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Green synthesis of metallic nanoparticles and its potential to enhance production of agricultural crops: A review

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Nanoscience and nanotechnology have gained much attention in recent years in the agricultural field. The small size (1-100 nm) and large surface area of nanomaterials unlocks their applications in several potential functions. The chemical and physical nature of metallic nanoparticles is different as compared to non-metallic nanoparticles. Green synthesis of metallic nanoparticles is less costly and not harmful to the environment. Therefore, applications of these metal-based nanoparticles are very effective and quite safe in the development of agricultural crops. Sustainable agriculture is the need of the hour. Review also shows the impact of nanomaterials on seed germination, crop growth and quality improvement. Agricultural crops diseases are one of the major factors that can limit crop productivity and have a serious impact on the economic output of a farm. This paper provides a compilation of technologies involved in the green synthesis of metallic nanoparticles and an overview of the application of nanotechnology in agriculture with a special focus on plant protection products and nano-pesticides.

Keywords: Nanotechnology, Green synthesis, Metallic nanoparticles, Agricultural field

INTRODUCTION

Many practical applications of metallic nanoparticles (particles sized less than 100 nm) are studied due to their number of special properties [1-4]. Different processes are widely used to synthesize metallic nanoparticles (NPs). Metallic nanoparticles involved zinc (Zn), cooper (Cu), silver (Ag), gold (Au) and their oxides, etc. However, the production of these metallic nanoparticles through chemical and physical methods is usually very costly, labor-intensive and they are very dangerous to the ecosystem [5. 6]. Thus, there is the need for an alternative method, which is cost-effective and at the same time environment-friendly and less toxic, that is known as green nanotechnology. In the past years, many biological systems like plants, fungi, bacteria, algae, human cells, etc. are used for the synthesis of metal nanoparticles. These biological systems contain proteins and metabolites that can be reduced to inorganic metal ions and form metal nanoparticles. This formation of metallic NPs through metal ions involves a capping process.

Agriculture is an important field of economics development where new techniques are often applied to enhance crops' productivity and quality. Application of nanoparticles in agriculture area called nano-agriculture i.e., advanced technology is often applied to increase the yield [7]. Synthesized NPs through various biological sources can be used in agriculture [8]. The use of metallic nanoparticles (NPs) in the sector of agriculture was found to be very effective in controlling biotic and abiotic stresses, decreasing the use of agrochemicals like pesticides and fungicides, and supervising the use of insecticides in a good and non-polluting manner. Farmers use many agrochemicals such as insecticides, herbicides, fungicides, either by spaying or by broadcasting at different time intervals. A large quantity of fertilizers is lost-because of various factors, namely, leaching, decomposition, photolysis, hydrolysis and microbial reduction, etc. Therefore, there is a need for non-toxic agrochemicals that can stay for long time on agricultural land. The major techniques of nanoparticle applications on crops include traditional approaches such as direct exposure to seeds and through culture media or by soil, spraying the NPs on the surface of plants, hydroculture (culture in water) and many more. New approaches for introducing NPs include cell isolation, protoplast incubation, biolistics etc. The support of nanotechnology in phytopharmaceutical products has increased exponentially, which may assure increased crop yield.

Rouhani *et al.* have carried out an *in-vivo* study for understanding the metallic NPs and chemical suspensions efficiency on cotton plants, affected by aphid that can be taken as a reference [9]. The results showed that NPs solution slows down the speed of action in the plant in comparison to the chemical solution but on the other hand, NPs solution was better in increasing the insertion in the plant [10].

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NPs can insert into the crop by various pathways, and the uptake rate of NPs depends on the size, shape, concentration, and charge present on the surface of nanoparticles [11]. NPs present on shoot surfaces of crops initiate the interaction with aerial parts. The use of NPs was found to have a positive impact on crop parameters of growth like germination, length, development, etc. Application of NPs like carbon-based, metal- and metal oxide-based shows effects on crop development (number of seminal rooting, elongation of root, length of shoot, seeds quantity, and quality of the flowers), leading to enhanced crop biomass and productivity [12-14].

The application of NPs into the soil can proceed directly to the soil or indirectly by nano fertilizers and pesticides [15, 16]. Study and monitoring of activity of microbes and diversity shows the effects of NPs on the soil. The activity of microorganisms fully depends on the NPs features and properties (category, amount, size, and functional groups present in the NPs).

The present compilation article gives a brief glimpse of a present global scenario on the effective utilization of bioinspired metallic nanoparticles and their research in the agricultural field. There are the following important elements for obtaining productive results: i) ability of nanofabricating novel materials, and its mechanism; ii) understanding the plant and soil interaction with nanoparticles; iii) micronutrient's deficiency improvement, and their availability increases; iv) environment safety and environmental obedience. Nanotechnology can sustainably reduce production costs in agriculture. Nano-farming has become a truly revolutionary area for the future of sustainable agriculture.

Raw materials for food industries are dependent upon the important and stable sector that is 'Agriculture'. Growth of the world population increases with the limitations of natural non-renewable resources (productive land, water, soil). That's why necessities claim for agricultural development to be economically strong, viable, eco-friendly and efficient. The improvement in the field of agriculture is mandatory for removing poverty and hunger. Therefore, new, sustainable and cost-effective techniques should be adopted for better agricultural production [17]. Sustainable growth of agriculture totally depends upon the new and innovative technologies just like nanotechnology. In order to ensure sustainable development of agriculture some important points are listed below [18-20]:

1. Specialized institutes with trained expertise can be established to assess the biosafety of NPs on the field and also reduce farming problems. With the passage of time, people become more trained for practical applications in agriculture.
2. For monitoring and evaluation of NPs based system, strict and clear guidelines should be followed in the context of food safety.
3. Evaluation of NPs-mediated toxicity on the environment and organisms should be properly documented for the researchers and for the farmers.
4. More research and collaboration should be carried out for better development of portable, easy-to-use nano-sensor and NPs-based applications.
5. Controlled and naturally produced NPs through plant root endophytes and *mycorrhizae* fungi must be studied for a better understanding of the interaction of NPs with plants.

The reason behind applying nanoparticles in the field of agriculture is to reduce chemicals amount, minimize nutrient loss due to fertilizers and increase production with good quality. Nanotechnology has the ability to advance NPs techniques for controlling crop pests and diseases with improved nutrient absorbing capacity. The significant interests of using nanotechnology in the agricultural field include fertilizers with NPs suspension and pesticides with NPs for obtaining less harmful products and to increase nutrient level without impurities in soil, water and protection against crop diseases. Nitrogen loss from leaching, emission and microbial degradation can be recovered due to NPs techniques. Nanotechnology may act as a detector for observing soil quality in the agricultural fields and hence to maintain the health of agricultural crops. Nano farming techniques do not contaminate water and soil while improving the productivity of crops.

NATURE OF METALLIC NANOPARTICLES

Nanoparticles have properties (physical and chemical) through which they can be applied in agricultural industries. Though it's very difficult to understand the nature of nano-scale particles but their properties are different and unique as compared to the bulk materials [21, 22]. For the application in agriculture, NPs production, characterization and mechanism must be well understood.

Physical properties

Physical properties of NPs include many features as shown in Fig. 1 but size, shape, surface area and size distribution are few important factors that can control the uptake of nanoparticles like lead, copper, zinc, cadmium, etc. [23-25]. Cell wall permeability and size of the stomata can affect the transportation of the nanoparticles.

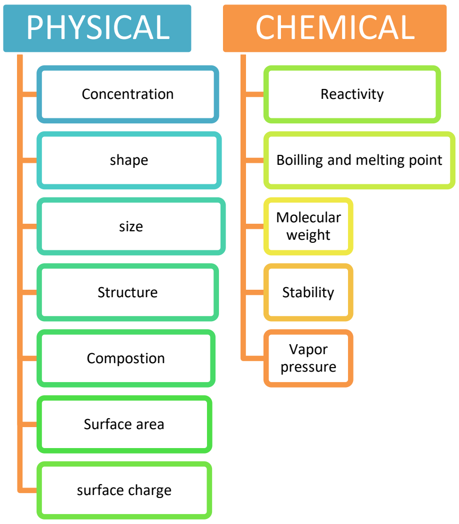

Figure 1. Physical and chemical nature of nanoparticles

Size and shape. The size and shape of nanoparticles are identified as important properties. It was postulated that nanoparticles size below 20-30 nm are thermodynamically unstable and are full of energy at the surface [26]. As the size of nanoparticles decreases, the surface area of the molecules present in the material increases in an exponential trend. The studies showed the different effects of nanoparticles size ranging from 50-200 nm on the growth of the *Arabidopsis* plant [27]. Different shapes of synthesized metallic NPs like square, tube, spherical, etc., are gaining lot of attention. The optical features of NPs also depend on the shape and size of the NPs.

Surface and size distribution of nanoparticles. Scanning electron microscope (SEM) and Brunauer–Emmett–Teller (BET) are the techniques that detect surface structure and area of synthesized NPs. The large surface area of NPs has faster effects as compared to the bulk materials. Dynamic light scattering (DLS) used to calculate the size distribution of NPs, and zeta potential can be used to evaluate the charge present on the surface of the synthesized NPs. Charge present on NPs affects the interaction of NPs with the plant cell membrane [28]. Cellular uptakes by plants are usually dependent on the surface hydrophobicity, size and charge of the solution. NPs with positive charge are taken up faster by plant cells as compared to neutral or negatively charged NPs. The diffusion of NPs in a liquid solution mainly depends on the surface charge of these NPs.

Chemical properties

Properties like structure, composition, phase identity, surface chemistry and reactivity are the chemical properties of metallic nanoparticles. Chemical features also include the surface chemistry and photocatalytic properties of nanomaterials in which elemental composition is studied by zeta potential [29, 30]. Property of NPs is understood by the kind of electronic motion occurring in the particles. There are many varieties of NPs that are contributing different chemical properties [31]. Metallic NPs have flexible properties which can be modified by their own, when they are interacting with other materials.

During synthesis, nanoparticles can control over their size and shape. They can also change their morphology, encapsulation freedom and optical properties while it is limited to selected NPs only. While synthesizing the metal oxide nanoparticles, they show these unique chemical properties because of their size and high density of corner surface. Size of the NPs also affects many features of any matter. Morphology feature includes shape, area and size which all are related to the electronic nature of metal oxide NPs [32]. Nanotechnology can have huge impact in agriculture production. Optimizing of process parameters can help in formulating nanoparticle-based fertilizers [33].

SOURCES AND GREEN SYNTHESIS OF METALLIC NANOPARTICLES

As compared with chemical (toxic) synthesis of NPs, the green method is innovative, simple (easy), economic and re-usable and gives stable products. Green nanomaterials can be synthesized mainly by plants and microorganism sources, Fig. 2. The green synthesis of NPs through plants parts is easier to be realized in large scale in comparison to the synthesis by microorganisms.

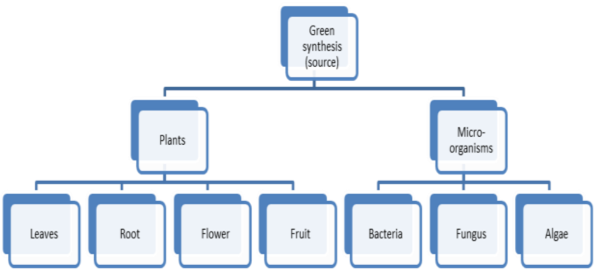

Figure 2. Different sources of synthesis of nanoparticles through a green method.

Eco-friendly and non-toxic route of bioinspired nanomaterials is advantageous in agriculture field [33]. Improvement in germination, growth and productivity along with the improvement of quality of crops has been reported with the use of green nanomaterials [34, 35, 38]. Consequently, the applications of metal-based nanoparticles are very effective and safe for the development of agricultural cultures.

METHODS OF USING NANOPARTICLES ON AGRICULTURAL CROPS

Nanoparticles exposure on crops has gained attention in recent years. Numerous studies were done on the effect of metallic nanoparticles on different varieties of agricultural crops. The method by which NPs are introduced on the crops gives profitable effect on the interaction of NPs and plants. NPs availability, collection, storage and movement (translocation) by plants also get affected. Though the nanoparticles-plant interactions seem lucrative, the ultimate availability, translocation, accumulation, and subsequent effects of nanoparticles depend primarily on the mode of their administration in addition to the element's availability, uptake and storage capacity of plants. Consequential human exposure of NPs represents an important pathway that considers carrying and assimilation of nanoparticles in plants. Therefore, the techniques that were used for good and efficient NPs–plant interaction need more attention and consideration in consequential process [39]. The major methods of using nanoparticles on agriculture crops include traditional methods such as direct seed and seedling exposure, spaying, hydroculture, etc., while modern techniques include isolated cells, protoplast incubation and biolistics. Some techniques are discussed below.

Seed exposure

Germination of the seed is basically described as the inhibition of water and nutrient which leads to sprouting of radicle and plumule by puncturing the coat of seeds [40]. Protection of the seed from biotic and abiotic factors can be done by the selective permeability of the seed cover. The nature of the seed coat is selectively permeable for definite size, shape and charge of outsider particles that were trying to reach at the sensitive parts of the seed. There have been reports conducted to understand the effects of NPs on the sprouting of seeds (germination), and uptake of the NPs [41, 42]. Primary methods of NPs introduction in seeds are either soaking the seeds in NPs solution for some days or direct germinating seeds in nanoparticle-spiked media or soil.

Application of 5 kinds of NPs (carbon nanotube (MWCNT), Al, alumina, Zn, and ZnO_2) on different seeds, *viz*., rape (*Brassica napus),* radish (*Raphanus sativus*),), lettuce (*Lactuca sativa*), ryegrass (*Lolium perenne*), maize (*Zea mays*), and cucumber (*Cucumis sativus*) were recorded by an incubation process in which seeds were soaked in NP solution, and then transferred in different petri plates with distilled water and put in an incubator [43-46]. Seeds with NPs solution give bettwe results as compared to the normal soaking. It has been reported that the process of soaking is good and less time consuming [47].

Spraying

Recently, many studies are involved in NPs-plant exposure *via* roots, either directly or during the stage of germination. Although the knowledge of responding after contacting plant foliar part and leaves with atmospheric NPs is limited, so more research is required in this field. The significant responses of crop leaf are unavoidable because of collecting of atmospheric particles or by applications of purpose-built NPs [39].

The spraying process of nanoparticles that was used in large-scale field is same as that used by farmers for controlling pests. The NPs spays are safe for the crops and can resist against the pest for a long time. Plant protection technologies are more successful when applied by foliar spraying of NPs in comparison to traditional soil-root treatment. To further advance this technology, it is also necessary to look at significant elements that inhibit the uptake of NPs by foliage, such as wax deposits on leaf surfaces, environmental conditions (such as light, temperature, and humidity), and the physical and chemical characteristics of NPs.

Biolistics

Direct introduction of DNA or RNA into plant cells defines the biolistic transformation technique. In this method, artificial/modified DNA or RNA was constructed by coating onto metallic NPs like gold. Coated DNA or RNA was released through gun with high pressure helium gas that directly inserts in the host cell wall. Torney *et al*. have reported a coated DNA from Type-II MSNs (mesoporous silica nanoparticles system) for endocytosis experiments in which 1 mg of filtered plasmid DNA was incubated with 10 mg of MSN with 50 ml of water for 2 h. The MSNs were washed with W5 media for isolating protoplasts [48]. Y-segmented petri dishes were used in the germination of plants. After bombardment with nanoparticles the plants were evaluated for 48 hrs. This method is also very modern and innovative, but it cannot be used for a large number of crops [48].

NANOPARTICLES' EFFECT ON SEED GERMINATION, CROP GROWTH AND QUALITY IMPROVEMENT

Due to special physiochemical properties of nanomaterials, they provide many opportunities in the agricultural sector. The interconnection of NPs with plants shows several physiological, morphological, and genotoxic changes, and their interpretation is important for the productive use of nanotechnology in agriculture. Metallic nanoparticles can be inserted in plants through various ways. NPs can be produced by itself or by metal ions oxidized by metal oxide in soil solution and followed by the reduction in plant system and transferred as ions [49]. Different biotic and abiotic stresses influenced the growth of plants.

Physicochemical properties of NPs like shape, size, charge, composition, surface modification and reactivity give subsequent effect on NPs-plant interaction [50, 51]. Along with other factors, concentration of NPs is also giving effect on NP-plant relation and the effect is varying from plant to plant.

Seed germination

Germination of the seed is the premier stage of a phytology. Interaction between plant system and NPs mainly occurs through seeds as they are the first point of interaction. Seed germination and growth can be estimated by the appearance of radical and plumule in seed. The effect of NPs on the seed growth can be estimated by the seed germination as the 1st stage of primary database. It was reported by Siddiqui et al that when low concentration of silica NPs (SiO_2 NPs) was introduced on tomato seeds, improved germination was occurred [52]. It was also reported that when the SiO_2 were mixed with growth medium and absorb by maize seeds with adequate pH turn the rate of germination increases and give positive effects on better nutrient availability [52, 53]. Seed germination and growth of roots of zucchini seeds were cultured in hydroponic medium augmented with ZnO NPs which showed no adverse effects [54] whereas in the case of rye grass (*Lolium perenne*) and maize (*Zea mays*), the seed sprouting was improved by Zn NPs with 35 nm in size and by ZnO_2 with 15–25 nm, respectively [55]. Zheng *et al.* (2007), Hong *et al.* (2005), Yang *et al.* (2007) and Gao *et al.* (2008) showed positive effects of TiO_2 NPs on plants [56-59]. TiO_2 NPs have been recorded to improve the germination and enhance the radicle and plumule growth of canola (*Brassica napus*) seedlings [60]. When TiO_2 NPs were inserted in the spinach seeds improved germination was observed with enhanced vigor [56].

Growth of crops

After germination of seeds, enhancement in plant length (shoot and root) describes the growth of plant. Growth of crops is also characterized by its shoot and root length, number of laterals and leaves and size of leaves with total biomass. When NPs interact with the plant roots, they either promote the growth of the roots and other parts of the plants after translocated to higher tissues or block the channels of penetration of the nutrient supply through the root. A few reports are available on the movement of NPs in plant tissues, therefore the mechanism behind the movement is also not clearly understood. Overall, the effects observed are related to the interaction of NP with roots, facilitating or preventing nutrient supply and transport to higher tissues [61].

When SiO_2 NPs were introduced into Changbai larch (*Larix olgensis*) seedlings, the rate of growth was increased, involving shoot height, root collar diameter, length, number of root laterals and it also gave effect on the chlorophyll synthesis [62]. In another research, rice plants were treated with bare quantum dots (QDs) and silica-coated QDs and found that silica-coated QDs significantly promoted root growth [63].

Au NPs showed good results in increasing the number of leaves and area, shoot height and the amount of chlorophyll of the treated plant [64, 65]. In the previous studies it was witnessed that Ag NPs can improve the growth of mustard, bean (*Phaseolus vulgaris*), and maize and the area of their leaves also increases [66, 67]. Copper NPs (Cu NPs) were mixed with agar media for testing of seeds of mung bean and wheat [68]. During the experiment it was observed that mung bean shows higher sensitivity to Cu NPs as compared to the wheat plant, noticeable inhibition in the growth of seedlings being observed [68].

Quality improvement

The physical and chemical changes taking place in the plant spread light on the efficiency and metabolic process that were actively happening in the plant system which includes growth, reproduction and development. These parameters are much affected by biotic and abiotic factors of environment along with NPs. Application of metallic and metal oxide NPs gives positive result in growth parameters which ultimately lead to high productivity and quality.

When Ag NPs were applied in the soil of wheat crops, an improvement in growth and yield was reported [69].

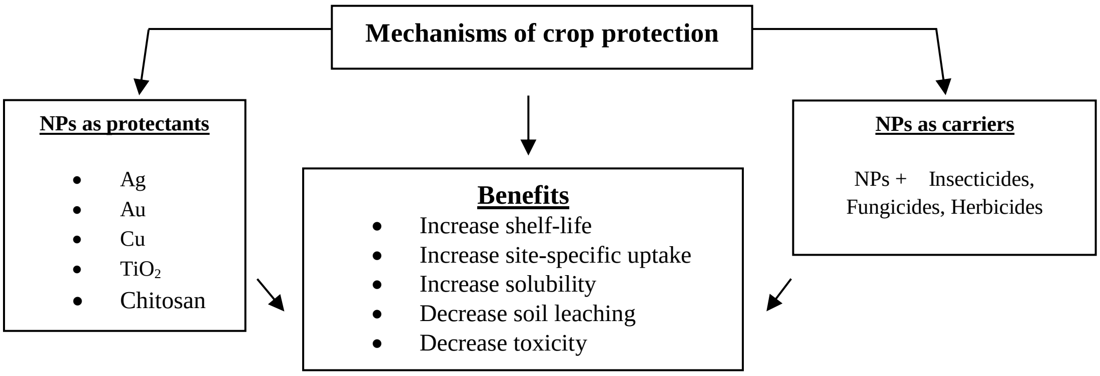

Figure 3. Crop protection by nanoparticles

Comparing with normal growth of wheat crops exposed to 25 to 50 ppm Ag NPs give better results in height and dry weight. Similar effects were shown in Indian mustard (*Brassica juncea*) where improvement in root and shoot length was reported and chlorophyll contents were also good [67].

NANOMATERIALS IN CONTROLLING CROPS PATHOGENS

Every 20% to 40% crops are destroyed due to pest and pathogens [70]. Nanotechnology offers advantages over toxic pesticides which could have positive impacts on environment. The use of NPs to protect crops can occur *via* two different mechanisms: a) NPs themselves providing crop protection b) NPs as carriers for existing pesticides, Fig. 3.

Nanoparticles as pesticides

Metallic nanoparticles can be applied on crops for the management of harmful pests and weeds and NPs can be used for preparing nano pesticides, nano fungicides and nano herbicides [70].

Insecticides. Insects are common creatures which are found all over the ecosystems. They almost depend on all the varieties of agricultural crops. Important crops like wheat, maize, rice, barley, etc. are facing lots of problems due to insects which spread diseases [71]. Nanotechnology offers a wide number of metallic NPs which can be synthesized by green methods and can be used as insecticides in controlling insects [72].

Stadler *et al.* reported that alumina NPs activity on two varieties of stored grains, namely *Rhyzopertha dominicoorzae* and *Sitophilus oryzae*, results show that NPs action is based on physical phenomenon instead of biochemical phenomenon in which insects become dead due to dehydration [73]. Silica NPs of 0.5 mg/cm killed the larvae of *Spodoptera litura* [74]. Researchers reported that a 5-25 mg/l concentration of Ag NPs killed adult *Hematophagous* flies, *Hippobosca maculate*, cattle ticks, and *Rhipicephalus* (Boophilus*) microplus* [75].

Fungicides. Fungi are the reason of damaging many crops by spreading fungal diseases [76]. It is evaluated that 85% crops diseases are due to fungus. To combat fungi, farmers have been using many chemical fungicides. This can lead to damage of the human body system. NPs that were made by green methods are less harmful when used as fungicides. Recently, *in vitro* assay conducted by many researchers showed strong inhibitory effects of biosynthesized Ag NPs against various fungal diseases [77-79]. Eco-friendly solutions of nanoparticles and fungicides enable smaller amounts of the nano-fungicides to be applied in given time period. In that way the modified NPs helps to protect the environment.

Herbicides. Herbicides that were made up of NPs can take the place of herbicides which were made of chemicals and are very much hazardous if the consumption becomes high. Nanoparticles-based herbicides improve the solubility and decrease the toxic effect when compared with chemical herbicides. The synthesis of herbicides made with particular NPs targeted at the point of root where the weeds are born. Nano-herbicides enter the root of the weeds and inhibit the cycle of glycolysis of the weed. This inhibition action generates deficiency of nutrients in the targeted weed and thus the weed become dead.

CONCLUSION

Nanoscience and nanotechnology have attracted a great deal of attention in recent years in the field of agriculture. The green synthesis route of metallic nanoparticles is more cost-effective, environmentally friendly and sustainable for agricultural development. The diseases of agricultural crops are one of the main factors that can restrict the productivity of crops and have a serious impact on the economic production of an agricultural enterprise. This article presents a compilation of technologies involved in the green synthesis of metallic nanoparticles, including an overview of the application of nanotechnology in agriculture with particular emphasis on phytopharmaceutical and nano-pesticide products. Green nanomaterials have potential to substitute a conventional agricultural practice as they can enhance the crop productivity in a targeted way without the release of any harmful chemicals with maintenance of soil fertility. Although there is a huge potential of green nanomaterials in crop productivity and disease resistance, systematic and detailed study needs to be carried out to understand exact mechanism pathways along with its long-term effect in future.

REFERENCES

1. M. C. Roco, *Curr. Opin. Biotechnol*., **14**, 337 (2003).
2. L. Zhang, F. X. Gu, J. M. Chan, A. Z. Wang, R. S. Langer, O. C. Farokhzad, *Clin Pharmacol Ther.*, **83**, 761 (2008).
3. M. C. Daniel, D. Astruc, *Chemical Reviews*, **104**, 293 (2004).
4. T. S. Wong, U. Schwaneberg, *Curr. Opin. Biotechnol*., **14**, 590 (2003).
5. K. B. Narayanan, N. Sakthivel, *Adv. Colloid Interface Sci*., **156**, 1 (2010).
6. P. P. Gan, S. H. Ng, Y. Huang, S. F. Li, *Bioresour. Technol*., 113, 132-5 (2012).
7. J. S. Duhuan, R. Kumar, N. Kumar, P. Kaur, K. Nehra, S. Duhan, Nanotechnology: The new perspective in precision agriculture Biotechnology Reports, 2017, p. 11.
8. P. Kaur, R. Thakur, J. S. Duhan, A. *Chaudhary, Journal of Chemical Technology and Biotechnology*, **10**, 1002 (2018).
9. Rouhani, S. Mohammad, K. S. Mohammad, *Journal of Agricultural Research*, **10** (1), 590 (2012).
10. A. L. Boehm, I. Martinon, R. Zerrouk, E. Rump, H. Fessi, *J. Microencapsul*., **20**, 433 (2003).
11. J. C. Tarafdar, Y. Xiang, W.-N. Wang, Q. Dong, P. Biswas, *Appl. Biol. Res*., **14**, 138 (2012).
12. C. M. Rico, S. Majumdar, M. Duarte-Gardea, J. R. Peralta-Videa, J. L. Gardea-Torresdey, *J. Agric. Food Chem*., **59**, 3485 (2011).
13. H. Feizi, P. R. Moghaddam, N. Shahtahmassebi, A. Fotovat, *Biol. Trace Elem. Res*., **146**, 101 (2012).
14. N. Bala, A. Dey, S. Das, R. Basu, P. Nandy, *Iran. J. Plant Physiol.* **4**(3), 1061 (2014).
15. P. Gajjar, B. Pettee, D. Britt, W. Huang, W. Johnson, A. Anderson, *J. Biol. Eng*., **3**, 9 (2009).
16. M. V. Khodakovskaya, B. Kim, J. N. Kim, M. Alimohammadi, E. Dervishi, T. Mustafa, C. E. Cernigla, *Small*., **9**, 115 (2013).
17. C. Yunlong, B. Smit, *Agric. Ecosyst. Environ.*, **49**, 299 (1994).
18. G. Pandey, *Environmental Technology & Innovation*, **11**, 299 (2018).
19. A. Acharya, P. K. Pal, *Nano Impact*, **19**, 100232 (2020).
20. R. Prasad, A. Bhattacharyya, Q. D. Nguyen. *Frontiers in Microbiology*, **8**, 1014 (2017).
21. D. L. Slomberg, M. H. Schoenfisch, *Environ. Sci. Technol*., **46**, 10247 (2012).
22. S. Honary, F. Zahir, *Trop. J. Pharmaceut. Res*., **12**, 255 (2013).
23. A. Cadden, *J. Food Sci*., **52**, 1595 (1987).
24. C. Rao, K. Biswas, *Annu. Rev. Analyt. Chem.*, **2**, 435 (2009).
25. G. Schmid, Wiley-VCH, Weinheim, Germany, 2011.
26. P. Ayyub, V. Palkar, S. Chattopadhyay, M. Multani, *Phys Rev B*., **51**, 6135 (1995).
27. D. Nath, P. Banerjee, B. Das, *J. Nanomedicine Biother. Discov*., **4**, 1 (2014).
28. K. M. Manjaiah, R. Mukhopadhyay, R. Paul, S. C. Datta, P. Kumararaja, B. Sarkar, in: M. Mariano, S. Binoy, L. Alessio, (eds.), Modified Clay and Zeolite Nanocomposite Materials, Elsevier, Amsterdam, The Netherlands, 2019, p. 309.
29. M. V. Khodakovskaya, A. S. Biris, *U.S. Patent Application*, 13, 509,487 (2010).
30. A. Joshi, S. Kaur, K. Dharamvir, H. Nayyar, G. Verma, *J. Sci. Food Agric.*, **98**, 3148 (2018).
31. C. Lu, C. Zhang, J. Wen, G. Wu, M. X. Tao, *Soybean Sci.*, **21**, 168 (2002).
32. H. A. Kordon, *J. Biol. Educ*., **26**, 247 (1992).
33. K. Parveen, N. Kumar, L. Ledwani, *Chemistry Select*., **17**, e202200415 (2022).
34. K. Ibrahim, S. Khalid, K. Idrees, *Arabian Journal of Chemistry*, **12**, 908 (2019).
35. K. Parveen, N. Kumar, L. Ledwani, *ChemistrySelect*, **7**, e202200415 (2022).
36. M. Khodakovskaya, E. Dervishi, M. Mahmood, Y. Xu, Z. Li, F. Watanabe, A. S. Biris, *ACS Nano*., **3**, 3221 (2009).
37. A. Shelar, A.V. Singh, R.S. Maharjan, P. Laux, A. Luch, D. Gemmati, V. Tisato, S.P. Singh, M.F. Santilli, A. Shelar, M. Chaskar, R. Patil, *Cells*, **10**, 2428 (2021).
38. A. Maity, *Proc. Natl. Acad. Sci. India Sect. B Biol. Sci*., **88**, 595 (2018).
39. C. Kole, D. Kumar, Sakthi, M. V. Khodakovskaya, Plant Nanotechnology: Principles and Practices, 1st edn., 2016.
40. H. A. Kordan, *J. Biol. Educ*., **26**, 247 (1992).
41. W. Mahakham, P. Theerakulpisut, S. Maensiri, S. Phumying, A.K. Sarmah, *Sci. Total Environ*., **573**, 1089 (2016).
42. J. Banerjee, C. Kole, in: C. Kole, D. Kumar, M. Khodakovskaya, (eds.), Plant Nanotechnology. Springer; Cham, Switzerland: 2016. p. 1.
43. M. H. Lahiani, E. Dervishi, J. Chen, Z. Nima, A. Gaume, A. S. Biris, M. V. A. C. S. Khodakovskaya, *Appl Mater. Interfaces*, **5**, 7965 (2013).
44. A. Srivastava, D. Rao, *Eur. Chem. Bull.*, **3**, 502 (2014).
45. M. V. Khodakovskaya, A. S. Biris, *U.S. Patent Application.* 13, 509,487, 2010.
46. A. Joshi, S. Kaur, K. Dharamvir, H. Nayyar, G. J. Verma, *Sci. Food Agric.*, **98**, 3148 (2018).
47. D. Lin, B. Xing, *Environ. Pollut.*, **150**, 243 (2007).

48. , F. Torney, B. G. Trewyn, V. S. Y. Lin, K. Wang, *Nat. Nanotechnol*., **2**, 295 (2007).
49. C. M. Rico, S. Majumdar, M. Duarte- Gardea, J. R. Peralta-Videa, J. L. Gardea-Torresdey, *J. Agric. Food Chem*., **59**, 3485 (2011).
50. X. Ma, J. Geiser-Lee, Y. Deng, A. Kolmakov, *Sci. Total Environ*., **408**, 3053 (2010).
51. M. V. Khodakovskaya, K. de Silva, A. S. Biris, E. Dervishi, H. Villagarcia, *ACS Nano*., **6**, 2128 (2012).
52. M. H. Siddiqui, M. H. Al-Whaibi, M. Faisal, A. A. Al Sahli, *Environ. Toxicol. Chem*., **33**, 2429 (2014).
53. R. Suriyaprabha, G. Karunakaran, R. Yuvakkumar, V. Rajendran, N. Kannan, *Curr. Nanosci*., **8**, 902 (2012).
54. D. Stampoulis, S. K. Sinha, J. C. White, *Environ. Sci. Technol*., **43**, 9473 (2009).
55. D. Lin, B. Xing, *Environ. Pollution*, **150**, 243 (2007).
56. L. Zheng, M. Su, C. Liu, L. Chen, H. Huang, X. Wu, X. Liu, F. Yang, F. Gao, F. Hong, *Biol. Trace Elem. Res.*, **119**, 68 (2007).
57. F. Hong, P. Yang, F. Q. Gao, C. Liu, L. Zheng, *Chem. Res. Chin. Univ*., **21**, 196 (2005a).
58. F. Yang, C. Liu, F. Gao, M. Su, X. Wu, L. Zheng, F. Hong, P. Yang, *Biol. Trace Elem. Res*., **119**, 77 (2007).
59. F. Gao, C. Liu, C. Qu, L. Zheng, F. Yang, M. Su, F. Hong, *Biometals*, **21**, 211 (2008).
60. H. Mahmoodzadeh, M. Nabavi, H. Kashefi, *J. Ornam. Hortic. Plants*, **3**, 25 (2013).
61. B. Nowack, R. Schulin, B. H. Robinson, *Environ. Sci. Technol*., **40**, 5225 (2006).
62. L. Bao-shan, D. Shao-qi, L. Chun-hui, F. Li-jun, Q. Shu-chun, Y. Min, *J. Forest Res*., **15**, 138 (2004).
63. A. Wang, Y. Zheng, F. Peng, *J. Spectrosc.*, 169245 (2014).
64. S. Arora, P. Sharma, S. Kumar, R. Nayan, P. K. Khanna, M. G. H. Zaidi, *Plant Growth Regul*., **66**, 303 (2012).
65. K. Gopinath, S. Gowri, V. Karthika, A. Arumugam, *J. Nanostruct. Chem*., **4**, 1 (2014).
66. H. M. H. Salama, *Int. Res. J. Biotechnol*., **3**, 190 (2012).
67. P. Sharma, D. Bhatt, M. G. Zaidi, P. P. Saradhi, P. K. Khanna, S. Arora, *Appl. Biochem. Biotechnol*., **167**, 2225 (2012).
68. W. M. Lee, Y. J. An, H. Yoon, H. S. Kweon, *Environ. Toxicol. Chem*., **27**, 1915 (2008).
69. A. Razzaq, R. Ammara, H. M. Jhanzab, T. Mahmood, A. Hafeez, S. A. Hussain, *J. Nanosci. Technol*., **2**, 55 (2016).
70. R. K. Mujeebur, F. R. Tanveer, *Plant Pathology Journal*, **13**, 214 (2014).
71. E. C. Oerke, *J. Agric. Sci.*, **144**, 31 (2006).
72. M. Ramezani, F. Ramezani, M. Gerami, in: D. Panpatte, Y. Jhala (eds.) Nanotechnology for Agriculture: Crop Production & Protection. Springer, Singapore. 2019.
73. T. Stadler, M. Buteler, D. K. Weaver, *Pest Manag. Sci*., **66**, 577 (2010).
74. N. Debnath, S. Mitra, S. Das, A. Goswami, *Powder Technol*., **221**, 252 (2012).
75. T. Santhoshkumar, A. A. Rahuman, A. Bagavan, S. Marimuthu, C. Jayaseelan, A. V. Kirthi, C. Kamaraj, G. Rajakumar, A. A. Zahir, G. Elango, K. Velayutham, M. Iyappan, C. Siva, L. Karthik, R. K. V. Bhaskara, *Exp. Parasitol*., **132**, 156 (2012).
76. T. Giraud, P. Gladieux, S. Gavrilets, *Trends Ecol. Evol*., **7**, 387 (2010).
77. C. Krishnaraj, R. Ramachandran, K. Mohan, P. T. Kalaichelvan, *Spectrochim. Acta A, Mol. Biomol. Spectrosc.*, **93**, 95 (2012).
78. V. Gopinath, P. Velusamy, *Spectrochim Acta A, Mol. Biomol. Spectrosc*., **106**, 170 (2013).
79. K. J. Lee, S. H. Park, M. Govarthanan, P. Hwang, Y. S. Seo, M. Cho, W. H. Lee, J. Y. Lee, S. K. Kannan, *Mater. Lett*., **105**, 128 (2013).