

REVIEW ARTICLE

Eco-designing of nano-materials to enhance crop productivity and improve soil remediation

Pranav Anil Patil¹ , Rajeev Kumar Gupta1*, Sreethu S¹& Shaifali²

¹Department of Agronomy, School of Agriculture, Lovely Professional University, Punjab -144411, India ²Department of Horticulture, Lovely Professional University, Punjab, 144411, India

*Email: rajeev.30662@lpu.co.in

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Abstract

The advent of climate change has presented unprecedented challenges to global agricultural systems. Advanced nano-engineering is a valuable tool for promoting sustainability and enhancing crop productivity to ensure food security. Nanotechnology, in particular, is a technology that can be beneficial for crop production. It can minimize losses in resources, improve the targeted and controlled delivery of fertilizers or agrochemicals based on specific needs, prolong the effectiveness of agrochemicals, and reduce recommended dosages and associated losses to boost agricultural productivity. Additionally, nanotechnology's unique characteristics of high reactivity, selectivity, and versatility make it highly promising for addressing complex issues and developing innovative approaches for soil remediation. Nano-particles enhance growth, expedite crop maturation, and enhance a plant's resilience to stress, becoming valuable instruments in regions susceptible to drought and flooding. In addition, they possess the ability to eliminate toxic contaminants, specifically heavy metals and pesticide residues. Nano-particles have a reduced long-term impact on the environment, humans, and plants compared to normal agrochemicals. This review will be highly valuable for future researchers as they strive to understand and harness the potential of nano-materials for enhancing food security and promoting sustainable agriculture.

Keywords

Food security; nanotechnology; crop yield; soil remediation; sustainability

Introduction

A wide range of hazardous substances, including pesticides, pharmaceuticals, personal care products, antibiotics, hormones, organic compounds, nano-compounds, endocrine disruptors, steroids, surfactants and their byproducts, industrial additives, and heavy metals, have built up in different environmental systems due to widespread industrialization, urbanization, and modern agricultural practices (1,2). Pollutant accumulation in different ecosystems can occur due to human activities such as healthcare, industrial operations, electricity generation facilities, oil refineries, mining, inadequate waste management, agriculture, and domestic practices. The concentration of pollutants might vary from 1 μg/ kg to 10 mg/kg (3). Scientific and regulatory bodies worldwide are concerned about the significant rise of these pollutants in the environment due to the severe and long-lasting health risks they pose to humans. To efficiently clean polluted surroundings, several physiochemical and biological methods have been developed, such as adsorption, advanced

oxidation techniques, sonocatalysis, nano-filtration/ reverse osmosis, and bioremediation (4).

In recent times, several researchers have directed their attention toward utilizing nano-substances to develop more efficient methods for remediation (5, 6). The distinctive physical properties of nano-materials, including their favourable surface-to-volume ratio, enhanced reactivity, surface chemistry modification capabilities, reduced intra-particle diffusion distance, superior contaminant removal efficiency, stability, and potential for reusability and recycling, have recently made nanobiotechnology a subject of significant interest for environmental applications (7). Eco designing is a design strategy based on ecological principles suggested to facilitate the creation of novel engineered nano-materials, including those used for environmental purposes. This method aims to achieve a balance between the effectiveness of these engineered nano-materials and the absence of any harm to marine species and humans. Hence, this article provides a critical analysis of both the consequences and potential scenarios for ecologically safe future uses of nano-materials. Specifically, it explores creative ecosafe nano-based technologies for monitoring and mitigating the presence and hazards posed by legacy contaminants in the environment (8).

Applying nanotechnology to enhance agricultural productivity

Nanotechnology is believed to offer potential solutions to various problems in agriculture. Consequently, a unique and innovative approach to farming has been developed, utilizing this technology, to increase agricultural productivity (9, 10). Nanotechnology enhances crop yields through the use of various delivery agents, such as nanopesticides, nano-fertilizers, nano-fungicides, nanoherbicides, and nano-sensors. These agents are employed for tasks such as detecting crop diseases, genetically modifying plants, monitoring the health of plants and animals, and managing post-harvest production (10) (Fig. 1). In addition, the advancement of nanotechnology has offered potential solutions for precision agriculture, which is currently facing numerous unprecedented challenges such as reduced crop productivity due to biotic and abiotic stresses like nutrient deficiency and environmental pollution (11). Nanotechnology also provides advanced solutions to an expanding range of environmental issues. The development of nano-sensors presents numerous possibilities for monitoring environmental stress and enhancing plants' resistance to disease (12). Hence, there is significant potential for extensive societal and fair advantages resulting from continuous progress in nanotechnology, specifically in terms of identifying issues and adopting collaborative strategies to achieve sustainable agricultural development. Nano-materials possess diverse applications and are commonly known as "intelligent delivery systems". They exhibit unique characteristics such as a high surface-area-to-volume ratio, which enhances their ability for retention, and unquestionably a size that enables easy cellular entry. The various effects of nano-formulations on ecology and plant physiology are depicted in Fig. 2 and Table 1.

Research findings indicate that nano-materials have the potential to enhance crop yield by augmenting various aspects of plant growth and development, including seed germination, seedling growth, plant photosynthesis, nitrogen metabolism, carbohydrate synthesis, and protein synthesis. Use of single-walled carbon nano-tubes enhanced the seed germination, improved seedling growth in barley, rice, maize soybean and tomato (13). The germination performance can be influenced by the

Fig. 1. Application of nanotechnology in the field of agriculture.

Fig. 2. Effect of nano formulation application and its impact.

Table 1. Impact of nanoparticle treatment on crop physiology.

CS- chitosan and TPP- tripolyphosphate

concentration of the nanoparticle suspension. Smaller size of nano particles leads to an increase in the area of contact between SiNPs and seeds of tomato, resulting in the expansion of the hydrophilic space around the seeds and improving the process of imbibition. This, in turn, promotes early germination (14).

The progress in nanotechnology has opened up possibilities to circumvent the constraints of traditional approaches. Nanoparticles (NPs) show great potential for the species-independent passive transport of DNA, RNA, and proteins. Nanotechnology is being utilized to enhance the growth of genetically modified organisms (GMOs) by employing NPs as nanocarriers. These NPs form a binding complex with biomodifier molecules, such as the CRISPR/ Cas system, and facilitate their distribution into plant cells (15). Nanomaterial engineering has become a state-of-theart technique for the development of crops in sustainable agricultural systems. Nano-devices and nano-materials (NMs) have the potential to mitigate the impact of substantial pressures on food and energy generation, while optimizing the utilization of scarce resources such as water and nutrients.

Nano-fertilizers: An efficient method for delivering balanced crop nutrition

To improve crop yield and soil fertility, it is typically necessary to supply essential nutrients (16). Accurate fertilizer management is a vital necessity for the development of sustainable agriculture. Nano-fertilizers deliver nutrients in a regulated manner when subjected to different stimuli, such as heat, moisture, and other nonliving factors. Nano-fertilizers are created using various chemical, physical, mechanical, or biological processes. They can be modified versions of bulk fertilizer ingredients, traditional fertilizers, or plant derivatives derived from different parts of plants. Nano-fertilizers are engineered to enhance efficiency compared to traditional fertilizers by delivering readily available elements with low bioavailability, such as phosphorus and zinc, while minimizing the leaching of mobile nutrients, such as nitrate, into the soil (17). Nano-fertilizers can be categorized into two types: nano-materials that function as nutrients themselves composed of either macro or micronutrients, and nano-materials that serve as transporters of macronutrients, containing loaded nutrients or improved fertilizers. The purpose of nanofertilizers is to improve soil fertility, increase agricultural productivity, and enhance the quality of agricultural output. Nano-particles, due to their smaller size, can penetrate plant surfaces more effectively than the pores in plant roots and leaves, resulting in increased nutrient uptake and efficiency. Numerous studies have shown that nano-fertilizers have positive effects on crop growth, yield, and quality, ultimately leading to higher crop yields and improved quality for human and animal consumption. Nano-materials are mostly used to encapsulate nutrients to produce nano-fertilizers. Both top-down and bottom-up strategies are employed to generate the first nanomaterials, utilizing physical and chemical approaches, respectively. The specific nutrients are transported in the

form of particles or emulsions with nano-scale dimensions. This is true for cationic nutrients. For anionic nutrients, they are provided after undergoing surface modification (11, 18). Multiple researches have indicated that nano-enabled fertilizers had the capacity to enhance the efficiency of nutrient transportation to plants.

Engineered nano-materials possess a large surface area and the ability to penetrate, which gives them the potential to be more effective in terms of nutrient use compared to traditional fertilizers. Regarding this matter, the regulated or gradual release of macro nutrients, such as nitrogen (N), has been accomplished using substances like nano-enabled urea-coated zeolite chips and ureamodified hydroxyapatite (19). According to reports, when wheat plants were exposed to a composite of NPKnanochitosan at concentrations of 10-100 mg $L⁻¹$, made by the polymerization of methacrylic acid and chitosan their lifetime was dramatically reduced by 40 days. Additionally, the grain production increased by 51% and 56% compared to the control group and conventional NPK, respectively (20).

Nano-material synthesis

There are three ways, namely physical, chemical, and biological, used to manufacture nano-particles (Fig. 3). Currently, chemical and physical techniques are the primary approaches for producing nano-materials on a wide scale. However, these procedures have detrimental impacts on the environment and human health, require significant energy consumption, and are costly. The utilization of green synthesis techniques for the production of nano-particles is a highly promising and ecologically sound method to create materials that possess distinctive characteristics. Herbs, bacteria, fungi, and agricultural waste are employed as natural reagents in the green synthesis of nano-materials, replacing harmful chemicals and minimizing the carbon emissions associated with the synthesis procedure. Microorganisms have the ability to use reductase enzymes to convert metallic salts into nanomaterials. In recent years; there has been an increasing interest in green synthesis for the study and advancement of nanomaterials (NMs) as a way to tackle the environmental sustainability issues associated with traditional methods. The main objective of green synthesis of NMs is to manufacture NMs while mitigating the environmental issues caused by human activities and minimizing the adverse effects of known pollutants. Green synthesis of NMs is considered environmentally friendly and safe in comparison to traditional approaches. This is because it involves the utilization of biological components in the synthesis process, resulting in the production of biocompatible products without the need for hazardous chemicals. Consequently, scientists have directed their attention towards the environmentally friendly production of NMs, with particular emphasis on cerium oxide $(CeO₂)$, copper (Cu), manganese (Mn), zinc oxide (ZnO), gold (Au), and silver nanoparticles (Ag).

The physical methods used include ion sputtering scattering, arc discharge method, laser ablation,

Fig. 3. Various synthetic methods available for the production of metal nanoparticles.

hydrothermal method, ion implantation, spray pyrolysis, and mechanical grinding. Co-precipitation, pyrolysis, solgel process, phytochemical method, electrochemical, chemical reduction, and hydrothermal synthesis are examples of chemical procedures. Nano-particles can be synthesized using a biological approach by utilizing enzymes and agricultural waste, such as grain husk, to extract substances from plants, bacteria, fungi, algae, and cyanobacteria (21, 22). In addition, the synthesis of nanoparticles may be summarized using two methods: topdown and bottom-up (23, 24). Top-down approaches include the partitioning of bigger, more substantial substances into smaller, more easily handled molecules. Top-down approaches encompass micro-fabrication methods that entail the manipulation of nano-particles by cutting, grinding, and moulding processes to get the desired shape (25). The bottom-up technique involves the gradual construction of a material by adding atoms or molecules one by one through processes such as aggregation, deposition, or self-assembly. To limit their size to the nano-range, the nano-particles produced using the bottom-up method need to be stabilized with a capping agent or stabilizer (26).

Applying nanotechnology for soil remediation

The process of soil degradation and contamination has been expedited as a result of heightened industrialization and excessive urbanization (27). Different remediation techniques are available based on the type and concentration of pollutants in soil and other areas. These methods include bio-remediation using microorganisms, phytoremediation using plants, nano-remediation, nanobioremediation, and nano-phytoremediation, which involve the use of plants and nano-materials (28). Soil remediation often involves the use of in situ approaches. In the past, microorganisms and crops have been used to remove heavy metals from contaminated soils through biosorption and bioaccumulation. Recent evidence

indicates that the use of nano-particles (NPs) in the remediation of heavy metals (HMs) has shown remarkable outcomes (29). Positive results have been seen when NPs are utilized together with microorganisms, either sequentially or simultaneously (30). Carbon-based and non-carbon-based nano-particles, as well as metallic and magnetic nano-particles, have commonly been utilized in the treatment of soil contaminated with heavy metals. Extensive research has been conducted on carbon nanotubes (CNTs) and nano-zero-valent iron for their potential in soil remediation (6, 31, 32). The effectiveness of CNTs in removing heavy metals is influenced by various factors, including the rate of CNTs application, contact time, presence of organic matter, silt and clay content, pH, and temperature of the surrounding environment. It was found that a significant proportion of Cd^{2+} is eliminated at a pH of 3.0 (33), while (34) reported that 99.9% of Zn^{2+} is removed by CNTs (0.05 g) at a pH of 10.0. FeS nano-particles exhibited a 99.65% removal efficiency for $Cr⁶⁺$ at a pH of 6.0. However, the elimination rate of FeS nano-particles decreased significantly at high pH levels (>10.0) (35). The remarkable efficacy of nano zero-valent iron (nZVI) in eliminating heavy metals is attributed to the inclusion of zerovalent iron shells, which consist of $Fe²⁺$ and $Fe³⁺$, within the nZVI structure (36). This elucidates the efficacy of nZVI-NPs in eradicating heavy metals from polluted areas. Utilizing nZVI at a high dosage successfully eliminates several HMs including chromium, lead, uranium, zinc, and vanadium from polluted areas (37). The utilization of nZVI at 5% and 10% concentrations resulted in a 70% increase in the efficiency of arsenic immobilization at the 5% dose level. The highest degree of mercury immobilization was seen when applying 10% nZVI, as reported by (38). nZVI has shown excellent efficacy in removing contaminants such as trichloroethene, hexavalent chromium, nitrate, lead, cadmium, and DDT throughout the remediation process (39). nZVI in conjunction with biochar led to

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elimination of zinc, lead, and cadmium (40). They discovered that the confinement of these metals is significantly influenced by the synergistic effects of both combinations. Studies on nano-biochar have confirmed that using nano-biochar to treat heavy metalcontaminated soils is a promising approach due to its unique characteristics, including its ability to disperse in water and its large surface area. The main mechanism by which nano-biochar works is its ability to effectively immobilize non-degradable heavy-metal contaminants in the soil rhizosphere (41). Various researches confirm that nano-myco-remediation is considered a cutting-edge and evolving approach with significant potential as a means of naturally eliminating pollutants from soil systems (42, 43).

Enhancing soil quality using nano-particles

Currently, nano-particles are utilized in various products such as DNA delivery, agrochemical distribution, nano insecticides, and nano-fertilizers. These products can synergistically enhance soil quality, crop output, and productivity. The soil is the greatest NP receptor because of its numerous applications. A study found that the application of plant extract-synthesized silver nanoparticles to soil resulted in a shift toward a neutral pH. Furthermore, significant enhancements in water retention, cation exchange capacity, and N/P availability were observed (44). Improper application of pesticides and insecticides in agricultural systems not only degrades soil quality and health but also contaminates the air and water (45). Research also concluded that the inclusion of 0.2% multi-walled carbon nano-tubes in clayey soil resulted in enhanced hydraulic conductivity and reduced soil fractures (46). Prior studies have been conducted that explore the use of Se nano-particles as a means to enhance soil fertility. The most significant increase in plant growth occurred at values of 5 and 10 μ g kg⁻¹, as reported by (47). Hence, the incorporation of nano-particles could potentially modify the microorganisms present in the soil and result in diverse responses in the enzymatic functions of beneficial microbes. These changes could modify the soil's pH and accelerate the release of nutrients to plants, presenting a fresh prospect for enhancing soil health (6, 48). The physio chemical properties of soil can be modified with the application of nano fertilizers (Fig 4).

Fig. 4. Summary of impact of nano-particles on soil physiochemical properties.

Enhancing nutrient availability

Enhancing the availability of nutrients in soil is another important function of nano-materials (49). Plants that receive nano-fertilizers, which consist of nutrient particles with a nano-scale size, have higher nutrient uptake efficiency. These materials offer a regulated release of nutrients, which minimizes leaching and increases crops' continuous nutrient availability.

Water retention and soil structure

Nano-materials support the structure and water retention of soil. Water stress in agricultural ecosystems can be reduced by using nano-particles, such as hydrogels, which can absorb and hold water before releasing it gradually to plants. Additionally, some nano-materials help to improve water infiltration, aeration, and soil structure (50).

Controlled release systems

Nano-materials are used as carriers to release pesticides and fertilizers under controlled conditions. Agro-chemicals can be delivered precisely, thanks to nano-encapsulation, which also lessens environmental effects and boosts input effectiveness. By releasing the active ingredients gradually following the plant's growth stages, this method lowers the frequency of applications overall (51).

Impact on soil microbial activity

Microbial communities in the soil can be impacted by nano -materials. While some research points to possible benefits for microbial activity, other studies raise concerns about the possible ecotoxicological hazards connected to specific nano-materials (52).

Impact of nano-particles on soil characteristics

Soil physical properties

According to studies on physical properties, iron, magnesium and zinc nano-particle administration can decrease the distance between soil particles and increase hydraulic conductivity and soil porosity (53, 54). Consequently, nano-particles contribute to the formation of a more rigid matrix, thereby promoting an increase in agricultural productivity and fostering a safer and healthier living environment. It was concluded that the excellent adhesiveness, specific surface, activity, and reaction capacity of MgO ENPs led to an improvement in the physical and mechanical properties of the soil upon application (55). Similarly, on comparing the effect of MgO nano-particles and Fe3O⁴ nano-particles, MgO ENP caused more reduction in soil bulk density. When Pt-engineered nano-particles of 3 nm were added to 300 mg $^{-1}$ soil at concentrations of 0.1, 1, and 10 μg, it was also observed an increase in the strength of the water molecule bridges and the structural rigidity of the soil. Nonetheless, they reduced the water content retained SOM at concentrations of 100-1000 µg by 300 mg⁻¹ soil.

Soil chemical properties

Soil chemical properties are altered by the addition of nano-particles into the soil. It was observed that claytextured soil's CEC increased by 17% when compared to control soil with the addition of 2000 mg L^{-1} of Fe₃O₄ ENPs

(56). The kind of material used has a significant impact on the changes indicated by CEC values. It was observed that when Fe ENPs-compost-biochar composite was added to the northern Spanish soil, the CEC increased by 7.8 and 6.8 times, respectively, in comparison to the control soil (57). Alteration of metabolites in the soil by exposure to Ag ENPs led to an increment of soil pH from 5.28 to 5.33 (58). According to certain research, adding engineered nanoparticles to soil resulted in a minor drop in pH. It was noticed that the pH of the rhizosphere dropped from 7.3 to 7.1 when 50 and 100 mg $kg⁻¹$ of TiO₂ ENPs were added to the soil (59). The kind of nano-particle and the characteristics of the matrix determine how the presence of ENPs alters the pH of the soil. Engineered nano-particles like ZnO, CuO, and TiO₂ have been shown in numerous studies utilizing various soil types to raise the EC values (59 –61). It was observed a modest drop in EC values when ZnO and $SiO₂$ ENPs (2% and 6%, respectively) were applied to saline soils as compared to the control soil (62). Numerous investigations have assessed how OM (SOM and DOM) affects the mobility, toxicity, and transformations of ENPs (63-64). The application of nano-particles into the soil also affects the soil nutrient availability. ZnO ENPs raised the amount of phosphate that was bio-available in the soil by increasing the secretion of P mobilizing enzymes (65). Composites of $CeO₂$ -functionalized maize straw biochar increased the TP content of the upper soil layer by 7.22% (66).

Nano-materials and its impact on soil microbiota

Understanding the potential impact of higher nanoparticle levels in the environment on the survival of crops as well as soil microbes in the root zone is crucial. Soil microorganisms have a crucial impact on the soil ecosystem, health, and plant yield. The impact on soil's beneficial activities, such as the microbial nitrogen cycle, symbiotic relationships, iron metabolism (siderophores), and the synthesis of antifungal chemicals, is particularly concerning for crop production that relies on microorganisms. Nevertheless, the detrimental impacts on the microbial population are greatly influenced by both the specific nano-materials being studied and the characteristics of the soil (67).

Constraints associated with the utilization of nanotechnology in the agricultural industry

While nanotechnology has significant promise for various applications in agriculture, it also entails certain inherent risks and drawbacks (Fig. 5). Nano-particles have the potential to accumulate in the soil, water, and air upon their discharge into the environment, hence presenting an ecological hazard. Enforce strict rules on the manufacturing, utilization, and disposal of nanoparticles to reduce their emission into the environment. Another method to reduce the accumulation of nano particles in soil and environment can be attained by the adoption of green synthesis of nano particles. There is a widespread agreement that in order for nanotechnology to fully develop, it is necessary to perform studies to comprehend and manage any possible dangers to health and the environment that may arise from exposure to nanomaterials.

Specifically, these nano-particles can disrupt the balance of macro and microbes in the soil, leading to a decrease in fertility (68). In addition, nano-particles have the potential to accumulate in plants and animals, leading to potential adverse effects on health (69). In order to assure the safety of animals and the quality of food, it is necessary to have a clear understanding of the mechanism by which metallic/metal oxide nano-particles are used in animal feed. Additionally, further experiments should be conducted to establish the safety of these nano-particles for human consumption.

Fig. 5. Illustration representing the various constraints associated with the repetitive application of nano-formulations.

Table 2. Nano particles in managing various stresses in different plants with diverse responses.

Furthermore, there is a possibility that certain broad-spectrum nano-particles may have unintended detrimental impacts on non-target organisms. Whether deliberately or unintentionally, the use of nano-particle formulations without proper adherence to safety measures has resulted in their entry into the lungs, from where they later migrated to the circulation and other vital organs (70). In the rapidly approaching nano era, it is crucial to identify species that exhibit a strong resistance to nanoparticles and have the ability to gather, utilize, degrade, or immobilize such particles.

Moreover, the utilization of nanotechnology in agriculture requires a substantial and occasionally costly commitment to research and development. The application of nanotechnology in agriculture raises ethical concerns regarding the integrity and safety of food (71). Nano-materials, due to their comparable size to DNA, have the potential to interact with biological specimens, leading to possible adverse effects (72).

Conclusion

The application of nanotechnology in agriculture has led to improvements in farming methods and increased crop production, while also enhancing the quality of crops. The introduction of engineered nano-materials and their use in sustainable agriculture has resulted in significant changes in the global agricultural industry, marked by innovation, rapid expansion, and the ability to meet the anticipated rise in food requirements. Microbes have the potential to manufacture nano-particles that are very suitable for various therapeutic and biological purposes due to their accurately measured bio-compatible sizes and unique properties. Biosynthesis approaches offer advantages due to the frequent presence of bio-molecule entities or a lipid layer on nano-particles, which contribute to stability and physiological solubility. Unlike conventional methods, this review demonstrates that these nanofactories are environmentally beneficial, economical, and easily scalable. It can be suggested that the green synthesis of nano particles acts as an environmental solutions and more research in the green synthesis of NMs from where others have left off needs to be carried out. Nano-materials offer the potential for a new environmentally friendly

revolution in agriculture by reducing the risks associated with farming. The application of nanotechnology in agriculture is becoming increasingly popular due to its specific and focused uses, such as the use of nanopesticides, nano-fungicides, nano-herbicides, and nanoinsecticides to enhance crop production by following the products closely. To summarize, the utilization of nanotechnology can improve both the quality and output of crops. Furthermore, the use of nanotechnology to restore polluted soils is highly efficient.

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Authors' contributions

Conceptualization, supervision, editing, final drafting: RKG; Conceptualization, experimentation, manuscript writing: PAP and SS; Data recording: SS and S. All authors approved the final manuscript.

Compliance with ethical standards

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