Nanotechnology-based controlled release of sustainable fertilizers. A review

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Abstract
The rising population is increasing food demand, yet actual crop production is limited by the poor efficiency of classical fertilizers. In particular, only about 40–60% of fertilizer nitrogen, 15–20% of phosphorus and 50–60% of potassium are used by crop plants, the rest ending polluting the environment. Nanofertilizers are promising alternatives. Here, we review plant nutrients, synthesis of zinc oxide nanoparticles, encapsulation of nanoparticles in fertilizers, and effect on plants.

Keywords Nanotechnology · Sustainable agriculture · Nanofertilizer · ZnO nanoparticle · Green synthesis and precision agriculture

Introduction
The earth population is increasing so fast that by 2050, it is expected to cross 9 billion. This may create a lot of problems, especially in the production of agricultural goods. The demand for food is expected to increase by 70–80% due to this upsurge (Bahar et al. 2020). Currently, the agricultural sector all around the world is severely affected by the poor yield of crops. This has occurred due to shortage of nutrients, soil organic matter, micronutrients, with additional factors including pest and insects attack and ineffective fertilizer (Prost 2021). The statistics gathered by the Food and Agriculture Organization of the United Nations (FAO) reports that the reduction in water resources and increase in soil salinity depleted the arable land for crop cultivation. This creates a serious challenge towards the growth of food and agricultural goods for meeting the demand and supply gap created by the increasing population (Rajam 2020).

Nanoscience and technology are the emerging field of science that has revolutionized many engineering branches such as the electronic industry, medicinal science, power sector, and automotive industries. This technology has a huge perspective in botanical and remedial fields like smart drugs release, biosensors, tissue synthesis, and nanofertilizers as shown in Fig. 1. Nanoparticles possess higher surface to volume fractions and distinctive features that build them very appropriate for use as compared to their bulk counterparts. The joint venture of nanotechnologies with agricultural and food science is emerging as a potential approach to increase plant growth and yield (Cheng et al. 2016; Moulick et al. 2020). With the help of this technology, farmers can utilize the nanoparticles effectively and precisely with other limited resources like water and costly synthetic fertilizers. Precision farming helps agriculture to become sustainable and greener by minimizing the usage of energy resources.
and waste (Duhan et al. 2017). Table 1 has categorized and tabulated different nanomaterial applications in the past decade.

The nanotechnology application in the form of nanofertilizer used both bulk and nanoscale materials. The nanoparticles normally range from 1 to 100 nm in at least one dimension (e.g., Zinc nanoparticles, and Iron nanoparticles) while the carriers of nanoparticles are at the bulk scale with more than 100 nm in size (Askary et al. 2017; García-Gómez et al. 2020). Therefore, the data presented in this review are related to nanomaterials and their utilization as a fertilizer. The major focus of this review is on the micronutrients utilized for the growth of plants. The most frequently used micronutrients are Zn and Fe; therefore, detailed literature regarding Zn nanoparticles is presented in this study. The novelty of this work is that up to our knowledge, no study has been conducted yet which highlights the data related to Zn nanoparticles and their usage as nanofertilizer. The literature discussed here allows the readers to understand the benefits of Zn nanoparticles or the development of crops through sustainable and precision agriculture.

**Plant nutrients**

Increasing population enforced farmers to enhance crops yield to meet the demand and supply gap of food in the developing world. Farmers used synthetic fertilizers in fields to promote the higher production of crops. Nutrient loss associated with the higher dissolution of fertilizers contributes towards financial loss and environmental pollution, along with lower crop productivity with poor dietary content for humans and domestic animals. Although fertilizers are well-known to increase crops yields; however, due to their higher solubility, the nutrient release from those particles are unable to match the sequential needs of crops (Meyer et al. 2018). For example, excessive nutrient nitrogen is wasted in the environment by ammonia emissions, leaching, runoff, and volatilization. On the other hand, extra phosphorus content remains present in the soil and get fixed by making a chemical bond with soil trace metals like calcium, magnesium, aluminium, iron and zinc. This bonding makes these essential micronutrients unavailable for plants’ uptake for their growth (Zhang et al. 2021).

This mismatch of nutrient release causes severe problems like fertilizer burns, ammonia volatilization, and leaching losses. The mismatch occurs due to lower nutrient requirements at different stages of plant growth, especially the initial stage. The plant uptake efficiency is very low due to the conversion of nutrients into unsolvable forms in the fields. Crops only utilize about 40–60% of nitrogen, 15–20% of phosphorus, and 50–60% of applied potassium products due to the above-mentioned problems (Chinta et al. 2020). The substances fixation, leaching, and volatilization cause both water and air contamination. These nutrients losses not only affect crop yield but also conversely misbalance the earth nutrient equilibrium and diminish the natural fertility of the top soil (Fertahi et al. 2021; Le et al. 2021). Therefore, it is
| Nutrients | Ionic/molecular form of nutrients in plant | Functionality | Scarcity signs | References |
|-----------|------------------------------------------|---------------|---------------|------------|
| Nitrogen  | Ammonium ion \((\text{NH}_4^+)\), nitrite \((\text{NO}_2^-)\) and nitrate ions \((\text{NO}_3^-)\) | Helps in building of protein and genital materials | Yellowish colour of leaves | Razaq et al. (2017), Ahmed et al. (2018) |
| Phosphorous | Ortho-phosphorous anion \((\text{PO}_4^{3-})\) | Major portion of nucleic acid, phospholipids and components of membranes, cell walls and adenosine triphosphate | Cell death, poor growth rate and distinctive violet shade | Emami et al. (2018), Malhotra et al. (2018) |
| Potassium | Potassium ion \((\text{K}^+)\) | Maintains turgidly in plants, increase ability to fight against diseases, enhance enzymes activation, respiratory system and increase the ability towards food formation like sugars, protein, starch and carbohydrates | Spots leading to necrosis and high chances of disease | Hafsi et al. (2017), Hassan et al. (2017) |
| Sulphur  | Sulphide \((\text{S}^-)\), and sulphate \((\text{SO}_4^{2-})\) | Major constituents of amino acid and vitamin A | Decrement in plant chlorophyll and lower protein production | Yue et al. (2020) |
| Calcium  | Ca\(^{2+}\) cations | Helps in building of plant cell wall during cell division and control cell membranes structures | Deficient root growth and low crop yield | Thor (2019), Mulaudzi et al. (2020) |
| Magnesium | Mg\(^{2+}\) ionic form | Activate enzymatic, physical, and biochemical reactions help in promoting photosynthesis reactions | Loss in green colour of leaves | Guo et al. (2016), Yan and Hou (2018) |
| Sodium   | Na\(^{+}\) cation | Activate plant development by cell expansion, maintains water content and maintains various essential solutes | Loss in green colour of leaves | Nieves-Cordones et al. (2016) |
| Silicon  | In the form of \(\text{SiO}_2\) | Major portion of plant cell wall, part of endoplasm and reticulum | Enhancement of leaves falling and fungus started on leaves | Souri et al. (2020), Prabha et al. (2021) |
| Chlorine | Chloride ion \((\text{Cl}^-)\) | Necessary during photosynthesis process and cell splitting process | Sudden drying of leaves and leaves dropping | Geilfus (2018) |
| Iron     | Fe\(^{2+}\) and Fe\(^{3+}\) cations | Required for oxidation and reduction reactions and helps in production of chlorophyll content and proteins | White spots on leaves | Rout and Sahoo (2015) |
| Boron    | Borate \((\text{H}_2\text{BO}_3^-)\) | Necessary for nucleic acid production, cell membrane and cell wall properties enhancement | Inhibits growth of the lateral buds | Shireen et al. (2018) |
| Manganese | Mn\(^{2+}\) cation | Acted as activators for enzymatic reactions and photosynthesis reactions | Loss in greenery of leaves and branches | Schmidt et al. (2016) |
| Zinc     | Zn\(^{2+}\) ion | Essential element of many enzymatic reactions, strengths ribosome structures and cell membranes | Smaller leaves and shoot growth | Sturikova et al. (2018), Umair Hassan et al. (2020) |
| Molybdenum | Mo\(^{4+}\) anion | Part of enzyme And promotes nutrient nitrogen assimilation | Loss in plant greenery | Manuel et al. (2018), Rana et al. (2020) |
| Nickel   | Ni\(^{2+}\) cations | Constituent of urease | Buildup of urea, burning of leaves, and drying of plants | Miri et al. (2017), Fatima et al. (2021) |
need of the hour to develop a method that is sustainable and environmentally friendly for the delivery of nutrients to the soil with minimum use of resources and fertilizers. Whereas common synthetic fertilizers are used in bulk quantities in the agriculture fields generally ranging from 80 to 140 kg per hectare of land. On the other hand, nanoparticles as a fertilizer reduce this huge quantity to a greater extent.

Nanofertilizer possesses properties that stop nutrient loss which increases the nutrient use efficiency and optimal plant growth. In the present scenario, “smart drug delivery carriers” are gaining much interest in the delivery of nutrients to the fields for the replenishment of exhausted minerals. Nanoparticles of the desired micronutrients are loaded on the bulk carrier acted as a substrate. Nanoparticles under a smart drug delivery system will control the solubility of macronutrients and decrease the adsorption and fixation while promoting bioavailability in soil (Solanki et al. 2015; Polman et al. 2020). The nanoparticles are being loaded in macronutrients fertilizer with absorption, attachment via mediated ligands, encapsulation, or entrapment. After nanoparticles loading on fertilizers, nutrient(s) discharge could be controlled, which might enhance the nutrient use efficiency. The mass production of nanofertilizers for crop improvement is still debatable due to safety and economics-related issues with nanoparticles (Dubey and Mailapalli 2016).

Techniques to improve plant growth

Biotic and abiotic stresses are involved all around the world for the poor growth of crops causing 50% yield decline. The biotic stresses occur because of living organisms like bacteria, viruses, fungi, parasites, beneficial and harmful insects, whereas, include excessive heat, rain, winter, salinity, nutrients scarcity and chemical toxicity (Mareri et al. 2019; Ahmed et al. 2021). Both these factors adversely affect the growth and productivity of plants. In addition, they change the physical, chemical, and molecular nature of plants (Atkinson and Urwin 2012). Therefore, different strategies are used to remove these stresses. The most adopted technique includes foliar spray or application of some active ingredients via soil. Plants need CO₂, H₂O along with sunlight for their growth. CO₂ and H₂O are composed of carbon, hydrogen, and oxygen; therefore, not classified as mineral nutrients. Additionally, 16 other essential plant nutrients are required in small amounts (Fe, Cu, Zn, Mn, B, Mo, Ni, Na and Cl) and fewer are necessary for higher concentration (N, P, K, Mg, Ca, S and Si) for their growth. After the application of these nutrients, the effects of stresses can be minimized or even eliminated. After passing through roots, they move to various parts of plants where their transformation takes place (Klaic et al. 2021). Through fertilizer application, these micro- and macronutrients reach their designated positions for necessary chemical reactions for crop improvement as shown in Fig. 2.

Due to the low efficiency of the applied fertilizers, most of these plant nutrients are lost to the surrounding environment which causes damages and loss in terms of productivity as explained in Table 1. For boosting the plant yield, these micro- and macronutrients, nanotechnology could be coupled with conventional fertilizers. These improved fertilizers might, therefore, be more efficient and meet the sequential need of plants. Nanofertilizers are supposed to be less harmful to crop plants as well as to the environment since their discharge rate for specific nutrients is slow (Monreal et al. 2016; Kottegoda et al. 2017). There are various technologies developed for the synthesis of nanofertilizers. Initially, nanoparticles of target nutrients are made and after that coupling of those nanoparticles are done with some substrates or base materials like urea or DAP fertilizer (Pohshna et al. 2020; Ramírez-Rodríguez et al. 2020). Nanofertilizers (encapsulated with nanoparticles and essential crop nutrients) can deliver the active ingredients due to their nanosize to the crops in an efficient way using slow-release techniques compared to bulk materials or ionic compounds of nutrients. These nanomaterials meet the plant need with higher target effective discharge in crop fields (Guo et al. 2018; Pirzadah et al. 2019).

Synthesis of nanoparticles

The outcome of nanomaterials on crop growth is dependent upon intrinsic and extrinsic interactions of the nanoparticles. The synthesis methods of nanomaterials also affect their properties greatly. The synthesis of nanomaterials is a very important task in the field of life sciences, medical, agricultural, environmental, and engineering applications. Two different strategies are used for the synthesis of nanoparticles from various sources as shown in Fig. 3. These sources include metallic and non-metallic substances (Subramanian et al. 2015). Under these strategies, further classification is done which includes two main classes, i.e., wet and dry synthesis methods. The wet method includes sol–gel, hydrothermal, precipitation, green synthesis using microorganisms and reversed micelles, whereas mechanical attrition and aerosol techniques come under the umbrella of the dry synthesis approach. (Kaul et al. 2012; Tarafdar and Raliya 2013; Dubey and Mailapalli 2016).

In the bottom-up approach, nanomaterials are built from smaller atoms and molecules which assemble themselves chemically by the principle of molecular recognition (Ariga et al. 2012). Nanomaterials are synthesized gradually atom by atom on a larger level like in the synthesis of nitrate salts metallic layer deposition in electronics industries. Each nanomaterial possesses distinctive properties as a result
of different production and processing techniques under the bottom-up approach (Rajput 2015). The conventional
adopted technique for the synthesis of nanoparticles is a wet-chemical method. The process takes start in a liquid media consists of different materials. For the prevention of agglomerates during the synthesis step, stabilizers are applied along with reactants (Ealias and Saravanakumar 2017; Nishida et al. 2018). In the bottom-up approach, a substantial number of nanomaterials are formed with minimal production cost. The major drawbacks associated with the bottom-up approach include dangerous by-products co-generation due to toxic solvents. Additionally, the final product gets contaminated due to starting materials (Jadoun et al. 2021).

The top-down approach yields nanomaterials that are synthesized from bigger molecules lacking atomic-level control (Khan 2020). Mechanical attrition is used widely to synthesize nanoparticles using a ball mill or planetary mill. The factors affecting final nanoparticle properties include the nature of the material, time of attrition, and attrition conditions. Another method other than attrition is pyrolysis in which an organic compound is enforced to pass through an orifice under high temperature, pressure conditions of 1000 °C and 10–15 bar, respectively (Rajput 2015). The major drawback with the top-down approach is

![Diagram of nanoparticles synthesis methods](image-url)
non-uniformity of nanoparticles and surface imperfections due to mechanical operation (Ealias and Saravanakumar 2017). The nanoparticles utilized as fertilizer application must be produced on large scale with such adaptive technology which is economical and yield particles with superior physicochemical properties.

**Synthesis of zinc-based nanoparticles**

Zinc is the most essential micronutrient required by animals and plants for their optimum growth. It plays a vital role in many cell functions especially in protein and enzyme synthesis reactions (Khan 2020). Most of the places around the world possess very low levels of plant available zinc. This shortage in the soil spreads zinc deficiency among the growing crops (Alloway 2009; Ahmed et al. 2021). In addition to the above, approximately 33% of the world population has taken zinc-deficient diets due to large intakes of cereals (Rehman et al. 2018; Aziz et al. 2019). Therefore, continuous efforts are required to address the zinc deficiency and more focus is needed for increasing the zinc micronutrient in crops and humans (Gomez-Coronado et al. 2016; Paradis-one et al. 2021). Different schemes are available for increasing the zinc content in growing crops as shown in Fig. 4 (Nakandalage et al. 2016). Biofortification (modifications in seeds) and the use of fertilizers with zinc have been identified as the most effective methods to remove zinc deficiency (Zaman et al. 2018; Du et al. 2019). Zinc fertilization is the fastest approach to meet the zinc demand among the crops in comparison to biological modification which is the time taking process.

On the other hand, zinc blended fertilizer does not always yield optimum results. The most important factor that affects fertilizer performance is the soil pH. High soil pH increases the negative charges on soil particles which increases the zinc exchange capacity of the soil and vice versa. Thus, the alkaline soil needs small zinc content for the removal of zinc deficiency continuously for greater fertility efficiency (Gomez-Coronado et al. 2016; Guo et al. 2018). Many research studies have been carried out using zinc sulphate as a zinc source either used directly to the soil or as a foliar spray. The soil application of fertilizer is the most effective technique, but ZnSO4 salt is unable to meet the requirement of plants and results in environmental pollution. So, there is a need to address the issue by identifying new smart fertilizers containing zinc as a micronutrient with high efficiency that has a lower risk factor of environmental pollution (Kopittke et al. 2019; Priyanka et al. 2019). Therefore, more research has been carried out to use nanotechnology for replacing conventional fertilizer with new nanomaterials containing Zn as nanoparticles in it (Kopittke et al. 2019).

Zinc oxide (ZnO) possesses very distinctive chemical and physical characteristics like higher physiochemical stability, high chemical coupling ability, a wide range of radiation absorptivity, and higher photo-stability (Shankar and Rhim 2019; Song et al. 2020). The rigidity and hardness of ZnO nanomaterials make them popular in ceramic engineering and manufacturing. At the same time, due to the negligible level of toxicity, biocompatibility, and biodegradability of ZnO are widely used for medicinal purposes. ZnO nanoparticles also show promising usage as micronutrient fertilizer and replacing conventional zinc salts fertilizers (Ludi and Niederberger 2013; Sabir et al. 2014; Panpatte et al. 2016). In this article, different preparation methods of zinc nanoparticles are reviewed. Zinc nanoparticles can be derived or synthesized from different zinc salts using different techniques including vapour deposition, water precipitation method, hydrothermal synthesis, the sol–gel method, and mechanical size reduction as shown in Fig. 5. Each salt possesses distinctive chemical and physical characteristics. Products obtained from different processes show a wide range of particles sizes, shapes, and structures. Additionally, the application of zinc nanoparticles in the agricultural

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**Fig. 4** Methods for removing zinc deficiency from plants such as zinc supplementation, food fortification and biofortification. Biofortification methods are sub-divided into two major techniques i.e., applying fertilizers (either through foliar spray or soil blend) and through genetic engineering

[Diagram showing methods of zinc deficiency removal]
sector has been discussed with its encapsulation in the polymer matrix as nanofertilizer.

**Controlled precipitation**

This technique is extensively applied for the synthesis of zinc nanoparticles from different raw materials with diverse properties as shown in Table 2. The process starts

| Raw materials                                           | Process parameters                                           | Product characteristics and dimensions                      | References                  |
|---------------------------------------------------------|--------------------------------------------------------------|-------------------------------------------------------------|-----------------------------|
| Zinc acetate, potassium hydroxide, and deionized water  | Operating temperature: 20–80 °C and temperature of drying: 120 °C | Particle size: 160–500 nm Brunauer–Emmett–Teller: 4–16 m²/g | Lanje et al. (2013)          |
| Zinc nitrate, and sodium hydroxide                       | Operating temperature: 100 °C for 2 h and drying period of 2 h at 100 °C | Particle diameter 40 nm and particle shape: spherical       | Lanje et al. (2013)          |
| Zinc acetate and aqueous ammonia                         | Precipitate at 85 °C and drying period at 60 °C for 10 h     | Particle diameter: 200 nm                                   | Jia et al. (2012)            |
| Zinc oxide powder and ammonium bicarbonate              | Temperature: 25 °C for 2 h and dry for 2 h at 80 °C and calcination at 350 °C for 1 h | Diameter 15–25 nm Brunauer–Emmett–Teller: 50–70 m²/g Hexagonal shape | Khoshhesab et al. (2012)     |
with a spontaneous reduction reaction of zinc precursor salt in the presence of a strong reducing agent with precipitation step as shown in Fig. 5. The development and properties of nanoparticles are controlled with the addition of a reducing agent. The impurities present in precursor salts are removed using high temperature, post-treatment steps with a milling operation. The precipitation of Zn nanoparticles is optimized by varying pH, temperature, reducing agent amount, and time. Lanje et al. (2013) adopted controlled precipitation for the preparation of zinc nanoparticles using zinc nitrate as precursor salt with sodium hydroxide. The starch molecules are used to eliminate agglomerates as hydroxyl functional groups hold the nanoparticles in the nucleating phase. The precipitation process requires surfactants to control the production of nanoparticles from precursor salts. These chemicals perform multiple functions and act as coagulants and flocculants. Suresh et al. (2018b) used the biocompatible precipitation method to develop ZnO nanoparticles using zinc nitrate and leaf extracts from Costus pictus plant. The schematic illustration of their method is shown in Fig. 6.

**Sol–gel method**

The sol–gel methodology for the synthesis of zinc nanoparticles possesses many advantages due to lower operational cost, process ease with reliability and reproducibility of a similar product. The reaction requires milder conditions for the production of nanoparticles using sol–gel route (Benhebal et al. 2013; Ismail et al. 2019). Yue et al. (2013) prepared zinc oxide nanoparticles using sol–gel technique with zinc 2-ethylhexanoate as precursor salt and Propan-2-ol as a solvent. Tetra Methyl Ammonium Hydroxide with a pH of ~14 was added by the authors, dropwise, in the solution of zinc salt and solvent. The reaction mixture was placed for 30 min, and then, washing was done with ethanol and water for removal of any impurities present in it. The transmission electron microscopy depicted the size of the nanoparticles.
in the range of 20–50 nm. The concentration of precursor salt in the solution did not affect the properties of nanoparticles. Likewise, Taghavi Fardood et al. (2019) fabricated ZnO nanoparticles using Arabic gum as stabilizing and reducing agent using a novel sol–gel method as depicted in Fig. 7. The properties and process parameters of sol–gel process are shown in Table 3.

**Hydrothermal synthesis**

The synthesis of nanoparticles via the hydrothermal route can easily be pursued in the absence of organic solvent with no post-treatment steps. Lack of organic solvent and calcination treatment makes this process greener, cleaner, and benign. The preparation of nanoparticles takes to starts with auto calving of the reaction mixture at a temperature ranging from 100 to 300 °C. This process continues for a few days. The reaction mixture cools after heating, which forms crystals due to nucleation phenomena. This process continues till the growth of nanocrystals. The hydrothermal process possesses several operational benefits due to the lower temperature and pressure of reaction media especially, with no post-treatment step as tabulated in Table 3 along with sol–gel method. Furthermore, a wide range of products are formed during the hydrothermal process in terms of shape and size (Tofa et al. 2019, Bulcha et al. 2021). Many studies have been carried out using microwave-assisted reactor for heating purposes in hydrothermal processes. Microwave-heated reactors make the system efficient with minimal loss. These efficient systems enhance the reaction rate with better product yield. The schematic diagram of the hydrothermal method is shown in Fig. 8.

**Physical methods**

Zinc oxide nanoparticles can also be prepared using other techniques different from chemical synthesis processes. These techniques include mechanical milling operation,

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Table 3 Sol–gel and hydrothermal methods to synthesize zinc oxide nanoparticles

| Raw materials                                      | Process parameters                                      | Product characteristics and dimensions                  | References                  |
|----------------------------------------------------|---------------------------------------------------------|---------------------------------------------------------|-----------------------------|
| Arabic gum, and zinc nitrite                        | Process temperature 75 °C and calcination at 500 °C     | Uniform spherical morphology particle size: 10 nm       | Taghavi Fardood et al. (2019)|
| Zinc acetate, ethanol, and sodium hydroxide         | Process temperature 60 °C pH of solution 8 and calcination at 500 °C for 4 h | Flake-like formation crystallite size 21.84 nm          | Manikandan et al. (2018)    |
| Zinc acetate, sodium hydroxide, methanol and aquabidest | Process temperature 25 °C sonication for 30 min pH ranges from 7 to 12 and calcination at 800 °C | Particle size at pH 7:1.3 nm and pH 12:73.8 nm          | Rochman and Akwalia (2017)  |
| Zinc 2-ethyl hexanoate, tetra methyl ammonium hydroxide, ethyl alcohol and 2-propanol | Process temperature 25 °C dry at 60 °C                  | Diameter of particles: 25–30 nm                         | Yue et al. (2013)           |
metallurgical processes, microwave-assisted thermal processes, etc. In the metallurgical process, zinc oxide nanoparticles are obtained by the roasting of zinc ore at high temperatures. International organization of standardization (Kołodziejczak-Radzimska and Jesionowski 2014) classifies zinc oxide from the metallurgical process into two types. Type A zinc oxide nanoparticles are formed via a direct process also known as the American process whereas indirect or French process yields Type B zinc oxide nanoparticles. In a direct process, the zinc ore reduces in the presence of coal within situ oxidation in the reactor. The bed in a reactor is divided into two separate layers. The top layer comprises of coal while the bottom layer constitutes a mixture of coal and zinc ore. The zinc ore is reduced with the help of carbon monoxide supplied with the hot air.

The only drawback associated with this process is low zinc oxide purity due to the presence of different metallic compounds. The presence of metal oxides like those of lead, iron and cadmium affect the white colour of zinc oxide nanoparticles. In the indirect synthesis technique, metal zinc is melted down in furnaces at around 910 °C. The vaporized zinc reacts with oxygen to form zinc (oxide) nanoparticles. The synthesized particles are cooled down in a cooling duct and are captured in the filter bag. Shi et al. (2014) prepared zinc oxide nanoparticles using a combination of chemical and mechanical processes to yield particles size of 21 nm. The milling process lasts for 6 h and produced zinc carbonate as a zinc oxide starting material. The post-treatment step of nanoparticles was carried out at 600 °C. The morphology of zinc oxide nanoparticles was affected by the duration of milling and temperature of heat treatment.

Green synthesis

Green synthesis is a cleaner and greener approach to produce zinc nanoparticles using renewable raw materials for example plants, microorganisms, algae, etc. as shown in Fig. 8. This synthesis mechanism is safer, environment friendly and economical in terms of raw materials and solvents requirements (Salam et al. 2014; Jamdagni et al. 2018). The biggest advantage of the green approach is the absence of harmful impurities with the synthesized nanoparticles (Agarwal et al. 2017). Green synthesis uses more benign chemicals which make particles more active and safer to use (Fakhari et al. 2019). Different green plants are used for the synthesis of nanoparticles (Baker et al. 2017). Mostly plant roots, shoots, leaves, barks and fruits are used for the synthesis process (Adelere and Lateef 2016; Saratale et al. 2018). Along with the wide range of applications, zinc oxide nanoparticles are safer and easier to produce with cheaper manufacturing processes (Jayaseelan et al. 2012). Different green sources are available for the synthesis of zinc oxide nanoparticles. These sources include plant extract, bacteria, algae, and other biological sources as illustrated in Fig. 9. A wider range of literature is available about different sources for the synthesis of zinc oxide nanoparticles. Few natural sources for zinc oxide nanoparticles are shown in Table 4.
Encapsulation of zinc oxide nanoparticles in fertilizers

Encapsulation of nanoparticles is the biggest challenge due to their smaller size with higher surface area and energy. Generally, encapsulation is applied for coating food ingredients, nanoparticles, and biological substances on a micro-level. This technique is mostly used in pharmaceuticals to control the release of active agents (Morin-Crini et al. 2019; Rajan et al. 2020). Control release system offers many advantages including shielding effect from degradation, targeted delivery, and controlled release of active agents. The reason behind encapsulation is to isolate the core material from an external environment or to release the active agent from the core in a controlled manner (Anita and Ramach 2012; Tamanna et al. 2015). For example, the urea core is encapsulated using polymers for the slow release of nitrogen. The encapsulation also decreases the solubility of urea (Arjona et al. 2018; Ibrahim et al. 2019; Beig et al. 2020a).

Table 4 Green plants for obtaining zinc oxide nanoparticles by green synthesis

| Plant (family)                  | Common name | Part taken for extraction | Size (nm) | Reference                                |
|--------------------------------|-------------|---------------------------|-----------|------------------------------------------|
| Azadirachta indica (Meliaceae) | Neem        | Fresh leaf                | 18        | Elumalai and Velmurugan (2015)           |
| Azadirachta indica (Meliaceae) | Neem        | Fresh leaf                | 10–30     | Madan et al. (2016)                      |
| Agathosmabetulina (Rutaceae)   | Buchu       | Dry leaf                  | 12–26     | Thema et al. (2015)                      |
| Aloe vera (Liliaceae)          | Aloe vera   | Leaf extract              | 8–20      | Ali et al. (2016)                        |
| Aloe vera (Liliaceae)          | Aloe vera   | Freeze-dried leaf peel    | 25–65     | Qian et al. (2015)                       |
| Gossypium (Malvaceae)          | Cotton      | Cellulosic fibre          | 13        | Aladpoosh and Montazer (2015)            |
| Trifolium Pratense (Legumes)   | Red clover  | Flower                    | 60–70     | Dobrucka and J (2016)                    |
| Coccus nucifera (Arecaceae)    | Coconut     | Coconut water             | 20–80     | Krupa and Vimala (2016)                  |
| Plectranthus amboinicus (Lamiaceae) | Mexican mint | Leaf extract             | 50–180   | Fu and Fu (2015)                         |
| Phyllanthus niruri (Phyllanthaceae) | Bhuimla, stone breaker | Leaf extract            | 25        | Paulkumar et al. (2014)                  |

Fig. 9 Green synthesis of zinc nanoparticles utilizing neem leaf extract. ZnO NPs is the abbreviation of zinc nanoparticles. Reprinted from Ref. (Haque et al. 2020) with permission from Nano Express. Copyright © 2020 Nano Express
Zinc nanoparticles are one of the most important and widely used metallic oxide nanoparticles. These nanoparticles are frequently applied due to their peculiar behaviour and chemical characteristics (Jiang et al. 2018). The only drawback of these metallic nanoparticles is their inherent thermodynamic instability due to reactive surfaces. The biggest challenge towards the synthesis of metallic nanoparticles is to kinetically stabilize their reactivity. This reactivity in the field of agriculture as a micronutrient source is because of their quick release (Dapkekar et al. 2018; Dimkpa et al. 2019; Phan and Haes 2019). The quick release of zinc nanoparticles might result in the wastage of micronutrients (zinc). The quick release of micronutrients would not match with the plant sequential needs and thus reduce the efficiency of nano-zinc-fertilizers (Madzokere et al. 2021). For minimization of nanoparticles reactivity, different techniques are available. The most used and applied method is an encapsulation of the zinc nanoparticle using a suitable material. These materials include polymers and mineral salts (Petchthanasombat et al. 2012; Zeng et al. 2019).

Polymeric encapsulation

Polymeric materials are widely applied for the controlled release of different substances subjected to a variety of intended applications (Kumar et al. 2021). These polymers have a wide range of applications in retarding the release of target elements for insecticides, pesticides, fungicides, germicides, and growth stimulants. The usage of these polymers is highly dependent on different other impactive parameters such as cost, climatic condition, biocompatibility, biodegradability, and ease of processing (Madzkore et al. 2021). Moreover, these polymers contribute towards the controlled release of the target material by self-degradation (Choudhary et al. 2019). The target material discharge rate is highly dependent on the dissolution of polymers in the environment (Roy et al. 2014; Beig et al. 2020b). Generally, the control release process is divided into two major steps: encapsulation of active material with the help of polymer matrix and complex molecular structure formation (comprised of polymeric back bones) with active material.

Many different polymers including natural, and synthetic like carboxymethyl cellulose (Davidsson et al. 2013), cellulose acetate phthalate (Mukherjee and De 2016), gelatin (Wilson et al. 2018), gum Arabic (De Oliveira et al. 2018), polyvinyl alcohol (PVA), and polyacrylamide (Paradelo et al. 2019) are widely used for encapsulation. The controlled release systems are highly dependent on the molecular weight and cross-linking of polymeric materials (> 10,000) (Frizzo et al. 2019). The higher cross-linking and weight of polymers favour better results in terms of discharge. The encapsulated materials are termed as nanomaterials due to the nanosize of target materials. Mainly, polymeric materials are used to encapsulate metallic nanoparticles in the agriculture sector for controlling the release of particles (Prasad et al. 2017). The metallic nanoparticles usually used are copper, zinc, iron, and titanium for the healthy growth of crop plants (Aslani et al. 2014; Tan et al. 2018; Ponnamma et al. 2019). This encapsulation enhances the effectiveness by reducing the dissolution and protecting biologically active molecules against early degradation. In this way, the overall efficiency of the fertilizer system increases with very little dose applied in the field (Venkatachalam 2017). Additionally, these nanomaterials are expected to reduce the toxicity level associated with these metallic nanoparticles (Thumrugunta et al. 2018).

Effects of Zn-based nanoparticles on plants

Zn regulates the functions of enzymes present in plants (Noulas et al. 2018). Different studies on zinc oxide nanoparticles have reported that these are imperative in boosting enzyme activities which would promote the growth and biomass yield in long term. Dhole et al. (2013) checked the effect of zinc oxide nanoparticles on the mung bean (Vigna radiata) seeds. The application of nanoparticles on mung bean increases the biomass content of roots and plant tissues. Dimkpa et al. (2017) also evaluated the performance of bulk zinc and zinc oxide nanoparticles on the development of sorghum. Different methods of fertilizer application (soil and foliar spray) were also studied and compared to check its effect on yield, nutrient use efficiency and Zn content in grains. The foliar spray of both samples considerably improved the sorghum yield and Zn content in grains. Subbaiah et al. (2016) carried out experiment on maize using zinc oxide nanoparticles with a particle size of 25 nm. The maize growth was checked on different concentrations of Zn ranging from 50 to 2000 ppm. The 1500 ppm ZnO nanoparticles gave the optimum results which increase the germination rate by 80% and the seedling index.

On the other hand, the dose of 2000 ppm of nanoparticles has no inhibition effect on seed germination whereas the same value of zinc sulphate bulk salt stops the germination of maize. Zn oxide nanoparticles also reduce the effect of stress on plants, e.g., effect of salinity, drought and cadmium stress (Taran et al. 2017; Dimkpa et al. 2019). Haripriya et al. (2018) reported the reduction in stress by the foliar spray of ZnO nanoparticles on the finger millet cultivated on saline land. Zhang et al. (2017) used ZnO nanoparticles and ZnSO4 to check their effect on tissue generation in wheat. The zinc concentration increases in the tissues of wheat. The grain zinc concentration is considerably higher in the case of nanoparticles. The results show that the nanoparticles were more efficient in comparison to bulk salt of zinc. Zhao et al. (2015) also presented the results using ZnO–NPs.
(400 or 800 mg/kg) which yield higher Zn concentration in roots of corn by approximately 30-fold in comparison to control. Du et al. (2019) reported the soil-based experimentation results of zinc nanoparticles. The results show the increased zinc content of wheat, but no zinc was reported in the plant tissues. The investigation results were more promising for acidic soils as compared to alkaline ones (Watson et al. 2015).

Conclusion

We reviewed the synthesis of zinc nanoparticles for plant application to increase growth and disease resistance. Surface modification can be done with metal oxide nanoparticles to alter the properties as per requirement for the desired application. In recent times, more focus is given to developing nanoparticles based on green methods. Few research has been carried out showing the benefits of metallic nanoparticles for sustainable agriculture, but the mechanism of delivery and usage are at their early stage.

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Availability of data and materials Not applicable.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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