CHAPTER 7

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NANOTECHNOLOGY IN SUSTAINABLE AGRICULTURE, SOIL CHEMISTRY AND REMEDIATION OF POLLUTED SOIL

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In the present time, the world is facing many grave issues especially associated with climate and we may witness more adverse events in the coming time. Uncontrolled population growth is adding further challenges to it, especially to the food security and sustainability of life. In the last decade, the world had a 690 million population undernourished and the COVID19 pandemic has added almost 83-132 million furthermore (Kah et al., 2019). The United Nations (UN) has projected that the population of the world will reach up to 10.9 billion by the year 2100 that would cause a 50% increased demand for food (Gerland et al., 2014). To cope up with food security, the UN has set a "Zero Hunger" goal under the sustainable development goals (SDGs) of the UN and the world would strive to achieve it by the year 2030 (Griggs et al., 2013).

Improving the yield and optimum utilization of resources has always been an approach to sustainable agriculture. Nanotechnology has been greatly appreciated for its contribution to the agriculture sector by improving the growth and yield of plants. Metals-based nanoparticles (NPs) that include Fe, Zn, and Cu act as micronutrients for the plants.

Some NPs are interestingly able to provide tolerance to various abiotic stresses. Such tolerance helps to restore the degraded land employing nanophytoremediation approaches. This chapter has highlighted the role of NPs in the efficient utilization of resources and enhancing the yield and of NPs in the agriculture sector. It also discussed the impact of NPs on soil and the restoration of degraded land using nanophytoremediation techniques.

1. INTRODUCTION

To achieve the food security goals it is of utmost necessity to bring scientific and technological innovations in the food and agriculture sector (Tanaka, 1999). Though the green revolution and biotechnology have strengthened the agriculture sector in the past at the same time, we have inevitably and heavily become reliant on agrochemicals knowing their adverse impact on the environment and ecosystem (Pimentel, 1996; Sandin and Moula, 2015).

The current agriculture practices also require a huge amount of water resources for irrigation, costlier agrochemicals, and manpower. Moving ahead towards the future with such strategies in agriculture is highly unlikely to achieve the UN SDG of “Zero Hunger” by 2030. Adopting eco-friendly agriculture with better yield, appropriate land use planning, efficient irrigations, phasing-off the use of harmful agrochemicals, and opting for integrated pest management (IPM) would certainly ensure sustainability in agriculture and also in living (Kah et al., 2018; Singh et al., 2016).

Nanotechnology (NT) is a rapidly rising area of science and technology that has enormous possibilities and also ensures to solve the key challenges associated with agriculture. By the year 2024, the NT market value may reach up to 125 billion USD (Liu and Xia, 2020; Rajput et al., 2020a). Nanotechnology has been easily accepted in the bioscience and agriculture sector; however, the hugeness of applications in the agriculture sector defines the NT as a budding stage (McNeil, 2005; Roco, 2003).

Nanoparticles (NPs) distribution in plants embraces a characteristic pathway that provides a better ability in protecting plants (Schwab et al., 2016). Such attributes of NPs are greatly contributed by their physicochemical characteristics such as size, surface-volume ratio, optical properties, etc. (Biju et al., 2008; Islam, 2019). Nano-pesticides, nano-herbicides, and nano-fertilizers with control release have been successful in grabbing the attention of the community. In the case of plant interaction with pathogens, NT offers an effective defence mechanism by delivering systemic chemicals such as jasmonic acid, salicylic acid, benzothiadiazole to the respective specific sites (De et al., 2014; Kashyap et al., 2015).

There are further applications of NT in agriculture which include mitigation of natural and bio-pesticide, measured and controlled release of nanomaterial assisted fertilizers, micronutrients, nano-sensors (Birthal, 2013; Khot et al., 2012; Rai et al., 2012; Rameshaiah et al., 2015).

Soil is an essence of agriculture and degraded soil quality is highly susceptible to affect yield qualitatively and quantitatively. Uncontrolled and mismanaged application of agrochemicals downgrade the soil quality and that can further affect the microenvironment and ecology of the soil (by affecting the beneficial soil microbes) (Timoshenko et al., 2021). It also affects non-target organisms (aquatic and terrestrial organisms) (Rajput et al., 2018b).

Nanoparticles used in agriculture release their constituent elements in the soil, elements like Zn, Cu, and Fe are readily utilized by the plants as micronutrients however metals like Ti and Cd may affect the physicochemical characteristics of the plants (Rajput et al., 2019a) as well as soil (Wani et al., 2017).

Nanoparticles have also been reported to have potential application in the remediation of pollutants from the soil. They are utilized to enhance the uptake of pollutants through plants generally termed nanophytoremediation (Peer et al., 2005). This chapter has discussed the key aspects of the application of NPs in agriculture specifically about enhancing the yield efficient utilization of resources. It also suggested the application of NPs in the remediation of soil through various recent approaches.

2. NANOTECHNOLOGY IN AGRICULTURE

Nanotechnology has got an immense application in agriculture and has been acknowledged in the agricultural community for a short time (Prasad et al., 2017; Subramanian and Tarafdar, 2011). Nanotechnology has been able to solve many conventional issues of agriculture essentially related to improving the efficacy and usage of pesticides, fertilizers, and other agrochemicals (Kah et al., 2018). Nanoparticles are capable of protecting the plant and promoting its growth (Biju et al., 2008; Islam, 2019). In agriculture, one of the best applications of NPs is the nano-encapsulation of agrochemicals with control release (Kah et al., 2018; Rameshaiah et al., 2015). Active ingredients can be delivered specifically to desired sites using the NPs and that is an excellent example of its application in agriculture. Such efforts ensure the improvement in the usage and efficiency of agrochemicals thus also protects the non-target organisms (El-Ghamry et al., 2018; Petosa et al., 2017). Application of NPs in biofertilizers (Rehmanullah et al., 2020), micronutrient (Monreal et al., 2016), assessment of toxic chemicals in agriculture produce (Chhipa, 2019; Ditta, 2012; Rai and Ingle, 2012; Usman et al., 2020) and nano-sensors (Birthal, 2013; Kaushal and Wani, 2017) are also advancement in the application of NPs in agriculture. Nanotechnology has done incredible efforts towards two basic aspects of agriculture that are key factors ensuring food security are: (a) improving the yield, and (b) efficient utilization of resources.

2.1 Efficient utilization of resources

The enhanced yield of the crops is a great aid to global food security, but it requires ideal crop nutrition. The modern agriculture system is completely dependent on fertilizers that ensure the availability of macronutrients (N, K, Mg, P, S, Ca,) as well as micronutrients (Cu, Mn, Fe, B, Cl, Mo, and Zn) (Broadley et al., 2012, 2007). Commercial fertilizers are claimed to impart nutrition to 30-50% of total crop yield (Snapp et al., 2005). Factors affecting nutrient use efficiency (NUE) are physico-chemical properties of soil, leaching of fertilizers, vaporization, and also the characteristics of the fertilizers (Baligar et al., 2001). The lower efficiency of the fertilizers signifies the high production cost as more amount of fertilizer would require maintaining nutrient availability. This would in turn affect the environment and ecosystem (Eriksen and Kjeldby, 1987). Higher productivity, profit along environmental production is considered as the best agriculture practices. Nanotechnology has strengthened the agriculture community in various terms including the use of nano-formulated fertilizers or smart fertilizers (Rameshaiah et al., 2015). Nano-careers are nano-structured NPs that carry the fertilizer and nutrients, and permit their controlled release in the soil (Worrall et al., 2018). The release event is dependent on the types of career and used fertilizers, thereby reducing the loss.

The application of nutrients can be done in various ways however some of the popular methods of applications are: (a) delivery as nano-scaled particle or emulsion and (b) encapsulation for allowing control release. In the latter case, the encapsulation is prepared in such a way that the shell can open only after receiving the desired stimulus from the environmental factors or man-induced signals.

Mechanism of the nutrient delivery are as follows:
Slow-release type: The capsule opens slowly and delivers the content; it is synchronized with assimilation by plants and leaching limits from the soil (Chhowalla, 2017).

Quick release: The encapsulated contents are released with the capsule encounters the surface of the leaves (Liu et al., 2018).

Specific/ recognition release: Such mode of delivery is meant for delivering the content when the capsule interacts with a specific receptor, that can be a molecule, or a functional group attached on the shell surface. Recognition of those receptors by the target triggers the release (Yang et al., 2014).

Moisture release: The encapsulated content is being delivered when it encounters water and releases the nutrient (Yoon et al., 2020)

pH release: The fertilizer containing encapsulation opens at particular pH, either an alkaline or acidic environment inside the plant tissues or cells triggers the release.

Magnetic/ultrasonic pulses: This type of encapsulation is man-controlled system and a magnetic or ultrasonic pulse triggers the release of fertilizers (Taurozzi et al., 2011).

These nano-structures allow control release of content as a function of time or interaction with a suitable environment for which those nano-structures have been created. Currently, studies have been done for testing the potential material for nano-careers. Zeolites, chitosan, and polyacrylic acids are mostly studied for this purpose (Dimkpa and Bindraban, 2017; Ditta and Arshad, 2016; Marchiol, 2018)**.**

2.2 Improving the crop yield

Improving the agriculture yield and rate of production have always been a matter of concern to global food security. Photosynthesis efficiency in C3 and C4 plants are different due to the undesirable role of ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO) (Qu et al., 2021). Around 85% of the plant population are C3 plants. C4 plants (e.g. maize, sugarcane, sorghum) have been reported to have nearly 50% higher photosynthetic capacity than the C3 plants (wheat, rice, barley, and potato) (Kajala et al., 2011). Recent studies have confirmed that it is realistic that enhancing the efficiency of photosynthesis can significantly improve crop yield. Improving the yield by modulating photosynthesis limits has been a matter of discussion for years.

In the past efforts are made to manipulate the process by (a) engineering C3 plants to utilize the C4 photosynthetic process (Hibberd et al., 2008; Kajala et al., 2011) (b) alternation in the size of chlorophyll antenna present in the photosystems (Melis, 2009), (c) enhancing the efficacy of RuBisCO(Amthor, 2007), (d) broadening of light waveband (Qiang et al., 2002), and refining the photoinhibition rate (Evans, 2013).

Many studies have confirmed the significant role of NPs in enhancing the photosynthetic process. Anatase crystal (TiO_2) has higher photocatalytic activity hence it was hypothesized that it can play a role in the absorption of light by the plant leaves thereby improving photosynthesis (Gao et al., 2008; Ji and Luo, 2019; Thomas and Syres, 2012).

The concept of nano-bionics in agriculture is to embed the NPs into plants to unleash some of their abilities that they cannot achieve without those NPs. Nanobionics modulate fast-growing plants to develop the important aspects to have an artificial photosynthetic system (Noji et al., 2011; Singh and Bell, 2016).

The role of single-walled carbon nanotubes (SWCNTs) as nano-bionics in *Spinacia oleracea* and *Arabidopsis thaliana* as nanobionics was shown. The study confirmed that SWCNT-chloroplast assembles and boosts the photosynthesis by thrice compare to control. It also increased the rate of electron transport (Clevers, 2011).

The role of TiO_2 NPs has also been reported to protect the chloroplast from photochemical stress. Such photochemical stress can lead to the aging of the chloroplast (Hong et al., 2005). It has also been involved in the activation of carboxylation RuBisCO that in turn increases the rate of photosynthesis (Qu et al., 2021; Suganami et al., 2021). Enhanced activity of RuBisCo in *Ocimum basilicum*, *Arabidopsis thaliana* and *Spinacia oleracea* (Kiapour et al., 2015; Lei et al., 2007).

Apart from photosynthesis, the conductance of water in leaves and the transpiration process is also enhanced. Titanium dioxide (TiO_2) has also been reported enhancing the chlorophyll content in the *Solanum lycopersicum*, and *Brassica napus* (Lei et al., 2007; Raliya et al., 2015).

Table 1. Application of various nanoparticles as nanobionics and their impact on photosynthesis.

No	Type of NPs	Effects	Mode of Action	References
1	Zinc oxide NP	Adverse	Zn NPs prevents the biogenesis of chlorophyll and affects PS-I thereby reducing the rate of photosynthesis	(Wang et al., 2016)
2	Copper (II) oxide	Adverse	Reduces the number of thylakoids in the granum. Also stops the expression of key proteins of the PS-I Higher concentration destroys PS-II	(Da Costa and Sharma, 2016)
3	Carbon nanodrops	Beneficial	Enhances the transport of electrons in PS I and II	(Sezgin et al., 2019)
4	Super paramagnetic Fe NP (Fe_3O_4, Fe_2O_4)	Adverse	They induce the production of ROS that destroys chlorophyll and components of PS-II thereby completely stopping photosynthesis	(Barhoumi et al., 2015)
5	TiO_2 NP NP	Adverse	Reduces the chlorophyll content and hampers the efficiency of PS-II. Does not affect the RuBisCO or Total sugar content (TSS)	(Dias et al., 2019)
6	Ag NP	Adverse	Leads to oxidation of chlorophyll and the apparatuses of Photosystem. It also affects the growth of the plant.	(Li et al., 2018)
7	Au NPs	Adverse	Induces the reabsorption of photoemission from PS-II. Improves photosynthesis	(Torres et al., 2018)
8	Silicon dioxide NPs	Beneficial	Allow plants to nurture in contaminated soil with metals. It reduces the uptake of contaminant metals and protects antioxidant system.	(Moura et al., 2020; Rizwan et al., 2019)
9	Aluminium oxide NPs	Adverse	Causes oxidative stress and affects the pigments of photosystem	(Vardar and Yanık, 2018)

Gold NPs (Au-NP) have also been studied for their effect on the photosynthetic abilities of the plant and it was found that Au NP increases photosynthesis by boosting the reabsorption of photoemission from photosystem II (Torres et al., 2018). Table 1 is appended below that exhibits the beneficial and adverse effects of NPs on the plant's photosynthetic ability.

3. RESTORATION OF DEGRADED SOIL

Several anthropogenic activities such as industrial, agricultural, and wastewater play a crucial role in contaminating the soil with persistent organic pollutants (POPs) (polyaromatic hydrocarbon, polychlorinated biphenyls, and pesticides), heavy metals, and also excess nutrients due to misuse of chemical fertilizers (Dror et al., 2017; Safari et al., 2020). Industrial expansion and expanding cities/urban are adding more of solid wastes, chemicals, and solvents, and many POPs. Soil consists of a matrix that has solid and aqueous phases having considerable amounts of colloids (Theng and Yuan, 2008).

Nanoparticles released in the soil can have different fates such as adsorption on soil particles, run off with water and leaching through the pores and making way to the groundwater (Rajput et al., 2020b). A fraction of the NPs can undergo degradation by physicochemical and biological processes. Some NPs get dispersed in the aqueous medium and then aggregate in various particle sizes (Tourinho et al., 2012) and absorbed easily compare to their respective bulk compounds/elements (Rajput et al., 2020a).

Soil pH positively affects the absorption of the NPs and gravitational force along with Brownian motion are playing a key role in the transport of NPs in the soil (Tourinho et al., 2012). The higher ionic strength of the aqueous phase allows stabilization of NPs, it also helps in aggregation and sedimentation (Peng et al., 2011). Metal-based NPs, e.g., Zn/ZnO, CuO, Fe, after their dissociation easily gets absorbed as micronutrients (Yusefi-Tanha et al., 2020).

Soil properties such as pH, soil structure, texture, organic matter content, degree of compactness, and soil microbial community greatly affect the bioavailability of metal-based NPs in soil (Rajput et al., 2018a; Timoshenko et al., 2021). The ionic strength of the soil also affects the mobility of NPs (Liu et al., 2016). The effect of NPs on soil is also dependent on the type of soil, the concentration of NPs, enzymatic activities, and soil microbiota (Rajput et al., 2018b). A schematic representation of fate of metal-based NPs in the soil has been illustrated by figure 1.

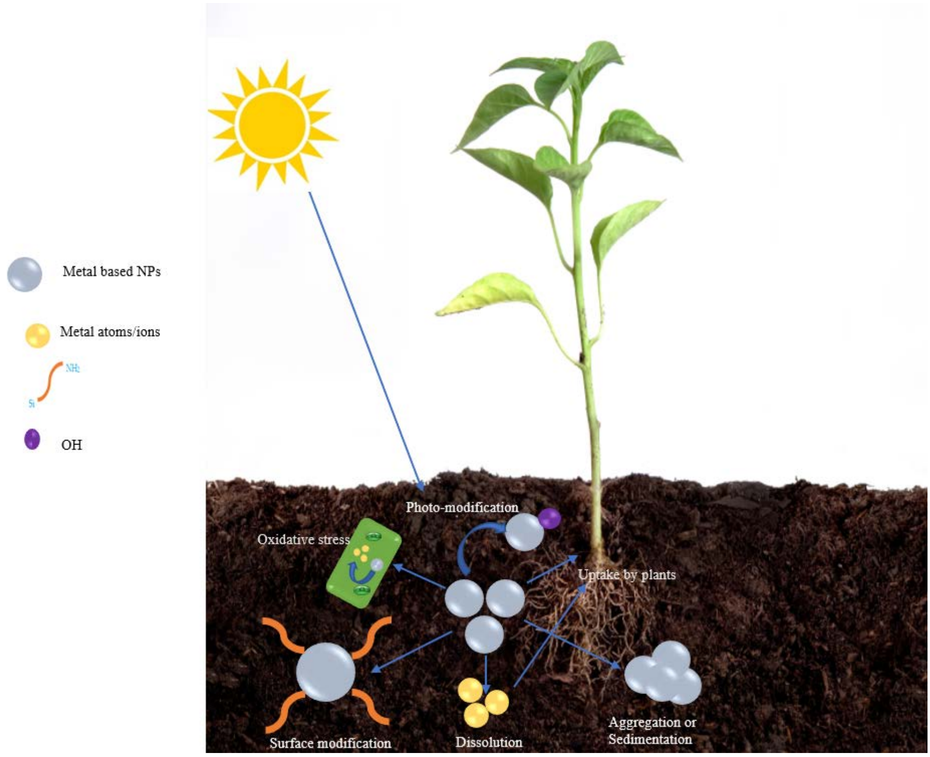

Figure 1. Schematic representation of fate of metal-based nanoparticles in soil

3.1 Improvement of contaminated soil using nanoparticles

Nanotechnology plays a significant role in soil remediation. Nanoparticles can be processed the target up to nanoscale. It increases the surface area per unit mass of the target material allowing it to come into contact with surrounding materials. This affects and enhances reactivity. It also reduces the activation energy prerequisite and makes the chemical reactions feasible.

Another physical phenomenon exhibited by surface plasmon resonance is used for the detection of toxic materials. Metal based NPs have advantages of their size because they possess the ability to diffusion and penetrate at very nanoscale and higher reactivity to redox-amenable contaminants.

A study on contaminant carbon tetrachloride reports that oxide-coated Fe NPs form a weak outer-sphere complex with it. Coating of oxide increases its reactivity and due to electron transfer, the carbon tetrachloride is being broken into carbon monoxide and methane. Similarly, benzoquinone, trichloroethene as well as other aliphatic hydrocarbon having chlorines can be broken down into smaller compounds with comparatively lesser toxicity (Windt et al., 2005).

Another similar example of pentachlorophenol degradation by *Shewanella oneidensis* using Palladium (Pd) as a biocatalyst. The NPs of Pd is being accumulated on the cell wall as well as inside of the cytoplasm of the organism. The Pd accumulated is charged with radicals using electron donor substrates hydrogen and acetate. The pentachlorophenol comes in contact with Pd carrying radicals and reacts with it catalytically by removing the chlorine from the compound (Quan et al., 2005).

Nanoparticles are aggressively used for remediation purposes (table 2). There have been reports use of NPs for remediation of various environmental media polluted with heavy metals, dyes, VOCs, POPs, pesticides, and PAHs.

Metal and metal oxide NPs are known for the removal of organic pollutants. An *in-situ* study using nanosized zero-valent iron (nZVI) NPs of Fe has shown excellent remediation properties for trichloroethane (a PCBs) and nitrobenzene (Zhao et al., 2016). The remediation rate can be further enhanced by altering those NPs with chemical functional groups, which can also provide target-specific degradation in water and air (Araújo et al., 2015; Qiao et al., 2019).

Table 2. Areas of environmental remediation where NPs are exclusively used.

Area of remediation	Target	NPs used	Reference
Dye removal	Rhodamine B	Iron (Fe)-doped ZrO_2	(Reddy et al., 2020)
	Rose Bengal dye	Hydrophilic polymeric membrane supported on Ag NPs	(Mofradi et al., 2020)
	Azo dye (Remazol Brilliant Blue R)	MgO NPs	(Moussavi and Mahmoudi, 2009)
Metal removal	Lead	Ag-doped TiO_2 nanofibres	(Srisitthiratkul et al., 2011)
		Fe_3O_4	(El-Kassas et al., 2016)
	Arsenic	Dispersed TiO_2 NPs anchored on Fe_3O_4	(Deng et al., 2019)
		Cobalt ferrite NPs aggregated	(Dey et al., 2014)
	Mercury	Au-graphene oxide-iron oxide (Au-GO-Fe_3O_4) nanoparticle	(Sanchez et al., 2020)
		Magnetic NPs coated with amino organic ligands and yam peel biomass	(Marimón-Bolívar et al., 2018)
Organic removal	2,4,6-Trichlorophenol	Ag-doped TiO_2	(Rengaraj and Li, 2006)
	Chlorpyrifos	Fe_3O_4	(Srinivasan et al., 2020)
	Oil removal	PVP-coated iron oxide NP	(Alabresm et al., 2018)
	γ-hexachlorocyclohexane	Fe-Pd bimetallic NPs	(Nagpal et al., 2010)

Future challenges are to develop NPs with better resistance to variation like pH, conductivity, and the concentration of pollutants for better stability, time, and cost-effectiveness (Zhang et al., 2019).

3.2 Phytoremediation of polluted soil assisted with nanoparticles: nanophytoremediation

Phytoremediation, i.e., remediation of pollutants from the soil using the plant at low-cost by applying effective method. Plants and related microbiome especially rhizobacteria helps in the modifications of soil in such a way that it becomes easier for the plants to eliminate, accumulate, or degrade the pollutants (Ashraf et al., 2019). The process is also used for the removal of contaminants from water bodies (surface water, and groundwater), and sludge (Chandra et al., 2017). Several approaches have been tried in the past to enhance the efficiency of phytoremediation, for example, the use of chemical additives, genetic engineering tools to alter the rhizobacteria helpful in phytoremediation (Gerhardt et al., 2017). But the use of NPs has added another dimension in the phytoremediation of soil (Gong et al., 2018).

Nanophytoremediation is an improved way of phytoremediation that includes nanotechnology and phytoremediation collectively. Nanoparticles owing to their physicochemical properties, help the process to occur at the nano-scale and improves the adsorption and degradation of pollutants (Mehndiratta et al., 2013). The use of NPs in phytoremediation is broadly studied but most studies are based on uses of carbon-based and metal-based NMs (Cai et al., 2019; Chen et al., 2017; Gong et al., 2009). Enzymes that are helpful in degradation are also used in nano-encapsulated forms and they possess better potential in the removal of complex POPs long-chain hydrocarbons are hard to degrade by microbial or plant remediation process (Chauhan et al., 2020**.** Zero valent iron (nZVI) is greatly known for its remediation potential and used for both metals and organic pollutant remediation. It is also used for the remediation of Trinitrotoluene (TNT) from soil using *Panicum maximum* (Guinea grass) and a 1/10 ratio of nZVI was able to remove all the TNT from the soil in 60 days.

Few successful field applications of NPs have been done in past for phytoremediation of soil. Ryegrass (*Lolium perenne* L.) has been widely used for the nanophytoremediation of Pb from the soil with 0.2% (w/w) nano-hydroxyapatite ((nHAP@BC) (Liang et al., 2017), Nano zerovalent iron (nZVI) and nZVI NPs (500-1000 mg/kg) (Zand and Tabrizi, 2020). The TiO_2 NPs has been reported to be useful for the removal of Cd from the soil using *Glycine max* (Singh and Lee, 2016). *Noccaea rotondifolia* subsp. Cepaeifolia is one of the most hyperaccumulator plant for the metals, especially Pb (Golestanifard et al., 2020).

Though phytoremediation couples with nanotechnology are advancing the remediation process certain challenges are ahead such as, the plant used for phytoremediation should be a fast grower with higher biomass, highly branched, and well-developed root system, it should also have the potential to tolerate, accumulate and degrade pollutants. Those plants must not be consumed by the human in any forms.

A review study has demonstrated that NPs are very helpful in providing tolerance in various abiotic stress conditions. It simulate germination, growth, and yield in various plants, enhances uptake of water, starch metabolism, improves photosynthetic ability, modulate plant hormone levels and oxidative stress, and also improves nutrient uptake (Rajput et al., 2021). However, the accumulation of NPs in soil even in plant tissues are growing challenge in recent days. It can induce stress and toxicity in the plants (Ranjan et al., 2021) and also affects the cellular and structural integrity of the plant and soil microbial community (Rajput et al., 2019b).

3.3 Future research directions

The scope of application of NPs in several sectors including agriculture is expanding exponentially. Agriculture has a huge scope of NPs application as fertilizer, growth promoter, and as plant health protector. On the one hand, it has been reported to be useful for the plant in optimum concentration whereas, on the other hand, it can harm the crop potentially. Unmanaged application of NPs can certainly become pollutants in the agricultural soil and aquatic system. The future direction of the work must be focussed the devising the permissible limits of various NPs in each sector, especially agriculture where the application is directly related to the many food chains, environment, ecosystem, and human lives. At the same time, it is necessary to establish the standard analytical methods for the detection of NPs in various environmental media. Further attention must be given to the formulations of NPs for agricultural applications to bring more novel products. The future scope of the research also should be focussed on the advancement of the remediation process in terms of new material, new eco-friendly methods for the synthesis of NPs, and exploring the NP-based remediation of pollutants that have not been explored.

4. CONCLUSION

Nanoparticles can modulate plant growth by affecting seed germination, root growth, and increased biomass in a dose-dependent manner. The application in agriculture, especially precision agriculture to reduce the resource utilization, and as nano-pesticides or nano-fertilizers to enhance the yield are increasing. It could also provide tolerance capability to plants to combat or cope up various environmental stresses. Such tolerance is helpful in the remediation of soil by those plants that are hyperaccumulators (heavy metals as well as organic pollutants). Since NPs have huge potential in agriculture therefore future aspects of the use of NPs in agriculture should be define the safe limits for application. Soil remediation using NPs is another aspect associated with agriculture; however, studies are pertaining to the identification and assessment of hyperaccumulator plants in the presence of NPs.

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