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REVIEW PAPER

Selenium nanoparticles: Green synthesis using algae and their potential applications for sustainable agriculture

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Abstract

Selenium is a trace and essential micronutrient for human, animal, and microbial health. Many researchers have recently become interested in selenium nanoparticles (SeNPs) because of their biocompatibility, bioavailability, and low toxicity. Selenium nanoparticles are widely used in biological applications because of their high bioactivity. Physical, chemical, and biological approaches can all synthesise selenium nanoparticles, but biologically synthesised SeNPs are less toxic, cost-effective, and eco-friendly. Algae have several beneficial physiologically active compounds that can reduce selenium and participate in nanoparticle coating, making them an effective tool for generating SeNPs. Researchers have widely investigated various selenium nanoparticle-based formulations for plant health management and soil improvement, including nanosized fertilisers, pesticides, and resistant plant diseases. This review paper covers SeNPs synthesising using algae and their wide agricultural applications.

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Introduction

Jöns Jacob Berzelius, a Swedish physicist, discovered selenium in 1817. Initially, the scientific world viewed selenium as hazardous; however, in the 1950s, it emerged as an essential element for living forms. Since organisms cannot produce it, they must obtain it through diet. This dietary component promotes healthy thyroid gland function, protects cells, and strengthens the immune system (Zhang *et al.*, 2005). Selenium deficiency causes various diseases, including Kashin-Beck disease, thyroid, cardiovascular, or fertility disorders (Wang *et al.*, 2020; Tinggi, 2008; Mistry *et al.*, 2012). Selenium is present in proteins that include amino acids such as selenomethionine, selenocysteine, and methyl selenocysteine (Flohe, 2009). Many enzymes, such as glutathione peroxidases and thioredoxin reductases, require selenium as a cofactor (Benko *et al.*, 2012). In addition to the numerous benefits, high Se consumption levels have certain drawbacks, such as gastrointestinal problems, poor dental health, a metallic taste in the mouth, tingling and inflammation of the nose, the typical garlic odour of the breath, diseased nails, dermatitis, loss of hair, fluid in the lungs, pneumonia, lack of mental alertness, and peripheral neuropathy (Fordyce, 2005; Smith *et al.*, 1937; WHO, 1987). To prevent the adverse effects of excessive dosages, reduce the dose by its consumption, as SeNPs may be an appropriate solution (Ramamurthy *et al.*, 2013). Nanotechnology concerns sub-microscopic particles with at least one dimension less than 100 nm. The adage "small is the new big" perfectly describes the role of nanotechnology-based delivery systems in modern therapies. Researchers (Liong *et al.*, 2008; Brigger *et al.*, 2012; Das *et al.*, 2016; Sun *et al.*, 2002; Sangomla *et al.*, 2018; Saifi *et al.*, 2018; Kumari *et al.*, 2018) have used various types of polymers, dendrimers, liposomes, metal nanoparticles (Ag, Au, Ce, Cu, Eu, Fe, Se, Ti, Y, etc.), silicon, and carbon nanomaterials to create effective therapeutic and drug delivery vehicles. The production and application of selenium nanoparticles (SeNPs) are generating interest due to several benefits such as chemical stability, biocompatibility, and low toxicity. SeNPs, like other nanoparticles, have crucial chemical, physical, and biological properties and perform specific functions due to their nanoscale size (Zang *et al.*, 2001; Wang *et al.*, 2007).

The cyanobacteria are photosynthetic prokaryotes, which can be colonial, filamentous, or unicellular. Because they produce a broad range of primary and secondary metabolites, cyanobacteria and their byproducts have previously been the subject of substantial research for ecological and agricultural uses (Garlapati *et al.*, 2019; Sami and Fatma, 2019). These metabolites may also help Cyanobacteria convert metal ions into metal nanoparticles. So far, most research on cyanobacteria-mediated nanoparticle biosynthesis has been about making gold and silver nanoparticles (Singh *et al.*, 2013; Patel *et al.*, 2015; Husain *et al.*, 2015; Parial *et al.*, 2016). Yang *et al.* (2012) synthesised and characterised the Spirulina polysaccharides-based SeNPs for the first time (Hnain *et al.*, 2013). This review focuses on the green synthesis of selenium nanoparticles and their roles in regulating biotic and abiotic stressors, as well as improving a variety of agricultural techniques, with a particular emphasis on nano farming. We will also cover the effects of nano-postharvest, nano-germination, and nano-stress (biotic/abiotic and pollution) on crop quality.

Synthesis of selenium nanoparticles using algae

Algae have several beneficial physiologically active compounds that can participate in the coating of nanoparticles and reduce selenium, making them a useful tool for producing SeNPs. Phycobilins (found in algae extracts and helps lower selenium and stabilise nanoparticles), proteins, polysaccharides, antioxidants (polyphenols and tocopherols), and antioxidants (polyphenols and tocopherols) are just a few of the things that can help with this kind of synthesis (Muthusamy *et al.*, 2017). The biosynthesis of selenium nanoparticles uses sodium selenite, sodium selenate, selenious acid, and selenium dioxide as precursors (Fig. 1).

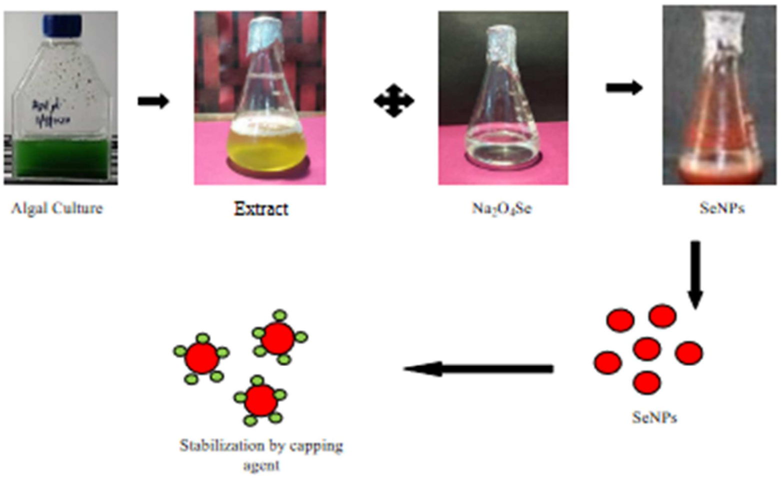

Fig. 1. Algae synthesise selenium nanoparticles

Cyanobacteria, also known as blue-green algae, undergo both intracellular and extracellular synthesis (Afzal *et al.*, 2021). Selenate reductases and selenite reductases do the synthesis inside cells, and different phytochemicals with a reducing potential start the synthesis outside of cells (Afzal *et al.*, 2021). For instance, *Spirulina platensis* (Elsaied *et al.*, 2021), *Arthrospira platensis* (Cepoi *et al.*, 2023), and *Anabaena variabilis* (Afzal *et al.*, 2021) all indicate extracellular synthesis. Furthermore, Alipour *et al.* (2021) looked at how well *Spirulina platensis*-based synthesis worked in the exponential growth phase as a way to make a lot of SeNPs quickly and efficiently. Researchers found that the capping agent composition for both brown and blue-green algae included alkenes, alcohols, phenolic groups, carbonyl-unsaturated ketone amides, amino acids, esters, and proteins in the case of *Polycladida myrica* (Tauliabah *et al.*, 2022), and polysaccharides like Fucoidan in the case of *Sargassum angustifolium* (Tehrani *et al.*, 2020).

Characterization of Selenium nanoparticles

Selenium Nanoparticle characterisation reveals crucial features such as size, shape, surface charge, and structure. These characteristics have a significant influence on nanoparticle behaviour and usage. The characterisation of selenium nanoparticles is significant for a variety of reasons, including nutrient management, disease resistance, soil health, agricultural productivity, and environmental impact. Selenium nanoparticles' potential toxicity may be assessed by proper characterization. Understanding their physical and chemical qualities enables researchers to predict and counteract any negative impacts on health and the environment.

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM), used to estimate the size and shape of SeNPs, can be distinguished as widely used methods for assessing the biosynthesized selenium nanoparticle properties: transmission electron microscopy (TEM), UV/Vis spectrophotometry, and dynamic light scattering (DLS) to evaluate the nanoparticle physical properties; scanning electron microscopy (SEM) to analyze the morphology of the nanoparticles; X-ray diffraction measurements to study the nanoparticle structure; as well as FTIR analysis (Fourier transform infrared spectroscopy) providing the opportunity to characterize biomolecules involved in SeNP synthesis and stabilization (Dwivedi *et al.*, 2013; Bunaciu *et al.*, 2015; Husen *et al.*, 2014).

Selenium nanoparticle applications in sustainable agriculture

Best crop management practices are critical for crop production employing advanced agriculture technology (Ahmad and Sharma, 2023) or new applications, such as nanomaterials (Abd El-Halim *et al.*, 2022). Aguirre-Becerra *et al.* (2022) and Abdelraouf *et al.* (2023) say that nanomaterials can help plants deal with abiotic and biotic stressors, as well as phytopathogens like *Fusarium* wilt infection. You can also use nanomaterials as nano fungicides. As a result, there has been a lot of interest in the potential applications of nanotechnology in agriculture, specifically nano-enabled pesticides and fertilizers (Adisa *et al.*, 2019), nano-enabled agro-strategies to enhance food production and quality (Gomez *et al.*, 2021), and nano-enabled agro-practices to increase plant resistance to abiotic stresses (Manzoor *et al.*, 2022) (Fig. 2).

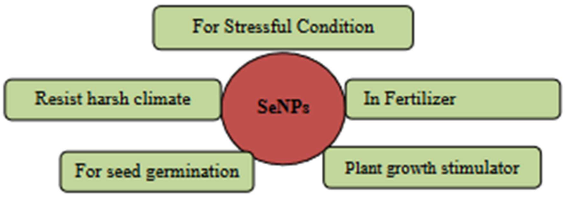

Fig. 2. Different Applications of Selenium Nanoparticles in Agriculture (Song *et al.*, 2023)

Researchers Domokos-Szabolcsy *et al.* (2012) and Husen and Siddiqi (2014) also studied the phytouptake of several metal or metal oxide nanoparticles, including Se. The majority of data showed that nanoparticles may adhere to plant roots and influence plants' absorption of chemicals or substances (Aslani *et al.*, 2014). The most widely accepted theory explaining the translocation of artificial nanomaterials is that they are capable of passing through tissues intra- or extracellularly until they reach the xylem. Although the exact process by which these nanomaterials traverse the Casparian strip and enter the xylem is still unknown, one potential entry point is the meristematic zone or root apex. Once it enters the vascular system, water transpiration and nutrient flow may transport a designed nanoparticle to the plant's aerial sections (Zhang *et al.*, 2015). The plant's cell wall prevents any external substance, including nanoparticles, from easily entering plant cells. The cell wall's pore diameter, ranging from 5 to 20 nm, regulates the sieving characteristics (Lin *et al.*, 2009).

SeNPs' remarkable properties and nanostructure make them highly transportable in plant cells and even organelles. SeNPs have a variety of applications in plants, including delivering balanced crop nutrition (nano fertilizers), pesticide-based plant protection (nano-pesticides), and accelerating plant responses to abiotic stresses, among others.

Fertilisers containing selenium nanoparticles

One of the most important elements in raising crop production, agricultural productivity, and food security is fertiliser. Bindraban *et al.* (2015) predicted that the fertiliser sector is fully capable of participating in the nanotechnology revolution. According to Marstronardi *et al.* (2015), there are numerous opportunities for nanotechnologies to intervene in the field of fertilisers and plant nutrition, providing an overview of the field's current nanotechnology status. According to Severin *et al.*, there has been an upward trend in the number of patents and products utilising nanomaterials for crop nutrition and protection (Severin *et al.*, 2015; Bindraban *et al.*, 2015). Published studies have compared nano-Se and other inorganic Se forms in higher plants (Premarathna *et al.*, 2010; Domokos-Szabolcsy, 2011; Domokos-Szabolcsy *et al.*, 2012; Haghighi *et al.*, 2014; Domokos-Szabolcsy *et al.*, 2014). These investigations analyzed the physiological and biological effects on a variety of plants, including giant reed (Domokos-Szabolcsy *et al.*, 2014), tomato (Haghighi *et al.*, 2014), tobacco (Domokos-Szabolcsy, 2011; Domokos-Szabolcsy *et al.*, 2012), and rice (Premarathna *et al.*, 2010). Tobacco callus cultures and rooted tobacco plantlets may have also absorbed selenium nanoparticles. The roots of plantlets that had been grown from seeds took in a mixture with 100 mg kg^{-1} selenium nanoparticles. This was at very high concentrations (2947 mg kg^{-1} DW). In plant tissue culture, selenium nanoparticles had distinct biological effects than selenate ions (SeO_3^{-2}). Researchers discovered that selenium nanoparticle concentrations ranging from 50 to 100 mg kg^{-1} significantly stimulated organogenesis and root system growth, while selenate did not exhibit these effects at any concentration and completely inhibited both callus growth and root regeneration at 50 to 100 mg kg^{-1} concentrations. This prior concentration induced root initiation, elongation, and biomass production (Domokos-Szabolcsy *et al.*, 2012). Therefore, further research is necessary to comprehend the various biological effects of selenium nanoparticles on plants, including phytouptake, translocation, and plant nano nutrition.

Selenium nanoparticles as pesticides

We used SeNPs 0.5 g/ml, AgNPs 150 g/ml, and K_2SO_4 (2%) to manage early blight disease in potatoes. SeNPs 0.5 g/ml, AgNPs 150 g/ml, and K_2SO_4 (2%) reduced disease severity (12.63%) while improving all plant parameters, including physiological parameters and yield. The conclusions suggest the use of AgNPs and SeNPs in plant foliage to prevent disease and boost yields (El-Batal *et al.*, 2016).

Selenium nanoparticles promote Seed germination

Several recent studies have shown the potential of nanomaterials for nano priming (Anand *et al.*, 2020; Antony *et al.*, 2021; Nile *et al.*, 2022; Khan *et al.*, 2023; Liang *et al.*, 2023). Studies have focused on its synergistic effect in enhancing seed germination under stress conditions. Biological selenium nanoparticles (150 µ mol L^{-1}) helped rapeseed seedlings deal with salt stress by increasing the expression of aquaporin genes (BnPIP1-1 and BnPIP2-1), making the plants take in more water, and controlling the uptake of Na^+ and K^+ (El-Badri *et al.*, 2022). More than 30 mg L^{-1} of nano-Se was added by Sarkar and Kalita in 2022. This increased flavonoids level lowered salt stress (200 mM NaCl) and increased the activity of antioxidant enzymes (SOD, CAT, APX, and POX).

Selenium nanoparticles for stressful conditions

Agriculture is the primary source of food and feed for households, animals, and people. However, several issues, such as pests, climate change, and environmental stressors like salt, drought, and waterlogging, affect agricultural output and put crops under stress, thereby posing a threat to the world's food security. Global agro-production is under attack from about 22,000 species of phytopathogens, insects, weeds, and mites at the farm level (Adisa *et al.*, 2019). Environmental contamination also poses a serious threat to human health and the global agroecosystem (Brevik *et al.*, 2020). The Nano Food Lab at Debrecen University (Hungary) has spent the last 15 years researching and developing viable techniques for manufacturing and examining biological selenium nanoparticles on farms to improve healthy food production and safeguard agricultural output from biotic and abiotic challenges. Only a few studies have published on the protection of cultivated plants from heavy metal stress by selenium nanoparticles. Researchers have found that SeNPs enhance the growth of some cultivated plants under stress, such as sorghum under high-temperature stress (Djanaguirama *et al.*, 2018), strawberry under salinity stress (Zahedi *et al.*, 2019), and rice under Cd and Pb toxicity (Joy *et al.*, 2019).

Selenium nanoparticles for postharvest and quality

The application of selenium nanoparticles before crop harvesting has several advantages, such as enhanced crop yield and quality, reduced production expenses, increased nutrient uptake, and support for sustainable production. Selenium nanoparticles are easily dissolved, kill bacteria, and aren't very harmful when given in smaller amounts than normal mineral forms of Se (El-Ramady *et al.*, 2014). Selenium nanoparticles promote plant growth, development, and secondary metabolism (Huang *et al.*, 2023b). Numerous studies have demonstrated the influence of selenium nanoparticles sprayed during production on increasing the postharvest quality of numerous crops, including:

1. Applying selenium nanoparticles (5.0 mgL^{-1}) from outside the plant made sugarcane more resistant to *Xanthomonas albilineans* infection by controlling the jasmonic acid pathway and raising the quality of the sugarcane juice (Shi *et al.* 2023). Selenium nanoparticle fertilisers (7.5 mgL^{-1}) made summer tea better by increasing the biofortification of Se in tea leaves, lowering the amounts of catechins and caffeine, and increasing the amounts of theanine (Huang *et al.*, 2023b).

2. Adding 5.0 mgL^{-1} of selenium nanoparticles to melon plants increased cucurbitacin B content, which increased antioxidant capacity and made the plants more resistant to insects. It also increased the activities of ascorbate peroxidase, β-1,3-glucanase, peroxidase, phenylalanine ammonia-lyase, and chitinase (Kang *et al.*, 2022).
3. Biological nanofertilizers such as Se (100 mg L^{-1}) and nano-CuO (100 mg L^{-1}) improved banana seedling development by increasing survival rate, photosynthetic pigments, and antioxidant enzymatic activities (CAT, PPO, and POX) for acclimation (Shalaby *et al.*, 2022).
4. Applying selenium nanoparticles (10 µM SeNPs) from the outside reduced leaf electrolyte leakage and the buildup of malondialdehyde and H_2O_2. This improved secondary metabolites in lemon verbena when the salt level was raised from 40 to 160 mM NaCl. In salty conditions, it also improved the production of secondary metabolites like total phenolic content, essential oils, and flavonoid compounds (Ghanbari *et al.*, 2023).
5. Small amounts of selenium nanoparticles (1.0 mgL^{-1}) can help tomato fruits when they are still immature, green and improve their flavour when they are exposed to penthiopyrad, a chiral carboxamide fungicide. They do this by lowering the MDA content and the plant damage caused by this fungicide and raising the amounts of volatile compounds, soluble sugars, and nutrients (Liu *et al.*, 2022).

Conclusion

Green approaches to synthesizing selenium nanoparticles (SeNPs) using algae provide a sustainable alternative to traditional chemical procedures. Because algae-based synthesis uses natural resources and produces no harmful byproducts, it is environmentally beneficial and cost-effective. This method uses the bioactive components of the algae to turn selenium ions into nanoparticles, making it a productive and affordable solution. According to research, SeNPs have antioxidant properties that can promote plant tolerance to adversity and illness, as well as the health of the soil. It seems promising to use SeNPs made from algae in sustainable agriculture. Future research should aim to optimize nanoparticle stability and efficacy by improving synthesis conditions. To assess the long-term effects on crop productivity and soil health, field studies are required. Furthermore, investigating how different soil types interact with SeNPs can enable customised applications for diverse agricultural contexts.

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