Potential and Risk of Nanotechnology Application in Agriculture *vis-à-vis* Nanomicronutrient Fertilizers

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Abstract

Nanotechnology had a wide potential of its novel applications in the fields of plant nutrition to meet the future demands of the growing population because nanoparticles (NPs) have unique physicochemical properties, i.e., high surface area, high reactivity, tunable pore size, and particle morphology. Management of optimum nutrients for sustainable crop production is a priority area of research in agriculture. In this regard, nanonutrition concerns with the provision of nanosized nutrients for sustainable crop production. The application of nanomaterials for delivery of nutrients and growth-promoting compounds to plants has become more and more popular and their utilization at the proper place, at the proper time, in the proper amount and of the proper composition affects the use efficacy of fertilizers. Using this technology, we can increase the efficiency of micronutrients delivery to plants. In the literature, various NPs and nanomaterials (NMs) have been successfully used for better nutrition of crop plants compared to the conventional fertilizers. This review summarizes the synthesis of nanofertilizers, characterization of nanofertilizers, NPs, and NMs as micronutrient fertilizers and describing their role in improving growth and yield of crops, uptake, translocation, and fate of nanofertilizers in plants and environmental hazard of NPs and NMs application.

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A. Rakshit et al. (eds.), *Soil Science: Fundamentals to Recent Advances*,
https://doi.org/10.1007/978-981-16-0917-6_26

Keywords

Health hazard · Nanomicronutrient fertilizers · Nanonutrition · Nanotechnology · Risk assessment

26.1 Introduction

Nanotechnology is one of the unique technologies of the twenty-first century. In the last decade, a large variety of nanomaterials (NMs) have been developed and used under the umbrella of nanotechnology in multifaceted sectors (Lien et al. 2017). The basis of nanotechnology was laid by Nobel laureate Richard P. Feynman through his popular lecture "There's Plenty of Room at the Bottom" (Feynman 1960). Taniguchi (1974) first coined the term nanotechnology and stated that nanotechnology consists of the processing, separation, consolidation, and deformation of materials by one atom or one molecule. The term "nanotechnology" is based on the prefix "nano" which hails from the Greek word meaning "dwarf." It is usually employed for materials having a size ranging from 1 to 100 nm (NNI 2009). Several researches had been awarded Nobel Prize for the development of nanotechnology (Table 26.1).

Nanotechnology, according to Joseph and Morrison (2006), is the modification or self-assembly of individual atoms, molecules, or molecular clusters into structures in order to produce materials devices with new or drastically different properties. Nanotechnology is the design, fabrication, and utilization of materials, structures, devices, and systems through control of matter on the nanometer length scale and exploitation of novel phenomena and properties (physical, chemical, biological) at that length scale in at least one dimension. Table 26.2 enlisted the size distribution of various natural and fabricated nanoparticles (NPs). At nanoscale, the chemical and physical properties of material change and surface area of material are large compared to its volume. This makes material more chemically reactive and changes the strength and electrical properties of material compared to the bulk counterpart. The synthesis protocols for diverse nanoparticles (NPs) were established and advanced to the molecular level (Gugliotti et al. 2004).Generally, it works by following the top-down (includes reducing the size of the smallest structures to the nanoscale) or

Table 26.1 Prizes for elucidating atoms and subatomic particles

Winners	Achievement	Nobel prize in the year
Gerd Binnig and Heinrich Rohrer	Scanning tunneling microscope	1986
Hans Dehmelt and Wolfgang Paul	Traps to isolate atoms and subatomic species	1989
George Charpak	Subatomic particle detectors	1992
Clifford Schull and Bertram Brockhouse	Neutron diffraction technique for structure determination	1994
Steven Chu, Claude Cohen Tannoudji, and William Phillips	Methods to cool and trap atoms with laser light	1997

Table 26.2 Comparison in size between natural and fabricated nanoscale objects

Object	Diameter (nm)
Hydrogen atom	0.1
Buckminsterfullerene (C_{60})	1.0
Six carbon atoms aligned	1.0
DNA (width)	2.0
Nanotube	3–30
Proteins	5–50
Quantum dots (of CdSe)	8.0
Dip pen nanolithography features	10–15
Microtubules	25
Ribosome	25
Virus	75–100
Nanoparticles range from	1–100
Semiconductor chip features	90

the bottom-up (comprises manipulating individual atoms and molecules into nanostructures with nearly similar chemistry or biology) approach.

Nanotechnology has emerged as a cutting-edge technology, acting as a convergent science that attracts a plethora of disciplines (environmental science, energy, plant science, agriculture, materials physics, and nanomedicine) and sectors closely linked with human welfare (Gruère 2012; Dasgupta et al. 2016). The application of nanotechnology in various fields anticipated to be advantageous for society and the environment, reduce the cost of input and cause inflation, boost the quality of goods, open opportunities for jobs (Hansen et al. 2008). A wide range of applications of nanotechnology have emerged into the “agrifood sector” which include the nanosensors, tracking devices, targeted delivery of required components, food safety, new product developments, precision processing, smart packaging, nanofertilizers, and others (McClements et al. 2009; Huang et al. 2010; Ranjan et al. 2014; Dasgupta et al. 2016). Nanotechnology can also improve the water solubility, thermal stability, and bioavailability of the functional compounds of food (McClements et al. 2009; McClements and Li 2010). The use of NPs imparted tremendous efficiency compared to bulk particles or particulate matter (PM) because of their large specific surface area, diverse functionalities, easy functionalization, the presence of active sites on the surface, extraordinary electrical and optical properties, extremely high stability, and high adsorption capacity (Boparai et al. 2011; Zhao et al. 2014; Choi et al. 2015; Jiang et al. 2015; Kumar et al. 2015).

26.2 Applications of Nanotechnology in Agriculture

The present day agriculture is facing many challenges, such as changing climate due to the greenhouse effect and global warming; urbanization due to life pattern changes; non-judicious use of resources like petroleum, natural gas, high-quality rock phosphate, etc., that are non-renewable; and environmental issues like run off,

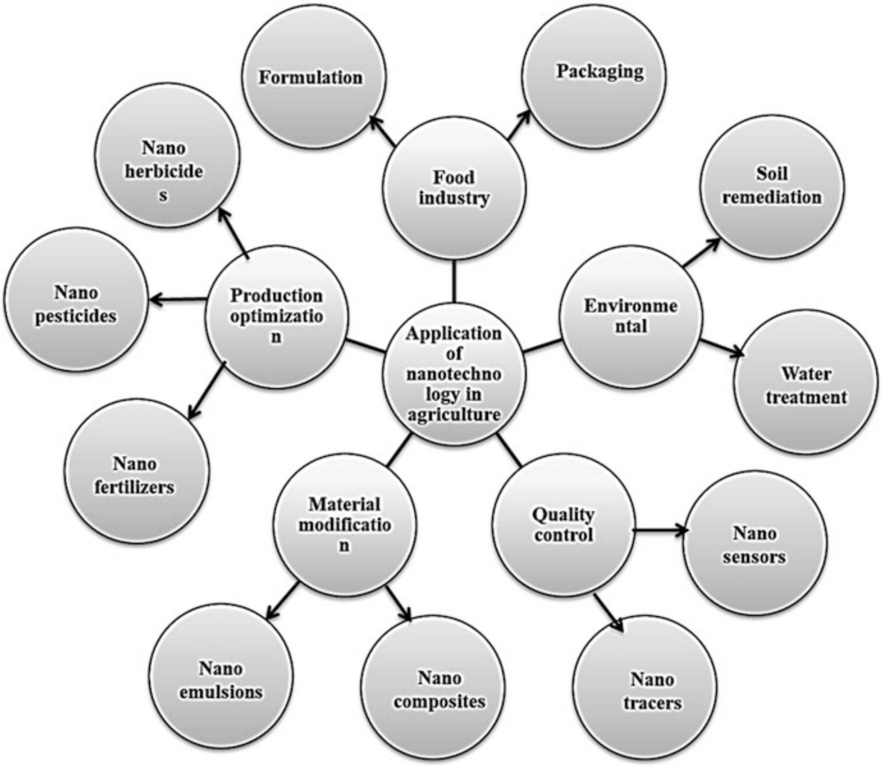

Fig. 26.1 Nanotechnological developments in agricultural field

eutrophication related with the application of more chemical fertilizers than required. These problems get more intensified by the world population, which is increasing at an alarming rate and is expected to reach 9.6 billion by the year 2050 (Desa 2008). The demand for global food production has increased during the last two decades. An increase by 70% in global grain production is required to feed this increasing world population (FAO 2009). Agriculture has always been the backbone of most of the developing countries to fuel the growth of economy. According to 2014–2015 estimates, India's population is 1.27. With the concern of providing food to such a big population, there is a need of new technology in agriculture giving more yields in short period.

A significant increase in agricultural production could be achieved through utilization of nanotechnology for efficient nutrient management system, good plant protection practices, efficient photocapturing system in plants, precision agriculture, and many others (Tarafdar et al. 2013; Prasad et al. 2014) (Fig. 26.1). Table 26.3 showed the cosmparison between nanofertilizers and conventional products. Applications of nanotechnology in materials science and biomass conversion technologies applied in agriculture are the basis of providing food, feed, fiber, fire,

Table 26.3 Property comparison between nanofertilizers and challenges in their applicability

Property	Nanofertilizer	Challenges	References
Controlled release	Nanofertilizers can control the speed and doses of nutrient solution release	Reactivity and composition variations due to environment factors	Duhan et al. (2017)
Nutrient loss	Leakage and waste caused by application of fertilizers can be reduced	Environmental effects after conclusion of the nanofertilizer life cycle	Chinnamuthu and Boopathi (2009)
Duration of release	Nanofertilizers can extend the duration of nutrient release in comparison with regular fertilizers	Phytotoxicity effects due to the dose and time of exposure	Servin and White (2016)
Efficiency	The uptake ratio is increased and the release time of nanostructures is reduced	Long-term environmental effects, as well as chronic effects on final consumers	Ditta and Arshad (2016)
Solubility and dispersion	Absorption and fixation of nutrients by the soil are improved, increasing their bioavailability	Complete ecotoxicological profiles, taking into account the consequences for health and the environment	Prasad et al. (2017)

and fuels. Nanotechnology provides a number of cutting-edge techniques for improving precision agricultural practices and allowing precise monitoring at the nanoscale level. In agriculture two types of nanomaterials are mostly used: (1) carbon based single- and multi-walled carbon nanotubes, (2) metal based aluminum, gold, zinc, and metal oxide based ZnO, TiO_2, and Al_2O_3. Single and multi-walled carbon nanotubes are used as nanosensors and plant regulator to enhance plant growth (Khodakovskaya et al. 2012). Nanosilica is used in filtration of food and beverages and packaging. Metal oxides like ZnO, TiO_2, and Al_2O_3 are used in nanofertilizers to boost the crop growth (Gogos et al. 2012; Sabir et al. 2014).

Application of nanotechnology has been regarded as an innovative and promising technology for sustainable agriculture, to feed the ever-increasing population of the world. It has revolutionized agriculture with innovative nutrients in the form of nanofertilizers (NFs), nanopesticides, and efficient water management system (Ditta and Arshad 2016). Conventional fertilizers with low use efficiency (20–50%) and cost-intensive increase in application rates have increased to develop and promote the use of NFs (Aziz et al. 2006). Many scientists worldwide have focused on this innovative field and have developed such NPs and NMs that could serve as nutrients for the plants (Liu and Lal 2015).

For agricultural use, it is preferable to have particle having size less than 20 nm, polydispersity index less than 1, zeta potential value apart from +30 mV and −30 mV, and mostly cubed shaped particle to enter through the plant pores (Tarafdar et al. 2012). Nanoparticles can be synthesized by physical, chemical, physicochemical (aerosol), and biological techniques. Grinding, thermal evaporation, sputtering, and pulse laser deposition technique are important physical methods. Chemical synthesis includes the technique like sol gel, co-precipitation, microwave synthesis, micro-encapsulation, hydrothermal methods, polyvinylpyrrolidone (PVP) method, and sonochemistry.

26.3 Nanofertilizers

Nanofertilizers are modified fertilizers synthesized by chemical, physical, or biological methods using nanotechnology to improve their attributes and composition, which can enhance the productivity of crops (Singh et al. 2017; Mahto et al. 2021). Nanofertilizers are nanomaterials that can supply one or more nutrients to the plants and enhance plant growth and yields or those that can improve the performance of conventional fertilizers but do not directly provide crops with nutrients. There are several advantage of using nanoformulation of fertilizers in agriculture (Table 26.4). Nanofertilizers can be classified as macronutrient nanofertilizers and micronutrient nanofertilizers (Fig. 26.2). Compared with the conventional fertilizers, these nanofertilizers are expected to significantly improve crop growth and yields, enhance the efficiency of fertilizer use and reduce nutrients losses, and/or minimize the adverse environmental impacts. Various benefits of using nanofertilizers are:

- Higher product quality with minimum remnants.
- Eco-friendly synthesis.
- Custom-made products.
- Lower-cost production, reducing the amount of fertilizers used.

Table 26.4 Advantages related to nanotech-modified formulation of conventional fertilizers

Desirable properties	Examples of nanofertilizers-enabled technologies
Controlled release formulation	The so-called smart fertilizers might become reality through transformed formulation of conventional products using nanotechnology. The nanostructured formulation could allow fertilizers to intelligently monitor nutrient release speed to fit crop uptake trends
Solubility and dispersion for mineral micronutrients	Nanosized formulation of mineral micronutrients may improve solubility and dispersion of insoluble nutrients in soil, reduce soil absorption and fixation, and increase the bioavailability
Nutrient uptake efficiency	Nanostructured formulation might increase fertilizer efficiency and uptake ratio of the soil nutrients in crop production and save fertilizer resource
Controlled release modes	Both release rate and release pattern of nutrients for water soluble fertilizers might be precisely controlled through encapsulation in envelope forms of semi-permeable membranes coated by resin-polymer, waxes, and sulfur
Effective duration of nutrient release	Nanostructured formulation can extend effective duration of nutrient supply of fertilizers into soil
Loss rate of fertilizer nutrients	Nanostructured formulation can reduce loss rate of fertilizer nutrients into soil by leaching and/or leaking

Source: modified from Cui et al. (2010)

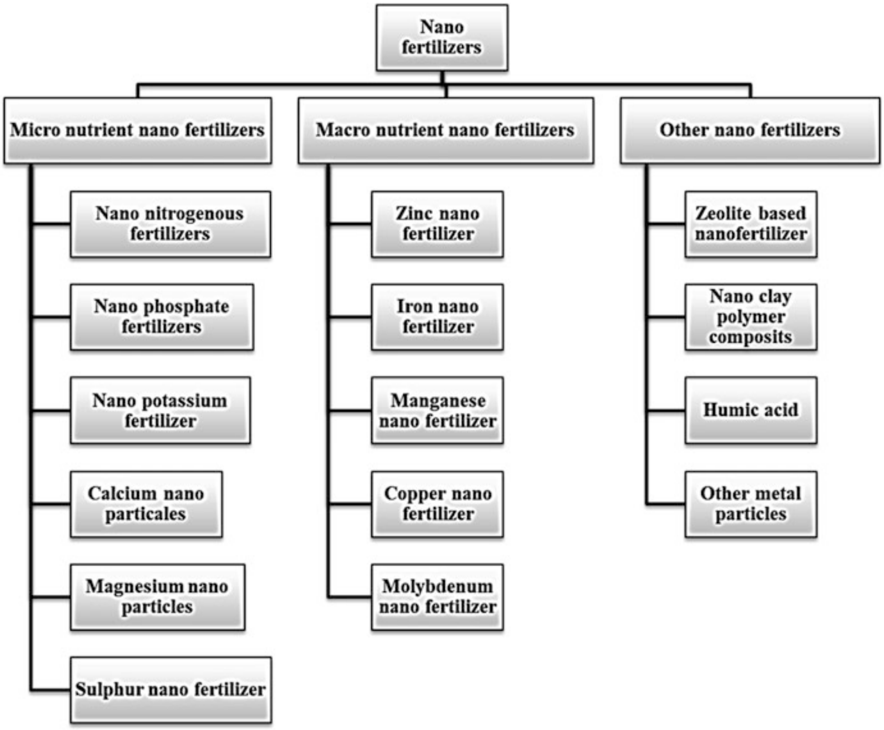

Fig. 26.2 Different types of nanofertilizers

- Less negative impacts and toxicity.
- Controlled release of plant nutrients.

Small size of the NFs facilitate its effective absorption by the plants due to the tremendous increase in the surface area (Fig. 26.3). Moreover, these have the ability to enter into the cells directly as these materials are small sized, which reduces/ bypasses the energy-intensive mechanisms of their uptake/delivery into the cell. Similar to the conventional fertilizers, NFs are dissolved in the soil solution and the plants can directly take them up. However, their solubility might be more than that of related bulk solids found in the rhizosphere due to their small size. These are more efficient compared to the ordinary fertilizers, as these reduce nutrient loss due to leaching, emissions, and long-term incorporation by soil microorganisms. Moreover, controlled release NFs may also improve fertilizer use efficiency (FUE) and soil deterioration by decreasing the toxic effects associated with over application of traditional chemical fertilizers (Suman et al. 2010). There are also reports about the use of nanoencapsulated slow release fertilizers. Recently, biodegradable, polymeric chitosan NPs (~78 nm) have been used for controlled release of NPK fertilizer sources such as urea, calcium phosphate, and potassium chloride (Corradini et al.

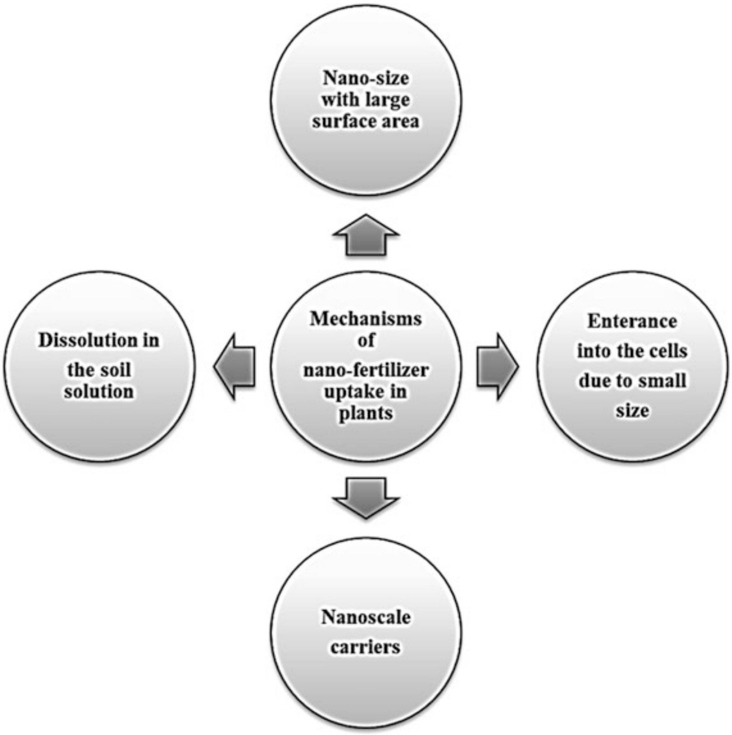

Fig. 26.3 General mechanisms employed by NFs for better uptake in plants

2010). Other NMs like kaolin and polymeric biocompatible NPs could also be utilized for this purpose (DeRosa et al. 2010).

26.3.1 Synthesis of Nanofertilizers

Nanofertilizers are synthesized by top-down (physical) or bottom-up (chemical) approaches. Top-down approach is a commonly used method. In top-down approach, the adsorbent or substrate used for synthesis of nanofertilizers such as zeolite or any other carrier is ball milled for several hours to achieve nanodimension. Usually, natural zeolite measures a range of 1000–3000 nm, and grinding using high-energy ball mill reduced the size of the particles. Manik and Subramanian (2014) reported that the ball milling of zeolite at 1, 2, 4, and 6 h had reduced the dimension 1078, 475, 398, 357, and 203 nm, respectively. The size reduction closely coincided with the increase in the respective surface area of 41, 55, 72, 83, and 110 $m^2 g^{-1}$. This phenomenal increase in the surface area provides extensive surface for nutrient adsorption and desorption. Despite the physical method of nanoparticle synthesis is very simple, the product is heterogeneous and particles often get agglomerated. To prevent agglomeration, stabilizing agents such as polymers or surfactants are used. Synthesis, characteristics, and nutrient release capability of some nanofertilizers are presented in Table 26.5.

The studies on slow release fertilizers (SRFs) based on zeolites are limited to nutrients, which can be loaded in cationic forms such as NH^{4+} and K^+. However, if the nutrients are in anionic forms such as $SO_4{}^{2-}$, NO^{3-}, and $PO_4{}^{3-}$, the loading is negligible on unmodified zeolites. Therefore, it is imperative that the material should have adequate affinity for anions so that the anionic nutrients can be efficiently loaded for its use as SRFs. Anionic properties can easily be imparted on the zeolitic surface using the concept of surface modification using surfactant. Surface modification facilitates the loading of anion into the zeolite's surface by the anion exchange process. Haggerty and Bowman (1994) reported that surfactant modified zeolite (SMZ), a type of inexpensive anion exchanger has been shown to remove anionic contaminants from water. Hexadecyltrimethylammonium bromide (HDTMABr), a cationic surfactant, was used for surface modification of zeolite. It has been found that HDTMABr loading with a maximum of 200 mmol kg^{-1} corresponds to 200% of the zeolite's effective cation exchange capacity. A surfactant bilayer forms and the surface reversed to positive (Li and Bowman 1997). Li et al. (1998) revealed that SMZ has been studied extensively in the last 15 years due to its high capacity of sorption and retention of oxyanions. The surfactant molecules (HDTMABr) form bilayers on zeolite external surfaces with the lower layer held by electrostatic interaction between the negatively charged zeolite surface and the positively charged surfactant head groups, while the upper layer is bound to the lower layer by hydrophobic forces between the surfactant tail groups in both layers (Bowman 2003). Surface modified zeolite showed positive results on the retention of chromate (Krishna et al. 2001) and phosphate (Bansiwal et al. 2006). Li and Zhang (2010) reported that the loading capacity of sulfate compared to nitrate on SMZ may be attributed to the charge effect of the anions. Each HDTMABr molecule contributes one positive charge, which needs only one negative charge to balance. Sulfate is divalent and thus needs two HDTMABr molecules to neutralize. Meanwhile, the HDTMABr surface configuration is not rigid because of the surfactant tail–tail interaction. Thus, bridging two HDTMABr molecules with one sulfate may be less favored compared to 1:1 neutralization of HDTMABr by nitrate.

26.3.2 Characterization of Nanofertilizers

Synthesized nanofertilizers are to be characterized using particle size analyzer (PSA), zeta analyzer, Fourier transform infrared spectroscopy (FTI-IR), Raman spectroscopy, X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDAX), transmission electron microscope (TEM), and atomic force microscope (AFM) to confirm the size, shape, charge distribution, functional groups, elemental composition, and attachment. The synthesized nanofertilizers have been characterized using the set of equipment (Table 26.6). Extensive studies had been undertaken to characterize nitrogenous

Table 26.5 Synthesis, characteristics, and nutrient release from nanofertilizers

Nutrients	Adsorbent	Approach	Size	Nutrient release (h)	References
N	Zeolite	Physical	25–30 nm	1200	Subramanian and Sharmila Rahale (2013)
	Montmorillonite	Physical	35–40 nm	400	
	Zeolite	Chemical	200 nm	–	Komarneni (2010)
	Surface crosslinked superabsorbents (hydrogels)	Chemical	40–80 nm	672	Liu et al. (2006a, b)
	Zeolite	Physical	420 μm	16	Li (2003)
	Hydroxyapatite nanoparticles + *Gliricidia Sepium*	Biological	19–25 nm	1440	Kottegoda et al. (2011)
	Zeolite	Physical	60 nm	1176	Selva Preetha (2011)
	Zeolite	Chemical	7–10 nm	480	Mohanraj (2013)
	Zeolite	Physical	87 nm	1152	Manik and Subramanian (2014)
	Montmorillonite	Chemical	50 μm	240	Bortolin et al. (2013)
P	Zeolite	Physical	25–30 nm	1104	Subramanian and Sharmila Rahale (2013)
	Montmorillonite, bentonite	Physical	35–40 nm	284	
	Zeolite	Physical	60 nm	1000	Selva Preetha (2011)
	Zeolite	Chemical	2–3 μm	1080	Bansiwal et al. (2006)
K	Zeolite	Physical	25–30 nm	1176	Subramanian and Sharmila Rahale (2013)
	Montmorillonite, bentonite	Physical	35–40 nm	216	
S	Zeolite	Physical	70–93 nm	816	Thirunavukkarasu (2014)
	Zeolite	Physical	420 μm	55	Li and Zhang (2010)
	Zeolite	Physical	60 nm	1520	Selva Preetha et al. (2014)
Zn	Zeolite	Physical	25–30 nm	1176	Subramanian and Sharmila Rahale (2013)
	Montmorillonite, bentonite	Physical	35–40 nm	312	
	Nano-Zn	Chemical	35 nm	–	Nair et al. (2010)
	Nano-ZnO	Chemical	20 nm	–	Mahajan et al. (2011)
B	Zeolite	Physical	60 nm	1,500	Selva Preetha (2011)

Table 26.6 Application of different instruments in characterization of nanoparticles

Instruments	Use in characterization
Particle size analyzer (PSA)	Measure particle size of suspensions or dry powders based on different technologies, such as high definition image processing, analysis of Brownian motion, gravitational settling of the particle, and light scattering (Rayleigh and Mie scattering) of the particles
Zeta analyzer	Measure effective electric charge on the nanoparticle surface and used as an indicator of dispersion stability
Fourier transform infrared spectroscopy (FTI-IR)	Identify different functional groups that are present in a system by measuring the vibrational frequencies of the chemical bonds involved
Raman spectroscopy	The use of inelastic scattering of light falling on a substance is used for non-destructive, microscopic, chemical analysis, and imaging of materials
X-ray diffraction (XRD)	X-ray diffraction (XRD) is a nondestructive technique that provides detailed information about the crystallographic structure, chemical composition, and physical properties of materials
Scanning electron microscope (SEM)	Measure surface topography and composition
Energy dispersive X-ray spectroscopy (EDAX)	Measure elemental analysis or chemical characterization of a sample
Transmission electron microscope (TEM)	TEM is the preferred method to directly measure nanoparticle size, grain size, size distribution, and morphology
Atomic force microscope (AFM)	3D characterization of nanoparticles with sub-nanometer resolution

(Subramanian and Sharmila Rahale 2013; Mohanraj 2013; Manik and Subramanian 2014), phosphatic (Bansiwal et al. 2006; Adhikari 2011; Behnassi et al. 2011), potassic (Subramanian and Sharmila Rahale 2012), sulfatic (Selva Preetha et al. 2014; Thirunavukkarasu 2014), and zinc (Subramanian and Sharmila Rahale 2012) fertilizers.

26.4 Micronutrient Nanofertilizers

Micronutrients play an important role in many physiological functions of plants. These are required in a very small amount ($\leq$100 ppm) but have a very critical role in various plant metabolic processes. These include chloride (Cl), iron (Fe), boron (B), manganese (Mn), zinc (Zn), copper (Cu), molybdenum (Mo), and nickel (Ni). These are applied to the plants either as Hoagland solution (Hoagland and Arnon 1950) or as foliar or applied in soil depending on crop species and also on the nutrient to be applied. These are also applied to the crop plants with composite fertilizers containing multiple macronutrients like NPK. Micronutrients present in these composites usually provide enough nutrients and cause little environmental risks. However, their availability is severely affected by small changes in pH, soil texture, and organic matter (Fageria 2009). So, it is most likely that under such circumstances, their optimum availability could be achieved through the application of NFs containing these micronutrients. A summary of the studies conducted regarding the investigation of the efficacy of each micronutrient-containing NPs is given in Table 26.7.

26.4.1 Zinc Nanofertilizer

Many researchers around the world have focused on finding the effect of ZnO-NPs on the growth and productivity of crops. Out of all the micronutrients, it is the most widely studied in plant science worldwide. For example, optimal concentration of ZnO-NPs significantly enhanced the growth and yield parameters of mung bean and chickpea (Mahajan et al. 2011). Optimal concentration of ZnO-NPs to be applied depends on the nature of the crop. With the application of 20 mg L^{-1} ZnO-NPs to mung bean plants, an increase of 42%, 41%, 98%, and 76% in root length, root biomass, shoot length, and shoot biomass, respectively, was recorded. Moreover, the application of higher doses of ZnO-NPs caused a decrease in the growth rates of mung bean and chickpea. In another greenhouse experiment, the application of ZnO-NPs at the rate of 400 and 800 mg kg^{-1} caused a significant increase in the growth and yield parameters of cucumber (*Cucumis sativus*) (Zhao et al. 2014). The results clearly showed an increase of 10% and 60% in plant root dry mass with the application of 400 and 800 mg kg^{-1}, respectively, as compared to control (without ZnO-NPs). However, the same rates caused a slight increase of 0.6% and 6% in the dry fruit weight, respectively, as compared to the control. Similarly, Lin and Xing (2007) reported a significant increase in the root elongation of germinated seeds of radish (*Raphanus sativus*) and rape (*Brassica napus*) with the application of ZnO-NPs at 2 mg L^{-1}, in comparison to control (deionized water). The authors also found a significant improvement in the growth parameters of ryegrass (*Lolium perenne*) with the application rate of 2 mg L^{-1} metallic Zn-NPs. Seed germination was improved with the application of lower concentrations of ZnO-NPs in peanut (Prasad et al. 2012), soybean (Sedghi et al. 2013), wheat (Ramesh et al. 2014), pearl millet (Tarafdar et al. 2014), tomato (Raliya et al. 2015), and onion (Raskar and Laware 2014). In another experiment, a significant improvement in *Cyamopsis tetragonoloba* plant biomass, shoot and root growth, root area, chlorophyll and protein synthesis, rhizospheric microbial population, acid phosphatase, alkaline phosphatase, and phytase activity in cluster bean rhizosphere was recorded with the application of ZnO-NPs (Raliya and Tarafdar 2013). Similarly, Helaly et al. (2014) found that ZnO-NPs supplemented with MS-media promoted somatic embryogenesis, shooting, regeneration of plantlets, and also induced proline synthesis, activity of superoxide dismutase, catalase, and peroxidase, thereby improving tolerance to biotic stress. In contrast to these studies, many researchers have reported phytotoxicity of the application of Zn-NPs in various crop plants (Mahajan et al. 2011; Lin and Xing 2007; Lee et al. 2010; López-Moreno et al. 2010). However, phytotoxicity depends on the nature of crop plants. Overall, most

Table 26.7 Nanomicronutrient fertilizers and their effects on plant growth parameters

Nutrient provided	Crop and experimental conditions	Size	Rate of application	Comments	References
Zn	*Vigna radiata* and *Cicer arientinum*, incubated 60 h in agar medium	20 nm	ZnO at 1–2000 mg L^{-1}	Growth and yield parameters in both improved	Mahajan et al. (2011)
	Cucumis sativus, 53 days greenhouse pot study	10 nm	ZnO at 400 and 800 mg kg^{-1} soil	Root dry mass, fruit starch, glutelin, and Zn contents significantly improved	Zhao et al. (2014)
	Brassica napus and *Lolium perenne*, 5 days germination	ZnO NP 20 nm and metallic Zn 35 nm	ZnO at 1–2000 mg L^{-1} applied to *Brassica napus* and metallic Zn at 1–2000 mg L^{-1} applied to *Lolium perenne*	Improved root elongation in both and Zn-NPs at levels higher than the optimum showed phytotoxicity	Lin and Xing (2007)
	Arachis hypogaea germination and field trial during 2008–2010	nZnO 25 nm	nZnO at 1000 ppm and chelated bulk zinc sulfate ($ZnSO_4$), a field experiment with nZnO applied at 15 times lower dose compared to chelated $ZnSO_4$	Promoted both seed germination and seedling vigor, early flowering, higher leaf chlorophyll content, pod yield per plant compared to chelated bulk $ZnSO_4$; in field experiment, there was higher pod yield compared to chelated $ZnSO_4$	Prasad et al. (2012)
	Glycine max L.	–	nZnO at 0, 0.5, and 1 g L^{-1}	Increased germination over control; greater radicle length and fresh weight in stressed seedling	Sedghi et al. (2013)
	Triticum aestivum L.	–	nZnO at 20–50 nm	Significantly increased chlorophyll and protein content	Ramesh et al. (2014)
	Pennisetum americanum	15–25 nm	Biosynthesized Zn-NPs sprayed at 16 L ha^{-1} after 2 weeks of germination at 10 ppm	Improved growth, physiological, biochemical, and yield parameters over control in 6-week-old plants	Tarafdar et al. (2014)
	Solanum lycopersicum L.	25 ± 3.5 nm	TiO_2- and ZnO-NPs at 0–1000 ppm	Promoted growth and development	Raliya et al. (2015)

(continued)

Table 26.7 (continued)

Nutrient provided	Crop and experimental conditions	Size	Rate of application	Comments	References
	Allium cepa	–	ZnO-NPs at 0.0, 10, 20, 30, and 40 g mL^{-1}	Low concentrations increased seed germination but decreased under higher ones	Raskar and Laware (2014)
	Cyamopsis tetragonoloba L.	–	Biosynthesized nZnO foliar sprayed at 10 ppm	Improved growth, yield, and quality parameters	Raliya and Tarafdar (2013)
	Musa acuminata in vitro cultures	–	nZn and nZnO	Somaclones accumulated more proline, chlorophyll, antioxidant enzymes activity, and developed more dry weight than the control	Helaly et al. (2014)
	Arabidopsis thaliana (mouse-ear cress)	–	nZnO at 400, 2000, and 4000 mg L^{-1}	nZnO was most phytotoxic; inhibition of seed germination depended on particle size at equivalent concentrations	Lee et al. (2010)
	Medicago sativa, *Cucumis sativus*, and *Solanum lycopersicum*	–	nZnO at 0–1600 mg L^{-1} and Zn^{2+} at 0–250 mg L^{-1}	While it decreased in Medicago sativa and Solanum lycopersicum, observed highest Zn content in alfalfa with 1600 mg L^{-1} nZnO and 250 mg L^{-1} Zn^{2+}	de la Rosa et al. (2013)
	Lolium perenne	–	nZnO and nZn^{2+}	Reduced biomass, root tips shrank, and root epidermal and cortical cells highly vacuolated/collapsed; nZnO was observed in apoplast and protoplast of the root endodermis and stele	Taran et al. (2014)
Fe	*Vigna unguiculata* subsp. *unguiculata*, foliar application, field study	–	Fe-NPs at 0.25 and 0.5 g L^{-1}	More 1000-seed weight, leaf Fe, and chlorophyll content compared to regular Fe salt	Liu et al. (2005)

	Glycine max greenhouse test 7 days, perlite medium, nutrient solution	18.9–20.3 nm	Superparamagnetic iron oxide NPs, Fe_3O_4 at 30, 45, and 60 mg L^{-1}	Chlorophyll contents increased up to 45 mg L^{-1} but decreased at 60 mg L^{-1}	Fageria (2009)
	Cucurbita pepo cultivated in vitro	–	Carbon-coated Fe-NPs	–	Malekian et al. (2011)
Mn	*Vigna radiata* 15 days in growth chamber, perlite medium, nutrient solution	20 nm	Metallic Mn at 0.05, 0.1, 0.5, and 1.0 mg L^{-1}, $MnSO_4$	Metallic Mn increased growth and physiological parameters more compared to $MnSO_4$; Mn-NPs did not show phytotoxicity	Ghafariyan et al. (2013)
Cu	*Phaseolus radiatus* and *Triticum aestivum*		nCu	The 2-day median effective concentrations for *P. radiatus* and *T. aestivum* exposed to nCu were 335 and 570 mg L^{-1}, respectively	Lee et al. (2008)
	Cucurbita pepo		Bulk and Cu-NPs and Ag-NPs were directly compared	Bulk and NP Cu were highly phytotoxic; humic acid (50 mg L^{-1}) decreased the ion content of bulk Cu solution but increased Cu^{2+} of NP solutions	Musante and White (2012)
	Lactuca sativa, 15-day germination, soil	50 nm	Metallic Cu at 130 and 600 mg kg^{-1} as Cu	Increased shoot:root ratio, total N, and organic matter at 130 mg kg^{-1}	Shah and Belozerova (2009)
	Elodea densa planch, 3-day incubation, water	30 nm	70% CuO and 30% Cu_2O at 0.025, 0.25, 0.5, 1, and 5 mg L^{-1} as Cu, $CuSO_4$	Increased photosynthesis rate but leaf Cu at <0.5 mg L^{-1} $CuSO_4$ inhibitory at all concentrations	Nekrasova et al. (2011)
Mo	*Cicer arietinum*, rhizosphere soil examination	100–250 nm	Mo at 8 mg L^{-1}, others unknown	Improved nodule number/mass, activity of antioxidant enzymes, and symbiotic bacteria	Taran et al. (2014)

of the crop plants usually require merely 0.05 mg L^{-1} soil solution. The researchers in these studies applied metallic Zn-NPs at a very high rate, ranging from 400 to 2000 mg L^{-1}, which was the main reason for their toxic effects. Even the application of Zn-NPs at 10 mg L^{-1} to ryegrass proved harmful for normal growth (Lin and Xing 2008). In another study, among cucumber, alfalfa, and tomato, the application of ZnO-NPs only enhanced seed germination of cucumber (de la Rosa et al. 2013).

26.4.2 Iron Nanofertilizer

In a greenhouse study under a hydroponic system, application of lower concentrations of Fe-NPs (30, 45, and 60 mg L^{-1}) significantly improved the chlorophyll contents of the sub-apical leaves of soybean compared to the regular application of Fe-EDTA (Ghafariyan et al. 2013). The results suggested that Fe-NPs could serve as an efficient source of Fe compared to the regular Fe-EDTA applied at <45 mg L^{-1} as Fe, thereby reducing the chloratic symptoms caused by its deficiency in soybean. Moreover, the uptake efficiency of Fe-NPs in the plant body was enhanced, which ultimately increased the chlorophyll contents of soybean plants. In another experiment, growth and yield parameters of black-eyed peas were significantly improved when Fe-NPs were applied as foliar at 500 mg L^{-1} (Delfani et al. 2014). Moreover, the application of Fe-NPs improved the effect of another fertilizer nutrient applied in the form of Mg-NPs. Previously, Hoagland and Arnon (1950) found that most of the plants generally require 1–5 mg L^{-1} Fe in soil solution.

26.4.3 Manganese Nanofertilizer

A hydroponic culture experiment was conducted to find out the comparative efficacy of Mn-NPs and commonly used Mn-salt, i.e., $MnSO_4$, on the growth and yield parameters of mung bean (Pradhan et al. 2013). Both were applied at 0.05, 0.1, 0.5, and 1.0 mg L^{-1}. The results showed that application of Mn-NPs at 0.05 mg L^{-1} significantly improved growth and yield parameters compared to the control with no Mn applied. At higher doses, Mn-NPs did not show toxicity to the bean plants, while $MnSO_4$ applied at 1 mg L^{-1} showed toxic effects like necrotic leaves, brown roots, and gradual disappearance of the rootlet after 15 days of treatment. Moreover, greater oxygen evolution and photophosphorylation in Mn-NP-treated chloroplasts was noted compared to the control. Greater oxygen evolution was caused by enhanced splitting of water in the oxygen-evolving center located in the chloroplast. The authors concluded that Mn-NPs could serve as a potential modulator of photochemistry in the agriculture sector.

26.4.4 Copper Nanofertilizer

Previously, it has been clearly found that the application rate of Cu-NPs at Cu 0.02 mg L^{-1} in Hoagland solution is optimum for normal growth and yield of crops. Scientists around the world have found toxic effects of the application of Cu-NPs, as they have applied them at higher rates than required (Lee et al. 2008; Musante and White 2012). They found that Cu-NPs applied at the rate of 200–1000 mg L^{-1} caused toxic effects on seedling growth of mung bean, wheat, and yellow squash. Similarly, reduced biomass of zucchini by 90% compared to that of the control (without Cu) after the seedlings were incubated in Hoagland solution for 14 days was recorded with the application of metallic Cu-NPs at 1000 mg L^{-1}. However, researchers like Shah and Belozerova (2009) recorded a significant increase of 40% and 91% in 15-day lettuce seedling growth rate with the application of Cu-NPs at 130 and 600 mg kg^{-1}, respectively. Similarly, a 35% increase in photosynthetic rate of waterweed was recorded in a 3-day incubation study using a low concentration of Cu-NPs applied at ≤ 0.25 mg L^{-1} (Nekrasova et al. 2011).

26.4.5 Molybdenum Nanofertilizer

Molybdenum is essential for legumes as it is involved in biological nitrogen fixation (BNF), being the component part of nitrogenase enzyme. For normal metabolism of crop plants the concentration of soil solution Mo should be ≈ 0.01 mg L^{-1}. Taran et al. (2014) conducted a pot experiment using different combinations of N-fixing bacteria and Mo-NPs (water, Mo-NPs, microbial inoculation with nitrogen-fixing bacteria, and a combination of the microbes and Mo-NPs). The control was treated with distilled water. Chickpea seeds were soaked in each of the treatments for 1–2 h. The results clearly showed that the combined application of microbes and Mo-NPs significantly improved the microbiological properties of the rhizosphere, including all groups of agronomically important microbes. The same combination significantly improved the root number, nodule number per plant, and nodule mass per plant compared to control.

26.5 Risk of Nanoparticle Application on Environment

Application of nanomaterials in agriculture is not always beneficial. It has number of negative effects on soil, plant, and aquatic life and most importantly human because of long food chain and easy motion of nanoparticles. Study of behavior of nanoparticles at different sizes with different concentrations in soil, plant, and water is as under:

26.5.1 Risk of Nanoparticle Application on Soil

Soil is prima facie receiver of fertilizers with nanoparticles. There is harmful chemical reactions and contamination by these nanoparticles to soil ecosystem and change in soil structure due to their large surface area and Brownian motion. Nanoparticles used through fertilizers could be harmful to soil biota and fertility (Ranallo 2013). They affect microbes, microfauna of soil, and digestive system of earthworm. An adverse effect of nanoparticles on soil health is presented in Table 26.8.

The potential harmful effects of nanoparticles Ag, TiO_2, ZnO, CeO_2, Fe_3O_4 include reduction in growth, fertility, survival, and increased mortality of earthworm and soil bacteria. Size is the main factor for ecotoxicity. To find out the relationship between size and toxicity, Roh et al. (2010) have initiated a study with TiO_2 and CeO_2 nanoparticle on *Caenorhabditis elegans*. It is a free-living, transparent nematode, about 1 mm in length that lives in temperate soil environments. They found that smaller size of TiO_2 (7 nm) and CeO_2 (15 nm) nanoparticles are more toxic compared to larger size (TiO_2 of 20 nm and CeO_2 of 45 nm). It has been found that higher doses of ZnO nanoparticle become toxic for soil (Hu et al. 2010). Whereas, the amount of ZnO in the soil is increased from 1 g kg^{-1} to 5 g kg^{-1}, ZnO nanoparticles bioaccumulate within the earthworm and cause DNA damage.

26.5.2 Risk of Nanoparticle Application on Plant

Toxicity of nanoparticles depends upon various factors like plant species, size, and concentration of nanoparticles in different stages of crop. Toxic effect of nanoparticles also depends upon their composition and size. Small sized nanoparticles are more reactive and toxic compared to large sized and affect the respiration or photosynthesis process (Navarro et al. 2008). Hund-Rinke and Simon (2006) worked on different sizes of photocatalytic active TiO_2 nanoparticles and its ecotoxic effect on algae (EC50: 44 mg L^{-1}) and daphnids with maximum concentration of 50 mg L^{-1} and found that ecotoxicity of nanomaterials depends upon nature of particles. Toxicity found in algae is more than daphnids. Lin and Xing (2007) worked on phytotoxicity of nanomaterials. They used MWCNT, Al, Al_2O_3, Zn, and ZnO in their experiment on radish, rape, ryegrass, lettuce, corn, and cucumber and found that seed germination of corn and ryegrass is affected by nanoscale ZnO and Zn, respectively. Aluminum oxide (Al_2O_3) nanoparticles showed phytotoxicity only on corn, which reduced the root elongation by 35%. Aluminum (Al) improved root growth of rape and radish and inhibited root elongation of ryegrass and lettuce but had no effect on cucumber. Some of the toxicological studies on the effect of nanomaterials are presented in Table 26.9.

The level of toxicity in plants due to nanoparticles is in direct relation with size and nature of the particles. Zinc oxide (ZnO) nanoparticles easily dissolve in soil and uptake by plant and TiO_2 nanoparticles accumulate in soil and retain for long time and stick with the cell wall of wheat plant. Both reduced the biomass of wheat crop

Table 26.8 Adverse effects of nanoparticles on soil health

Nanoparticle	Size (nm)	Effect	References
Ag	9–21	The activity of nitrifying bacteria was reduced by 50%	Okkyoung and Zhiqiang (2008)
C_{60} fullerene	50	Fast growing bacteria and protozoa were reduced by 20–30%	Johansen et al. (2008)
Ag, CeO_2, and TiO_2	7–45	Growth (9–21%), fertility (11–28%), and survival (20–30%) of Caenorhabditis elegans (species of nematode) were reduced	Roh et al. (2009, 2010)
TiO_2 and ZnO	10–20	Traces of ZnO (~50 μg g^{-1} weight) and TiO_2 (~32 μg g^{-1} weight) were found inside the earthworm	Hu et al. (2010)
ZnO, Zn, and Zn^{2+}	50	Soil enzymes (dehydrogenase, phosphatase, and β-glucosidase) were reduced by 17–80%	Kim et al. (2011)
Ag	10	Culturability of beneficial soil bacterium *Pseudomonas chlororaphis* O_6 was reduced	Calder et al. (2012)
Zero-valent iron (nZVI)	20–100	Mortality of *Eisenia fetida* and *Lumbricus rubellus* species of earthworm was 100% at 750 mg kg^{-1}	El-Temsah and Joner (2012)
CeO_2, Fe_3O_4, and SnO_2	50–105 (CeO_2), 20–30 (Fe_3O_4), and 61(SnO_2)	Microbial stress was noticed	Antisari et al. (2013)
Cr_2O_3, CuO, Ni, and ZnO	<100	The activity of enzyme (60%), dehydrogenase (~75%), and urease (44%) was reduced	Jośko et al. (2014)

(Du et al. 2011). Phytotoxicity was studied by Mazumdar and Ahmed (2011) on rice crop. They found that silver nanoparticle accumulated inside the root cell and damage the cell walls during penetration of particles due to complex mechanism and small size of particles, it damaged the external and internal portion of cell wall. The other factor for plant toxicity is the concentration of nanoparticle because a nanoparticle of same size in different concentration changes its chemical properties. Zinc oxide nanoparticle showed great toxicity in different concentrations (Boonyanitipong et al. 2011). They found that ZnO starts showing adverse effect on rice plant from 100 mg L^{-1} and fully inhabits root growth and biomass at 500–1000 mg L^{-1} concentration.

26.5.3 Risk of Nanoparticle Application on Water

The nanoparticles can easily be released in water body or air and uptake by living organisms, create toxic effect for human, animals, and also for aquatic life. Titanium

Table 26.9 Toxicological effect of nanoparticles on plant

Nanoparticle	Size (nm)	Crop	Adverse effect	References
TiO_2 and ZnO	20–100 (TiO_2) and 40–50 (ZnO)	Wheat (*Triticum aes*tivum)	Wheat biomass was reduced by 7.6% due to TiO_2. No significant result due to ZnO	Du et al. (2011)
ZnO and TiO_2	–	Rice (*Oryza sativa* L.)	75% reduction in root as concentration of ZnO increased from 10 to 1000 mg L^{-1}. No significant reduction with TiO_2	Boonyanitipong et al. (2011)
TiO_2	<100	Corn (*Zea mays*)	Aberration index increased from 0.5% to 2.5% with control and 4% concentration, respectively. Inhibits root elongation by 34%	Castiglione et al. (2011)
Au	25	Rice (*Oryza sativa* L.)	Damage of internal and external cell wall of root due to deposition of Au through xylem	Mazumdar and Ahmed (2011)
Aluminum oxide (Al_2O_3)	–	Tobacco (*Nicotiana tabacum*)	As concentration of Al_2O_3 increased as 0–1%, the average root length, biomass per seedling, and germination rate significantly decreased as 93%, 83%, and 2%, respectively	Burklew et al. (2012)
ZnO and Fe-ZnO	18.4 (ZnO) and 13.4 (Fe-ZnO)	Green pea (*Pisum sativum* L.)	Chlorophyll and ROS (reactive oxygen species) production were reduced by 27% and 50%, respectively	Mukherjee et al. (2014)

oxide (TiO_2) reduced the light to entrap the algal cell and thus reduce the growth (Sharma 2009). The toxicity study of Ag, Cu, Al, Ni, TiO_2, and Co nanomaterials on algal species, zebrafish, and daphnids revealed that Ag and Cu nanoparticles cause toxicity to all organisms (Griffitt et al. 2008) and the metal form is less toxic than soluble form of nanoparticles. Table 26.10 describes the aquatic toxicity of use of nanomaterials release in surface water body. It has been proved from different studies that nanoparticles like Ag, Cu, Al, Ni, and TiO_2 cause unrecoverable toxic effect on aquatic ecosystem. Silver, iron oxide, and copper nanoparticle adversely affected health of zebrafish. It enhances mortality, hatching, and reduces heartbeat and survival rate affect normal development (Asharani et al. 2008; Griffitt et al. 2007; Zhu et al. 2012). Therefore, the level of nanotoxicity in soil, plant, and water mainly depends on the composition, size (<20 nm), and concentration (>100 ppm) of the nanoparticle.

Table 26.10 Adverse effects of nanoparticles on aquatic species

Nanoparticle	Size (nm)	Aquatic species	Effect	References
Fullerene (nC_{60})	10–200	Daphnia	Mortality was increased by 40% and offspring production was reduced by 50%	Oberdörster et al. (2006)
Cu	80	Zebrafish	NKA (Na/K ATPase) activity was reduced by 88%	Griffitt et al. (2007)
TiO_2	21	Rainbow trout	Glutathione level was reduced by 65%	Federici et al. (2007)
Ag	5–10	Zebrafish	Heartbeat (150–50 beat min^{-1}) was decreased from 150 to 50 beat min^{-1} and mortality rate was 10%	Asharani et al. (2008)
TiO_2	10–100	Marine phytoplankton	Toxic to the aquatic life in sunlight	Miller et al. (2012)
Ag	18	Freshwater fish *Cyprinus carpio*	Mortality was 100% at 1 ppm NP's concentration	Hedayati et al. (2012)
FeO	30	Zebrafish	About 75% of fishes were killed at high concentration (50 mg L^{-1}) of NP	Zhu et al. (2012)

26.5.4 Risk of Nanoparticle Application on Human Health

The emerging field of nanotechnology has created an interest on human health risk associated with nanoparticles. These particles create new challenge for researchers to understand and find risk associated with human health. Exposure of these materials occurs through inhalation, ingestion, and dermal exposure during synthesis, manufacturing, and application of these nanomaterials. Table 26.11 shows the adverse effects of nanomaterials on human health.

The most common way of exposure is inhalation of airborne nanoparticles. Greatest emission risk occurs in the manufacturing process with poor filtering and ventilation system (AFSSET 2006). Factors that affect inhaled dose are particle geometry and physiochemical properties, lung morphology, respiration physiology, and environmental condition (Shade and Georgopoulos 2007). Nanoparticles deposit in respiratory traces after inhalation increases the total deposition fraction (TDF) in the lungs with decrease in particle sizes. Nanoparticles can also be taken-up in the brain through the olfactory epithelium (Borm et al. 2006; Jaques and Kim 2000). Ultrafine airborne particles may increase respiratory and cardiovascular morbidity and mortality (Shade and Georgopoulos 2007).

Ingestion is another source of entry of nanoparticles into human body. The nanoparticles entered through gastrointestinal tract directly through intentional ingestion or indirectly via water, food, animal food, and fish (Bergin and Witzmann 2013). Mucociliary escalators may be excreted as inhaled particles or absorbed into the gastrointestinal tract; however, absorption is dependent on particle size and physicochemical characteristics (Hagens et al. 2007). Jani et al. (1990) found that

Table 26.11 Adverse effects of nanoparticles on human health

Nanoparticle	Size (nm)	Body part	Effect	References
MWCN and carbon nanofibers (CNFs)	20 (MWCN) and 150 (CNFs)	In vitro on lung tumor cells	MWCN and CNFs reduced the living cells by 33% and 58%, respectively	Magrez et al. (2006)
TiO_2, Ag, Al, Zn, and Ni	–	Alveolar epithelial cells and apoptotic damage	Cell damage was observed in all cases	Park et al. (2007)
ZnO	30	Epidermal cells	Glutathione (51–59%), catalase (55–64%), and superoxide dismutase (72–75%) were reduced	Sharma et al. (2009)
Ag	<10	Hepatoma cells	Cytotoxicity (oxidative stress) was noted	Kim et al. (2009)
CuO	<50	Lung epithelial cells A549	Cell viability was decreased by 40%	Moschini et al. (2010)
TiO_2	1–200	Mammalian cell	Reactive oxygen species production, cytokines level, apoptosis, and genotoxicity were increased and cell viability and proliferation were reduced	Iavicoli et al. (2011)
Cadmium sulfide (CdS)	~3	*Escherichia coli* and HeLa cells	Oxidative stress in both *Escherichia coli* and HeLa cells. Reduced growth of *E. coli* by 50%	Hossain and Mukherjee (2013)
Ag	10–80	Lung cell (via inhalation)	Cell viability was decreased by 20–40%, oxidative stress in cells	Nguyen et al. (2013)
Ag	10–50	–	The Ag particles of size 10 nm were found more cytotoxic than other size	Gliga et al. (2014)
Cu	23.5	Nerve cells and astrocyte cell	Central nervous system was damaged	Bai et al. (2014)

particle size less or equal to 50 nm had more uptake or absorbed across gastrointestinal tract and can be passed to the liver, spleen, blood, and bone marrow by the momentary lymph supply and nodes. Plants have more resistance to prevent translocation of nanoparticles than mammalian barriers (Birbaum et al. 2010).

Dermal exposure is an import route to absorb nanoparticles via the skin. Skin constitutes about 10% of the body's weight and acts as a buffer against external impurities, as well as shielding, preserving homeostasis, digestion, synthesis, and deposition functions (Crosera et al. 2009). Penetration of nanoparticles depends upon physicochemical characteristics of nanoparticles and medical condition of skin such as eczema, dermatitis, and skin irritation. Absorption between epidermis and dermis or permeability increases in damage skin (Nielsen et al. 2007). Dermal exposure of small size nanoparticles lower than 10 nm is more dangerous. This size of particles may cause erythema, edema, and eschar formation. Further larger size particles cannot penetrate into the skin from transappendageal routes (Gautam et al. 2011).

Thus, it has been established that nanoparticles adversely affect human health and the potential routing could be through inhalation, ingestion, and dermal exposure. It is understood that the nanoparticles show significant health complications in human when exposed to the size of particles less than 50 nm.

26.5.5 Asian Prospects of Micronutrient Nanofertilizer

Nanotechnology is considered as one of the key technologies in the twenty-first century that promises to advance traditional agricultural practices and offers sustainable development by improving the management and conservation tactics with reduced waste of agricultural inputs (Dubey and Mailapalli 2016; Shang et al. 2019). In 2018, both public and private sectors of worldwide had invested about US $1055.1 million on nanotechnology market which is projected to reach $2231.4 million by 2025. The exponential growth of global investment in nanotechnology research closely coincides with the number of patents relating to nanoproducts. Recent statistics suggests that 88% of the patents are generated from just seven countries comprising US, China, Germany, France, South Korea, Switzerland, and Japan (Subramanian and Tarafdar 2011). The Government of India is currently spending Rs.1000 crores under Nano Science and Technology Mission (Nano Mission) during the Eleventh Five-year Plan period to promote research and development in all flourishing sectors of nanotechnology, and agriculture is one of them. Within the sphere of agricultural sciences, nanotechnology application in relation to soil and crop management is in its nascent stage and over the next few years it is expected to grow exponentially.

Fertilizers play a pivotal role in agricultural production. It has been unequivocally demonstrated that fertilizer contributes to the tune of 35–40% of the productivity of any crops. Without the fertilizer input, it is hardly possible to sustain agricultural productivity of any country. Thus, attempts are being made to synthesize nanofertilizers in order to regulate the release of nutrients demand of crops and overcome the uncertainty of crop production sector with limited natural resources (Godfray et al. 2010). Based on their actions, nanofertilizer could be classified as control or slow release fertilizers, control loss fertilizers, magnetic fertilizers, nanocomposite fertilizers as combined nanodevice to supply wide range of macro- and micronutrients in desirable properties (Panpatte et al. 2016; Lateef et al. 2016). A very few nanofertilizer formulations have been synthesized in China, Taiwan, India, Germany, and the USA and are being tested under laboratory conditions. Liu et al. (2006a, b) an associate from Chinese Academy of Agricultural Sciences (CAAS) have shown that nanocomposites containing organic polymer intercalated in the layers of kaolinite clays can be used as a cementing materials to regulate the release of nutrients from conventional fertilizers. This process increases the nutrient use efficiencies, besides preventing environmental hazard. Bansiwal et al. (2006) reported the use of surface modified zeolite as a carrier of slow release phosphatic fertilizer for the first time in India.

As a promising interdisciplinary research field, nanotechnology has aroused its enormity in agriculture. Micronutrients like zinc (Zn), copper (Cu), iron (Fe), manganese (Mn), boron (B), chlorine (Cl), molybdenum (Mo) also play an integral role in steady increase of crop productivity. However, numerous factors, such as soil pH, cation exchange capacity, soil texture, calcium carbonate content, water content, etc. stimulate their deficiencies in crop production with extensive farming practice (Ghormade et al. 2011). The deficiency of micronutrients decreases not only the productivity of crops, but also affects human health through the consumption of micronutrient-deficient foods (Swaminathan et al. 2013; Monreal et al. 2016). In contrast, the supplementation of nanoformulated or nanoentrapped micronutrients for the slow or controlled release of nutrients would stimulate the uptake process by plants, promote the growth and productivity of crops, and contribute to maintaining soil health as well (Peteu et al. 2010). Although the exact mechanism behind promotion of plant growth and enriched quality is not clear, it may be at least partially explained by the potentialities of nanomaterials to absorb more nutrients and water that in turn helps to enhance the vigor of root systems with increased enzymatic activity (Dubey and Mailapalli 2016; Shojaei et al. 2019). Therefore, the developing countries of Asia come forward to adopt these high potential technologies to ameliorate micronutrient deficiency in crop production and secure the nutritional security to the human being. The government of Myanmar is the first to undertake a program to include micronutrient nanofertilizers in their national fertilizer regimen. Later on, several other Asian countries like, India, Taiwan, Thailand, Malaysia, Iran also approved to commercialize the micronutrient nanofertilizers and Table 26.12 shows some approved micronutrient nanofertilizers currently used in these countries (Dimkpa and Bindraban 2017; Prasad et al. 2017; Elemike et al. 2019).

Nanoform of micronutrients improves their bioavailability to the plants and shows a significant improvement in plant growth and nutrition quality and some recent advancement in micronutrient nanofertilizer research in Asian countries is summarized in Table 26.13. Among the various micronutrients, Zn is the most important one, as it requires for structural component or regulatory co-factor for various enzymes and proteins in plants (Noreen et al. 2018). The foliar application of Zn and B nanofertilizers at 636 and 34 mg tree^{-1}, respectively, increased fruit yield by 30% in pomegranate trees (Khot et al. 2012). Similarly, foliar application of nano Zn and B fertilizers was found to increase fruit yield and quality, including 4.4–7.6% increases in total soluble solids (TSS), 9.5–29.1% decreases in titratable acidity (TA), 20.6–46.1% increases in maturity index, and 0.28–0.62 pH unit increases in juice pH on pomegranate without affecting any physical fruit characteristics (Davarpanah et al. 2016). Cucumber seedlings grown in nutrient solution including rubber type nanomaterial as a Zn source increased shoot and fruit yield compared

Table 26.12 List of various micronutrients nanofertilizer products available in market

Country	Nanofertilizer	Constituents	Manufacturer
India	Nano micro nutrient (eco star)	Zn, 6%; B, 2%; Cu, 1%; Fe, 6%; EDTA Mo, 0.05%; Mn, 5%; AMINOS, 5%	Shan Maw Myae Trading Co. Ltd.
	Nano fertilizer (eco star)	N, 8.2%; K_2O, 2.3%; organic matter, 75.9%; C:N, 5.4	Shan Maw Myae Trading Co. Ltd.
	Nano green	Extracts of corn, grain, soybeans, potatoes, coconut, and palm	Nano Green Sciences Inc.
	Nano N/P/K/S/Mg/Zn	Concentration 500 ppm N/P/K/S/Mg/Zn	Kanak Biotech
	IFFCO Nano N/Zn/Cu	–	Indian Farmers Fertiliser Cooperative (IFFCO)
	NanoMax-NPK/ NanoMax-Potash/ NanoMax-Cal/ NanoMax-Zinc	Multiple organic acids chelated with major nutrients, amino acids, organic carbon, organic micronutrients/trace elements, vitamins, and probiotic	JU Agri Sciences Pvt. Ltd
	TAG Nano NPK	Proteino-lacto-gluconate formulation, formulated with organic and chelated micronutrients, vitamins, probiotics, seaweed extracts, humic acid besides N, P, and K	Tropical AgroSystem Pvt. Ltd.
	TAG nano phos	Proteino-lacto-gluconate based P in nanoform	
	TAG nano potash	Proteino-lacto-gluconate based K in nanoform	
	TAG nano cal	Proteino-lacto-gluconate formulation, containing bio-available Ca, Mg, and S	
	TAG nano zinc	Proteino-lacto-gluconate based Zn in nanoform	
	Nanomol (S) micronutrient		Alert Biotech
	Nanomol (F) micronutrient	Contains Fe, Mn, Zn, Cu, Mo, and B	
	Nano zinc	Contains 21% Zn	
	Nano bor	Contains 20% B	
	Nano ferrous		
	Nanomag	Contains 9.6% Mg	
Malaysia	PPC nano	M protein, 19.6%; Na_2O, 0.3%; K_2O, 2.1%; $(NH_4)_2SO_4$, 1.7%; diluent, 76%	WAI International Development Co. Ltd.

(continued)

Table 26.12 (continued)

Country	Nanofertilizer	Constituents	Manufacturer
Iran	Biozar nano-fertilizer	Combination of organic materials, micronutrients, and macromolecules	Fanavar Nano-Pazhoohesh Markazi Company
Taiwan	Nano ultra-fertilizer	Organic matter, 5.5%; total N, 10%; total P_2O_5, 9%; total K_2O, 14%; AC-P_2O_5, 8%; CA-K_2O, 14%; CA-MgO, 3%	SMTET Eco-technologies Co., Ltd.
	Nano organic compound fertilizer	Organic matter, 41%; total N, 11%; total P_2O_5, 10%; total K_2O, 17%; water soluble MgO, 2%	Lazuriton Nano Biotechnology Co., Ltd.
	Nano high nitrogen Compound fertilizer	Total N, 26.7%; total P_2O_5, 17.8%; total K_2O, 11.5%	
	Nano low nitrogen High phosphorus high potassium compound fertilizer	Total N, 6.8%; total P_2O_5, 29.5%; total K_2O, 23.4%; water soluble MgO, 0.4%	
	Nano High phosphorus High potassium compound fertilizer	Total N, 2.4%; total P_2O_5, 19.9%; total K_2O, 44.2%; water soluble MgO, 1.2%	
	Nano organic fertilizer	Organic matter, 87.6%; total N, 4.8%; total P_2O_5, 2.6%; total K_2O, 2.5%	
Thailand	Plant nutrition powder (green nano)	N, 0.5%; P_2O_5, 0.7%; K_2O, 3.9%; Ca, 2.0%; Mg, 0.2%; S, 0.8%; Fe, 1.0%; Mn, 49 ppm; Cu, 17 ppm; Zn, 12 ppm	Green Organic World Co., Ltd.
	Supplementary powder (the best nano)	N, 0.5%; P_2O_5, 0.7%; K_2O, 3.9%; Ca, 2.0%; Mg, 0.2%; S, 0.75%; Fe, 0.03%; Mn, 0.004%; Cu, 0.007%; Zn, 0.004%	The Best International Network Co. Ltd.
	Hero super nano	N, 0.7%; P_2O_5, 2.3%; K_2O, 8.9%; Ca, 0.5%; Mg, 0.2%; S, 0.4%; pH 12.08	World Connect Plus Myanmar Co. Ltd.
	Nano capsule (the best)	N, 0.5%; P_2O_5, 0.7%; K_2O, 3.9%; Ca, 2.0%; Mg, 0.2%; S, 0.8%; Fe, 2.0%; Mn, 0.004%; Cu, 0.007%; Zn, 0.004%	The Best International Network Co. Ltd.

with those grown in commercial $ZnSO_4$ fertilizer (Mattiello et al. 2015). Application of Zn nanoparticles in pearl millet significantly enhanced grain yield by 38%, which was also associated with an improvement of 15% in shoot length, 4% in root length, 24% in root area, 24% in chlorophyll content, 39% in total soluble leaf protein, and 12% in plant dry biomass compared to the control in a period of 6 weeks (Moghaddasi et al. 2017). It was also observed a considerable yield increase using Zn nanoparticles as a nutrient source in rice, maize, wheat, potato, sugarcane, and

Table 26.13 Indicative list of beneficial effects of micronutrients nanofertilizer application in various agro-climatic zones of the Asia

Nanofertilizer	Crops	Amount	Benefits	Reference
Zn	Ryegrass	1–2000 ppm	Root elongation	Lin and Xing (2008)
	Cucumber	1000 mg kg^{-1}	Root tip deformation and growth inhibition	Zhao et al. (2014)
	Garden pea	500 mg kg^{-1}	Decreased chlorophyll and H_2O_2 contents	Nair and Chung (2015)
	Spinach	1000 mg L^{-1}	Growth reduction	Zheng et al. (2005)
	Tomato, eggplant	1 mg mL^{-1}	Reduced fungal disease	Khan and Siddiqui (2018)
	Chili pepper	100, 200, 500 ppm	Improved germination	Tantawy et al. (2015)
	Coriander	0–400 mg kg^{-1}	Improved pigment contents and defense responses	Ahmed et al. (2018a, b)
	Onion	5, 10, 20 mg L^{-1}	Inhibition of root growth	
ZnO	Mung bean and chickpea	1–2000 ppm	Plant growth increased at 20 ppm in mung bean and in check pea at 1 ppm	Mahajan et al. (2011)
	Cucumber	400–800 ppm	Root dry weight and fruit gluten increased	Lin and Xing (2007)
	Rape seed	1–2000 ppm	Root elongation	
	Peanut	1000 ppm	34% increment in pod yield per plant	Prasad et al. (2012)
	Chickpea	1.5 ppm	Improved shoot dry weight and antioxidant activity	Burman et al. (2013)
	Maize	10 ppm	Improved plant height and dry weight	Adhikari et al. (2015)
	Cluster bean	10 ppm	Improvement in plant growth and nutrient content	Raliya and Tarafdar et al. (2013)
	Arabica coffee	10 mg L^{-1}	Enhanced growth, biomass accumulation, and net photosynthesis	Rossi et al. (2019)
	Wheat	20 mg L^{-1}	Increased grain yield and biomass accumulation	Du et al. (2019)
	Guar	10 mg L^{-1}	Improved plant growth, biomass accumulation, and nutrient content	Raliya and Tarafdar (2013)
	Tobacco	0.2 µM and 1 µM	Positively affected growth physiology, increased metabolites, enzymatic activities, and anatomical properties of plants	Tirani et al. (2019)

(continued)

Table 26.13 (continued)

Nanofertilizer	Crops	Amount	Benefits	Reference
S-NS, ZnO-NS	Mung bean	–	Increased dry weight, increased leaf area	Pradhan et al. (2013)
Nano-ZnCuFeO FeO-NS, ZnO-NS	Mung bean	–	Increased root and shoot length, increased accumulation of biomass	Dhoke et al. (2013)
Fe	Cucumber	50, 500, and 2000 mg L^{-1}	Dose-dependent effects on biomass and antioxidant enzymes	Moghaddasi et al. (2017)
	Lettuce	10, 20 mg L^{-1}	Reduced growth and chlorophyll contents and increased antioxidant enzyme activities	Trujillo-Reyes et al. (2014)
	Garden pea	30–60 ppm	Improved seed mass and chlorophyll content	Giorgetti et al. (2019)
Fe/SiO_2	Barley and maize	0–25 ppm	Improved mean germination time	Najafi Disfani et al. (2017)
	Groundnut and maize	15 mg kg^{-1}	Enhanced plant growth and biomass accumulation	Disfani et al. (2017)
FeO	Soybean	30–60 ppm	Chlorophyll increased	Ghafariyan et al. (2013)
FeS_2	Daucus, mustard, and sesame	80–100 μg mL^{-1}	Increased germination and crop yield	Srivastava et al. (2014) Das et al. (2016)
Cu	Lettuce	130–600 ppm	Shoot and root length increased	Shah and Belozerova (2009)
	Squash	0, 100, 500 mg L^{-1}	Higher ionic Cu found in media amended with bulk Cu than with nCu	Musante and White (2012)
	Lettuce	130, 660 mg kg^{-1}	Increased shoot/root length ratio	Hong et al. (2015)
	Lettuce	0, 10, 20 mg L^{-1}	Negative effects on nutrient content, dry biomass, water content, and seedlings growth	Trujillo-Reyes et al. (2014)
	Cucumber	0–1000 mg L^{-1}	Reduced growth and increased antioxidant enzymes	Kim et al. (2012)
	Radish, grasses	10–1000 mg L^{-1}	DNA damage, growth inhibition	Atha et al. (2012)
	Tomato	50–500 mg L^{-1}	Improved fruit firmness and antioxidant content	Ahmed et al. (2018a, b)
	Cilantro	0, 20, 80 mg kg^{-1}	Reduced germination and shoot elongation	Zuverza-Mena et al. (2015)

(continued)

Table 26.13 (continued)

Nanofertilizer	Crops	Amount	Benefits	Reference
	Bean	100, 250, 500 ppm	Growth inhibition and nutrition imbalance	Alsaeedi et al. (2017)
	Garden pea	100–500 mg L^{-1}	Reduced plant growth and enhanced ROS production and lipid peroxidation	Tripathi et al. (2017)
CuO	Maize	10 ppm	51% increase in plant growth	Adhikari et al. (2016)
	Spinach	200 mg kg^{-1}	Improved photosynthesis and biomass production	Wang et al. (2019)
Mn	Mung bean	0.05–1 ppm	Shoot length, chlorophyll content, and the photosynthesis rate increased	Pradhan et al. (2013)
	Rice	–	Improved Zn uptake 5.66 mg $hill^{-1}$	Yuvaraj and Subramanian (2015)
Mo	Chickpea	8 ppm	Plant mass and number of modules increased	Taran et al. (2014)

sunflower (Monreal et al. 2016; Chhipa 2017). Under Zn deficient soil, application of nano ZnO at low doses positively influences the growth and physiological responses, such as shoot and root elongation, the fresh dry weight, and photosynthesis in many plant species compared to the control (Ali et al. 2019; Asl et al. 2019). Kale and Gawade (2016) reported that application of nano ZnO with other fertilizer in Zn deficient soil not only promotes nutrient use efficiency but also increases barley productivity by 91% compared to the control. Nanoparticles of ZnO showed a significant improvement in biomass, shoot length, root, chlorophyll and protein content, and phosphatase enzyme activity in *Vigna radiate*, *Cicer arietinum*, *Cucumis sativus*, *Raphanus sativus*, *Brassica napus,* and *Cyamopsis tetragonoloba* (Lin and Xing 2007; Mahajan et al. 2011; Zhao et al. 2013; Raliya and Tarafdar 2013).

Iron is also an important nutrient required by plants in minute quantities for maintaining proper growth and development (Palmqvist et al. 2017). Delfani et al. (2014) reported that use of nano Fe on blacked eyed pea recorded 10% increment in chlorophyll content in leaves. In *Glycine max* chlorophyll content was increased significantly by nano Fe application at 30–60 mg kg^{-1} (Ghafariyan et al. 2013). Disfani et al. (2017) also found that Fe/SiO_2 nanomaterials have significant potential to improve seed germination in barley and maize. Application of 50 mg L^{-1} nano FeO in *Citrus maxima* plants significantly improved the chlorophyll contents and root activity by 23% and 24%, respectively, compared to controls (Sharma 2006). Yousefzadeh and Sabaghnia (2016) demonstrated that the application of nano Fe fertilizer not only increased the agronomic traits of *Dracocephalum moldavica* with sowing density, but also improved essential oil contents of plants. Elfeky et al.

(2013) found that foliar application of nano Fe_3O_4 could significantly enhance total chlorophyll, total carbohydrate, essential oil levels, iron content, plant height, branches per plant, leaves per plant, fresh weight, and dry weight of *Ocimum basilicum* plants compared to that of soil application. Disfani et al. (2017) demonstrated that 15 mg kg^{-1} of nano Fe and SiO_2 increased shoot length of barley and maize seedlings about 8.25% and 20.8%, respectively.

Application of nano Cu improved photosynthesis in *Elodea desaplanch* by 35% at low concentration (Nekrasova et al. 2011) and seeding growth up to 40% in lettuce (Shah and Belozerova 2009). Spray of nano Mn on *Vigna radiata* increased 52% root length, 38% shoot length 71% rootlet, and 38% biomass at 0.05 mg kg^{-1} concentration in comparison with bulk $MnSO_4$ (Pradhan et al. 2013). However, MnO nanoparticles and FeO nanoparticles were not only less toxic than their ionic counterparts but they also stimulated the growth of lettuce seedlings from 12% to 54%, respectively (Lü et al. 2016). Molybdenum nanoparticle also showed improved microbial activity and seed growth in chickpea after combined treatment with nitrogen fixation bacteria (Taran et al. 2014). In addition to germination, nanomaterials, such as ZnO, FeO, and ZnFeCu-oxide, are reported to increase crop growth and development with quality enhancement in many crop species including peanut, soybean, mung bean, wheat, onion, spinach, tomato, potato, and mustard (Dubey and Mailapalli 2016; Shalaby et al. 2016; Shojaei et al. 2019; Zulfiqar et al. 2019).

The basic economic benefits of the use of micronutrient nanofertilizers are reduced leaching and volatilization associated with the use of conventional fertilizers. Simultaneously, the well-known positive impact on yield and product quality has a tremendous potential to increase growers' profit margin through the utilization of this technology. Biosynthesized nanoparticles-based fertilizers and nanobiofertilizers should be explored further as a promising technology in order to improve yields while achieving sustainability.

26.6 Conclusion

The opportunity for application of nanotechnology in agriculture is prodigious. Research on the applications of nanotechnology in agriculture needs to be initiated in all sectors of agriculture. Nanotechnology promises a breakthrough in improving nutrient use efficiency through nanoformulation of fertilizers, breaking yield and nutritional quality barriers through bionanotechnology, surveillance and control of pests and diseases, understanding the mechanism of host–parasite interactions at the molecular scale, development of new-generation pesticides and safe carriers, preservation and packaging of food and food additives, strengthening of natural fiber, removal of contaminants from soil and water bodies, improving the shelf-life of vegetables and flowers, and use of clay minerals as receptacles for nanoresources involving nutrient ion receptors, precision water management, regenerating soil fertility, reclamation of salt-affected soils, checking acidification of irrigated lands, and stabilization of erosion-prone surfaces, to name a few. The use of nanomaterials for delivery of pesticides and fertilizers is expected to reduce the dosage and ensure controlled slow delivery. Nanotechnology has the potential to revolutionize the fertilizer use and has the ability to play an important role in crop nutrition. The usefulness and effectiveness of nanofertilizers to enhance the growth and yield has been clearly demonstrated. Nanomaterials could preferably be used for foliar application but can also be used as seed treatment or for soil application. Nanomaterials perform better under lower concentration and can enhance the nutrient use efficiency and improve soil fertility in an eco-friendly manner. However adverse impact of its use has also been reported. There is very limited knowledge about its long-term adverse effect on soil, plants, and ultimately on human. It is required to study about the non-toxic limit of nanoparticles related to its size and concentration. The positive benefit of nanoparticles should be selected on the basis of their risk related to environment and human.

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