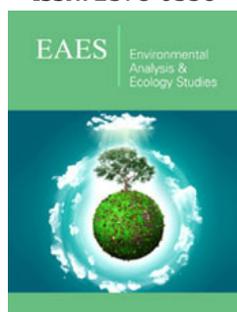


Plant Mediated Green Synthesis of Nanoparticles and their Role in Mitigation of Abiotic Stress in Crop Plants: A Review

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Abstract

In a developing country like India, with significant number of people living under poverty line, agriculture is the mainstay for the livelihood of more than 50 per cent population. To meet the food requirement of increasing population, although a large acreage of land is under cultivation of a range of crop species, the average yield every year, however, has not been as anticipated. Plants have failed to realize their full growth potential owing to varying abiotic stress conditions like high salinity, drought, extreme temperatures, presence of heavy metals, water logging etc. Efforts have been made and are underway to devise strategies/methodologies that could evoke defensive response in plants when exposed to stress conditions. In the recent past, the use of nanoparticles has emerged as a ray of hope in providing solution for combating this obstacle that hamper crop plants from realizing their full growth potential. Nanoparticles are small particles with dimensions satisfying the nanometer scale. Although nanoparticles have been synthesized using physical and chemical methods, these methods are not only expensive, but also are non-eco-friendly and hazardous to health. Of late, a safer approach (green approach) of synthesizing nanoparticles, using plant extracts, have been adopted and has found wide acceptance among the agricultural scientists. Nanoparticles have large surface area, show quick absorbance/penetration with precision delivery to the target site. Use of nanoparticles like Fe, Cu, Zn, Ag, Au, silica etc. have shown positive response in plants manifested in increased germination, high chlorophyll content, increased proline synthesis, photosynthesis etc. The encouraging response seen in plants has led to the resurgence in efforts to try a range of nanoparticles synthesized from myriad plant species. This communication reviews the efforts made by various scientific groups using nanoparticles and the results achieved

Keywords: Green synthesis; Plant, Nanoparticles, Biotic and abiotic stress

Introduction

The ever-increasing population in the world and particularly in the developing countrylike India, has intensified the demand for enhanced food production. With the population expected to escalate by 34 percent by 2050, The global crop production will have to rise from the present 2.1 billion tons to about 3 billion tons [1]. Although to cater to the needs of ever-increasing population, a vast area of land has been brought under cultivation of various food crops, the agricultural yield, every year, has not been up to the mark due to varying biotic and abiotic stresses. Among the common natural abiotic stresses, that has despicably thwarted efforts to have a bumper harvest, have been the soil salinity, drought, and extreme temperatures.

Although to overcome these obstacles, efforts have been and are being made to devise and/or strategize scientific methods that could ameliorate the growth conditions of the crop

plants, the results obtained, have been far from satisfactory. Of late, Nanotechnology has emerged as a potent tool that has helped in resolving a range of problems hitherto unresolved [2]. It has offered an eco-friendly mechanism that has proved pivotal in overcoming some of the problems confronting the agricultural scientist. It uses the physio-chemical properties of a substance at molecular level to explore biological and material world at nano meter scale. Nanoparticles, being tiny in size (1-100nm), show unique physio-chemical characters such as large surface area, improved/enhanced reactivity, increased solubility and penetration via the membranes that enable them target any cell organelle and diverse morphology as compared to bulk particles [3,4].

Owing to all these attributes that the small size bestows on a chemical component, the nanoparticles are suitable for chemical delivery that has the quality of reaching the target site with precision. For example, the chemical fertilizers, which are applied in large doses to enhance the productivity of crop, usually are not target specific and/or are not absorbed completely by plants resulting in their accumulation in soil making it toxic. Use of nanoparticles has given a fillip to the plant growth and productivity by enhancing the availability and absorption/penetration of nutrients into the plants. Nanotechnology holds promise in overcoming the stress related problem faced by the crop plants. However, it can be effectively used once its full potential is identified and particularly, their role in mitigation of various types of stresses faced by plants and their mechanism of action [5]. Realizing the pivotal role that plant based nanoparticles can play in alleviating the problems confronting the mankind, it was considered worthwhile to write this review in order to summarize and address the advancements in the field of green synthesis of nanoparticles.

Plant Mediated Green Synthesis of Nanoparticles

Nanoparticles, on account of its unique physiochemical properties, have wide applications in agriculture, engineering, environmental remediation, biotechnology, microbiology, medicine, electronics, mechanics, optics, and material science [6]. Methods employed thus far, to synthesize nanoparticles, can be broadly categorised into two. The first category includes the top-down approach and the second includes the bottom-up approach. While in top-down approach, bulk materials are reduced to the nano-dimensions by employing lithographic techniques or etching, mechanical processes such as high energy ball milling, laser pyrolysis method, machining, grinding, etc., in the bottom-up approach, the chemical methods such as gas phase method, hydrothermal method, sol-gel method etc. are used for the synthesis of nanoparticles from simple atoms or molecules [7,8]. The bottom-up approach seems more promising and effective method for synthesis of nanoparticles, as it provides the options to form nanoparticles of desired shape and size depending upon the subsequent application by controlling the precursor concentrations, pH, temperature etc. [6,7].

Need for green synthesis

Various approaches adopted for the synthesis of nanoparticles have its limitations. The mechanical and physical methods are not able to give nanoparticles of expected size. Moreover, the maintenance of high temperature and pressure required during the synthesis incurs heavy expenditure. The chemical methods involve use of organic solvents and a range of other chemicals as capping and reducing agents which are non-ecofriendly, toxic health hazard and hard to degrade. Commonly used chemicals in the synthesis process include sodium borohydride and hydrazine hydrate. This apart, while chemicals like ammonium ions, citric acid, carbon monoxide, formaldehyde, hydrogen, hydrogen peroxide, hydroxylamine hydrochloride, sodium carbonate etc. are used as reducing agents, Cetyltrimethylammonium bromide (CTAB), Dodecyl amine (DDA), Ethylene diamine tetra acetic acid (EDTA), Oleic acid, Polyetherimide (PEI), Polyethylene glycol (PEG), Polyamidation (PAMAM), Polyacrylic acid (PAA) etc. work as capping agents.

Realizing the serious consequences, the continuous use of nanoparticles synthesized using physical and chemical methods can lead to, it became imperative to invent an alternative method(s) which was least invasive. Of late there has been a resurgence in efforts in adopting a greener approach toward nanoparticle synthesis [8,9]. The greener methods (Green chemistry) involve the use of natural products (plant extracts/ bacterial- fungal extracts) restricting the use of toxic chemicals to the minimum.

The principles of green chemistry were established in 1998 considering the main objectives to reduce environmental hazards, and risk to human health with enhanced next generation applications. Environmentally benign, green method of nanoparticle synthesis is simple and cost effective with high rate of reproducibility of more stable material concomitant with low risk of contamination of the product [8,10]. Furthermore, it is very straightforward to scale up. Although the green methods of nanoparticle synthesis encompass the use of various microorganisms (bacteria, fungi, yeast, etc.) besides the plants, the methods involving exclusively the microbes (bio-assisted methods) is slow with less reproducibility and offers limited number of size and shape when compared to routes that use plant-based active ingredients [8].

The use of plant extracts as the production assembly of various types of nanoparticles have drawn attention, due to the active ingredients of plant metabolites like polyphenols, flavonoids, tannins, saponins, resins, essential oils, terpenes, terpenoids etc., which help in conversion of metal ions into nanoparticles by behaving as reducing and capping agents [11]. The plant extracts provide a rapid, non-toxic, non-pathogenic, biodegradable and economical single step technique for the biosynthetic processes involved in making of various metallic and non-metallic nanoparticles. (Table 1) lists the plants that have facilitated nanoparticle synthesis.

Table 1: Plant mediated green synthesis of silver, gold, iron and copper nanoparticles.

| Plant (Family) | Active ingredients | Nanoparticles synthesized and size (nm) | Experimental condition | Activity studied | |
|--|---|---|---|---|-----------|
| <i>Camellia sinensis</i> -Tea) (Theaceae) | Polyphenols and flavonoids and small amount of gallic and tannic acid | Silver (Ag) and Gold (Au) (20-60nm) | Aqueous extract of Tea leaves and coffee powder at room temp. | oxidation of 4-nitrophenol to 4-aminophenol | [12]-[14] |
| | | Ag (4nm) | Dried leaf extract | Antimicrobial activity | [15] |
| | | Iron (20-90nm) | Oolong tea extract at room temp. | Degradation of malachite green | [16] |
| | | Iron NPs | Green tea extract with Eucalyptus leaf extract | Removal of nitrate from aqueous solution | [17] |
| | | Hybrid NPs: graphene oxide-Ag | Green tea extract at room temp. | catalytic reduction activity of 4-nitrophenol | [18] |
| | | Iron NPs | Green tea extract at room temp. | Degradation of malachite green activity | [19] |
| | | Iron oxide (20-90nm) | Green tea extract at room temp. | Oxidation of cationic and anionic dye activity | [20] |
| | | Fe and Fe/Pd bimetallic | Green tea extract | Reductive degradation of chlorinated organics | [21] |
| | | Iron | Tie Guanyin Tea Extract | Degradation of bromomethyl blue | [22] |
| | | Fe and Fe oxide | Green tea extract | Degradation of malachite green | [23] |
| | | Iron | Green tea extract | Cytotoxic effects of tumour cell lines | [24] |
| | | Iron (5-15nm) | Tea powder | Degradation of bromomethyl blue | [25] |
| | | Iron(II,III)-Polyphenol Complex NPs | Green tea extract | Ecotoxicological impact | [26] |
| | | Iron | Green tea extract | -- | [27] |
| | | Iron (dependent over the amount of tea extract) | Green tea extract at room temp. | NA | [28] |
| | | Iron (20-40nm) | Green tea, oolong tea and black tea extract at room temp. | Oxidation of monochlorobenzene | [29] |
| | | Metal Oxide NPs: CuO | Microwave condition (540W) | Antibacterial activity against human pathogenic bacteria | [30] |
| | | Iron, Silver and Copper (26-40nm) | Black tea leaf extract | Antibacterial, antifungal and aflatoxin B1 absorption activity | [31] |
| <i>Emblica officinalis</i> - Amla (Phyllanthaceae) | ascorbic acid B and polyhydroxy flavanoids | Gold (Au) and silver (Ag) NPs | Aqueous fruit extract at room temp. | Phase Transfer and Transmetallation in an Organic Solution | [32] |
| | | Silver | Aqueous fruit extract at room temp. | Antibacterial activity | [33] |
| | | MgO | Ethanollic fruit extract at room temp. | Antibacterial activity | [34] |
| | | ZnO | Methanolic fruit extract at room temp. | Antimicrobial activity against six bacterial and two fungal pathogens | [35] |

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|---|---|---|--|---|------------|
| Aegle marmelos-Bael (Rutaceae) | Polyphenols, alkaloids, terpenoids and phenylpropanoids | Ag | Leaf extract under ambient conditions | NA | [36] |
| | | Ag (13nm) and Au (23nm) | Leaf extract under ambient conditions | NA | [37] |
| | | Ag (4-10nm) | Green leaves at room temp. | NA | [38] |
| <i>Azadirachta indica</i> -neem (Meliaceae) | Coumarin, tannins and flavonoids | Ag | Aqueous extract | NA | [39] |
| | | Mono-metallic and bimetallic NPs of Ag and Au | Aqueous extract | Antibacterial activity | [40]-[44] |
| | | Ag (below 30nm) | autoclave assisted extract of neem gum | Antibacterial activity | [45] |
| | | ZnO nanotubes (25nm); ZnO NPs (9.6-29.5nm) | Aqueous leaf extract | Antibacterial activity against E. coli | [46]-[49] |
| | | MgO NPs | Aqueous leaf extract | Enhanced seed germination in <i>Cicer arietinum</i> and <i>Solanum lycopersicum</i> | [50] |
| Sapindusmukorossi-raw reetha (Sapindaceae) | Saponins, triterpenoids and other polyphenols | Ag-Mo/CuO | Aqueous leaf extract | solar photocatalytic and antimicrobial activities | [51] |
| | | CuO (48nm) | Aqueous leaf extract | Antibacterial activity | [52] |
| | | CuO | Aqueous leaf extract | -- | [53] |
| | | CuO (36±8nm) | Leaf extract | Apoptosis in cancer cells | [54] |
| | | CuO (232-236nm) | Leaf extract | Degradation of methylene blue | [55] |
| | | CuO (220-235nm) | Leaf extract | Antioxidant and anticancer activity | [56] |
| | | CuO (48nm) | Leaf broth | -- | [57] |
| | | CuO (29.9nm) | Aqueous fruit extract | -- | [58] |
| | | CuO | Aqueous neem extract | catalytic degradation of Reactive red 120 dyes | [59] |
| | | nano cubes of potassium zinc hexacyanoferrate | Aqueous fruit extract | Photocatalytic activity and degradation of harmful organic dyes | [60] |
| | | Au | Aqueous fruit pericarp extract | -- Catalytic reduction of p-nitroaniline | [61], [62] |
| | | MnO | Aqueous fruit pericarp extract | Worked as catalysts in the oxidation and polymerisation of aromatic amines. | [60] |
| <i>Curcuma longa</i> -Turmeric (Ziniberaceae) | flavonoid curcumin, cardiac glycosides and phenols | Ag | Aqueous leaf extract | Antibacterial activity against V. cholera | [63] |
| | | Au | Aqueous leaf extract | -- | [64] |
| | | Iron oxide | Aqueous leaf extract under microwave assisted conditions and calcination | COD removal capacity and antimicrobial activity | [65] |
| | | ZnO | Aqueous leaf extract under microwave assisted conditions and calcination | Photodegradation of methylene blue dye | [66], [67] |
| | | CuO (30-80nm) | Aqueous leaf extract | Photocatalytic degradation | [68] |

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| Calotropis procera -ark (Asclepiadaceae) | Antioxidant enzymes | Au | Aqueous extract of latex | -- | [69] |
| | | ZnO | Aqueous leaf extract | Antimicrobial activity against human and plant bacterial pathogens | [70] |
| | | ZnO | Aqueous extract of latex | -- | [71] |
| | | CuO (15-20nm) | Aqueous leaf extract | Absorptive activity of Chromium | [72] |
| | | CuO (9.8-10.77nm) | Leaf extract | Morphological and optical activities | [73] |
| <i>Polyalthia longifolia</i> -Ashoka (Annonaceae) | Antioxidant enzymes | Ag | Aqueous leaf extract at room temp. and 60 °C | Antibacterial activity | [74] |
| <i>Abutilon indicum</i> -Mallovs (Malvaceae) | carbohydrates, glycosides, steroids, tannins, flavonoids, and Phenolic compounds | CuO (725nm) | Leaf extract | Antimicrobial, antioxidant and photocatalytic dye degradation activity | [75] |
| <i>Acasianilotica</i> -Gum Arabic tree (Fabaceae) | Gallic acid, ellagic acid, epicatechin, rutin | Ag (20-30nm) | Aqueous pod extract | Electrocatalytic Reduction of Benzyl Chloride | [76] |
| <i>Ailanthus altissima</i> | -- | CuO (20nm) | Aqueous leaf extract | Antibacterial activity | [77] |
| <i>Aloe vera- Aloe vera</i> (Asphodelaceae) | Vitamins A, C and E, sugars, lignin, saponins, salicylic acids, amino acids, folic acid, and choline | NixCu _{0.25} Zn _{0.75} -xFe ₂ O ₄ Polycrystalline powder (15-40nm) | Simple solution of metal nitrates and Aloe vera plant extract | Capable to degrade trichloroethylene (TCE) pollutant | [78] |
| | | CuO (15-30nm) | Aloe vera plant extract | -- | [79] |
| | | In ₂ O ₃ (5-50nm) | Aloe vera plant extract | Optical properties | [80] |
| | | Ag (11-20nm) | Aloe vera plant extract | -- | [81] |
| | | ZnO (8-20nm); (25-65nm) | Leaf extract; Freeze dried leaf peel | Antibacterial activity | [82], [83] |
| | | CuO (20-30nm) | Leaf extract | Antibacterial Activity (Fish BacterialPathogens) | [84] |
| <i>Aloe barbadensis</i> Miller (Asphodelaceae) | Vitamins A, C and E, sugars, lignin, saponins, salicylic acids, amino acids, folic acid, and choline | ZnO (25-40nm) | Aqueous leaf extract at room temp. | Optical properties | [85] |
| <i>Alternanthera dentate</i> — Joseph's coat (Amaranthaceae) | Flavonoids and phenolics | Ag (50-100nm) | Aqueous leaf extract at room temp. | Antimicrobial activity | [86] |
| <i>Anisochilus carnosus</i> -Lavender (Lamiaceae) | Flavonoids, saponins, tannins, phytosterols, triterpenoids | ZnO (9.6 -56.14nm) | Leaf extract | -- | [87] |
| <i>Arachys hypogea</i> - Ground nut (Fabaceae) | Reducing sugars | Cu ₂ O (15-30nm) | Aqueous leaf extract | Antibacterial activity against E. coli | [88] |
| <i>Acanthophyllum Bracteatum</i> - (Caryophyllaceae) | -- | Ag (29-68nm) | Aqueous extract of plant at 25-90 °C | -- | [89] |
| <i>Agathosmabetulina-buchu/bucco</i> (Rutaceae) | limonene, menthone, psi-diosphenol and pulegone | Zn (15.8nm) | Dry leaf extract | -- | [90] |
| <i>Aglai elaeagnoidea</i> -droopy leaf (Meliaceae) | carbohydrates and terpenoids compounds | CuO (20-45nm) | Fruit extract | Catalyst activity | [91] |
| <i>Annona squamosa- sweetsops</i> (Annonaceae) | Glycoside, alkaloids, saponins, flavonoids, tannins phenolic compounds, phytosterols | Ag (20-100nm) | Aqueous young leaf extract | NA | [92] |

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|---|---|--------------------------------------|---|---|-------|
| <i>Anthemis nobilis</i> -Daisy (Asteraceae) | phenolic acids, triterpenes, flavonoids, catechins, coumarins, sesquiterpenes, hydroperoxides, polyacetylenes, and steroids | CuO (18-60nm) | Flower extract | A3 coupling reaction activity | [93] |
| <i>Argemone Mexicana</i> -Mexican poppy (Papaveraceae) | Alkaloids (Berberine) | Ag (10-50nm) | Aqueous leaf extract at room temp. | Antimicrobial activity | [94] |
| <i>Asparagus adscendens</i> Roxb. -Shatavari (Asparagaceae) | Asparosides A, B, C and D; Adscendosides A and B; Asparanins A, B, C, D; Adscendins A and B | CuO (10-15nm) | Aqueous leaf and root extract | Antimicrobial activity | [95] |
| <i>Astragalus gummifer</i> -Tragacanth gel (Fabaceae) | Tragacanthin and bassorin | CuO (18-35nm) | Gum extract | -- | [96] |
| <i>Bauhinia tomentosa</i> -orchid tree (Fabaceae) | flavones, flavonol glycoside, triterpene, phenanthraquinone | CuO (22-40nm) | Leaf extract | Antibacterial activity | [97] |
| <i>Cammelia japonica</i> (Theaceae) | Phenolics, tannins | CuO (17nm) and ZnO (20nm) | Leaf extract | Optical sensor application | [98] |
| <i>Cinnamomum Camphora</i> -Camphorwood (Lauraceae)- | Phenolic compounds | Pd (3.2 -6.0nm) | Aqueous leaf extract | -- | [99] |
| | | Ag | continuous-flow tubular Microreactor at 90 °C temp. | Antibacterial activity | [100] |
| <i>Cacumen platycladi</i> - Arborvitae/ tree of life (Cupressaceae) | Kaempferol (Antibacterial) | Au-Pd bimetallic NPs (7nm) | Aqueous leaf extract | -- | [101] |
| <i>Capparis Zeylanica</i> -Ceylon Caper (Capparaceae) | alcohol, alkaloids, amyirin, anthocyanins, betulin, flavonoids, glycosides, saponins, steroids, sterol and terpenes | CuO (50-100nm) | Leaf extract | -- | [102] |
| <i>Capsicum annuum</i> - peppers (Solanaceae) | Proteins/enzymes, polysaccharides, amino acids, vitamins | Ag (8-12nm) | Aqueous fresh leaf extract | -- | [103] |
| <i>Carica papaya</i> -papaya (Caricaceae) | papain, flavonoids, cystatin, chymopapain, ascorbic acid, tocopherol, cyanogenic glucoside and glucosinolates | CuO (140nm) | Leaf extract | Photocatalytic dye degradation | [104] |
| <i>Centella asiatica</i> L.- Asiatic pennywort (Apiaceae) | Terpenes, flavonoids, phenylpropanoids, tannins, alkaloids, carbohydrates, vitamin, mineral and amino acid | CuO (570nm) | Leaf extract | Catalytic degradation of organic dyes and nitroarenes | [105] |
| <i>Coptidis Rhizoma</i> -Huang Lian (Ranunculaceae) | Alkaloids (Berberine) | ZnO (2.9-25.9nm) | Dried rhizome extract | -- | [106] |
| <i>Citrus sinensis</i> - Orange (Rutaceae) | Vitamin C, flavonoids, acids, volatile oils | Ag (33±3nm at 25 °C, 8±2nm at 60° C) | leaf extract at various temp. | -- | [74] |
| <i>Citrus medica</i> Linn. (Rutaceae) | Vitamin C, flavonoids, acids, volatile oils | CuO (33nm) | Fruit extract | Antimicrobial activity | [107] |
| <i>Citrullus colocynthis</i> - bitter apple (Cucurbitaceae) | Vitamin C, flavonoids, acids, volatile oils | Ag (31nm) | Aqueous leaf extract at room temp. | -- | [108] |
| <i>Coccinia grandis</i> (Cucurbitaceae) | Triterpenoids, alkaloids, tannin | Ag (20-30nm) | Fresh leaf extract | -- | [109] |
| <i>Coffea arabica</i> -Coffee (Rubiaceae) | Caffein, flavonoids and tannins | CuO (20-60nm) | Coffee powder extract | -- | [96] |

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|--|---|---|-------------------------------------|--|--------------|
| <i>Cocos nucifera</i> -Coconut (Arecaceae) | vitamin B, nicotinic acid, pantothenic acid (B5) biotin, riboflavin(B2) folic acid, pyridoxine, thiamine, amino acids, L-arginine | ZnO (20-80nm) | Coconut water | -- | [110] |
| <i>Coriandrum sativum</i> - coriander (Apiaceae) | Carotene, thiamine, riboflavin, niacin, oxalic acid, sodium | Ag (26nm) | Fresh leaf extract | -- | [111] |
| <i>Dalbergia sissoo</i> -Indian rosewood (Fabaceae) | Polyphenols and hydroxyflavonoids | Mono-metallic and bimetallic NPs of Ag and Au | Aqueous and methanolic leaf extract | -- | [112], [113] |
| <i>Dalbergia spinosa</i> —liana(Faboideae) | Flavonoids, isoflavonoids, neoflavonoids, steroids, terpenoids | Ag (14-22nm) | Shade dried leaves | -- | [114] |
| <i>Drypetessepia</i> - Hedge Boxwood (Putranjivaceae) | flavonoids, chalcone glycosides, saponins, tripterpenoids, phenolics, alkaloids | CuO (25nm) | Leaf extract | Catalytic activity | [115] |
| <i>Ecliptaprostrata</i> -Bhringraj (Asteraceae) | Esters, Oleic acid, eicosyl ester | CuO (30-32nm) | Leaf extract | Antimicrobial and cytotoxic activity | [116] |
| <i>Eichornia crassipes</i> -water hyacinth (Pontederiaceae) | Inorganic minerals | ZnO (32-36nm) | Leaf extract | -- | [117] |
| <i>Eukalyptus</i> -Safeda (Myrtaceae) | essential oils (1,8-cineol and α -pinene) | Fe (50-80nm) (40-60nm) (20-80nm) | Leaf extract | -- | [118]-[120] |
| <i>Eukalyptus camaldulensis</i> - Safeda (Myrtaceae) | essential oils (1,8-cineol and α -pinene) | CuO (89.24nm) | Leaf extract | Biofilm formation | [121] |
| <i>Euphorbia Chamaesyce</i> - <i>Euphorbia</i> (Euphorbiaceae) | triterpenoids, diterpenoids, flavonoids, tannin and polyphenol | CuO (36-40nm) | Leaf extract | Catalytic degradation of p-nitrophenol | [122] |
| <i>Euphorbia esula</i> L.- <i>Euphorbia</i> (Euphorbiaceae) | triterpenoids, diterpenoids, flavonoids, tannin and polyphenol | CuO (20-110nm) | Leaf and flower extract | Catalytic activity | [123] |
| <i>Falcaria vulgaris</i> -sickleweed (Apiaceae) | β -caryophyllene and 1,8-cineole | CuO | Leaf extract | Cytotoxic, antifungal, antibacterial, antioxidant and cutaneous wound healing activities | [124] |
| <i>Ferulagoangulata</i> -Boiss (Apiaceae) | (Z)- β -ocimene, α -pinene, p-cymene, sabinene, β -phellandrene, and α -phellandrene | Cu (44nm) | Leaf extract | Photocatalytic degradation of Rhodamine B (RhB) | [125] |
| <i>Ginkgo biloba</i> Linn- Ginkgo (Ginkgoaceae) | terpene trilactones, flavonol, glycosides, biflavones, proanthocyanidins, alkylphenols | CuO (15-20nm) | Leaf extract | Catalytic activity | [126] |
| <i>Gloriosa superba</i> L.-flame lily (Colchicaceae.) | Colchicine, b-sitosterol, fatty acids and benzoic acid. | CuO (5-10nm) | Leaf extract | Antibacterial activity | [127] |
| <i>Glycine max</i> -Soyabean (Fabaceae) | Proteins, carvacrol, (E,E)-2,4-decadienal, p-allylanisole, p-cymene, and limonene | Pd (15nm) | Aqueous leaf extract at room temp. | -- | [128] |

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|---|---|--|--|---|-------------|
| <i>Gossypium</i> - cotton (Malvaceae) | carbohydrates, flavonoids, tannins, steroids, terpenoids, saponins, resins, phenols and proteins | ZnO (13nm) | Cellulose fibers | NA | [129] |
| <i>Hagenia abyssinica</i> (Brace) JF. Gmel.-kousso (Rosaceae) | phenols, saponins, flavonoids, anthraquinones, terpenoids, alkaloids, steroids, glycosides, and tannins | CuO (34.76nm) | Aqueous leaf extract at room temp. | Antibacterial activity against <i>E. coli</i> , <i>Pseudomonas aeruginosa</i> , <i>Staphylococcus aureus</i> , and <i>Bacillus subtilis</i> | [130] |
| <i>Hibiscus rosa-sinensis</i> - rose mallow (Malvaceae) | Proteins, vitamin C, organic acids, flavonoids, anthocyanins | Ag(13nm) | Aqueous leaf extract | -- | [131] |
| <i>Ixoro coccinea</i> -jungle flame (Rubiaceae) | Triterpenes, monoterpenes, sesquiterpenes | CuO (80-110nm) | Aqueous leaf extract | -- | [132] |
| <i>Jatropha curcas</i> -barbados nut (Euphorbiaceae) | Curcain and curcacycline A curcacycline B | TiO ₂ (20-100nm) Ag (30-50nm) | titanium isopropoxide solution with aqueous leaf extract Seed extract | -- | [133] |
| <i>Lantana camara</i> - wild/red Sag (Verbenaceae) | Phenolics, flavonoids, terpenoids, alkaloids, lipids, proteins, carbohydrates | Ag (14-27nm) | Fresh leaf extract | -- | [15] |
| <i>Lawsonia inermis</i> -henna (Lythraceae) | alkaloids, phenolic, coumarins, flavonoids, saponins, terpenoids, quinones, xanthonnes, and tannins. | CuO (27nm) | Leaf extract | Electrical conductivity | [135] |
| <i>Leucaena leucocephala</i> L.-white leadtree (Fabaceae) | ficaprenol-11 (polyprenol), squalene, lupeol,-sitostenone, trans-coumaric acid | CuO (10-25nm) | Leaf extract | Antimicrobial activity | [136] |
| <i>Malus domestica</i> -Apple (Rosaceae) | Terpenes, phenolics and aliphatic hydrocarbons | CuO (28-35nm) | Leaf extract | Antibacterial activity against <i>E.coli</i> , antioxidant activity and DNA cleavage activity | [42] |
| <i>Melia dubia</i> -malaivembu (Meliaceae) | Alkaloids, carbohydrates, glycosides, phenolic compounds, tannins, gums, mucilages | Ag (7nm) | Aqueous fresh leaf extract | <i>In vitro</i> anticancer activity | [137] |
| <i>Memecylonedule</i> — delekbangas (Melastomataceae) | Triterpenes, tannins, flavonoids, saponin | Ag(50-90nm) | Shade dried leaf extract | -- | [138] |
| <i>Millingtonia hortensis</i> — neem (Bignoniaceae) | alkaloids, tannin, flavonoid and phenolic | Ag (2-8nm) | Dried leaf extract | Anti cardio toxicity in male wistar rats | [139] |
| <i>Mimusops selengi</i> (Sapotaceae) — Spanish cherry | Ascorbic acid, gallic acid, pyrogallol, resorcinol | Ag (12-30nm) | Seed Extract | Antimicrobial and antioxidant activities | [140] |
| <i>Morinda citrifolia</i> L.- Drumstick (Moringaceae) | Phenolic compounds | Ag (20-50nm) | Aqueous silver nitrate extract with leaf extract at various temp. | Antibacterial activity | [141] |
| <i>Morinda morindoides</i> - Drumstick (Moringaceae) | Phenolic compounds | CuO (16-21nm) | Leaf extract | Catalyst (Organic dye) | [142] |
| <i>Moringa Oleifera</i> (Moringaceae)- | Phenolic compounds β -sitosterol, caffeoylquinic acid, quercetin, kaempferol | Ag (50nm) | Aqueous silver nitrate extract with leaf extract at various temp.; Fresh stem bark extract | Antibacterial activity | [143]-[145] |

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|---|---|------------------------------|--|---|-----------------|
| <i>Moringa Oleifera</i> (Moringaceae)- <i>Mukiamaderaspatana</i> - Madras pea pumpkin (Cucurbitaceae) | Phenolic compounds β -sitosterol, caffeoylquinic acid, quercetin, kaempferol flavonoids, saponins, carbohydrates, steroids, tannins and phenolic compounds | CuO (6-61nm) | Leaf extract | Nitrate removal activity | [146] |
| | | Ag (13-34nm) | Fresh leaf extract | Insecticidal activity against <i>Culex</i> <i>quinquefasciatus</i> and <i>Aedes aegypti</i> (Diptera: Culicidae) | [147] |
| <i>Musa accuminata</i> -Cavendish banana (Musaceae) | Starch, carbohydrates, sugars | CuO (50-85nm) | Peel extract | Photocatalytic activities | [148] |
| <i>Nelumbo nucifera</i> — sacred lotus (Nelumbonaceae) | Betulinic acid, steroidal pentacyclic tri- terpenoid, procyanidins | Ag (25-80nm) | Fresh leaf extract | larvicidal activity against malaria and filariasis vectors | [149] |
| <i>Nephelium lappaceum L.</i> (Sapindaceae) | Proteins, lipids, carbohydrates | ZnO | Fruit peel extract | Antibacterial activity | [150] |
| <i>Nyctanthes</i> -tree of sorrow (Oleaceae) | Alkaloids, glycosides, glycerides of linoleic, oleic, lignoceric, stearic, palmitic and myristic acids; nyctanthic acid | TiO ₂ (100-150nm) | titanium isopropoxide solution with aqueous leaf extract | -- | [151] |
| <i>Ocimum sanctum</i> — Tulsi (Lamiaceae) | Phenolic compounds, Alkaloids, glycosides, tannins, saponins, aromatic compounds | Ag | Aqueous silver nitrate extract with leaf extract at various temp, | Antibacterial activity against <i>Escherichia</i> <i>coli</i> , <i>Klebsiella</i> <i>pneumoniae</i> and <i>Pseudomonas</i> <i>aeruginosa</i> | [152], [153] |
| <i>Ocimum basilicum L. var.</i> <i>purpurascens</i> (Lamiaceae) | Phenolic compounds, Alkaloids, glycosides, tannins, saponins, aromatic compounds | ZnO (50nm) | Leaf extract | -- | [154] |
| <i>Olea europaea</i> - Olive (Oleaceae) | Essential oils (betulinic acid, uvaol, ursolic acid, maslinic acid) and flavonoids | CuO (20-50nm) | Leaf extract | Toxicity activities | [155] |
| <i>Origanum vulgare</i> - oregano (Lamiaceae) | Essential oils and phenolic compounds | Ag (63-85nm) | Fresh leaf extract | Antibacterial and anticancer activity | [156] |
| <i>Parthenium hysterophorus L.</i> -white to weed (Asteraceae) | germacrene-D, trans- β - ocimene | ZnO (22-90nm) | Leaf extract | Antifungal activity | [157] |
| <i>Phaseolus vulgaris</i> -kidney bean (Fabaceae) | Proteins and starch | CuO (26.6nm) | Black bean extract | Anticancer activity against human cervical cancer cells | [158] |
| <i>Phyllanthus niruri</i> - stone breaker (Phyllanthaceae) | alkaloid, flavonoid, terpenoids, cardiac glycoside, saponins, tannins, cyanogenic glycosides | ZnO (25.61nm) | Leaf extract | Photocatalytic activity | [87] |
| <i>Piper longum</i> - pipli (Piperaceae) | Piperidine, alkaloids, tannins, dihydros, stigmasterol, sesamim, terpenines | Ag (46nm) | Dried fruit powder | Antioxidant, antibacterial activity and cytotoxic effects | [159] |
| <i>Plantago asiatica</i> -asiatic plantain (Plantaginaceae) | lavonoids, alkaloids, terpenoids, phenolic acid derivatives, iridoid glycosides, fatty acids, polysaccharides and vitamins | CuO (7-35nm) | Leaf extract | Catalytic activity | [160] |
| <i>Plectranthusamboinicus</i> -indian borage (Lamiaceae) | Antioxidants and Eugenol | ZnO (50-180nm) | Fresh leaf extract | Photocatalytic activity | [161] |
| <i>Pongamia pinnata</i> (Legumes) | Sterols and fatty acids | ZnO (26-100nm) | Fresh leaf extract | Antibacterial activity | [162] |

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|---|--|--|-------------------------|--|----------------------------|
| <i>Pterocarpus santalinus</i> (Fabaceae) – sandalwood | Phenolic compounds (cedrol, Propanoic acid, 2-methyl-, 3- P-Cresol, (-) - Spathulenol) | Ag (20-50nm) | Fresh leaf extract | Antibacterial activity | [163] |
| <i>Pterospermum acerifolium-kanakchampa</i> (Malvaceae) | Saponins, tannins, flavonoids | CuO (15-30nm) | Aqueous leaf extract | Studied for toxicity against <i>Daphnia magna</i> | [164] |
| <i>Punica granatum-Anar</i> (Punicaceae) | ascorbic acid, citric acid, and malic acid, and phenolics, flavonoids and anthocyanins | CuO (15-20nm) | Leaf extract | antimicrobial activity against opportunistic pathogens | [165] |
| <i>Punica granatum-Anar</i> (Punicaceae) | ascorbic acid, citric acid, and malic acid, and phenolics, flavonoids and anthocyanins | CuO (40-80nm) | Seed extract | Photocatalytic activity | [166] |
| | | <i>Quercus- oak</i> (Fagaceae) | CuO (34nm) | Aqueous fruit extract | Photocatalytic degradation |
| <i>Rhizophora mucronata-asiatic mangrove</i> (Rhizophoraceae) | Alkaloids, flavonoids, polyphenols, terpenoids | Ag (60-95nm) | Fresh leaf extract | mosquito larvicidal activity | [168] |
| <i>Rheum palmatum L. -Chinese rhubarb</i> (Polygonaceae) | Anthraquinone and antioxidants | CuO (10-20nm) | Leaf extract | Catalytic activity | [169] |
| <i>Rosa canina- dog rose</i> (Rosaceae) | sugars, organic acids, pectins, flavonoids, tannins, carotenoids, fatty acids, vitamins | ZnO (21-243nm) | Fruit extract | Antibacterial activity | [170] |
| <i>Ruellia tuberosa - Meadow weed</i> (Acanthaceae) | -- | CuO (83.23nm) | Aqueous extract | Antibacterial and dye degradation activity | [171] |
| <i>Sambucus nigra- European black elderberry</i> (Adoxaceae) | Polyphenol anthocyanins | Ag (20-80nm) | Frozen fruit extract | Anti-inflammatory activity | [172] |
| <i>Santalum album- chandan</i> (Santalaceae) | alpha- and beta-santalol, cedrol, esters, aldehydes, phytosterols | ZnO (70-140nm) | Leaf extract | Apoptosis induction in human breast cells | [173] |
| <i>Saraca indica -Ashoka tree</i> (Fabaceae) | Flavonoids, terpenoid, lignin, cardiac glycosides, phenolic compounds, tannins | CuO (13-15nm) | Leaf extract | Photoluminescence Studies | [174] |
| <i>Solanum nigrum- black nightshade</i> (Solanaceae) | Flavonoids, phenolic compounds | ZnO (20-65nm) | Fresh leaf extract | Antibacterial activity | [175] |
| <i>Solanum tuberosum- potato</i> (Solanaceae) | Flavonoids, phenolic compounds | Magnetic nanoparticles (MNPs) | Potato extract | Dye (RhB) degradation activity | [176] |
| <i>Sesbania grandiflora - hummingbird tree</i> (Fabaceae) | Carboxylic compounds, flavonoids, terpenoids, polyphenols | Ag (10-50nm) | Fresh leaf extract | Antibacterial activity | [177] |
| <i>Sesbania grandiflora - hummingbird tree</i> (Fabaceae) | Carboxylic compounds, flavonoids, terpenoids, polyphenols | Ag (10-25nm) | Leaf extract | Antibacterial activity against many human pathogens | [178] |
| | | <i>Sesuvium portulacastrum— salt marsh</i> (Aizoaceae) | Polyphenol anthocyanins | Ag (5-20nm) | Callus and leaf extract |
| <i>Sorghum vulgare-millet/jowar</i> (Poaceae) | Amino acids | Fe (40-50nm) | Sorghum bran extract | -- | [180] |
| <i>Spathodea campanulate- African tulip tree</i> (Bignoniaceae) | Essential oils (α-humulene, β-caryophyllene, farnesyl acetone, aromadendrene, α-gurjunene and tricosane) | ZnO (30-50nm) | Fresh leaf extract | -- | [181] |

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|---|--|--------------------|---|--|----------------|
| <i>Stachys lavandulifolia</i> - betony/ woundwort (Lamiaceae) | Essential oils (germacrene-D, β-phellandrene, β-pinene, myrcene, α-pinene and Z-β- ocimene) | Cu (72-88nm) | Flower extract | Antibacterial activity | [182] |
| <i>Stachys lavandulifolia</i> - betony/ woundwort (Lamiaceae) <i>Syzygiumcumini</i> — jamun (Myrtaceae) | Essential oils (germacrene-D, β-phellandrene, β-pinene, myrcene, α-pinene and Z-β- ocimene) Gallic acid, p-coumaric acid, quercetin,3,4- dihydroxybenzoic acid | Ag | Herbal tea extract and modified iron oxide NPs | Antibacterial activity and 4-nitrophenol reduction activity | [183] |
| | | Ag (40-100nm) | Air dried seed extract | Activity against high glucose-induced cardiac stress | [184] |
| <i>Syzygiumaromaticum</i> (Myrtaceae) | Gallic acid, p-coumaric acid, quercetin,3,4- dihydroxybenzoic acid | Cu (12nm) | Bud extract | Antimicrobial activity | [185] |
| <i>Syzygiumalternifolium</i> (Wt.) Walp(Myrtaceae) | Gallic acid, p-coumaric acid,quercetin,3,4- dihydroxybenzoic acid | Cu (17.5nm) | Leaf and fruit extract | Antiviral activity | [186] |
| <i>Tabernaemontanadivaricata</i> - pinwheelflower (Apocyanaceae) | alkaloids, triterpenoids, steroids, flavonoids, phenyl propanoids and phenolic acids | CuO (48±3nm) | Leaf extract | Antibacterial activity (Urinary tract) | [187] |
| <i>Terminalia catappa</i> - Indian almond (Combretaceae) | alkaloids, quinone derivatives, gallic acid | CuO (21-30nm) | Leaf extract | Antibacterial test | [188] |
| <i>Thymus vulgaris L.</i> -Garden Thyme (Lamiaceae) | Essential oils (p-cymene, γ-terpinene thymol) | CuO (Various size) | Leaf extract | Catalytic activity | [189] |
| <i>Thymus vulgaris L.</i> -Garden Thyme (Lamiaceae) <i>Tinospora cordifolia</i> - <i>Guduchi</i> (Menispermaceae) | Essential oils (p-cymene, γ-terpinene thymol) Giloin, Tinosporan acetate, Tinosporal acetate, terpenoid, alkaloid, lignans, steroids. | CuO (30nm) | Leaf extract | Catalytic activity | [190] |
| | | CuO (50-130nm) | Fresh leaf extract | Catalytic degradation | [191] |
| <i>Tinospora cordifolia</i> - <i>Guduchi</i> (Menispermaceae) <i>Tephrosia tinctoria</i> — alu pila (Fabaceae) | Giloin, Tinosporan acetate, Tinosporal acetate, terpenoid, alkaloid, lignans, steroids. Phenol, flavonoids | CuO (6-8nm) | Fresh leaf extract | Photocatalytic, antibacterial and antioxidant activities | [192] |
| | | Ag (73nm) | Shade dried stem extract | antidiabetic activity | [193] |
| <i>Thymbra spicata</i> -Mediterranean thyme (Lamiaceae) | Essential oils, flavonoids and polyphenols | CuO (10-20nm) | Flower extract | Catalyst activity | [194] |
| <i>Trifolium Pratense</i> - Red clover(Fabaceae) | isoflavones, flavonoids, pterocarpan, coumarins, and tyramine | ZnO (60-70nm) | Flower extract | Antibacterial activity | [195] |
| <i>Vitex Negundo</i> - Chinese chaste tree (Lamiaceae) | Phenolic compounds | Ag (75-80nm) | Aqueous silver nitrate extract with leaf extract at various temp; flower extract | Antibacterial activity; Growth inhibitory effect on human colon cancer cell lines | [66], [196] |
| <i>Vitis vinifera</i> - Grapes (Vitaceae) | tannins, flavonoids, procyanidins organic acids, lipids, enzymes and vitamins | CuO (3-6nm) | Leaf extract | Antimicrobial Activity against <i>Escherichia coli</i> and <i>Bacillus subtili</i> | [197] |

| | | | | | |
|--|---|--------------|--|------------------------|-------|
| <i>Zingiber Officinale</i> -Zinger (Zinziberaceae) | Phenolic compounds (gingerols, shogaols, and paradols) and polyphenols | CuO (3nm) | Stem extract | -- | [198] |
| <i>Ziziphus spina-christi</i> (L.) Wild-Buckthorn (Rhamnaceae) | 1-Hexadecanol, hexadecenoic acid, ethyl ester (Ethyl palmitate) and 1-Hexadecanol, 2-methyl | CuO (8-15nm) | Aqueous fruit extract | triphenylmethane | [199] |
| <i>Porphyra vietnamensis</i> (Red algae) | -- | Ag | Sulphated polysaccharide was isolated from red algae | Antibacterial activity | [200] |

Limitations of plant mediated green synthesis

Although the use of plant extracts as source of nanoparticles holds promise, there is no clarity about the exact mechanism of nanoparticle synthesis using plant extracts [8,11]. Here it will be apt to mention that the plants of the same species occupying varying habitats vary in their chemical compositions that may lead to different results and interpretations in different laboratories. This

can be considered as a major limitation associated with plant based biogenic methods. However, the green method of nanoparticle synthesis has far more advantages than these minor limitations.

Abiotic Stress Interactions and Nanoparticles

The effect of nanoparticles, whether harmful or advantageous, depends upon the type and concentration of nanoparticles used as well as the plant species [11-200].

Uptake and translocation mechanism of nanoparticles in crops

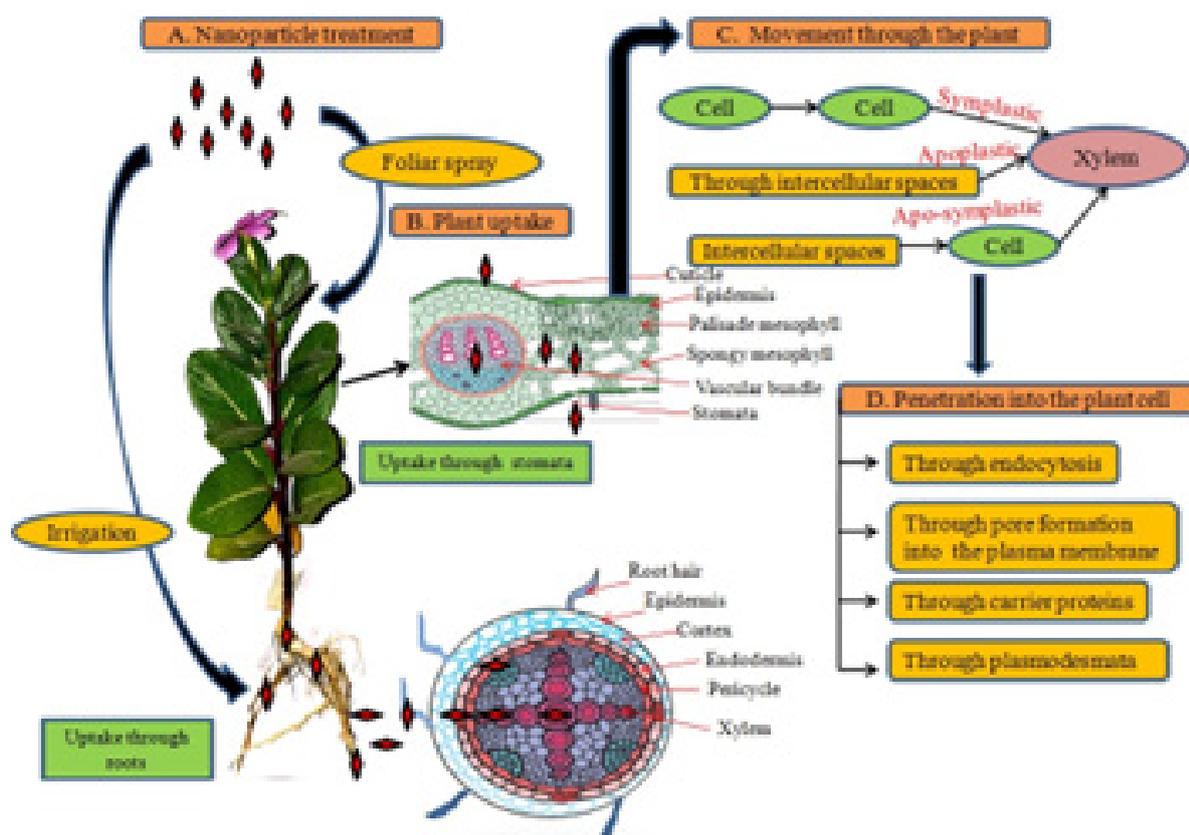


Figure 1: Shows the mechanism of absorption, uptake, transport and penetration of nanoparticles in plants. (A) Treatment methods of nanoparticles: Foliar spray (Flowers, leaves, hydathodes etc.) and irrigation through roots. (B) Uptake of nanoparticles is hampered by many barriers such as cuticle, epidermis, endodermis, casparian strips. Roots hairs on roots, stomata, hydathods and lenticels provide passage to nanoparticles into the plant system. (C) Nanomaterials can follow the apoplastic, symplastic and or apo-symplastic pathways for moving up and down the plant (D) Nanoparticles penetrate into the plant cell through several mechanisms such as endocytosis, pore formation, through plasmodesmata and can be mediated by carrier proteins.

Source: Modified after Pérez-de-Luque [208].

Generally, lateral roots of the plant absorb the nanoparticles from the soil from where they enter into the vascular system through the cortex and pericycle of the roots [201]. While the nanoparticles that are smaller than the pore of the cell wall pass easily through it [202,203], the larger nanoparticles fail to penetrate the cell wall of root cells. Instead, the cell wall opening of flowers, stigmas, hydathodes, and stomata provide an easy passage to the larger nanoparticles which interfere with the metabolic pathways of these cells (Figure 1) [204]. A body of data is available which suggest that nanoparticles move within the plant body by 1) Binding with ion channel proteins, (2) endocytosis through newly formed pores, (3) binding with some organic molecule, and/or by aligning with membrane transporters [205-207]. Nevertheless, further investigation is required to explain the selectivity and uptake mechanism of nanoparticles among types of plants, which is still not very clear.

Mechanistic Interaction of Nanoparticles under abiotic stress in plants

Plants, owing to their rooted and sedentary nature, cannot escape unpredictable changes happening within and outside the lithosphere. Any exposure to stress conditions result in an outburst of Reactive Oxygen Species (ROS) that cause the oxidative breakdown of myriad biomolecules central to the structural integrity of the cell and its photosynthetic machinery/metabolism [209]. Although plants are fortified with an inbuilt defence mechanism to overcome the negative effects of stress conditions,

by way of inducing a battery of genes/ proteins into action and/or by stimulating the production of stress busting molecules like proline, glycerol, inositol, glycine, trehalose etc., the decline in overall growth and productivity despite all the defences, more often than not, get accentuated [210]. While soil salinity and drought lead to osmotic stress in plants, waterlogging creates hypoxia conditions for roots which is usually overcome by a shift in starch metabolism to fermentation that manifests in reduced growth. Similarly, the presence of heavy metals in soil stimulates the accumulation of metal chelates, polyphosphates and organic acids which extenuates the severity of impact, the growth, nevertheless, is affected.

Nanoparticles, owing to various structural/functional attributes, have the potential to mitigate the disruptive effects of abiotic stresses on plants by 1) imitating the activities of antioxidant enzymes that scavenge the ROS [211], 2) by binding to the heavy metals thereby preventing it from getting incorporated into the plant system, 3) by improving the rate of photosynthesis by protecting the photosystems [212], [213], and 4) by alteration of expression of the genes involved in plant defence responses. However, the response of plants to nanoparticle types and the concentration used varied from species to species [214]. This has opened many avenues to explore a range of nanoparticles that could help plants overcome the abiotic stress induced barriers. In the recent times there has been a spate of reports which prove the potential of nanoparticles in mitigation of abiotic stresses in plants. (Table 2) sum-up the role of nanoparticles in circumventing abiotic stresses.

Table 2: Role of nanoparticles in mitigation of abiotic stresses in crop plants.

| Name Of Crop | Type of Stress | Type of Nano Treatment | Effect of Nano Treatment | References |
|---|--|--------------------------------|--|------------|
| Tomato (<i>Lycopersicon esculentum</i>) | Salt stress | Nano-silica | Increased seed germination and reduction in time for germination | [217] |
| Tomato (<i>Solanum lycopersicum L.</i>) | Salt stress | SiO ₂ nanoparticles | Improved tolerance to salt stress | [212] |
| Lentil (<i>Lens culinaris Medik.</i>) | Salt stress | Nano-silicone | Increase in seed germination, overall growth | [220] |
| <i>Cucurbita pepo L.</i> | Salt stress | SiO ₂ nanoparticles | Enhanced plant growth and tolerance to salt stress | [213] |
| Rice (<i>Oryza sativa</i>) | Salt stress + <i>Fusarium</i> (fungal infection) | SiO ₂ nanoparticles | Improvement in the biochemical status of rice plants under both the stresses | [219] |
| Maize (<i>Zea mays</i>) | Salt stress | Chitosan nanoparticles | Improved plant growth under salt stress | [302] |
| <i>Brassica napus</i> | Salt stress | Cerium oxide nanoparticles | Enhance salt tolerance and increased growth of plants | [303] |
| Rice (<i>Oryza sativa</i>) | Salt stress | Copper oxide nanoparticles | Cu accumulation resulted in toxic effects | [304] |
| Broccoli/Cabbage (<i>Brassica oleracea</i>) | Salt stress | Carbon nanotubes | Enhanced water uptake by plants and improved growth of plants | [226] |
| <i>Solanum Lycopersicum L.</i> | Salt stress | Nano-silicon (N-Si) | Enhanced tolerance to salt stress | [305] |
| Sunflower (<i>Helianthus annuus</i>) | Salt stress | ZnO nanoparticles | Improvement in plant tolerance to salt stress | [306] |

| | | | | |
|---|--|---|--|-----------------------|
| Maize (<i>Zea mays</i>) | Salt stress | Chitosan nanoparticles | Improvement in tolerance to salinity | [302] |
| Wheat (<i>Triticum aestivum L.</i>) | Salt stress | Silver nanoparticles | Improvement in tolerance to salinity | [218] |
| Rice (<i>Oryza sativa</i>) | Salt stress | Silica nanoparticles | Nanoparticle treatment activated antioxidant defense systems and induced osmolyte production | [307] |
| Common bean (<i>Phaseolus vulgaris</i>) | Na ⁺ ion stress Salinity | Silica nanoparticles | Nanoparticle treatment alleviated the effects Na ⁺ -derived salt stress | [221] |
| <i>Triticum aestivum L.</i> | Salt stress | ZnO nanoparticles | Enhanced tolerance to salt stress | [231] |
| Potato (<i>Solanum tuberosum L.</i>) | Salt stress | SiO ₂ nanoparticles | Enhanced tolerance to salt stress | (Gowayed et al. 2017) |
| Cucumber (<i>Cucumis sativa</i>) | Salt stress | SiO ₂ nanofertilizer | Improvement in plant tolerance to salt stress | [224] |
| <i>Phaseolus vulgaris</i> | Salt stress | Nano chitosan | Improvement in growth, physiological and biochemical parameters | [308] |
| Tomato (<i>Solanum lycopersicum L.</i>) | Salt stress | SiO ₂ nanoparticles | Improved plant growth under salt stress | [309] |
| Grape (<i>Vitis vinifera</i>) | Salt stress | Iron nanoparticles and potassium silicate | Improvement in plant tolerance to salt stress | [227] |
| Tomato (<i>Solanum lycopersicum</i>) | Salt stress | Chitosan-polyvinyl alcohol hydrogels and copper nanoparticles | Increase in salt tolerance | [228] |
| Maize (<i>zea mays</i>) and <i>Faba Bean (Vicia fabaL.)</i> | Salt stress | Nano silica | Foliar spray of nano silica helped in mitigation of salt stress | [310] |
| Fenugreek (<i>Trigonella foenum-graceum L.</i>) | Salt stress | SiO ₂ nanoparticles | Improvement in plant growth | [311] |
| <i>Triticum aestivum L.</i> | Salt stress | Silver Nanoparticles | Enhanced tolerance to salt stress | [230] |
| Tomato (<i>Solanum lycopersicum</i>) | Salt stress | Cu nanoparticles (Foliar spray) | Induce tolerance to salinity | [229] |
| Potato (<i>Solanum tuberosum L.</i>) | Salt stress | Silicone nanoparticles | Helped in mitigation salt stress | [223] |
| Chickpea (<i>Cicer arietinum</i>) | Cold stress | TiO ₂ nanoparticles | TiO ₂ NPs treatment increased tolerance to cold stress. | [312] |
| <i>Arabidopsis thaliana</i> | Cold stress | Silver nanoparticles | Increased upregulation of stress related genes | [255] |
| Chickpea (<i>Cicer arietinum</i>) | Cold stress | TiO ₂ nanoparticles | Increased energy efficiency under cold stress | [250] |
| Chickpea (<i>Cicer arietinum</i>) | Cold stress | TiO ₂ nanoparticles | Increased tolerance in plants against cold stress | [312] |
| Saffron (<i>Crocus sativus</i>) | Water logging | Silver nanoparticles | Root growth increased | [272] |
| Soybean (<i>Glycine max</i>) | Water logging | Silver nanoparticles | Increased the seedling growth | [313] |
| Soybean (<i>Glycine max</i>) | Water logging | Al ₂ O ₃ nanoparticles | Improvement in plant growth | [273] |
| Tomato (<i>Lycopersicon esculentum</i>) | Heat stress | Multi-walled carbon nanotubes | Increased expression of various heat shock proteins | [262] |
| Maize (<i>Zea mays</i>) | Heat stress | CeO ₂ nanoparticle | Increased expression HSP70 | [258] |
| Maize (<i>Zea mays</i>) | Heat stress | TiO ₂ nanoparticles | Helpful in the alleviation of heat stress | [260] |

| | | | | |
|--|--------------------------------------|--|---|--------------|
| Tomato (<i>Lycopersicon esculentum</i> Mill. cv. 'Halil') | Heat stress | Selenium nanoparticles | Low concentration of Selenium helped in the alleviation of heat stress | [259] |
| Wheat (<i>Triticum aestivum</i>) | Heat stress | Silver nanoparticles | Treatment with silver nanoparticles improved morphological growth under heat stress | [261] |
| Soybean (<i>Glycine max</i>) | Drought stress | ZnO nanoparticles | Enhanced percent seed germination and improved plant growth | [236] |
| Tomato (<i>Solanum lycopersicum</i> L.) | Drought stress | Nano-silica | Helped in mitigation of drought stress | [212] |
| Safflower (<i>Carthamus tinctorius</i>) | Drought stress | Iron nanoparticles | Foliar application improved tolerance against drought | [238] |
| Strawberry (<i>Fragaria ananassa</i>) | Drought stress | Iron nanoparticles | Helped in mitigation of drought stress | [227] |
| Lentil (<i>Lens culinaris</i>) | Drought stress | Silver nanoparticles | Increased plant growth index | [241] |
| Sugar beet (<i>Beta vulgaris</i>) | Drought stress | Fullerenol | Adversely affected plant growth | [314] |
| <i>Brassica napus</i> | Drought stress | γ -Fe ₂ O ₃ (Maghemite nanoparticles) | Helped in mitigation of drought stress | [239] |
| Barley (<i>Hordeum vulgare</i>) | Drought stress | MWCNTs (multi-walled carbon nanotubes) | Helped in mitigation of drought stress | [242] |
| <i>Prunus mahaleb</i> | Drought stress | SiO ₂ nanoparticles | Helped in mitigation of drought stress | [234] |
| Soybean (<i>Glycine max</i>) | Drought stress | CeO ₂ nanoparticles | Increased plant growth | [243] |
| Sunflower (<i>Helianthus annuus</i>) | Drought stress | Maghemite (γ -Fe ₂ O ₃) | Increased plant growth | [240] |
| Cucumber (<i>Cucumis sativa</i>) | Drought and salt stress | SiO ₂ nanoparticles | Helped in mitigation of water deficit and salt stresses | [237] |
| Spinach (<i>Spinacia oleracea</i>) | UV-B stress | Anatase-TiO ₂ | Helped in mitigation of oxidative stress | [276], [277] |
| Wheat (<i>Triticum aestivum</i>) | UV-B stress | Cd-telluride quantum | Retarded growth of root and shoot | [274] |
| <i>Triticum aestivum</i> | UV-B stress | Silicon nanoparticles | reduced oxidative stress. | [315] |
| <i>Pisum sativum</i> | Chromium (VI) phytotoxicity | SiO ₂ nanoparticles | Protection against Cr(VI) phytotoxicity | [268] |
| Sunflower (<i>Helianthus annuus</i> L.) | Boron toxicity | CeO ₂ nanoparticles | Reduced the Boron phytotoxicity | [270] |
| <i>Zea mays cultivar</i> | Arsenate toxicity-25 uM & 50uM | Silicon NPs | Si NPs effective in reducing Arsenate toxicity, making plant more resistant | [267] |
| <i>Arabidopsis thaliana</i> | Excessive light, heat, dark chilling | Spherical Cerium oxide Nanoparticles (Nanoceria) | Nanoceria treatment helped in the protection of photosynthesis | [263] |
| <i>Moringa oleifera</i> | Cd & Pb toxicity | Silver nanoparticles | Ag NPs helped in mitigation of Cd and Pb toxicity | [271] |

Salinity stress: Saline soils are physiologically dry soils. High concentration of salt in soil makes the soil water potential more negative that reduces the potential gradient between the soil and the roots. This hampers the uptake by roots that culminates in the build-up of ionic toxicity and nutritional imbalance in plants. Besides, vital processes like lipid metabolisms, protein synthesis, photosynthesis are also affected [215]. Reports are available on the potential of Si and SiO₂ nanoparticles and silicon fertilizer in the alleviation of salt stress in several plants such as Basil [216]; Tomato

[212,217]; Wheat [218]; Rice [219]; Lentil [220]; Common Bean [221]; Potato [222,223]; Cucumber [224] etc. A significant increase in the plant growth, chlorophyll content, proline level, antioxidant enzyme system, photosynthetic rate and other vital processes, subsequent to nanoparticle treatment, have been observed.

Silica nanoparticles help in the mitigation of salinity stress by decreasing the Na⁺ absorption by different plant tissues. Decreased levels of Na⁺ concentration in tissues maintain the osmotic potential

of plants which improves the absorption of water and minerals from the soil, that stimulates the plant growth and development under salt stress [225]. In broccoli, use of multiwalled carbon nanotubes helped in alleviation of salt stress by slight alteration in plasma membrane properties and aquaporin transduction, transportation that increased water uptake and net assimilation of CO₂ [226]. Other nanoparticles used effectively in mitigation of salt stress includes iron nanoparticles in Grapes [227], chitosan in Tomato [228], Copper oxide in Tomato [229], silver in Wheat [230], ZnO in Wheat [231], Maghemite in peppermint [232] etc. which showed the similar response like silica nanoparticle.

Drought stress: Drought causes wilting of plants. With little or no water available in the surroundings although some plant species undergo rolling of leaves to prevent the loss of water by exposing less leaf surface to dry air, this nevertheless, reduces growth, vigour and the rate of photosynthesis [233]. Treatment of silicon in Sorghum and silica nanoparticles in hawthorn (*Crataegus sp.*) showed improved drought tolerance. The seedlings of hawthorn treated with different concentrations of silica nanoparticles, showed a positive response on photosynthesis, water, proline, carbohydrate, Malondialdehyde (MDA) and chlorophyll content [234]. Similarly, treatment of two cultivars of Sorghum with silicon nanoparticles improved the water uptake by improving shoot to root ratio in both the cultivars irrespective of their susceptibility for drought stress [235,236]. The use of silica nanoparticles have also helped in mitigating the adverse effects of drought stress in Tomato, Prunus and Cucumis by improving the water uptake and mineral absorption [212,234,237]. In drought stressed soybean seeds enhancement in seed germination and shoot to root ratio was observed upon treatment with ZnO nanoparticles [236].

Due to drought and salinity stress, it becomes difficult to absorb iron from the soil which is an important micronutrient for the plants. The deficiency of iron besides causing significant damage to metabolism, leads to chlorosis in plants. Several studies have been conducted to reveal the mitigating effects of Fe nanoparticles under drought stress. Foliar application of iron nanoparticles in safflower and irrigation of strawberry with solution containing iron nanoparticles improved the resistance against drought in both the plants [227,238]. Similar results were obtained when Brassica napus and sunflower seeds were treated with γ -Fe₂O₃ (Maghemite nanoparticles) [239,240]. Promising role of nanoparticles in the improvement of physicochemical attributes and agronomic traits under drought conditions have also been recorded in Lentil, Barley, Soybean and Wheat upon treatment with silver nanoparticles, multiwalled carbon nanotubes, CeO₂ and TiO₂ nanoparticles, respectively [241-244].

Chilling stress: Exposures to very cold temperatures have had varying effects on the functioning of plants. Freezing temperature damages the plant cell by distortion of permeability and leakage of ions from the membrane which reduces the germination of seeds and the growth of plants [245]. Chilling stress also adversely affects photosynthesis in plants by damaging rubisco enzyme

and by reducing chlorophyll content, CO₂ assimilation and rate of transpiration [247,248]. It is only the cold tolerant species that show less damaging effect of chilling [246]. Application of nanoparticles helps in the alleviation of damaging effects of chilling stress by (1) decreasing the membrane damage and reducing the ion leakage [249]; (2) Enhanced production of Rubisco enzyme and gene expression of chlorophyll binding gene [250], (3) Increasing ability of chloroplast to immerse light [251], (4) Increasing the antioxidant enzyme activity [252] and by (5) inhibiting the ROS production [253]. Application of TiO₂ in Chickpea [250,254] and silver nanoparticles in Arabidopsis [255] increased upregulation of stress related genes that increased tolerance against cold stress.

Heat Stress: Exposure to high temperatures cause denaturation of proteins that hinder metabolic processes. Heat stress increases oxidative stress, which causes degradation of membrane lipids, leakage of ions, reduced rate of photosynthesis, decreased chlorophyll content and protein degradation [256,257]. Although, plants have overcome the harmful effects of elevated temperatures by the production of molecular chaperones and heat shock proteins (HSPs), the adverse effects of heat stress persist still in some plants. The use of nanoparticles like Cerium oxide and TiO₂ in Maize [258,260], Selenium in Tomato [259] and silver nanoparticles in Wheat [261] improved the tolerance of plants against heat stress. Application of Selenium, CeO₂, TiO₂ and multiwalled carbon nanotubes have been reported to enhance the upregulation of heat shock proteins such as HSP70 and HSP90 [258,260,262]. Treatment with Spherical Cerium oxide nanoparticles (Nanoceria) in Arabidopsis reduced the stress caused by light, heat, dark and chilling conditions [263].

Heavy metal stress and other stresses: Heavy metal stress disturbs the uptake of nutrients and vital supplements by the plants. This apart, besides suppressing the activity of the enzyme, it disturbs the uptake causing reduced plant growth due to the deficiency of essential nutrients [264]. Presence of heavy metals in environment cause oxidative stress in plants which degrade the plant metabolism. Treatment of TiO₂ and Al₂O₃ nanoparticles in tobacco plants increased the upregulation of miRNA expression which in result improved the plant tolerance against heavy metal stress [265,266]. Similarly, while application of silicon nanoparticles in maize reduced the arsenate toxicity [267], in Pea and bamboo it reduced chromium toxicity and lead toxicity respectively [268,269]; SeO₂ reduced boron toxicity in Sunflower [270]; Silver nanoparticles reduced lead and cadmium toxicity in Moringa [271].

Waterlogging chokes the root system by depleting the oxygen content of soil. This causes accumulation of carbon dioxide which ceases germination and growth. Application of silver nanoparticles in Saffron and Soybean and Al₂O₃ nanoparticles in Soybean has improved the corm and seed germination, respectively, and increased the plant growth under water logging stress [272,273]. Treatment of Cd-telluride quantum dots and silicon nanoparticles in wheat proved successful in alleviating the UV-B stress by reducing

oxidative stress [274,275]. A similar response was observed in spinach with the treatment of Anatase-TiO₂ nanoparticles under UV-B stress [276,277].

Mechanism of Action of Nanoparticles under Abiotic Stress

The chemical and physical interaction of nanoparticles with biological systems such as plants is mainly due to their intrinsic catalytic reactivity, nano size and large surface area. Generation of reactive oxygen species (ROS), during the interaction of nanoparticles with plants under abiotic stress, is a common phenomenon [260,278]. Besides inducing ROS, nanoparticles have triggered the upregulation of a number of stress related genes [211]. Furthermore, it can imitate the antioxidant enzymes and other signalling molecules that result in transcriptional changes and alteration in secondary metabolite production. Changes in the metabolic pathway subsequent to nanoparticle treatment has improved the tolerance of plants against the stress conditions [279]. There are very few studies on the effect of nanoparticles on antioxidant enzymes and their interaction at the molecular level. Antioxidant enzymes play an important role in the defence mechanism of plants against all stresses. It helps in the scavenging of ROS and reactive nitrogen species (RNS) which cause oxidative stress in biological systems. The commonly present antioxidant enzymes include catalase (CAT), peroxidase (POD), superoxide dismutase (SOD), ascorbate peroxidase (APX), guaiacol and

glutathione reductase (GR), glutathione peroxidase (GPX) etc. Application of gold nanoparticles in Brassica juncea [280]; CeO₂ nanoparticles in kidney bean [281] and silver nanoparticles in Spirodela polyrhiza have enhanced the production of these enzymes [282].

Under stress conditions, the defence system is activated by signalling network. Calcium ions play a major role in signal transduction pathway and are called the second messenger. Stimulus of any kind of stress elevates the level of cytosolic Ca²⁺ concentration through calcium ion channels which eventually bind with Ca²⁺-binding protein (CaBP) and activate them (Figure 2). The activated CaBPs directly bind to promoters of specific stress related genes and causes the repression or induction of their expression and accordingly, induce tolerance against the stress. Nanoparticles can imitate Ca²⁺ ions and bind with the CaBPs. It can cause overexpression of CaBPs that triggers the activation of plant defence system through expression of stress related genes [283]. Silver nanoparticles bind with Ca²⁺/Na⁺ ion pumps via calcium ion receptors or calcium ion channels and instigate the signaling cascade in plants [284]. In addition, C60 nanocrystals activates the Ca²⁺/calmodulin-dependent protein kinase II [285]; cadmium sulfide QDs induced overexpression of calcium-binding protein CML45 as well as calcium-dependent protein kinase 23 [286]. These CaBPs play an important role in the development of resistance in plants against abiotic stresses [287,288].

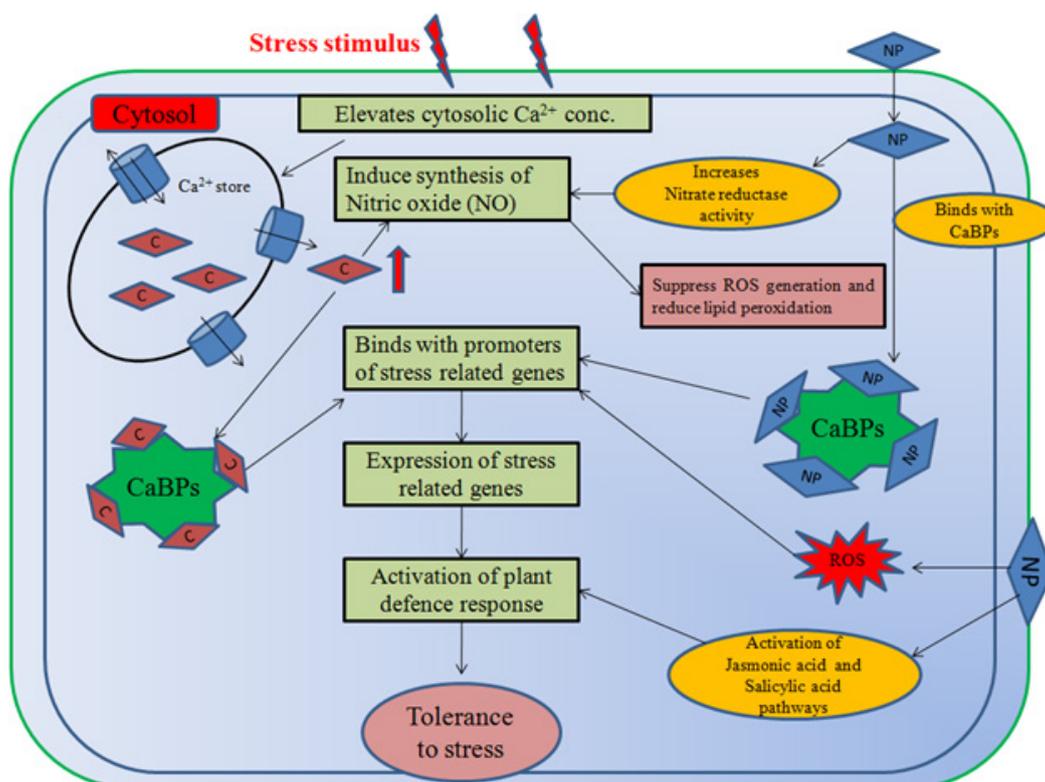


Figure 2: Shows the mechanism of action of nanoparticles in plants under stress stimulus. NP- Nanoparticles; C- Ca²⁺ions; CaBPs- Calcium binding proteins; ROS- Reactive oxygen species.

Source: Modified after Khan et al. [283].

It has been observed that Nitric Oxide (NO) modulates the antioxidant gene expression and suppresses the generation of ROS and eventually reduces lipid peroxidation. Treatment of nanoparticles can elevate the level of Ca^{2+} in the cytosol which induces the synthesis of Nitric oxide (NO). In addition, nanoparticles can increase the nitrate reductase enzyme activity in plants which enhances the concentration of NO to activate the immune response in plants under biotic and abiotic stress conditions [289,290].

Under biotic stress conditions plant induces two types of resistance (1) Acquired systemic resistance (ASR) via the Salicylic acid (SA) signaling pathway and (2) induced systemic resistance (ISR) through the Jasmonic acid (JA) and/or ethylene signaling pathways [291]. Jasmonates and salicylic acid interact with hormones such as Auxins, Ethylene, and Gibberellins that regulate plant growth as well as defense responses to various stresses [292,293]. Application of Chitosan nanoparticles induces plant defense response through the SA pathway under biotic stress [294] and the JA pathway under abiotic stress conditions [295]. In a study the activation of ISR in wheat through JA pathways with the treatment of TiO_2 nanoparticles was reported [296]. In another study, Chitosan-PVA and Chitosan-PVA + Cu NPs promote the expression of SOD genes and JA in tomato under salinity stress [228].

The mechanism of action of nanoparticles is still not well known. However, it is envisaged that the genomic and proteomic studies can help in elucidation of the exhaustive mechanism of nanoparticles under abiotic stress conditions. In a study the modification in the proteins involved in the metabolism of sulphur in roots of *Eruca sativa* following the treatment with silver nanoparticles was reported [297]. Application of polyvinylpyrrolidone (PVP) coated silver nanoparticles induced the expression of stress related genes in *Arabidopsis thaliana* [298]. The transcriptional response of this model plant was analyzed by cDNA expression microarrays which showed the upregulation of 286 genes including metal and oxidative stress related genes and downregulation of 81 genes including ethylene signalling pathway. Treatment of TiO_2 and Al_2O_3 nanoparticles on tobacco plants showed the upregulation of miRNA which plays a significant role in abiotic stresses [265,266].

The proteomic study of rice with the treatment of silver nanoparticles showed 1) The upregulation of stress related genes, 2) Ca^{2+} regulation and signalling, 3) Induction of oxidative stress response pathway, 4) Cell division and cell wall synthesis, 5) Protein degradation, and 6) Apoptosis [284]. The exposure of ZnO, TiO_2 , and fullerene soot in the roots of *Arabidopsis thaliana* and multiwalled carbon nanotubes in Tomato resulted in the upregulation of biotic and abiotic stress related genes [299,300]. Sores et al. reported that NiO nanoparticles induced oxidative stress in *Hordeum* while the treatment of NiO in combination with SiO_2 nanoparticles helped in mitigation of oxidative stress indicating the protective role of SiO_2 nanoparticles in abiotic stress [301].

Conclusion

Nanoparticles have emerged as potent tool endowed with qualities of eliciting the defensive response in plants under stress

conditions. Its small size, large surface area, easy absorbance/penetration and the ease of finding the target site has given it an edge over the other conventional methods employed to overcome stress related problems. The positive response shown by a range of crop species under varying stress conditions like high salinity [302-315], presence of heavy metals, extreme temperatures, and drought conditions, subsequent upon nanoparticle treatment, underpins the positive role played by the nanoparticles in alleviating stress induced complications. Although nanoparticles are being widely used, its mechanism of action is still not yet clear. It is surmised that any insight gained into the mechanism of nanoparticle action will be pivotal realizing that agriculture in India contribute about 18 per cent of the GDP while providing employment to more than 50 per cent workforce. A thorough understanding of the mechanism of nanoparticle action will pave the way for developing new strategies to tackle a range of stress related problems confronting the agriculturists.

Author Contribution Statement

Dr. Savita- Searching of literature and compilation of data in the form of tables.

Dr. Anju Srivastava: Editing and expert inputs.

Dr. Reena Jain: Editing and expert inputs.

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Dr. K.K. Koul: Editing and expert inputs.

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