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An Overview on Green Synthesis of Nanomaterials and Their Advanced Applications in Sustainable Agriculture

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Abstract

The excess use of unsafe pesticides and mineral fertilizers in agriculture has led to serious health problems and environmental pollution. Nanotechnology has been solving these problems by providing nanoparticles (NPs) with excellent performance. By green synthesis of nanoparticles from plants, animals, and microbes, the use of hazardous and toxic chemicals has become limited. Nanoparticles have excellent performance in many fields such as electronics, cosmetics, automobiles, catalysis, biosensors, bioengineering, etc. NPs also showed excellent performance in agriculture by improving crop production and food quality. Various nano-based agroparticles that have conducted many smart and efficient agricultural systems involving nanopesticides, nanofertilizers, nanoherbicides etc. Apart from enhancing the food production, these materials operate some other functions like as identifying disease in plants, control release of nutrients, delivery of nutrients at target sites, etc. various nanofertilizers such as Fe, Mn, N, K, Mo, P, CNTs and P showed excellent targeted delivery performance. Nanopesticides and many nanoformulations have showed excellent pest protection performance. Here we reviewed the sources of nanomaterials and their excellent performance in agriculture.

Keywords: nanoparticles, nanopesticides, nanofertilizers, nanoherbicides, sustainable agriculture, nanotechnology.

Contents

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1 Introduction

Nanoparticles have dimension in the range of 1 to 100 nanometer and enact as a tie between materials of different magnitude and molecular or atomic entities [1]. They manifest exceptional and miraculous attributes because of their higher reactivities which in turn is due to their large surface areas and smaller sizes [2-4]. Beginning of the nineteenth century has brought the attention of scientists towards the capacity of biological entities to curtail the metal antecedents but the processes are still undetermined. Population explosion, urbanization and speedy industrialization have ended up in the ruin of earth's atmosphere and tremendous amount of unhealthy matter is in air. More knowledge is to be discerned about the secrets of nature and its natural products which would lead to the advancements in the field of nanoparticles' synthesis. Nanoparticles are widely implied in different era of research and most significantly in the field of agriculture. Nanomaterials has mny applications in different fields such as paints, semi-onducting devices, cosmetics, medicines, etc. illustrated in figure 1. So, such synthesis processes need to be developed that do not utilize toxic reagents. Hence, green synthesis of nanoparticles turns out to be a suitable alternative to physical and chemical methods [5]. Nanoparticles manufactured through biological methods have gained much favor over nanoparticles synthesized from physical or chemical methods. NPs synthesized from physico-chemical methods come out with many problems such as the utilization of toxic reagents and hazardous by-products [6]. Plant based (green) synthesis of nanoparticles is evidently not a hazardous method as metal salt is synthesized by the use of plant extract.

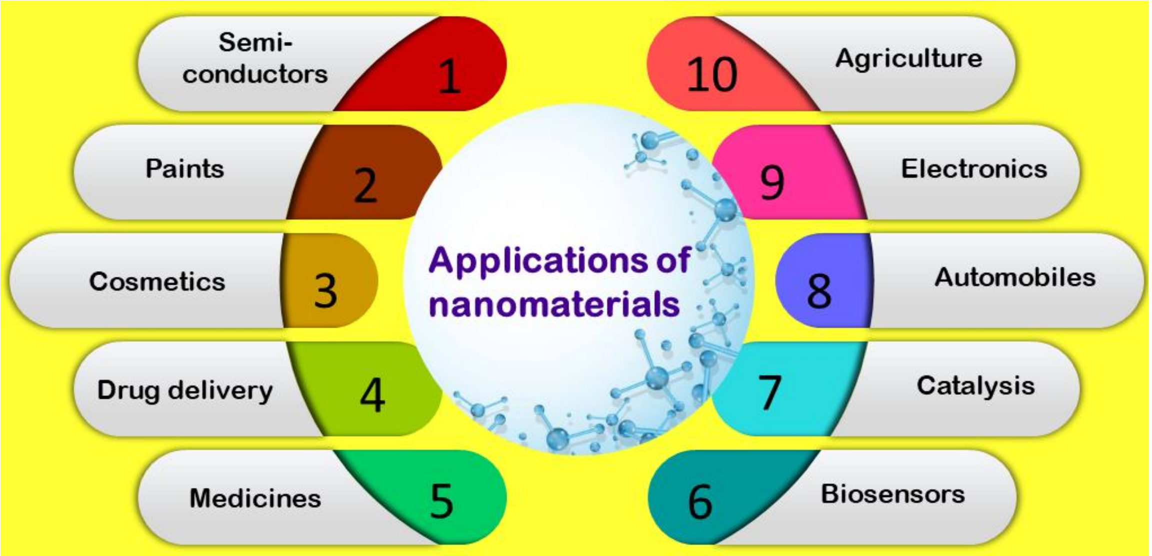

Figure 1. Applications of nanomaterials in different fields.

Green synthesis is the procedure for the development of nanoparticles which makes use of natural resources such as plant extracts, micro-organisms and energy conserving processes in a more economical, non-toxic and sustainable way [7, 8]. Green nano-technology is an energy efficient and safer process. It minimizes wastes production and green-house gas emissions. Renewable material utilization for such products is very beneficial and has lesser environmental impacts in terms of energy and pollution and so is termed as eco-friendly. In order to be utilized for specific applications, extracts from different plants are used in the production of NPs with characteristic functionalities. Micro-organisms like bacteria, yeasts, algae and fungi are used. Choice of micro-organisms depends on functionalities, size and type of the desired nanoparticles [9]. Green synthesis which utilizes biological molecules from plant extracts has turned out to be of much significance as compared to chemical means as plants are safe, promptly available and diverse which makes it fit for a sustainable bio-resource. The reaction rates for plant mediated synthesis of nanoparticles are higher ranging from few minutes to hours and reaction primarily can take place at room temperature. The exercise of plant extracts to manufacture high quality nanoparticles is in huge practice because of simple steps involved in recovering nanoparticle. The steps are abstraction of plant, extract filtration and metal NP salt addition. Resultant solution is stirred and NPs are eventually recovered from precipitate[7].

Involvement of nanotechnology in agriculture sector has inclined to be a vital factor for sustainable development. It has a great potential to transform the whole agricultural sector with innovative means which enhance the agricultural productivity of plants through adept supplements in the mode of nano-nutrients for nano-fertilizers, nano-pesticide and nano-herbicides by the plants [10]. Nano-materials are utilized for plants' protections as nano-herbicides, nano-pesticides and nano-sensors as well. Nano-nutrients or nano-fertilizers have tremendous effects on growth, rate of germination, phytotoxicty of various field crops and vegetables [11].

Nanoparticles being comparable to virus in size may be inhaled by humans and may end up in bloodstream or other sites in the human body like heart, blood cells or liver [12, 13]. As toxicity of the NPs depends on origin, many of the NPs may have non-toxic or positive effects on health. Exposure to NPs might have general acute toxic effects which include protein denaturation, generation of reactive oxygen species, perturbations in phagocytic functions and also in mitochondrial disconcertion. Other common and chronic toxic effects of NPs may include neo-antigens' generation which results in enlargement or dysfunctioning of the organs [13].

2 Synthesis of Nanoparticles:

The biological preparation of Nanoparticles via the green method utilizes the plants and animals to cause the conversion of metallic ions into neutral atoms. Green synthesis (GS) is also done by the elimination of toxic chemicals. Hence, the green synthesized nanoparticles (NPs) offers you the improved biocompatibility in dealing with the biomedical application as compared to the chemically synthesized ones.

There are multiple plant species and groups, among which the Angiosperms and Algae are widely studied. The green-synthesis from the plants-derived materials such as chitin and silk also reported in the past. Different kinds of researches in the past have proved the capability of various plants' specie in green synthesis of nanoparticles and their capping behavior. Not just the plants but the animal-derived biomolecules are also responsible for this.

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2.1 Plant-based synthesis of Nanoparticles:

This section will highlight all the signs of progress made towards the green synthesis of nanoparticles via the plant species. Most commonly, the plant species having medicinal applications play a major role in the green synthesis process. Plant-based nanomaterials are listed in table 1.

2.1.1 Angiosperms:

The plant's lineage has the angiosperms at the top and hence these are widely utilized for the green synthesis of NPs. Their easy access, wide applications, availability all over the world have further favored this synthesis. Also, the Angiosperms play an essential role in dealing with human and animal diseases [14]. The nature of Angiosperm plants have aided in processing the natural reducing ability in improving this green domain. The green Synthesis has received many updates in its library especially in the Asian Countries due to enriched plant resources. But not all the plant's species can do justice with the green synthesis of plants.

Most of the researches made on the angiosperm species have revealed that the synthesis of Gold and Silver Nanoparticles is quite common as compared to the other magnetic Nanoparticles. The reason behind this fact is the poor capability of converting the metal cation into lower reduction potential. Various researches have contributed to the plant-based production of nanoparticles. A well-explored plant named *Camellia Sinensis* has been considered an advantageous plant's specie in GS of NPs. The purification of living molecules present in this plant's species viz. catechins, theaflavins, and their isolation has confirmed their role in green synthesis of Au NPs [15, 16]. Similarly, the pure tea polyphenol is utilized for the synthesis of Pt NPs. Another plant's specie named *Jatropha curcas L* is responsible for the reduction of metal cations via the cyclic peptide molecules [17]. Therefore, the overall research progress that has been completed recently in this newly-emerged green synthesis domain is quite impressive as compared to the conventional methods.

2.1.2 Gymnosperms:

Gymnosperms were the first to have the seeds in plants category, hence they are of much importance. Each group of plants further have distinct metabolites. These metabolites are further responsible for the reduction of metal ions to synthesize the nanoparticles. The studies regarding the green synthesis of NPs from gymnosperms is quite restricted but evident to some extent. Various researches have been made in this sense, and the NPs synthesized from the gymnosperms have different sizes, morphology, and quantity depending on plant type [18-22]. Noruzi et al have synthesized the Au NPs from the *Thuja orientalis* extract in just a 10-minutes of reaction time. The overall efficiency was found out to be 90% and the produced Nanoparticles were round in shape and crystalline in nature [23].

2.1.3 Algae:

The three main criteria to synthesize and hence achieve the efficiency in the GS of NPs are mainly the reducing agent, stabilizing capping agent, and acceptable solvent [24]. The algae-based

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preparation of nanoparticle is one such process. These are photoautotrophic in nature [25]. Hence, the bio-reduction of algae can synthesize the metal and metal oxide NPs [26-30]. *Spirulina platensis* is a kind of edible blue-green alga that is utilized to synthesize the gold and silver NPs [31]. Senapati et al. have synthesized the gold NPs via *Tetraselmis kochinensis* plant [32].

Table 1. List of nanoparticles derived from plants.

Plant	**Nanoparticle**	**Size (nm)**	**Ref.**
Allium cepa L.	Au	~100	[33]
Allium sativum L.	Ag	4 .4 ± 1.5	[34]
Achyranthus aspera L.	Ag	20-30	[35]
Anacardium occidentale L.	Au	-	[36]
Andrographis paniculata Nees.	Ag	28	[37]
Astragalus gummifer Labill.	Ag	13.1±1.0	[38]
Azadirachta indica A. Juss.	Au	2-100	[39]
Camellia sinensis L.	Au	25	[40]
Carica papaya L.	Ag	15	[41]
Centella asiatica L.	Ag	-	[42]
Chenopodium album L.	Ag Au	12,10	[43]
Coleus aromaticus Lour.	Ag	40–50	[44]
Cinnamomum zeylanicum Blume.	Pd	15 to 20	[45]
Cinnamomum camphora L.	Pd	3.2-6.0	[46]
Citrullus colocynthis L.	Ag	31	[47]
Datura metel L.	Ag	16 - 40	[48]
Desmodium triflorum (L) DC.	Ag	5-20	[49]
Diopyros kaki	Pt	2-12	[50]
Dioscorea bulbifera L.	Ag	8-20	[51]
Dioscorea oppositifolia L.	Ag	14	[52]
Elettaria cardamomom (L) Maton.	Ag	-	[53]
Gardenia jasminoides Ellis.	Pd	3-5	[54]
Glycyrrhiza Glabra L.	Ag	20	[55]
Hibiscus cannabinus L.	Ag	9	[56]
Hydrilla verticilata (L.f.) Royle.	Ag	65.55	[57]
Jatropha curcas L.	ZnS	10	[58]
Justicia gendarussa L.	Au	27	[59]
Lantana camara L.	Ag	12.55	[60]
Leonuri herba L.	Ag	9.9 - 13.0	[61]
Macrotyloma uniflorum (Lam) Verdc.	Au	14-17	[62]
Mentha piperita L.	Ag, Au	90, 150	[63]

Mirabilis jalapa L.	Au	100	[64]
Morinda pubescens L.	Ag	25-50	[65]
Ocimum sanctum L.	Ag	4–30	[66]
Parthenium hysterophorus L.	Ag	10	[67]
Pedilanthus tithymaloides (L) Poit.	Ag	15-30	[68]
Piper betle L.	Ag	3-37	[69]
Piper nigrum L.	Ag	5 - 50	[70]
Plumeria rubra L.	Ag	32 -220	[71]
Sesuvium portulacastrum L.	Ag	5-20	[72]
Solanum xanthocarpum L.	Ag	10	[73]
Sorghum Moench.	Ag, Fe	10, 50	[74]
Soybean (Glycine Max) L.	Pd	~15	[75]
Swietenia mahogany (L) Jacq.	Ag	-	[76]
Syzygium aromaticum (L) Merr. & Perr.	Au	5-100	[77]
Terminalia catappa L.	Au	10-35	[78]
Trianthema decandra L.	Ag	10-50	[79]
Tridax procumbens L.	CuO2	-	[80]
Vitus vinifera L.	Pb	661	[81]
Zingiber officinale Rosc.	Ag Au	10	[82]

2.2 Green synthesis of Nanoparticles from Animal-derived material:

Polymer nanomaterials have their unique and distinct properties depending on their surface area, microbial encumbrance, and the size of pores. Many animals' species either unicellular or multicellular are involved in the synthesis of NPs.

2.2.1 Silk Proteins:

Multiple species of insects and spiders made the silk fibroin which is a semi-crystalline polymer containing amino acids like glycine, alanine, and serine. This material is employed in the tissue engineering of bones, skin, muscles, and blood vessels. The basic reason is its non-toxic, less harmful, and non-immunogenic nature. Multiple evidences have been found regarding the green synthesis of nano-composites via the utilization of fibroin. The most common is the fibroin-TiO_2 [83] nano-composites and the nano-hydroxyapatite silk fibroin [84]. All the obtained nanocomposites were crystalline in nature and 100 mm in length. Another component named sericin, which is present in the effluents of silk industries is also responsible for the synthesis of NPs. The nano-sericin powder is obtained via the ultra-sonification which reduces the particle size [85].

2.2.2 Chitosan:

The invertebrate chitin is responsible for providing you the multiple applications in various fields. For example, the chitosan nano-fibers are perfect to colorize the textiles. Moreover, the medical filed is also benefited from this peptide. It is involved in the slow release of vaccines as well as cancer treatment. Nano-chitosan also plays a noteworthy role in reducing the contamination of environment. Furthermore, Sahab et al have synthesized the PAA NPs of the 50 nm size which have the anti-fungal uses [86].

The magnetic chitosan plays a major role in removing the organic dyes from the wastewater. The large quantity of hydroxyl as well as amino groups present in chitosan are responsible for a good adsorption rate against the organic dyes when used with the magnetism of Fe_3O_4 [87]. Similarly, synthetic dyes can also be removed via the bentonite-chitosan nano-composites [88].

2.3 Microbes-based synthesis of Nanoparticles:

There had been a number of techniques and processes employed to obtain the nanoparticles by different precursors [89, 90]. Some of the techniques were not budget-friendly while some were toxic due to the excessive use of chemicals, while the rest synthesize the NPs via the UV radiation or aerosol spray [90, 91]. Hence, to minimize all these problems, the microbes-based synthesis of NPs is practiced significantly [91]. The microbes-based synthesis of NPs has now become an interesting research to make and has a bright future ahead as well due to the number of applications [89, 91, 92].

The nanomaterials are obtained from the microbes via two different methods including the intracellular and extracellular [89, 93]. Their mechanism is different as per the species and NPs you want to obtain. The intracellular mechanism is based on the transfer of positive metal ions through the cell wall which is due to the negative ions already present in the cell wall of bacteria. These ions were then reduced by the specific proteins i.e. enzymes into the NPs. While, in fungi the extracellular mechanism takes place. In this approach, the metal ions are converted to their respective NPs via the nitrate-reductase synthesis method [93]. *F.oxysporum* produces the silver-gold NPs via this extracellular approach when reacts with the Tetrachloroaurate and Silver Nitrate [94]. Also, *Aspergillus flavus* is involved in the green synthesis of Ag NPs having a size of 8 nm approximately[95]. Biosynthesis of nanoparticles from microbes is listed in table 2.

Table 2. Biosynthesis of nanoparticles from microbes.

Sr. No	Microorganism	Nanoparticle	Size (nm)	Ref.
1	*Lactobacillus sp.*	Ti	40-60	[96]
2	*P. boryanum UTEX 485*	Pt	30-0.3	[97]
3	*Corynebacterium sp. SH09*	Ag	10-15	[98]
4	*Desulfovibrio desulfuricans*	Pd	50	[99]
5	*Lactobacillus sp.*	Au	20-50	[100]
6	*Pseudomonas stutzeri AG259*	Ag	<200	[101]
7	*Klebsiella pneumoniae*	CdS	5-200	[102]
8	*Aquaspirillum magnetotacticum*	Fe_3O_4	40-50	[103]
9	*Bacillus subtilis 168*	Au	5-25	[104]
10	*Coriolus versicolor*	Ag	25-75	[105]
11	*Aspergillus flavus*	Ag	8.9	[106]
12	*V. luteoalbum and isolate 6–3*	Au	<10	[107]
13	*F. oxysporum*	$BaTiO_3$	4	[108]
14	*F. oxysporum*	Pt	10-50	[109]
15	*F. oxysporum*	Si	6-13	[110]
16	*F. oxysporum*	Ti	5-15	[110]
17	*F. oxysporum*	Au, Ag	8, 14	[111]

3 Sustainable Agriculture

The idea of sustainable development of agriculture gained immense importance after Brundtlant Report in 1987. Tough its meaning is little vague, United States Department of Agriculture 2012 defined it "agriculture is basically about livestock and production of various crops having impact on environment". The basic concept behind sustainable development of agriculture is to maintain balance between need of food and protecting the environmental resources from declining resources and harmful effects. There are many other aims associated with this sustainable approach like less usage of inorganic fertilizers, protection of water resources, conservation of biodiversity, minimizing waste production etc. [112, 113]. Ecofriendly fertilizers have been recognized to increase the crop yield along with better condition of soil [114-117]. To help farmers financially, helping them to implement new techniques and providing them better facilities to upgrade their quality of life is also included in their objectives of sustainable approach[118]. Figure 2 illustrate the different parts of sustainable agriculture.

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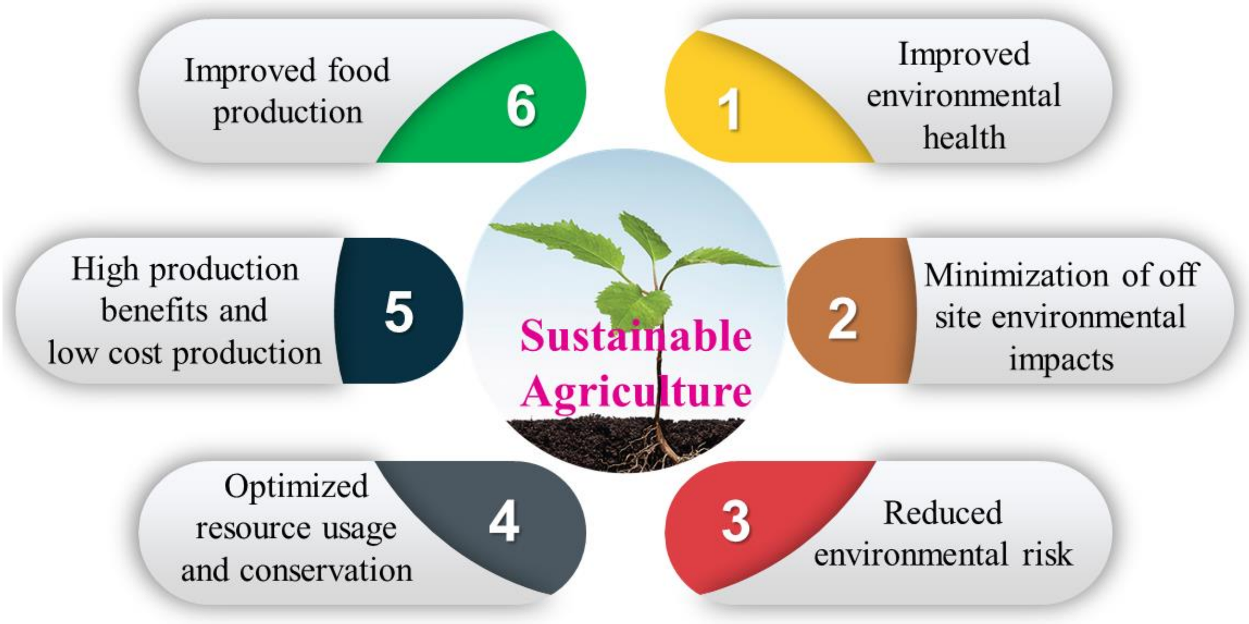

Figure 2. The different parts of sustainable agriculture.

Various farming techniques can be applied to make it better to a certain level. Nanotechnology is one of the progressive and successful techniques to produce highly efficient fertilizers which brings no harm to biodiversity. Agriculture is one of the areas which is totally shifted from conventional techniques to nanotechnology. Use of nano-fertilizers has taken the place of inorganic pesticides because they tend to enhance crop yield and also stimulated sustainable approach widely.

4 Nanoagriculture a Way Towards Sustainable Agriculture

Modern agriculture demands sustainable and high crop yield without use of inorganic chemical fertilizers which has adverse effects on health and environment. Hazardous chemicals found in such fertilizers reach under the soil bed via leaching and contaminate water which leads to detrimental outputs. However, preventing measures should be taken to reduce the unwanted and harmful risks produced by chemical fertilizers[119]. Agricultural approach based on nanotechnology is a successful method to obtain attractive yield[120] and production of nanodevices like nanobiosensors(that senses the disease in crops) is a major innovation in the field of agriculture[121]. Other features have been introduced into the nanobiosensors to detect any toxicity caused by microorganisms in plants. Moreover, the very small size of this device make it very easy to use in agricultural lands and fields and these bionanosensors are also used to detect toxicity cause d by fungi [121-123]. Hence , use of nanoparticles in the conventional agriculture system has gained immense importance due to its countless benefits which includes improved quality of soil, smart monitoring, enhanced enzymatic activity, increased nutrients uptake etc. and now this approach is known as nanoagriculture. Figure 3 illustrates the role of nanoparticles in agriculture.

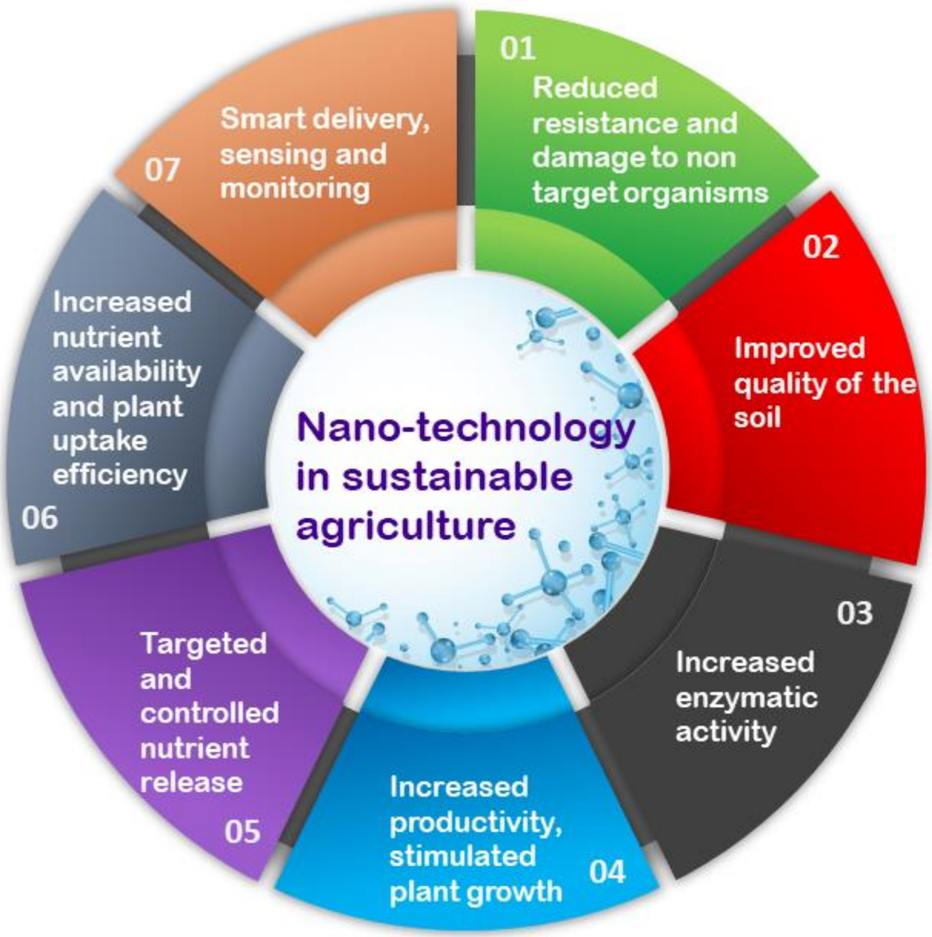

Figure 3. Role of nanoparticles in agriculture.

NPs reduce the nutrient loss thus enhancing the crop production via precise control of nutrients[124, 125]. The present condition of agricultural system is not suitable for better yield but incorporation of nanotechnology with present system would be able to make it better with use of efficient nanodevices and nano-fertilizers considerably[126]. Sustainable methods of agriculture are getting attention recently for its many advantages and environmental friendly nature.

5 Applications of Nanoparticles in Agriculture

5.1 Weed Control by Nano-herbicide

Herbicide resistance is quite common in the cropped environment due to number of reasons. One most common reason that results in the poor weed control and herbicide resistance is the multi-specie approach. Plants can get exposed to one herbicide in one season while a different one in another season. It develops the resistance against the herbicides. Weeds can be controlled by producing an herbicide that attacks the roots of target weeds. Developing this specific herbicide molecule requires the nanoparticle (NP) encapsulation which then enters the roots of weeds to inhibit the glycolysis process. It'll create the starvation condition and particular weed get killed [127]. Applying herbicide in the soil which doesn't have sufficient moisture will lead to

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unfavorable results. Encapsulated herbicide acts by controlled release which takes care of the competing weeds. Moreover, there are adjuvants available for the herbicide. These adjuvants have the nanomaterial employed.

Herbicide paraquat may need a carrier system for action. Silva et al. have prepared the chitosan nanoparticles for this purpose [128]. The characterization of these synthesized nanoparticles was done by the physio-chemical techniques. Next, the process is followed by the evaluation of pH, zeta potential, and size. For this purpose, various techniques have been employed including the TEM, FTIR, and differential Scanning Calorimetry. Therefore, all these techniques were performed to study the release action of 1, 1'-Dimethyl-4, 4'-bipyridinium (Paraquat), an herbicide containing the chitosan NPs. The results depicted that the parquat and herbicide release action is altered via the alginate or chitosan nanoparticles.

5.1.1 Detoxification of Herbicides Residues

Crops can sense the damage by the excessive use of herbicides. Whenever herbicides are used in large amounts, the residues can be left behind in the soil. Therefore, using the herbicide over the years will eventually develop the herbicide resistance in the weed growing in that soil and then shift in the weed flora. Broadleaf and grassy weeds have a half-life of nearly 125 days and are also mobile in some soils. These kinds of weeds can be controlled via an herbicide named as Atrazine. This s-triazine-ring herbicide is used globally for this purpose and is now at threat due to residual problems. TNAU, India has raised the hope recently from their study that remediation of residuals of Atrazine is possible within a short time. Silver modified NPs of CMC were applied to remediate the Atrazine residuals from soil and results showed the 88% success rate of degradation of herbicide [129].

5.2 Nanomaterial in Seed Germination

New scientific innovations utilize many approaches and contributed much to the field of nanosciences recently. This situation has been a one step further towards the nanotech applications in agriculture. Nanoscience helped in enhancing the growth of crops, the process of seed germination, and adapting to different environments. Population dynamics and well-being of all the species depends significantly on the seed germination process. Therefore, the germination of seeds is not just a sensitive but important process in the plant's lifecycle. Seed germination, in turn, depends upon multiple factors and attributes i.e. moisture level in soil, nutrients, and soil's compatibility with species [130]. Many studies have been made in this regard and it has been shown that nanomaterials have contributed much to increasing the plant's growth and overall production of crops. It has been depicted that the utilization of Carbon nanotubes (multi-walled) has shown positive effects on the seed development process of soybean, tomato, corn, barley wheat, and more [131-134]. Similarly, nano silicon dioxide (SiO_2), Titanium Dioxide (TiO_2), and Zeolite have already influenced the seed germination process in a positive manner for various kinds of crops [130, 135]. Another research conducted in this regard depicted that the Iron or Silicon Dioxide nanoparticles play an important role in improving the overall seed germination of particular types of crops mainly Barley and Maize [136]. There has been enough evidences now

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concerning the advantageous influences of nanomaterials on seed germination but the actual process behind this is unclear yet. Some studies have reported that after application of nanomaterial, the NPs have the capacity to pass through the seed coat. After passing, they enhance the ability of absorption of water by the seedling. This way, the seedling is better able to grow and germinate under favorable conditions.

Quality enhancement and increase in the crop's yield is also described by employing multiple kinds of nanomaterials. Such nanomaterials include Zinc oxide, Titanium dioxide, carbon nanotubes, Iron Oxide, and ZnFeCu-Oxide [137-139]. Similarly, studies have stated the benefits of the crop growth of OH-functionalized fullerenes via the utilization of carbon nanotubes. Gao et al. studied the growth of hypocotyl in fullerenes in *Arabidopsis* via the cell division [140]. Therefore, Fullerol has been found responsible for the enhancement in fruit's growth, size, and the overall yield as well. The increase found out to be 128% and also it cause an increase in the production of bioactive compounds. These bioactive compounds include the Amarine, ψ,ψ-Carotene, charantin, and Chicory Extract [141]. Yousefzadeh and Sabaghnia described that the nano-iron fertilizer enhanced the essential oil contents of plants[142]. In the same way, the nano-zinc and boron fertilizers are employed for improving the fruit yield and quality. It includes the process of decreasing the total soluble solids by 4.4 - 7.6%, an increase in the titratable acidity by 9.5 – 29.1%, and 0.28-0.62 pH increase in the pomegranate [143]. These evidences are enough to prove the role of nanomaterials in increasing the crop's production and quality. However, the mechanism by which the nanomaterials enhance the growth and quality of plants is still unknown. Some evidences have been found that the nanomaterials increase the intake of nutrients and water and nutrients to improve the root system via increases enzyme activity [137, 138]. Moreover, the studies have also revealed the phenomenon of control or slow release of nanofertilizers in water or soil which helps in availability of nutrients for all the time during cultivation of crops. This availability of nutrients helps to improve the seed sprouting, development, blossoming/flowering, and more [144]. Like, a urea fertilizer (nano-coated in this case) named as hydroxyapatite release the nitrogen contents needed for plant growth at a very slow rate. It releases these contents continuously for 60 days. On the other hand, the traditional fertilizer will end up in 30 days and that too with an unbalanced release. It'll adversely affect the plant's growth and quality of production [145]. In a study, Zheng et al [146] researched about the photosynthesis in spinach. They found out that when TiO_2 nanofertilizer is applied, the photosynthesis rate increases by 3.13% but decreased beyond the 4%. Similarly, Disfani et al [136] made a research on the size of barley and maize seedlings and depicted that the application of nanomaterial i.e. nano Fe/SiO_2 caused an increase in length by approx. 8.3% and 21% respectively. But the shoot length have a negative impact on reaching the concentration level above 0.025 g/kg. This means that the growth of crops depend on the nanomaterials. El Feky et al. [147] suggested that the crop's development and quality also depends upon the application of nanomaterials. The foliar applications of nano Fe_3O_4 can increase the total production of chlorophyll, carbohydrate and essential oils content, height, shoot and branches length, and many other factors in *Ocimum basilicum* plants.

5.3 Nano-fertilizers

These are regarded as the nanomaterials which are capable enough to provide nutrients and certain elements to the plants which are needed for their growth and production [148]. Nanofertilizers are categorized as subject to the type of nutrients plants need. Various nanofertilzers are listed in table 3.

5.3.1 Macronutrient Nanofertilizer

As mentioned in the name, this fertilizer is for the soil where nutrients are obligatory in the large amount, especially for the traditional framing. Macronutrients such as Nitrogen, Phosphorus, Sulphur, Magnesium, Potassium, and Calcium are needed for proper growth. Demands for the production of food are increasing continuously which tends to increase the need for nanofertilizer to 263 MT by 2050 [149]. Nanomaterial has a high volume-to-surface ratio. This brings the utmost efficiency to the applications of macronutrient fertilizer rather than the traditional ones. Therefore, many researchers are working continuously to improve the macronutrients fertilizer to use it at the field scale. In this regard, Liu et al. [148] and Ditta et al. [150] have studied the applications of nanoparticle-based fertilizer. Controlled release of Nitrogen has been achieved by the zeolite chips (Urea coated) and urea-modified hydroxyapatite nanoparticles [145, 151]. Similarly, Liu and Lal [152] have researched on the Calcium and Phosphorus hydroxyapatite nanoparticles which showed an increase of approx. 20.5% and 34% in the Glycine max seed yield. Liu et al. [153] have noticed a 15% increase in the biomass of *Arachis hypogeae* by the application of Ca NP as compared to the conventional Calcium macronutrient. Moreover, Delfani et al. [154] studied the seed weight of Vigna unguiculata. They found the enhancement by 7% in the seed weigh after the application of synthesized Mg NP. The effects of nanofertilizers on plant and soil is illustrated in figure 4.

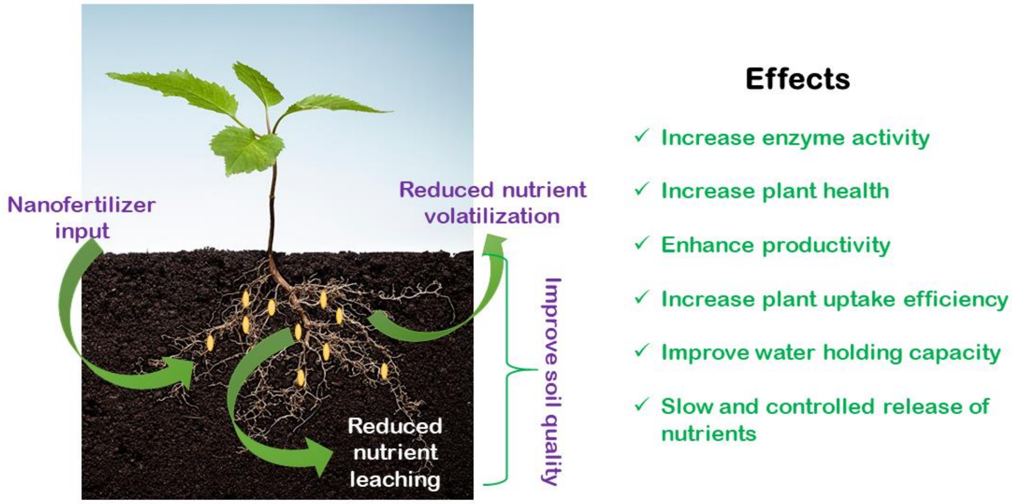

Figure 4. The effects of nanofertilizers on plant and soil.

5.3.2 Micronutrient Nanofertilizer

Though micronutrients are required in smaller quantities but necessary for the metabolic process. The bioavailability to the plants is significantly improved in the case of micronutrients and hence enhances the growth and quality of crops. Delfani et al. [154] have made another research on the chlorophyll contents of black-eyed pea after the application of Fe NP which is improved by 10%. Similarly, Ghafariyan et al. [155] have found out 30-60 ppm concentration increase in the chlorophyll content in G. *max*. Using bulk Manganese Sulfate will not provide sufficient increase in growth and quality. Therefore, spraying the Mn NP will enhance the biomass by 37-38%, root length by 52-53%, and shoot length by 38-39%.

Zinc element is responsible to carry out the regulatory mechanism for all the enzyme activities in plants. Zinc Oxide NPs are responsible to enhance or upsurge the contents of biomass, shoot length, root length, and overall growth by improving the protein content. These improvements can be seen in the Vigna Radiate, Cucumis sativas, Raphanus sativus, Brassica napus, and Cluster bean [156-159]. Molybdenum NPs when used in combination with the nitrogen fixation bacteria tend to improve the overall seed growth in chickpea [160].

5.3.3 Nano-particulate Fertilizer

Nanoparticles including the Titanium Dioxide, Silicon Dioxide, and carbon nanotubes are significantly responsible to increase the plant's growth and quality of crops. A mixture of Titanium Dioxide, Silicon Dioxide NPs have been seen to improve the seed growth and germination process along with an enhancement in nitrogen fixation in G. *max* [135]. Only the Titanium Dioxide NPs have the ability to improve the chlorophyll, protein, and nitrogen content of the Spinacia oleracea [161]. Carbon Nanotubes have been widely used as the fertilizer for diverse species of plants and vegetables. Carbon nanotubes follow the same principle as the nanoparticles and penetrate the seed coat to enhance the water uptake resulting in better growth [162].

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Table 3. Various nanofertilizers are used in agriculture and their impact on crops.

Sr. No	Plant	Nano-fertilizer	Amount of nano-fertilizer (PPM)	Highlights of the study	Ref.
1	*Pennisetum glaucum*	Au	50	Seedling growth and seed germination	[163]
2	*Arachis hypogaea*	Ca	-	Plant growth and nutrient contents	[164]
3	*Cucumis sativus*	CeO_2	400	Globuline content and food quality	[165]
4	*Phoenix dactylifera*	CNTs	0.05-0.1	Leaf number and shoot length	[166]
5	*Lactuca sativa*	Cu	130-600	Shoot length, germination of seeds and effect on soil microbe community	[167]
6	*Zea mays*	CuO	10	Plant growth and roots	[168]
7	*Glycine max*	FeO	30-60	Effects of NPs on chlorophyll	[169]
8	*Pisum sativum*	FeO	250-500	Increased chlorophyll	[170]
9	*Vigna unguiculata*	Mg	2.5	Increased chlorophyll	[170]
10	*Vigna radiata*	Mn	0.05-1	Increased chlorophyll	[171]
11	*Oryza sativa*	Mn	-	Zn uptake improved	[172]
12	*Cicer arietinum*	Mo	8	Increased plant mas	[173]
13	*Glycine max*	P	100	Growth rate increased	[174]
14	*Spinacia oleracea*	TiO_2	0.25-4	N_2 fixation improved	[175]
15	*Lolium*	Zn	1-2000	Root elongation	[176]
16	*Vigna radiata*	ZnO	1-2000	Growth rate increased	[177]

5.4 Nano-pesticide

The pesticide industry has an ongoing demand for nanoformulation. In this process, the nanoformulation of traditional pesticide with polymers or metal NPs have advantageous factors to consider. In this regard, the nanoencapsulation of pesticides makes sure the slow release of the ingredients over a prolonged time. This way, you can also reduce the run-off of pesticides [178, 179]. Nanocarriers have a similar advantage of site-specific delivery. Another method named as nanoemulsion is getting thoughts of professionals [180]. In this method, the nanoemulsion process can enhance the overall solubility and absorbing capacity of pesticides in soil. The impact of nano pesticides on plants is explained in table 4.

Table 4. Impact on nanopesticides on plants.

Nanoparticles	**Pathogen**	**Plant disease**	**Effect**	**Ref.**
Ag	*Xanthomonas campestris pv.campestris*	Bacterial blight	Improved bacterial reduction	[181]
Ag core-DHPAC shell	*Phytophthora nicotianae*	Fungal disease	Growth inhibition	[182]
FeO	*F. oxysporum*	Fungal disease	Growth inhibition	[183]
Chitosan	*Colletotrichum capsici*	Diseases in chilli	Reduce mycelia growth rate	[184]
	Macrophomina phaseolina	Fungal disease	Stopped spore germination	[185]
Cu	*Fusarium sp*	Fungal disease	Antifungal	[186]
	Phytophthora infestans	Disease in tomato	Antifungal	[187]
	Xanthomonas axonopodis pv. punicae	Bacterial blight	Improved bacterial growth inhibition	[188]
Silver-GO composite	*Xanthomonas performance*	Bacterial Spots	Improved bacterial growth inhibition	[189]

Silver NPs are one of the nanopesticides which is active against the number of pests in a diverse range of plants including *Botrytis cinerea*, *Colletotrichum*, *Phoma*, and more. Similarly, a combination of Silica and Silver NPs has been proven utmost effective against the powdery mildew [190-193]. Cu nanoparticles are also proven effective against the gram-positive and negative bacteria in low concentration. These NPs were also used against the fungal disease pathogens including *Fusarium sp.*, *Phytophtora infestance* and more [194]. The impact of nanoformulation based materials on pest control are listed in table 5.

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Table 5. Impact of nanoformulation based materials on pest control.

Nano-formulations	**Pesticides**	**Pathogen**	**Plant disease**	**Effect**	**Ref.**
Porous hollow silica	Validamycin	-	-	36% loading capacity increased	[195]
Cellulose/silica nanocomposites	Tebuconazole	Moulds and rust	Leaf decay	Enhanced release rate	[196]
$CaCO_3$	Validamycin	*Rhizoctonia solani*	-	Controlled release	[197]
Lignin	Diuron	-	-	Controlled release	[198]
TiO_2	With Ag and Zn	Xanthomonas perforans	Disease in tomato	Improved bacterial reduction	[199]

Zn NPs is another in the category which was proven effective as nano fertilizer but also as an anti-fungal agent. These NPs were used and found effective against the *Penicillium expansum*, *B. cinerea*, *Apergillus flavus* and more [200, 201]. Zinc Oxide NPs have another benefit of being less harmful against the silver NPs. Before making these methods of nanomaterial application to the crops and plants commercial, the control action should be practiced. The Nano-pesticide act must be structured by the centralized organizations in this regard.

5.5 Nanotechnology vs. Traditional carry out

Target framing is getting common these days in nano-agriculture field in which nanoparticles are applied to increase the growth and crop eminence [202, 203]. In terms of seed development or germination and plant growth promotion, the CNTBs (carbon nanotubes) have replaced all other traditional methods [146, 204]. Cu bactericides were used in the past which is now replaced by the nanosized bacteriophages. Their smaller size along with the greater surface to volume ratio makes them more proficient as compared to all other traditional practices. A comparison of nanomaterials and conventional materials is illustrated in figure 5. NPs work in a manner by penetration through the apoplast and then into the epidermal and cortical layers. They accumulate inside as an aggregation [158, 205]. Similarly, Rico et al. [206] studied another penetration pathway i.e. symplastic, and found out as more organized and regulated.

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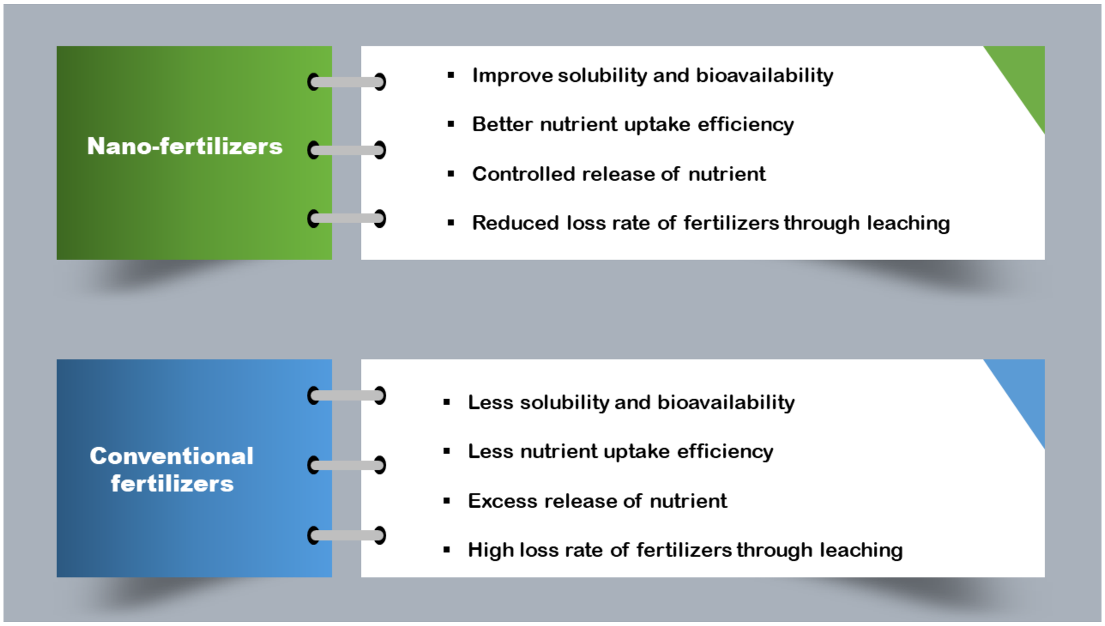

Figure 5. A comparison of nanomaterials and conventional materials.

6 Nanomaterial toxicity to crops

6.1 Uptake and movement of nanomaterial

Nanoparticles play a vital role in the study of how a plant responds to different aspects like size, height, and uptake of NPs, and 40-50 nm absorption is observed in the literature[207, 208]. Moreover, coating materials also contribute significantly to the absorption and uptake of nanoparticles. Different species of plants require different quantities of nanoparticles to absorb in a specific time and concentration is provided[208]. A plant can take up nanoparticles via symplastic movement or apoplastic or both[209-211]. Symplastic movement is a result of endocytosis and occurs when nanoparticles cross the outer membrane[212]. NPs are taken up by the plant and reach out to several parts of plants it could be edible like fruits or non-edible like stem, leaf, and roots[213, 214].

6.2 Toxicity to crops

Nanoparticles can cause harm to plants in both direct and indirect ways. The high exposure of NPs to plants may adversely affect the growth of roots and leaves and the process of germination as well.[215, 216]. The most harmful biochemical reactions of nanoparticles include the production of reactive oxygen species in higher amount which affects uptake and movement of water in plants, cause OS(oxidative stress) and problems in photosynthesis and other chemical reactions[217, 218]. Many genetic changes were observed in the response to using various nanoparticles on N. Tabacam and A. cepain. The toxicity of titanium oxide nanoparticles was compared with copper oxide NPs and cadmium oxide NPs [219, 220].

It was concluded that TiO_2 NPs are the least toxic among them and CuO_2 NPs cause high damage to DNA with the formation of $8OH_2$'dG. Hong et al studied that exposure of $nCeO_2$ over Cucumis Stivus causes changes in the enzymatic behavior of plants [216]. Damage to chloroplast, destruction of vascular bundle, and variation in uptake of nutrients occur when nan- ceria is applied is provided to cotton plants [221].

7 Detoxification mechanism in crops induced by nanomaterial

Formation of reactive oxygen species (ROS) is an important harmful mechanism of NPs which badly affects the normal functioning of crops. Nanoparticles are very small in size and have higher activity due to large surface areas which results in higher induction of reactive oxygen species by NPs. Prevention from damages and in the regulation of ROS antioxidants (both enzymatic and non-enzymatic) plays a vital role.

Major antioxidant enzymes are peroxides, SODs, and CAT and GSH and phenolics are the chief non-enzymatic antioxidants. Use of nanoparticles causes changes in the behavior of antioxidants. It has been revealed by studies that exposure of Ag NPs with R.Communis results in higher production of reactive oxygen species[222]. The toxic effect of Ag NPs in A.thaliana is a disturbance in water levels and photosynthesis(by effecting chlorophyll content badly)[223].

Exposure of CuO NPs on A.thaliana revealed that toxicity is caused by the release of copper ions [224]. Servin et al. reported that exposure of tin oxide NPs on cucumber cause induction of catalases but no APX activity[214]. The effect of Nd(III) oxide NPs in pumpkin cause higher activities of peroxidase and superoxide dismutases but decreases in the activity of catalases and APX (Chen et al. 2016). Rico et al. studied that use of nanoceria in rice has adverse effects on GSH resulting destruction of membranes and photosynthesis. Servin described that upon exposure of tin oxide NPs(250-750mg L-1) cause an increase in catalases activity but no effect on APX activity[214].

8 Threats of Nanotechnology

The higher growth rate of nanoparticles production and its applications in various areas are well known[225]. The present level of usage and mixing of nanoparticles is not harmful but it cannot be ignored that there is a chance in increasing the concentration of NPs in the coming years[226, 227].

Nanotechnology has its own merits and demerits [228]. NPs can be obtained directly (via natural sources) or indirectly (via anthropogenic production). Nanoparticles are present in soil via rain or supply through agricultural activities. The concentration of NPs is high in the soil as compared to water and air, due to slow movement in soil NPs continue to stay there for a longer period of time[229]. Nano-fertilizers are major source of nanoparticles contamination because plants uptake NPs present in soil and NPs move through the plant and reach to various parts of plants and ultimately to human when human consumes the product of that plant. The adverse effects of NPs include a higher rate of reactive oxygen species, chromosomal aberration, genetic defects, and cause harm to different organs in humans. There are many sites of entry for nanoparticles into the human body. They can enter via breathing, eating, and even by injecting during the medical processes. The major issue is the activities and responsibilities of NPs inside the human body like how nanoparticles behave with tissues and different organs[228]. Chances of cytotoxicity increases when a high concentration of nanoparticles are used. During the past few decades, nanoparticles are being produced on a very large scale and they end up causing toxicity in the environment. Researchers revealed that Ag NPs are used in the making of socks because they help to lessen smell but they affect adversely when released in the wash[230]. Ag NPs are bacteriostatic they may destroy other bacteria which are helpful for the degradation of organic material in waste treatment farms. By knowing the threats of NPs, authorities such as EPA(environmental protection agency) and FDA(food & drug administration) have started taking preventing measures to reduce the risks produced by NPs[228].

9 Conclusion

As the need for food grows rapidly, it is important to enhance the productivity of crops. Regarding to improved crop production, it is important to find an advanced solution that can accelerate productivity and not pollute the environment. The integration of nanotechnology in agriculture has provided the final solution needed for the development of the agricultural sector. Nanoparticles modify conventional agricultural particles as they target, control the release of chemicals that are not harmful to soil microorganisms, and unmarked organisms, including crop plants, and ultimately they are not natural. As nano fertilizers release nutrients slowly and consistently, they also reduce the high cost of continuous application of fertilizers. Furthermore, nano fertilizers are highly capable of controlling the environmental pressure of the soil and the active ingredients as required. Although these unique properties of nano-based agricultural particles have made them a viable candidate, nanotechnology is still in its infancy in agriculture. A detailed study of the ecological pathways of these advanced organisms is not yet known and is being explored. When their adverse effects on ecosystems are fully understood and their long-term effects are well explored, the full potential of nanoparticles can be utilized.

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