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Research Article

Nanomaterial's synthesis, types and their use in bioremediation and agriculture

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Diseases, pests and pollutants are the major factors of agricultural production. They reduce a large proportion of agricultural production by reducing plant growth and development. Nano science can be utilized in the remediation of these problems in agriculture, as it provides a safer, efficient and effective way of agrochemicals delivery to the plants, resulting in increased agricultural production. Nanoparticles are widely used in the agricultural sector because of their distinctive properties. Studies have shown the influence of nanoparticles on plant growth and production. Nanoparticles act as effective carriers in the delivery of agrochemicals to plants. They provide site targeted delivery of nutrients and thus, prevent wastage of nutrients applied for plant growth and productivity. Bioremediation of pollutants is an emerging technology that provides Bio-Nano Materials for the protection of agriculture from pollution. This review aims to present and focus on the latest techniques used for the reduction of environmental pollution and improved agricultural production. This review speculates about the biosynthesis of nanomaterials from different sources like plants, fungi and bacteria along with chemical and organic synthesis from carbon, silver and gold. The role of nanoscience in detecting plant diseases and removal of heavy metals. Application of Nanoscience in storing, production, processing and transport of agricultural materials. It is also emphasized that Nanoscience may transform agriculture through innovation of new techniques like Precision farming, improvement of plants to engross nutrients, targeted use of inputs, detection and control of diseases and withstand environmental pressures. Further, efforts have been made in describing that nanoparticles may act as a better substitute for agricultural plant's growth and nutrition improvement by lowering the content of pollutants and pre-detection of diseases in plants. The biosynthetic route of nanomaterial synthesis could emerge as a better and safer option for environmental pollution reduction. Thus, nanoscience may increase agricultural production to feed a huge population in near future.

Key words: Bioremediation; nanomaterials; biosynthetic; sustainable; ecofriendly

INTRODUCTION

The challenging task of the 21st-50th century is to clean the environment in an eco-friendly and sustainable way, so, that the agricultural production can be increased. Although it is a new area still it is rapidly growing. Microbes are the emerging Nano-factories and have potentials for environmental clean-up methods. Most of the biogenic nanomaterials yielded satisfactory results. They can increase the production in an agricultural system. India is an agricultural dependent country. Its economy is also dependent on agricultural production. All animals, directly or indirectly, depends on agricultural production, for their food supply. Thus any change in agricultural production may affect the development and economy of any country like India. Diseases, lack of nutrients and pollution are three major reasons for the reduction in agricultural production. Among diseases, microbial diseases are becoming a vast problem in agriculture and the chemicals used in the remediation of these diseases are producing problems in animals that are consuming them. These toxic chemicals (*Fungicide, Herbicide and Bactericide*) causes a major loss of animal species like honey bee and birds which are beneficial for agricultural production (Wiyaratn, et al. 2012). These toxic chemicals also cause loss of beneficial bacteria's from soil which is involved in the decomposition of various waste materials and thus increasing soil fertility (Mandal, et al. 2006). Nowadays farmers adding nutrients more than their requirement by the

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plants. This extra quantity of nutrients are becoming wastage and directly affecting the farmer's income from agricultural production. Among pollutants, heavy metals are becoming a major problem in agricultural production. Heavy metals cause harmful effects to the agricultural plants and reduce their production. Heavy metals enter animals through food sources from plants and cause toxicity in them also. In short, if we are gaining on one hand but we are losing more on the other hand. So, as an outcome, we are losing a lot. This loss of agricultural production can be prevented by employing nanoparticle science technology for providing nutrients, diseases protection and protection from heavy metals pollution. Nanoscience or nanotechnology is a branch of science dealing with studies involving nano size (10-9 size of meter) particles. Nano can be applied to any unit of measure for example you can consider nanograms and nanoliters. The concept of nanoscience was first time driven by Richard Feynman in 1959 and from then it was growing very fast in all areas of research and development worldwide (Jain, et al. 2010). Nowadays, nanoscience is the subject of extensive research in all areas (Li, et al. 2007). It may bring the next industrial as well as the green revolution in the world (Satishkumar, et al. 2009). Nanoscience provides many environmental benefits to agriculture. These may be divided into nano-fertilizer, disease remediation and reduction of pollutants like heavy metals. The specific nanoscience application for onsite remediation of soil, air, groundwater and wastewater treatment are also in development. The size of nanoparticles has significance in their physiological and biochemical properties. It behaves completely different from its main part. The reduction in the size changes redox properties, thermodynamic properties and internal cohesive forces of the particle or material. It causes easy delivery and interaction of the particle with the active site (Li, et al. 2007). Nanoparticle synthesis using microorganisms comes under green nanoscience technology. It may provide a better alternative for diseases control in plants (Hsu, et al. 2015). Nanoscience is a persistent solution for our environment. It is needed to utilize new methods like nanoparticle science for better development in agriculture. Nanoscience can help us to design new materials with peculiar properties and reproducibility for agricultural development (Ndlovu, et al. 2020). In this concern, the scientific community should continuously focus on a very challenging and relevant research's direction, which is the development of nanoparticles capable of heavy metal remediation from soil and water. The concept of nanoscience may help us to understand the mechanism of transformation of heavy metals into plants and animals, more accurately at the molecular level. The synthesis of materials at the nanosize dimension will facilitate us to design new useful systems for heavy metal removal from plants. This review will provide information on different systems and methods which may be utilized to overcome heavy metal toxicity among agricultural lands across the globe.

NANOPARTICLES

The particle of very small size (<100 nm), of any material, is called a nanoparticle of that particular element. They are atomic or molecular aggregates of 1-100 nm dimension and their physicochemical properties modify drastically as compared to the bulk material. The properties of nanoparticles depend and may vary with their size i.e. the size of nanoparticles define their properties. Nanoparticles are more mobile and more reactive. They are roughly divided into organic and inorganic. The first category of organic nanoparticles comprises carbon nanoparticles. The second category inorganic nanomaterials comprise magnetic nanomaterials, noble metal nanoparticles like silver, gold nanoparticle and semiconductor nanoparticles like titanium dioxide, zinc oxide. Nanomaterials are also produced naturally by volcanic and lunar eruptions (Li, et al. 2013). These are known as natural nanoparticles but there are other classes of nanoparticles that are produced by anthropogenic activities like the exhaust of diesel, coal combustion and fumes of welding works; these are known as incidental nanoparticles. The nanoparticles synthesized by man are called engineered nanoparticles. The man-made or engineered nanoparticles includes nano zinc, nano aluminium, TiO_2, ZnO, quantum dots etc (Hočevar, et al. 2013). The smaller size of nanoparticles makes them more useful for use as sensors that can be easily deployed in remote locations. Currently, nanomaterials are being proved successful both in efficiency as well as cost-effective and also in the environmental friendly way in utilizing them as an alternative for current treatment materials for agricultural remediation (Rao, et al. 2007; Rodríguez-León, et al. 2013). The use of biologically synthesized nanomaterials has been increasing in the field of agriculture and medicine because of their stable, eco-friendly and cost-effective nature (Popescu, et al. 2010). They should be utilized in wider applications. The biological synthesis of nanomaterials is more advantageous over other methods due to ease of fast synthesis, ease of toxicity control, ease of size control, cost-effective and environmentally friendly methodology (Umashankari, et al. 2012). Nanoscience is being utilized extensively for the protection of agriculture from bacterial disease and pollutants including chemicals like heavy metals (Petla, et al. 2012).

UNIQUE PROPERTIES OF NANOPARTICLES AND THEIR CONTRIBUTION TO PLANT PRODUCTION AND GROWTH

The properties of nanoparticle changes with its size. Nanoparticles show different and unique properties when compared with their bulked product. Some examples are sown here below-Table 1. These properties showed a way to encapsulate and slow the release of agrochemicals used in plant growth and protection. The major roles of nanoparticles in increasing agricultural production are summarized in Table 2.

Table 1. Properties of nanoparticles along with their bulked forms.

Materials	Nanoparticle	Bulked
Copper	Hard	Soft
Gold	Chemically active	Chemically inactive
Silicon	Conductor	Insulator
Titanium dioxide	Colourless	White

Table 2. Contribution of nanoscience in plant production and growth.

Sl. No.	Contribution of Nanoscience
1.	Nano Materials (NM) can be effectively used in plant germination and growth.

2.	The carbon nanotubes can be used as regulators of seed germination and plant growth.
3.	Multi-Wall Carbon Nanotubes (MWCNTs) can enhance the growth of tobacco cell culture by 55-64% when compared to control at a wide range of concentrations from 5-500 µg ml-1.
4.	At low concentrations, activated carbon enhanced cell growth.
5.	Nanotechnology provides controlled and efficient use of fertilizers, pesticides and other agrochemicals for better growth and production of plants (Gudkov SV, et al. 2020).
6.	Chitosan nanoparticles are proved more effective anti-fungal agents against the pathogen (Fusarium solani).
7.	Silver nanoparticles act as antimicrobial agents and protect plants from microbial diseases.
8.	Copper nanoparticles may act as bio-pesticides and protect plants from pests.
9.	Zinc based nanoparticles inhibit fungal growth by damaging conidiophores.

SYNTHESIS OF NANOPARTICLES

Traditionally, there are several methods for generating nanoparticles, including gas condensation, abrasion, chemical precipitation, ion embedding, pyrolysis, and hydrothermal production. In abrasion, macro- or micro-scale elements are crushed in a ball mill, an earthly ball mill, or other size-reducing apparatus. The resulting particles are air categorized to recover nanoparticles. In pyrolysis, a vaporous precursor (liquid or gas) is forced through an orifice at high pressure and burned. The resulting solid (a version of soot) is air categorized to recover oxide particles from by-product gases. Old-style pyrolysis often results in aggregates and agglomerates rather than single primary particles. Ultrasonic nozzle Spray Pyrolysis (USP) on the other hand aids in preventing agglomerates from forming. These methods are costly for nanoparticle synthesis, there are other methods to produce nanoparticles cheaply as:

BIOGENIC PRODUCTION OF VARIOUS NANOPARTICLES

The microorganisms and plant extracts are used generally for a cheaper synthesis of nanoparticles (Figure 1). The main reaction involved in the biosynthesis of the nanoparticle is the oxidation/reduction reaction. It is a bottom-up approach for the synthesis of the nanoparticle. The biochemical antioxidants in the plant sample and biochemical enzymes in the microbial sample are responsible for the reduction of metal into their nanoparticles. Currently, there is million tons of production of nanoparticles worldwide and is probable to increase intensely in the near upcoming (Sekhon, 2010). The nanomaterials are materials having a particular dimension between 1-100 nm, so along with vascular plants; the microorganisms like bacteria, yeasts, algae, fungi, and actinomycetes may be used for nanoparticles biosynthesis (Saxena, et al. 2014).

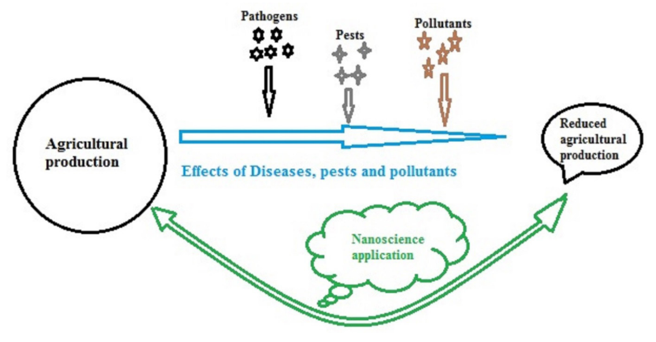

Figure 1. Effects of diseases, pests and pollutants.

NANOPARTICLES PRODUCED BY PLANTS

Nanoparticle synthesis from plant extract is called a green synthesis of the nanoparticle (Shebl, et al. 2019, Hassan, et al. 2020). Currently, it is gaining prominence because of the single-step involved in biosynthesis. So, it is a time-saving process along with no toxicants and the presence of natural capping agents (Saxena, et al. 2014). Plants material is easily available, they are safe to handle and possess a large variability of metabolites that aid in reduction. All these reasons make plants more advantageous over others for nanoparticle synthesis. Currently, there are many plants are being investigated for their importance in nanoparticles synthesis (Table 3). Phytochemicals consume less time for the reduction of metal ions, compared to fungi and bacteria. It shows plants materials as a better candidate for the biosynthesis of nanomaterials, compared to bacteria and fungi. By utilizing plant tissue culture and downstream processing techniques, one can synthesis nanomaterials of metallic and oxide at an industrial scale if the metabolic status of the plants are addressed appropriately. It is found that the nature of nanoparticles produced from this method varies with the plant to plant, mode of application, size, and quantity (Mathew, et al. 2010). It is revealed by the scientist that the investigation on nanoscience basically for plants is in its early stages; more depth study is required to reveal about biochemical, physiological and molecular mechanisms of plants in concern to nanomaterials and more work is required to explore the mechanism of nanomaterials actions, their behaviour towards biomolecules and their effect on gene regulation and expressions in plants. Generally, plant-based nanoparticles involve three mechanisms viz. adsorption, reduction and desorption mechanisms in the heavy metal removal process from plants, soil and water (Figure 2).

Table 3. Plants used for the synthesis of nanoparticles.

Nanoparticles	Plants species	References
Gold and silver nanoparticles	*Citrus sinensis*	Siddiqui MH, et al. 2015
	Diospyros kaki (Persimmon)	Sathyavathi R, et al. 2010
		Sweeney RY, et al. 2004
	Pelargonium graveolens	Pope JH, et al. 2000
	Hibiscus rosa sinensis	Parida UK, et al. 2011
	Coriandrum sativum	Arfin T,et al. 2013, Reddy MC,et al. 2015
	Emblica officinalis	
	Phyllanthium	Ankamwar B, et al. 2005
	Mushroom extract	Kavitha KS, et al. 2013
Gold nanoparticles	*Terminalia catappa*	Philip D, et al. 2009
	Banana peel	Ankamwar B, 2010
	Mucuna pruriens	Bankar A, et al. 2010
	Cinnamomum zeylanicum	Arulkumar S, et al. 2010
		Jung JY, et al. 2011
	Medicago sativa	Blaney LM, et al. 2007,
	Magnolia kobus and	Reddy MC, et al.2015
	Dyopiros kaki	Kathad U, et al. 2014
	Allium cepa L.	Pavani KV, et al. 2012
	Azadirachta indica A. Juss.	Parashar V, et al. 2009
		Boruah SK, et al. 2012
	Camellia sinensis L.	Dwivedi AD, et al. 2011
	Chenopodium album L.	Fazaludeena MF, et al. 2017
	Justicia gendarussa L.	
	Macrotyloma uniflorum (Lam) Verde	Aromal SA, et al. 2012
		Wiyaratn W, et al. 2012
	Mentha piperita L.	MubarakAli D, et al. 2012
	Mirabilis jalapa L.	
	Syzygium aromaticum (L)	Philip D, 2009
	Terminalia catappa L.	Raghunandan D, et al. 2010
	Amaranthus spinosus	

Silicon-Germanium (Si-Ge) nanoparticles	*Freshwater diatom Stauroneis sp.*	Yadav KK, et al. 2017, Roychoudhury A, 2020
Silver nanoparticles	*Elettaria cardamomom* *Parthenium hysterophorus* *Ocimum sp.* *Euphorbia hirta, Nerium indicum* *Azadirachta indica* *Brassica juncea* *Pongamia pinnata* *Clerodendrum inerme* *Gliricidia sepium* *Desmodium triflorum* *Opuntia ficus indica* *Coriandrum sativum* *Carica papaya (fruit)* *Pelargoneum graveolens* *Aloe vera extract* *Capsicum annum* *Avicennia marina* *Rhizophora mucronata* *Ceriops tagal* *Rumex hymenosepalus* *Pterocarpus santalinus* *Sonchus asper*	Fazaludeena MF, et al. 2017 Gurunathan S, et al. 2009, Vankar PS, et et al. 2010 Mandal D, et al. 2006 Gericke M, et al. 2006 SweeneyRY, et al.2004, Pugazhenthiran N, et al. 2009, Pavani KV, et al. 2012 Arfin T, et al. 2013 Vahabi K, et al. 2011 Raut Rajesh W, et al. 2009 Farooqui MA, et al. 2010 Monica RC, et al. 2009 Ahmad N, et al. 2011 Sekhon BS, 2010 Babu MG, et al. 2009 Jain D, et al. 2009 Jain PK, et al. 2006 Chandran SP, et al. 2006 Lin D, et al. 2007 Jain D, et al. 2010 Gnanajobitha G, et al. 2012 Rodríguez-León, et al. 2013 Dhas SP, et al. 2013 Kasthuri J, et al. 2009
Palladium nanoparticles	*Cinnamomum zeylanicum Blume.* *Cinnamomum camphora L.* *Gardenia jasminoides Ellis. Soybean (Glycine Max) L.*	Gudkov SV, et al. 2020 Pavani, KV, et al. 2012 Tang WW, et al. 2012 Jiang S, et al. 2009
Magnetic Nanoparticles	*Aloe vera*	Philip D, 2010
Lead Nanoparticles	*Vitus vinifera L.* *Jatropha curcas L.*	Petla RK, et al. 2012 Priya MM, et al. 2011
Nanoparticles of silver, nickel, cobalt, zinc and copper	*Brassica juncea, Medicago sativa and Helianthus annuus*	Juibari MM, et al. 2011
Platinum nanoparticles	*Diopyros kaki* *Ocimum sanctum L.*	Jung JY, et al. 2011 Sathyavathi R, et al. 2010

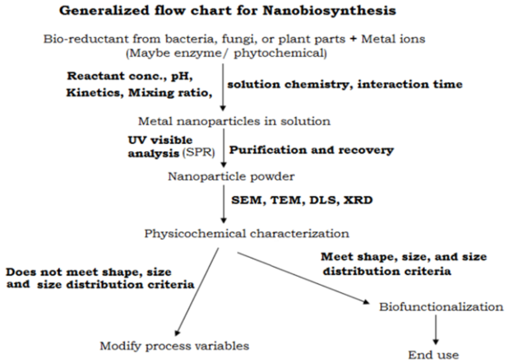

Figure 2. General outline for the biosynthesis of nanoparticles.

NANOPARTICLES PRODUCED BY BACTERIA

Bacteria possess the peculiar property of mobilization and immobilization of elements and in some cases, they may precipitate metals even in nanometer size. Therefore, Bacteria are called bio-factory for the production of nanomaterials like silver, gold, palladium, titanium, magnetite, cadmium and platinum. It is a new method of nanoparticle synthesis. In this method, bacterial enzymes are involved in catalyzing a specific breakdown reaction and produce nanoparticles (Bali, et al. 2006). The polysaccharides, vitamins, enzymes, biodegradable polymers and biological systems may be utilized for the synthesis of nanoparticles in the same way. The enzymes which are produced in extracellular secretion possess more advantage of the production of a large number of nanomaterials ranging size between 100-200 nm in a comparably pure form, and free from other materials like cellular proteins. These nanomaterials may be further purified by filtration easily. The metal binding and S-layer properties of bacteria make them more useful in the technical application of bioremediation and nanoscience. The different types of bacteria used for nanomaterials are shown (Table 4). The mechanism involved in silver nanoparticle synthesis by Pseudomonas aeruginosa is explained in Figure 3. The quality of nanoparticles produced by these techniques may be controlled by optimization of bacterial growth controlling parameters like enzymatic activities and cellular activities. Thus, there is a lot more to study to make proper use of this technique for nanomaterial synthesis. It is a more appealing field because of an ecofriendly, more stable, safe and less expensive process.

Table 4. Bacteria are used for the synthesis of nanoparticles.

Nanoparticles	Bacterium species	References
ZnS nanoparticles	Sulphate reducing bacteria of the family Desulfobacteriaceae	Sintubin L, et al. 2009, Smitha SL, et al. 2009, Lee JH, et al. 2007, Zhong LS, et al. 2007, Raut RW,et al. 2010, Srivastava NK, et al. 2008
CdS nanoparticles	Clostridicum thermoaceticum Klebsiella aerogens Escherichia coli	Olenin AY, et al. 2011 Wang P, et al. 2016 Robinson T, et al. 2001
As-S nanotubes	Shewanella sp.	Li S, et al. 2007
Palladium nanoparticles	Desulfovibrio desulfuricans NCIMB 8307	Nanda A, et al. 2009
Gold nanoparticles	Alkalothermophilic actinomycete Thermomonospora sp. Pseudomonas aeruginosa Lactobacillus strain	Sathishkumar M, et al. 2009 Sathishkumar M, et al. 2009 Ingale AG, et al. 2013 Sintubin L, et al. 2009
Magnetic nanoparticles	Magnetosirillium magneticum Sulphate reducing bacteria	Mathew L, et al. 2010 Gnanadesigan M, et al. 2012

Gold nanowires	Rhodopseudomonas capsulate	Husseiny MI, et al. 2007
Silver nanoparticles	Bacillus cereus Oscillatory willei NTDMO1 Escherichia coli Pseudomonis stuzeri Bacillus subtilis Bacillus sp. Bacillus cereus Bacillus thuringiensis Lactobacillus strains Pseudomonas stutzeri Corynebacterium Staphylococcus aureus Ureibacillus thermosphaericus	Pope JH, et al. 2000 Murugadoss G, et al. 2009 Li H, et al. 2011 Klaus-Joerger T, et al. 2001, Priya MM, et al. 2011, Joglekar S, et al.2011 Jampílek J, et al. 2011 Rathore KS, et al. 2008 Gardea-Torresdey JL, et al. 2002 Li L, et al. 2004 Lee JH, et al. 2007 Klaus-Joerger T, et al. 2001 Monica RC, et al. 2009 Narayanan KB, et al. 2008 Velammal SP, et al. 2016

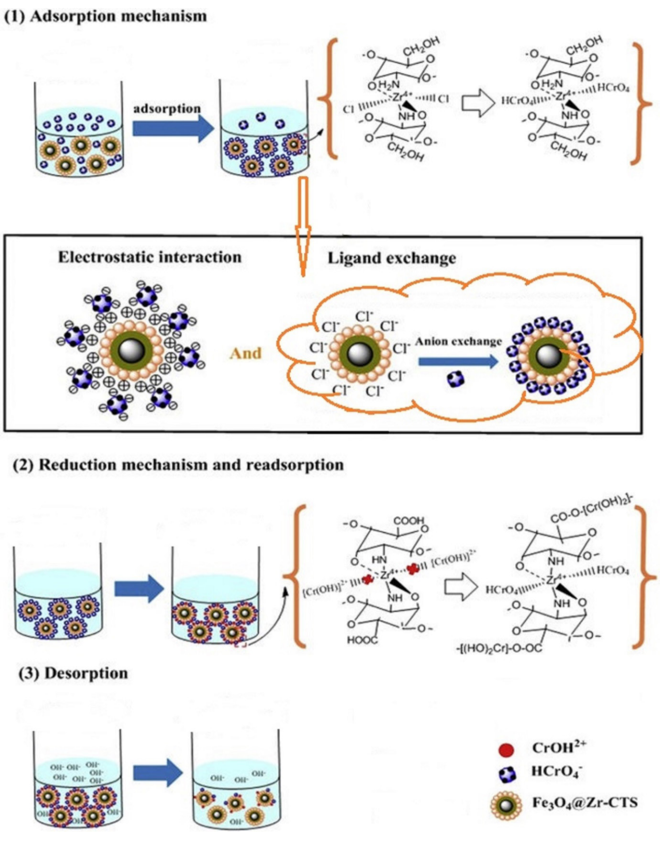

Figure 3. General mechanisms involved in heavy metal removal by plant-based nanoparticles from plants, soil and water.

NANOPARTICLES PRODUCED BY YEAST AND FUNGI

Fungi produce a larger amount of extracellular enzymes than bacteria, which shows more influence on nanomaterial synthesis. The documented mechanistic aspect governing nanoparticle synthesis by using fungi is explained here. The nanomaterials with well-defined dimensions can be synthesized by using fungi. Compared to bacteria, fungi can be used for larger production of nanomaterials because fungi secrete a larger amount of proteins which directly increases the formation of nanomaterials (Mathew, et al. 2010). Moreover, the protein isolates from fungi can also be used for nanoparticle formation. The enzymes produced by fungi during metal nanoparticle synthesis reduce salts to their metallic solid nanomaterials by the catalytic effect (Sweeney, et al. 2004). It is major weaknesses of this synthesis method by microorganisms and if need be corrected if this method is to participate with other methods. The other disadvantage of this method is that it generates nanomaterials at a slower rate than detected when plant extract is used. The other thing to be considered for the fungal synthesis of nanomaterials is that fungi should possess certain properties like high production of required metabolites/enzymes, high growth rate, easy handling in large scale production and require low cost for production techniques(Roychoudhury, 2020). Generally, fungi are observed as the best source for nanomaterial synthesis over other biological systems because of their easy handling, cost-effectiveness, and wide diversity. Genetic engineering may be employed for an ecofriendly and improved method of nanoparticle synthesis (Shankar, et al. 2003). In terms of the quality of nanomaterials and utilization of nutrients for microbial growth, yeast strains have assured benefits over bacteria (Popescu, et al. 2010).

ROLE OF NANOSCIENCE IN DETECTING PLANT DISEASES

There is a strong need to detect plant diseases in the early stage so that they can be protected from microbial agents and a great loss of food and agriculture can be prevented. Plant diseases are the most limiting factor for reducing crop productivity; the initial requirement to achieve control of plant disease is to recognize their causal organisms correctly. The identification process by involving traditional methods consumes a lot of time and inputs. But nanotechnological techniques such as nanoparticles and Quantum Dots (QDs), nano-imaging, nanostructured platforms, and nanopore tools for DNA sequencing requires less time and can be used for enhancing crop production and to ensure high-quality monitoring. In recent years, nanotechnology has emerged as a new diagnostic tool. Nano diagnostic kits help in preventing any epidemics at a much early stage which quickly detect the potential of plant pathogens and allows experts to help the farmers, thus nanotechnology can be applied for more cost-effective, quick, and accurate diagnostic plans of plant diseases. Nanotechnology may also be used for the delivery of pesticides at targeted/infected plant tissues, for pathogen detection and control of wound healing in plants. Nanoscience can be utilized in real-time monitoring systems, distributed throughout the fields, to monitor soil conditions and crop conditions, by providing or connecting an autonomous nanosensor to a GPS. This technique reduces the time required for observation of the crop in fields. It provides results within a few hours that are more accurate, simple and portable. This technique does not involve any complicated procedures and is so simple to be utilized by the farmers. The union of nanoscience with sensors technology may create new methods which allow early detection of diseases development and environmental changes.

Nanoscience provides a new way of changing crop management methods and improving plant nutrition. It reduces the problem of leaching, photolytic degradation, hydrolysis, and microbial degradation. It has reduced the wastage of nutrients by providing how a very low amount of required minimal effective concentration, reach the target site of crops.

NANOMATERIALS FOR HEAVY METALS REMOVAL

Heavy metals are distributed among soil, air, and water by natural or human activities like weathering, biodegradation, volcanic eruptions and mining, agrochemical industries; respectively. Heavy metals are increasing with human civilization. Any element having an atomic weight greater than 63.5 and has a specific gravity greater than 5.0 can be called heavy metal (Mueller, et al. 2012). Heavy metals are divided into toxic metals (Hg, Cr, Pb, Zn, Cu, Ni, Cd, Co, Sn); precious metals (Pd, Pt, Ag, Au, Ru) and radionuclides (U, Th, Ra, Am) (Kim, et al. 2013). These metals are non-biodegradable and very difficult to eliminate naturally from soil, air, and water. Generally, all metals are toxic when their values increase from their permissible limits. Heavy metals cause toxic effects in human's body when it exceeds the permissible limits. Various technologies have been used for heavy metal remediation like precipitation, reverse osmosis, advanced oxidation, coagulation, photoelectrochemistry, and flocculation. Each differs in the degree of remediation efficiency (Hočevar, et al. 2013, Turhan, et al. 2013). Currently, nanoscience has provided a great approach for heavy metal toxicity remediation by providing different nanomaterials. This technique is very beneficial over other techniques, some of the benefits are increased efficiency, reduced consumption and substation of more abundant and less toxic materials than ones used before. Generally adsorbing nanomaterials have shown great and effective work against heavy metal toxicity removal (Popescu, et al. 2010). Nanoparticles for heavy metal removal are divided into carbon-based nanoparticles (carbon nanotubes and graphene) and inorganic nanoparticles (based on metal oxides and metals). Different combination of nanoparticles is also developed for heavy metal removal. The disposal of nanoparticles may lead to release in the aquatic ecosystem which may prove harmful for them, this should be solved. The plants utilized in heavy metal removal are summarized in (Table 5). The interaction of nanoparticles with plant's biomolecules and removal of heavy metal cations and anions is explained in Figure 4.

Table 5. Plants utilized for nanoparticle generation and their role in bioremediation of heavy metals.

Plant species used for Nanoparticle generation	Best heavy metal bioremediation	Reference
Noaea mucronata	Pb(98%), Zn(79.03%), Cu(73.38%), Cd(72.04%) and Ni(33.61%)	Sekhon B.S, 2010
Euphorbia macroclada	Pb(92%), Zn(76.05%), Cu(74.66), Cd(69.08%) and Ni(31.50%)	Kalavathy H, 2010

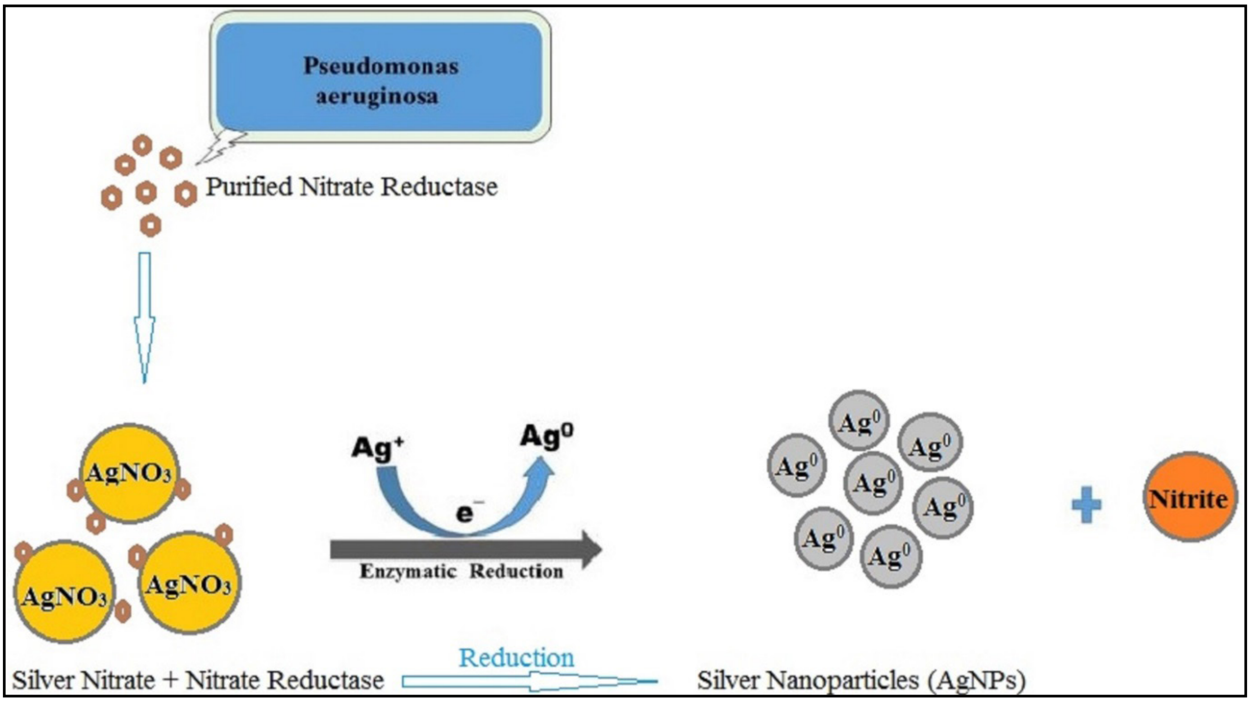

Figure 4. Mechanistic illustration of silver nanoparticle synthesis by bacterial involvement.

Carbon-based nanomaterials

Activated carbon: Activated carbon is produced from freely available carbonaceous precursors such as wood, coal, coconut shells and agricultural wastes. They possess high porosity and a large surface area. They are broadly used in wastewater treatments. These nanomaterials possess a high potential for the removal of organic and inorganic pollutants from contaminated water. Activated carbon has a significant weak acidic ion-exchange character which is involved in the removal of trace metal contaminants from wastewater by adsorption. (Zhong, et al. 2009) in his work observed the adsorption of pentavalent arsenic on granular activated carbon. The activated carbon synthesized from coconut tree sawdust was observed as an adsorbent for Cr (VI) and removes from wastewater (Nazeruddin, et al. 2016). Activated carbon is investigated for adsorption and stability of mercury on it (He, et al. 2008). The adsorption ability of powdered activated carbon was tested against Cu (II) and Pb (II) and was found 0.85, 0.89 µmol g-1; respectively. A new sodium polyacrylate grafted activated carbon was synthesized by gamma radiation to enhance functional groups on its surface. This procedure may be applied to other adsorbents to enhance the efficiency of metal ions adsorption by activated carbon (Ewecharoen, et al. 2009). Because of the low cost and high adsorption ability of activated carbons, they are appropriate materials for heavy metal removal.

Carbon nanotubes: Carbon nanotubes are like pillars for nanoscience. They are generally used in nanomaterial synthesis. Carbon nanotubes are divided into two groups as single-walled and multiwall nanotubes (Mallikarjuna, et al. 2012). Their potential as a superior adsorbent for heavy metals has been studied widely (Nair, et al. 2002; Lu, et al. 2006; Ahmaruzzaman, 2011; Zhu, et al. 2016). Currently, scientists are focusing on nanomaterial synthesis which shows specific adsorption towards a single solute in the target material and ignoring the interaction potentials between mixtures that may affect the adsorption process (Rao, et al. 2007, Wang, et al. 2009, Yang, et al. 2010, Hong, et al. 2012, Li, et al. 2007). Carbon nanotubes have been used as a better adsorbent for the removal of heavy metals like Pb2+, Cd2+, Ni2+, and Cu2+ (Petla, et al. 2012). The mechanism involved in heavy metal removal by carbon nanotubes comprises electrostatic attraction, adsorption, precipitation and chemical interaction between the metal ion and functional group present on the surface of carbon nanotubes. The drops in pH of the solution, when metal binds to carbon nanotubes indicate the transfer or release of the proton from carbon nanotubes where metal binds to it. Sometimes phenolic groups are also involved in heavy metal binding to carbon nanotubes. Moreover, an increase in metal ion concentration also increases the pH values of the solution and indicates the adsorption of heavy metal (Rao, et al. 2007). Various carbon nanotubes have been synthesized to improve adsorption capability and minimize weaknesses under different environmental circumstances, for the removal of heavy metals. The combination of magnetic properties of iron oxide with adsorption properties of carbon nanotubes may prove rapid, effective and promising technology for hazardous heavy metals removal (Kasthuri, et al. 2009). The maximum adsorption capacity of different heavy metals on carbon nanotubes differs among different heavy metals.

Graphenes: Graphene-based adsorbents have a great adsorption capacity for removing heavy metal pollutants from water and soil (Park, et al. 2005, Zhang, et al. 2003). Many researchers are focusing on and putting their efforts into investigating the potential application of graphene oxide nanomaterials in eliminating heavy metals from water and soil. The adsorption properties of graphene nanomaterials may be improved if graphene nanomaterial is synthesized by employing the Hummers method which incorporates many oxygen-containing groups like carboxyl and hydroxyl groups on the surface of nanomaterials (Mueller, et al. 2012). These functional groups increase the surface area of graphene oxide nanomaterial which further increases the adsorption capacity of nanomaterials for heavy metals. The mechanism of heavy metal removal by graphene nanomaterials is the same as was discussed for carbon nanotubes. The high dispersion nature of graphene oxide nanomaterials makes it more advantageous over carbon nanotubes. The other nanomaterials that have been studied include carbon fibre, carbon, nanoporous carbon and their complexes (Ahmed, et al. 2018, Prabhu, et al. 2012). They show exceptional adsorbent capacity for heavy metal removal and the rates of removal are persistent with pollution control requirements. Their efficiency depends on well-developed internal pore structures, large specific surface areas, and the presence of functional groups on surface nanomaterials.

Other nanomaterials: Along with carbon-based nanomaterials, other nanomaterials such as iron-based nanomaterials, photocatalytic nanomaterials, silica, alumina, and manganese dioxide nanomaterials are also explored for heavy metal pollutant removal. These nanoparticles have been engrossed for their outstanding adsorption properties. Some other nanomaterials which are utilized in the removal of heavy metal from soil, air and water are TiO_2 -Based Nanomaterials, ZnO –based nanomaterials, Iron oxide nanomaterials, bimetallic nanoparticles, and Metal based-nanomaterials (Pejman, et al. 2015). All possess excellent efficiency for the removal of heavy metal pollution from agricultural lands and irrigation water. But still, a lot of further research is required on nanoscience to remove heavy metals more efficiently and significantly from agricultural lands and water.

Nanotechnology has an enormous role in the field of nano-fertilizer. Nano-based fertilizer can do balanced nutrient supply, stimulated crop growth, improved crop quality, regulate nutrient migration to the environment, reduction of cost of production due to its less requirement per hectare (Mikula, et al. 2020), helps in precision farming, increased nutrient use efficiency of plants, increased drought and salt stress tolerance to plants (Kalia, et al. 2020). The two most important applications of nanotechnology in nano-fertilizers include the controlled release of fertilizers and the bio-availability of nutrients (Muhammad, et al. 2020). Apart from these two roles nanotechnology can also be used for the target modulation and regulation of Plant Growth-Promoting Rhizobacteria (PGPR) at the genetic or proteomic level (Fu, et al. 2020). In India, nano-fertilizers are used mostly to boost zinc uptake in wheat and other cereals, but there is a gap in research and its application by the farmers. Agriculture is facing various challenges such as climate changes, environmental issues, urbanization, sustainable use of resources and accumulation of pesticide and fertilizers. More research and work is needed to make these solutions possible at ground level i.e. to the farmer's level. There should be subsidized programs on the use of these technologies by the farmers so that maximum benefits of these technologies can be seen on ground level reality. All farmers should be made aware of the use and benefits of these products for their crops and particular farming process. Without these efforts the gap between research and its application by the farmers cannot be filled. Dr. G. Pandey in his review has shown the application and challenges of nanotechnology for sustainable agriculture in India (Pandey, 2020). The impact of different nano-fertilizers on the yield and growth characteristics of particular crops is illustrated in Table 6 and Table 7.

Nanotechnology has a promising approach in controlling the diseases of crops. It is beneficial over conventional approaches, such as reduced input requirements, better efficacy and lower eco-toxicity (Usman, et al. 2020). Nanomaterials may act as antimicrobial agents, biostimulants that induce plant innate immunity, and as carriers for active ingredients such as elicitors, micronutrients, and pesticides in controlling diseases (Rehmanullah, et al. 2020). Thus nanotechnology may provide potential benefits in the field of disease management and agricultural adaptations shortly.

The use of nanomaterials as agrochemicals either as fertilizers or pesticides is scientifically being explored before it could be used in agriculture for a general farm practice. The properties of nanomaterials such as type of material, shape, size, crystal phase, solubility, exposure and dosage concentrations are considered to be of the potential risk to human health (Shukla, 2019). However, some experts point out that food products containing nanomaterials available in the market are probably safe to eat, then also this area needs to be investigated more actively because detailed studies are required to address the impact and safety concern of nanomaterials within the human body when exposed to nanomaterials *via* food (Guha, et al. 2020).

Researchers have to develop proper assessment approaches to assess the impact of nanomaterials or nano-fertilizers on biotic and abiotic components of the ecosystem (Heinisch, et al. 2019). Amongst the different issues concerning the use of nanomaterials in agriculture, the nature of accumulation of nanomaterials in the environment and the focus on the edible part of plants might be the important issues before their use.

Nevertheless, Dr. S.K. Singh in his review has discussed the impending use of nanotechnology in the fields of food and agriculture such as nano-fertilizer, plant nutrition, and plant protection and suggested that nanoparticles may be toxic to the environment and biological system due to their changed physicochemical properties (Singh, et al. 2020). Thus while considering the benefits of nanomaterials researchers should also focus on the probable risk that may arise due to that nanomaterials.

Role of nanoparticles in precision farming

Advanced biosensors for precision farming are possible only by nanoparticles or nanochips. The modern nanotechnology has the potential to address the problems of conventional agriculture and can revolutionize this sector. The potential uses and benefits are enormous that includes insect pest management *via* formulations of nanomaterial based pesticides and insecticides, increase in agricultural productivity using nanoparticles encapsulated fertilizers for slow and sustained release of nutrients and water. Precision agriculture uses AgTech to collect detailed field and crop data, mainly using sensing technologies combined with geo-referencing. Over the last few decades, many new technologies have been developed for precision farming (Duhan, et al. 2017). Some of these are Satellite Positioning (GPS) system, remote sensing, automated steering system, geo-mapping and variable Rate Technology (VRT). Some other roles of nanoparticles in precision farming are listed in Figures 5 and 6.

Table 6. Impact of nano-fertilizers on yields of different crops under varying climatic conditions.

Nanofertilizers	Crops	Yield increment (%)
Nanofertilizer+urea	Rice	10.2
Nanofertilizer+urea	Rice	8.5
Nanofertilizer+urea	Wheat	6.5
Nanofertilizer+urea	Wheat	7.3
Nano-encapsulated phosphorous	Maize	10.9
Nano-encapsulated phosphorous	Soybean	167
Nano-encapsulated phosphorous	Wheat	28.8
Nano-encapsulated phosphorous	Vegetables	12.0-19.7
Nano chitosan-NPK fertilizers	Wheat	14.6
Nano chitosan	Tomato	20.0
Nano chitosan	Cucumber	9.3
Nano chitosan	Capsicum	11.S
Nano chitosan	Beet-root	8.4
Nano chitosan	Pea	20
Nanopowder of cotton seed and ammonium fertilizer	Sweet potato	16
Aqueous solution on nanoiron	Cereals	8-17
Nanoparticlesof ZnO	Cucumber	6.3
Nanoparticlesof ZnO	Peanut	4.8
Nanoparticlesof ZnO	Cabbage	9.1

Nanoparticlesof ZnO	Cauliflower	8.3
Nanoparticlesof ZnO	Chickpea	14.9
Rare earth oxides nanoparticles	Vegetables	7-45
Nanosilver+allicin	Cereals	4-8.S
Iron oxide nanoparticles+calcium carbonate nanoparticles + peat	Cereals	14.8-23.1
Sulfur nanoparticles+silicon dioxide nanoparticles+synthetic fertilizer	Cereals	3.4%-45%

Table 7. Impact of different nano-fertilizers on different growth and survival characteristics of particular crops.

Nanofertilizers	Crops	Imparted characteristics
Nanoparticles of ZnO	Chickpea	Increased germination, better root development, higher indoleacetic acid synthesis.
Nano silicon dioxide	Maize	Drought resistance, increment in lateral root roots number along with and shoot length.
Nano silicon dioxide	Maize	Increased leaf chlorophyll
Nano silicon dioxide	Tomato	Taller plants and increased tuber diameter.
Colloidal silica+NPK fertilizers	Tomato	Increased resistance to pathogens.
Nano-TiCi	Spinach	Improved vigor indices and 28% increased chlorophyll.
Polyethylene+indium oxide	Vegetables	Increased sunlight absorption
Polypropylene+indium-tin oxide	Vegetables	Increased sunlight utilization
Gold nanoparticles+sulfur	Grapes	Antioxidants and other human health benefits.
Kaolin+Si02	Vegetables	Improved water retention
Bentonite+N-fixing bacteria inoculation	Legumes	Improved soil fertility and resistance to insect-pest.
Nanocarbon+rare earth metals+N fertilizers	Cereals	Improved nitrogen use efficiency
Stevia extract+nanoparticles of Se+organo-Ca+rare-earth elements + chitosan	Vegetables	Enhanced root networking and root diameter
Nano-iron slag powder	Maize	Reduced incidence of insect-pest
Nano-iron+organic manures	Cotton	Controlled release of nutrients acts as an effective insecticide and improves soil fertility status.

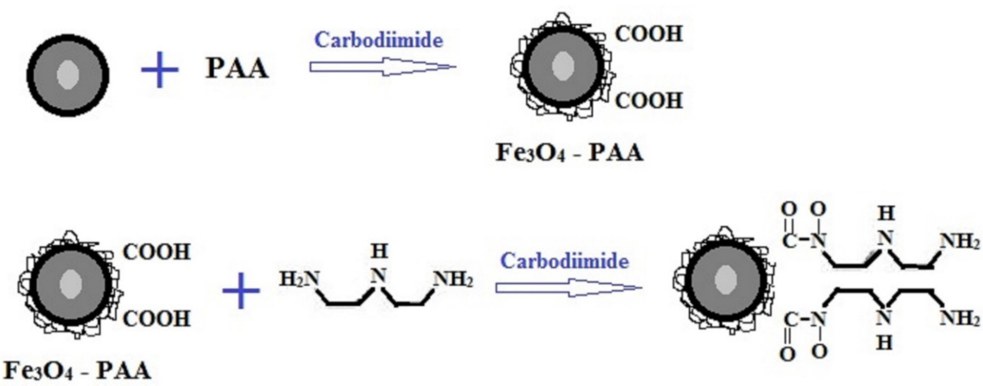

Figure 5. Iron oxide nanoparticle generation and activation of Poly-Acrylic Acid (PAA) by amino-functionalization on iron oxide nanoparticles as a new approach in making magnetic nano-adsorbent for metal cation and anions removal.

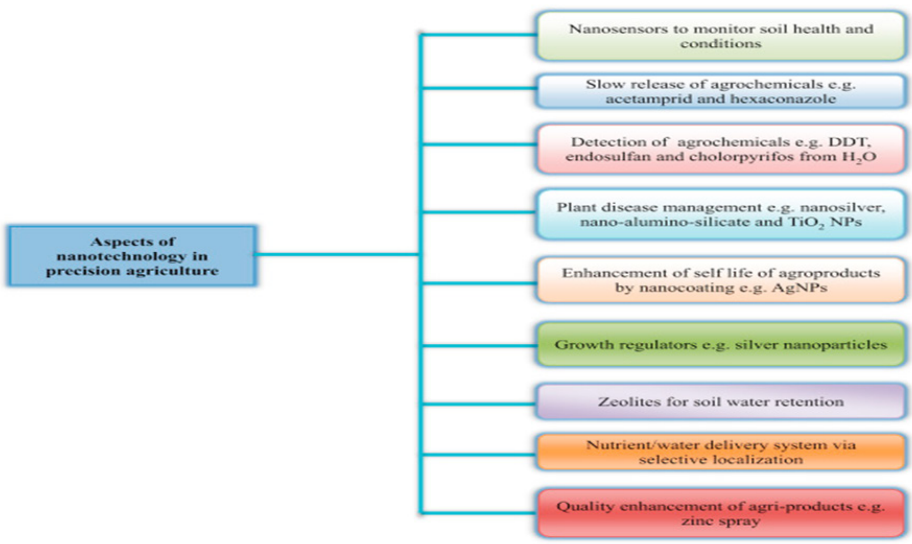

Figure 6. Applications of nanotechnology in precision agriculture.

FUTURE SCENARIOS

Nanotechnology is a capable domain of recent times. Metallic nanoparticles are mainly produced during enzymatic reactions. Mechanistic understandings may provide control over morphology, stability, and rate of synthesis of nanomaterials. Environmental contaminants are remediated by biologically synthesized nanomaterials (Masood, et al. 2013). Heavy metal pollution has been seen as a significant concern because of its hazardous impacts and non-biodegradable nature (Wu, et al. 2016). Bioremediation of heavy metal pollution has been preferred over other methods such as chemical precipitation and electrochemical methods (Diaz, et al. 2015). Microbes have been evolved and can offer inventive bio-based clean-up methods (Engel, 2017). Metal reducing microbes promotes precipitations, minerals dissolutions and transformations such as geochemical agents (Neumann, 2017). Microbial reduction methods have delivered a new way to explore nanotechnology. Bio-mineralization is among, one of them which controls the environmental impact of heavy metals (Kang, et al. 2017). The enzyme metal interaction here provides detoxification of heavy metals by a biotransformation process. Microbes that produce nitrate reductase can enhance the efficacy of the bioremediation process. Other enzymes along with nitrate reductase have been studied for further possibilities of heavy metal remediation. Microbe metal interaction and the importance of their enzymes still required further investigation (Waseem, et al. 2019). The studies of these microbial interactions at the genetic level may provide new genetic tools for bioremediation. These findings may assist in clarifying new phenomena such as antibiotic resistance (Ghosh, et al. 2012). The upsurge in antibiotic resistance is becoming a serious concern all over the world for modern medicine. The combination of metallic nanomaterials with antibiotics may overcome these problems such as bacterial resistance (Jang, et al. 2018). However, the co-occurrence of antibiotic resistance and metallic resistance genes has been reported recently. Thus microbes may play a critical role in controlling heavy metal pollution. The use of microbial nanomaterials for renewable energy needs further investigation.

CONCLUSION

Development in engineering and nanoscience technology may prove more helpful for generating new chances to develop more cost-effective and environmentally safe agricultural technologies. Nanoparticle has peculiar properties which make them more suitable to solve pollution problems. Current findings have indicated that nanomaterials are beneficial particles for heavy metal removal because of their unique and efficient properties in removing heavy metals from the agricultural system. The microbial threats to agricultural quality and production may also be removed with the help of nanotechnology. Zinc, chitosan and copper-based nanomaterials possess antimicrobial and antifungal properties which in turn can solve these microbial problems in agriculture and may increase agricultural production. Thus further research must be made in this direction to develop nanoparticles with greater stability, specificity and capability for simultaneous removal of multiple contaminants, and microbial pathogens from agriculture. It is not clear that why and how different species of plants show dissimilar resistance properties to nanoparticles. It is recommended to discover the effects of environmental factors on the uptake and accumulation of nanoparticles by different plant species. The route of nanoparticles movement in plant's cells and their effect on the genetic system of plants should be investigated.

CONFLICT OF INTERESTS

We do not corroborate that this work is original and has not been published elsewhere nor is it currently under consideration for publication elsewhere. We have no conflicts of interest concerning the publication of this paper.

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