



The Role of Nanotechnology in Plant Nutrition. A Review

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Abstract

Nanotechnology is a type of science that deals with a tiny volume of material ranged from 1 to 100 nanometers. Nanoscale materials (NSs) acquires new properties compared to the original form of the same material. These phenomena are attributed to a surface area dedicated to nanoparticles (NPs). Regarding this type of fertilizers, through which they are used as smart delivery systems, they are manufactured by chemical, physical or biological methods, for improving their properties and composition, which in turn improves crop productivity. Also, these nanometric fertilizers are superior than traditional fertilizers in the efficiency of their absorption (Nutrient Use Efficiency) and activation of the metabolic processes inside the plant due to the higher surface area of their molecules, use of less quantities with greater effectiveness and their supply to plants with their needs of nutrients for longer periods compared to the traditional forms of nutrients and positively improve the biochemical content of crop and its quality. Regarding the role of nano-fertilizers in the development of crops, several researchers have shown that the use of nano-fertilizers can deliver nutrients directly to the zone of roots by avoiding swift changes in the chemical composition of soil nutrients, thereby reducing loss of nutrients, and improving the efficiency of use. In addition, to preserving depression by reducing the loss of nutrients that cause pollution, but one must be careful in applying its rate. Based on the above, we may infer that nanotechnology has made a significant and effective contribution to plant nutrition, especially through the use of smart fertilizers such as NFs, which have been suggested to improve total nutrient usage efficiency (NUE) values by regulating and slowing nutrient release in order to help manage the long-term nutrient needs of crops.

Keywords: Nanotechnology, Nanoscale materials (NSs), Nanoparticles (NPs), Nanofertilizers (NFs), plant nutrition.

Introduction

Sustainable and high productivity agriculture is critical to risk reduction hunger and increased food security. The production and distribution of food around the world is under increasing pressure due to climate change, population growth and the decline of fertile land and freshwater resources (Usman *et al.*, 2020). This challenge can be met through technological developments that are accompanied by significant changes in current global food production systems (Shang *et al.*, 2019).

To increase crop yields with declining nutrient efficiency values, this led to intensive use of synthetic fertilizers (Guo *et al.*, 2018). However, this widespread use of artificial fertilizers will lead to significant environmental risks in the long term, such as air pollution, soil depletion, nutrient enrichment and pollution of groundwater (Seleiman *et al.*, 2020). In addition, the over use of artificial fertilizers increases production costs and lowers profit margins for farmers (Diatta *et al.*, 2020). Low NUE values and increased environmental risks associated with increased use of artificial fertilizers have been a long-term obstacle to achieving sustainability in agriculture (Diatta *et al.*, 2020). Low NUE values are usually triggered by higher levels of synthetic fertilizer release than plant uptake levels, or shifts in nutrient types into those that are not bioavailable to plants. As a result, agricultural sustainability can be achieved

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through the introduction and application of creative techniques (Shang *et al.*, 2019) that can increase global food production while preserving natural and environmental resources. Nanotechnology, according to recent studies, has the potential to transform the current synthetic structure used in industrial agricultural processes by increasing the efficiency of novel agrochemicals and providing solutions to environmental and agricultural problems (Usman *et al.*, 2020).

As a result, agricultural researchers have been increasingly interested in the use of nanoparticles (NPs) in recent years (Kah *et al.*, 2019). In this context, there is a scientific interest in developing novel fertilizer sources with the goal of increasing fertilizer usage performance (Van Eerd *et al.*, 2018). Nanotechnology has the potential to produce modern innovative types of fertilizers, such as nano fertilizers (NFs), to expand global food supply and feed the world's increasing population in terms of sustainable agriculture (Feregrino-Pérez *et al.*, 2018).

The term nano fertilizer refers to a nanomaterial that is either a plant nutrient in and of itself (micro- or macronutrients) or a carrier of a plant nutrient. NFs are nutrients that have been encapsulated or covered by nanomaterials (DeRosa *et al.*, 2010). NFs may be made from industrial materials (e.g., adapted versions of conventional fertilizers) or from green plant components using nanotechnology and a variety of chemical, mechanical, and biological processes (Singh and Kumar, 2017). NFs are used to improve soil fertility, plant nutrient bioavailability, and product consistency (Singh and Kumar, 2017).

Nanotechnology's application in plant science and agriculture has developed in recent years. Technological advances have improved methods for handling nano particles of physiologically important metals on a wide scale, which are now used as "smart distribution systems" to optimize fertilizer formulation by reducing nutrient loss and plant cell uptake (Naderi and Danesh- Shahraki 2013). These "nano fertilizers" are a smart distribution mechanism because they have a wide surface area, high sorption potential, and controlled-release kinetics to specific locations. Via mechanisms such as targeted delivery, slow or managed release, nanostructured fertilizers can improve nutrient utilization efficiency. They were able to precisely release their active ingredients in response to environmental cues and biological demands (Seleiman *et al.*, 2020).

1. Concept and definition of nanotechnology

Nanotechnology is the fast-growing science of the ultra-small; it is creating geometric particles in the size range 1 to 100 nanometers (Paul, 2008). This technology is being used increasingly in numerous areas of agricultural production.

In many areas of agricultural production, nano scale materials are classified as a collection of substances with at least one dimension less than approximately 100 nanometers. Nano-scale materials are those that have at least one dimension that is less than about 100 nanometers (a nanometer is a millionth of a millimeter) (Fig.1).

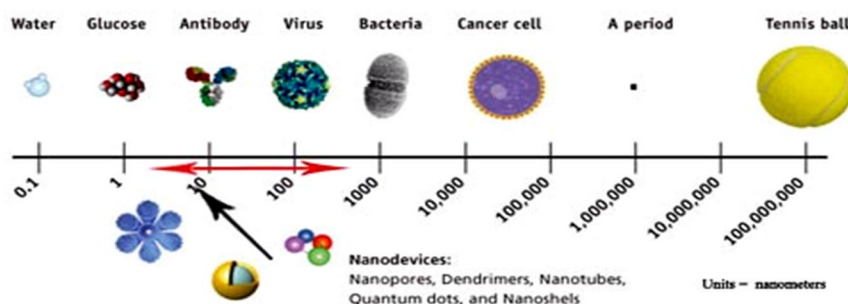


Fig.1: Units in nanometers (µm)

The term "nanotechnology" refers to materials with a size range of 0.1 to 100 nanometers (Fig. 1); but, because of their small size, these materials are bound to have different properties than bulk materials. Physical resistance, chemical reactivity, electrical conductance, magnetism, and optical effects are among the distinctions. According to Royal Society, "Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale". These new materials are designed to have specific physical or chemical properties due to their small size, form, surface area, conductivity, or surface chemistry, and have been used in a variety of fields (Smith *et al.*, 2007). 'Nano-material' means, according to another description,

a normal, tangential, or manufactured substance containing particles in an unbound, aggregated, or clumped state and containing, in the range of 1-100 nm, 50 percent or more of the particles in a number-size distribution or more of the outer dimension. (The European Commission, 2011).

2. Classification of nanomaterials

Nanomaterials are extremely thin, with one dimension of less than 100 nanometers. Nanomaterials can have one dimension (e.g., surface films), two dimensions (e.g., filaments or fibers), or three dimensions (e.g., particles), as shown in the diagram (Fig.2). It may take the form of a single, compact, aggregated, or lumpy shape, as well as circular, tubular, or irregular shapes. Common types of nanomaterials are nanotubes, dendrites, quantum dots, and fullerenes (Table 1).

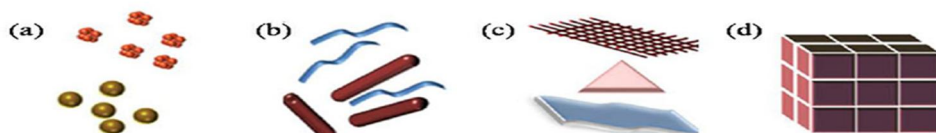


Fig. 2: Categorizing of nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.

Table 1: Classification of nanomaterials (Farzad *et al.*, 2014)

Categories of nano-materials	Description
Nano-particles	Particles less than one micrometer in size or even one micrometer in size can be obtained as high performance radiation resistant materials, magnetic materials, solar battery materials, packaging materials, and magnetic fluid materials.
Nano-tubes and nanofibers	Long linear nanofiber material, optical materials, microconductors, microfibers, PEEK, PET and PTFE nanotubes
Nano-film	Membranes are used as gas catalysts
Nano-block	The nanocrystalline materials are manufactured with great precision and develop a controlled crystallization or nanoparticles
Nano-composites	Composite nanomaterials that use nanoscale enhancements in place of traditional fibers or particles
Nano-crystalline solids	Polycrystals with a size of 1 to 10 nm and 50% or more solids consist of an inherent interface between the crystals and different directions. Clusters that are formed by homogeneous nucleation and that grow by fusion and fusion of atoms.

3. Mechanism's synthesis and properties of the nano particles

From synthetic materials nanoparticles can be developed from adjusted synthetic fertilizer styles, or synthetic materials which produced by different chemical, mechanical, or biological processes of green plants parts by nano technology (Singh and Kumar, 2017). There are two main methods of synthesizing nanoparticles: (1) top-down and (2) bottom-up as shown in (Fig. 3). However, in the top-down approach, the nano particles are produced by splitting the cluster to produce nano-size. In bottom-up method, nano particles are synthesized using smaller molecules, atoms, and monomers. A non-toxic green synthesis is environmentally friendly method, since living organisms such as plants, fungi and bacteria are used to synthesize the nanoparticles. These microorganisms act as reducing and stabilizing agents and contain no used impurities or chemicals (Lee *et al.*, 2020). On the other hand, the top-down or bottom-up chemical method uses mineral, decreasing agents and hazardous chemical compounds to stabilize nano materials that, when disposed of, lead to adverse effects on humans and the environment (Irvani *et al.*, 2015).

On other hand, there are two main factors that lead to the fact that nanomaterials differ in their properties from those of other materials which are their higher relative surface area and quantitative effects as shown in (Fig. 4).

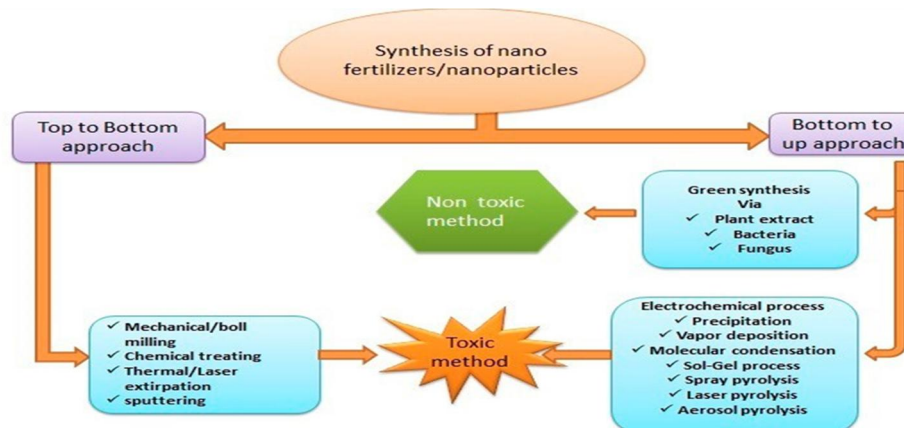


Fig. 3: Main approaches for the synthesis of nano-fertilizers (NFs) or/and nanoparticles (NPs).

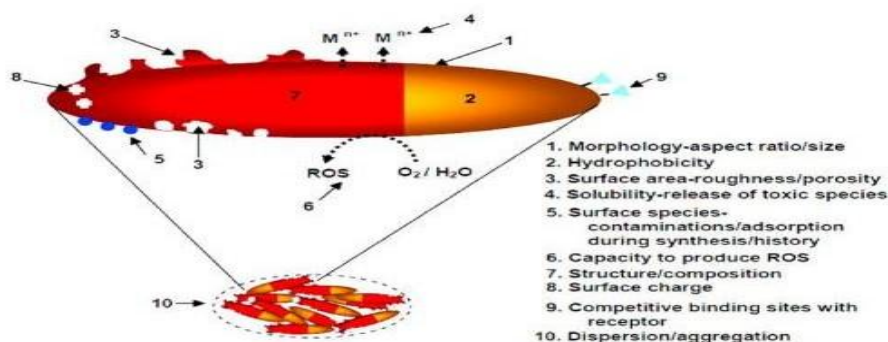


Fig. 4: The properties of nanoparticles

Substantial properties of nanoparticles are morphological/volume aspect ratio, hydrophobicity, solubility - release of toxic species, surface area/roughness, contamination/absorption of surface species, during synthesis/history, reactive oxygen species (ROS) O/HO, ROS production ability, structure/synthesis, competitive binding sites with receptors and dispersion/aggregation and all of them are the significant properties of nanoparticles (Somasundaran *et al.*, 2010). Nanomaterials have a higher surface area to volume ratio than traditional materials, which can result in a larger chemical reaction and a reduction in power. Quantum effects in determining material properties can become much more significant at the nanoscale, resulting in new optical, electrical, and magnetic activity.

4. Mechanisms of nano-fertilizers uptake by plants

The transport and absorption of NF elements from the soil to plants must be investigated, as this information will reveal how NFs are suitable for plants. For example, if NFs or NPs prefer to be transported via the xylem, the irrigation system is the best way to apply them. External and effective application is advised if NF travels around the phloem (Pitambar and Shukla, 2019). The formation of NFs, the size of the NPs, plant physiology, and the cell wall pore diameter (5-20 nm) all have an effect on the transport and accumulation of nutrients released from NFs in plants. Rico *et al.* (2011) have provided a graphical representation of multiple nanoparticles' absorption, transition, and biotransformation routes, as well as potential cell uptake patterns in the plant system, as shown in Fig. 5.

4.1. Root exposure and uptake of nano-fertilizers in plants

Many factors influence NP absorption by roots, including plant morphology, growth stage, exposure conditions, particle size, and root processes. Slomberg and Schoenfisch (2012) discovered that silicon nanoparticles (SiO₂) with diameters of 50 and 200 nm penetrate *Arabidopsis thaliana* roots. TiO₂ NPs, on the other hand, persisted between 36 and 140 nm in the wheat root parenchyma without access to the vascular system, while NPs smaller than 36 nm in diameter were accumulate in the wheat root and transferred to plant (LaRue, 2012). The surface charge influences NP absorption and transport

in plants as well (Lv *et al.*, 2019). Furthermore, various plant species demonstrated varying NP uptake capabilities, presumably due to variations in physiological functions and metabolism. When added to the soil, NPs or NPs are taken up by the roots, and when applied foliar to the leaves, they are taken up by the leaves. External application of NPs or their aggregates in smaller diameters allows better entry to the epidermis via the glacial pathway as compared to larger NPs. However, between plant species, differences in leaf morphology, as well as the number and size of stomata, can affect the absorption of different NPs with different diameters. Translocation of NF or NP from a soil application may occur through apoplastic or symplastic pathways. The apoplastic pathway allows NPs to penetrate the cell wall pores and then translocate into the intercellular space. However, NPs larger than 20 nm cannot move through the apoplastic pathway due to the cell wall's pore diameter. In foliar application, the diameters of NFs and/or NPs must be smaller than in soil application.

Finally, aside from some significant studies on TiO₂ and ZnO nanoparticles, the majority of absorption, translocation, and aggregation studies in plants are only carried out in plants up to the germination point. As a result, nothing is understood about the fate of nanoparticles in the plant environment (Rico *et al.* 2011). The details of storage in the plant facility are still being worked out.

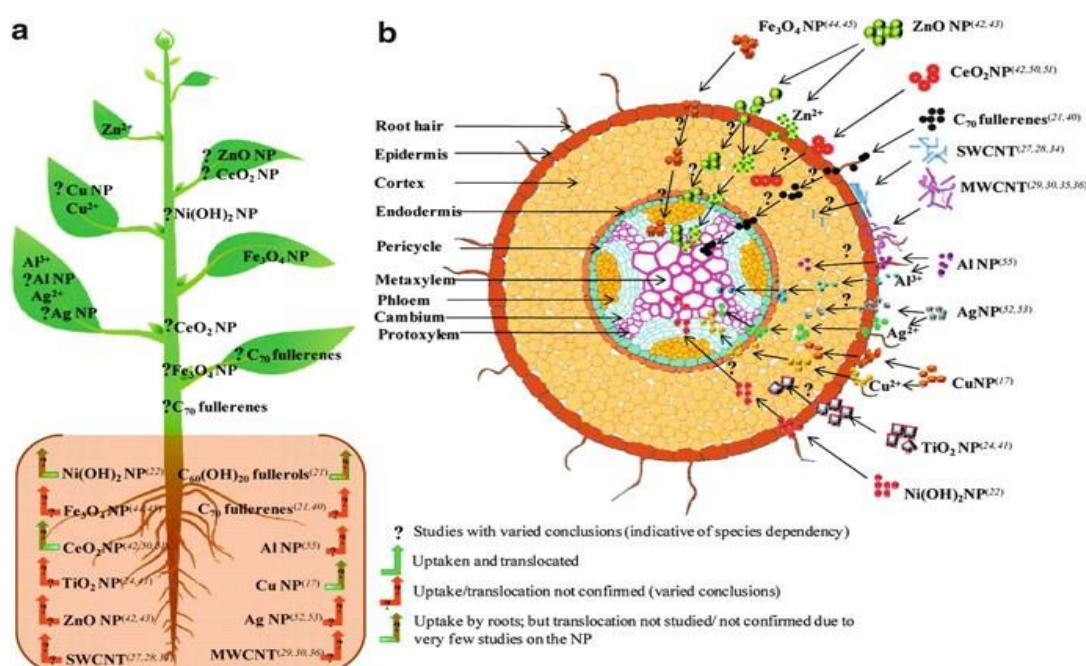


Fig. 5: Absorption, translocation, and biotransformation pathway of various nanoparticles in the plant system: (a) Plant with selective absorption and translocation of nanoparticles; (b) Cross section of the root absorption area showing the different interactions of nanoparticles upon exposure.

4.2- Foliar exposure and uptake of nano-fertilizers

NPs penetrate the skin barrier before reaching plant tissues in foliar applications. The epidermis is a waxy coating on the leaves with two points of entry: the lipophilic skin and the hydrophilic stomata. The lipophilic pathway is intended for non-polar solutes that can diffuse between leaves, while the hydrophilic pathway is intended for polar solutes (Eichert *et al.*, 2008). As a result, NPs or their aggregates with a diameter of less than 4.8 nm can quickly pass through the glacial's course to enter the epidermis. However, several studies have demonstrated that NPs larger than 5.0 nm can reach plants via foliar application (Lv *et al.*, 2019). Polar nanoparticles, on the other hand, will join via the stomata or hydrophilic pathway. NP absorption by leaves may be affected by differences in leaf morphology and the number and size of stomata between species (Wiesner *et al.*, 2009). Stomata are about 25 meters long and 3–10 meters wide in morphological terms (Eichert *et al.*, 2008). However, the maximum exclusion of the actual stomatal hole of NP diffusion remains uncertain due to the physiological function and special geometric structure of stomata. Nanoparticles can fly long distances across the plant's vascular system by following the stomatal pathway after joining the leaf apoplast (Lv *et al.*, 2019). Nutrients or photosynthates that migrate to shoots (xylem) or roots (phloem) do not return to their

original locations because plant vascular systems are unidirectional and non-circulatory (Lough and Lucas 2006). As a consequence, foliar-applied nanoparticles can only be absorbed through the phloem system.

Wang *et al.* (2012) found that foliar-applied micronutrient oxide NPs (24–47 nm in diameter) penetrating the leaves through the stomatal pathway and reaching the roots through sieve tube phloem penetrated the leaves via the stomatal pathway. Zhao *et al.* (2016) discovered that after foliar spraying CuO NPs onto lettuce, 97-99 percent of the trapped copper is confined to lettuce leaves, whereas the remaining 1-3 percent is only present in root tissues. According to Wang *et al.* (2012), CuO NPs (20–40 nm) applied in soil is transported from maize roots to shoots via the xylem and then back to the roots via the phloem. Wang *et al.* (2012) discovered that foliar-applied micronutrient oxide NPs (24–47 nm in diameter) penetrated the leaves through the stomatal pathway and reached the roots via sieve tube phloem.

5. The role of nano-fertilizers in plant nutrition

Nano-fertilizer technology is a very innovative technology that seeks to improve fertilization production because the nutrient utilization efficiency of traditional fertilizers for N, P, and K is around 30-35 percent, 18-20 percent, and 35-40 percent, respectively. Nutrient transporters known as nano-fertilizers are created on substrates of nanoscale measurements ranging from 1 to 100 nm. The nanoparticles have a wide surface area and can hold a large amount of nutrients while slowly and gradually releasing them, enabling the absorption of nutrients that meet the needs of various crops while having no detrimental effects on the use of fertilizers (Pirzadah *et al.*, 2019).

Nano-fertilizers have some specific properties that enable increased nutrient utilization efficiency. The important features are: 1) Nano-fertilizers have a smaller particles size (less than 100 nm) which lead to an increase in the specific surface area and the number of particles per unit area and offer more opportunity for the nano fertilizer to come into contact to the plant system (roots and leaves) which leads to more penetration and absorption, i.e., high use efficiency of fertilizer. All of these facilitate the different metabolisms and more photosynthesis in the plant system while consuming lesser amounts of fertilizers, 2) It has high solubility in various solvents such as water, 3) Fertilizer elements encapsulated in nanoparticles increase the availability of phytonutrients and thus, their uptake by crops, and 4) Zeolite-based nano-fertilizers can slowly release nutrients to the crop, which increases the nutrient availability of the crop despite the growth phase.

The following advantages of nano-fertilizers in plant nutrition are as follows:

Solubility and dispersion of nutrient

In comparison to traditional fertilizers of large particle size, which have lower solubility and therefore lower bioavailability for plants, nanoscale mineral composition can boost the solubility and distribution of insoluble nutrients in the soil, minimize soil adsorption and stabilization, and increase bioavailability.

Nutrient uptake efficiency

If the bulk compound in traditional fertilizer applications is not available to roots, reducing productivity, the nanostructured formula would increase fertilization efficiency and soil nutrient uptake ratio in crop production while saving fertilizer resources.

Effective duration of nutrient release

Although traditional fertilizers were used at the time of plant dispensing and converting the remainder to insoluble salts in the soil, the nano-structural formula will extend the effective length of nutrient supply of fertilizers into the soil.

Controlled release modes

Unlike traditional fertilizers, which can cause toxicity and disrupt the ecological balance of the soil, the rate and pattern of nutrient release from water-soluble fertilizers can be precisely regulated by encapsulating them in laminated types of semi-permeable membranes coated with polymer resin, wax, and sulfur.

Release pattern of nutrients as follow:

Slow release: The nano capsule releases nutrients gradually over a set period of time.

Quick release: Nano-particle shell breaks upon contact with a surface (such as striking a leaf).

Specific release: A nanoparticle shell breaks when it comes into contact with a surface (such as striking a leaf).

Moisture release: In the presence of water, the nanoparticle degrades and releases nutrients.

Heat release: The Nano-particle releases nutrients when the temperature exceeds a set point

PH release: Only under particular acid or alkaline conditions does the Nanoparticle degrade.

Ultrasound release: An external ultrasound frequency ruptures the nanoparticle.

Magnetic release: a magnetic Nano-particle ruptures when exposed to a magnetic field.

Effective duration of nutrient release

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Fertilizer nutrient loss rate

The nano-composite formula can lower the rate of fertilizer nutrient loss in soil through leaching and/or infiltration. Conventional fertilizers, on the other hand, have a high rate of loss due to seepage, leaching, run-off, precipitation, and erosion. Plant nutrition can be improved by providing necessary nutrients to plants in the form of nano fertilizers in two ways:

1) Nanostructured elements are encased in a carrier complex, which may be a nanomaterial or not. By absorption or adsorption, it is absorbed into a matrix such as chitosan, polyacrylic acid, cement, or zeolite, and

2) using the requisite nutrient elements in nanostructured formulations (either in suspension or encapsulated). In certain situations, seed mineral nutrition is determined by the abundance of one or more elements to crop plants rather than the quantity of one or more elements found in the soil. As a result, scientists have been investigating the possibility of encapsulating fertilizer components and other compounds in inorganic nanomaterials. Carbon nanotubes, clay montmorillonite-urea nanocompounds, SiO₂ nanoparticles, nano porous or mesoporous silica, and natural or synthetic zeolites are a few instances (Ditta and Arshad, 2016).

6. Nano-technology applications in agriculture

Applications of nanotechnology in agriculture as shown in (Fig. 6) aims to reduce the number of chemical products used by active ingredients delivery, to reduce nutrient losses during fertilization and increase yields through optimizing nutrient and water managements (Gogos *et al.*, 2012). In the areas of plant breeding and genetic transformation, devices derived from nanotechnology are also being studied (Torney *et al.*, 2007).

Agricultural materials, such as wheat straw and soybean hulls, can also be used to make bio-nanocomposites with better mechanical and physical properties (Alemdar and Sain 2008). Nano-particles produced with the help of nanotechnology can be used in the value chain of the entire agricultural production system.

On the other hand, Parisi *et al.*, (2015) provide an overview of the most relevant applications of agricultural nanotechnology (Table 2).

Plant growth, yield, and productivity are all improved by controlled nano-fertilizers. To increase yields, a nano-based approach to target delivery (gene transfer) is used. Nano-pesticides can be used to protect plants effectively. Precision agriculture is made possible by the use of nanosensors and highly computerized controls. Nanomaterials may also be used to enhance plant resistance to stress and soil quality.

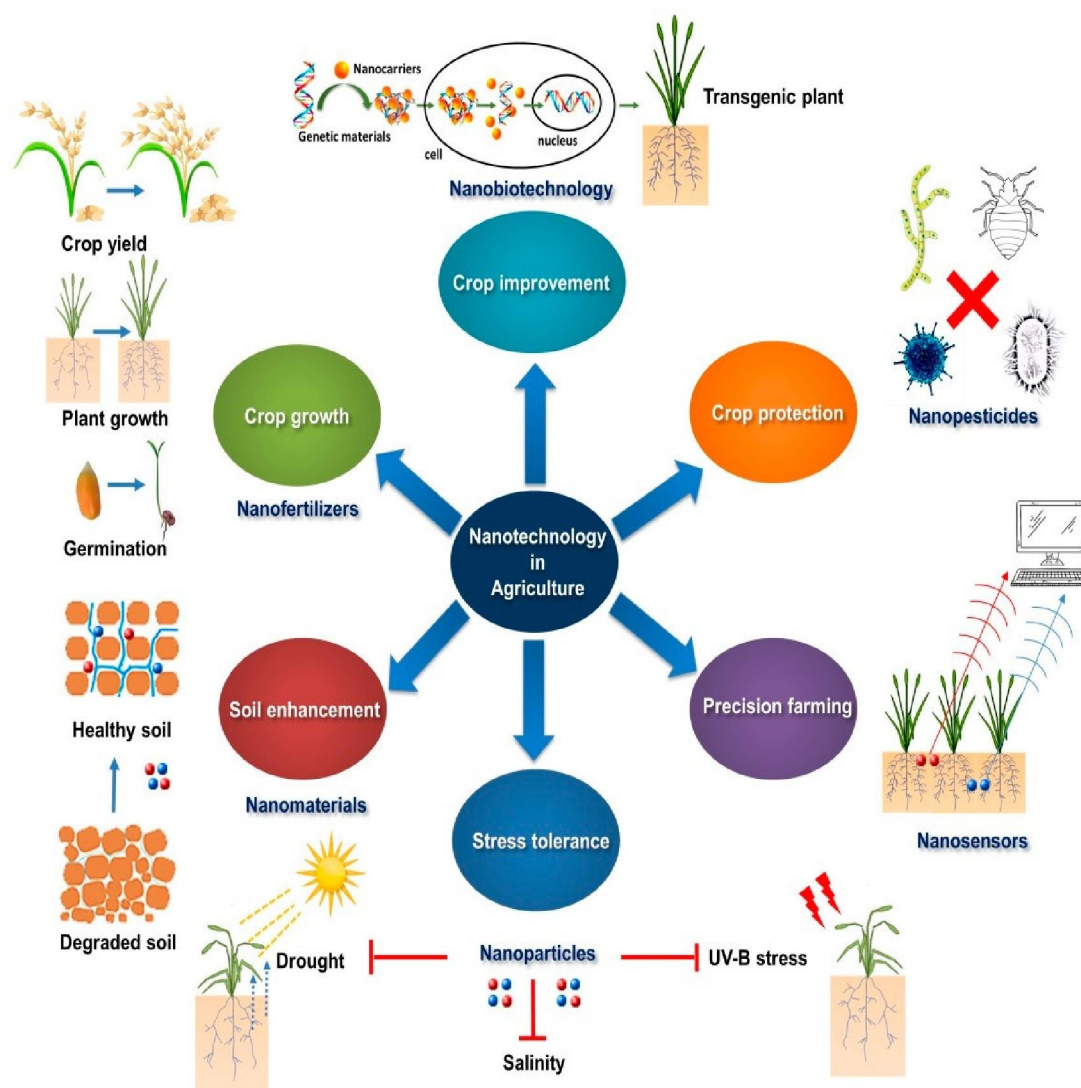


Fig. 6: Applications of nanotechnology in agriculture

Table 2: Relevant applications in agricultural nanotechnology and examples of successful applications at small scale.

at small scale.		
Definition	Example	
Crop production		
Plant protection products	Nano-capsules, nanoparticles, nanoemulsions and virus capsules as intelligent delivery systems for active ingredients to combat diseases and pests in plants	Neem oil (Azadirachta Indica), a nanoemulsion as a larvicidal agent (VTT University, IN)
Fertilizers	Nanocapsules, nanoparticle and virus capsules to improve the uptake of nutrients by plants and the supply of nutrients to certain areas	Large scale nutrient fertilizer coated with zinc oxide nanoparticles (University of Adelaide, AU CSIRO Land and Water, AU Kansas State University, USA)
Soil improvement		
Water/liquid retention	Nanomaterials, for example zeolite and nanoclays, hold back water or liquid agrochemicals in the soil for their slow release in plants	Soil improvement product based on a component made of nanoclay to retain and release water (Geohumas-Frankfurt, DE)

Water purification		
Water purification and pollutant remediation	Nanomaterials for example nanoclays, filter and bind to as variety of toxic materials. including pesticides, to remove them from the environment	Filters coated with TiO ₂ nanoparticles for the photolysis of agrochemicals in contaminated water (University of Ulster, UK)
Diagnostic		
Nano-sensors and diagnostic devices	Nanomaterials and nanostructures (such as electrically active carbon nanotubes nanofibers and fullorene) are highly sensitive biochemical sensors for the precise monitoring of environmental conditions as well as plant health and growth	Detection of pesticides with a liposome-based biosensor (University of Crete, Georgia)
Plant breeding		
Plant genetic modification	DNA- or RNA-carrying nanoparticles are released to plant cells For genetic transformation or to stimulate defense reactions that are activated by pathogens	Porous silicon dioxide nanoparticles that transport DNA to transform plant cells (Iowa State University, USA)
Nano-materials from plant		
Nano- particles from plants	Manufacture of nano-materials through the use of technical equipment or microbes and through the treatment of waste from agricultural products	Wheat straw and soy husk nano fibers used to make bio - nanocomposite production (Canadian Universities and Ontario Ministry of Agriculture, Food, and Rural Affairs in Ontario, California)

Conclusion

An increase in food production occurs because of the use new and innovative fertilizers using nanotechnology to face the increase in population, from the perspective of sustainable agriculture. Where, the literature reported strongly suggests that nano-sciences are likely to play a critical role in the development of smart delivery systems. NFs can help to reduce fertilizer losses due to volatilization, filtration, runoff, and energy consumption during processing by intelligently supplying active ingredients, increasing nutrient absorption and NUE levels, and reducing fertilizer losses due to volatilization, filtration, runoff, and energy consumption during processing. Nano fertilizers can release their nutrients in 40-50 days, while only in 4-10 days for synthetic fertilizers. Research has shown, however, that NFs release nutrients 12 times more slowly than synthetic fertilizers and may increase crop yields and quality characteristics. Research-based use and the wisdom of NF should be studied in more detail before NF is commercialized or distributed on a commercial scale. This enables plants to grow more biomass without any negative effects on the environment using the nutrients available in the root region. Controlled and sustained nutrient release helps to increase the efficiency of nutrient usage. Nutrient release is governed by physical and chemical processes, but the biological sense of nutrient release is unclear.

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