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Review article

Nanofertilizer use for sustainable agriculture: Advantages and limitations

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ABSTRACT

Nutrient fertilization plays a critical role in maintaining soil fertility and improving crop productivity and quality. Precise nutrient management of horticultural crops is a major challenge worldwide as it relies predominantly on chemical fertilizers. Traditional fertilizers are not only costly for the producer, but may be harmful to humans and the environment. This has led to the search for environmentally friendly fertilizers, particularly those with high nutrient-use efficiency, and nanotechnology is emerging as a promising alternative. Nanofertilizers offer benefits in nutrition management through their strong potential to increase nutrient use efficiency. Nutrients, either applied alone or in combination, are bound to nano-dimensional adsorbents, which release nutrients very slowly as compared to conventional fertilizers. This approach not only increases nutrient-use efficiency, but also minimizes nutrient leaching into ground water. Furthermore, nanofertilizers may also be used for enhancing abiotic stress tolerance and used in combination with microorganisms (the so-called nano-biofertilizers) provide great additional benefits. However, although the benefits of nanofertilizers are undoubtedly opening new approaches towards sustainable agriculture, their limitations should also be carefully considered before market implementation. In particular, the extensive release of nanomaterials into the environment and the food chain may pose a risk to human health. In conclusion, although nanofertilizers use in agriculture is offering great opportunities to improve plant nutrition and stress tolerance to achieve higher yields in a frame of climate change, not all nanomaterials will be equally safe for all applications. The risks of nanofertilizers should be carefully examined before use, and further biotechnological advances are required for a correct and safe application of nanomaterials in agriculture.

1. Introduction

Agriculture, including horticultural crops, is a major economic sector related to the production and provision of a wide range of specialty crops for food, feed, and ornamental purposes and it currently represents a worldwide multitrillion dollar industry [1]. Limited resources and the rapidly-increasing human population, which is predicted to reach 9.6 billion by 2050, pushes the sector forward demanding the development of a very efficient agriculture while allowing reduction of worldwide poverty and hunger [2]. Chemical fertilizers provide plants with nutrients for optimal growth and productivity; however, current production practices cannot fulfill the growing demand of food without reliance on the extensive use of fertilizers [2]. Given the limited amount of additional arable lands and scarce water resources globally, the use of more efficient mineral fertilizers is a necessary approach to fulfill the increase in food production required to feed this increasing population and support economic development. Furthermore, intensive application of conventional fertilizers over extended periods of time has caused serious environmental constraints worldwide including ground water pollution, water eutrophication, soil quality degradation, and air pollution [3].

Limited nutrient use efficiency and environmental constraints associated with the use of chemical fertilizers remain a major problem and a hindrance for achieving reasonable sustainability in agriculture. Additionally, cost increases resulting from over-application of chemical fertilizers reduce profit margins for growers. Low nutrient use

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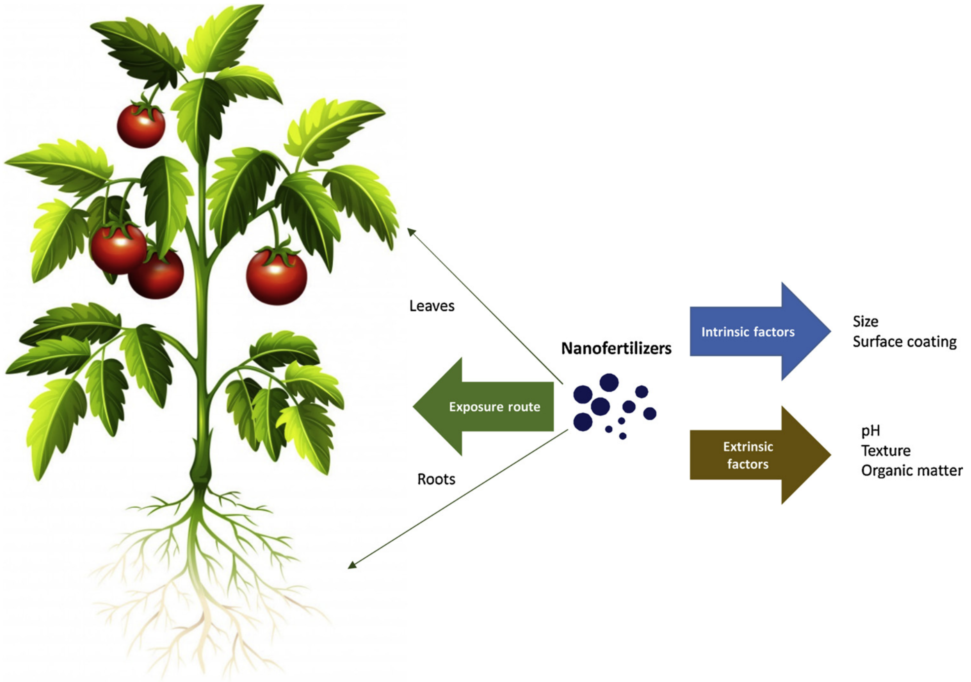

Fig. 1. Factors that influence uptake, distribution and accumulation of nanofertilizers in crops. Intrinsic factors (nanofertilizers), extrinsic factors (soil) and exposure route.

efficiencies are typically the result of high release rates of conventional fertilizers overwhelming the actual nutrient absorption rate by plants, and/or the transformation of fertilizers/nutrients to forms that are not bioavailable to crops [4]. As such, there is a great interest towards the development of new innovative fertilizer sources in order to increase the fertilizer use efficiency [5]. Several strategies have been proposed to increase fertilizer use efficiency, such as the use of precision fertilization, split or localized application, fertigation, and the use of nanofertilizers [6]. In the context of sustainable agriculture, application of nanotechnology for the development of new types of fertilizers is regarded as one of the potentially promising options for significantly boosting global horticultural production to meet the growing food demands of population with the added benefits of sustainability under the current scenario of climate change [7,8]. A correct application of nanofertilizers can feed plants gradually in a controlled manner [9] along with the benefits of increasing the fertilizer use efficiency, minimizing volatilization and leaching, and lessening environmental hazards [10]. Several studies, which will be discussed here, have revealed that some nanofertilizers have the potential to increase crop productivity by enhancing seed germination, seedling growth, photosynthesis, nitrogen metabolism, and protein and carbohydrate synthesis, aside from improving stress tolerance. Among other advantages, nanofertilizers can be applied in a comparatively smaller amount, ultimately reducing the transport expenditures and increasing ease of application. However, nanofertilizers may also have some disadvantages, which can limit their full implementation in the market.

2. Advantages of nanofertilizers

There is a growing pressure on the agriculture sector to fulfill the continuously increasing demands of the consistently growing human population. Chemical fertilizers are thought to be indispensable for improving crop productivity and are extensively applied through different methods [8]. However, crop usage is generally less than half of the applied amount of fertilizer [11], and the remaining amount of minerals intended to reach the targeted site may leach down, so that they become fixed in soil or contribute to water pollution [12]. For instance, it has been reported that key macronutrient elements, including N, P, and K, applied to the soil are lost by 40–70 %, 80–90 % and 50–90%, respectively, causing a considerable loss of resources [8,10,11]. Furthermore, growers tend to use repeated applications of these fertilizers in order to achieve desired higher yields, which contrarily can lead to a decrease in soil fertility and increase salt concentrations thereby causing future crop losses. Furthermore, uneven use of fertilization without control on nutrient release can deteriorate product quality. Hence, it is crucial to develop slow/control release fertilizers not only to increase crop production and quality, but also to enhance the sustainability in horticultural production [8]

The horticulture sector today is facing an intense pressure for achieving considerable efficiency in food security using alternatives to chemical fertilizers [12]. New approaches and technologies are required if global horticultural production and demand are to be fulfilled in an economically and environmentally sustainable manner. Materials that are of up to 100 nm particle size in at least one dimension are generally classified as nanomaterials [13,14] and are the basis for nanotechnology [15]. There are various types of nanomaterials such as single or multiwalled nanotubes, magnetized iron nanoparticles, copper (Cu), aluminum (Al), silver (Ag), gold (Au), zinc (Zn) and zinc oxide (ZnO), silica (Si), cerium oxide (Ce_2O_3), and titanium dioxide (TiO_2), among others [16–19]. Given the unique properties of nanomaterials such as high surface-to-volume ratio, controlled-release kinetics to targeted sites and sorption capacity, nanotechnology has a high relevance for the design and use of new fertilizers [8]. Nanofertilizers are nutrients encapsulated/coated with nanomaterial for the control and slow delivery of one or more nutrients in order to satisfy the imperative nutrient requirements of plants [20]. These “smart fertilizers” are currently being regarded as a promising alternative [21], to the extreme that they are in several cases considered to be the preferred form of fertilizers over the conventional ones [22,23].

The interaction of nanomaterials and fertilizers, due to the high reactivity of nanomaterials, results in an increased and effective absorption of nutritional elements and essential compounds for plants [24]. The efficiency of nanofertilizers depends on several factors (Fig. 1). Uptake, distribution and accumulation of nanofertilizers in crops will strongly depend on both intrinsic and extrinsic factors, and the exposure route. Particle size and surface coatings are the most important intrinsic factors influencing the efficiency of nanoparticles application, and extrinsic factors, such as organic matter, soil texture or soil pH will also strongly affect its potential application [25,26]. In addition, nanofertilizers can be absorbed through both plant roots or leaves, so that the exposure route and mode of application significantly influence the behavior, bioavailability, and uptake of nanofertilizers in crops [25].

Nanofertilizer applications in agriculture may serve as an opportunity to achieve sustainability towards global food production. There is a tremendous food production pressure on the sector as nutritional deficiencies in human populations are mainly because of using less nutritious food and a low dietary intake of fruits and vegetables [27]. Important benefits of nanofertilizers over conventional chemical fertilizers rely on their nutrient delivery system [12]. They regulate the availability of nutrients in crops through slow/control release mechanisms. Such a slow delivery of nutrients is associated with the covering or cementing of nutrients with nanomaterials [10]. By taking advantage of this slow nutrient delivery, growers can increase their crop growth because of consistently long-term delivery of nutrients to plants. For example, nutrients can be released over 40–50 days in a slow release fashion rather than the 4–10 days by the conventional fertilizers [11]. In conventional nutrient management systems, half of the applied fertilizer is lost in leaching or becomes unavailable for the plant because of excessive availability hindering the roots to uptake or sometimes causing toxic effects on the plant. Furthermore, nanofertilizers reduce the need for transportation and application costs [28]. Another advantage of using small quantities is that the soil does not get loaded with salts that usually are prone to over-application using conventional fertilizers on a short- or long-term basis [29]. Another advantage for using nanofertilizers is that they can be synthesized according to the nutrient requirements of intended crops [30]. In this regard, biosensors can be attached to a new innovative fertilizer that controls the delivery of the nutrients according to soil nutrient status, growth period of a crop or environmental conditions [29]. Plants are sensitive towards micronutrient availability during crop growth and negative effects result in the form of fruits and vegetables with poor nutrition [31,32]. In conventional nutrient management system, it is very difficult to control the micronutrient delivery to a specific crop, but nanofertilizers provide the opportunity to the growers for supplying adequate amounts of nutrients [8,33]. For instance, most of the horticultural growing areas worldwide are deficient in certain micronutrients (*e.g.* Zn and Fe [31]), so nanofertilizers can act as effective and efficient fortification products for crop and fresh food products. Nanofertilzers increase the bioavailability of nutrients through their high specific surface area, miniature size and high reactivity [12]. On the other hand, by providing balanced nutrition, nanofertilizers enable the plant to combat various biotic and abiotic stresses, with overall clear advantages. However, the extensive use of nanofertilizers in agriculture may have some important limitations, which must also be considered and will be discussed later in detail.

3. Production and use of nanofertilizers

Nanomaterials or nanoparticles for nanofertilizers can be synthesized by different approaches, top-down, bottom-up or using biological approaches (Fig. 2). The top-down approach is based on the reduction of size to nanoscale well-organized assemblies from the bulk materials. Top-down is a physical method based on milling materials. The limitation in this approach is the low control in the size of nanoparticles and a greater quantity of impurities. The bottom-up approach begins at the atomic or molecular scale to build up nanoparticles using chemical reactions. It is a chemically controlled synthetic process, therefore, this method controls the particle size better and reduces impurities [34,35]. In addition to chemical and physical approaches, nanoparticles can be synthesized biologically, the so-called biosynthesis approach. There are several natural sources for this purpose, some of them are plants, fungi and bacteria based. The advantage in this approach is the greater control of the toxicity and size of the particle [25,36]. For every application the most recommended approach will require a synthesis capable of producing mass scale particles with controlled physico-chemical properties resulting in a homogeneous and target-specific nanoformulation. Consequently, bottom-up is in most cases the most effective approach used nowadays for nanofertilizer production [7,34].

Scientists are under enormous pressure to deliver unique technologies that not only fulfill the grower's production demands, but also meet the economic budget of both the growers and production industry [1]. Nanoscience may provide the solution to cater these challenges by providing nanomaterials of high performance [23,37]. As discussed earlier, these innovative fertilizers aim to control the nutrient active ingredient release at a very slow pace in accordance or commensurate with crop growth. The main aim of using these nanofertilizers is to increase the nutrient use efficiency thereby leading to precision agriculture. In this context, nanofertilizer smart technology is expected to lead to a step forward to make the agriculture sector sustainable [38,39]. These fertilizers can be an excellent replacement for the conventional fertilizers that are required in bulk quantities, and additionally can save the soil and water from nutrient pollution [23]. The use of different nanofertilizers including N, P, K, Cu, Fe, Mn, Mo, Zn and carbon nanotubules have shown an excellent control release for a targeted delivery efficiency [10,12]. Various forms of nanoparticles, their oxides nanoparticles, and nanoformulations of conventional nutrients have been converted into valuable inputs in nanofertilizer form. Conversion of these nanoparticles have depicted promising results when applied at a specific concentration on different crops [40].

Nanoparticles are made from organic and inorganic nanomaterials. Additionally, their synthesis also varies in terms of physical or chemical methods employed. The inorganic nanomaterials include the metal oxides such as ZnO, TiO_2, MgO and AgO, and others. On the other hand, the organic nanomaterials include lipids, polymers and carbon nanotubules. Nanoparticles of different materials are of usually four types, *i.e.* silver, gold, alloy and magnetic [(like Fe_3O_4 (magnetite) and Fe_2O_3 (maghemite)]. In this regard, the nanofertilizers are classified on the basis of the nutrient categorization. Hence, there are classically two types of nanofertilizers, *i.e.*, micronutrient nanofertilizers and macronutrient nanofertilizers. Furthermore, nanobiofertilizers are also emerging as an additional approach [12,8].

3.1. Macronutrient nanofertilizers

Macronutrients (*e.g.*, nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), sulphur (S) and calcium (Ca) have been combined with nanomaterials for the purpose to deliver an accurate amount of nutrients to the crops and minimize their bulk requirements with extra-benefits of decreasing purchasing and transportation costs [4,41]. These macronutrient nanofertilizers comprise one or more nutrients in encapsulated form with specific nanomaterial. NPK consumption in the agriculture sector is projected to increase 265 million tons in 2020 [42]. As such, there is an urgent need to carry out research from a practical point of view to develop new fertilizers with high nutrient efficiency and being friendly to the environment to replace the conventional macronutrient fertilizers. As a nitrogen source, urea-modified zeolites, hydroxyapatite and mesoporous silica nanomaterials have been investigated as slow/control release nanofertilizers showing promising results [12,15]. Biosafe nanofertilizer was developed as a source of P that is a nanostructured water-phosphorite suspension (particle size of 60–120 nm). It was the first phosphatic nanofertilizer acquired from raw phosphorite of Tatarstan's Syundyukovskoe deposits through ultrasonic material dispersion. In this experiment, it was observed that the morphometric indices, fresh yield and fruit yield as well as production quality of tested plant species increased several-fold [43].

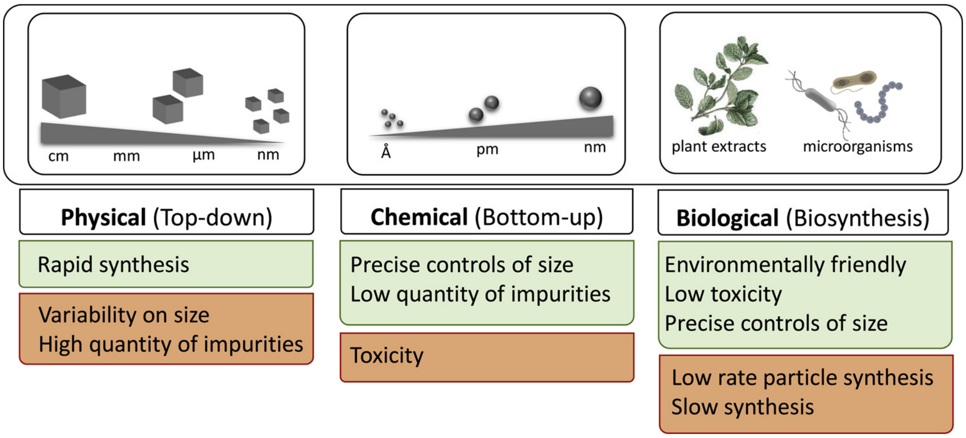

Fig. 2. Methods for the synthesis of nanofertilizers. Physical (top-down), chemical (bottom-up) and biological approached for the production of nanofertilizers.

3.2. Micronutrient nanofertilizers

Micronutrients are those elements that are required by the plant in trace/low quantities, but are essential to maintain vital metabolic processes in plants [44]. Plant growth is highly dependent on zinc (Zn) because it is a structural part or regulatory co-factor for various enzymes and proteins [45]. This micronutrient is also involved in the synthesis of carbohydrates, protein metabolism, and the regulation of auxins, and provides defense to plants against harmful pathogens [46]. On the other hand, boron (B) is not only involved in the biosynthesis of plant cell wall and its lignification, but also plays an important role in plant growth and various other physiological processes [47]. Hence, it is imperative to apply the proper amounts of Zn and B to horticultural crops for attaining maximum yields with good quality. The effect of foliar application of two micronutrient nanofertilizers of Zn and B at three different concentrations was tested and it was observed that low amounts of B (34 mg tree^{-1}) or Zn nanofertilizers (636 mg tree^{-1}) increased fruit yield by 30% in pomegranate trees (*Punica granatum* cv. Ardestani) [38]. It was also reported that cucumber seedlings grown in nutrient solution including rubber type nanomaterial as a Zn source increased shoot and fruit yield compared with those grown in commercial Zn-sulfate fertilizer [48]. Likewise, application of Zn nanoparticles as nanofertilizer in pearl millet (*Pennisetum americanum*) significantly enhanced crop production (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 [49]. Also, it was observed a considerable yield increase using Zn nanoparticles as a nutrient source in rice, maize, wheat, potato, sugarcane and sunflower [15]. Moreover, stabilized maghemite nanoparticles applied through irrigation in solution form in soil as a nanofertilizer improved the growth rate and chlorophyll contents compared to the control (chelated iron) in *Brassica napus* [50].

Iron (Fe) is also an important nutrient required by plants in minute quantities for maintaining proper growth and development. Although it is required in trace amounts, its deficiency or excess leads to impairment in key plant metabolic and physiological processes, thereby leading to reduced yield [51]. Therefore, application of Fe is imperative to optimize yields in horticultural crops. In this respect, the effect of iron oxide nanoparticles and ferric ions was studied at different concentrations on the physiological and molecular changes in *Citrus maxima* plants. It was observed that iron oxide nanoparticles entered the plant roots, but their translocation from root to shoot did not occur. Among the different levels used, 20 mg/L iron oxide nanoparticles had no impact on plant growth, while 50 mg/L significantly improved the chlorophyll contents and root activity by 23% and 24%, respectively, compared to controls. In contrast, 100 mg/L negatively influenced all these characteristics, thus indicating that the effect of iron oxide nanoparticles is concentration dependent [52].

Manganese (Mn) plays a vital role not only in metabolic and physiological processes but it also provides the plant with the ability to endure various environmental stresses by acting as a co-factor of various enzymes. It is also essential for photosynthesis, the biosynthesis of ATP, chlorophyll, fatty acids and proteins, as well as secondary metabolites such as lignin and flavonoids [51]. The effects of laboratory-prepared Cu, Zn, Mn, and Fe oxide nanoparticles was assessed in low concentrations ($<$ 50 mg/L) as micronutrients, on the germination of lettuce (*Lactuca sativa*) seeds. The results showed that CuO nanoparticles were slightly more toxic than Cu ions, while the toxicity of ZnO nanoparticles was similar to that of Zn ions. 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% [6]. Other micronutrient nanofertilizers have also been tested in a number of crops (see Table 1 for additional examples).

3.3. Nanobiofertilizers

Biofertilizers are formulations or preparations containing one or more microorganisms enhancing soil productivity, by fixing atmospheric nitrogen, solubilizing phosphorus or stimulating plant growth through synthesis of growth-promoting substances [70–72]. Therefore, nanobiofertilizers could be defined as the integration of biofertilizers with nanostructures or nanoparticles in order to improve the growth of plants [73]. To achieve this goal is essential to control the delivery of biofertilizers in the soil and extend the useful life of formulations (Fig. 3).

Some of the most important aspects in nanobiofertilizers development are the interaction between nanoparticles and microorganisms, the shelf life of biofertilizers and its delivery. The interaction between gold nanoparticles and plant growth promoting rhizobacteria was shown to exert positive effects [74,75]. By contrast, silver nanoparticles cannot be used with biofertilizer because it causes adverse effects on biological processes in microorganisms, like alteration of cell membrane structure and functions [76]. On the other hand, the shelf life of biofertilizers is a limiting factor in these formulations and the use of nanomaterials can improve it. Use of nanoformulations can be helpful to enhance the stability of biofertilizers with respect to desiccation, heat, and UV inactivation. For example, polymeric nanoparticle coatings can be used to develop formulations resistant to desiccation and consequentially improve the useful life of these products [73,77]. Moreover, nanomaterials can be used to improve the delivery of biofertilizers to soil and plants. Trials using hydrophobic silica nanoparticles to the water-in-oil emulsion have shown an improvement in

Table 1
Impact of different micronutrient nanofertilizers on various crops under non-stressful conditions. Abbreviations: ROS, reactive oxygen species.

Type	Conc.	Crop	Effect	Ref.
Fe	50, 500 and 2000 mg/L	Cucumber	Dose-dependent effects on biomass and antioxidant enzymes	[49]
Fe	10, 20 mg/L	Lettuce	Reduced growth and chlorophyll contents, and increased antioxidant enzyme activities	[53]
Fe	30-60 ppm	Garden pea	Improved seed mass and chlorophyll content	[54]
Cu	0, 100, 500 mg/L	Squash	Higher ionic Cu found in media amended with bulk Cu than with nCu	[55]
Cu	130, 660 mg/Kg	Lettuce	Increased shoot/root length ratio	[56]
Cu	0, 10, 20 mg/L	Lettuce	Negative effects on nutrient content, dry biomass, water content and seedlings growth	[53]
Cu	0-1000 mg/L	Cucumber	Reduced growth and increased antioxidant enzymes	[57]
Cu	10-1000 mg/L	Radish, grasses	DNA damage, growth inhibition	[58]
Cu	50-500 mg/L	Tomato	Improved fruit firmness and antioxidant content	[59]
Cu	0, 20, 80 mg/Kg	Cilantro	Reduced germination and shoot elongation	[60]
Cu	100, 250, 500 ppm	Bean	Growth inhibition and nutrition imbalance	[61]
Cu	100-500 mg/L	Garden pea	Reduced plant growth and enhanced ROS production and lipid peroxidation	[62]
Zn	1000 mg/Kg	Cucumber	Root tip deformation and growth inhibition	[63]
Zn	500 mg/Kg	Garden pea	Decreased chlorophyll and H_2O_2 contents	[64]
Zn	1000 mg/L	Spinach	Growth reduction	[65]
Zn	1 mg/ mL	Tomato, eggplant	Reduced fungal disease	[66]
Zn	100, 200, 500 ppm	Chili pepper	Improved germination	[67]
Zn	0-400 mg/Kg	Coriander	Improved pigment contents and defense responses	[68]
Zn	5,10, 20 mg/L	Onion	Inhibition of root growth	[69]

the delivery of the product, as well as an enhancement in shelf life by reduction of desiccation [78]. Nevertheless, there is a fundamental problem in nanobiofertilizers production, since the nanoscale constructs are usually smaller than cells. In this regard, macroscopic filters made of radially aligned carbon nanotube walls, which can absorb *Escherichia coli*, could be used as a promising technology to collect other microorganisms from fermentation processes and deliver them to the plants [73,79]. Therefore, nanobiofertilizers can solve some limitations of biofertilizers, but this technology still requires further research and development.

4. Nanofertilizers for abiotic stress tolerance

Plant productivity depends on a combination of various vital factors such as soil fertility, good quality irrigation water, and an appropriate light intensity and temperature, among other environmental factors, so that any deviation in one or more of these factors causes adverse effects on plant productivity [80]. Unfortunately, during the crop growth cycle, a plant has to constantly face several biotic and abiotic stresses. Drought, heat, salinity, waterlogging, and cold, among others, are major abiotic stresses that cause huge losses to agriculture globally by reducing yield and product quality [81]. Being sessile in nature, plants must combat these stresses *in situ*. These stresses either individually or in combination, negatively affect the morphological, physiological, biochemical and molecular changes in plants that ultimately decrease productivity [82]. In recent years, in view of climate change the severity of these abiotic stresses is expected to increase in the upcoming decades that clearly depict a threat for crop production [81]. In this context, there is an increased interest towards the use of nanotechnology in the agriculture sector [83]. Different types of nanomaterials have been evaluated for their possible role in managing different abiotic stresses, and a summary of their positive, negative and neutral effects on various crops under various abiotic stresses is shown in Table 2.

Numerous studies have been performed for the endurance of abiotic stresses with different nanomaterials resulting both in positive or negative impacts on plant growth under abiotic stress conditions [38,102]. Applications of silver (Ag) nanoparticles (20 nM; 0.05, 0.5, 1.5, 2 and 2.5 mg L^{-1}) suspensions were tested on germination and growth of *Solanum lycopersicum* L. under two levels (150 and 100 mM) of salinity and observed that the germination rate, germination percentage, seedling fresh and dry weights and root length were improved under salinity. Furthermore, evaluation of salt stress-related genes using semi-quantitative RT-PCR showed that exposure to AgNPs caused upregulation of four genes (*AREB, P5CS, MAPK2* and *CRK1*) and downregulation of three genes (*TAS14,* ZFHD1and *DDF2*) under salt stress [100]. Also, the nanotoxicity of AgNPs was evaluated and compared to $AgNO_3$ (both at 500 μM and 1000 μM applied with nutrient solution) in *Cucumis sativus* and reported that increasing concentration of both AgNPs and $AgNO_3$ posed adverse effect on seedling growth, but the

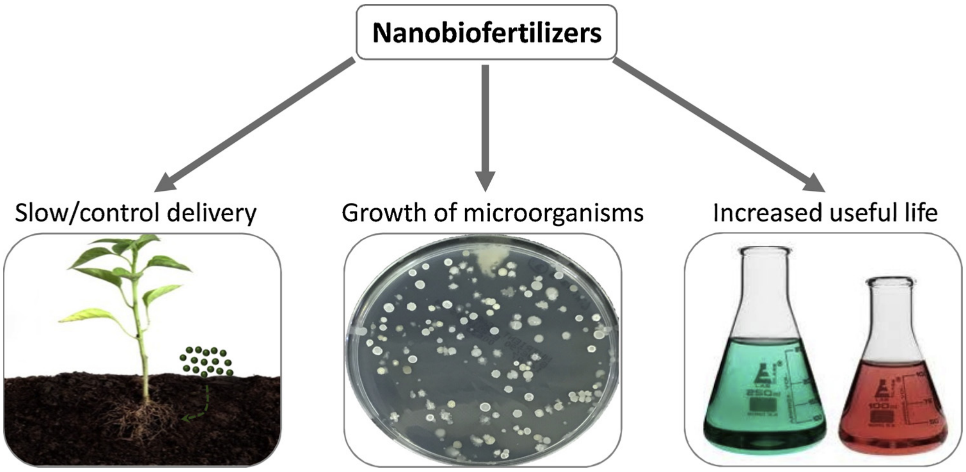

Fig. 3. Mechanisms of action of nanobiofertilizers in crops. A diagram indicating the major beneficial effects of nanobiofertilizers.

Table 2

Impact of different nanomaterials on various crops under stressful conditions. Abbreviations: MDA, malondialdehyde; MWCNT: Multi-walled carbon nanotubes; SWCNT: Single-walled carbon nanotube; NP: Nanoparticle; ROS, reactive oxygen species; SOD, superoxide dismutase.

Application method	Type	Concentration	Plant species	Type of stress	Effects	Reference
Pre-sowing	MWCNT	10, 20, 40, 60 mg/L	Cabbage	Salinity	Increased growth, water uptake and net assimilation of CO_2. Induced alterations in lipid rigidity, composition and permeability in the root plasma membranes	[5]
Pre-sowing	SiO_2	0, 1.5, 3.0, 4.5, 6.0, 7.5 g/L	Pumpkin	Salinity	Enhanced seed germination, growth, photosynthetic parameters and antioxidant enzymes activity. Reduced MDA, H_2O_2, chlorophyll degradation and oxidative damage	[84]
Pre-sowing	Nano-silicon	10 mg/L	Hollyhock	Salinity	Increased germination, plant height, relative water content, fresh and dry weights, relative growth rate, total soluble sugars and membrane stability	[85]
Pre-sowing	Nano-urea modified with hydroxyapatite	0, 25, 50, 100%	Almond	Salinity	Increased germination and length, diameter, and number of secondary roots/plant	[86]
Pre-sowing	TiO_2	0. 25%	Spinach	Excessive light	Increased antioxidant enzymes activity, decreased accumulation of reactive oxygen species and MDA.	[87]
Pre-sowing	Ag	0, 40, 80, 120 mg/L	Saffron	Flooding	Increased root growth, dry leaf weight and root length	[88]
Pre-sowing	Hydroxyapatite	0,5,10,20 g/kg	Bok choy	Cd stress	Increased biomass, levels of chlorophyll and vitamin C, activities of SOD, CAT, and POD, and decreased the levels of MDA	[89]
Pre-sowing	MWCNT	0, 125, 250, 500, 1000 µg/mL	Zucchini	Drought	Reduced germination percentage, vigor index, biomass accumulation, root and shoot length in a dose-dependent manner	[90]
Pre-sowing	Nano-selenium	1, 4, 8, 12 µM	Ajwain	High and low temperature	Improved plant growth, chlorophyll and leaf relative water content	[91]
Post-sowing	TiO_2	0.05, 0.1, 0.2 g/L	Tomato	Heat stress	Enhanced photosynthesis by regulating energy dissipation, and caused cooling of leaves through inducing stomatal opening	[92]
Pre-sowing	CuO, Al_2O_3, TiO_2	0, 20, 200, 2000 µg/mL	Onion	Oxidative stress	Induced chromosomal aberrations effect SOD and POD activities as well	[69]
Pre-sowing	SiO_2	0.05, 0.5, 1.5, 2, 2.5 mg/L	Tomato	Salinity	Up-regulated the expression profile of salt stress genes (*AREB, TAS14, NCED3* and *CRK1*).	[93]
Pre-transplanting	Ag	10, 20, 40 mg/L	Tomato	Salinity	Negatively affected the plant height, number of branches and fruit traits (diameter, weight and number of fruits).	[94]
Post-transplanting	Chitosans-PVA, Cu	10 mg of Cu along with 1 g Cs-PVA	Tomato	Salinity	Enhanced plant growth, promoted expression of jasmonic acid and the enzyme SOD genes.	[95]
Post-transplanting	Si	1, 2, 4, 5 cm^3/L	Chili pepper	Salinity	Significantly regulated the plant to endure salt stress.	[67]
Post-transplanting	Nano-Ca	0.5, 1, 2, 3 g/L	Tomato	Salinity	Lower level significantly reduced the negative effects of salinity	[96]
Post-transplanting	Monopotassium phosphate, nano-calcium	0.5, 0.75, 1 g/L	Tomato	Salinity	Medium concentration of NMs improved stem diameter and number of flowers.	[97]
Post-transplanting	Nano-silicon	0, 1, 2 mM	Tomato	Salinity	Improve fresh weight, chlorophyll concentration, photosynthetic rate and leaf water content	[98]
Post-transplanting	Na_2SiO_3	10 µM SiNP	Pea	Cr (VI)	Reduced uptake of Cr (VI) and oxidative stress, up-regulated antioxidant defense system and enhanced accumulation of nutrients	[99]
Foliar application	Nano-silicon	1, 2 mM	Peregrina	Salinity	Enhanced vegetative parameters and chemical constitutes, meanwhile decreased accumulation of Na, Cl and total phenolics and flavonoids in leaves	[100]
Foliar application	Ag	0.4, 40 mg/plant	Cucumber	Oxidative stress (Nanotoxicity)	Enhanced respiration, inhibited photorespiration and reduced inorganic nitrogen fixation.	[101]

severity of $AgNO_3$ was greater than that of AgNPs. Moreover, prominent disintegration of endodermis and degeneration of root cortical cells was observed in seedlings exposed to $AgNO_3$. Therefore, AgNPs was less toxic than $AgNO_3$ and possess more potential for *C. sativus* production [103]. Recently, the role of nano-calcium (LITHOVIT ®), glycinebetaine (GB), acetylsalicylic acid (aspirin) and monopotassium-phosphate fertilizers were evaluated for relieving salt stress in *Solanum lycopersicum*, and it was found that LITHOVIT® was the most effective, increasing the fruit number and yield by 76% [104].

The effect of 0, 10, 50 and 100 mg L^{-1} of SiO_2 nanoparticles (10–15 nm size) were studied on vegetative, physiological and biochemical characteristics of *Prunus mahaleb* under drought. High doses of SiO_2NPs suspensions provided with irrigation water before imposing drought treatments were more effective than low doses in alleviating drought stress to *P. mahleb* [102]. The effects of iron nanoparticles and salicylic acid (SA) were examined for drought tolerance under *in vitro* conditions in *Fragaria* × *ananassa* Duch [105]. They reported that applied iron NPs in suitable concentrations increased the drought stress tolerance by optimizing iron nutrition and alleviated the negative effects associated with drought conditions. In another study, it was reported that *Ocimum basilicum* plants were better able to endure drought stress under the combined effect of gibberellin (GA_3) and TiO_2 [106]. Although AgNPs showed no positive impact on yield in *Carum copticum* [107], SiNPs could improve tomato plants performance under a short-term exposure to heat/cold stress [91]. In another study, multi-walled carbon nanotubes (MWCNTs) showed negative effect on germination percentage, vigor index, biomass accumulation, and root and shoot lengths in a dose-dependent manner in *Cucurbita pepo* under drought and well-watered conditions. The authors inferred that the poor germination and growth of seedlings fed with different concentrations (0, 125, 250, 500 and 1000 μg mL^{-1}) of MWCNTs were associated with changes in the activation of antioxidant enzymes [90]. Similarly, application of cobalt ferrite ($CoFe_2O_4$) nanoparticles also showed a varied effect in tomato grown in hydroponics [62]. They found that $CoFe_2O_4$ NPs had no effect on germination and growth of tomato plants, whereas their highest level (1000 mg L^{-1}) enhanced root growth. At 250 mg L^{-1} or higher $CoFe_2O_4$ NPs concentrations, reduced translocation of Mg and Ca was observed. Catalase activity also decreased in the leaves and roots of L. *esculentum* on exposure to $CoFe_2O_4$ NPs. Therefore, keeping in view the positive and negative effects on crops, it is mandatory to explore the role of different nanomaterials in a dose-dependent and plant species manner under both laboratory and field conditions before recommending any practical advice for their use in agriculture [108].

5. Limitation of nanofertilizers

In the context of sustainable agriculture, recent progress is undoubtedly witnessing the successful use of some nanofertilizers for achieving enhanced crop productivity. However, the deliberate introduction of this technology in agricultural activities could result in many unintended non-reversible outcomes [13]. In this scenario, new environmental and unintended health safety issues can limit the use of this technology in horticultural crops' productivity. Nanomaterial phytotoxicity is also an issue in this regard since different plants respond differently to various nanomaterials in a dose-dependent manner [84]. Hence, it is crucial to consider the advantages of nanofertilizers, but also their limitations before market implementation (Fig. 4).

Importantly, nanomaterials are very reactive because of their minute size with enhanced surface area [101]. Reactivity and variability of these materials are also a concern. This raises safety concerns for farm workers who may become exposed to xenobiotics during their application [109]. These include not only those exposed to nanofertilizer manufacturing but also nanofertilizer application in the field. Considering the anticipated benefits, there is consequently a need to explore the feasibility and suitability of these new smart fertilizers. Indeed, a considerable concern about their transport, toxicity and bioavailability as well as unintended environmental impacts upon exposure to biological systems, limit their acceptance to adoption in sustainable agriculture and the horticulture sectors [8]. Risk assessment and hazard identification of the nanomaterials including nanomaterial or fertilizer life cycle assessment are critical as well as establishing priorities for toxicological research. This is particularly true considering the accumulation of nanoparticles in plants and potential health concerns. Indeed, the use of nanofertilizers derived from nanomaterials have raised serious concerns related to food safety, human and food security [110,111].

Some studies have reported phytotoxic effect of nanoparticles [112], and the uptake, translocation, transformation and accumulation (phytotoxicity) of NPs in plants is dependent on species, dose and application method as well as type of NPs (composition, size, shape, surface properties) [112]. Examination of the degree of toxicity of each NP in any given crop is important to study and understand the uptake and translocation of nanofertilizers, the possible transformation of nanoparticles when they interact with soil and plant compounds, and the accumulation of NPs in different plant tissues [113].

5.1. Uptake and translocation of nanomaterials

Nanofertilizers can be absorbed by crops through the roots or leaves. NPs can penetrate root epidermis and endodermis reaching the xylem vessels, allowing it to be transported to the aerial part of the plant. Moreover, NPs can be absorbed by leaf stomata and transported to other plant parts through the phloem [112]. In both cases, NPs must penetrate the cell wall by pores, and pore sizes may rage 3–8 nm. Therefore, only NPs smaller than 8 nm could pass through pores and reach the plasma membrane. Accordingly, NPs or aggregates bigger than 8 nm cannot enter into cells [114]. It was recently shown that tomato roots can absorb 3.5 nm Au NPs but not 18 nm Au NPs [2]. It has been shown that CeO_2 NPs can be absorbed by cucumber leaves and consequently transported to different plant tissues [115] and Ag NPs could be absorbed and distributed throughout the plant after foliar exposure in lettuce plants [116].

The uptake and translocation of nanoparticles may vary from plant to plant depending on its particular physiology and several mechanisms of their uptake, transport and distribution within the plant [117]. In several cases, plants activate defense responses against NPs. This appears to be particularly true for the metallic oxide-based nanofertilizers, in which the plant faces the parent nanomaterials effects as well as the metal ions produced by the dissolution of engineered nanofertilizers [111,118]. An experiment with carrots comparing metal oxide nanoparticles (ZnO, CuO, or CeO_2) and metal ions uptake demonstrated that uptake of both nanometal oxides and metal ions occurred. Such uptake and accumulation in edible parts may impose not only problems to the physiology of plants, but also pose serious risks to human health [110]. It was shown in this study that metal oxide nanoparticles accumulated in the outer layer of carrot and did not enter the fleshy part, while metal ions entered the fleshy edible part and were potentially more toxic to human health. It was suggested that this outer layer acts as a barrier to restrict the inward penetration of engineered nanoparticles in the edible tissues [110]. Therefore, peeling the outer layer of root and tuberous vegetables will be required to reduce the toxic exposure to these metal nanoparticles [111].

5.2. Transformation of nanoparticles

Nanomaterials are highly reactive. Therefore, when nanofertilizers are used in crops and they interact with different components in the environment, they are subject to transformations and changes in their physicochemical properties [119]. NPs interact with organic and inorganic substances in the soil, as well as with various plant components that may alter the behavior, fate, and toxicity of NPs. When nanofertilizers are used in roots, NPs are exposed to root exudates in

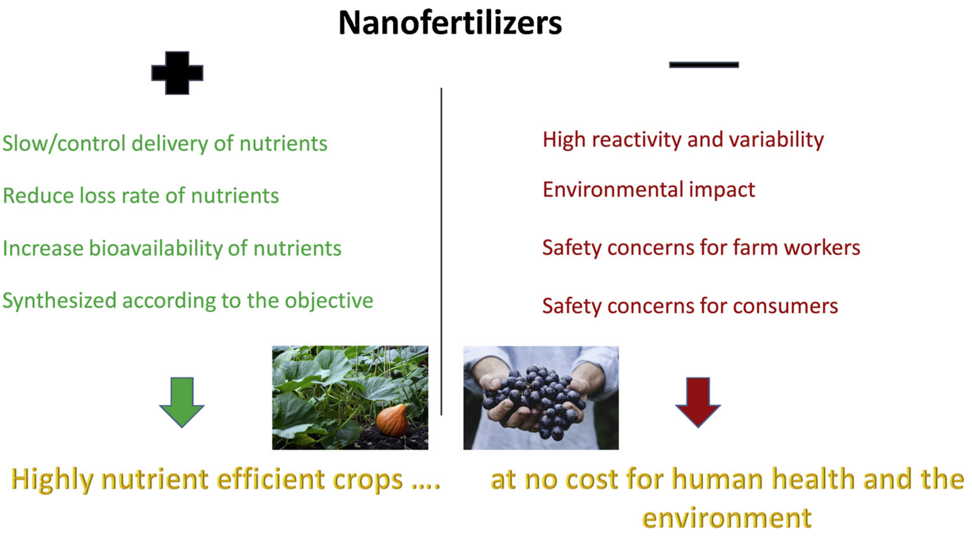

Fig. 4. Advantages and limitations of nanofertilizers. A correct use of nanofertilizers to improve crop yields requires before market implementation a careful examination not only of their advantages for the physiology of plants, but also of their potential limitations for the environment and human health.

rhizosphere that can determine the behavior and toxicity of heavy metals. For example, mesquite plants treated with Ni-$(OH)_2$ NPs had Ni$(OH)_2$ in the roots but contained Ni NPs in the shoots and leaves, demonstrating the biotransformation process of this nanoparticle inside the plant [120].

Other cases of biotransformation have been observed using CeO_2 NPs in cucumber plants. Results showed 15% of Ce(IV) being reduced to Ce(III) in the roots and 20% to Ce(III) in the shoots [26]. However, another study showed that CeO_2 NPs biotransformation did not happen in cucumber roots, suggesting that NPs biotransformation requires specific conditions in the plant rhizosphere [121]. Biotransformation was also demonstrated in Ag NPs applied on lettuce plants. Ag NPs were oxidized and Ag^+ ions formed Ag complexes with thiol-containing molecules [122]. Also, in another experiment using Ag NP in lettuce, it was found that 33% of the NPs was transformed to Ag-glutathione [123].

5.3. Accumulation of nanoparticles

Among the various issues, the most important might be the accumulation of nanoparticles in plants and their food parts. The accumulation of nanoparticles depends on many factors, but mainly on plant species, tissue/organ that will be used directly as food or for food processing, and nanoparticle type and size. Because of the variability in interactions between NPs and plants, nanomaterials used in nanofertilizers can accumulate in plants and, in some cases, they can cause toxicity problems, not only to plants but also to humans [118]. For example, multi-walled carbon nanotubes induce phytotoxicity in red spinach (*Amaranthus tricolor* L.) causing growth inhibition, production of reactive oxygen species and cell death [68]. CeO_2 nanoparticles can accumulate and shut down the nitrogen fixation potential of soybean [113], thus not only threating the future of leguminous crops in agriculture but also can cause human health problems. Further, in another experiment, application of C_{60} (fullerene) to zucchini, soybean, and tomato plants increased the accumulation of dichlorodiphenyldichloroethylene (DDT) [124].

5.4. Further research and strategies to cope with toxicity problems

Nanofertilizers present a great opportunity in agriculture, but it is necessary to work on strategies that cope with their accumulation and potential risks for human health and the environment, while adopting the advantages of using nanoparticles in crops. This young field of research is achieving important goals and present an opportunity in the future. Thus far, *in vitro* analyses have been developed to help in the standardization of the correct dose and type of nanofertilizer recommended for each application and crop species, so that any potential toxicity to the environment, crops and food is minimized [125]. Another important issue to take in account, but still little explored to date, is not only the specific accumulation of NPs in edible parts of crops but the bioavailability of the accumulated NPs to the next trophic level. In this regard, specific studies of NPs bioavailability in edible parts are urgently needed to use nanofertilizers safely.

6. Conclusions and future prospects

Nanofertilizers have a significant impact in the agriculture sector for achieving enhanced productivity and resistance to abiotic stresses. Thus, promising applications of nanofertilizers in the agrifood biotechnology and horticulture sectors cannot be overlooked. Furthermore, the potential benefits of nanofertilizers have stimulated a great interest to increase the production potential of agricultural crops under the current climate change scenario. The basic economic benefits of the use of 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. However, despite the exciting outcomes of nanofertilizers in the field of agriculture, so far, their relevance has not yet been focused towards marketability. Uncertainty related to the interaction of nanomaterials with the environment and potential effects on human health must be explored in detail before spreading nanofertilizers at a commercial scale. Future studies must be focused on generating comprehensive knowledge in these underexplored areas in order to introduce this novel frontier in sustainable agriculture. Consequently, nanofertilizer application safety and the study of the toxicity of different nanoparticles used for nanofertilizer production must be a research priority. Furthermore, an in-depth evaluation of the effect of nanofertilizers in the soils with different physio-chemical properties is necessary in order to recommend a specific nanofertilizer for a specific crop and soil type. Biosynthesized nanoparticles-based fertilizers and nanobiofertilizers should be explored further as a promising technology in order to improve yields while achieving sustainability.

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