charge

2016). Although, various techniques are being used to achieve detoxification of waste water, only a few have the property of being both conventional and effective. One such includes, the CuNPs that hold good for waste water treatment. The efficacy of CuNPs has been highly effective compared to other NPs for treating waste water. Since, the NPs have high mobility in the solution, the heavy metals, organic pollutants, inorganic anions, and bacteria have been reported to be successfully removed by CuNPs (Lu et al. 2016).

CuNPs have shown immense antimicrobial activity against bacteria, that includes both Gram-positive as well as Gram-negative bacteria. This antibacterial property of the green engineered CuNPs is been useful in treating of waste water free from pathogenic as well as non-pathogenic bacteria. It has been observed that the technique involving agar well diffusion for the antibacterial analysis using CuNPs against both Gram-positive (*Streptococcus mutans* and *Staphylococcus aureus*) and Gram-negative (*Pseudomonas aeruginosa*, *Klebsiella pneumonia* and *Escherichia coli*) reported a highly effective toxicity of CuNPs on these tested pathogens by inhibiting their growth. This bactericidal activity by CuNPs is due to the development of highly reactive oxygen species, like OH, $H_2O_{2,}$ and O^{2-}, adsorb on the surface of the CuONPs that caused the death of the pathogens (Akintelu et al. 2020). These properties of CuNPs can be altered easily according to the actions necessary. For instance, in order to remove the residual metals or heavy metals from waste water in order to treat it, adsorption technology can be used along with CuNPs. By passing a charge through the waste water sample heavy metal residues can be adsorbed onto the surface of the NPs, thereby treating the water free of heavy metals and making it easier for further purification (Waris et al. 2021) as in Fig. 4.

4.2 Bioremediation

CuNPs have shown promising experimental progress in inducing apoptosis as well as stop the procreation of cervical cancer cells. They also exhibit cytotoxicity towards cervical cancer cells (HeLa cells) which is a useful property whilst considering bioremediation using CuNPs. They are economical and hence can be used in bulk whilst considering any bioremediation or bioaugmentation. CuNPs possess excess surface to volume ratio that interacts well with other particles. This enables them to serve as a better option in using them as catalysts, biosensors, antibacterial substances, and to build super strong materials for various applications that can be used over a long period of time. They have an excellent antibacterial property to inhibit the growth of bacteria that includes *Escherichia coli* and *Staphylococcus aureus* by entering through their cell walls (Agrawal et al. 2019).

CuNPs have antibacterial properties that are effective against bacteria and their metabolites. These CuNPs infiltrate the bacterium and cause malfunctions in the cell physiology causing destruction of the bacteria. A similar mechanism can be observed in case of algae that cause eutrophication. CuNPs are potentially useful in bioremediation process, they practically work by decreasing significant growth rate with the increased production of intracellular reactive oxygen species (ROS) in algae. Further, the process leads to the death of the organism in question. The toxicity of CuONPs to unwanted algae and bacteria is due to their high adsorption rate and intracellular interactions in various microorganisms (Fathi et al. 2020).

In the case of contamination of a water body by nitrates, CuNPs as adsorbents can help to eradicate the nitrate from a specific water body. Activated carbon has been used as an adsorbent for remediation process. However, the efficiency of the activated carbon can be increased by impregnating it with green engineered CuNPs. This process is beneficial in terms of reducing the treatment generations, use of dangerous by-products for human health and the atmosphere, cost effective and environmentally friendly, without the need for high pressure, energy, or temperature. Furthermore, it has been shown that CuNPs are an environmentally feasible and conventional method to eliminate the contaminants from the waste water resources (Paixão et al. 2018). However, bioremediation makes use of microbes to remediate the contaminated environments, a proper interaction between NPs and living organisms is essential. Some aspects are of immense importance that includes, the nanotoxicity, size of NPs, and nanonutrition that may have an effect on the living organisms which in turn may affect the whole bioremediation process (Vázquez-Núñez et al. 2020).

CuNPs exhibit antifungal properties along with aforementioned antibacterial properties. This is another aspect that can be utilised in terrestrial bioremediation of the environment along with aquatic bioremediation. Since, they are toxic to bacterial and fungal cells, CuNPs can be engineered to target the specific microbes. Due to their physical and chemical characteristics, they can be effective against both Gram-negative and Gram-positive bacteria. They are also potentially effective in producing antioxidant properties by using radical scavenging assay. CuNPs can be used as heat transfer liquids since, they have unique properties of exhibiting greater thermal conductivity in water and ethylene glycol. These characteristics are used to synthesise air-resistant CuNPs used in biological applications such as bioremediation or bioaugmentation, as well as certain industrial applications (Radha and Balajee 2021). (1) Accumulation of the CuNPs on the cell surface from pits which causes cell leakage; (2) DNA damage due to interaction of CuNPs; (3) Interaction of Cu ions with sulfhydryl group of proteins; (4) Entry of CuNPs and Cu ions inside the cell develops oxidative stress, which leads to cell death; (5) Interaction of CuNPs with cell membrane decreases the transmembrane electrochemical potential, which affects membrane integrity; (6) Inhibition of ATPase activity; (7) Interfering with motility of flagella; (8) Triggering of ROS enzymes; (9) Blocking DNA replication.

4.3 Photo Catalytic Degradation of Dyes in Effluents

Since the past decades it has been seen that NPs are used in numerous applications in several fields like catalysis, environmental bioremediation, degradation of toxic waste products, etc. Amongst all NPs, CuNPs have attracted the most attention based on efficacy due to the fact that it is not an expensive element along with abundant availability. In recent times, CuNPs have expanded considerably for their activity as photolytic degradation of waste water pollution due to their exceptional physicochemical and biological properties, cost efficacy and being sustainable towards the environment (Noman et al. 2020).

CuNPs have been proven to degrade dyes such as safranin which is present in effluents. A number of reactive species such as hydroxyl radicals, holes, and superoxide anion radicals, being potentially accountable for the photocatalytic degradation of the dye safranin. However, a study, showed that OH and H^+ reactive species have the dominant role in the degradation process followed by O^{2-} radicals. The CuNPs get photo-excited upon UV irradiation leading to the surface plasmon resonance phenomenon with a very high efficacy rate in the removal of safranin dye from the waste effluents. Hence, the CuNPs are classified as photocatalysts based on their mechanism of action on degradation of dyes (El-Berry et al. 2020).

CuNPs have been shown to have photocatalysed a number of dyes (Fig. 5), that includes methyl red, methylene blue, crystal violet, methyl orange, Coomassie brilliant blue, Congo red, etc. Removal of these dyes from the waste water effluents with either physical or chemical methods is definitely a herculean task. However, tiny CuNPs have been a promising solution to their photocatalytic degradation and ultimately help to remove these dyes from the effluents and water sources (Hashmi et al. 2021).

The other conventional methods of dye degradation, such as methylene blue are not as effective as using CuNPs due to the fact that other methods are unable to completely degrade the dyes present in effluents. Instead of complete degradation, the dyes are just converted from one form to another and further stay as pollutants. CuNPs ensure that these dyes are completely degraded through photocatalysis. Biosynthesised CuNPs that have less particle sizes exemplify higher photocatalytic activity that is due to the fact that separation of photogenerated charge carriers is extremely efficient along with improvised light absorption with respect to larger specific surface area (Muthuvel et al. 2020). CuNPs under optimal conditions have a very high potential efficacy of 97% dye degradation for methyl red, methyl orange, and phenol red in 5 min (Raina et al. 2020). Furthermore, CuNPs have shown a very

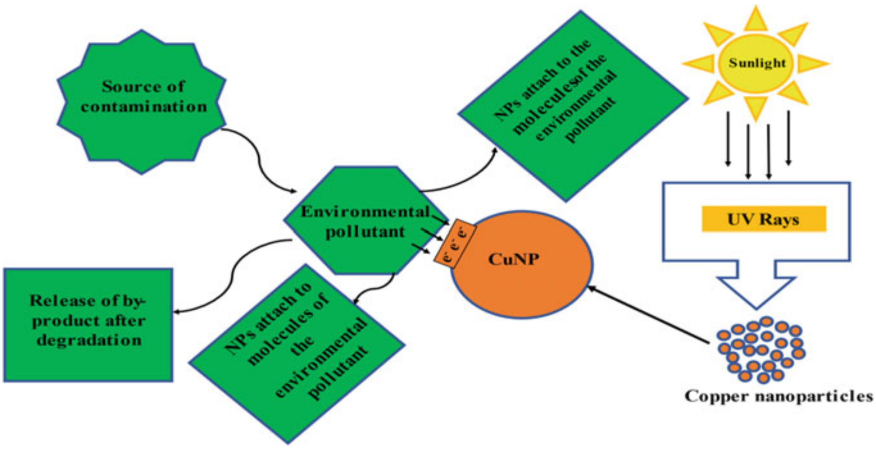

Fig. 5 Representation of degradation of an environmental pollutant using CuNPs

high degradation efficacy of about 91.53% against methylene blue dye (Fathima et al. 2018). Therefore, it can be concluded that CuNPs are immensely useful in aspects of waste water treatment, bioremediation, and photo catalytic degradation of dyes in effluents. They have shown very high potential efficiency and are environmentally friendly, economically feasible bioremediating agents.

Certain CuNPs synthesised using chemical synthesis in laboratories have efficient activity of catalysis than the available commercial CuNP powders or particles. Hence, these CuNPs can be used to increase the rate of Ullmann's reaction and also for the preparation of binary alloys of metallic clusters. Also, employed as intermediates for manufacturing various nano-based drugs. CuNPs are used in the field of sensors for chemicals and catalysis in size-controlled manner that is potentially beneficial in the field of bioremediation as well as bioaugmentation of terrestrial as well as aquatic ecosystems. These chemically synthesised CuNP are soluble in water and possess anti-fungal properties. Furthermore, their high antibacterial potency has been exhibited against *Escherichia coli*, a Gram-negative bacterium as compared to other metallic NPs. CuNPs derived from the plant sources have various uses such as antibacterial activity, photo-catalytic degradation of dyes, antiviral activity, antifungal activity, mycotoxin reduction activity (aflatoxin B1), cytotoxicity towards certain Gram-positive as well as Gram-negative bacteria like *Escherichia coli*, *Staphylococcus aureus*, *Proteus mirabilis*, *Bacillus* spp. etc. They have exhibited a higher fungicidal activity on *Penicillium spp*. Comparatively, *Klebsiella pnuemoniae*, *Pseudomonas aeruginosa*, *Propionibacterium acnes*, and *Salmonella typhi* CuNPs had greater inhibition to *Escherichia coli*. These NPs were adsorbed on the cell surface of *Escherichia coli* and interacted with the cell wall causing impairment to the cell membrane further, leading to an increase cell permeability and decrease in the viability of bacteria. Although the exact mechanism which allows for the antimicrobial effect of CuNPs on bacteria and certain fungi is not fully understood, it is currently subjected to research and need to be further determined (Radha and Saranya 2019).

4.4 Agriculture and Plant Pathology

About 1.3 billion tons of eatable food and raw materials formed for the utility of human being are wasted globally in a year. According to 2018 report from Food and Agriculture Organization FAO, food wastage estimation is seen more in medium compared to high-income countries (FAO 2015). This need has to overcome by the expansion of several conditions like drought, insect and pest-resistant crop or plant varieties and also development of several supplements and disease management strategies fungicides, fertilisers, and pesticides specific to target and have greater impact compared to chemical counterparts existing in the commercial establishments (Dubey and Mailapalli 2016). To fulfil this, metal NPs like copper, silver etc. are extensively used in agro-industries as pose superb antimicrobial agents to prevent the pathogens in food causing food borne infections and also improve the shelf life of food. In recent times, CuNPs have engrossed a great importance in agrochemical industry across all the countries due to its excellent broad-spectrum antimicrobial activity. However, Cu is more preferred because it is comparatively cheaper, ubiquitously available, and cost effective in comparison to Ag and Zn (Ingle et al. 2014). The major concern in agriculture is the crop loss because of several of pathogens which are evidently the microbes. Several of the soil-borne phytopathogens, insect pests, parasites, and predators damage the crops as they directly affect, feeding on them causing the loss for the food industry as well.

Currently nanotechnology opens up the nanoparticle formulated products which can be used in preventing and protecting the agriculture and food industries like the crop yield along with its improvement. Apart from this, Cu also plays a key role as micronutrient towards the development and growth of the plants. Presently, fertilisers and herbicides with CuNPs have been a boon on agriculture as they facilitate easy absorption by the plants. Several studies have demonstrated potential activity by CuNPs against insect pests and fungal pathogens of the crop plants like nanopesticides, nanoherbicides, and nanofertilisers (Dubey and Mailapalli 2016). Nanocopper inhibits the microbial growth by the formation of Cu-oxychloride which forms the complex with chitosan with pathogens like *Fusarium graminearum*, *Alternaria alternate,* and *Curvularia lunata* synergistically with nanohydrogels formed by the Cu-based bio-pesticides to exhibit antifungal activity. The mode of action includes formation of reactive hydroxyl radicals which tend to damage biomolecules such as lipids, DNA, and proteins to prevent of disease by the death of pathogen which is responsible for huge crop loss (Fig. 6) Cu nanocomposites are successful antibacterial agents as Cu ions released by the composite interaction with bacterial outer membrane in turn couples with groups containing carboxyl and amines of the peptidoglycan layer and sulfhydryl groups causing the denaturation of the protein. Similarly, DNA strands are cross-linking with disorganisation of the helical structure causing endocytosis of

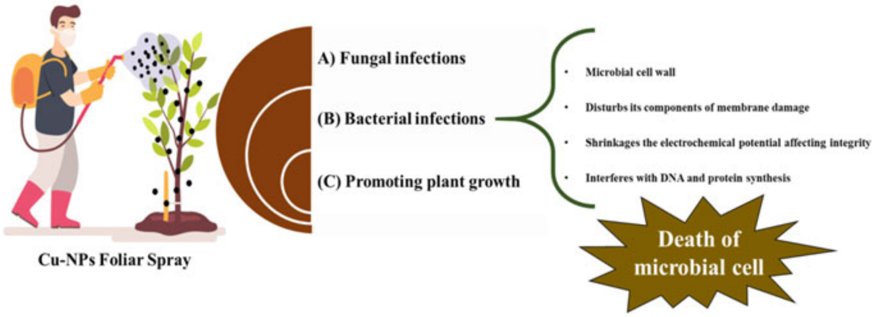

Fig. 6 Probable avenues take part in using CuNP-based formulation in minimising the pathogen and crop management microbial cell death

bacterium. The microbicidal action of CuNPs also favoured by several parameters like particle size, electrostatic hold formed between bacterial cell and CuNPs, cell wall and cell membrane composition of the microbe with the number of hydrophobic and hydrophilic interaction amongst microbial and NPs (Wang et al. 2017). It's been proven that several commercial crops like tea, banana, cocoa, citrus, coffee, and other faced microbial diseases have been succeeded by the action of Cu-based fungicides. Hence, Cu-based bio-pesticides are greatly recommended nanoformulation of nanofertilisers and nanopesticides (Shende et al. 2015). Therefore, CuNPs can be recommended for managing several insects and pests but also can overcome the pathogens that are accountable for food damage. Thus, the use of CuNPs may revolutionise the field of food and biosafety in the coming years.

5 Future Prospectives

CuNPs, due to their exceptional physicochemical characteristics, high electric conduction, and good biocompatibility have been promising factor for nanodevices, in medical, agricultural, and other applications. Currently, newer techniques involving metal NPs are being researched to find new properties and to used varied. Microemulsion has been the most common method for CuNP synthesis using tensioactive substance and organic solvents involving lot of energy and costs (Chandra et al. 2014). This led to the advancement of new techniques that are environmentally friendly, cost effective by including low toxic substrates like alginate as stabilising agent or chitosan-silver-copper organometallic to form the bimetallic particles (Ghorbani 2014). Investigators have been developing new systems using NPs to offer least possible harm to the environment, inexpensive with increased efficacy.

CuNPs have potent antimicrobial activity against pathogens; hence they are used against food spoilage microbes. Future can hold for the benefits of bimetallic NPs, that have been gaining interest due to their increased effectivity like Zn–Cu and Ti–Cu approved by FDA could be used as food preservative and that also has effect on the food pathogens thus expanding the shelf life of the food product. Bimetallic NPs are also effective against the pest hence, can be used as plant protector, utilised as vehicle for enzyme delivery, drugs, antioxidants and anti-browning agents. CuNPs can be used to target specific pesticides and further to enhance its antimicrobial activity it can be stabilised with polyvinylpyrrolidone. CuNPs can be incorporated in polymers like nanocomposites made up of silicates to improvise the efficacy of antimicrobial activity, thermal stability of the film and the physical strength that can be used to enhance the preservation. CuNPs have high efficacy to inhibit against fungal species and insect-pests of crop plants. Therefore, CuNPs can be formulated and can be used as CuNP-based nanopesticides, nanoherbicides, and nanofertilisers that can favour the use in very low quantities. This can further help to eliminate the toxic effects caused by the use of excessive pesticides and fertilisers. CuNP-based biosensors help to manage the pests and also detect the pathogens. It has been estimated that in 2020, NPs have been produced with focus on nanomaterials as high as 20 times than compared in earlier10 years (Ghorbani 2014). It can be very well noted that the use of CuNPs may help to reform the applications in the field of food, medicine, agriculture, bioremediation etc.

6 Conclusions

NPs from natural extracts have gained an immense popularity in the field of nanotechnology worldwide as greener process better consequences without any toxins effecting environment and human health. With being eco-friendly and chemical free, they have managed to be useful in varied applications in major fields of science and technology. The methods need proper consideration with respect to pH, temperature, incubation time to optimise the bio-based synthesis of NPs as these methods are safer, have stability and commercially acceptable. Major synthesis of metal NPs for their effective applications is based on the secondary metabolites from the bio-based extracts with varying concentrations as reducers and stabilisers used for capping. NPs with polymer-based have also been emerging with development in nanotechnology. These green synthesised NPs are a boon due to the various factors like antimicrobial, antifungal, anti-cancer, catalytic, textile, cosmetics, water remediation etc. CuNPs can be the future aspects and help in demanding from them for the welfare of humans and environment.

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Plant Mediated Nanocomposites for Water Remediation

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Abstract The usage of nanocomposites has grown significantly in recent years, due to their exceptionally tiny size and high surface area, which contribute to their mechanical and physiochemical properties with respect to bulk materials of equal chemical composition. Nanomaterials are often synthesized by a combination of physical, chemical, and biological methods. Among them, plant mediated synthesis offers unique properties such as sustainability, biocompatibility, biodegradability, and also many new functionalities in an environmentally friendly manner. Currently, environmental pollution remains a serious global problem that is inextricably associated with various types of anthropogenic activities. Water quality in the modern world is substantially harmed by numerous pollutants and toxins from diverse sources and it can be overcome by the plant-derived nanocomposites as it provides an efficient and cost-effective solution in preventing further pollution and in improving the quality of the water. Thus, this chapter mainly summarizes the purification and remediation of contaminated water with the aid of various plant-derived nanocomposites.

Keywords Nanocomposites · Plant-derived · Water · Remediation · Green synthesis

1 Introduction

1.1 Nanotechnology and Nanocomposites

Nanotechnology has evolved into a multidisciplinary technology as it allows scientists to manipulate the tiny particles of chemical elements and convert them into

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structures of various sizes and shapes to exhibit outstanding properties to satisfy the requirements of various fields (Naushad et al. 2019; Roy et al. 2021a; Nagore et al. 2021; Pandit et al. 2022). Green nanotechnology, as a subset of nanotechnology, has the capability of making a substantial contribution to address environmental issues while promoting sustainable development (Roy et al. 2021b, 2022). Moreover, the commercialization of nanotechnology-based products has advanced in recent years due to their wide range of significant applications (Thacker et al. 2019).

Novel structures of nano-sized materials including metal nanoparticles (MNPs), carbon nanotubes (CNTs), graphene, quantum dots (QD), and their composites have become innovative functional nanomaterials in nanoscience and technology (Singh et al. 2018; Raina et al. 2020). MNPs are suitable to apply in a broad spectrum of disciplines due to their distinctive features such as surface plasmon resonance, optical, electrical, and magnetic properties, mechanical strength, and catalytic activities that may be exploited to execute a number of tasks (Kumar and Gunasundari 2018; Ahmed et al. 2021). Besides, these MNPs can be created and modified with a variety of functional groups, and let them attach to antibodies, ligands, and medicines in the biomedical field.

A QD is a nm-sized semiconductor particle with a core-shell structure that holds electrons in all three directions. Besides, they are widely used due to their unique optical properties as they emit light at specific wavelengths of energy. These wavelengths of light can be fine-tuned by changing various properties of particles, including shape, material composition, and size (Maxwell et al. 2019). Carbon-based nanoscale tubular formations with a significant length-to-diameter ratio are known as CNTs. Mainly, single-walled carbon nanotubes (SWCNTs) with diameters less than 1 nm and multi-walled carbon nanotubes (MWCNTs) with diameters greater than 100 nm are the two types of CNTs reported so far and they are composed of several concentrically linked nanotubes. Graphene-based nanomaterials including graphene oxides and reduced graphene oxides exhibit remarkable electrical, thermal, mechanical, optical, and chemical properties that are responsible for potential applications in the biomedical field, sensors, and solar cells (Popov 2004).

Nanocomposites (NCs) are organic or inorganic materials that are widely studied in recent decades. NCs are prepared by combining two or more substantially distinct nanometer-sized materials, which can include a variety of types including one-dimensional, two-dimensional, three-dimensional, and amorphous materials (Kumar and Gunasundari 2018). Moreover, one or more discontinuous phases are distributed in a single continuous phase and usually are harder and exhibit superior mechanical properties than a continuous phase. The discontinuous phase includes several types of nanofillers including silica, clay, carbon-based materials (CNTs, carbon black), alumina silicate, polymers, biopolymers (cellulose, starch, chitin), etc. (Kumar and Gunasundari 2018; Malaki et al. 2019). The most commonly studied types of nanoscales reinforcing agents are NPs, nanoplatelets, nanofibers, and CNTs. These are often added to the appropriate matrix to raise the modulus of elasticity and yield strength. Furthermore, as the particle size is lowered to the nanometer scale, new materials with novel properties are created. The matrix and the reinforcing agents assembled together, thus the resulting composite material exhibits the average properties of the two phases. Furthermore, the mechanical, thermal, electrical, optical, catalytic, and magnetic properties of NCs will differ from those of individual phases in the composite (Kumar and Gunasundari 2018).

NCs may be divided into three major categories, metal matrix nanocomposites (MMNCs), ceramic matrix nanocomposites (CMNCs), and polymer matrix nanocomposites (PMNCs), depending on the types of matrix employed (Krasno and Swathi 2018).

MMNCs comprised of a metal as the matrix and ceramic or metals as the reinforcement developed to enhance the mechanical properties of light alloys. Ceramic or carbon-based reinforcing agents in MMNCs contribute to the metal matrix's ductility and toughness, as well as the high strength and stiffness of the reinforcement (Malaki et al. 2019). CMNCs consist of ceramics matrix reinforced with ceramic/metal fibers to develop the strength and mechanical properties of the composite. CMNCs mainly composed of Al_2O_3 or SiC systems, as well as the matrix based on Al_2O_3 provide a noticeable strength to the composite (Kumar and Gunasundari 2018). Polymers are frequently employed in a variety of sectors owing to their ease of processing, low weight, and ductility. When NPs are homogeneously incorporated with polymeric matrices, the properties of synthetic polymer NCs are superior to that of the single NPs or single polymer thus improving the mechanical properties (Tyagi and Tyagi 2014; Shameem et al. 2021). PMNCs, composed of polymer or copolymer materials, are a matrix that are packed with inorganic compounds, to increase their physicochemical properties (Shameem et al. 2021). Since the filler of the composite includes nanofillers such as CNTs, nanofiber fillers (plate-like nanofillers, inorganic fillers), and clay, improvement of thermal and moisture stability, solvent resistance, biodegradability, barrier properties, fire retardancy and extraordinary flexibility are observed (Song et al. 2017).

1.2 The Synthesis Process of Nanocomposites

NCs are formed by incorporating NPs, which are synthesized using one of two methods: the top-down approach, where larger materials are converted into nano-sized particles, and the bottom-up approach, in which atoms are combined to form the bulk materials. Physical, chemical, and biological processes can all be manipulated to synthesize NPs within the framework of these two primary approaches. The NPs synthesized from above methods could be incorporated for the synthesis of NCs (Mulvaney 2015; Thacker et al. 2019).

Given the importance of NC materials, various methodologies have been utilized to upgrade the synthesis process. The synthesis of NCs involves primarily physical, chemical, and biological synthetic approaches, the most significant of which are detailed here.

The sol-gel technique is frequently utilized in chemical processes for the synthesis of MMNCs, and it comprises mostly two primary reactions: hydrolysis and condensation. In particular, numerous bimetallic NCs including Au–Ag, Au–Pd, Au–Pt, etc. are prepared through sol-gel method. The chemical precipitation method converts the substance into the insoluble form using additional chemical reagents (Gatos and Leong 2016).

The electrochemical reduction technique is another way that is widely utilized since it is less expensive than other physical methods. The electric current is the driving or controlling force for the formation of MNPs with high purity and controlled particle size where the current density and simple operation methods are optimized. Sputtering is a method to eject NPs from the surface of the target material by utilizing high-energy external impulses. The hydrothermal method is responsible for a pure product with a high yield involving high temperature and low pressure (Gatos and Leong 2016; Malaki et al. 2019). Basically, a polydispersity of the final product and impurities that may be contained in the final products during the milling process are a few drawbacks associated with the techniques mentioned above (Parveen et al. 2016; Hernández-Díaz et al. 2021).

Though several approaches have been invented for the preparation of CMNC, the general methodologies, as utilized, are conventional powder method, polymer precursor route, spray pyrolysis, vapor techniques and chemical methods, which include the sol-gel process, colloidal and precipitation approaches and the template synthesis.

Intercalation of the polymer or pre-polymer from solution, in-situ intercalative polymerization, melt intercalation, direct mixing of polymer and particulates, template synthesis, and in-situ polymerization sol-gel method are all used to synthesize PMNCs. It should be noted that according to the level of penetration of the polymer chains into the silicate galleries, a range of NCs with structures covering from intercalated to exfoliated can be formed during the intercalation processes. Hence, this method has been identified as the industry standard for preparing polymer-layered silicate mixtures (Shameem et al. 2021).

The biological method is referred to as the green synthesis method, is a prominent method that has gained considerable attention for the synthesis of NCs. The biological approach is an eco-friendly, non-toxic, cost-effective, and cleaner methodology for the synthesis of NCs. It is a novel route with the use of plants and microorganisms to convert metal ions into MNPs, which are the reinforcing agents and are regarded as an important tool which is receiving a lot of attention in current research (Kalpana and Devi Rajeswari 2018; Hernández-Díaz et al. 2021).

Many novel methods have been discovered to prepare the NCs to achieve the required composition, size, and shape which influence the distinctive properties of the corresponding composite (Sharifzadeh and Amiri 2021). Direct compounding is utilized for a large-scale production of nanomaterials and polymers. Moreover, this method has some drawbacks since NPs have a high tendency to form aggregates that hinder the homogeneous dispersion of NPs in polymeric matrices. However, to address the aforementioned limitations of NPs, the synthesis of NCs has recently gained immense attention.

Currently, a great advancement has been made in the evolution of bio-based NCs since they are ecologically friendly (Kalpana and Devi Rajeswari 2018). Polymers derived from biosources, such as plant oils, lignin, cellulose, sugars, terpenes, and have been investigated to develop polymer materials with properties comparable to those of synthetic polymers (Song et al. 2017). The biodegradability properties of biopolymers make an effective way for the advancement of NCs that can be used for environmental remediation. For instance, alginate (ALG)-based biopolymer NCs have many applications related to environmental remediation due to its properties including biocompatibility, low toxicity, chelating activity, and hydrophilicity (Kloster et al. 2020). Among the biopolymers, polysaccharides and polypeptides are identified as the suitable candidates due to their low cost and non-toxic nature. (Orta et al. 2020).

Compared to the physicochemical techniques for the preparation of NCs, the green nanotechnology-based NCs synthesis is an ideal solution to minimize the obstructive consequences of the production of nanomaterials while reducing the risks associated with nanotechnology (Shafey 2020).

1.3 Green Synthesis Approach for Nanotechnology

Green synthesis is a concept that is introduced to define the method for synthesizing NCs in an environmentally acceptable manner. Here, the synthesis through plants and microorganisms offers many benefits, including sustainability, widespread availability, and intrinsic incorporation of chemical functionality, biocompatibility, and biodegradability as illustrated in principles of green chemistry (Fig. 1). Recent considerations are given for the preparation of NCs using bacteria, fungi, algae, viruses, and biomolecules for achieving various applications (Mohammadinejad et al. 2015; Parveen et al. 2016; Roy and Bharadvaja 2019). However, the key drawbacks associated with the synthesis of NPs using microorganisms over plant-based synthesis are difficulty in purifying them and poor understanding about the mechanisms, led the researchers to concern more on plant-based biosynthesis of NPs (Mohammadinejad et al. 2015).

Hence, plant mediated synthesis attracted the researchers immensely as it offers significant advantages, including renewability, biodegradability, biocompatibility, cost-effectiveness, reliability, versatility, simplicity, and ease of handling. Most plants function as sustainable and renewable suppliers, as they are able to capture light energy and convert it into chemical energy when compared to microbes and enzymes. In addition, in the same medium phytochemicals and biopolymers consist of the plant extract act as reducing, capping, and stabilizing agents that are essential for the synthesis of NPs and subsequently for NCs.

Plants contain countless reducing agents that are responsible for the synthesis of NPs. As living organisms, plants exhibit an abundance of biomass that could be effectively used for the green synthesis. Primary and secondary metabolites of the plants act as the main bioreactors and molecular suppliers, thus performing a significant

Fig. 1 Concepts of green chemistry for the synthesis of nanomaterials through the sustainable process (Mohammadinejad et al. 2015; Shafey 2020)

role in the NPs synthesis (Mohammadinejad et al. 2015; Hernández-Díaz et al. 2021). Numerous water-soluble plant metabolites such as phenolic compounds, flavonoids, alkaloids, quinones, terpenoids, catechins, organic acids, and co-enzymes are efficaciously utilized for the preparation of NPs in environmentally friendly manner (Ahmad et al. 2019; Hernández-Díaz et al. 2021). Phytochemicals such as vitamin B_1, vitamin B_2, vitamin C, tea and wine phenols act as both reducing and capping agents. Besides, there are numerous green stabilizers that are responsible for stabilizing and functionalizing metallic NPs without adversely affecting the environment and biosynthesis process. In addition, enzymes, vitamins (B, C, D, and K), polyphenols, citric acid, biodegradable polymers, and silica play a role as stabilizing agents (Shafey 2020).

Though, the plant mediated synthesis directly helps to improve the environmental friendliness, through synthesis, regulation, control, clean up, and remediation, it has some major drawbacks such as longer reaction times, tedious purification steps, greater sizes of all NPs, and poor understanding of the fundamental mechanisms (Shafey 2020).

2 Plant-Derived Nanocomposites

Plant mediated NPs which are components of NCs are synthesized by different methods. The intracellular method, where the synthesis and the diffusion of NPs occurs through the cell walls of the plant, the extracellular method, where the NPs are synthesized within cell free extract or supernatant. Generally, NPs are synthesized by combining the plant extract with the precursor salt solution where water is used as the solvent for the extraction, thus, this is a simple, non-toxic, and greener method for the production of NCs (Fig. 2) (Mohammadinejad et al. 2015; Shafey 2020; Bukhari et al. 2021).

The plant extracts are made from various plant parts (leaves, stem, bark, flower, roots, fruit, seeds, peels, pulp, gum). The extract of the plant material is obtained either in aqueous or sometimes organic (mainly used ethanol as a solvent) medium through hot or cold extraction methods (Mohammadinejad et al. 2015).

Most biopolymers, including cellulose, starch, gums etc., are utilized as matrix phases in the synthesis of NCs. Cellulose-fiber-reinforced polymer NCs have gained enormous consideration due to their low density, non-abrasive, combustible, non-toxic, low cost, and biodegradable properties. Cellulose fibers are pretreated to modify the fiber surface, such as chemical functionalization, to protect the moisture absorption process and maximize the surface roughness. There has been a great

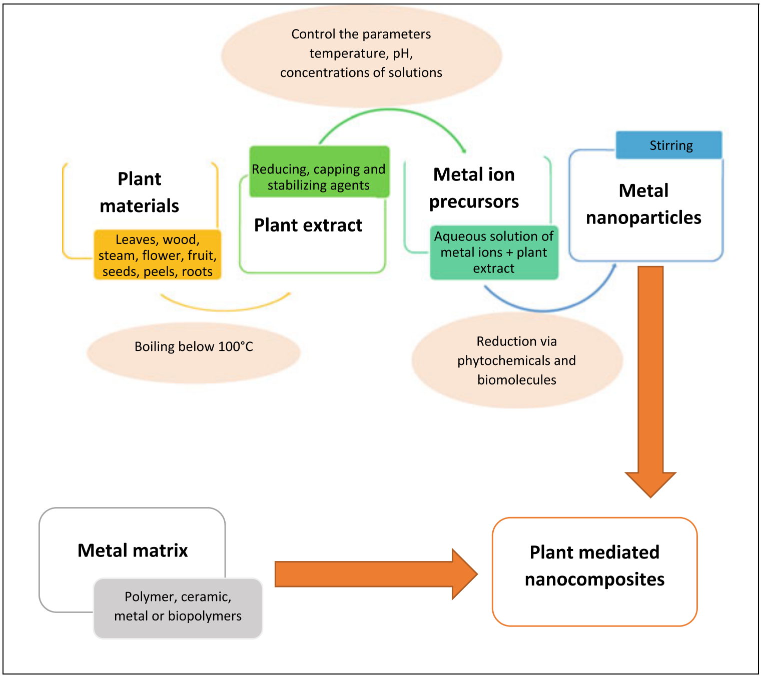

Fig. 2 Synthesis of plant mediated nanocomposites

interest in gum bio-based NCs in the past five years (Nazarzadeh Zare et al. 2019). Gums contain a lot of hydroxyl groups, which when mixed with water, generate hydrogen bonds that impart high viscosity and thickening to the solutions. Gums are also used for production of hydrophilic matrix pills as they have high capability of swelling, and are non-toxic and inexpensive (Pal et al. 2015).

Polymer-layered silicate NCs have been efficaciously synthesized by the addition of clay into triglyceride-based polymers which are derived from plant oils, can increase the applicability of new bio-based NCs by enhancing their mechanical properties (Lu et al. 2004).

Several parameters affect the formation of NCs, including temperature, pH, concentrations of metal ion solutions and plant extract, irradiation methods, etc. Irradiation methods such as UV, microwave, and solar irradiations are also applied for the synthesis of NCs, where it produces NPs with various shapes, sizes, and yields (Bukhari et al. 2021). Moreover, the microwave irradiation method is responsible for the rapid synthesis of NPs due to the generation of enormous amounts of heat that occur with high-frequency electromagnetic radiations (Shafey 2020). The homogeneous heating via microwaves generates the direct nucleation process of NPs and that results in the rapid and uniform synthesis of NCs. Using the aforementioned procedure, MNPs or MONPs are obtained as nanofiller or reinforcing agents. The prepared NPs are incorporated into a metal, ceramic or polymer matrix for the purpose of synthesizing NCs (Singh et al. 2018; Bukhari et al. 2021).

3 Plant-Derived Nanocomposites for Water Treatment

3.1 Basic Sources of Water Pollution

The environmental damage is worsening day by day as a result of unavoidably detrimental anthropogenic activities that cause an imbalance in the ecosystem via depletion of natural resources and extinction of wildlife. The continued spread of industrialization and urbanization processes leads to the generation of huge amounts of harmful wastes that contaminate the air, water, and soil, which result in a slew of consequences for human wellbeing and environment (Ibrahim et al. 2016; Orta et al. 2020).

Contamination of aquatic systems is caused by harmful pollutants that are primarily found in domestic wastage, urban run-off, industrial sewage, hospital waste, and agricultural wastewater, which originated from sources such as food processing, pulp/paper manufacture, textile, surgeries and laboratories, agriculture, aquaculture, and so on. Toxic and persistent effluents such as inorganic pollutants (heavy metals), organic pollutants (toxic dyes, pesticides, herbicides, fertilizers, hydrocarbons, phenols, plasticizer, detergents, oil etc.) are discharged into the environment by the aforementioned sources (Ibrahim et al. 2016; Singh and Gupta 2017). For human beings, and flora and fauna, water resources are fundamental for confirming survival on the earth. However, with the rapid growth of population with their requirements, industrial activities have developed without the corresponding care of the environment. As one of the negative circumstances of it, the pollution of hydric resources in detrimental ways are currently unbearable (Schweitzer and Noblet 2018).

Nowadays advancement of the nanomaterials from the field of environmental remediation has gained much attention especially in remediation of wastewater, drinking water, and groundwater.

3.2 Nanocomposites for Water Treatment

The use of clean water is an essential components of the survival of living beings and their associated activities. Thus, the water quality must be improved and which could be accomplished by removing hazardous chemicals from contaminated water via physiochemical, and biological processes. The primary conventional physical methodologies for removing pollutants from water bodies include coagulation, ion exchange, membrane filtration, reverse osmosis, and adsorption. Chemical approaches that can be used for wastewater treatment include oxidation, ozonization, photochemical, and electrochemical processes (Zinicovscaia 2016; Yu et al. 2021). However, due to the outstanding properties of NCs, such as large surface area, magnetic, and photocatalytic capabilities that accountable for polluted water treatments, they play a key role in overcoming challenges with the effectiveness of pollutant removal via physical and chemical conventional techniques.

Hence, nanomaterials-based techniques for removing contaminants from water bodies are developing as potential alternatives to current water treatment systems. For an instance, the water quality is enhanced through various novel materials such as nanoclays and ceramics, bioactive NPs, nanocatalyst-based procedures including nanostructured catalytic membranes, nanofiltration, and CNT-based techniques (Moreno-Sader et al. 2019; Ali et al. 2020). These nano-sized materials are responsible for achieving the anticipated quality of the water with respective to the selectivity, high capacity, and recyclability of ligands for toxic metal ions, organic and inorganic solutes, radionuclides, etc.

3.3 Plant-Derived Nanocomposites for Water Treatment

NCs synthesized by utilizing plant-derived materials (husks, woods shavings, straw, etc.) contribute to the sustainable development as most of the agro waste are utilized for the synthesis of NCs as a value addition. For example, husk, an agricultural waste, includes significant floristic fiber, protein, and functional groups (carboxyl, hydroxyl, and amidogen) which allow for the adsorption of contaminants from wastewater processes. It has also been used successfully to eliminate colored components and metal ions from contaminated water (Nakbanpote et al. 2007). Further, polyaniline/rice husk NCs was synthesized for the removal of arsenic ions from aqueous solutions by batch sorption method (Lashkenari et al. 2011).

Plant-based carbon sources are considered as biodegradable, renewable, non-toxic, largely available resource materials for the production of NCs. Due to the high stability, physiochemical strength, pine wood shavings have been exploited as a renewable carbon supply matrix. Reduced iron oxide NPs impregnated magnetic pine wood shavings NCs was developed as an adsorbent for the removal of phosphorous from contaminated water with 100% removal efficiency (Ramasahayam et al. 2012).

Due to their superior adsorption properties, the incorporation of binary metal oxides including titanium-iron oxide, cerium-iron oxide, iron-manganese oxide, iron-tin oxide, iron-zirconium oxide, and other inorganic materials into carbon framework to produce NCs has made significant progress in water purification (Siddiqui and Chaudhry 2017). Keeping these in mind $MnFe_2O_4$/biochar, *Nigella sativa* seeds-based NCs has been developed as an effective adsorbent for water treatment providing clean and affordable drinking water (Siddiqui and Chaudhry 2018). Hence, it is imperative to employ remedial measures for the proper treatment of contaminated water by applying novel nanoscience technologies (Patients et al. 2012).

3.4 Remediation Processes of Contaminant from the Eco Systems

3.4.1 Nanoadsorbents Mediated Waste Water Treatment

The adsorption process is the most widely used technique of water filtration. Several economical nano range adsorbents generated from agricultural and industrial by-products, natural materials, or modified biopolymers have recently been prepared and utilized to eliminate heavy metals from contaminated water by adsorption process.

The adsorbing phase is the adsorbent that removes impurities from a fluid using a solid adsorbent in the adsorption process. Figure 3 depicts the adsorbate, which is made up of components that have been adsorbed on the phase's surface. Adsorption is an appealing option for reducing the quantity of heavy metals in wastewater, which might be readily accomplished due to the adsorbents' availability, cheap cost, eco-friendliness, and high efficiency. Furthermore, these new adsorbents have been created to increase the selectivity, capacity for adsorption, and durability of classic adsorbents for massive-scale use (Qalyoubi et al. 2021).

Nanosorbents are nanoscale organic or inorganic particles that absorb other substances owing to their distinct characteristics, such as their huge surface area and high substance specificity, which aid in the removal of targeted pollutants rapidly and specifically. Polyaniline, carbon materials (activated carbon, CNTs, biochar), anion exchanger (zeolites), anthracite, biopolymers, metal oxides such as TiO_2, and other

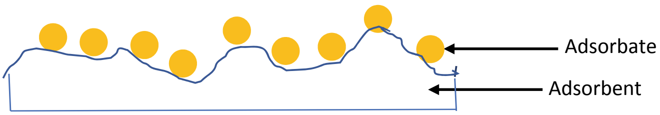

Fig. 3 Adsorption process

adsorbents have been widely employed to remove contaminants from polluted water bodies (Qalyoubi et al. 2021).

NCs generated from zero valent iron (ZVI) NPs have been utilized to clean up water pollution due to their remarkable features such as biodegradability, low toxicity, magnetic sensitivity, and dual redox properties in water. The increased reactivity of ZVI NPs in the wastewater remediation process is due to their large specific surface area, high density of reactive surface sites, and higher intrinsic surface reactivity. However, due to the magnetic property of the iron NPs, the aggregation of ZVI NPs is increased, hence decreasing the desired reactivity of ZVI NPs (Ibrahim et al. 2016). To circumvent this hindrance, stabilizing and capping chemicals are added to protect the NPs from aggregating. This is possible through the plant mediated synthesis of iron NPs, and there are numerous Fe-containing NCs invented recently and are used in the environmental remediation process (Table 1) (AlSalhi et al. 2020; Puthukkara et al. 2021). Furthermore, as per the published literature, most of the agro waste such as sorghum bran, eucalyptus leaf, pomegranate leaf, banana peel etc. have been utilized in the preparation of iron-based NPs for adoption of heavy metals (Herlekar et al. 2014). Applying leaf extract of eucalyptus prepared from its leaf litter, polydisperse iron NPs such as nanoscale ZVI, Fe_3O_4 and Fe_2O_3 were synthesized. These synthesized NPs are responsible for removing significant amounts of nitrogen, P and chemical oxygen demand (COD) from eutrophic wastewater bodies (Herlekar et al. 2014).

As per the published literature, ZVI NPs-based NCs used to remove a variety of water pollutants including antibiotics and drug residues, halogenated organic compounds and nitro compounds contained agro chemicals, inorganic ions, heavy metals, dyes, and radioactive elements. The typical reaction between ZVI NPs with oxygen and water is given below:

$$2Fe^0 + 4H^+ + O_2 \rightarrow 2Fe^{2+} + 2H_2O$$
$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$$

Though pollutants are allowed to settle by attaching to ZVI NPs-based NCs, Fe^{2+} ions are responsible for eliminating toxic pollutants from the wastewater bodies. Several modifications are implemented during the synthetic process to enhance the desired activity of the ZVI NPs, such as encapsulation of ZVI NPs in a matrix such as silica, activated carbon, etc. and emulsification of ZVI NPs using oils, doping the ZVI NPs with other catalytic metals, coating ZVI surface with polymer, surfactants, and natural products (Aragaw et al. 2021; Puthukkara et al. 2021).

Table 1 Plant mediated NCs for environment application

Pollutant	Nanocomposite	Plant materials for biosynthesis	Particle size of the reinforcing agents	References
Removal of toxic dyes				
Methylene blue	Sugarcane bagasse, hickory chips-derived CNT-(biochar)BC NC	bagasse of *Saccharum officinarum*	50–100 nm	Chausali et al. (2021)
Congo Red Azo dye	Ag–Au bimetallic NC	Commercially available *Camellia sinensis*	20–200 nm	Kang and Kolya (2021)
Methylene blue	MMT/Ag	*Sida acuta* leaves extract	NA	Anjum et al. (2019)
Methyl orange	Fe–Ni NC	*Eucalyptus* leaf extract	20–50 nm	Weng et al. (2017)
Malachite green	Ni/Fe_3O_4 NC	*Moringa oleifera* leaf extract	16–20 nm	Prasad et al. (2017)
Azo dyes (adsorption)	Fe-Polyphenol NCs	*Eucalyptus tereticornis*	40–60 nm	Wang (2013)
Azo dyes (degradation)	Fe-Polyphenol NCs	*Eucalyptus tereticornis, Melaleuca nesophila*, and *Rosemarinus officinalis* extracts	40–60 nm	Wang (2013)
nitroarenes in an ethyl alcohol	Cu/Fe_3O_4	*Silybum marianum* L. seed extract	8.5–60 nm	Sajadi et al. (2016)
Acid black acid brown	Iron oxide/Pd NC	*Piper nigrum* seeds extract	NA	Wang (2013)
Removal of heavy metals				
Pb (II), Cu (II), and Zn (II)	Rice straw-derived HAP-BC NC	Straw of *Oryza sativa*	4.6–29.2 nm	Chausali et al. (2021)
Cr (VI)	nZVI and Fe-oxide NCs	*Eucalyptus* leaf extracts	NA	Manquián-Cerda et al. (2017a)
As	Fe (oxide, hydroxide), and nZVI	*Vaccinium corymbosum* leaves	61.1–106 nm	Manquián-Cerda et al. (2017b)
Cr (VI) and Copper ions	nZVI, Fe-oxide NCs	*Eucalyptus* leaf extract	NA	Zeng et al. (2011)
As (III)	Fe/Clay supported NC	Commercially available *Camellia sinensis*	48–70 nm	Tandon et al. (2013)

(continued)

Table 1 (continued)

Pollutant	Nanocomposite	Plant materials for biosynthesis	Particle size of the reinforcing agents	References
As (III), (V)	Fe/Chitosan supported NC	*Mentha spicata* L. extract	20–45 nm	Prasad et al. (2014)
As (V)	Fe/Chitosan supported NC	*Eucalyptus globulus*	48–70 nm	Saif et al. (2016)
Removal of organic pollutants				
Nitrobenzene	Copper supports on Fe_3O_4 nanocatalysts	*Silybum marianum* L. (plant seeds)	8.5–60 nm	Sajadi et al. (2016)
Cyanation of aldehydes	$Cu/RGO/Fe_3O_4$	*Euphorbia bungei boiss* leaves	46–78 nm	Nasrollahzadeh et al. (2017)
4-nitrophenol	Pd/RGO/ Fe_3O_4 NC	*Withania coagulans* L. extract	7–13 nm	Atarod et al. (2016)
4-nitrophenol	Ag–Au bimetallic NC	Commercially available *Camellia sinensis*	20–200 nm	Kang and Kolya (2021)
Ipso-hydroxylation of boronic acid in water	Fe_2O_3/SiO_2 NC	*Zanthoxylum rhetsa* fruit extract	5–21 nm	Saikia et al. (2017)
Removal of inorganic pollutants				
Phosphate removal	SiO_2–biochar NC	Vermiculite treated algal biomass VBC	5.7 nm	Chausali et al. (2021)
Fluoride removal	Fe-Al bimetallic NCs	*Syzygium aromaticum* extract	458.9 nm	Mondal and Purkait (2019)

NA—Not available

3.4.2 Nanophotocatalytic Process for Removal of Biodegradable Pollutants from the Wastewater

Photocatalysis is solar-based physicochemical technique that is used to photodegrade organic contaminants. The procedure is an ecologically benign, sustainable, and energy-saving technology that was developed as an alternate method for degrading numerous organic contaminants. The capacity of a material to generate an electron–hole pair as a result of exposure to solar radiation is referred to as photocatalytic activity (Petronella et al. 2017; Lin et al. 2020).

The photo-oxidation process of nanoscale semiconductors has received a lot of attention since of their potential applications in the field of environmental protection. Further, semiconductor-based photocatalytic oxidation processes can potentially be used in photocatalysis, environmental treatment, self-cleaning, novel generation solar cells, etc. Additionally, semiconductors are commonly used in photocatalysis processes because they may generate electron-hole pairs upon photoexcitation of the bandgap. Photogenerated e-/h+ species are capable of creating reactive oxygen species (ROS), which could result in pollutant photocatalytic conversion. Due to their unique optical and electric properties of plasmonic metals, the use of plasmonic MNPs such as Au and Ag NPs with semiconductors has resulted in increased photocatalytic efficiency (Petronella et al. 2017).

The oxidation process is applied for wastewater treatment through photocatalysis. As the reinforcing agents, NPs in the NCs such as Ag, Au, Fe, iron oxides synthesized by greener methods are extensively used as photocatalysts for the remediation of organic dyes (Table 1) (Petronella et al. 2017). As the first photocatalyst discovered, TiO_2 has long been used to remove pollutants from water sources due to its high chemical stability and excellent catalytic properties.

For instance, TiO_2 NPs prepared by using leaf extract of *Syzygium cumin* were highly effective in removing Pb from waste water, where TiO_2 NPs act as the photocatalyst (Sethy et al. 2020). Furthermore, the use of biological derivatives, derived from plants such as starch, cellulose, and so on has been reported for the straightforward green synthesis of TiO_2 NPs (Irshad et al. 2021). Starch has been reported to be used in the synthesis of TiO_2 with strong photocatalytic properties. Also, cellulose fibers were used to efficiently synthesize homogenous TiO_2 nanowires. It also revealed the advantages of cellulose fiber recovery without morphological alteration and use as the matrix phase of the NCs for waste water treatment (Muniandy et al. 2017).

The breakdown of organic contaminants used with visible light irradiation to assess the sample's photocatalytic activity. The two major processes for effective pollution removal are adsorption and photocatalytic degradation (Petronella et al. 2017; Lin et al. 2020; Trinh et al. 2021).

3.5 *Removal of Organic Contaminants and Toxic Dyes*

Organic pollutants in the environment, such as dyes, drug residues, phenolic compounds, herbicides and pesticides, phthalate esters, and polycyclic aromatic hydrocarbons, are exceedingly hazardous and detrimental to both humans and the environment (Pai et al. 2021). Montmorillonite (MMT)/Ag NCs, for example, is used to remove methylene blue from contaminated water. MMT's exceptional features, such as surface area, mechanical stability, swelling capabilities, and high cation exchange capacity, aid in the effective removal of contaminants from contaminated water. Ag NPs synthesized from *Sida acuta* leaves extract have been utilized as a reinforcing agent for NCs to catalyze the degradation of textile dyes. As a result, the efficacy of NCs containing Ag NPs in the elimination of dyes from contaminated water is enhanced (Anjum et al. 2019).

One of the most concerning challenges encountered while addressing environmental contamination is the release of reactive dye effluents as toxic and persistent pollutants into the adjacent water bodies. Not only are reactive dyes harmful to the environment, but they are also linked to health issues such as cancers, severe inflammatory responses in the gastro intestinal tract, methemoglobinemia, irritation in the eyes, etc. (Das 2014). Furthermore, such toxins enter to the food chains, and causing significant health problems to human.

Ionic, anionic, and non-ionic dyes are the three types of dyes that are classified according to the charge under the aqueous solution, where dyes form positively charged ions called cationic/ionic dyes, and negatively charged ions are anionic dyes. Vat dyes and disperse dyes are non-ionic dyes (Das 2014). Organic dyes are mostly discarded by nearby industrial effluents such as paper production, plastic, leather, pharmaceutical, cosmetic, textile, and food sectors. Removing dyes from wastewater is critical in avoiding negative impacts on human health and the eco system. Further, dye molecules are dangerous and persistent due to their complicated and stable chemical structure of chromogen-chromosphere, which makes biodegradation difficult. The chemical components in dyes are extremely resistant to solar irradiation, microbial attack, and for the oxidizing agents. As a result, these chemicals are difficult to decompose and produce safe products for humans and the environment (Aragaw and Bogale 2021; Mittal and Roy 2021).

Conventional dye removal methods include coagulation-flocculation, biodegradation, electrochemical oxidation, ion exchange, Fenton oxidation, reverse osmosis, ozonation, and adsorption. Among them, adsorptions are the most efficient dye removal processes as they bind the particles on the adsorbent's surface through physical and chemical forces (Aragaw and Bogale 2021). In terms of cost, efficiency, feasibility, and negative environmental effect, each physical and chemical water treatment process has benefits and drawbacks. To overcome such constraints, a combination of several treatments is frequently utilized to attain the targeted water quality in the most cost-effective manner (Crini and Lichtfouse 2019). However, owing to its unique features, plant-derived NCs-based water treatment is now developing as an exceptional strategy for effective waste water treatment.

Recent research shows that hydroxyapatite (HAP) NCs can remove dyes from polluted waterways mainly by adsorption of cationic dyes by the electrostatic attraction adsorption mechanism. The adsorption of cationic dye in wastewater has been boosted by nanobiochar generated from the pyrolysis of reed straw biomass combined with HAP (Tan and Sen 2020; Pai et al. 2021).

Most of the hazardous dyes are colored substances that contain aromatic compounds which are difficult to degrade and prevent sunlight and oxygen in to the waterbodies which is detrimental to the survival of aquatic forms (Kang and Kolya 2021).

3.6 Removal of Heavy Metals

As heavy metals are harmful and cancer causing, substantial emphasis is paid to the cleanup of polluted water bodies. The adsorptive removal through nano-sized materials like MOs, metal organic frameworks, zeolite, and carbon-based materials is commonly available due to their outstanding properties such as large active surface area, numerous functional groups, and high chemical and thermal stability (Qalyoubi et al. 2021).

Heavy metal ions such as Cu, Zn, Pb, I, Cr, Se, Hg, and Cd are frequent inorganic pollutants found in industrial and drinking water. They are basically classified into two main groups as divalent, where the oxidation number of the metal is two (Cu (II), Cd (II), Pb (II), Zn (II),) and multivalent, where the oxidation number is more than two (As (V), Cr (III), Cr (VI), Co (II), Se (IV), Se (VI)) (Jung et al. 2021). When compared to divalent heavy metals, multivalent heavy metals contain in waste water bodies inflict more harm to the human health. For instance, several multivalent heavy metals, such as As (V), undergo biotransformation, resulting in the formation of hazardous and carcinogenic methylation compounds. Inorganic As compounds are transformed enzymatically into methylated arsenics by bacteria, algae, fungus, and humans during the biotransformation process. Hexavalent chromium (Cr (VI)) penetrates the cell membrane more effectively than Cr (III), and these chromates are causing serious problems for human health such as DNA mutations, cancers, and so on (Crini and Lichtfouse 2019).

Adsorptive NCs membranes that are made up of the dispersion of nano-sized adsorbents (MOs, carbon-based materials etc.) in the polymer matrix (biopolymers, zeolite etc.) are a good solution for removal of heavy metals efficiently. Photocatalytic materials such as semiconductors and MOs (TiO_2, ZrO_2, ZnO and WO_3) are involved in the oxidation and reduction of heavy metal ions. Heavy metals from wastewater have been removed by using MOs NPs such as SiO_2, TiO_2, ZnO, and Fe_2O_3. Plant-derived NCs are primarily prepared by the use of biopolymers such as cellulose, which function as matrix phase in the composite. Further, NPs such as Fe NPs synthesized from plant extract are employed in the removal of heavy metals from polluted water sources (Table 1) (Kumar et al. 2021). For instance, *Eucalyptus globulus* leaf extract was used as the bio reducing agent for synthesize nanoscale ZVI and those act as adsorbents for sufficient removal of hexavalent Cr within 30 min (Herlekar et al. 2014). According to the findings, tea polyphenols are employed as a bio-reducing, capping, and stabilizing agent in the synthesis of ZnO nanorods for the effective adsorption of Pb^{2+} from waste water bodies (Zhang et al. 2018).

Removal of heavy metals from contaminated water can be carried out through several currently used strategies such as ion exchange, solvent extraction, physical and chemical precipitation, reverse osmosis, membrane filtration, electrochemical precipitation, and adsorption process (Jung et al. 2021). Due to their high cost and intricate approach, the majority of these treatments are complicated. As a result, the need for the development of a new technique that takes advantage of the availability of low-cost materials for heavy metal ions removal has arisen. The adsorption method has been discovered to be one of the most successful and feasible ways for heavy metal remediation from polluted water bodies (Pai et al. 2021). Heavy metal adsorption is accomplished by chemisorption and physisorption, which are based on the interaction of adsorbents with heavy metal ions. The attraction that may be formed between positively charged heavy metal ions and negatively charged nanoadsorbents is known as electrostatic interaction (Nasir et al. 2019).

There are several factors including contact time, pH of the solution, initial heavy metal ions concentration, adsorbent dosage, and temperature that basically affect the adsorption process of heavy metals. The pH of a solution can affect the ionization degree of an adsorptive molecule as well as the adsorbent's surface properties. The binding speed of heavy metals into adsorbent is responsible in order to remove harmful contaminants from wastewater which is determined by the contact time. The initial concentration of heavy metal ions is an important adsorption rate parameter and probable interactions between heavy metal ion concentration and accessible sites on the adsorbent surface. The adsorbent concentration in relation to the adsorbent capacity to absorb metals with the least amount of adsorbent is a critical parameter. If the adsorption dose rises with rising temperature, the process is endothermic. As the temperature rises, it caused the high mobility of both ions of heavy metals and numerous active sites of the adsorbent (Yousef et al. 2020).

4 Challengers and Future Prospective

The water remediation techniques such as photocatalytic/chemical catalyzed degradation, adsorption of pollutants, pollutant sensing and detection methods through NCs that are prepared via a greener approach could have numerous applications. However, the mechanisms of interactions between the contaminated water and the composite which comprises the matrix and incorporated nanofiller are needed to be studied further. Further, large-scale synthesis of plant mediated NCs and more practical uses remain viable options. Extensive use of plant-based NCs in water remediation has demonstrated their potential to adsorb metals and organic contaminants from polluted water. More progress must be made in the use of water remediation for selectivity in material removal, resistance to variations in pH and concentrations of chemicals present in polluted water, long-term stability, and cost optimization. Thus the long-term efficiencies of the plant mediated NCs which is an important practical aspect that should be addressed much more in future.

5 Conclusion

Plant mediated NCs are widely used for many key applications in numerous industrial fields however, there are many technical and economic barriers to their widespread adoption for commercialization. Hence, innovative technologies must be invented to synthesize materials that exhibit unique properties and upgrade performance for industrial applications. Consequently, sustainable, greener, and low-cost methods should be developed to meet the growing demands arising from advances in science and technology. Apart from the physiochemical methods for synthesizing NCs, the use of plant extracts, a biological method is an alternative approach to study the shape controlled and broad size distributions of the NPs and NCs. NCs exhibited applications in water reclamation, discharge of heavy metals, organic pollutants, drug residues, dyes, and elimination of pesticides from the contaminated eco system. Plant-derived NCs as environmentally friendly, biocompatible, and efficient materials in terms of water remediation, basically through adsorption and photocatalytic techniques, are highly applicable in the wastewater treatment.

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Photocatalytic Degradation of Dye from Various Metal/Metal Oxides Derived from Diverse Plants

Mahendra Pratap Singh, Prakash Baburao Rathod, and Subodh Kabirdas Sakhare

Abstract Toxic dyes are rapidly becoming a big issue in terms of water/soil pollution, as they have an effect the purity of world water bodies, human health and creatures. Unscientific management of industrial dye waste is the primary cause of water pollution. The dyes that come from industries kept a lot of impact on aquatic ecosystems. The ingestion of these dyes through food, vegetables and fish has long-term negative consequences, making them toxic to human health. Therefore, it is a pressing necessity to obtain a simple, quick and low-cost technique for detecting, identifying and purifying these dyes in aqueous medium or from any other source. Various processes, such as sorption, photocatalytic degradation and conversion, can be used to handle industrial waste dyes. Compared to sorption and conversion, photocatalytic degradation has various advantages, including environmental protection and total pollution degradation. Photocatalytic degradation is possible with both metal and non-metal nanoparticles. There are numerous papers on the use of CNTs, ZnO, TiO_2 and other nanoparticles for dye degradation, but the preparation of this both metal and non-metal are required harsh reaction condition and which cause a harmful impact on the environment. The production of nanoparticles using various plant extracts (phyto-nanoparticles) has a cleaner approach. To use of such nanoparticles in the dye degradation process has more impact.

Keywords Environmental pollution · Metal/Non-metal nanoparticles · Dye degradation

1 Introduction

Nanoscience and nanotechnology are primarily represented through the synthesis of NPs of various chemical compositions, shapes, sizes and balanced dispersity, as well as their potential uses in human health. Because of changes in their natures like a size, shape, size modification and big surface cover to volume ratio, nanoparticles (NPs)

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get novel and better applications with respect to bulk analogues (Pandit et al. 2022). A primary step in nanotechnology research is the production of metallic and semiconductor NPs via different ways. Nanoparticles have huge number of surface atoms, resulting in a large surface area have lately produced and contributed considerably to the generation of a variety of distinct synthetic metal nanoparticles (MNPs). There are numerous ways to synthesise a nanoparticle but nanoparticles made from variety of extracts from plant components has a positive approach toward green synthetic root. In the current decade a lot of published research articles have demonstrating the value of plant-based green nanoparticle manufacturing. Plant phytochemicals show the quality to both reduce the size of the nanoparticles and have capacity to stabilise nanoparticles.

Water resources have been disproportionately harmed by modernisation and new industrial advances due to these humans and aquatic organisms may be at risk (Verma et al. 2020). More use of organic dyes results to adverse environmental effects, particularly on water resources such as rivers and ponds, as well as groundwater. The introduction of new chemicals has transformed the structure of wastewater streams from the past some decades. Silver and copper nanoparticles are the most investigated and prospective nanoparticles among several noble metals operating as nanoparticles that have been identified for a long time. The catalytic characteristics of silver and copper nanoparticles are good which can be useful in the remediation of water. Iron-based nanoparticles have sparked a lot of interest in contaminated land and groundwater cleanup in recent years because of their enormous surface per volume proportion.

In comparison to physical and chemical approaches, biological nanoparticle production has recently gotten more attention because of their positive impact on environment. Plant extracts and microorganisms are commonly used to make nanomaterials. In comparison to microorganisms, the synthesis of NPs taking plant extracts is advantageous since it deletes the arduous methods of sustaining cell cultures and could be scaled up successfully for large-scale NP processes.

NPs have several applications in the areas of physics, chemistry, biology, bio labelling, antimicrobials, electronics, catalysts, optical fibres, agriculture and sensors. Metal and Metal Oxide Nanoparticles (MONPs) are appealing to a wide spectrum role in nanoscience and nanotechnology. The nanobiotechnology industry is rapidly increasing, necessitating extensive research into the environmental effects of this nanomaterial.

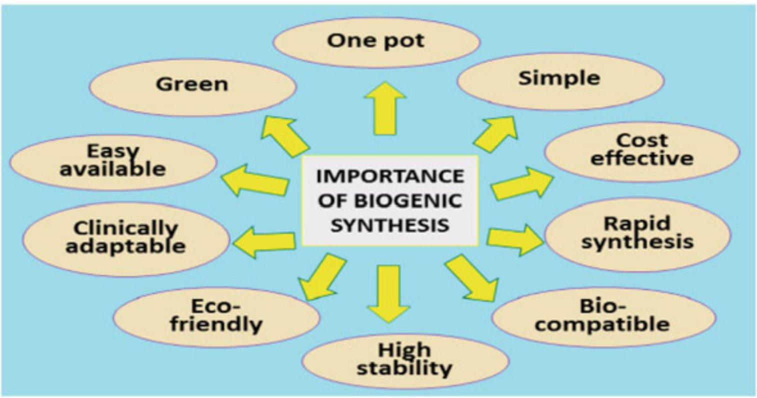
The use of green-produced metallic nanoparticles as an effective catalyst for the degradation of different dyes has been extensively investigated in this regard (Rasheed et al. 2018). Metal nanoparticles' unique physical, chemical and electrical properties suggest that they are ideal material for the organic dye reductive degradation, making them a viable alternative to traditional dye contamination removal procedures. Green-produced silver nanoparticles are currently being utilised extensively to minimise dye stuffs in aqueous media (Roy et al. 2021a, b). The photocatalytic dye degradation from various metal/metal oxides generated from various plants was the subject of this chapter.

2 Importance of Plant-Mediated Route Over Other Routes

Sonochemical methods, solvothermal, phyto-synthesis, thermo-decomposition, photochemical synthesis, laser-abiliated technique, physio-chemical process, flow process, microwave technique, reduction in solution, wet chemical and electrochemical among others are frequently used to synthesise MNPs with desired properties. In terms of synthetic pathways, environmental consequences and cost effectiveness, MNPs synthesised by bacteria, plant extract and fungi kept more importance than traditional approaches. Because of its simplicity, cheap cost, nontoxicity and eco-friendly, biological nanoparticle production utilising plant extracts has gotten increased attention. Plant-medicated nanoparticle production offers various advantages over other approaches, including being a fast method for extracellular nanoparticle creation on a large scale (Roy et al. 2022). Importance of biogenic/green synthesis was shown in Scheme 1.

Microbes and plants both have antioxidant and reducing abilities, which are responsible to reduce metals to metal nanoparticles in plant synthesis. Plant-based synthesis of MNP is favoured over biological approaches due to ease of availability and lower production costs. It does not require any expensive equipment and not obtain a dangerous by-products. The plant-based biosynthesis of AgNPs utilising a number of plant extracts has received a lot of focus. Microbe-mediated and Plant-mediated, nanoparticle production approaches have recently been popular. However, microbe-mediated methods are multi-step, time-consuming procedures (Roy et al. 2021a, b).

Plant phytochemicals have the ability to both reduce and stabilise nanoparticles. When compared to nanoparticles made with sodium borohydride, magnetic nanoparticles made with green technologies have been determined to be non-toxic. The different phytochemicals, acting in the form of reducing agent in the synthesis of Metal Iron Oxide Nanoparticles (MIONPs) from iron salts, obtained from



Scheme 1 Importance of biogenic synthesis of NPs (Ahmed et al. 2017)

Cynometraramiflora fruits according to the researchers. Furthermore, the synthesised MIONPs were characterised using a variety of methodologies and the photocatalytic capacity of nanoparticle was determined by degrading a pollutant dye.

Traditional methods are no longer suitable due to unable to reduce the toxicity of wastewater contaminants, high level of energy consumption and capital expenditure. In current years, biological synthesis has arisen as a viable substitute than standard catalyst nanoparticle synthetic methods. Nanoparticles obtained with a different range of sizes, shapes, compositions and properties by biological objects, acting as biological factories, is a non-toxic, clean and eco-friendly technology. Plant extract nanoparticle synthesis is simple, easy to obtain for large-scale nanoparticle manufacturing and advantageous strategy because it does not require any specific, sophisticated, or multi-step methods like isolation, culture preparation (Swami et al. 2004).

Green technology has overcome physical and chemical methods because of its more eco-friendly environment, has the ability to be synthesised on a big scale, is cost-effective and does not take higher temperatures, pressures, or energy as well as harmful substances. The probability of generating nanomaterials from water bodies has been newly investigated using stabilising or capping agents.

For reduction and capping, both processes require a lot of energy and harmful chemicals and they're not easily scalable. The use of toxic chemicals in these synthetic processes compromises with biocompatibility of nanoparticles and these chemicals remain on the nanoparticles surface after numerous time of washing, which is a major problem. Due to the participation of plant-based biological entities (carbohydrates, proteins, glycoproteins, macromolecule proteoglycans, biological polyacids and nucleic acids) in the synthesis process, reduce the possibility of biocompatibility of nanoparticles being compromised.

3 Need of Degradation of Dyes from Aqueous/Nonaqueous Medium

To eliminate hazardous substances from water bodies. Electrolysis, electron beam treatment, flocculation, activated carbon, redox processes, precipitation, froth flotation, coagulation and photo electrochemical action have all been investigated for industrial pollutant-water effluents treatment but these processes frequently transmit contaminants produce secondary phase pollutants like carcinogenic aromatic amines, which can create other major human issues.

Organic dyes from the textile industry are among the many substances that are actively poisonous, bio recalcitrant, indestructible, carcinogenic, mutagenic and resistant to fading when exposed with light. These dyes are commonly applied in paper, plastic, pharmaceutical, culinary, cosmetic and textile sectors. Which could endanger our ecosystem and water supplies. Methylene blue, Methyl orange, Acridine orange, Congo red, Eosin Y, Methyl red, Phenol red, Bromophenol blue and other dyes are extensively employed in industries. Because of intricate structure, dyes are particularly stable in water, before expulsion of industrial waste complete eradication of dyes are compulsory to reduce aqueous contamination. Textile dye discharge into water bodies is now a major source of worry, as it causes substantial environmental problems and harms both human and aquatic life. Only the textile industry uses about 20% of the total dye generated in the globe. Because these dyes have a limited biodegradability and a lengthy shelf life, they have a lot of time in water bodies as absorption form, polluting the water. This impure water is detrimental to humans as cancer problem and a variety of skin illnesses, but also to aquatic life, as it depletes oxygen in the water and causes aquatic creatures to die.

There is a need to increase the availability of useful and drinkable water through eliminating different dyes from aqueous bodies, thereby increasing the overall quality of life. Adsorption and photocatalytic degradation are two strategies for dye removal that have been proposed. Although adsorption is non-expensive and handy, it is not reusable and remained harmful wastes. Photocatalytic method is simple but slightly more expensive than previous method, it can be reused and produces best results than adsorbents (Roy and Bharadvaja 2019). When sunlight is available, photocatalytic degradation can take energy from the sunlight, which breakdown dyes; this property gets degradation very inexpensive. In most circumstances, the procedure is highly useful and safe because it can filter water with certain colour pollutants without producing harmful intermediate products.

Variety of particles were used in photocatalytic degradation. Nanoparticles are the most commonly utilised and easiest to manufacture due to their enormous surface area. Metallic nanoparticles have been demonstrated to behave as photocatalytic agents in studies. ZnO, SnO_2 and ZnO_3 are some of the other metal oxides employed for photocatalytic degradation (Kyung et al. 2005).

Metal oxide NPs are often effective at degrading organic water pollutants when exposed to ultraviolet (UV) radiation or when hydrogen peroxide is present (Wong and Chu 2003). In wastewater treatment, a photocatalyst with improved dye degradation capabilities (even without UV irradiation or an extra oxidising agent) is very desirable. Furthermore, employing a green strategy may aid in boosting the application of such systems. We show that CuO NPs produced in this study are effective in degrading colours without the need of artificial light. As a result, this research adds to the growing body of knowledge in the area of green photocatalysts for removing toxic dyes from polluted industrial water with more degrading capacity while posing no threat to the environment.

These Semiconductor nanoparticles (ZnO/TiO_2) can generate electron–hole pairs at a specific wavelength in presence of light, which found a chain of oxidation and reduction reactions to obtain hydroxyl groups, which act as oxidising agents to break down organic substances from dyes into photocatalytic products. TiO_2, Zn(II)O, Cu(II)O and a variety of other photocatalysts have all been studied throughout the years. Due to photoactive ability, it's oxidise these dyes as green compounds, titanium dioxide has been widely employed and investigated in various research, despite some obstacles like low surface area and quantum effect.

In other words, Zinc oxide is increasingly gaining attraction as a viable alternative to titanium dioxide for photocatalytic degradation of dye-polluted water, owing to the limitations faced by titanium dioxide. This is because, as compared to titanium dioxide, it has good photoactivity and photoluminescence capabilities, as well as a comparatively high surface area and quantum yield (Carraway et al. 1994). The sol–gel technique was used to synthesise ZnO NPs without usage capping ligands, which found increased photocatalytic activity. Zinc oxide nanoparticles photoactivity was investigated by employing as a catalyst under UV light for Rhodamine B photo-induced degradation at various calcination temperatures. Finally, the degradation rate as the catalyst quantity increased had investigated using Rhodamine B, as well as the catalyst's reusability.

Plant-based copper oxide nanoparticles are a suitable, stable, biologically safe and cost-effective way for incorporating a wide range of bioactive compounds (Laha et al. 2014). Dyes and their derivatives have been linked to a variety of health issues, including central nervous system, kidney and liver disorders and poisoning in living organisms, skin irritation. The use of CuONPs to photodegrade methyl violet B and crystal violet inhibits their bioaccumulation in the environment. CuONPs produced with *R. tuberosa* were tested for antibacterial properties, photodegradation of crystal violet (CV) dye and coating materials. Adsorption, biological treatment and some of the ways like heterogeneous photocatalysis are applied for colours elimination from pollutant water.

Because of more chemical oxygen demand of effluent, the bacterial use in biological impure water treatment is bounded and most colours are poisonous to the microbial cell. As a result of high surface area, NPs have efficiency to absorb dyes and can be tweaked to boost their chemical affinity against specific substances (Jain et al. 2009). Heterogeneous nanomaterials have also bounded adsorption, while desorption characteristics are severely lacking. Aside from that, photocatalysis has a number of gains than adsorption technique. MONPs like TiO_2, ZnO and SnO_2 (Shahwan et al. 2011) has been mostly applied as catalysts for removing dye micropollutants from air and water by photodegradation methods.

4 Current Progress in Phyto-Nanotechnology Towards Dye Degradation

MNPs have intensively investigated because of their numerous uses in medicine, catalysis, drug delivery and biosensing, among other fields. Because of their unusual physicochemical features, silver nanoparticles (AgNPs) have attracted a lot of attention (Singh et al. 2019). Colloidal Ag-particles antimicrobial activity with respect to viruses and bacteria has been observed. They also have promise catalytic activity, allowing them to destroy potentially toxic synthetic dyes like Methylene red, Congo red, Methyl blue and Methyl orange. They have been also found to be effective sensors in the detection of Hg and Cu ions (Uddin et al. 2017). Due to employment of toxic and non-biodegradable reducing and stabilising agents, both synthesising previous methods constitute a harmful environment. Although, green-synthesised AgNPs have been regarded as a novel approach because of numerous gains likes environmental friendliness, large-scale production feasibility, ease of production and toxic chemicals absentee. Plant extracts or microorganisms are used to synthesise AgNPs in the biological technique. Plant-mediated preparation of Ag-nanoparticles are believed to be low cost and better than microbial synthesis from the standpoint of commercial practicality because handling and maintaining microbial cultures is frequently time-consuming (Vanaja et al. 2014).

Several studies have effectively synthesised AgNPs from fresh plant extracts such as Tulsi, Spinach, Coffee, Neem Babunah, Aloe Vera and others.

Although, vegetable and fruit wastes have been used to synthesise Ag-nanoparticles, with reducing massive environmental impact targetedly. Because of its inappropriate disposal, biowaste as vegetable or fruit waste has create a large environmental hazard. India is the world's second-largest producer of cauliflower, about over 35% of complete production (Khedkar et al. 2017). In India, cauliflower (Brassica oleracea var. botrytis) is a staple of the diet. Before cooking, leaves of cauliflower is scraped off floret and discarded as is customary. In addition, a large number of surplus cauliflower leaves are plucked before being sold in vegetable markets and then improperly disposed. As a result of this inappropriate disposal, dangerous germs develop unnecessarily. These vegetable wastes are examining extensively in order to find alternative uses for them such as biofuels, compost and so on, due to their negative consequences. Cauliflower leaves are high in polyphenols, which, as previously stated, are promising for creation of nanoparticles as reducing agents. Previous research has revealed that AgNPs can be made from fresh cauliflower and have antifungal and antibacterial properties with respect to pathogens such as *E. coli*, *Klebsiella pneumoniae*, *Staphylococcus aureus*, *Bacillus subtilis*, *Aspergillus sp* and *Candida albicans* (Singh et al. 2018). Study founds, Ag-nanoparticles made from fresh cauliflower floret extract have promising cancer-fighting effects and antioxidant.

Silver nanoparticles have increased a lot of attention from scientists in recent decades due to their critical usage as catalytic, antibacterial, polymers and textile fabrics to destroy germs (Fouad et al. 2019). In this evolved and populous period, comfort and convenience of life have boosted industrial zones and the rate of output is expanding day by day due to people's desires. Dyes are one of the most common types of contaminants found in wastewater. Methyl orange, Methyl red and Congo red are among the most regularly used dyes in many sectors on a large scale due to their simplicity of application.

Congo Red (CR) is an extremely poisonous and carcinogenic anionic dye made from benzyl amine that belongs to the azo dye family. The CR dye presentation in impure water will be highly hazardous to aquatic bodies. Degradation of dye has become a difficult task for both scientists and environmental engineers. To break down colours in effluent, scientists have tried a range of methods, including adsorption techniques, photocatalysis and biological degradation, among others.

Because of budget constraints, research has moved toward more ecologically friendly approaches.

Various scientists have used a variety of ways, although these methods are inefficient to remove contaminants due to the high load. As a result, more modern strategies for dealing with these types of contaminants are required. Due to their ability to totally digest many sorts of contaminants including dyes, nanotechnology is an advanced field that takes benefits of biodegradation by taking bacterial culture with plant extracts (Tomaszewska et al. 2013).

Enormous plant extracts can be used as capping and reducing agents for nanoparticle manufacturing, removing the need for hazardous chemicals and other remediation steps Cissus quadrangularis, Azadirachta indica, Catharanthus roseus, Phoma glomerata, Elettaria cardamom, Lantana camara flower (Kishore et al. 2020). Recently Ag-nanoparticles are synthesised using onion (O), tomato (T) and acacia catechu (C) and COT combined extracts as stabilising and reducing agents in a green manufacturing approach. Degradation of different dyes like Methyl red, Methyl orange and Congo red as well as $NaBH_4$ was examined by taking catalytic uses of all generated compounds.

C. albicans, *C. nonalbicans* and *C. tropicalis* have all been found to be susceptible to silver nanoparticles. Copper nanoparticles have gotten a more focus due to their inexpensive spend, easy availability and features that are similar to those of other MNPs (Nagar and Devra 2018). Copper nanoparticles are used in heat transfer fluids, sensors, catalysis and antimicrobial agents to some extent (Ahmed et al. 2016). Chemical reduction, sol–gel and other methods for nanoparticle manufacturing are known. Unfortunately, both procedures employ hazardous chemicals or necessitate a large amount of energy, both of which are time-consuming and produce hazardous waste.

Green chemistry biosynthetic approaches make use of microbes or plant parts, which have confirmed to be a simple and viable alternative to traditional processes. Green synthesis has the advantages of being environmentally friendly, having a one-step process, being cost-effective, being repeatable and frequently producing stable compounds. Proteins, flavonoids, polyphenols, terpenoids and other phytocompounds, found in extracts of plant, operate as capping and reducing agents (Ahmed et al. 2016).

Titanium dioxide has recently received a lot of interest due to its variety of applications in electric, environmental solutions, sensor-based equipments and other industries, as well as solar cells. TiO_2 is the mostly used in photocatalysis under most situations due to its great photoactivity, nontoxicity, high stability, water-insoluble characteristics and inexpensive cost. Anatase titanium dioxide has a greater photocatalytic activity compared to other forms of titanium dioxide.

The crystalline form of TiO_2 and structural characteristics such as shape, specific surface area and particle size determine its photocatalytic activity. Photocatalytic oxidation is advanced technique for pollution removal. Many metal oxide have been confirmed to be effective photocatalysts used for deprivation of organic pollutants and photocatalytic water splitting due to their outstanding ultraviolet trapping, robust chemical stability and nontoxicity. In comparison to previous physical and chemical procedures, a biological method has been shown to produce titanium dioxide nanoparticles (TiO_2NPs) at a faster rate. TiO_2NPs have been extensively investigated as a solution to environmental concerns such as degradation of organic dyes, CO_2 reduction and phenol due to their recyclability, highly reactive, nontoxicity, photostability chemically inert qualities and inexpensive.

Ag_2O semiconductors come in a variety of shapes and sizes, with reported bandgaps ranging from 1.2 to 3.4 eV. Because of its photosensitivity and irradiation instability, Ag_2O is frequently utilised as a main photocatalytic material as well as a supportive catalyst. Silver oxide NPs also work as moderate oxidising material in chemical transformation. In recent times researchers took significant efforts in the preparation of Ag and Ag_2O nanoparticles using a variety of chemical reagents. Chemical reduction (Barhoum et al. 2016), electrochemistry, electron irradiation, gamma irradiation. These approaches, on the other hand, frequently involve the use of either expensive or dangerous substances like stabilisers and reducing agents. Furthermore, remaining products may make both Ag, Ag_2O nanoparticles unsuitable for biomedical uses, while discrepancies in responses between both Ag, Ag_2O nanoparticles are to be expected due to diverse manufacturing techniques and the affectability of different cells (Karekar et al. 2019). Under visible light irradiation, silver halides nanocatalysts like AgCl, AgBr and AgI, carbonates (Ag_2CO_3) (Barhoum et al. 2016), phosphates (Ag_3PO_4) (Rehan et al. 2019), chromates (Ag_2CrO_4), oxides (Ag_2O) and because of its unusual electrical structure, crystal structure and band structure, Ag_2O is considered a good option.

Comparative experiments employing different metal oxide catalysts to photocatalysed the breakdown of visible-light-induced Methylene Blue (MB) have revealed their rate constants. A study team has used the green combustion approach to successfully produce Ag_2O NPs. Under UV light irradiation, these nanoparticles were employed for investigation of photocatalytic degradation of azo dye such as Acid orange-8 with a 70% degradation efficiency (Rashmi et al. 2020). By using an eco-friendly liquid like Pemodi's fresh leaf extract (Shah et al. 2019) investigated the photocatalytic ability of the produced Ag_2O nanoparticles. The Ag_2O NPs employed UV light to destroy the methyl blue about 97.8% with 0.0214 min^{-1} rates constant in 180 min (Shah et al. 2019). Ying and colleagues employed photocatalytic-assisted adsorption with the produced Ag_2O NPs to eliminate Congo red dye. After 35 min of visible light irradiation, Ag_2O NPs regenerate after the Congo red dye has entirely photodegraded, on behalf of the findings.

Using Phoenix dactylifera L. extract, this study studies an effective and sustainable approach for preparing Ag/Ag_2O NP from aqueous $AgNO_3$. The impact of variety of plant extracts with percentage volume ratios on silver or silver oxide nanoparticle production, optical properties and catalytic activity towards the degradation of Congo red and methyl blue dye was investigated. On the synthesised Ag/Ag_2O nanoparticles, the characteristics of the bioactive components were investigated using electron microscopy and spectroscopy (Barhoum and Luisa Garca-Betancourt 2018). Congo red is an anionic diazo dye based on benzidine that contains two azo linkages (–N = N) chromophores. Because Congo red and methyl blue are the extensively used azo dyes in the different industry therefore they were select for this study. Benzidine, a human carcinogen and mutagen, is known to be metabolised from this class of colours. As a result of its structural stability and severe toxicity, it is prohibited in many countries.

Preparing various shapes and sizes of semiconductor metal oxide nanoparticles for use in oxidation processes has attracted interest. Many transition metal oxides have been investigated as photocatalysts for hydrogen production and removal of colour, including TiO_2, NiO, CuO, ZnO and $BiVO_4$. Rare earth oxides have usual more focus than transition metal oxides because of their intriguing optical, electrical and catalytic features. CeO_2 has piqued interest as one of the most important earth oxides, with applications in solid oxide fuel cells, photocatalytic dye degradation, UV filters, electrochemical sensors, supercapacitors, optical materials and solar cells (Shajahan et al. 2020).

5 Review Based on the Recent Literature

Zhiqiang et al. (2014) used Panos extract to make four-way pedal Quaker ZnO nanoflowers through green route. To test the efficacy of ZnO in degradation of dye under UV light irradiation, Eosin Y, Methylene blue and Malachite green (MG) were used as reference dyes. The synthesis of ZnO nanoparticles was taken by the sol–gel approach, according to (Dodoo-Arhin et al. 2020). Without the usage of capping ligands, increased photocatalytic activity was achieved. Mariselvama et al. (2019) represented the preparation of Ag-nanoparticles from a lot of plant sources and the use of these Ag-NPs to degrade the AZO dye using an ultraviolet photocatalytic technique. Pure and Ag-decorated CeO_2 nanoparticles were produced and characterised using experimental procedures, according to (Murugadoss et al. 2021). The nanoparticles' crystallography, microstructure, optical and magnetic characteristics were all studied in depth. The photocatalytic behaviour of pure CeO_2 and Ag-coated CeO_2 nanoparticles was assessed using the photodegradation of Rodamine B dye in presence of visible-light irradiation. Muhammad et al. (2020) described the manufacture of nickel nanoparticles utilising Hordeum vulgare seed extract. The impact of various reaction conditions on nickel nanoparticle manufacturing was also investigated. In addition, a model reaction for methylene blue degradation is demonstrated in order to assess the catalytic ability. Anshu et al. (2018) described a simpler method for producing water-soluble red-emitting magnesium-nitrogen-embedded carbon dots from common decorative plant Bougainvillea leaves. Most importantly, the use of generated r-Mg-N-CD as a promising photocatalyst substance for the photodegradation of an impure dye known as methylene blue (MB) has been experimentally investigated. R-Mg-N-CD photodegrades MB at a six times faster rate when exposed to natural sunshine with respect to 100 W tungsten bulb. The as-obtained r-Mg-N-CD had a lot of expressions, which was linked to excitation-independent red emissions with a high quantum yield of 40% excellent photostability. Due to its high quantum yield and emission at a longer wavelength, this material was compared to the already existing red-emitting QD at 678 nm. Extremely fluorescent red-emitting carbon-based fluorescent nanoparticles are coloured as MB and are not employed in the photocatalytic destruction of organic contaminants created by sunlight.

Green manufacturing of CuONPs using aqueous *Abutilon indicum* leaf extract as a green fuel, as well as assessment of antibacterial, antioxidant and photocatalytic degradation of dye capabilities to the produced Nps. In situ-electro-biosynthesis was used to make the metal oxide catalysts, which are regarded as a great catalyst for malachite green (MG) dye degradation in aqueous medium (Norzahir et al. 2019). Using *Biebersteinia multifida* aqueous extract on MB dye, (Abdolhossien et al. 2018) showed photocatalytic ability of obtained Ag-NPs. Ag and Cu-NPs were obtained from *Centella asiatica* and their use in photocatalytic degradation of dye was investigated (Swati et al. 2020). The *C. asiatica* leaf extract has been used to develop copper and silver nanoparticles in a fast, eco-friendly and convenient approach. Nanoparticles were synthesised using various amounts of $AgNO_3$ and cupric sulphate, which were then used for dye degradation.

Ganeshan et al. (2016) described the preparation of titanium dioxide nanoparticles by taking an *A. altissima* leaf extract. (Sakeel et al. 2020) reported AI-MnO NAPs using *A. indicum* phyto-molecules as a reducing and stabilising content. The green-synthesised AI-MnO NAPs' antibacterial, anticancer, photocatalytic against methylene blue and adsorption removal of Cr(VI) metal ion capabilities were all examined further (Suresh et al. 2020) described a plant-based synthesis for the manufacture of Cu-nanoparticles by taking *C. paniculatus* leaf extract and testing antifungal effectiveness with respect to phytopathogenic fungus *F. oxysporum* and photocatalytic efficiency in organic dye degradation.

Kishore et al. (2020) used plant extracts for stabilising and reducing agents in green synthesis of Ag-nanoparticles. UV–Visible, FTIR, XRD, SEM, DLS, TEM and EDAX were taken for nanoparticles characterisation that were synthesised. The catalytic application of all produced compounds was also investigated for such distinct dyes, MR, CR and MO degradation as well as $NaBH_4$. Salah et al. (2021) investigated the detoxifying and biodegradable effects of green-produced Ag/Ag_2O-nanoparticles of CR and MB dyes degradation over a range of reaction periods.

CuNPs were made from *C. sinensis* leaves were used in dyes degradation via a photocatalysis method (Adeel et al. 2019). The CuNPs generated in presence of solar irradiation and their photocatalytic activity (PCA) was determined by measuring the degradation of BPB dye. Luminita and Bianca (2020) investigated silver nanoparticles from cranberry bush fruits as silver ion reducing and capping agents, as well as the catalytic activity of as obtained Ag-nanoparticles by testing in the degradation of harmful organic colourants such as tartrazine, carmoisine and brillian blue FCF by sodium borohydride.

Cerium oxide nanoparticles were prepared by *R. turkestanicum* extract and their photocatalytic activity for decolorising organic colours produced by industrial wastewaters were evaluated (Zahra et al. 2020). FeNps bio fabrication in Hibiscus sabdariffa aqueous extract with improved photocatalytic activity with respect to dye degradation was reported by Abdulmohsen et al. (2017). Green tea leaves were employed to make Fe-nanoparticles by Shahwan et al. (2011). They used the resulting materials to degrade MO and MB as Fenton-like catalysts. The production of FeNPs by taking sorghum bran extracts and green tea leaf was also reported by Nadagouda et al. (2010).

Synthesis of cerium oxide, silver and Au-nanoparticles by using *H. sabdariffa* flower extract was studied. Their use in the characterisation of the evaluation of cytotoxicity and physical properties with respect to U87 glioblastoma cells under catalytic reduction of 4-nitrophenol and hyperglycemic conditions were observed (Kalita and Ganguli 2017). However, developing adequate eco-friendly semiconductor photocatalysts is an important environmental component of wastewater cleanup.

Under UV–Visible light irradiation, green-catalytic RB dye degradation by Au and TiO_2-NPs taken on F. P. Polydimethylsiloxane S. was observed (Lee et al. 2020). Singh et al. (2020) taken newly created AuNPs to utilise the UW effect in cationic dye sorption like methylene blue and the results revealed that it had a more profound effect than the usual sorption procedure. The effectiveness of freshly obtained nanoparticles in dye removal was tested and an attempt was made to determine the dye removal mechanism. Using inedible fruit waste 'Cynometra ramiflora fruit extract' (Sahana et al. 2017) described a unique, eco-friendly produce magnetic FeO-nanoparticles (MIONPs) at room temperature. Photocatalytic efficiency of NPs was demonstrated by degrading a polluting dye like methylene blue in a variety of methods. Using Ferulago angulata (schlecht) boiss aquous extract by (Ebrahim et al. 2017) established a unique biological approach for CuO and ZnO-NPs synthesis. CuO and ZnO NPs were characterised by applying FTIR, FE-SEM and XRD. Using controlled degradation of RhB commercial dye in visual irradiated aqueous solution, we investigated photocatalytic activity of ZnO and CuO.

Rasheed et al. (2018) synthesised CA-AgNPs by *Convolvulus arvensis* plant extract, these AgNPs were used to reduce many azo dyes using $NaBH_4$ and CA-AgNPs catalytic efficiency has assessed using a UV–Visible spectrometer after the decrease in optical density. Tayyaba et al. (2019) investigated the antioxidant, antibacterial and hemolytic characteristics of green-produced CoNPs utilising *C. argentea* plant extract. Its ability reduces the MB dye in the absence and existence of surface modificator sodium dodecyl sulphate was also investigated.

Singh et al. (2019) used *P. guajava* leaf extract and copper acetate monohydrate to create an effective CuO NPs which under solar light irradiation utilises for NB and RY160 dyes degradation. The hard to degrade, industrial dyes like NB and RY160: The created catalysts were praised for their ease of recovery and reusability in addition to their excellent dye degradation efficiency. CuONPs made from *R. tuberosa* were investigated for their potential as coating materials and antibacterial agents also uses for crystal violet dye degradation (Seerangaraj et al. 2019). Lalitha et al. (2019) used Panos extract to make ZnO nanoparticles. Under UV radiation irradiation, efficacy of ZnO in Methylene blue, Malachite green and Eosin Y dye degradation were used as model dyes. Khalida et al. (2020) determined the manufacturing of biogenic CAg-NPs particles produced from citrus peel and their usage as catalysts for the degradation of several hazardous dyes like MG, MB, CR, 4-NP and RhB. For CR reduction, the recyclability and reusability of catalysts were also tested. UV–Vis, FTIR, DLS and TGA were used to examine biogenic CAg-nPs particles. Biogenic production of Fe_2O_3NPs utilising pomegranate seeds extract was reported by (Ismat et al. 2019).

6 A Comparative Study With Different Substrate

In comparison to physical and chemical approaches, biological nanoparticle production has recently gotten more attention. As a result, plant extracts and microorganisms are increasingly commonly used to make nanomaterials. In comparison to microorganisms, the obtaining process of nanoparticles by taking plant extracts are advantageous since it detects the arduous methods of sustaining cell cultures and can be successfully found for NP preparation (Singh et al. 2016). When compared to nanoparticles made with sodium borohydride, magnetic nanoparticles made with green technologies have been proven to be non-toxic. On the nanoscale scale, several varieties of metal nanoparticles with most active physicochemical nature can be successfully generated (Liang et al. 2019). The (AgNps) are a type of metallic nanoparticle that has a wide range of biological and environmental uses. AgNps have a great ability to degrade a variety of colours.

The nanoparticle prepared by using the plant extract has some good observation compared to nanoparticles made by physical and chemical root. Using *A. dentate* aqueous extract, green fast syntheses of spherical shaped 50–100 nm diameters Ag-nanoparticles were observed. This extract finished the reduction of silver ions in less than 10 min to AgNPs. Aqueous leaf extract synthesises extracellular Ag-nanoparticles, which are comparable to microbiological and chemical approaches in terms of simplicity, speed and cost (Ahmed et al. 2016).

AgNPs were rapidly produced by taking *Acalypha indica* leaf extract within 30 min (Krishnaraj et al. 2010). When stable Ag-nanoparticles are formed at various concentrations of $AgNO_3$, the particles are typically spherical, with varying from 15 to 50 nm diameters. The use of orange peel (Citrussinensis), to make a biomimetic polymer template green AgNPs have been described with the goal of making nanoscale research more environmentally friendly. From TEM image it is observed that the well-dispersed spherical NPs ranging in size from 3 to 12 nm but most of the particles has 6 nm diameters (Veeraputhiran 2013). Chenopodium album, a noxious weed, was found to have a simple and quick biosynthesis of AgNPs. The leaf extract was successfully used to synthesise AgNPs and AuNPs with 10–30 nm size (Dwivedi and Gopal 2010). Several research have discovered semiconductors like TiO_2**,** but not limited to other metal oxides, can be beneficial. AgO has a promising future in photocatalytic processes due to its capacity to break down a variety of contaminants under Ultraviolet, red/NIR and visible light irradiation in working conditions (Jiang et al. 2015). CuO photocatalyst has lately piqued scientist's interest due to its 1.7 eV band gap, cheap cost, minimal toxicity and widespread presentee. ZnO has received a lot of attention in the field of photocatalytic research to increase its performance as well as examining the quantum effect of photocatalyst materials (Sapawe et al. 2013). NiO is also extensively used as a catalyst because of its remarkable thermal, electrical, redox and catalytic properties as well as its high nontoxicity, photosensitivity and chemical stability and it can generation of OH radicals act as a promoter for the same (Venu and Sahle 2008). CuO NPs are the most widely employed Magnetic Nanoparticles (MNPs) for treatment of wastewater due to their better ability to degrade dye. Metal oxide NPs are often effective at degrading organic water pollutants when exposed to ultraviolet (UV) radiation or when hydrogen peroxide is present (Wong and Chu 2003). However, many of the pollutants targeted by businesses are either non-degradable or difficult to break down such as reactive yellow 160. (RY160) and Nile blue-like vibrant dyes. Furthermore, the use of ultraviolet light and hydrogen peroxide is not always feasible or safe. Because hydrogen peroxide consumption generates significant toxicity in human's central nervous system, MB and CR were utilised to examine the photocatalytic performance under irradiation solar light circumstances. Because of their enormous low diffusion rates and molecular weights, these dyes are difficult to break down. The newly developed catalysts were lauded for their ease of recovery and reusability, as well as their increased dye degradation efficiency.

Nanoparticles are employed in a multiple applications, including pharmaceuticals, biosensors, photocatalysis, biomarkers and medicinal, to mention a few. Non-metallic NPs are also employed in different applications, although metal NPs are the most stable and efficient (Hameed et al. 2016). Copper oxide nanoparticles have received a lot of focus recently because of their unique properties. Batteries, gas sensors, catalysis, optical, electrical and solar energy exchange devices are all examples of copper oxide Np uses.

Green-synthesised TiO_2 NPs were made from Jatropha curcas L. leaf extract and their photocatalytic treatment of TWW by biological treatment process was assessed in a parabolic trough reactor with 82.26% COD and 76.48% Cr removal rates.

Pandimurugan and Thambidurai (2015) reported photocatalytic degradation of anionic and cationic dyes MB and drimarene turquoise blue S-G by ZnO NPs obtained from various zinc sources such as zinc nitrate, zincacetate and zinc sulphate and Padina tetra-stromatica brown seaweed plants under direct sunlight. In addition, Anbuvannan et al. (2015) produced ZnO NPs from Anisochilus carnosus leaf extract and shown good photocatalytic degradation of MB dye. The extraordinary photocatalytic breakdown like 83.99% of MO azo-dye by ZnO NPs within 120 min under 364 nm wavelength UV light was achieved utilising Nephelium lappaceum L. fruit peel extract (Pandimurugan and Thambidurai 2015).

Eucalyptus leaves-Fe and Green tea-Fe extracts were used to make FeO core–shell NPs that have catalytic nitrate removal activity in swine effluent. In this comparative study, the reactivity of green-generated nanoparticles was investigated and compared to chemically made INPs. FeO core–shell nanoparticles made in a green way have a lot of potential for environmental remediation. For the decolorisation of MO and MB dye, iron oxide NPs produced from Amaranthus spinosus leaf extract exhibit a high catalytic activity. These particles are more proficient of decolorisation than chemically generated nanoparticles. Magnetite NPs made from Andean blackberry leaf extract were discovered to have catalytic activity for the MB, CR and MO dye degradation (Muthukumar et al. 2015).

7 Further Improvements Needed

Related to standard procedures, the nanoparticle manufactured using plant extract offers several advantages, including the absence of dangerous chemicals, low-cost technology, non-hazardous by-products and ease of degradation after usage. This advantage has a good impact on the environment, but it also has some drawbacks, such as plant extract reusability, nanoparticle sustainability for long periods of time and increasing the use of plant extract would ruin the ecosystem. The separation of plant extract is also a tedious job require long time for separation. However, regulating the form, size and mono-dispersity of the nanoparticles produced has proven to be a substantial technological challenge in this procedure. To mark plant-mediated synthesis a viable and inexpensive alternative to commercial NP synthesis, several difficulties must be solved. The type of plant used in the plant-mediated production of metal nanoparticles is also crucial. To find the best root, effective measurements in green synthesis, such as total reductive protein content and antioxidant capacity of the plant extract, has to be assessed, as these characteristics impact the plants' ability to generate nanoparticles. More study is needed to have a better understanding of the physicochemical characteristics, activity and stability of plant-mediated NPs in order to expand their practical uses.

There is still opportunity for development in this area. To make the extraction technique for extracting the plant content needed for nanoparticle manufacturing easier. To ensure that the plant extract and the rest of the plant are reused. To boost the long-term viability of produced nanoparticles, additional techniques must be implemented. To take the necessary steps and publicise them in such a way that they can improve the utilisation of plant extracts in comparison to traditional synthesis processes while also confirming the ecosystem's balance.

8 Future Scope of the Chapter

The scope of this chapter is to learn about the origins of nanoparticle synthesis and the benefits of using plant extract in nanoparticle synthesis. This chapter explains how to use nanoparticles in dye degradation studies and why dye degradation is important in terms of ecosystem and water remediation. This chapter provides a wealth of information on modern phyto-nanotechnology and its applications in several fields. This chapter will help researchers increase their academic wealth and will be valuable for future studies in the field of phyto-nanotechnology.

9 Conclusions

In this chapter, we discussed ongoing research on small-scale, cheap-cost, energy-saving and easy-to-scale-up technology (green root) based preparation of metal/metal oxide nanoparticles using diverse plant extract. Which provides environmentally friendly technologies that increase human well-being, dissipate pollutants and protect human and environmental health. This might be accomplished by the treatment of drinking water and wastewater, resulting in an eco-friendly environment free of numerous toxins such as dye and other harmful hazards from various sources around the world in both aqueous and nonaqueous bodies.

We reviewed the ability of various plant species to create green NPs and their usage in dye degradation. Plant-mediated NP synthesis has undeniably significant advantages over existing conventional approaches. Plant-mediated NP synthesis, despite its advantages, has substantial disadvantages, particularly in terms of regulating form, homogeneity and mono-dispersity. Optimisation studies and controlled reactions can be used to overcome these barriers. NP green synthesis has so far only been done on a modest scale in the lab. As a result, scale-up research for industrial manufacturing of these nanoparticles must be given special consideration in the near future.

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Phytonanotechnology for the Removal of Pollutants from the Contaminated Soil Environment

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Abstract Over-consumption of chemically synthesized components aids country toward industrial revolution, which symbolizes for economic prosperity. On the other hand, industrial revolution is responsible for soil pollution, due to its toxic effluents. The main source of soil pollutants includes fertilizers, pesticides, untreated wastewater used for irrigation, land application of sewage sludge due to rich organic content, petroleum leakage and leaching from landfills, etc. The crops grown out of this contaminated soil make the plant to changes its nutritional valve, bioaccumulates the chemicals, and also hinder with its vigor. Studies proved that prevent measures should prioritize in minimizing the adverse effect on the environment. Use of Phytonanotechnology in wastewater treatment, as nano fertilizer, nanotechnology-based biocontrol agents, and other areas before the hazardous chemicals entering soil. Green synthesized nanoparticles assist as excellent bio remedial agents as they are rich in biomolecules like carbohydrates, proteins, lipids, and several enzymes also determine its efficacy of action. Hence, this chapter highlights the various eco-friendly and inexpensive products or formulation used for removal of toxic and recalcitrant materials which are dreadfully risky to human health.

Keywords Pollutants · Green synthesis · Bioremedial agent · Biomolecules · Nanofertilizers

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1 Introduction

Wastewater discharged from industries encompasses a wide range of multifaceted and lethal metals, dyes, organics, phenolic products, recalcitrant chlorine, and pathogenic organisms, as well as a variety of potentially dangerous inorganic pollutants that are constantly used, and even has a negative impact on natural resources and poses significant well-being risks (Zainith et al., 2016; Roy and Bharadvaja 2021). Industrial and economic development have a significant impact on the soil environment by pay off large amounts of wastewater comprising of greater concentrations of toxic and fatal pollutants with low degradability, which have a significant impact on modern life's climate and living standards (Mishra et al., 2019; Garg and Roy 2022). Several distinct conventional treatment methods have been used for the management and supervision of unwanted waste generated from industrial activities (Fig. 1) since ancient times, comprising precipitation, adsorption, ion exchange, coagulation, bio-sorption, electro-dialysis, and several more. In modern times, innovative knowledge has been developed to improve the competence of pollutant removal. Phytonanotechnology for example, has been proven to be a novel and efficient technique for cleaning up pollutants in a variety of surroundings, as well as a relatively flexible management option that can be engaged on a larger scale (Verma et al., 2020). This technology is found to be very promising in treating several of pollutants of groundwater, wastewater and other sediments polluted containing heavy metals and hydrocarbons. These pollutants can be either organic or inorganic chemicals in earth, this method can cover a wider range of potential applications with lower budgets and minimal negative environmental implications (Archana et al. 2021; Vázquez-Núñez et al., 2020). Nanoparticles (NPs) are a superior choice for waste and sewage water treatment because they have unique qualities such as nano-size, large surface area, high reactivity, high solution mobility, strong mechanical capabilities, porosity traits, hydrophilicity, dispersibility, and hydrophobicity. Different NPs have been claimed to be successful in removing heavy metals for example Pb, Mo, and other organic and inorganic contaminants, as well as many hazardous microorganisms. According to the World Health Organization (WHO), about 1.7 million people have died as a result of water pollution, and four billion cases of various health conditions have been documented annually as a result of waterborne infections (Swift et al., 2019). According to 2017 WHO report done by Dr. Margaret Chan, Director-General said that "A polluted environment is a deadly one—particularly for young children "(WHO 2017). Their developing organs and immune systems, and smaller bodies and airways, make them especially vulnerable to dirty air and water." As a result, this chapter is a useful resource for learning about, speeding up, and enhancing the elimination of wastewater from industries, their pollutants, and waste products using NPs.

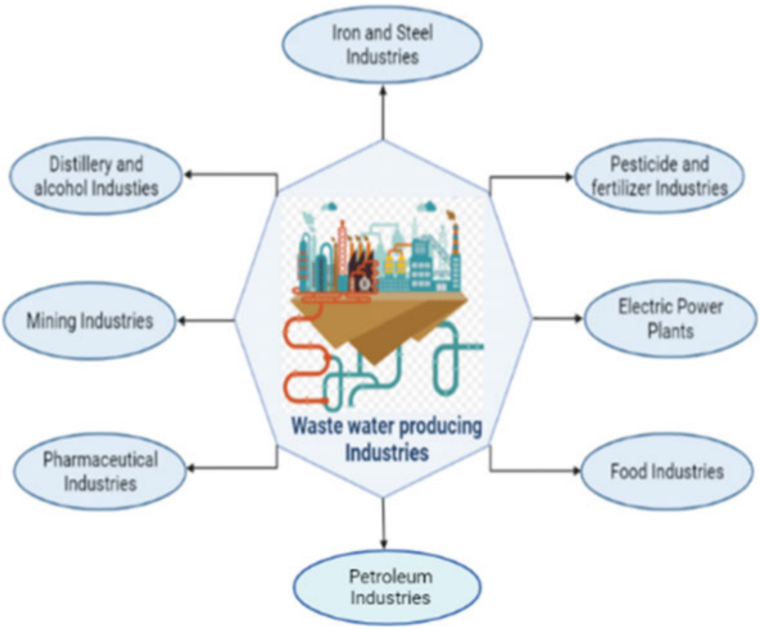

Fig. 1 Several of small and large scale industries produce greater quantity of wastewater causing contamination of soil and the environment

2 Photosynthetic Strategies of Nanoparticles

Particles having dimensioned lesser than the size arranging from 1 and 100 nm in diameter which can modify their physicochemical properties as associated to their original bulk material are referred to as NPs (Kataria et al., 2019; Roy et al., 2021a, b; Roy et al., 2022). Biologically NPs production is quite cost-effective and environmentally safe technology that can replace harmful and expensive physical and chemical methods (Roy and Bharadvaja 2019; Roy et al., 2021a, b; Nagore et al., 2021; Mittal and Roy 2021; Pandit et al., 2022). As a result, microbes and plant extracts have been used to make NPs. The use of plant extracts for NPs production has the potential to be more beneficial than microorganisms because of the ease with which biohazards can be scaled up and the complicated procedure of maintaining cell cultures (Prasad 2014; Roy and Bharadvaja 2017; Raina et al., 2020; Roy 2021).

Photosynthesis involves two phases light and dark cycles where the light energy is converted into chemical energy, which is carried out by all chlorophyllous organisms, such as bacteria, cyanobacteria/algae, and plants, and whose products are mostly consumed by humans and animals. Plant growth and development consume only 2–4% of the available photon energy generated by plants. The function of photosynthetic machinery can also be improved by nanotechnology. NPs have been shown to affect key plant life stages such as seed germination, photosynthesis, and flowering. In a recent study supported importance of iron when investigated the destiny and influence of iron oxide (Fe_3O_4) NPs with the size of 13 nm in Barley (*Hordeum vulgare*), a widely grown crop around the world (Kokina et al. 2021). The results showed that increasing doses of Fe_3O_4NPs steadily increased plant growth up to 500 mg/L, promoting fresh weight having 19% and 88% observed in leaves and root tissues, respectively, compared to the control. Even at high NPs levels, no phytotoxic effect was seen. Some phenological indices, including as types of chlorophyll pigments present, total soluble protein, chloroplasts number along with dry weight, were raised when NPs were added. High doses of NPs significantly lowered catalase activity and hydrogen peroxide concentration, implying that NPs may have a role as a nanozyme in vivo. Hydroponic culturing of barley seedlings for about three weeks with varied concentrations of Fe_3O_4NPs like 125, 250, 500 and 1000 mg/L revealed good assess to Fe with their uptake and translocation very well in the plantlets (Tombuloglu et al., 2019). The existence of Fe_3O_4NPs in the plants was confirmed by Transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM) techniques and by photosynthesis marker genes by RT-qPCR (Kawakami and Bhullar 2020).

2.1 *Chloroplast-Nanoparticle Interactions*

For biological applications, NPs can be composed of a variety of materials, including silica, gold, carbon, and polymers. Modifying the size and charge of NPs permits them delivery as cargo inside the plant cell as its coated with particles of our interest to different organelles such as chloroplasts get accepted as bio-recognition coatings Single-Walled Carbon Nanotubes (SWCNTs) which are also be coated with a single-stranded DNA for delivery to chloroplasts used for genetic engineering (Newkirk et al., 2021). Because of the quick transit of electrons and increased activity of plant signaling chemicals like nitric acid, NPs like SWCNT augmented three-fold higher photosynthetic yield in the chloroplasts. Additionally, the use of nano-mesoporous silica compounds in photosystem II (PSII) accelerated photosynthesis (Fig. 2). Silica, titanium oxide, and other NPs, for example, improve photosynthetic rate by improving oxygen transport or increasing light absorbance. Plant cell and organelle bio surfaces act as stumbling blocks in the delivery of NPs and their contents into chloroplasts. Several delivery methods have been used from decades to deliver micro-carriers inside the chloroplast genome like standard way of delivery by particle delivery methods and gene gun also called as particle bombardment which is dependent on factors like pressure and force (Economou et al., 2014).

2.2 *Silver Nanoparticles (Ag-NPs)*

Ag-NPs have received a lot of attention from researchers since Si bulk particles are known to boost photosynthetic efficiency. When plants are exposed to Si-NPs, the

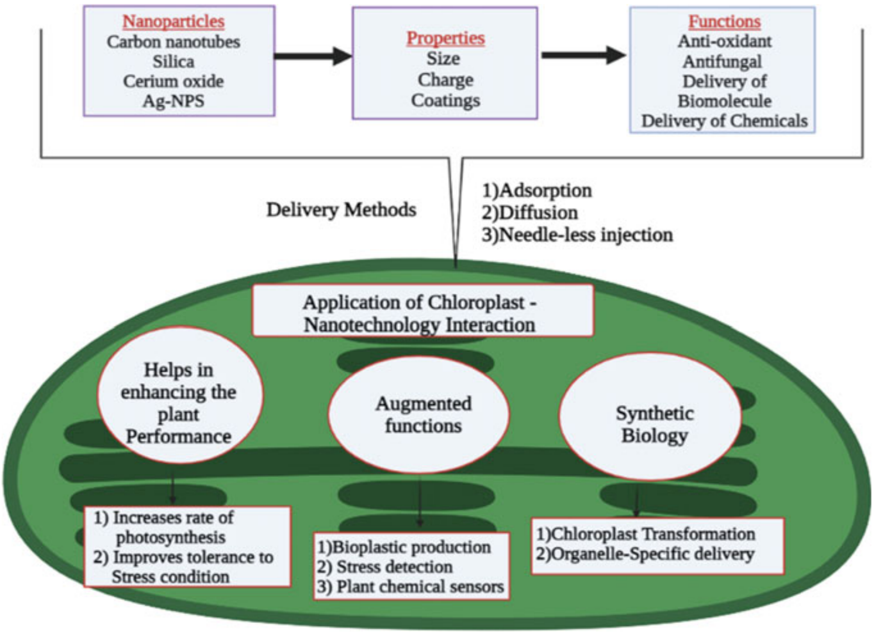

Fig. 2 Phytonanoparticles used as an effective tool for various positive effects of on Chlorophyll based structural and functional changes at genome level

light they receive is more efficiently utilized, and as a result, increases in photosynthetic pigment content may occur as a natural reaction (Siddiqui et al., 2020). Ag-NPs are known to be effective antibacterial agents, they could be employed as a disinfection alternative. In a wide range of products, Ag-NPs are increasingly used as biocides. NPs in silver form has a wide range of applications, from home paints to artificial prosthetic devices. The widespread use of Ag-NPs necessitates their eventual discharge into the environment. Released Ag-NPs, on the other hand, may constitute a threat to naturally occurring microbes. Because of its numerous applications and inexpensive manufacturing costs, Nanosilver has become one of the most popular NPs. Medical applications, water purification, antimicrobial usage, paints, coatings, and food packaging are just a few of the commercial goods that use it. Using Ag-NPs to impregnate other materials is a practical technique to take advantage of silver's germ-killing qualities (Bogumila et al., 2013). Ag-NPs operate as catalysts in redox reactions, affecting photosynthetic and respiratory processes in the process. Chlorophyll content and PSII efficiency are both improved by Ag-NPs (Sami et al., 2020) (Fig. 2).

2.3 Titanium Dioxide (TiO_2 NPs)

TiO_2 NPs is seen in three different crystal forms: rutile, anatase, and brookite, as well as non-crystalline (Samadi et al,., 2014). Plants have been treated with a range of NPs, including TiO_2 NPs, which have been shown to regulate a variety of processes. Stimulation of glucose biosynthesis, as well as increased plant growth and photosynthetic rate, are notable examples (Shabbir et al., 2019). At the right concentration, NP-TiO_2 and TiO_2 can boost photosynthesis, chlorophyll production, and nitrogen metabolism. NP-TiO_2 improves chlorophyll structure, increases light absorbance, facilitates pigment production, improves sunlight collection, and helps to transfer of light energy to active electrons making them to take part in chemical activities which are featured in the photosynthesis in liberation of energy needed for the plant (Samadi et al., 2014). Manipulation of anything related to photosynthesis-related enzymes can improve this process and efficacy more than normal. A group of scientist worked with Ribulose-1,5-bisphosphate carboxylase-oxygenase (RubisCo), enzyme very crucial in photosynthetic process which is game changer where the carbon dioxide is converted to biological compounds like glucose, vital for growth in most photosynthetic organisms as a part of dark cycle also called as Calvin cycle (Siddiqui et al., 2020) (Fig. 2). Since several studies have showed that TiO2 is a good light absorber and helps to tap more light; therefore it transmits energy to electrons. It also improves the activation of the RuBisCo enzyme (which is at the heart of the dark cycle or), resulting in increased carbon assimilation. Other NPs, such as iron oxide and silver, on the other hand, limit photosynthesis through their hazardous properties. Zinc oxide NPs (ZnO-NPs) restrict photosynthesis in a similar way by blocking photosynthesis-regulating genes (Poddar et al., 2020).

3 Remediation of Soil from Heavy Metals

In spite of many different types of contamination of soil, heavy metals are released from several industrial wastes. In contrast, if not adequately remediated to a harmless level, electronic wastes, and other wastes pose a severe concern to both human beings and animals in the environment. Heavy metal contamination, which is caused by different anthropogenic deeds such as electroplating, mining, energy and fuel production, wastewater sludge management, and farming, is one of the world's most serious environmental issues. Heavy metals, often known as trace metals, are a wide category of trace elements that are significant in both industry and biology. Heavy metals were once naturally present in soils as natural components, but their abundance in the environment has increased as a result of human activity. Excessive concentrations of heavy metals such as Zn, Cr, Cd, Pb, Cu, and Hg can be found in soils all over the world, posing a global problem. Heavy metals are found in a variety of food chains, with negative consequences for microorganisms, plants, animals, and humans.

Several strategies for adulterated soil treatment must be developed which include methods like physical, chemical, and photocatalytic degradation. Nevertheless, the majority of these approaches have considerable limitations when it comes to absolutely involved in remediating hydrocarbon-contaminated soil. Few of these processes produce daughter compounds that are more environmentally hazardous than the parent compounds. Biological treatment is the most eco-responsible technique to remediate hydrocarbon and heavy metal damaged seen in the earth. The ability the breaking down of the complex compound depends on the ability of consortium of native microbes like algae, fungi, bacteria, actinomycetes, and other plants association in the soil environment and ecosystem into harmless elements (Abioye 2011).

3.1 Bioremediation Technique

Out of numerous strategies used for cleaning up of soil pollution bioremediation is one of the most promising used for the safer removal of inorganic and organic pollutants without harming surroundings. This process utilizes several of microorganisms or plants to depollute the contamination caused, reduces the load of organic and inorganic xenobiotics from the location. Since this technology uses many living organisms for the remediation it is very well called as green technology where hydrocarbon and HM contaminants are removed. Bioremediation exhibits as very advantageous as its primary benefit is it being less expensive than conventional approaches. It is a longstanding treatment; several other additions include lesser cost, more effective, and also facilitate total mineralization of the noxious waste. Furthermore, it is a non-invasive process that has no undesirable effects on the environment (Perelo 2010).

3.2 Nano Bioremediation

Phytoremediation is a community-accepted, environmentally acceptable method that provides a natural remedy to pollutants. Nano-phytoremediation is green technology used for adsorption and degradation of pollutants followed by absorption of degraded pollutants by plant. This technology utilizes phytoremediation along with nanomaterials (Srivastav et al. 2018). Several NPs are proved to be efficient over traditional approaches for removal of toxic metals from environment. The "nanobioremediation" utilizes NPs for boosting the microbial activity for detoxification. Nanotechnology reduces the time as well as cost in order to clean up the contaminated sites on larger scale. The bio-fabrication of nano-objects or bifunctional macromolecules employed as tools to manufacture or manage nano-objects is known as "bionanotechnology" or "nanotechnology through biotechnology" (Dixit et al., 2015). The nanoscale modified biopolymers are one example of above technology which can be

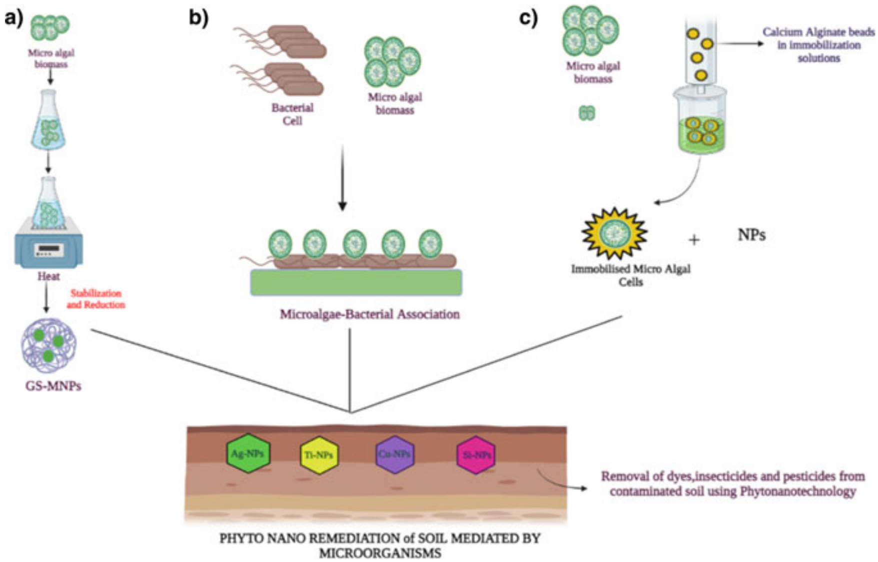

Fig. 3 Steps involved in synthesis of nanoparticles via greener approach for phytoremediation

produced by genetic and protein engineering of microorganisms. Furthermore, the size of these material scan be regulated at molecular levels. This technology is very efficient for combating environmental pollution with respect to inorganic pollutants (toxic metal ions) as well as organic pollutants (dyes, insecticides, and pesticides) (Ananda et al., 2021; Tripathi et al., 2022). The steps involved in phytoremediation of organic moieties (dyes, insecticides, and pesticides) contaminated soil has been illustrated in Fig. 3.

GS: Green Synthesized: GS-MNPs: Green Synthesized Metal Nanoparticles mediated by microorganisms. (1) The processing of algal extract in water or an organic solvent by heating or boiling it for a specified period of time is the first step in the synthesis of nanoparticles utilizing microalgae. (2) Microalgae-Bacteria Association shows mutualistic relationship in the environment and together helps in phytoremediation. The sustaining ability of microorganisms at higher metal concentrations triggered them to use in nanoparticle synthesis. Nitrogen, phosphate, heavy metals, pesticides, organic and inorganic pollutants, and pathogens may all be successfully removed from wastewater by a variety of microalgae species. (3) Gel Entrapment method can be used to immobilize the microalgae and later can be coated with GS-MNPs. The above method utilizes Calcium Alginate beads. These beads can be produced by treating calcium ions containing gel with alginate solution. Then membrane can be obtained by treating these beads with chitosan solution.

4 Remediation of Soil from Dyes

Dye-containing wastewater pollution of soils and groundwater is a major environmental hazard. Because of rising public awareness and concern about the release of synthetic dyes into the environment and their persistence there, remediation of these pollutants has gotten a lot of attention (Ali 2010). Light, pH, and microbial attack are among conditions that dyestuffs are designed to withstand. The stability of dye molecules to above-said conditions triggered to remove these stuff from wastewater before releasing into the environment.

The organic dye molecules and their intermediates are proved to be carcinogenic as well as mutagenic to humans. From last two decades, many interesting nanoscale materials like, metal oxides, bimetallic compounds, metallic nanoparticles, nanotubes, carbon fiber, and enzymes are employed for detoxification of these in environmental matrix (Benjamin et al., 2019) (Table 1).

The soil pollutants can be effectively neutralized by phytoremediation and has advantages like inherent sunlight activeness, cost-effectiveness, stable over longer times, and applicable to any open site which is not possible with other techniques (Rane et al., 2014). The catalytic degradation and removal of dyes can be done effectively with phyto nanoparticles. A large variety of plants have been reported for NPs synthesis in recent days. The AuNPs with 2–20 nm size were synthesized using the Live Alfalfa plants. Ag, Ni, Co, Zn, and Cu NPs were synthesized using the plants like *Brassica juncea* (Indian mustard), *Medicago sativa* (Alfalfa), and *Helianthus annuus* (Vanaja et al., 2014).

Mechanisms Involved in Remediation of Dye from Soil

1. **Adsorption**

   It is defined as, "A molecular or atomic film (the adsorbate) is created when a gas or liquid solute accumulates on the surface of a solid or liquid (adsorbent)". In most cases, the overall absorption of the adsorbent is fixed, with one solute being replaced by another.

   The pollutants form the polluted sites/water bodies can be adsorbed through electrostatic interactions (attraction between opposite charges), ligand-ion combination or binding to specific groups on surface of adsorbents. (Singh et al., 2019) (Table 1).
2. **Catalytic reduction**

   Synthetic AuNPs catalyze the reduction of aqueous methylene blue (MB) to leuco MB with $NaBH_4$ at ambient conditions. The process might well be monitored using UV-V spectrophotometry in the wavelength range of 450–750 nm. In aqueous solution, MB absorbs between 664 and 614 nm (Ganapuram et al., 2015) (Table 1). The mechanism of catalytic reduction of MB to leuco MB with AuNPs with $NaBH_4$ as reducing agent was illustrated in Fig. 4.
3. **UV-induced photocatalytic activity**

Table 1 Examples of Phytonanoparticles used in the remediation of contaminated soil (Galdames et al., 2020)

Phyto nanoparticles	NP size (nm)	Media treated	Source of concern	Contaminant type	Removal mechanism	References
Fe_3O_4	38–78	Soil	Ni (II)	Heavy metal	Surface adsorption	Wang et al., (2019)
nZVII	15–45	Soil (sandy)	Ibuprofen	Pharmaceutical	Chemical reduction	Wang et al., (2019)
Fe/Cu	60–120	Groundwater	Cr (VI)	Heavy metal	Catalytic reduction	Wang et al., (2019)
Fe/Pd	20–30	Groundwater	Trichloroethylene	Chlorinated solvent	Chemical reduction	Shrivastav et al., (2019)
Fe	40–50	Wastewater	Ibuprofen	Pharmaceutical	Adsorption (spontaneous and exothermic)	Shrivastav et al., (2019)
Fe_3O_4	38–42	Wastewater	Methylene blue	Dye	Adsorption	Shrivastav et al., (2019)
Fe	100–200	Wastewater	Ammonia N and COD*	Domestic wastewater	Chemical reduction and adsorption	Dhandapani et al., (2012)
Ag	25	Waste water	Methylene blue	Dye	Adsorption	Ghaedi et al., (2018)
Ag	25	Wastewater	Methyl orange	Dye	Adsorption	Ghaedi et al., (2018)
Au	40–50	Wastewater	Congo red	Dye	Adsorption	Ghaedi et al., (2011)
Pb	47	Wastewater	Malachite green	Dye	UV-Induced photocatalytic activity	Elango and Roopan (2015)
TiO_2	10–20	Surface water	Aquatic biofilm	Bacterial	Photocatalyst involving H_2O_2 generation	Dhandapani et al., (2012)

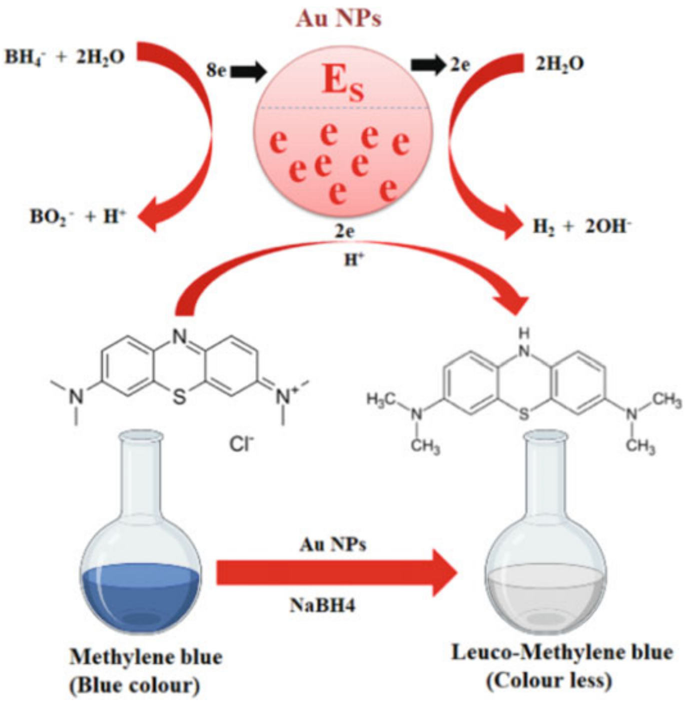

Fig. 4 The catalytic reduction of methylene blue to leuco-methylene blue with AuNPs along with sodium borohydride as a reducing agent

Under visible light irradiation (>420 nm), the $ZnCo_2O_4$ NPs show strong photocatalytic activity for the breakdown of MB. The capacity of $ZnCo_2O_4$ NPs to absorb bandgap photons under UV and visible light, as well as their nanoscale particle size, is credited with their photocatalytic activity (Cui et al., 2011; Yadav et al., 2021) (Table 1).

Various experiments conducted by researchers and scientists have proven the catalytic property of NPs produced by plant extracts in removing and degrading dyes from soil environment. They are as follows:

1. At room temperature, AgNPs and copper nanoparticles (CuNPs) isolated from *Cassia occidentalis* were utilized to reduce 4-Nitrophenol.
2. Photocatalytic activity of bio-synthesized AgNPs revealed Methylene blue degradation when exposed to sunlight greenly produced AgNPs efficiently eliminates the dye by almost 95% (Vanaja et al., 2014).
3. In chloroaurate solution, *Sesbania* seedlings generate gold NPs (AuNPs) in plant tissues. AuNPs catalytic characteristics are employed to decrease the hazardous contaminant 4-Nitrophenol (Fig. 4).
4. Photocatalytic capabilities of ZnONPs can decolorize and destroy acid red dyes (Fig. 5)

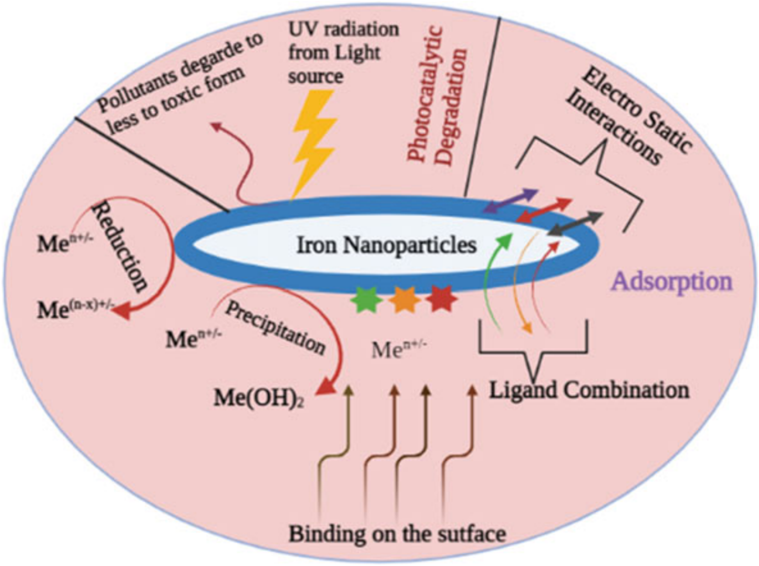

Fig. 5 Pollutant elimination by iron-based nanoparticles by adsorption and photocatalysis

5. Fe oxide and iron oxyhydroxide are found in iron nanoparticles isolated from green tea leaves (GT-Fe NPs). MB and Methyl orange dyes are removed from soil solution using these NPs, which function as a Fenton-like catalyst for the degradation of Congo red dye.
6. ZnONPs is used via the precipitation process utilizing oxalic acid and zinc acetate solution (Singh and Singh 2017) (Fig. 6).
7. The methyl orange dye was degraded to 72% by TiO_2 NPs produced by *Citrus paradisi* peel extract (Sreedharan et al., 2019).

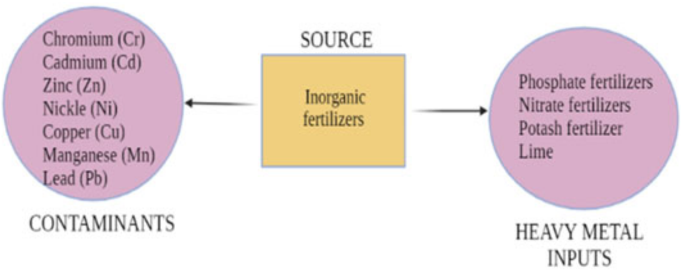

Fig. 6 Heavy metals get accumulated in the soil along with the inorganic fertilizers

5 Remediation of Soil from Inorganic Fertilizer Residues

Plants require nutrients in order to grow and produce. The inorganic fertilizers and organic manure, might be considered as effective options for preserving soil fertility in order to restore nutrients in the soil. Inorganic fertilizers, such as nitrogen, phosphorus, potassium, urea, DAP (Diammonium Phosphate), and MoP (Muriate of Potash), are readily available to crops in their inorganic form. Inorganic fertilizer pollutants on the other hand, disrupt the natural ecology of soil, affecting plant and animal life directly. Agrochemical pollution is a serious threat to the ecology. Exposure to agrochemicals has been related to health issues such nervous system damage and cancer. Nanotechnology has aided in the development of highly effective agrochemical cleanup technologies. NPs have become a common agent in agrochemical remediation due to their large reactive surface area and small packing space requirements. Surface-engineered NPs are gaining popularity as a way to completely remove agrochemicals from the environment. Nano sorbents assisted microbial breakdown of agrochemicals by immobilizing them in the soil. However, because many agrochemicals are persistent, photocatalysis is used to completely remove these residues (Sebastian et al., 2020).

Over 99% of soil phosphorus is present in plant-inaccessible forms. As a result, researchers are constantly looking for new ways to boost phytoavailable phosphorus. Effects of Phyto NPs on Phosphorous Availability play an important role in limiting inorganic phosphorus accumulation in soil and hence aid in its remediation. In one experiment, phytoavailable phosphorus increased by 56% when nano-TiO_2 was added to the mix compared to the control. The amount of phosphorus available was closely connected to the amount of NPs used (Archana et al., 2021; Hanif et al., 2015). Fertilizers with a sulfur nanocoating (100 nm layer) are good slow-release fertilizers because the sulfur content is beneficial. The coating's durability slows the pace of fertilizer disintegration and allowed for a long-term release of sulfur-coated fertilizer. In addition to sulfur nanocoatings, urea and phosphate encapsulation and release will be beneficial to address soil and crop demands. Other NPs with possible applications include kaolin and Phyto biocompatible NPs, which when applied will help to control the release of NPK fertilizer supplies such as urea, calcium phosphate, and potassium chloride using biodegradable NPs (Manjunatha et al., 2016). The absorption of NPs raises the content of other elements in crops as well as the content of absorbed elements. For example, a study on cucumber seedlings grown in sandy loam soil found that 0.5 g/kg of TiO_2 NPs exposure resulted in roughly 34% higher phosphorus and 35% more potassium content than those in the control group (Servin et al., 2012). Nanofertilizers improve crop yield by balancing nutrition throughout the life cycle.

6 Remediation of Soil from Pesticides and Insecticides

Bioremediation is a promising technique that makes use of microorganisms' ability to remove pollutants from the environment while remaining environmentally benign, cost-effective, and adaptable (Raffa and Chiampo 2021). The use of pesticides in large amounts disturbed ecosystem and also was found to be badly affected the environmental harmony besides its serious health effects as well (Bansal 2011; Khajezadeh et al., 2020). The principle bioremediation is to facilitate, and accelerate the natural degradation of the pesticides in the soil pesticides can be biodegraded using a variety of techniques, which can occur in aerobic or anaerobic conditions depending on the microorganisms used. Furthermore, depending on where the remediation treatment is performed, bioremediation procedures can be classified as in-situ, ex-situ, or on-site. In the in-situ method, the treatment takes place in the polluted zone, and the process is typically aerobic. Natural attenuation, bioaugmentation, biostimulation, bioventing, and biosparging are the most common in-situ approaches. Ex-situ procedures include removing contaminated soil from polluted locations and transporting it to another location for treatment. *Ex-situ* treatments include bioreactors, composting, land farming, and biopiles. The on-site treatment involves treatment of polluted soil in the nearby unpolluted place without affecting the nature of place while transporting (Morillo and Villaverde 2017).

Factor	Conditions required
Micro organisms	Aerobic or anaerobic
Natural biological processes of microorganisms	Catabolism and anabolism
Environmental factors	Oxygen content temperature, pH, Electron acceptor/donor
Nutrients	Carbon, Nitrogen, Oxygen, etc
Soil moisture	25–28% of water holding capacity
Type of soil	Low clay or slit content

Mechanism of Remediation of Soil from Pesticides and Insecticides

Bacteria/fungus of specific species or enzymes can be used in soil bioremediation to remove insecticides and pesticides (Raffa and Chiampo 2021). By taking into account of biological and chemical factors affecting pesticide biodegradability, bioremediation is considered as environmentally sustainable and cost-effective method for decontaminating and detoxifying a pesticide-contaminated environment (Bansal 2011). Photochemical, chemical, and microbiological processes can all be used to degrade pesticides and transform them into one or more metabolites.

The microorganisms completely mineralize the pesticides by utilizing them for their metabolic activities. Enzymes like hydrolases, peroxidases, and oxygenases, which influence and catalyze biochemical reactions, play an important role in biotransformation mechanisms.

Pesticide degradation can be divided into three phases, which can be stated as follows:

1. **Phase 1**: By the process of oxidation, reduction, or hydrolysis, pesticides are converted into less toxic and more water-soluble compounds.
2. **Phase 2**: The products in phase-1 are further transformed into more water-soluble and less toxic amino acids and sugars.
3. **Phase 3**: In this phase, the phase-2 metabolites are converted into secondary conjugates that are less toxic.

Bacteria or fungus are the microorganisms involved in the degradation process and can produce intra- or extracellular enzymes (Khajezadeh et al. 2020).

7 Future Perspectives

Various NPs have been shown in numerous studies to considerably detoxify or remediate organic, inorganic, and heavy metal contaminants in soils. Phytonanotechnology has the potential to give green and environmentally friendly options to environmental cleanup and management that do not affect the environment. Several plants, fungi, and bacteria have been found as hyperaccumulators, which have the potential to collect extremely high amounts of metals. For bioremediation of heavy metal-polluted environments, such plant, fungal, and bacteria species are of interest. NPs in many forms can be utilized to remove contaminants from the soil environment. Some heavy metals were removed from polluted places using nanoparticles made by these sorts of plants, fungus, and bacteria. Selection of appropriate plant species and nanomaterials for pollutant uptake, as well as agronomic management optimization, are required for a high-resolution cleanup process. To improve the dissipation of environmental pollutants, improve soil quality, and ensure human and environmental health, Phytonanotechnology must be applied.

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