Chapter 7
Deciphering the Enigmatic Praxis of Nano-fertilizers in Agro-food Industrial Landscape

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1 Introduction

Fertilizers, also referred to as plant feeders, have been employed for the past few decades in agriculture to assist the farmer community by fulfilling the requisite nutrition, vital for the evolution and expansion of plants. However, because of the burden of ever-expanding global population, which is expected to reach 9.6 billion by 2050, there is imperative prerequisite for the adoption of potent agricultural practices that would succour in accomplishing the world's right to food and alleviation of poverty and hunger. To meet such expectations, there is tremendous requirement for the implementation of good agricultural practices such as use of nano-fertilizers, which improve not only the crop yield but also the quality and shelf life. Further, traditional fertilizer practices are not only enhancing the cost burden but are also posing deleterious impact on the human as well as environmental health, apart from reducing the soil fertility, crop yield and overall development.

With the dawn of nanotechnology, it has presaged huge sway in all the realms of society including environment, healthcare, energy and electronics. Nowadays, nanotechnological practices (such as encapsulation and delivery of substances at targeted sites, enhancing the organoleptic properties, introduction of antibacterial nanoparticle coatings onto the food, enhancement of food shelf life, sensing contamination, improved food storage, tracking, tracing and brand protection) have been swamping the agro-food industry by enriching its nutraceutical potential,

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production yield, quality and safety levels to a superior level with the judicious application of fertilizers/manures, pesticides/insecticides, herbicides and plant growth factors.

2 Nano-fertilizers

Nano-fertilizers (NFs) facilitate the potential means to augment the crop productivity via delivering the nutrients to crops (in the dimensions of 1–100 nm) at their targeted site of application with controlled rate of release, thereby minimizing the illicit exposure of the fertilizers to the non-targeted areas. Further, the application of nano-fertilizers can also be harnessed to release the bulk materials together with nanoscale formations in order to develop new improved, potential fertilizers for improving the yield and nutritional value. Literature studies have shown that agriculture crops nano-enabled with fertilizers were proved to be significant in the accretion of nutrient use efficiency (NUE) by crops (Gogos et al. 2012; Anjunatha et al. 2016; Singh et al. 2021; Lowry et al. 2019; Bandala and Berli 2019). Therefore, apart from enhancing the crop productivity, the primary goal in the field of fertilizer research is also to prevent or minimize the nutritional loss for better crop development (Chhipa 2017). Nevertheless, specially designed nanostructures, which are generally expected to harmonize the nutritional needs of the crops, also allow the release of nutrients in a controlled fashion. Further, it is a matter of the fact that reducing the size of nanoparticles by physical or chemical means results in the enhancement of surface mass ratio of fertilizers. This strategy plays a critical role in the better absorption of nutrients from root which in turn allows the slow, targeted and efficient release of nutrients from NFs. Moreover, implementation of such NF's practices aids in the reduction of dosage quantity, cost of its application and nutrient losses, thus improving NUE by 20–30% compared to conventional approaches of fertilizer's use (Kah et al. 2018).

3 Manufacturing of NFs

NFs are primarily prepared from conventional fertilizers or extracts obtained from diverse plants or plant parts by coating/encapsulating them with nanomaterials regulating the release of nutrients in a controlled manner, thereby ensuring the productivity, fertility of the soil and agricultural product quality (Zulfiqar et al. 2019). Further, the physicochemical characteristics of nanomaterials permit superior encapsulation of the nutrients into nanosized form which can be released in a precise manner to expand the efficiency of crop plants with minimum impact to the environment. Furthermore, the interaction of nanomaterials with fertilizers improves absorption of nutrients and bolsters bioavailability of nutrients (due to the definite surface area, mini size and extra reactivity) and NUE, thereby preventing leaching, volatilization and environmental hazards such as soil fertility as well as safety of workers (Solanki et al. 2015; Chen and Wei 2018; Linquist et al. 2013). The manufacturing of nutrients/NFs into the nano-form can be done in three different ways (Iqbal 2019).

3.1 Entrapment or Encapsulation Within the Nanomaterials

The praxis of encasing a constituent within another material to produce particles with diameters of a few nanometres to a few micrometres is referred to as encapsulation. The absolute aim of encapsulation is to thwart the nonspecific outcomes by some nutrients when they come in contact with soil components and to prevent the instability of such nutrients in soil for prolonged period of time, thereby reducing their overall efficacy (Bratovcic and Suljagic 2019). Diverse forms of polymers have been employed for encapsulation for both NFs and nanopesticides which are usually of natural origin such as proteins (e.g. chicken egg albumin, zein, casein, α-lactalbumin, β-lactoglobulin, collagen, gelatin) and polysaccharides (e.g. alginate, carrageenan, xanthan gum, chitosan, modified starch) (Pestovsky and Martinez-Antonio 2017; Sabliov et al. 2015). The process of nanoencapsulation has also been exploited for hydrophobic NF or pesticide candidates (having poor or limited water solubility profile) in order to ensure better stability, improved dispersability in aqueous media and controlled release of the active compound. Further, nanoencapsulation improves pest control efficiency or nutrient delivery and restrains the amounts of dose/treatment in crops and human exposure (de Oliveira et al. 2015; Grillo et al. 2016; Nuruzzaman et al. 2016).

Literature studies have revealed the encapsulation of active agents by microspheres of starch on a matrix having nanopores which verified its flexibility precisely in distribution of the active agents to their target (Larue et al. 2012b). These nanocapsules or microspheres become attached to the heir of bees alike to pollens and keep parasites at bay owing to the controlled release of active agents in a gradual manner. Thus, dissemination and application of nanoencapsulation lead to the least possible usage of active agents and presented extreme defence to bees against parasites. Similarly, nanogels were also fabricated to assist the precise release of pheromones from insects for protection against diversified pests. Further, nanoencapsulation has also yielded favourable effects for improving the therapeutic efficacy of NFs with a substantial decline in the dose of energetic components (Larue et al. 2012a). In order to spot the pathogens and to extend the shelf life of packed foods, nano-biosensors have displayed promising outcomes. Although the extensive and multidimensional applications of nanomaterials in food production and preservation are still evolving, in the current scenario, it seems a far distant dream to fulfil the objectives of global food and nutritional security without the assistance of nanomaterial-based technologies in agro-food industrial sector.

3.2 Coating with a Layer of Nanomaterials

Nanoscale coatings comprise traditional fertilizers coated or loaded with nanoparticles, whereas nanomaterial coatings (also termed as nanomembranes) and porous NFs, respectively, help in slowing down the release of nutrients and include a network of capillary channels that delay nutrient solubility. Various biological microorganisms such as bacteria or fungi degrade these coatings composed of biodegradable polymers or synthetic polymeric materials, consequently permitting the discharge of nutrients and its fixation into the soil. These are generally termed as "controlled release fertilizers" (CRFs), and are available commercially for application to ornamental gardens or lawns for the last two decades in order to enhance the nutrient efficiency of fertilizers. In CRFs, the thickness of the polymer coating and the mix of nutrients that are coated govern the ejection rate of the fertilizer nutrients to the soil for the complete absorption by the plant. Such smart coating nanotechnology applications which allow greater control of the plant over the nutrient release rate have also been touted as "intelligent NFs" (Crawshaw 2010). Further, the large surface coatings of nanopolymers over the biofertilizers improve the distribution of constituent nutrients and act as reservoir for constant supply of plant nutrients. Furthermore, CRFs exhibit great solubility in comparison to slow release fertilizers, but they are covered with such type of components that significantly minimizes the acquaintance of active ingredient resulting in precise dissemination of nutrients.

3.3 Formation of Nano-emulsions

Application of herbicide- or pesticide-based nano-emulsions has been implemented with the aim of providing potential advantages over other conventional techniques, such as robust adhesion to surfaces, better permeability and wide-ranging applicability (Feng et al. 2018). Investigations employing hydrophobic silica NPs to the water-in-oil (w/o) emulsion reported enhancement in the distribution of the product, as well as an improvement in shelf life by reducing desiccation (Kaushik and Djiwanti 2017).

The overall efficiency of NFs is governed by three primary factors, namely, intrinsic (e.g. method of preparation of nano-formulation, particle size and surface coating), extrinsic (e.g. soil depth, soil pH, soil texture, temperature, organic matter and microbial activity) and route of exposure, which affect the overall performance of NFs (Zulfiqar et al. 2019; Solanki et al. 2015; Ma et al. 2018; El-Ramady et al. 2018). Moreover, the exposure route or mode of administration through plant roots or leaves (foliar) also plays a noteworthy role in the absorption, behaviour and bioavailability of NFs. Figure 7.1 describes the methods of preparation of NFs along with factors affecting the potential of NFs.

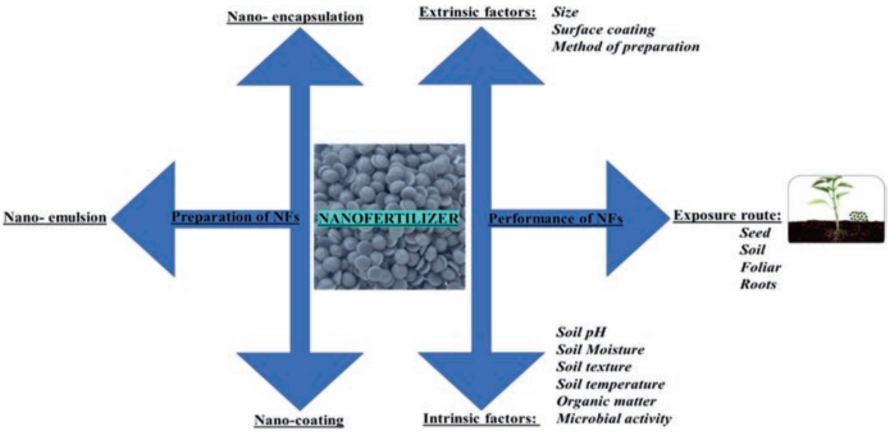

Fig. 7.1 Preparation methods and factors affecting the potential of NFs

4 Classification of NFs

The prime focus of nanotechnological tools in agro-food sector is to revitalize food production with ever-increasing population demand for food, with higher nutritional quotient, quality attributes and safety profile. Therefore, precise release of herbicides, pesticides and plant growth factors can be realized through utilization of nanocarriers as fertilizers which could serve as significant means to improve crop productivity.

Although the application of NFs is still in its infancy (Pulizzi 2019), their usage seems economically more rational as they limit the transportation requirement and application cost. Further, their miniature quantities of NFs used in the soil diminish the risk of loading undesirable salts in comparison to conventional fertilizers. Besides this, in current agriculture, NFs can be merely designed on the basis of nutritional requirements of target sites (León-Silva et al. 2018; Zulfiqar et al. 2019).

On the basis of specific nutritional requirements of plants and properties of nanomaterials employed, NFs can be categorized, namely, as macronutrient NFs, micronutrient NFs, nanoparticulate fertilizers and plant growth stimulating NFs. Apart from the safety and eco-friendly nature of nutrient loaded nanomaterials, these fertilizers coated/encapsulated in the nanocarriers can control the release of nutrients in a precise manner as well as be employed for many other applications, including pesticides, food and drug delivery (Chopra et al. 2014; Kumar et al. 2016; Sotelo-Boyas et al. 2017; Bernela et al. 2018). Figure 7.2 depicts the classification of NFs in accordance with the nutritional requirement of the plants.

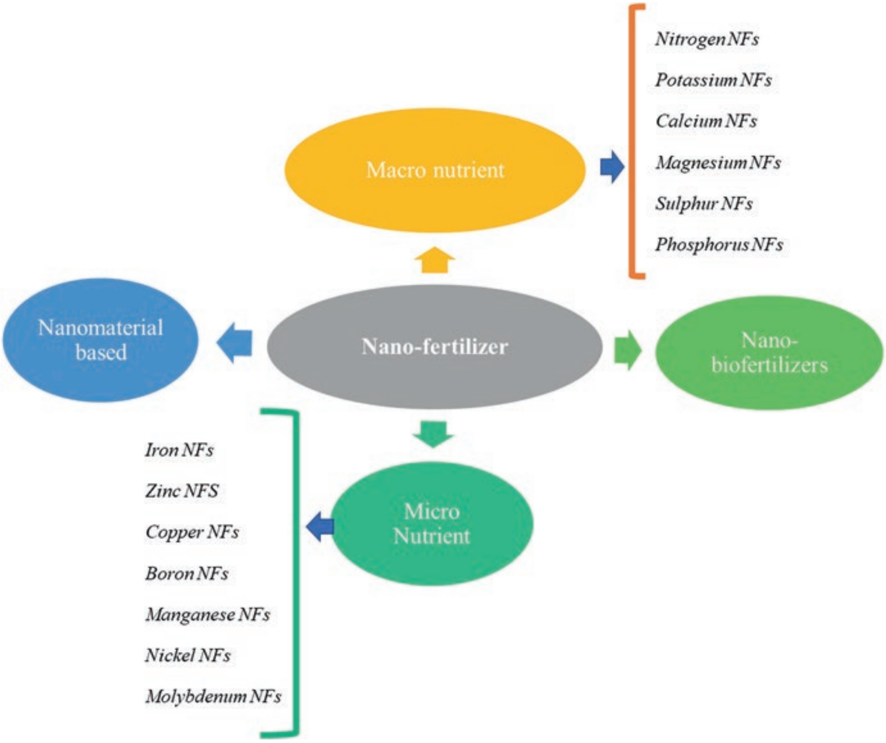

Fig. 7.2 Classification of NFs on the basis of nutrient requirements and nanomaterial properties

4.1 Macronutrient NFs

For plant nutrition, sufficient amount of macro- and micronutrients are indispensable, including oxygen, carbon, hydrogen, phosphorus, nitrogen, calcium, potassium, sulphur and magnesium. Among these, the three (oxygen, carbon, hydrogen) are structural elements and excerpted from the existing environment, while the remaining macronutrients are acquired from soil. Though all the macronutrients are imperative, few prime macronutrients are consumed in higher quantities in comparison to secondary ones. These essential macronutrients (nitrogen, phosphorus, potassium) are considered fertilizer vitals or labelled as “N-P-K” since many years as other macronutrients are considered as secondary.

Nitrogen NFs

Nitrogen is the first and foremost element considered as critical nutrient for plant growth worldwide for its vital role in metabolism and protein synthesis. In contrast to this, the nitrogen use efficiency in agronomical sector still remains <50% owing to loss of excessive nitrogen through denitrification, volatilization and leaching, thereby resulting in nitrogen overuse to accomplish the targeted crop yields and posing great concerns fiscally or ecologically at the global level (Mejias et al. 2021).

Primarily, nitrogen is applied as granulated fertilizers, which usually consequences in substantial losses through surface run-off/leaching, ammonia volatilization and nitrogen oxide emissions. Further, the pervasive practice of conventional nitrogenous fertilizers, such as urea (CH_4N_2O), has alarmed environmental concerns worldwide. The indefatigable efforts for advanced solutions have resulted in the synthesis of novel nanomaterials, ensuing in the growth of potent tools for the progress of innovative technological products. Therefore, nitrogen NFs have been designed to elevate nitrogen absorption by refining the efficiency of nitrogen distribution to plants and dropping its damages to the atmosphere. Further, the evidence on the efficacy of nitrogen NFs in agricultural crops is evolving, and the approaches that can be implemented to circumvent nitrogen losses are yet to be fully elucidated. New scenarios with environmental constraints offer ample opportunities for the application of nitrogen NFs. Hence, more innovative solutions such as NFs, to improve nitrogen use efficiency, to reduce leaching into the environment and for future considerations for agricultural crops, are considered obligatory that can achieve sustained release of nitrogen during crop production. Several studies have advocated the role of nitrogen NFs to obtain high production yield in contrast to conventional mineral urea while minimizing the shortcomings of conventional ones (Milani et al. 2012). The first studies concerning nitrogen NFs were investigated on urea, and use of nano-hydroxyapatite (nHAP) in fertilizer suggestions by Kottegoda et al. (2011) unbolted the pandora box for employing nitrogen carrying nanomaterials in agro-food sector. In this study, a nanohybrid structure based on nHAP encapsulated urea molecules was developed which exhibited significant sustained release of nitrogen from the NFs in contrast to conventional urea (Kottegoda et al. 2011). In another investigation, nHAP encapsulated urea molecules displayed significant impact on both germination of seedlings and early growth of plantlets of *Vigna radiata*, apart from better stability over the time for slower nitrogen release (Subbaiya et al. 2012).

Manikandan and Subramanian fabricated intercalated nitrogen NF formulation and found a consistent rise in growth, yield, quality and uptake of nutrients in maize crop with respect to traditional urea (Manikandan and Subramanian 2016). Further, it has been observed that nanocarriers such as zeolites, chitosan or clay can manage with plant's mandate and release of the nourishment at a retarded rate and ensure better plant uptake and prudent use of nitrogen (Panpatte et al. 2016; Aziz et al. 2016). Because of other parameters such as increase in surface area and capability to harmonize the proclamation of nitrogen, nanozeolites along with its combinations have been broadly exploited for the manipulation of NFs. Furthermore, zeolite-based nitrogen NF not only indicated higher accumulation of nitrogen in plants but also exerted positive effect on intrinsic factors such as soil pH, moisture and availability of nitrogen as compared to conventional fertilizers (Rajonee et al. 2016).

Phosphorus NFs

Phosphorus is another utmost vivacious nutrient for ideal plant growth, apart from its role in root growth and flowering stage. Some of the additional sources of phosphorus fertilizers include bone meal and industrial wastes like Thomas slag or basic slag. Phosphorus is essential for energy storage and energy transfer molecules such as ATP (adenosine triphosphate), ADP (adenosine diphosphate), phospholipids, photosynthesis execution and organic compound formation. It exhibits dynamic role in photosynthesis, respiration and the biosynthesis of DNA (Soliman et al. 2016). It also aids in the plant's ability to survive in unfriendly climatic situations such as resistance to diseases. Although the amount of phosphorus in soils may be much higher than the one desired for plant growth, several factors can limit its availability to plant (Sohrt et al. 2017), such as formation of its complexes with iron, aluminium hydroxides and calcium in the soil or its immobilization with dirt particles in the soil that restricts its availability (Bindraban et al. 2020). It is also a matter of fact that phosphorus in synthetic fertilizers is poorly available and only 10–20% of it is taken up by plants, whereas phosphorus in excess deteriorates the condition by altering the microbial biomass and its proportions with nitrogen and carbon (Fan et al. 2018).

Depending on their solubility profile, phosphorus fertilizers can be categorized into three types: (a) water soluble such as *ammoniated superphosphates* and *monobasic calcium phosphate*; (b) citric soluble, e.g. *Thomas slag*, *dicalcium phosphate*, basic *slag*, *defluorinated phosphate* and *fused magnesium phosphate*; and (3) sparingly soluble phosphate such as *tricalcium phosphates* (Diatta et al. 2018).

Literature studies have proposed the potential application of NFs or release-retarding materials like zeolites to augment the NUE of phosphorus that NFs can steadily distribute phosphorus for 40–50 days subsequent to their administration; on the other hand, traditional phosphorus fertilizers distribute all the components within 8–10 days after their application (Liu and Lal 2015).

Nanotechnological approaches such as nHAP-based NFs respectively resulted in 32.6% growth rate and 20.4% seed yield in soybean plants in contrast to other synthetic phosphorus fertilizers (Liu and Lal 2014). Soliman et al. observed the implementation of hydroxyapatite (HAP) nanocarriers for the delivery of phosphorus which resulted in significant improvement in the growth, chemical contents and anticancer properties of leaves of *Adansonia digitata* plants compared to different sources of phosphorus fertilizers (Soliman et al. 2016). Another study indicated several fold enhancements in fresh and dry biomass, amplified fruit yield, enriched quality and also improved NUE (Patra et al. 2013). Further, the usage of surface-modified zeolites has also been pronounced to endorse the phosphorus use efficiency (Preetha and Balakrishnan 2017). The encapsulation of phosphorus in biodegradable nanocarriers was studied for its activity, and it was found that phosphorus gets absorbed directly through leaves, which eliminates the necessity of binding phosphorus to the soil, so that excess phosphorus should not be accumulated in soil which does not benefit the crop production and yield (Husted 2018). Additionally, polysaccharides such as sodium alginate, carrageenan and carboxymethyl cellulose along with lignin have also been employed to coat water-soluble granular fertilizers in different mass ratios, which effectively controlled the phosphorus release in a sustained manner (Fertahi et al. 2020). Further, Dwivedi et al. have also suggested the role of zeolites as a carrier for improving the solubility and accessibility of phosphorus (Dwivedi et al. 2016). Thus, phosphorus NFs may possibly serve as an appropriate choice for smart agriculture practices, as it maximizes NUE as well as reduces the leaching of phosphorus into groundwater, thereby assisting in improving the crop yield.

Potassium NFs

The third prime macronutrient after nitrogen and phosphorus is potassium, as it exhibits a vigorous monitoring role in the biochemical procedures of plants (such as water uptake, reproduction, photosynthesis, synthesis of protein, activation of enzyme, stomata regulation, water intake, transport of the plant's reserve substances, augmentation of capacity, prompting of the absorption of nitrates, strengthening of cell tissue, encouragement of flowering, synthesis of carbohydrates or enzymes, etc.) which are indispensable for quality assurance, excellent appearance and substantial crop harvesting. Potassium deficiency hugely impacts the growth of root and shoot, the number of seeds inside fruits, size, shape, colour, taste, plant immunity towards diseases, resistance changes in temperature/wind, overall growth and the final crop yield (Preetha and Balakrishnan 2017). Plants with an acceptable level of potassium have been reported to be more resistant to abiotic stresses such as water stress and variable temperatures (Sohair et al. 2018; Wang et al. 2013; Taha et al. 2020). It has been observed that maximum use efficiency of potassium NFs typically ranges between 30 and 50% (Battaglia et al. 2018), which designates that about 50–70% of applied potassium NFs can be vanished, thus instigating considerable commercial losses and damaging effects on soil health and water quality (Czymmek et al. 2020). On the other hand, potassium NF formulation ensures slow potassium release rate as well as losses in soil and thus maintains uninterrupted supply of potassium to crops for a prolonged period (Kubavat et al. 2020).

Similarly, the use of potassium NFs for foliar administration pointedly enriched the growth, number of leaves, product quality, disease and pest resistance and drought tolerance in *Cucurbita pepo* (Gerdini 2016). Therefore, it can be postulated that potassium NFs exhibit the potential to protect soil strength and water quality improvement by dropping potassium losses into soil owing to leaching and thereby helping to enhance physiological and yield traits. Potassium NFs and potassium loaded zeolites were able to enhance the leaf area, grain yield, biological yield, harvest index, potassium concentration and chlorophyll (chl) content, respectively, in *Ocimum basilicum* (Ghahremani et al. 2014) and hot pepper (*Capsicum annuum* L.) (Li et al. 2013). In contrast to conventional fertilizers, potassium NFs delivered higher potassium content in the plants when treated at similar concentrations (Rajonee et al. 2016). In another study, *Lithovit* NF particles existed as a tinny layer on the surface of leaves and penetrated inside after getting mixed with dew droplets at night. It has been observed that these NF particles also promote the supply of carbon dioxide which further led to enhanced photosynthesis and ultimately improve the plant growth or productivity (Attia et al. 2016). It is also pertinent to note here that potassium NF application at the level of 150+150 ppm caused significant rise in the nutrient level of shoots and seeds in peanut plants compared to other treatments (Afify et al. 2019).

Magnesium NFs

Magnesium, a pulsating secondary element after N-P-K for plant growth, composes the central part of the chl molecule and acts as an enzyme activator crucial for photosynthesis. Unfortunately, magnesium has been an undervalued secondary nutrient (also referred to as *The Forgotten Element*) as its deficiency is rarely identified in crops (Cakmak and Yazici 2010). Magnesium NUE is quite low, as it escapes from the soil through leaching mobilization, and prejudiced use of nourishment. Further, its uptake gets affected in the occurrence of cations such as NH_4, Ca^{2+} and K^+ (Gransee and Führs 2013).

Delfani et al. evaluated magnesium and iron nanocarriers for foliar administration in black-eyed pea which exhibited noteworthy effect on yield, leaf iron content, stem magnesium content, stability of plasma membrane and chl pigments noticed for the combination of these two elements (Delfani et al. 2014). Further, it is a well-documented fact that N-P-K are the primary macronutrients; however, their excessive use may lead to disparity of other macro-/micronutrients and unwarranted usage of nitrogen or potassium and phosphorus respectively leading to deficiency of magnesium and disproportion of zinc. Furthermore, pretreatment of tomato roots with magnesium oxide NFs significantly inhibited development of bacterial wilt in tomato roots against *Ralstonia solanacearum* (Imada et al. 2016) and also played a pivotal role as antibacterial agent against *Ralstonia solanacearum* besides additional benefits such as nontoxicity and ease of availability (Cai et al. 2018). $Mg(OH)_2$ nanocrystals have also been exploited for their efficiency in seed germination and plant growth promotion on *Zea mays* which resulted in 100% seed germination and enhanced growth with high magnesium content (Shinde et al. 2018).

Sulphur NFs

Sulphur plays a significant role in plant growth, because it participates in chl formation and upsurges nitrogen efficiency along with plant defence against several diseases. Some of the common sources of sulphur include elemental sulphur (S_8) and sulphates (SO_4^2). Elemental sulphur (S_8) exhibit much higher sulphur concentrations (>90%) with larger particle size; however, it cannot be directly absorbed by the plants, until it is biologically oxidized by soil microorganisms. On the other hand, SO_4^{2-}salts undergo rapid absorption by plants, but it unveils low sulphur concentrations as well as SO_4^{2-} leaching, thereby resulting in significant loss which further leads to environmental toxicity (as the leftover is not sufficient amount required by the crop) (Valle et al. 2019). Therefore, oxidation rate of sulphur can be significantly amplified by reducing the particle size (Germida and Janzen 1993). Thus, to serve this purpose, the necessity of sulphur NFs becomes obligatory and a valuable approach.

Alipour et al. stated insignificant effect of sulphur NFs on different parameters of *Ocimum basilicum* after salt stress (Alipour 2016). Additionally, in a study, green synthesis of sulphur NPs was carried out employing leafy extract of *Ocimum basilicum*, subsequently applied to the seeds of *Helianthus annuus* and irrigated with $MnSO_4$ resulting in low manganese uptake, improved sulphur uptake, eradication of physiological drought and elevated water content of plantlets, which substantiates the efficiency of sulphur NFs (Ragab and Saad-Allah 2020). Besides this, sulphate and chitosan NPs-based N-P-K NFs revealed auspicious results as macronutrient fertilizers in agriculture (Dhlamini et al. 2020; Ha et al. 2019). Silver nanocarriers (Ag-NCs) having size <20 nm exhibit antibacterial properties by attaching to the sulphur-containing amino acids of the bacterial cell membrane which imparts greater permeability and are primarily responsible for its cell death (Slavin et al. 2017; Roy et al. 2019; Guilger Casagrande and Lima 2019). Furthermore, such nanocarriers also react with the phosphorus moiety of the DNA and inhibit its replication and metabolic processes, thereby disrupting cell functions (Liao et al. 2019).

Calcium NFs

Calcium plays a pivotal role in plant activities such as stabilization of cell wall, formation of seed, transportation of minerals in soil and counter-balancing of toxic substances. Foliar application of calcium in fruits with low efficiency did not enhance its concentration in fruits owing to limitations of calcium uptake or penetration in fruits, composition and occurrence of cuticle and lesser translocation of calcium in the phloem (Wojcik 2001; Conway et al. 2001; Mengel 2001; Danner et al. 2015).

Calcium NFs even at smaller calcium concentrations significantly reduced the cracking of fruit in comparison to higher concentrations of calcium chloride ($CaCl_2$). However, the foliar application of calcium did not show any significant changes on crop production, fruit yield and quality (Davarpanah et al. 2018). In contrast to this, calcium NFs sprayed on the apple fruit before harvesting significantly improved the fruit quality and quantity in comparison to spraying with $CaCl_2$ (Ranjbar et al. 2019). Further, foliar application of calcium carbonate in its nano-form resulted in 15 days prior to flowering along with increase in the number of flowers to >50% in *lisianthus* (Seydmohammadi et al. 2020).

Both crystalline and nanocrystalline forms of calcium phosphate (CaP) compounds exist in biological system as well as in the environment as mineral deposits (Dorozhkin and Epple 2002). CaP compounds constitute inorganic elements of biological tissues of living systems in the hydroxyapatite form, to maintain the stability, hardness and functioning of bone, teeth and tendons. CaP, in various crystal forms and their unusual property of hosting a variety of cations (K, Mg and Zn), makes it conceivable for broad applications (Epple 2018). Further, calcium peroxide NCs are capable of eliminating pollutants from soils, speeding up the response rates by augmenting the aspect percentage of responsive surfaces and rendering them applicable for nano-remediation (Khodaveisi et al. 2011). In an investigation, Supapron et al. reported slower release of calcium and magnesium from zeolites, thereby improving its content in soil (Supapron et al. 2007). Various other studies have also shown generation of oxygen during deprivation of NCs from contaminants which expedite an aerobic environment essential for bioremediation (Mueller and Nowack 2010; Sarkar et al. 2019).

Therefore, the application of NFs with all the primary (N, P, K) and secondary macronutrients (Mg, S, Ca) may improve the NUE, when administered at lower doses, and reduced their bulk requirements which escalates environment risk as verified by several investigators on a variety of macronutrient NFs as agricultural involvements (Chhipa 2017; Ditta and Arshad 2016).

Ramírez-Rodríguez et al. attempted the application of multi-nutrient NFs based on nitrogen and potassium ions-doped (CaP) NCs for the release of nutrients in controlled manner in order to devise smart agricultural practices (Ramírez-Rodríguez et al. 2020a). It was observed that NCs exhibited improvement in yield after using 40% lesser amount of nitrogen by weight for wheat plants in comparison to conventional methods. Further, urea-doped CaP NCs on *Triticum durum* plants also displayed superior prospect of nitrogen administration to plants in an extra safe and effective method (Ramírez Rodríguez et al. 2020b). Furthermore, sulphate-supplemented or chitosan-based N-P-K NFs have also indicated encouraging outcomes as macronutrient fertilizers on sustainable agricultural activities (Dhlamini et al. 2020; Ha et al. 2019). Table 7.1 summarizes the effect of different macronutrient-based NFs to improve the NUE and all other important parameters for different plants.

4.2 Micronutrient NFs

Secondary nutrients or micronutrients (e.g. iron, copper, zinc, boron, manganese, nickel, molybdenum, chlorine and selenium) are required in minor quantities, but are very much essential for crop nutrition and growth similar to primary macronutrients (e.g. nitrogen, phosphorus, potassium, calcium, sulphur and magnesium). The deficiency of micronutrients not only affects the crop yield but also results in low absorption of other macronutrients and causes structural problems. Although N, P and K serve as prime nutrients for crop production, their immoderations may also cause misbalancing of the micronutrients; for example, excess of nitrogen and potassium leads to deficiency of magnesium, whereas surplus of phosphorus causes imbalance of zinc.

Therefore, it is mandatory to combine the secondary micronutrients with primary nutrients (NPK), in appropriate dosage regimens and should be administered

Table 7.1 Effect of various macronutrient-based NFs on diverse crops/plants

Macronutrient/NFs	Technique used	Concentration (mg/L)	Plant/crop	Results obtained	References
NPK	Foliar	100	*Solanum lycopersicum*	Enhanced growth rate and yield	Panda et al. (2020)
	Foliar	10–100	*Oryza sativa*	Boosted rice grain yield by >49%	Dimkpa and Bindraban (2018)
P	Soil	NA	*Oryza sativa*	Greater physiological efficiency of shoots and roots and photosynthetic rate	Miranda-Villagómez et al. (2019)
K	Foliar	NA	*Triticum aestivum*	Improved dry matter yield in saffron	Amirnia et al. (2014)
MgO	Pretreatment of roots	0.007–0.01	*Solanum lycopersicum*	Diminished bacterial wilt disease caused by *Ralstonia solanacearum*	Imada et al. (2016)
$Ca(NO_3)_2$	Foliar	NA	*Vigna mungo*	Upsurge biomass of shoot along with nutrient content	Yugandhar and Savithramma (2013)
N	Soil	NA	*Pennisetum americanum*	Augmented N and P metabolizing soil microorganisms and improved biomass production	Thomas et al. (2016)
CaCO3	Seed treatment	NA	*Vigna mungo*	Enhanced growth root and shoot along with biomass production	Yugandhar and Savithramma (2013)
S	Soil	50–300	*Melia azedarach*	Improved shoot and root growth by 133% and 220%, respectively	Salem et al. (2016)
		150	*Arachis hypogaea*	Upsurge in nutrient content of shoot and root	Chhipa (2017)

(continued)

Table 7.1 (continued)

Macronutrient/ NFs	Technique used	Concentration (mg/L)	Plant/crop	Results obtained	References
Ca	Post-transplanting	500, 1000, 2000, 3000 and 500, 750, 1000	*Solanum lycopersicum*	Significantly lessened the detrimental effects of salinity, increased the diameter of stem and flower number	Zulfiqar et al. (2019)
	Seed	2.5	*Vigna unguiculata*	Raised magnesium content in stem, chl content and stability of plasma membrane	Chhipa (2017)
	Sand	160	*Arachis hypogaea*	Ca in stems, protein and soluble sugar upgraded	Bandala and Berli (2019)
Mg	Seed	2.5	*Vigna unguiculata*	More stable plasma membrane, improved chl, Mg content in stem and increased seed production	Chhipa (2017)
	Foliar	0.5	*Vigna unguiculata*	Photosynthesis improved, growth as well as yield	Dimkpa and Bindraban (2018)
K	Foliar	150	*Arachis hypogaea*	Significant rise in nutrient content of shoots and seeds	Afify et al. (2019)
NPK	Foliar	NA	*Solanum tuberosum*	Increased production and quality	Abd El-Azeim et al. (2020)

to crops in order to manage the deficiencies. These nutrients act contrarily in soils; few of them may exist in sufficient amount, but may not be accessible for absorption by plant (e.g. iron and manganese). On the other hand, boron may offer some difficulty to accrue, particularly in sandy soils due to its crusade (Sharma et al. 2017).

Iron NFs

Iron is an imperative cofactor for enzymes which deals with biological processes in plants (Tarafdar and Raliya 2013), and it is present in the soil in high amounts (Talaei 1998), but remains unavailable for the plants, owing to its insoluble form. Therefore, NFs are the sole alternatives for making the iron available for plants (Armin et al. 2014).

Hu et al. demonstrated the influence of diverse concentrations of iron oxide NFs and ferric ions on the physiological variations in *Citrus maxima* plants. Although the study revealed insignificant effect at very low concentrations, not much influence was reported by plants even at very high concentrations (Hu et al. 2017). In an investigation, the foliar application of *Vigna unguiculata* with iron NPs at 500 mg/L significantly enhanced the number of pods per plant by 47%, weight of seeds by 7%, iron content in leaves by 34% and chl content by 10% (Delfani et al. 2014).

In an additional study by Askary et al., the application of iron oxide NFs in plants treated with various concentrations caused a significant rise in growth parameters such as chl and total protein contents (Askary et al. 2017). Further, the evaluation of γ-iron oxide NFs (20–100 mg/L) in watermelon and *Zea mays* increased the chlorine content (Hu et al. 2018). Lower concentrations (0–0.75 g/L) of ferrous oxide NPs were reported to enhance the chlorine content and the levels of lipids and proteins, whereas reduction in these parameters was achieved at higher concentrations (0.75–1.0 g/L) in soybean plants (Sheykhbaglou et al. 2018). Another report which evaluated the effects of nanoscale zerovalent iron on a terrestrial crop, *Medicago sativa* (alfalfa), exhibited higher content of chl in 20-day-old seedlings, while the lignin and carbohydrate contents decreased slightly (Kim et al. 2019). The application of cornelian cherry fruit extract-synthesized ferrous oxide NFs unveiled significant root and shoot biomass encouragement (Rostamizadeh et al. 2020). Further, magnesium and iron oxide NPs have also displayed high photosynthesis proficiency of black-eyed pea (Delfani et al. 2014). Moaveni et al. showed the foliar administration of Mg and FeO NFs on sour tea, which produced alterations in physiological traits and mucilage yield and assisted in improving its physiological properties (Moaveni et al. 2020).

Zinc NFs

Zinc plays a dynamic role in plant growth which acts as a cofactor for several plant enzymes such as isomerases, aldolases, dehydrogenases, transphosphorylases and RNA and DNA polymerases (Hassan et al. 2020; Chaudhuri and Malodia 2017). This element protects the plants against several pathogens (Cabot et al. 2019) and is involved in cell division, tryptophan synthesis, photosynthesis and protein synthesis and also maintaining the membrane structure and potential (Chaudhuri and Malodia 2017). Apart from the limitations of zinc fertilizers in soil fixation, zinc NFs have shown great potential for improvement of crop production yield and quality (Wang et al. 2016). Therefore, appropriate amounts of zinc are essential for different plants for better quality and improved yield. Zinc NFs can be applied to plants using various simple and cost-effective techniques such as direct mixing in soil, foliar spray and seed priming (Narendhran et al. 2016; Sharifi et al. 2016; Khanm et al. 2018; Munir et al. 2018). Davarpanah et al. premeditated the effect of low as well as diverse concentrations of zinc NFs (636 mg) or boron NFs (at 34 mg) on pomegranate and found improvement in the fruit quality along with great yield (Davarpanah et al. 2016). In another study by Moghaddasi et al., the shoot growth and fruit yield were augmented in cucumber seedlings grown in zinc NFs containing nutrient solution in comparison to conventional zinc sulphate fertilizer (Moghaddasi et al. 2013). Also, zinc NFs were designed for the improvement of yield in pearl millet (*Pennisetum glaucum* L.), and it was observed that the development and production of the crop were boosted significantly (Tarafdar et al. 2014).

Zinc oxide NFs at low concentrations (≤100 mg/Kg) mixed with soil resulted in enhanced zinc uptake by cucumber plants, in contrast to higher concentrations (1000 mg/kg) which caused inhibition of plant growth (Moghaddasi et al. 2017). Furthermore, the foliar application of zinc oxide NPs on *lisianthus* enhanced anthocyanin and chl content with an improved number of leaf, branches and flowers (Seydmohammadi et al. 2020). Recently, Abbasifar et al. utilized foliar application of green-synthesized zinc NFs (at a dose of 4000 ppm) as well as copper NFs (at a dose of 2000 ppm), respectively, for basil plants. It was found that copper NPs significantly affected chl content of basil leaves along with maximum flavonoid and phenolic content and highest antioxidant activity with zinc NFs only (Abbasifar et al. 2020). Shebl et al. manufactured zinc, manganese and iron nano-oxide NFs for foliar application employing green chemistry technique with particle size around 20–60 nm and applied on squash plants. The results exhibited that the spraying of MnO NFs on the plants resulted in maximum development of root, shoot, leaf area, fruits, yield and the content of photosynthetic material. The content of organic matter such as protein, lipids and energy was reported highest in squash fruits sprayed with ferrous oxide NFs (Shebl et al. 2019). Iron and Mn NFs were biosynthesized via a rapid and simple technique using microorganism's supernatant containing auxin complex and evaluated as plant NFs. The synthesized NFs revealed to be apposite as micronutrient fertilizers for crop production. Among these, bimetallic manganese oxide/ferrous oxide NFs from bacterial supernatant exhibited the finest outcome on plant growth, especially in germination rates, root growth and fresh weight in maize plantlets giving an idea for using these as micronutrient NFs (de França Bettencourt et al. 2020).

Copper NFs

Copper can be considered as a crucial constituent for several important physiological functions, including respiration, cellular transportation, antioxidative activity, protein trafficking, photosynthesis, hormone signalling of plants (Priyanka et al. 2019) and cofactor of antioxidants such as ascorbate oxidase and superoxide dismutase (Rai et al. 2018). The deficiency of copper leads to various problems such as necrosis; stunted growth; low seed, grain and fruit number; and low crop production. Organic matter in soil impacts the accessibility of copper; therefore, the soil application of copper NFs may prove advantageous owing to their large surface area, high solubility and reactivity (Hong et al. 2015). The administration of copper ions in minor amounts has been suggested for serving the purpose of microelement and stimulating plant growth (Rajput et al. 2018). In recent studies, the field application of copper oxide NFs enhanced the propagation and root growth of soybeans and chickpeas (*Cicer arietinum* L.) (Adhikari et al. 2012). Likewise, the nanocrystalline powders of copper, cobalt and francium (at concentrations of 40–60 nm) had 65%, 80% and 80% sprouting rates of soybean-treated seeds (Ngo et al. 2014). Similarly, diverse concentrations of copper NPs augmented the development and yield of wheat due to expansions in leaf area, chl pigments, number of grains/spike and grain mass; however, enhanced flavonoid content, sulphur acclimatization and proline and glutathione content in *Arabidopsis thaliana* were observed after applying copper NPs with dose of 5 mg L^{-1} (Nair and Chung 2014).

The application of biosynthesized (using *Citrus medica* L. fruit extract) copper NPs (at doses ~20 μg/ml) improved the mitotic index in actively dividing cells of onion (*Allium cepa*) (Nagaonkar et al. 2015). Improvement in stress tolerance in wheat was achieved with the employment of copper nanoparticles as indicated by improved levels of proteins intricated in starch degradation and glycolysis, superoxide dismutase activity, sugar content and Cu content in copper nanoparticle-treated seeds (Yasmeen et al. 2017). A substantial increase in root length, height and fresh and dry weights of pigeon pea (*Cajanus cajan* L.) seedlings was noticed when treated with biogenic copper nanoparticles having 20 nm size (Shende et al. 2017). Encapsulation of copper nanoparticles in CSPVA hydrogels improved the yield, nutraceutical properties and total antioxidant capacity and showed higher lycopene content (Hernandez et al. 2017). Treatment of tomato plants with copper nanoparticles has been reported to produce fruits with more firmness along with enhancement in vitamin C, lycopene contents, antioxidant capacity and activity of superoxide dismutase and catalase (López-Vargas et al. 2018). Foliar spray of copper-chitosan nanoparticles or in combination with seed coating has boosted the yield and growth profile of finger millet plants as well as enhanced defence enzymes resulting in the suppression of blast disease (Sathiyabama and Manikandan 2018). Seed priming of *Helianthus annuus* with copper nanoparticles led to higher content of proteins and oil in seeds (Polishchuk et al. 2013).

Various metals such as copper and silver have been employed for regulating morbific microorganisms owing to their potent antimicrobial properties. Lately, some of the metal nanoparticles, viz. aluminium, copper, gold, magnesium, silver, titanium and zinc, have been revealed to have promising antimicrobial activity and exhibited inhibition of microbial growth through diverse mechanisms (Sánchez-López et al. 2020). The rare crystalline structure which exhibits great surface area enables copper oxide nanoparticles to be an effective antimicrobial agent (Mahmoodi et al. 2018). Further, the high concentrations of copper oxide nanoparticles are essential for their superior antibacterial action (Concha-Guerrero et al. 2014). Furthermore, copper oxide nanoparticles have been also reported to have antimicrobial activity against pathogenic bacteria such as *S. flexneri*, *E. coli*, *S. typhimurium* and *E. faecalis* (Ahamed et al. 2014). In another study, Amiri et al. also conducted an agar diffusion test to evaluate the antimicrobial efficacy of copper oxide nanoparticles against *Streptococcus* mutants and *Lactobacilli* and produced effective results against both the bacterial species (Amiri et al. 2017). Copper oxide NPs, biosynthesized by using papaya leaf extracts, resulted in outstanding antibacterial activity against *R. solanacearum*, a soil-borne pathogen (Chen et al. 2019). Moreover, copper oxide NPs damaged the cell wall of the micro bacteria resulting in leakage of the inner cellular components. It has also been reported to generate toxic hydroxyl radicals which lead to the expiry of the bacteria (Taran et al. 2017). Copper oxide nanoparticles biosynthesized by the actinomycetes and improved antagonistic activity for bacteria were conveyed against some bacterial pathogens (Nabila and Kannabiran 2018). Likewise, Qamar et al. manufactured copper oxide nanoparticles from *Momordica charantia* plants with enhanced antimicrobial activity against various bacterial pathogens such as *Bacillus cereus*, *Corynebacterium xerosis* and *Streptococcus viridians* (Qamar et al. 2020). Some studies have shown the great antimicrobial potential of copper nanoparticles against some bacterial species such as *Escherichia coli*, *Pseudomonas aeruginosa*, *Micrococcus luteus*, *Staphylococcus aureus* and *Klebsiella pneumoniae* and several fungal species such as *Candida albicans*, *Aspergillus flavus* and *Aspergillus niger* (Ramyadevi et al. 2012).

Boron NFs

Boron is also a key element for the development and enlargement of plants, as it involves biosynthesis of the cell wall and its lignifications (Wimmer et al. 2019). It also plays a substantial role in the elongation of pollen grains and tubes, formation of cellular walls, transfer of photosynthetic organisms from leaves to active sites and proliferation in flowers and fruit yields (Davarpanah et al. 2016; Ahmad et al. 2009). Further, it is also indispensable for the development of bark, the transmission of some active hormones that affect the growth of the stem and root levels, germination of pollen, flowering and increasing the level of carbohydrates and transfer to active areas of growth during the reproductive stages. The flowering stage requires its continuous supply, while it should be present in sufficient amount for effective nodulation and nitrogen fixation in legumes (Shil et al. 2007). Boron deficiency can be lessened with the help of fertilizers, but the harmful effect of recurrent fertilizer application disturbs soil fertility and results in environmental pollution. In this viewpoint, nanotechnology has been proposed as an alternative technique, which can be effectively used for boron acquisition (Shireen et al. 2018). Literature studies have implicated the role of boron NFs in improving plant growth and yield. Ibrahim and Al Farttoosi sprayed 0, 90 and 180 mg/L of boron NPs, in which 90 mg/L of boron NPs reported greater plant pod number and seed yield when correlated to conformist fertilizer on mung bean crops (*Vigna radiata*) (Ibrahim and Al Farttoosi 2019). Likewise, nano-boron (20 ppm) and nano-zinc sprayed (at 200 ppm) respectively on olive trees plants produced more fruits with improved oil content in seeds (Genaidy et al. 2020). Similarly, another study stated a larger number of fruits and a higher productivity yield in pomegranate (*Punica granatum*) after the application of boron NFs (at the rate of 34 mg boron per tree) (Davarpanah et al. 2016). Taherian et al. applied boron NFs to alfalfa (*Medicago sativa*) crop under calcareous conditions and harvested maximum yield with suitable forage quality. If concluded, boron NFs can massively improve the quality and yield of crops (Taherian et al. 2019).

Manganese NFs

Manganese possesses a dominant role in many physiological processes by acting as a cofactor of many enzymes; acts as an essential micronutrient in nitrogen metabolism, photosynthesis and the biosynthesis of fatty acids, ATP and proteins; and aids plants to manage different stresses (Palmqvist et al. 2017). Although previous reports have uncovered that the administration of manganese considerably advances the growth and yield of wheat, maize, sugarcane, soybean and common beans, higher doses of manganese may prove fatal to different plants (Fageria 2001; Dimkpa and Bindraban 2016). Manganese NFs can augment the root and shoot growth in mung bean (*Vigna radiata*) by 52% and 38%, respectively, in comparison to manganese sulphate salt, a conventional manganese fertilizer. Maximum growth increment was achieved by using manganese nanoparticles at 0.05 mg/L, and the increased effect was noted in shoot length by 10%, in root length by 2%, in fresh biomass by 8%, in a number of rootlets by 28% and in dry biomass by 100% with respect to manganese sulphate salt (Pradhan et al. 2013). Manganese treatments also boosted the yield of eggplant (*Solanum melongena* L.) by 22% (Elmer and White 2016) and pointedly amplified the root length of lettuce (*Lactuca sativa* L.) (Liu et al. 2016). Manganese NFs (0.1, 0.5, 1 mg/L), when evaluated as a nano-priming agent to improve salinity stress (100 mM NaCl during germination) in *Capsicum annuum* L., have been found to significantly improve the root growth in salt-stressed as well as non-salt seedlings (Ye et al. 2020). However, no prominent effect of manganese NFs on the root length of *Sinapis alba* (white mustard), the germination of seed in lettuce and yield of watermelon (*Citrullus lanatus*) was observed (Landa et al. 2016). At the physiological level, manganese nanoparticles clasp with the chl-binding protein (CP43) of photosystem II, and ultimately enhance the activity of the electron transport chain, affecting the overall efficiency of photosynthesis. Consequently, plants fertilized with manganese nanoparticles have shown a higher rate of nitrogen acclimatization and absorption in contrast to conformist substance applications (Pradhan et al. 2013).

Nickel NFs

Although nickel has been known as a trace element, its uptake is quite imperative for different enzyme activities, for maintenance of cellular redox condition, and several other activities responsible for development such as physiological, biochemical and growth responses (Yusuf et al. 2011). Nickel is required by the urease enzyme which absorbs urea nitrogen into ammonia inside the plant. It also controls absorption of minerals, enzymatic action and several other metabolic progressions of plant. Nickel deficiency induces urea toxicity in which urea gets accumulated inside the tissues which lead to necrotic regions on the leaf tips. Besides this, nickel also possesses systemic fungicidal activity for the management of cereal nuts. Besides this, they also contribute in increasing crop yields (Mahapatra et al. 2022). Nickel NFs of 5 nm at low concentrations of 0.01 and 0.1 mg/L exhibited no effect or stimulated growth in 10-day wheat seedlings although a little surge was noticed in the content of chl after the application of 0.01 mg/L (Zotikova et al. 2018). Biosynthesized nickel NFs' antimicrobial activities were also evaluated and enumerated against a host of pathogenic bacteria such as *Bacillus subtilis*, *Escherichia coli*, *Klebsiella pneumonia*, *Staphylococcus epidermidis* and *Salmonella typhi* and fungi such as *Aspergillus clavatus*, *Aspergillus fumigatus*, *Aspergillus niger*, *Candida albicans* and *Candida tropicalis* (Ameen et al. 2021).

There are a few investigations about the synthesis of nickel NFs from bacteria and fungus. Inoculated microbial strains in the broth along with 1 mM nickel sulphate after 2 days resulted in nickel NPs blend based on the production of subordinate metabolites and proteins, which could diminish the metal campuses to particular metals (Horeyalla et al. 2017). Nickel ferrite nanoparticles have displayed potent fungicidal activity against plant fungi and assist in management of plant disease by improvement in crop growth. These nanoparticles have obtained remarkable results in both plant protection and growth of the plant (Sharma et al. 2017). Such NPs have been appropriately assessed and verified for fungicidal activity against *C. gloeosporioides* and *F. oxysporum* which have been described to inhibit the occurrence of wilt caused by *Fusarium* in tomato, capsicum and lettuce.

Molybdenum NFs

Molybdenum is required in very small quantities (in ranges between 0.3 and 1.5 ppm) for most of plant tissues as low as 0.01 mg/L and 0.20 mg/L for a growing medium. Molybdenum deficiency or toxicity is rare, but its deficiency is commonly found in poinsettias (*Euphorbia pulcherrima*) (Thomas et al. 2017). Molybdenum is important for two enzymes that convert nitrate to nitrite and then to ammonia prior to its use in the synthesis of amino acids within the plant (Mendel and Hänsch 2002). In legumes, it is required by symbiotic nitrogen-fixing bacteria for the fixation of atmospheric nitrogen (Self et al. 2001). It is also used by plants for the conversion of inorganic phosphorus into organic forms. Due to the alluring benefits of NFs, attempts have been made to study the effects of molybdenum NFs as a fertilizer. Taran et al. established colloidal molybdenum NFs and colloidal molybdenum along with microorganisms NFs for chickpea where both were observed to be highly effective in terms of activity, yield and resistance against disease of legumes during unfavourable situations (Taran et al. 2014). Similarly, biosynthesized molybdenum NFs (2–7 nm) at dose of 4 ppm using a fungus *Aspergillus tubingensis* TFR29 have revealed significant development in root area, root diameter, root length, tip number, beneficial enzymes and microbial activities in the rhizosphere, biomass and grain yield (Thomas et al. 2017).

Selenium NFs

Selenium occurs in diverse forms comprising oxyhalides, selenides, halides, oxides, acids, oxyacids, selenoenzymes and selenium nucleic acids (Skalickova et al. 2017). Earlier data has reported it as a toxic element; however, modern investigations have reported its concentration-dependent toxicity (Uttam and Abioye 2017; Meetu and Shikha 2017). Selenium falls in the similar group as sulphur and may be present in different oxidation states. More than one billion people are affected by selenium malnutrition globally; thus, its supplementation in plants as well as animals becomes more crucial for human well-being (WHO 2009). Sewage waste, phosphate fertilizers and farmyard manures are the prominent reservoir of selenium micronutrient (Uttam and Abioye 2017). Selenium nanoparticles exhibit remarkable physicochemical properties and high bioavailability with some vital physiological functions like potential antimicrobial, anticancer or antioxidant properties. These are prominently employed as supplements in plants and food and also extensively utilized in nanomedicines owing to their less toxicity profiles (Hosnedlova et al. 2018). They also perform as detoxifying mediators once they come in contact with heavy metals such as mercury, cadmium or lead; these properties have empowered them to guard living organisms against numerous diseases. Selenium compounds could simply functionalize with ligands such as selenocystin binding with glutathione peroxidase that counteract the free radicals existing in cells, therefore eliminating the detrimental effect of the radicals. However, selenium nanoparticles barely interact with other complexes and are gently released into living systems (Carvalho et al. 2003). Broadly, selenium fertilization can remarkably magnify the production of biochemical compounds such as amino acids, flavonoids, glucosinolates, protein and phenolic compounds (Meetu and Shikha 2017). Schiavon et al. described the improvement in the flavonoid and phenolic content in selenium biofortified tomato fruit (Schiavon et al. 2013). Dinkova-Kostova et al. also reported an escalation in glucosinolates, which hydrolyses to form isothiocyanates that bears outstanding anticancer properties (Dinkova-Kostova 2013). Further, sodium selenite, selenous acid or selenium oxide can be utilized as the precursor compound for the synthesis of selenium nanoparticles and plant substrates from *Vitis vinifera* fruits, *Bougainvillea spectabilis* wild flowers, etc. have been employed (Sharma et al. 2014; Ganesan 2015).

Selenium nanoparticles biosynthesized by *Trichoderma species* unveiled growth-promoting characters in *Vigna radiata* plants (Keswani et al. 2014; Keswani et al.

2016; Barbieru et al. 2019). Table 7.2 summarizes the use of micronutrients as NFs and their impact on different plants. However, their immoderations are damaging the growth of crops, thereby resulting in various nutritional problems.

4.3 Nanomaterial-Enhanced Fertilizers (NEF)

Nanoparticles composed of chitosan and methacrylic acid employed for encapsulation of N, P and K were evaluated on garden pea. It was noticed that the rate of root elongation in plants reduced in a dose-dependent manner along with upregulation of some major proteins at lower concentrations (Khalifa and Hasaneen 2018). Few other NPs, such as TiO, silicon oxide and carbon-based NPs, have been potentially reported to promote the growth of the plant (Chhipa 2017). Similarly, *Lycopersicon esculentum* plants and *Glycine max* also exhibited enhancement in growth and accumulation of nitrogen or seed germination, respectively, once titanium oxide and zinc oxide nanoparticles were applied (Raliya et al. 2017; Changmei et al. 2002).

NPs such as chitosan, zeolites and polymers facilitate considerable enhancements in the absorption of organic nutrients through nanoencapsulation approaches, forming a sustainable rich source of nutrients for the plants (Qureshi et al. 2018).

4.4 Nano-biofertilizers (NBFs)

NBFs embrace a deliberate co-occurrence of a biocompatible nanomaterial and a biological source-driven fertilizer that aims to expedite slow and gradual release of nutrients over a prolonged period for improving NUE and better crop yield and productivity (Duhan et al. 2017; Thirugnanasambandan 2019). NBFs primarily comprise biologically suitable microorganisms like rhizobium, blue-green algae, mycorrhizae and bacteria (such as *Azotobacter*, *Azospirillum*, *Azorhizobium*, *Ascophyllum pseudomonas*, *Beijerinckia* and *Bacillus* species) which along with NFs act synergistically not only by curbing the nitrogen-fixing capacity but also by improving the solubility of insoluble complex organic matter to simpler form. This diverse microflora helps to maintain moisture-absorbing ability of host soil which aids in enhancing the nutrient availability to plants, by maintaining a homogeneous soil texture by replenishing soil and microbial content and augmenting soil aeration and natural fertilization (Itelima et al. 2018). The combined application of NBFs with nanoparticles along with beneficial microbes may ensure delayed/scheduled site-specific nutrient delivery to plants, thus improving the overall activity of NFs.

Although application of NBFs seems innovative and renewable, the assessment of traits such as susceptibility at the nanoscale, field stability, unstable environment conditions (such as fluctuations in temperature, pH sensitivity and radiation exposure), availability of required bacterial strains (along with their vulnerability towards desiccation) and the markedly high amount becomes indispensable for a big zone

Table 7.2 Effect of various micronutrient-based NFs on crops and plants

Micronutrient	Exposure route	Concentration of micronutrient	Plant/crop	Results	References
Fe_2O_3	Spray	0.25, 0.5, 0.75 and 1 g/L	*Glycine max*	Increase in dry weight of leaf, pod and yield	Sheykhbaglou et al. (2010)
	Growth medium	1 g/L	*Lactuca sativa*, *Cucumis sativus*	Increased iron adsorption on the seed surface	Wu et al. (2012)
	Soil	1–6 g/L	*Zea mays*	Improvement in chl pigments and growth	Pariona et al. (2017)
	Growth medium	0.5, 4 g/L	*Arachis hypogaea*	Protein levels improved	Suresh et al. (2016)
	Soil	0.002, 0.02 and 0.05 g/L	*Citrullus lanatus*	Augmented germination of seed, seedling and antioxidant enzyme activity	Li et al. (2013)
Fe	Foliar	0.25, 0.5 g/L	*Pisum sativum*	Improved seed protein, chl content and yield, decreased the firmness of plasma membrane	Alidoust and Isoda (2014)
	Soil	0.25 g/kg and 1 g/kg	*Pisum sativum*	chl and carotenoid content increased, the mass of fresh plant	Mukherjee et al. (2016)
	Foliar	0.05–2 g/L	*Zea mays*	Better growth, quality along with yield	Subbaiah et al. (2016)
	Seed	0.25, 0.50 and 0.75 g/L	*Capsicum annuum*	Heightened root and shoot, seed germination and growth of seedling	Afrayeem and Chaurasia (2017)
	Soil	0.002, 0.004, 0.008 and 0.016 g/L	*Lycopersicum esculentum*	Improved photosynthesis rate and growth, enzymes and proline content	Faizan et al. (2018)
	Foliar	2 g/L	*Helianthus annuus*	Improved leaf surface area, shoot dry weight, chl and Zn content, rate of CO_2 acclimatization	Torabian et al. (2016)
Fe NPs	Foliar	0.5 g/L	*Vigna unguiculata*	Significantly improved the pod number, seed weight, Fe content and chl content	Delfani et al. 2014

(continued)

Table 7.2 (continued)

Micronutrient	Exposure route	Concentration of micronutrient	Plant/crop	Results	References
ZnO	Hydroponic	0.025, 0.05, 0.075, 0.1 and 0.2 g L	*Gossypium hirsutum*	Improved protein content, plant growth, biomass, antioxidant activity, photosynthesis rate	Priyanka and Venkatachalam (2016)
	Soil	1 g/L	*Vicia sativa*	Length of shoot increased	García-Gómez et al. (2015)
	Hydroponic	0.1, 1 g/L	*Cucumis sativus*	Increased germination rate and variation at different concentrations	Zhang et al. (2015)
	Foliar	0.001 g/L	*Pennisetum glaucum*	Improved growth of root and shoot, chl pigments and leaf protein	Tarafdar et al. (2014)
	Foliar	0.001 g/L	*Coffea arabica*	Increased growth, higher biomass production and photosynthetic rate	Rossi et al. (2019)
	Mixed substrate	0.002 g/L	*Triticum aestivum*	Increased biomass production and yield	Du et al. (2019)
	Hydroponics	0.2 μm and 1 μm	*Nicotiana tabacum*	Increased metabolites, growth, enzyme activity	Shang et al. (2019)
	Distilled water	0.005 g/L	*Oryza sativa*	Increased the formation of reactive oxygen species in roots	Wang et al. (2015)
	Hydroponic	0, 0.01 and 0.02 mg/L	*Zea mays*	Improved growth	Adhikari et al. (2016)
	Hydroponic	0.025, 0.01, 0.05, 0.1 and 1 g/L	*Oryza sativa*	Enhanced activity of malondialdehyde, ascorbate peroxidase, superoxide dismutase and proline content	Da Costa and Sharma (2016)
	Soil	≤100 mg/kg	*Cucumis sativus*	Enhanced Zn uptake	Moghaddasi et al. (2017)
	Foliar	NA	*Lisianthus*	Enhanced anthocyanin and chl content with improved number of leaves, branches and flowers	Seydmohammadi et al. (2020)

Micronutrient	Exposure route	Concentration of micronutrient	Plant/crop	Results	References
CuO	After germination	2–100	*Zea mays*	No improvement	Wang et al. (2012)
	Soil	0.08 mg/kg	*Coriandrum sativum*	Accretion of Cu improved	Zuverza-Mena et al. (2015)
	Mixed with soils	<50 nM	*Cicer arietinum* L.	Better germination and root growth	Adhikari et al. (2012)
	Mixed with soils	20 μg/mL	*Allium cepa*	Improved the mitotic index in dynamically dividing cells	Nagaonkar et al. 2015
	Mixed with soils	0.2 g/kg	*Spinacia oleracea*	Enhanced photosynthetic rate and yield	Wang et al. (2019)
	Fruit spray	100 μg/mL	*Prunus domestica*	Limited the symptoms of grey mould (*B. cinerea*)	Malandrakis et al. (2019)
CeO_2	Hydroponic	0.4 g/L	*Cucumis sativus*	Improved content of globulin and scratch	Zhao et al. (2014)
TiO_2	Sand	0.25, 0.5, 1, 2 g/L	*Triticum aestivum*	Unpretentious	Ramesh et al. (2014)
	Nutrition pots	0.05, 0.1, 0.2 mg/L	*Solanum lycopersicum*	Photosynthetic rate, transpiration of water and its conductance improved	Qi et al. (2013)
	Foliar application	0.02, 0.03 g/L	*Oryza sativa*	Better growth and limited cadmium mobilization	Shang et al. (2019)
MnO	Seed	0.00025–0.05 g/L	*Lactuca sativa*	Improved the length of root	Liu et al. (2016)
Mn	Seed	0.05 mg/L	*Vigna radiata*	Increased shoot length by 10%, in root length by 2%, in fresh biomass by 8%, in number of rootlets by 28%	Pradhan et al. (2013)
S	NA	0.5–4 g/L	*Vigna radiata*	Increased dry weight	Patra et al. (2013)
Zn NPs	Foliar	4 g/L	*Ocimum tenuiflorum*	Increased chl pigments in leaves along with phenolic and flavonoid content and antioxidant activity	Abbasifar et al. (2020)
Cu NPs	Foliar	2 g/L	*Ocimum tenuiflorum*	Increased chl pigments in leaves along with phenolic and flavonoid content	Abbasifar et al. (2020)

which limits this technology to a certain extent (Mishra et al. 2017). Such issues also complicate the desired nutrient accessibility to the host plant, which causes a consistent possibility of environmental quality deterioration. Therefore, nanoscale biofertilizers resolve these issues by providing structural protection to biofertilizer nutrients and plant growth-promoting microbes, through nanoencapsulation/coating of nanoscale polymers (Golbashy et al. 2017). The heterogeneous impacts of NBF on soil texture and plant system enzymes manifest significant benefits in enabling improved growth and nutritional quality. The large surface coatings of NPs over the biofertilizer improve the distribution of constituent nutrients.

Further, increased surface area, nanoscale dimensions and higher chemical reactivity of NP-coated fertilizers enable improved interaction and stable chemical texture, thereby allowing efficient uptake via improved bioavailability. Moreover, the steady release from the nanocarriers also ensures long-term availability of administered fertilizers along the diverse stages of plant growth (El-Ghamry et al. 2018). The biological content (microbes) of NBFs gets synergistically benefitted via refining the soil's nutritional content, atmospheric nitrogen fixation, activities of plant roots or rhizobacterium and formation of siderophores for metal chelation, thereby improving the accessibility to plant root, or phosphorus solubilization through phosphorus solubilizing bacterial and fungal strains (Ahemad and Kibret 2014; Mala et al. 2017). The healthy response of NBF administration in crop plants has been reported in a wide array of studies, in terms of improved qualitative as well as quantitative plant growth parameters (Dhir 2017). Table 7.3 summarizes the typical role of NBFs in enhancing plant growth and nutritional content during the last decade.

5 Advantages of NFs over Conventional Fertilizers

NFs (also known as smart fertilizers) exhibit a lot of benefits over conventional fertilizers (as displayed in Table 7.4) for sustainable and eco-friendly crop production regardless of some concerns presented by few researchers regarding the adverse effects owing to their improper usage or application (Tarafder et al. 2020; Iqbal 2019; Zulfiqar et al. 2019; Qureshi et al. 2018; Basavegowda and Baek 2021).

6 Limitations and Risk Management of NFs

Recent progress in the field of NFs for achieving enhanced crop quality and better yield has emerged as one of the spectacular success stories in the agro-food industrial sector. Although the practice of NFs is indisputably opening fresh avenues for smart and sustainable agriculture, their possible menace to plants, soil microorganisms and humans should also be sensibly measured before their commercial application. The extensive use of NFs may have some significant limitations in terms of

Table 7.3 List of NBFs employed in diverse plant applications

NBFs	Exposure method	Concentration (%)	Plant/crop	Result	References
Zinc oxide (ZnO) + (*Pseudomonas fluorescens*)	Foliar	0.02	*Vigna radiata*	Revealed growth in shoot length, biomass of root	Dhoke et al. (2013)
Iron oxide (FeO) + (*Pseudomonas fluorescens*)	Precipitation	0.05	*Triticum aestivum*	The NBF improved the number of spikes and its length, seed number, weight and overall harvesting	Mardalipour et al. (2014)
Iron (Fe) + (*Pseudomonas and Azotobacter*)		0.02			
Zinc (Zn) + (*Pseudomonas and Azotobacter*)		0.04			
Manganese (Mn) + (*Pseudomonas and Azotobacter*)		0.08	*Zea mays* L.	Increased grain yield	Farnia and Omidi (2015)
Chelated (*Phosphorbarvar and Azetobarvar*)		0.03	*Zea mays* L.		
Zinc (Zn) + (*Pseudomonas* bacteria)		1.0	*Zea mays*		
Calcium (Ca) + (*Ascophyllum nodosum*)	NA	4.0	Forage sorghum	Highest Chl$_a$, Chl$_b$, carotenoid and carbohydrates were observed	Biosci et al. (2015)
NPK + (*Rhizobacteria*)	Sol-gel	5.29	*Vitis vinifera*	Overcome the consequences of the abiotic stress with improved quality and yield	Sabir et al. (2014)
Titanium (Ti) + (*Azorhizobium caulinodans*)		0.02	*Triticosecale*	Reduced the damaging effect of ROS along with higher grain yield and weight, chl content	Ghooshchi (2017)
NPK + (*Azotobacter*)	Ultrasonication	–	*Vigna radiata*	Enzyme activities as well as seed vigour index improved	Ruby Celsia and Mala (2014)

Table 7.4 Comparative benefit analyses of NFs versus conventional fertilizers

Advantages	Conventional fertilizer	NFs
NUE	High loss rate during drifting, leakage, overflow	Little loss of nutrients
Controlled release	Additional release of nutrients leads to extra toxicity and causes imbalance in soil	Controlled release
Modified and synthesis as per requirement	Not applicable	Can be manufactured/designed rendering to the nutrient requirements of specific crop
Application of biosensor	Not applicable	Biosensors can be attached to a new smart NFs which can control the delivery of the nutrients according to soil nutrient status
Effective cost	High	Small amounts are required which decrease the cost of transportation and field administration
Loss of nutrients	High	Low
Solubility/diffusion	Low	High
Bioavailability	Low	High
Dispersion of mineral micronutrients	Lesser solubility due to large size	Improved dispersion of insoluble nutrients
Effective duration of release	Used by the plant during administration; the leftover is transformed into an insoluble form	Effective and extended duration
The efficiency of nutrient uptake	Mostly not available for roots and if available the efficacy of nutrient absorption is low	Improved absorption ratio
Soil fertility	Not much involved	NFs improve the soil fertility and design a possible environment for microorganisms
Stress reliever	Low efficiency	Fights against various biotic and abiotic stresses
Soil contamination and environmental hazard	High	Reduced
Antimicrobial activity	Low	New NFs along with microbial flora can be designed for specific use
Fertilizer demand with time	High	Low
Cost-effective	High	Low
Precision	Low	High
Hazardous to the environment	High	Low

the biocompatibility of NFs, which must also be calibrated and assessed critically. In the early phases of crop development, the progress of the crop is directly proportional to the critical concentration of nutrient in the tissue (known as deficiency phase) followed by a rise in the nutrients and no more growth occurs (termed as adequacy phase) and finally when the increased concentration of nutrients in the tissue becomes detrimental for the crops (called as toxic phase) (Mahapatra et al. 2022).

With the dawn of nanotechnological applications in the agriculture arena, it has become fervently imperative to devise vibrant strategies for synthesis, storage, dose regimens, exposure route and proper risk management of NFs, as there is an absolute dearth of regulatory guidelines or standard praxis for the precise calculation of nano-contaminants in farming situation or criteria for their toxicity evaluation. It is a matter of fact that applications of NFs are still in nascent stages, and there are no acceptable scientific regulations that can guarantee or label NFs with no risk (Mahapatra et al. 2022). Therefore, the application of NFs like any other budding technology may have its pros and cons; however, the primary challenge is to reduce the limitations (such as large-scale production, higher cost of production and lack of standardization) after critical assessment of benefit versus environment risk (Aufan et al. 2009; Solanki et al. 2015; Iqbal 2019).

Further on the human health front, it is pertinent to note that NF nanoparticles may enter the human body through oral, respiratory or intradermal routes and even the accretion of these nanomaterials in the environment as well as the food chain could cause significant hazards to human health. Furthermore, it can be implied that these environmental and unanticipated health safety issues may pose obstacles in the application of nanotechnology in crop production. Hence, the design and use of NPs as fertilizers should be systematic in agriculture farming for their long-term effect of bio-accumulation and acquaintance in the plants, which might pose serious impact in the food chain as well (Bundschuh et al. 2018; Tiede et al. 2016).

Additionally, the employment of NPs as fertilizers should address all the safety and ethical concerns (such as exposure on human body or environmental risk) before their commercialization. Consequently, it becomes mandatory to analyse the practicability, risk assessment, risk identification and aptness of new smart NFs for the toxicity evaluation (Bratovcic et al. 2021). Various studies have proposed the pragmatic study of toxicity analysis of CuO and ZnO NFs on soil microorganisms or human health that should be taken into consideration before the application in agriculture settings (Rajput et al. 2020). Further, it was explicated that these NFs may also disrupt biological nitrogen fixation, may impair plant cells or may pose grave hazards to human health. Therefore, a comprehensive analysis of the phytotoxic effects of NFs in plants, their exposure routes, proper usage practices, effect on soil microorganisms and impacts on human well-being should be made mandatory before their possible application of nanomaterials (Seleiman et al. 2021).

7 Conclusions and Perspectives

It is needless to argue that the praxis of nanotechnology has whittled a niche in the agro-food landscape as one of the most expedient contrivances (despite few emerging agricultural and environmental challenges) predominantly associated with the necessities for augmented productivity, sustainability and security of agriculturally produced foods. Such avant-garde applications based on applied nanotechnology exhibit tremendous potential to concoct delivery systems for agrochemicals and plant breeding, thereby reducing the impact on environment and input costs while improving the quality as well as the scale of production yields. In contrast to these beneficial effects, myriad concerns have also emerged related to toxicological hazards and risks associated with application of NFs or nanopesticides (despite controlling the release of active compound, improved plant nutrition and stress tolerance) which primarily include release of nanomaterials into the environment. Several studies and research findings listed in this chapter also highlight the dearth of present level of understanding about the ecotoxicological effects of nanopesticides/NFs. Therefore, in the light of these aforementioned facts, it is warranted to examine the contributing risk factors of nanopesticides/NFs in comprehensive detail by elucidating the mechanism of fundamental steps involved in formulation design of NFs and pathways involved in plant physiology or plant nutrition for the precise and safe application of nanomaterials in agriculture.

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