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Importance of green synthesis of nanomaterials for sustainable agriculture

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With the advancement in science and technology, the branch of Nanotechnology has also grown up with time and today the applications of Nanotechnology is widespread in different fields like engineering, medicine, agriculture, environmental remediation etc. The scope of synthesis and the applications of the synthesized nanomaterials are immense in today's world. Common methodologies employed in the manufacturing of nanomaterials include top down approach and bottom up approach which are mainly physical and chemical processes.

Green synthesis

The processes in which an array of metallic nanoparticles (NPs) are synthesized using bioactive substances like crop residues, plant parts, microorganisms, eggshells, algal matter etc are referred to as green or biological nanoparticle synthesis. Green synthesis of nanoparticles has gained much popularity in the recent days. It has several advantages like lesser environmental impact, safer technology, more biocompatible, lesser production cost etc which makes green synthesis of nanoparticles a more attractive option for the production of nanomaterials. Examples of green synthesized nanoparticles are briefed below.

Salam *et al.* (2014) produced zinc oxide nanoparticle using a medicinal crop *Ocimum basilicum L. var. purpurascens* with hexagonal shape crystal structure and 50 nm size. High purity zinc oxide nanoparticles in a size range of 21.49 and 25.26 nm were manufactured following green synthesis methodology using *Laurus nobilis* leaves (Fakhari *et al.,* 2019). Jayarambabu *et al.* (2020) synthesized copper nanoparticles in the size range of 5 to 25 nm using turmeric (*Curcuma longa*) tuber extract. Mango peels which are normally considered as biowaste were utilized for the synthesis of silver nanoparticles by Zing *et al* (2021), the nanoparticles synthesized were spherical and rod shaped having dimension of 25-75 nm. It also exhibited certain antibacterial property against *Escherichia coli* and *Staphylococcus aureus* also. Zavaleta *et al* (2022) used *Eucalyptus globulus* leaves extract for the green synthesis of iron oxide nanoparticles and the particles were having spherical morphology with 2-4 nm in size.

Applications of green synthesized nanoparticles in agriculture

Applications of green synthesized nanoparticles are being reported in different fields of agriculture like in crop production, crop protection, crop improvement, environmental pollution remediation *etc,* in which some of them are briefed below.

Crop production

Green synthesized zinc oxide and zinc sulphide nanoparticles using chitosan biopolymer and its application to sunflower crop resulted in enhanced seed oil yields compared to the untreated control plants (Patel *et al.,* 2019). Foliar application of green synthesized zinc oxide nanoparticles from leaf extracts of *Phoenix dactylifera* L. var. Khalas indicated that photosynthethic pigments and activity of antioxidant enzymes were enhanced in the okra crop which contributed towards the tolerance of crop towards salinity stress (Alabdallah and Alzahrani, 2020). Seed priming with iron oxide nanoparticles synthesized using the flower extract of *Cassia occidentalis* indicated the beneficial effect of seed priming on germination, seedling vigour, length of root and dry weight of Pusa basmati rice (Afzal *et al.,* 2021). Spherical shaped *magnesium oxide nanomaterials with a size of 38 to 57 nm were green synthesized using Enterobacter bacteria, whose application in rice crop resulted in enhanced plant height, chlorophyll content, and antioxidative enzymes and decreased the arsenic concentration in the crop (Ahamed et al., 2021). While Chatterjee et al (2021) found that the green synthesized iron nanoparticles from Adiantum lunulatum, a* pteridophyte with around 5 nm size and quasi spherical morphology improved the performance of growth and vigour of rice seedlings and decreased the arsenic availability in the crop plant. Sahoo *et al* (2021) studied the impact of *Azadiracta indica* leaves mediated green synthesized zinc oxide nanoparticles and standard zinc oxide nanoparticles on greengram crop and found that green synthesized zinc oxide application has resulted in better seed yield, protein and zinc concentration in the seeds; hence better yield, quality and nutrient use efficiencies was achieved following the application green ZnO nanoparticles. *Ahamed et al (2022) reported that conjoint application of biosynthesized molybdenum nanoparticles from Bacillus sp. strain ZH16 bacteria and the Bacillus sp. strain ZH16 on wheat crop led to decrease in the arsenic translocation to an extent of more than thirty percent and increased indole acetic acid synthesis, solubiliztion of phosphate, and ACC deaminase activity.*

Crop protection

Silver nanoparticles (AgNPs) were biosynthesized through reductive processes facilitated by bacterial agents, particularly strains of *Bacillus pumilus, Bacillus persicus, and Bacillus licheniformis*. Nanoparticles, particularly those derived from *B. licheniformis*, exhibited remarkable in vitro antiviral properties against yellow bean mosaic virus which is an important pest attacking pulses (Elbeshehy *et al.,* 2015). *Rhodotorula glutinis* (BNM 0524) yeast extracted from apple peel was used for the synthesis of silver nanoparticels which was found to be having comparable efficacy like iprodione fungicide at 3 ppm concentration against many of the postharvest pathogens like *Botrytis cinerea*, *Penicillium expansum, Aspergillus niger* and *Alternaria sp.* (Fernandez *et al.,* 2016). Elamawi and Hendi (2018) reported that silver nanoparticles synthesized extracellularly using *Trichoderma longibrachiatum* fungus was having antifungal properties against many of the plant pathogenic fungi *viz Fusarium verticillioides, Fusarium moniliforme, Penicillium brevicompactum, Helminthosporium oryzae, and Pyricularia grisea,* in which around 90 percent of decrease in colonies. Ogunyemy *et al* (2019) synthesized zinc oxide nanoparticles from flower extacts of chamomile (*Matricaria chamomilla*), leaves of olive (*Olea europaea*) and fruits of tomato (*Lycopersicon esculentum*) and reported that zinc oxide nanoparticles synthesized from olive leaves exhibited more pronounced and significant antibacterial activity against *Xanthomonas oryzae* pv. oryzae (Xoo) strain GZ 0003, which is the causal pathogen causing bacterial leaf blight disease which is creating widespread damages to rice crop globally. *Ali et al (2020) reported that iron oxide nanoparticles at the rate of* 1.0 mg/ml *synthesized using neem tree leaf extract*

(Azadiracta indica) acted as capping, reducing and stabilizing agent were effective in the management of citrus brown rot disease in sweet orange caused by the pathogen Fusarium oxysporum. Agathosma betulina plant derived zinc oxide nanoparticle were hexagonal in shape with 27.5 nm in size and application of these green synthesized nanoparticles resulted in improved shoot length, dry weight, lesser Na^+/K^+ ratio and overall better crop growth under salt stressed conditions in *Sorghum bicolar* crop (Rakgotho *et al.,* 2022). Ahamad *et al.* (2023) found that application magnesium oxide nanoparticles synthesized from extracts of lemon fruits enhanced the biometric characters of the carrot crop and also decreased the leaf blight severity caused due to *Alternaria dauci.*

Crop improvement

Seed priming in onion utilizing gold nanoparticles resulted in substantial enhancement in the emergence percentage, which was recorded to be 63.2%, in contrast to the 37.4% in the unprimed control group. Furthermore, an average yield increase of 23.9% in AuNPs, treated onions was reported (Acharya *et al.,* 2019). Silver nanoparticles enhanced the tomato seeds germination by upto 70%, while simultaneously reducing the average germination duration when compared to the control group. The application of silver nanoparticles at various concentrations resulted in a substantial increase in shoot length to an extent of 25 to 80%, root length 10 to 60%, and fresh biomass from 10 to 80%) of the tomato plant. Besides, the total chlorophyll, carotenoids, flavonoids, soluble sugars, and proteins contents were higher in tomato plants treated with neem leaves mediated green synthesized silver nanoparticles compared to the control (Ansari *et al.,* 2023). Ullah *et al* (2023) indicated a green synthesized protocol for iron oxide nanoparticles of 2 to 7.5 nm from *Chenopodium album* and *Fumaria indica* and reported that modified Murashige and Skoog (MS) media incorporating iron oxide nanoparticles as a source of iron facilitated accelerated callogenesis and regeneration in comparison to conventional MS media in tissue culturing of rice plants. Besides these, the foliar application resulted in remarkable enhancement in biomass upto 133%, spike weight upto 350% and enhanced concentration of antioxidant enzymes like ascorbate peroxidase, superoxide dismutase, peroxidase, and catalase in rice crops. Nanopriming with magnetite nanoparticles green synthesized using orange peel extract enhanced biomass and iron uptake in *Solanum lycopersicum* making it an option for iron biofortification in tomato crop (Rojo *et al.,* 2024).

Environmental pollution remediation

Quality of irrigation water and the industrial effluents can have significant influence on the ecosystem. Titanium dioxide nanoparticles synthesized using *Jatropha curcas* crop as a capping agent showed that it could be effectively used after the solar photocatalytic treatment of tannery waste water for the removal of upto 82.26 percent of chemical oxygen demand and 76.48 percent of chromium (VI) ions, which is the more toxic form of chromium from the environmental perspective (Gautam *et al.,* 2018). In another study by Liu *et al* (2018) eucalyptus leaves extract were utilised for the synthesis of iron nanoparticles which exhibited around 100 percentage efficiency for the removal of hexavalent chromium ions in aqueous solution. Iron nanoparticles green synthesized using *Azadiracta indica* leaves extract and ferrous sulphate heptahydrate as precursor could remove 77 percent of chemical oxygen demand and 74 percent of nitrate on fifth day of treatment from petroleum refinery waste water (Devatha *at al.,* 2018). *Syzygium Cumini* leaves extract derived green synthesized zinc oxide nanoparticles was found very efficient in enhancing the seed germination of pearl millet (*Pennisetum glaucum*) and for the remediation of Rhodamine B polluted water with an efficiency of 98 percent (Rafique *et al.,* 2020).

Lin *et al.* (2020) reported that green synthesized iron nanoparticles using green tea leaves extract could be used for the removal of toxic divalent lead ions and rifampicin antibiotic from wastewater to an extent of 100 percent and 92 percent respectively. Root extract of *Sphagneticola trilobata* plant, utilized for the green synthesis of zinc oxide nanoparticles could remove more than eighty percent of chromium when applied at a concentration of 1g/L while also promoting the growth and seed germination of fenugreek plant (Shaik *et al.,* 2020). Khilji *et al.* (2022) found that zinc oxide nanoparticles derived from *Oedogonium* sp. was very effecting in the remediation of effluents from leather industries as it reduced 46.5%, 43.5%, 54%, 57.6%, and 59.3% of total dissolved solids, chlorides, chromium, cadmium and lead. Selenium nanoparticles were green synthesized utilizing the bacterial strain *Pseudomonas aeruginosa* JS-11, the spent culture supernatant effectively reduced soluble SeO_3^{2-} to insoluble red elemental selenium (Se^0) at 37°C, indicating that these red Se° nanospheres could function as biosensors for assessing nanotoxicity through the inhibition of SeO_3^{2-} bioreduction in NP-treated bacterial cell cultures as a toxicity endpoint (Dwivedi *et al.,* 2013).

Limitations

Green synthesis although having several advantages, it has certain disadvantages too. Availability of raw material like plant/parts should be ensured for the green synthesis process. As they are biological samples, seasonality, stage of the development and location specificity of the crop grown in a particular region can affect the adoption of the same technology in another part of the world. Green synthesis processes also often requires equipment's for preserving/treating the samples in a wide range of temperature based on the protocol being followed ranging from -24^{0}C to more than 600^{0}C which also requires lot of energy. The shape and size of green synthesized nanoparticles were reported differently even in same crops which may trigger in the adoption of those processes in large scale. The impact of green synthesized nanomaterials in the remediation of mixed heavy metals was lesser (Ying *et al.,* 2022).

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