

## NANOFERTILIZERS: AN OVERVIEW

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### Abstract

The adequate bioavailability of nutrients to plants is among the various difficulties of the agricultural sector. Thus, the existence of mechanisms for controlled release of the nutrients is essential for planting, as well as novel techniques that do not cause adverse effects. The use of nanotechnology in agriculture can bring many benefits, such as better use of nutrients by plants, reducing waste. Nanofertilizers are an emerging technology and a constantly expanding class of agrochemicals, representing possible solutions to the development of sustainable agriculture. Based on this, the present work aims to update and discuss some relevant topics about these nanomaterials, such as different synthesis approaches, possible mechanisms for the capture of nanofertilizers by plants, and the advantages and limitations of using these materials. Also, an overview of the main literature in the area is presented approaching current studies that use green chemistry concepts.

**Keywords:** sustainable agriculture, agrochemicals, emerging technologies, nanofertilizers, green chemistry.

### 1. Introduction

In the past two decades, numerous difficulties encountered in agriculture have become recurrent. Not due to the lack of space or even investment in technology, but due to the regular climatic instabilities caused by the worsening of global warming and the intense deforestation. Based on this, the precepts of sustainable agriculture have become important in agricultural research groups, such as the development of green nanomaterials, optimization of agricultural processes, breeding, rational use of pesticides, and others (DUHAN et al., 2017). Efforts by researchers around the world have been growing in the search for smart and greener solutions that can meet global food demands, due to population growth. Given this scenario, special attention is given to biodegradable materials, produced via clean and safe processes. Currently,

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a worldwide trend has been the manufacture of nanomaterials by green processes, whether using water as a solvent, minimizing the use of toxic reagents, or reusing agro-industrial waste. An important class of agrochemicals impacted by these precepts are fertilizers (USMAN et al., 2020).

Organic fertilizers are fundamental to the success of the crop, whether promoting major changes in the physical properties of the soil or increasing the productivity of the crop, which consequently increases the profitability of the producer. However, the use of this class of agrochemicals has limitations, such as low efficiency (ZULFIQAR et al., 2019). This disadvantage is common to conventional fertilizer application processes. It is estimated that around 50% of the applied nitrogen is lost to the environment, causing additional production costs and contamination of rivers, lakes, and groundwater. Therefore, the main challenges in the use of these fertilizer materials are in the strategic optimization of application, which must become more sustainable and must maintain or improve the levels of productivity and quality when used in different cultures. It is these challenges that are driving the development of nanofertilizers, seen as promising allies for the progress of agriculture (MAGHSOODI; GHODSZAD; ASGARI LAJAYER, 2020).

Nanofertilizers are nanomaterials that can consist of a carrier matrix of mineral elements. According to He, Deng and Hwang (2019), these compounds can be produced by nanoencapsulation of nutritional elements or as nanoparticulate nutrient itself. Nutrients are essential for the complete development of plants (HUSAIN JAAFERY et al., 2020) and the way they are bioavailable in the soil is crucial for the plant uptake. Another limiting factor is that these nutrients are not completely available in the soil in adequate quantities (ASGARI LAJAYER et al., 2019). For this, the producers carry out the necessary fertilization of the land according to the crop. The nutritional elements necessary for plants are divided into two major groups, micronutrients and macronutrients (ZHAO et al., 2020b). Micronutrients are minerals needed by plants in low amounts (ZHAO et al., 2020a). This group consists of iron (Fe), boron (B), chlorine (Cl), copper (Cu), zinc (Zn), manganese (Mn), and molybdenum (Mo), among others (NAIR; AUGUSTINE, 2018). The presence of traces of these elements is vital to the development cycle of plants since they are involved in the regulation of enzymes, proteins, and carbohydrates (BRIAT et al., 2020). Macronutrients are elements that must be present in plants in high quantities (SINGH; DWIVEDI, 2019). They are substances that play fundamental roles in the formation of plant tissues, fruits, and flowers, root development, conservation of water levels in the plant, and other functions (TUHY et al., 2015). This group is composed of nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), and sulfur (S) (LIU; LAL, 2015). Chart 1 shows the effects of some elements in different cultures.

**Chart 1.** Effects of nutrients in different cultures.

Element	Culture	Effects	Reference
N	<i>Phaseolus vulgaris L.</i>	Contributed to plant growth	(MEDEIROS et al., 2010)
P	<i>Brachiaria decumbens</i>	Promoted greater root growth	(DA SILVA et al., 2011)
K	<i>Vigna unguiculata L.</i>	Improved water balance and breathing	(PRAZERES et al., 2015)
Mg	<i>Musa spp.</i>	Application of this element recovered plant growth, nutrients and carbohydrates status	(HE et al., 2020)
Fe and Cu	<i>Lactuca sativa</i>	The elements act on growth, water content and catalase activity	(TRUJILLO-REYES et al., 2014)
Fe and Zn	<i>Cucumis sativus</i>	The elements act in the production of antioxidant enzymes	(MOGHADDASI et al., 2017)
Cu	<i>Solanum lycopersicon</i>	The element act on the antioxidant content	(AHMED; KHAN; MUSARRAT, 2018)
Cu	<i>Allium cepa</i>	The element act mainly on the mitotic index	(AHMED et al., 2018)

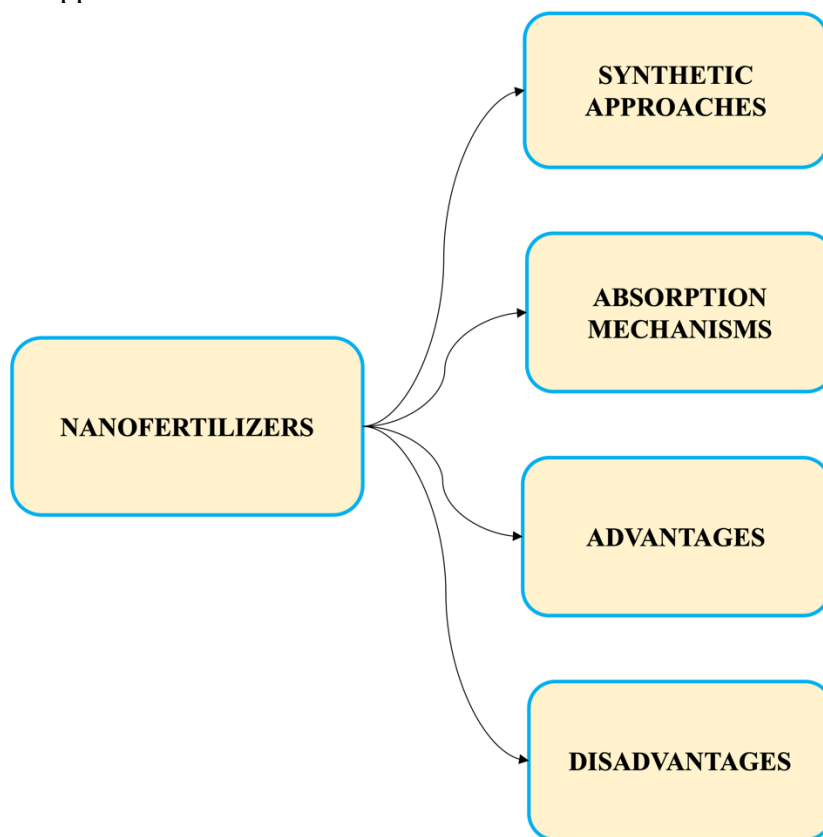
**Source:** Authors.

There are three main approaches to the production of nanofertilizers: top-down, bottom-up, and biological (PEREIRA et al., 2017). Each synthesis method has advantages and disadvantages in terms of the required process, ranging from the control of particle size, economic viability, even in the necessary yield for a given crop. Kah et al. (2018) observed an increase of approximately 30% in the absorption of nutrients with the application of nanofertilizers compared to the application of conventional fertilizers for different plant species. In the scientific field, this class of nutritional agrochemical is divided into three categories: nanostructured micronutrients, nanostructured macronutrients, and nanostructures that transport nutrients. Examples of these categories are hydroxyapatite, zinc oxide (ZnO) and chitosan nanoparticles (SAMPATHKUMAR; TAN; LOO, 2020).

Considering the issues addressed, the great potential of nanofertilizers in the revolution and future replacement of conventional technologies is notable. In this review, an overview of nanofertilizers will be presented, discussing the following topics: different synthesis approaches, possible mechanisms for the capture of nanofertilizers by plants, and the advantages and limitations of the use of these nanoparticles. Figure 1 presents an illustrative

scheme of the topics that were covered in the work. Also, the purpose of this review is to include the main research in the area regarding the production of these agrochemicals by green synthesis, which are unquestionable factors to reduce the impacts that modern agriculture has on the environment and on human health.

**Figure 1.** Topics approaches in the review.



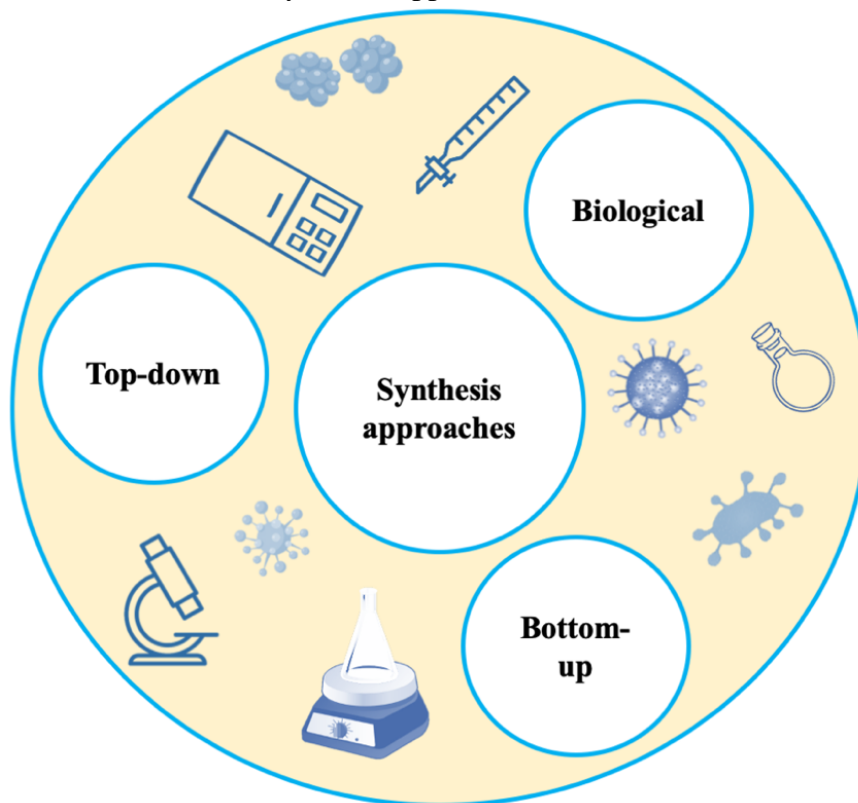
Source: Authors.

## 2. Nanofertilizer production

There are several ways to obtain nanofertilizers, such as top-down, bottom-up, and biological (Fig. 2). The top-down production process uses physical methods, starting from larger particles until reaching the nanometric scale (FEREGRINO-PEREZ et al., 2018). The techniques based on this concept have some limitations, for example, low control of uniformity and particle size. Another way of obtaining nanofertilizers is bottom-up, based on chemical reactions (ABDEL-AZIZ; RIZWAN, 2019). Bottom-up methods allow greater control of the size of the nanostructures and the reduction of impurities. Finally, another method used for the manufacture of nanofertilizers is the biological route. Microorganisms such as bacteria and fungi are used for biosynthesis. The advantage of obtaining nanofertilizers via biosynthesis is the low cytotoxicity of the final product (CAI et al., 2020). Therefore, it is noticed that there are numerous possibilities for the production of nanofertilizers and the challenges are diverse, such as the reduction of energy costs, better yields, and the synthesis of a material with high

efficiency. With the integration of these characteristics, it is possible to manufacture agrochemicals that present high performance and sustainable applications.

**Figure 2.** Different nanofertilizer synthesis approaches.



**Source:** Authors.

Nanofertilizers can be produced from organic or inorganic compounds. The development of inorganic nanostructures uses mainly metal oxides, such as zinc oxide (ZnO), magnesium oxide (MgO), and silver oxide (AgO). As for nanomaterials obtained from organic compounds, polymers, carbon, and others are used. Sharma et al. (2020) reported the effects of nanofertilizers in a chitosan matrix doped with copper and salicylic acid in the corn crop. The synthesis of the nanoparticles was based on the encapsulation of nutrients by chitosan ion gelation. They observed satisfactory results in the application of the nanofertilizer, such as the increase in the activities of antioxidant enzymes, reduction in the content of malondialdehyde, and the increase of chlorophyll content in the leaves.

Shebl et al. (2020) prepared ferrite nanofertilizers by microwave-assisted green hydrothermal route using hydrated zinc, manganese, and iron nitrates dissolved in water. After the appropriate mixtures and concentrations of each reagent, the medium was transferred to a 100 mL autoclave container and subjected to microwaves (750W). After microwave treatment, five ferrite samples were tested at different temperatures (100–180°C). Finally, the material was washed and dried at 100°C for 6 hours. The different nanomaterials they prepared were used in different concentrations (0, 10, 20, and 30 ppm) as leaf nanofertilizers during the pumpkin

planting process (*Cucurbita pepo* L). When the nanoferrite synthesized at 160°C was applied to the growing pumpkin culture at a concentration of 10 ppm, an increase in yield was observed when compared to untreated pumpkins, for two consecutive seasons.

Kottegoda et al. (2017) synthesized environmentally friendly nanoparticles of urea transporters as a nutrient for different cultures. In the study, nanostructured materials could be programmed and used as a nanofertilizer. Because of the high solubility of the urea molecules, the authors incorporated them into a hydroxyapatite matrix. For the production of the nanoparticles, the authors used the bottom-up methodology, in which phosphoric acid was dispersed dropwise in a suspension of calcium hydroxide and urea under mechanical stirring. Finally, techniques were used to purify the material until the nanofertilizers were obtained. Also, the authors evaluated the study of nitrogen release in aqueous media, in which it occurred for up to one week using the synthesized nanohybrid what happens when you use pure urea.

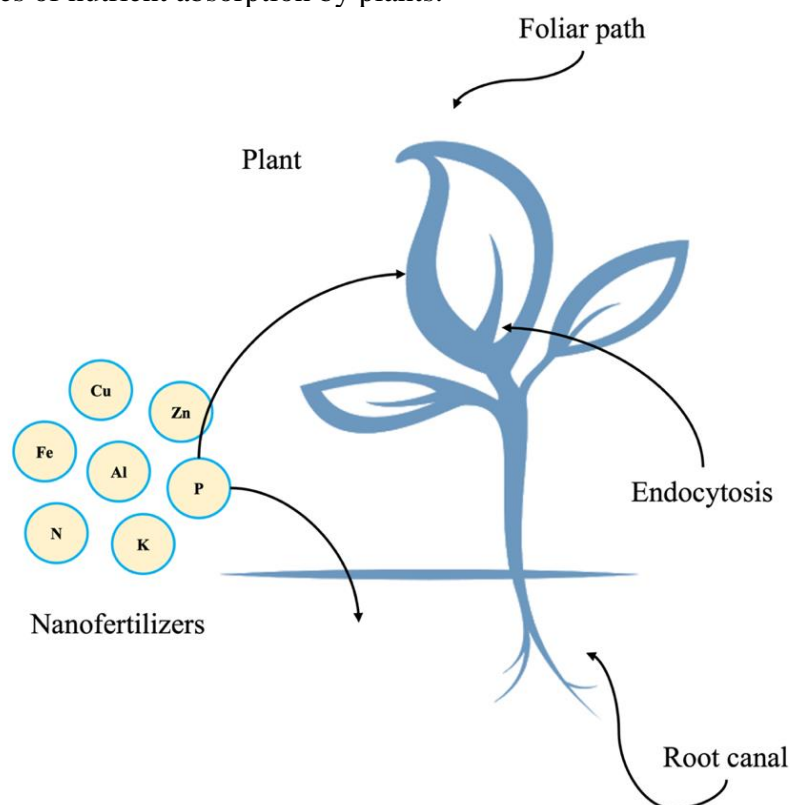
Kumar, Ashfaq and Verma (2018) developed a procedure for the polymeric synthesis of polyvinyl acetate (PVA) starch as a substrate for the slow release of copper and zinc nutrients transported by carbon nanofibers. The authors tested the effectiveness of nanofertilizers by applying different concentrations on chickpea culture. They reported that the use of the produced nanohybrid increased the yield of chickpea plants from 46% to 96%.

Therefore, it is observed that there are several alternatives for the production of nanofertilizers, making it necessary to choose the most appropriate method for each case and final application. The choice must be based on the economic viability of the production, use, preparation and final application. Another important factor to be evaluated is the performance of the final products, for this, it is necessary to know about the mechanisms of absorption of nutrients in the culture under analysis.

### **3. Mechanisms for nutrient uptake by plants**

There are countless possible mechanisms of uptake of macro- and micronutrients by plants. After releasing the nanofertilizers into the environment next to the crops, the elements can be absorbed by different routes, such as via root, leaf, endocytosis, and/or other (IOANNOU et al., 2020). Figure 3 shows a scheme with the different routes of nutrient uptake by plants. Absorption by the roots can greatly restrict the nutrients that are captured when treated in the soil, due to the size of the pores and the elements to be absorbed. Sartori et al. (2008) reported a study in which they compared two types of absorption to verify which one showed more significance in the orange crop (*Citrus sinensis* (L.) Osbeck). They evaluated the mechanisms of root and leaf uptake in the development of the plant after five years of treatment, with solutions using zinc as an essential micronutrient. As a result, they reported that the root canal proved to be more efficient.

**Figure 3.** Routes of nutrient absorption by plants.



**Source:** Authors.

Another important route is the leaf, through this route it is possible to carry out the application of pesticides and herbicides in the plantation simultaneously with fertilization. For this reason, foliar fertilization is highly efficient and minimizes contamination. However, it has some disadvantages such as nutrient mobility and penetration through leaf cuticles. Rios, Garcia-Ibañez and Carvajal (2019) evaluated the use of Zn nanobiocarriers as a potential nanofertilizer using the foliar pathway. They used broccoli and pak-choi plants (*Brassica rapa* subsp. *Chinensis*) hydroponically cultivated in the absence of zinc. The authors tested the use of the zinc nanofertilizer combined with surfactant (PMP) and plant vesicles to increase the bioavailability of the nutrient. After the tests with the fertilizers combined with vesicles derived from broccoli and PMP, the authors found significant differences in the crops analyzed. The application of the fertilizer without the surfactant caused a weak increase in the concentration of Zn in the leaves. However, the combined use of the micronutrient with the surfactant strongly increased its leaf concentration, approximately three times compared to the previous situation. The treatment with vesicles and surfactants showed the higher concentration between the tests, almost four times the value of plants when only zinc was used.

Abdel-Aziz, Hasaneen and Omer (2019) investigated the possible effects of using chitosan nanoparticles and modified carbon nanotubes in isolated form or loaded with NPK (nitrogen, phosphorus and potassium) as fertilizers in French bean plants. The authors

addressed two application techniques: seed priming, and leaf application. As a result, they observed that leaf fertilization was better than seed priming and that leaf treatment with chitosan nanoparticles reduced harvest days without reducing yield (80 days), when compared to control and seed priming treatment (110 days). The authors did not verify great changes in the results with carbon nanotubes when treated via leaf.

Although nanofertilizers enter plants mainly through the root and leaf pathways, there are other support mechanisms, such as endocytosis (SHINDE et al., 2020). The endocytosis process allows the transport of elements from the extracellular medium into the cell, through vesicles limited by membranes (FAN et al., 2015). Moghaddasi et al. (2015) conducted a study on the positive and negative effects of using rubber ash nanoparticles on plants as a zinc fertilizer. They investigated the absorption of Zn by the roots and the effects of these nanoparticles on the growth of cucumber. The authors reported that the capture of these nanostructures occurs at the root, for this, they used characterization techniques, such as Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The authors attributed the entry of zinc in the cucumber culture by the roots, but with the aid of a possible posterior mechanism of endocytosis.

Apodaca et al. (2017) used bean plants (*Phaseolus vulgaris*) grown with copper (Cu) nanoparticles combined with kinetin, a plant hormone. In the study, they verified the growth of the crop, the mechanisms of nutrient uptake, the copper concentrations in the roots and leaves, the chlorophyll content, and the enzymatic activity in beans with approximately 2 months of age. The authors evaluated the possible routes for the absorption of nutrients, especially copper, and found high concentrations of this element in the root tissue. The results of the research revealed significant levels of copper in the leaves when treated with kinetin. Thus, the role of the endocytosis mechanism in plants for the absorption of nutrients is notorious.

The works discussed above showed that some variables directly influence nutrient uptakes, such as particle size, chemical species, concentration, plant stage, external conditions of the environment, time of contact with the elements, and others. Therefore, in-depth studies of each crop are essential when using nanofertilizers as a source of nutrients.

#### **4. Benefits and challenges of using nanofertilizers**

Emerging technologies are constantly developing, specifically in modern agriculture. Concerns about the environment must be a fundamental factor, taking into account that natural resources are increasingly scarce, and the climatic effects are aggravated by the devastation caused by man. The search for progress and population growth generated important demands, such as high production of food in smaller spaces and less time. Therefore, the use of nanofertilizers in agriculture can serve as an ally to achieve sustainability, especially towards



world food production (HU et al., 2017). Chart 2 shows the advantages and disadvantages of using nanofertilizers in agriculture.

**Chart 2.** The advantages and disadvantages of using nanofertilizers in modern agriculture.

<b>Advantages</b>	<b>Disadvantages</b>
Possibility to act as a great nutrient release mechanism	Need for life cycle studies
Reducing nutrient loss to the environment	Food security
Numerous synthesis approaches	Lack of long-term environmental studies

**Source:** Authors.

In the last few years, the food sector has been experiencing great advances, specifically in the development of technology used in crops to supply nutrients lacking in the human diet, which is caused mainly by the advent of fast food and the low consumption of vegetables and fruits. Thus, the importance of using nanotechnology in the development of agrochemicals led to the conception of nanofertilizers. These nanoparticles act in the regulation of nutrients in different plants (HUSSAIN et al., 2018) using control mechanisms and the slow release of essential elements in the growth and germination of cultures. For example, there are studies that nanofertilizers release nutrients in up to two months, which, when compared to similar fertilizers that release in up to 10 days, have a great advantage. Another positive point of having a nutrient management system is that these elements are not lost to the environment (CYRIAC et al., 2020).

An additional advantage of using nanofertilizers is that they can be produced considering which nutrients are needed for a given crop because of the ease of production of these materials. Besides, the bioavailability of nutrients due to the high surface area of the nanoparticles, size, and reactivity is also a plus (REDDY PULLAGURALA et al., 2018). By providing the elements in a balanced way, nanoparticles cause cultures to eliminate several factors, such as biotic and abiotic stresses. However, the intense use of nanofertilizers in agriculture can have some disadvantages and limitations, which need special attention (YOUNES et al., 2020).

The overuse of nanofertilizers in agricultural activities can bring some unwanted and even irreversible environmental results. Also, the safety of these nanoparticles in the development of plants is another factor, as nanofertilizers can act differently in crops. Thus, the assessment of risks and the identification of the harmful effects of these nanostructures, including the evaluation of the life cycle, are essential. Another disadvantage of the indiscriminate use of nanofertilizers is their transformation in the environment due to high

reactivity, being subject to unwanted reactions and changes in properties (IAVICOLI et al., 2017). Ma et al. (2017) investigated the use of CeO<sub>2</sub> nanoparticles in cucumber plants by performing translocation and absorption analysis, which are often unwanted due to increased environmental toxicity when the nanoparticles are transformed into other species. They found that approximately 15% of cerium was reduced from Ce<sup>4+</sup> to Ce<sup>3+</sup> in the roots of cucumbers and the transformation products were transported by the phloem. This demonstrates that the use of nanofertilizers can cause numerous implications for the human health. Thus, the safety of food grown in the presence of nanofertilizers must be well evaluated.

## 5. Conclusion

The review approached nanofertilizers, which are a new topic in the literature under constant development. The research carried out in the area, although presenting more advantages than disadvantages in the use of these nanomaterials, is still preliminary and very specific. As a result, many studies still need to be carried out to contribute to the establishment of this technology as a viable, safe, and sustainable alternative for wide application in different cultures. The numerous synthesis approaches using renewable sources and green techniques are positive points. Also, simplicity of execution and no need for sophisticated equipment show advantageous paths for the effective insertion of these nanostructures in the field. For this, knowledge of all the limitations and benefits of the application of nanofertilizers is essential. These range from performance in a specific culture to the life cycle and transformations of chemical species in contact with plants. As the majority of the literature shows a promising future in the use of nanofertilizers for plant nutrition, research addressing this topic is a very active and encouraging area due to the many possibilities not yet explored.

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