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Review

Metal Nanoparticles in Agriculture: A Review of Possible Use

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Abstract: Deterioration of soils over the years has led to a decline in crop yields and nutritional qualities, resulting from the oversupply of conventional fertilizers, which are unsustainable, costly and pose a threat to the environment. Nanoparticles are gaining a reputation in the field of agriculture for the remediation of soil degradation in a sustainable way. Recently, they have been recognized as potential fertilizers with properties that make them more absorbable and readily available for plant use than their bulk counterpart. However, there is less literature elaborating on the use of nanoparticles as agro-inputs for crop nutrition and protection. This review, therefore, provides insights into the application of nanoscaled nutrient elements such as silver, zinc, copper, iron, titanium, magnesium and calcium as fertilizers. In addition, the review explains the need for utilizing green synthesized nanomaterials as one of the ways to palliate the use of environmentally toxic chemicals in the cropping system and discusses the various benefits of nanoparticles, ranging from plant growth stimulation to defence against pathogens.

Keywords: agriculture; nanoparticles; nanofertilizers; plant growth

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1. Introduction to Nanoparticles

Soil degradation has led to an imbalance between food and feed production, climate regulation, water retention and carbon storage in the ecosystem. On a larger scale, it has led to soil erosions and nutrient runoffs, leading to soil infertility, thus affecting human beings through malnutrition and other related diseases [1,2]. To increase productivity and improve soil quality, fertilizers have been used for decades by farmers worldwide on degraded soils affected by human factors [3,4]. However, their intensive usage has led to the pollution of both water and soil as the crop uses less than half of the applied amount [5,6]; the other remaining amount is lost through photolysis, hydrolysis, leaching and microbial immobilization and degradation [7]; thus, threatening the soil microorganisms, human health and the ecosystem, and reducing the profit margin of farmers [6,8,9].

Limited nutrient usage efficiency and environmental restrictions connected with the use of chemical fertilisers continue to be a key issue and obstruction to attaining adequate sustainability in agriculture [6,10]. Currently, the work of researchers is aimed at eco-friendly agricultural practices that can achieve sustainable food production in the long term without altering the environment and wasting resources [11]. The introduction of new technologies, such as nanotechnology, is a key to sustainable food production, hence protecting the environment [6]. Nanotechnology is known as the science of designing, producing and characterizing particles at the nanoscale [12]. These particles, of a size less than 100 nm, have presented numerous properties that allow them to be at the core of several fields, such as drug delivery, cancer diagnosis and treatment [13]. They are wonderful absorbents and catalysts owing to their area, they present a reduced risk of modification by temperature, a tuneable pore size, and easy adsorption and surface coating [14].

Nanotechnology is defined as the scientific knowledge to manipulate and control matter in the nanoscale range to make use of size- and structure-dependent properties and phenomena distinct from those at smaller or larger scales [15]. The use of nanomaterials dates from 4500 years ago. In some civilisations, nanofibers were used for the reinforcement of ceramic matrixes. In addition, the ancient Egyptians of the third century used NMs for the production of different forms of dyes [16]. The development of nanotechnology has resulted in the production of nanoparticles with many applications in different fields, such as the food industry, medicine and textiles [17]. In agriculture, their usage as fertilizers and pesticides has been reported in many studies. Elements such as silver, zinc, copper, iron, silicon, titanium, magnesium, and manganese have been supplied to plants in different forms, hence, having a beneficial effect on their growth and yield as they fight against infections and act as fertilizers or carriers of nutrients [18–23] Although scientific reports have demonstrated the applications of nanofertilizers and nanoparticles in crop nutrition and pest control, the adoption of this sustainable alternative is still in its infancy. Hence, this review, therefore, aims to provide insights into the broad agricultural applications of nanoparticles as nanofertilizers.

2. Synthesis Methods up to Date

Several methods have been proposed for the synthesis of metal nanoparticles. They are classified into two main groups, bottom-up methods and top-down methods, which include physical, chemical and biological methods. The precipitation method, microemulsion, ultrasound, hydrothermal synthesis, microwave synthesis, inert gas condensation, laser ablation, sputtering, sol-gel, mechanical milling, biosynthesis, etc., are among the ones that have been extensively used, as described in Table 1 [24–26]. Though these methods are usually easy to conduct, the chemical and physical ones present some concerns when it comes to the stability and monodispersion of the size of the nanoparticles. In addition, most of these methods are either costly or not energy and material efficient and present a risk to the environment due to the emission of toxic chemicals [27,28].

Table 1. Nanoparticle synthesis methods [25,29–33].

		Advantages	Disadvantages
Top-Down Approach			
Physical methods	Evaporation–condensation	High speed No use of toxic chemicals Purity Uniform size and shape.	Productivity, high cost, radiation exposure. Require high energy, temperature and pressure, A large amount of waste generation, highdilution, difficult size and shape tunability, lower stability, altered surface chemistry and physicochemical properties of nanoparticles.
	Arc discharge		
	Laser Ablation		
	Hydrothermal		
	Electron beam evaporation/lithography		
	Mechanical grinding		
	Ball milling		
	Spray pyrolysis		
	Vapour-phase synthesis		
	Inert gaz condensation		
	Ion implantation		
	Laser pyrolisis		

Table 1. *Cont.*

		Advantages	Disadvantages
	Flash spray pyrolysis		
	Sputtering		
	Pulse laser deposition		
Bottom-up approach			
Chemical methods	Chemical reduction	Cost-effective High versatility in surface chemistry, Easy functionalization High yield Size controllability Thermal stability Reduced dispersity	Difficult large-scale production Chemical purification of nanoparticles required Low purity, use of toxic chemicals and organic solvents, hazardous to human beings and the environment.
	Irradiation		
	Electrochemical (electrolysis) method		
	Microemulsion		
	Coprecipitation		
	Pyrolysis		
	Irradiation		
	Sonochemical method		
	Sol-gel		
	Solvothermal		
	Hydrothermal		
	Plasma-enhanced chemical vapour deposition		
	Chemical vapour synthesis		
	Photoreduction		
Biological method	Plant	Good reproducibility High yield Low-cost Use of less hazardous chemicals Stable nanoparticlesLess energy	Usually slow
	Bacteria		
	Fungi		

2.1. Green Synthesis Using Plants

The usage of living structures in nanoparticle production is a real alternative to physical and chemical processes owing to its environmental friendliness and cost-effectiveness. Biosynthesis of nanoparticles using plants has been demonstrated to be green chemistry that interconnects plant sciences with nanotechnology and helps achieve the synthesis of nanoparticles at room temperature, neutral pH and a low cost without the use of environmentally harmful chemicals [31]. Plants and their by-products have demonstrated essential properties in the synthesis process of nanoparticles as their usage is more beneficial than other systems [34]. They are increasingly being used because they facilitate the development of nanoparticles and increase the success rate of synthesis, as researchers strive to build upscaled processes of monodispersed and stable nanoparticles [35]. The conventional approach for making metallic nanoparticles from plants employs a reducing agent derived from dried plant biomass and a metallic salt as a precursor [31]. The photo components of plant extracts act as reducing as well as stabilizing agents. However, considering the phytochemistry of plants, it is difficult to precisely tell which chemicals act for the bioreduction and stabilization of NPs. Nevertheless, biomolecules such as phenolics, alkaloids, flavonoids, terpenoids, enzymes and proteins have been reported to be involved in the synthesis reaction [36]. Hence, it has been reported that the hydroxyl groups present in carbohydrates, amino acids, proteins and nucleic acids of plants act in the stabilization of

ENPs [37]. Green synthesis of nanoparticles is becoming a very insightful topic nowadays. There is rising attention to the use of organisms [38]. The biological production of metallic and metal oxide nanoparticles is less harmful to the environment than the current chemical or physical approaches. As shown in Figure 1, plant, bacterium, fungus and algae substrates are utilized to substitute chemical solvents and stabilizers to reduce the toxicity of both the product and the process [39]. Hence, plants have shown a large interest in expanding the biosynthesis of nanoparticles on a large scale as the plant-mediated nanoparticles are very stable and have diverse sizes and shapes compared to the ones produced through other biological systems [38]. Synthesized nanoparticles can be carbon-based or metal-based. The most produced and used metal-based engineered nanoparticles are zinc oxide (ZnO), titanium dioxide (TiO_2), gold (Au), silver (Ag), cerium oxide (CeO_2) and copper oxide (CuO) or dioxide (Cu_2O) nanoparticles. Other nanoparticles, such as Mn, Fe_3O_4, CuO, CaO and Fe_3O_4, are also widely used and produced [40].

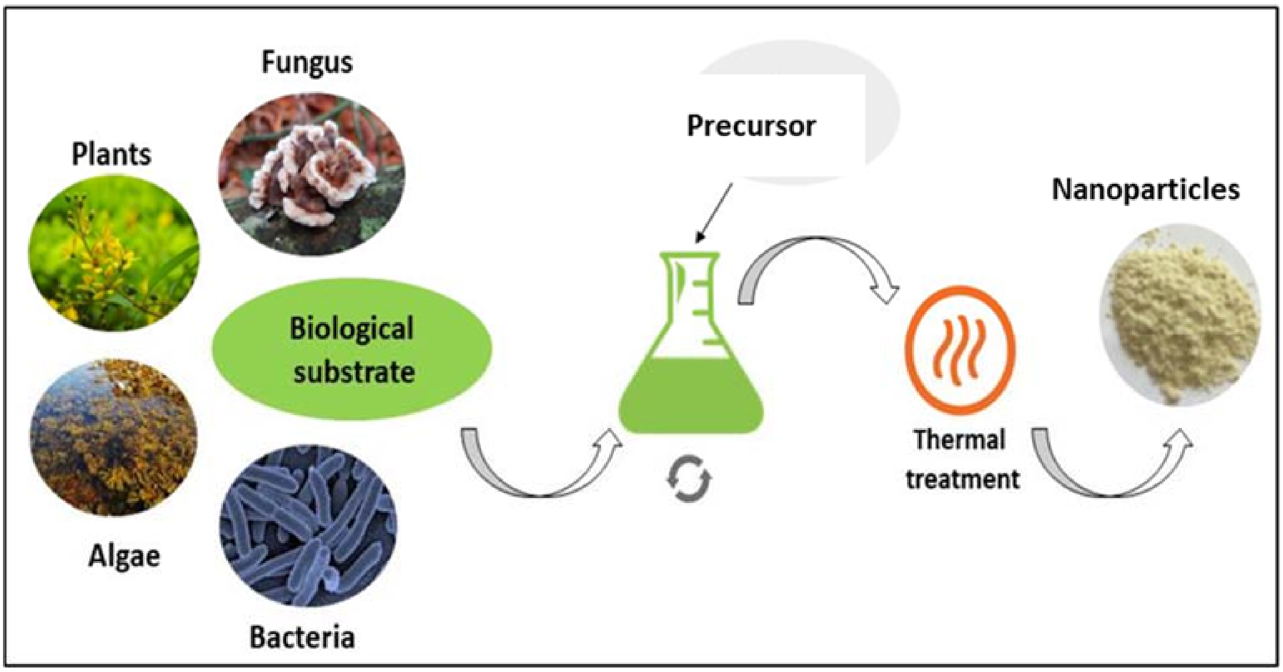

Figure 1. Summary of the green synthesis process of nanoparticles using the biological route [39].

Many plants have been used in nanoparticle production (Table 2). Based on the literature, plant-mediated nanoparticle synthesis has gained a reputation. The synthesis of zinc oxide nanoparticles through *Trifolium pratense* flower extracts can help to avoid the use of toxic chemicals. Hence, produced ZnO nanoparticles have proven antibacterial activities against *Pseudomonas aeruginosa* and show a larger spectrum than [41]. ZnO nanoparticles have been manufactured using a variety of plant species, including Moringa oleifera and *Aspalathus linearis* [42,43]. Furthermore, other nanoparticles such as pure massicot phase lead Oxide (PbO) using *Sageretia thea* [44]; silver nanoparticles with the capacity of rendering high antimicrobial efficacy against Gram-negative and Gram-positive bacteria, i.e., *Escherichia coli* and *Staphylococcus aureus* and hence has a great potential in the field of medicine [45]; and gold nanoparticles using extracts of *Chrysanthemum* and tea beverages [46], thus making plants a real asset for nanoparticle synthesis.

Table 2. Summary of the synthesis of nanoparticles using plant extracts as reducing/chelating agents.

Plant Species	Nanoparticles	Application/Properties	Reference
Agatosma betulina	ZnO	Quasi-spherical nanoparticles with 15.8 nm diameter	[47]
***Gloriosa superba*L.**	CuO	5–10 nm spherical nanoparticles. Antimicrobial activity against *Klebsiella aerogenes*, *Pseudomonas desmolyticum* and *Escherichia coli*	[48]
Plectranthus amboinicus	CuO	Protein denaturation of Egg albumin Antimicrobial activity against bacteria and fungi Antioxidant activity Inhibition of α-Amylase for the treatment of diabetes Anti-larvicidal activity against mosquito larva	[49]
Lantana camara	Fe_3O_4	Highly stable nanorod crystals Inhibition of *Pseudomonas* sp. Growth Enhancement of *Vigna mungo* seed germination at a concentration of 200 ppm	[50]
Laurus nobilis	TiO_2	Antimicrobial activity against bacteria and fungi Inhibitory antioxidant activity on DPPH radicals	[51]
Solanum nigrum	ZnO	29.79 nm nanoparticles. Antimicrobial (inhibitory) activity against *Staphylococcus aureus*, *Salmonella paratyphi*, *Vibrio cholerae* and *Escherichia coli*	[52]
Bush tea (*Athrixia phylicoides* DC.)	ZnO	Spherical nanoparticles with an average diameter of 24 nm	[53]
Simarouba glauca	Au	Inhibition of *Staphylococcus aureus*, *Streptococcus mutans*, *Bacillus subtilis*, *Escherichia coli*, *Proteus vulgaris* and *Klebsiella pneumonia* growth.	[54]
***Origanum majorana* L.**	CeO	Spherically shaped nanoparticles with a size of 10–70 nm. Antioxidant activity by free radical scavenging activity against DPPH and ABTS free radicals.	[55]
***Capsicum annuum* L.**	Ag	The secondary structure of the proteins in the plant extract changed after the reaction with silver ions.	[56]
Lemongrass (*Cymbopogon citratus*)	Al_2O_3	Complete growth inhibition of extended-spectrum β-lactamases and Metallo-β-lactamases isolates.	[57]
Populus ciliata	Co_3O_4	Maximum inhibition of *Klebsiella pneumoniae* and *B. subtillus* growth.	[58]
Mulberry (*Morus alba*) leaves extract	Ag	Effective antibacterial activity toward *Staphylococcus aureus* and *Shigella* sp.	[59]
Citron juice (*Citrus medica* Linn.)	CuNPs	Significant inhibitory activity against *Escherichia coli* followed by *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, *Propionibacterium acnes* and *Salmonella typhi.*	[60]
Rhododendron arboreum	CuO	Antimicrobial activities against *Escherichia coli*, *Streptococcus mutans* and *Proteus vulgaris*.	[61]
Pisidium guvajava* and *Aloe vera	MgO	Antibacterial activity against *E. coli* and *S. aureus.*	[62]

2.2. Targeted Elements

2.2.1. Silver Nanoparticles

Silver nanoparticles have been widely used in the medical, industrial and sporting fields owing to their inhibitory effect on the numerous bacterial strains and microorganisms commonly present in medical and industrial processes [63]. They present several optical, electrical and thermal properties, such as high electrical conductivity, and antimicrobial and catalytic properties [64]. Moreover, they have been incorporated into composite fibres, cryogenic superconducting materials, cosmetic products, the food industry and electronic components due to their unique properties such as chemical stability, good conductivity, catalyst and most important antibacterial, antiviral, antifungal and anti-inflammatory activities [65]. When applied, the Ag ions of silver nanoparticles directly react with plants, improving their morphology and physiology, hence improving their resistance to fungal, bacterial and nematode attacks [66]. In addition, Ag nanoparticles are believed to have the ability to improve the germination of plant seeds [67].

2.2.2. Zinc Oxide

Zincite has gained notoriety as it has been used in several industrial sectors. Due to their potential adaptation, ZnO nanoparticles have been incorporated into solar cell preparation, gas sensing, chemical absorbents, varistors, hydrogenation catalysts and photocatalytic degradation, as well as optical and electrical devices [68]. In addition to the various uses of ZnO nanoparticles, research has demonstrated that they have a stationary effect on the growth of *Escherichia coli* [69,70]; *Klebsiella pneumonia*, *Staphylococcus aureus* and *Candida albicans* and *Penicillium notatum* [71,72]; *Salmonella enterica Typhimurium*, *Aspergillus flavus*, *A. fumigatus and Candida albicans* [73], and many more, allowing them to be used in the agricultural sector and the food industry. The study led by [74] concluded that the application of ZnO nanoparticles on *Sesamum indicum* increased both the seeds' germination and the plant's vegetative growth.

The synthesis of ZnO nanoparticles, with different sizes and shapes, has been performed using a significant amount of plant species or their substrates, such as dry ginger rhizome (*Zingiber officinale*) [71]; the leave of *Agathosma betulina* and *Aspalathus linearis* [42,47,75]; orange and pomegranate fruit peel [72,76]; avocado seed extract [77] and the flowers of *Trifolium pratense*, *Nyctanthes arbor-tristis* and *Jacaranda mimosifolia* [41,78,79].

2.2.3. Copper Nanoparticles

Copper oxide nanoparticles are presented in two forms: copper (II) oxide (CuO) and copper (I) oxide (Cu_2O). The CuO form has been at the centre of numerous fields of research due to its useful properties, including superconductivity at high temperatures, spin dynamics and electron correlation, making them elements of choice in gas sensing devices, catalysis, batteries, high-temperature superconductors, solar energy conversion and field emission [80]. Due to their high surface-to-volume ratio, continuously renewable surface and fluctuating microelectrode potential values, nanoparticles are also frequently used as catalysts. Hence, their activity against microorganisms such as *Bacillus subtilis* has made them elements of choice in the field of medicine and wastewater treatment [81,82].

2.2.4. Iron Oxide

Iron is presented in three different forms in nature; most commonly, the oxides found are magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) and hematite (Fe_2O_3). Magnetic iron oxide nanoparticles, namely magnetite and maghemite, have received significant attention due to their low toxicity, superparamagnetic properties and simple separation methodology. They are especially fascinating in biomedical applications for protein immobilization during diagnostic magnetic resonance imaging, thermal therapy and drug delivery [83].

Iron oxide nanoparticles have a very high magnetism due to four unpaired electrons in their 3d orbitals, allowing them to be a key component in magnetic seals and inks, magnetic recording media, catalysts, ferrofluids, contrast agents for magnetic resonance imaging and therapeutic agents for cancer treatment [84]. The use of iron oxide nanoparticles in the field of agriculture is a novel technology that has been proven successful, though some improvements are necessary. For instance, Fe_2O_3 nanoparticles promoted growth by regulating phytohormone contents and antioxidant enzyme activity in peanuts, hence improving the availability of Fe in the soil and its accumulation in the plant cells [85]. Soil drenching and foliar application are the most frequently used methods for the application of iron oxide nanoparticles on plants, usually as a source of Fe nutrition [86].

The preparation of iron oxide nanoparticles is achieved through many methods, most of which are chemical, physical or biological [83]. The biosynthesis of iron oxide nanoparticles has been shown to be a cost-effective and environmentally friendly alternative to the physical and chemical techniques of production. This method produces non-toxic nanoparticles because sugars, antioxidants, amino acids and proteins present in the plants are used for the formation of the nanoparticles [86].

2.2.5. Magnesium Oxide

Due to its unique physicochemical properties, such as outstanding refractive index, excellent corrosion resistance, high thermal conductivity, low electrical conductivity, physical strength, stability, flame resistance, dielectric resistance, mechanical strength and excellent optical transparency, magnesium oxide (MgO) is an eco-friendly, economically feasible and industrially important nanoparticle [87]. It is regarded as a promising high-surface-area heterogeneous catalyst support, additive, and promoter for a variety of chemical reactions due to its unique properties, which include stoichiometry and composition, cation valence and redox properties, acid-base character and crystal and electronic structure [88].

Magnesium oxide nanoparticles are employed as semiconductors, organic catalysts, sorbents for organic and inorganic pollutants in wastewater, electrochemical biosensors, photocatalysts and refractory materials. They also naturally have antibacterial, anticancer and antioxidant properties [87]. Owing to its low toxicity for both plants and humans, and thermal stability, MgO nanoparticles can be used for plant protection and increased production. Furthermore, they possess antimicrobial properties against bacteria and fungi [89].

2.2.6. Calcium Carbonate

Recently, calcium carbonate has been highlighted among the other investigated nanomaterials [90]. Several characteristics have been associated with $CaCO_3$ nanoparticles; they include affordability, low toxicity, biocompatibility, cytocompatibility, pH sensitivity, sedate biodegradability and environmental friendliness [91]. $CaCO_3$ is a critical substance in both fundamental research and industry. It has numerous applications in various industrial fields such as plastic, paper, rubber, paints, textile, food and beverages. It has been used as a filler material in paints, pigments, coatings, paper and plastics, and it can be sculpted into complicated and beautiful shapes by creatures, such as bones, teeth, and shells [92,93]. In the medical field, they have been used for drug delivery, biosensors, bone replacement, biomineralization and enzyme immobilization [90].

The synthesis of $CaCO_3$ has been performed through many methods, such as aqueous precipitation [94], mechano-chemical treatment without further heat treatment [95], lysine biomineralization [96] and plant species such as *Myrtus communis* [97]. The application of calcium carbonate ($CaCO_3$) as a drug carrier to cancer cells has been gaining a reputation owing to its availability, low cost, safety, biocompatibility, pH sensitivity and slow biodegradability [98]. Hence, it has been proven that $CaCO_3$ can help fight against pests such as California red scale (*Aonidiella aurantii*) and Oriental fruit flies (*Bactrocera dorsalis*) when sprayed on *Citrus tankan* leaves [99]. In addition, in a study led by [100], the combination of calcium carbonate and hydroxyl apatite nanoparticles under full irrigation provided the highest yield compared to other treatments on soybean plants.

2.2.7. Titanium Dioxide

The oxide form of the titanium metal is TiO_2; it is naturally found as anatase, rutile or brookite minerals. TiO_2 nanoparticles have been produced worldwide and are mostly used in cosmetics, sunscreens, food preparation and drug delivery systems due to their absorption of ultraviolet light and higher refractive index, which empowers them to work as a material with various applications [101]. In agriculture, for instance, TiO_2 nanoparticles have been used as antimicrobial and growth-regulating agents as well as fertilizers. They present great potential as growth-promoting agents for plants and help prevent human food intoxication. Different plant and fruit pathogens are destroyed by TiO_2 nanoparticles. Moreover, TiO_2 nanoparticles can achieve the mineralization of residual pollutants, pesticides and organic compounds in hydroponic cultures and under simulated conditions [102]. Studies have shown that TiO_2 has a beneficial impact on plant growth and yield. The study led by [103] showed an increase in plant dry weight, chlorophyll content and photosynthetic rate of spinach plants after seed treatment with TiO_2 before planting. In addition, the application of TiO_2 on *Zea mays* resulted in an increased uptake of micro and macro-nutrient; however, higher concentrations decreased the dry biomass of plants [104].

3. Application of Nanoparticles on Plants as Fertilizers

Integrating cutting-edge nanotechnology into agriculture, including fertiliser creation, is considered one of the greatest feasible methods to significantly increase crop yield and sustain the world's constantly growing population [105]. The application of nanoparticles in agriculture as fertilisers is attributed to their improved characterization, absorption and responsiveness, as well as surface and adhesion effects [106]. Nanofertilizers are macro- or micro-nutrient fertilisers that are used to increase agricultural yields and have a particle size of less than 100 nm. Nanofertilizers are nanomaterials responsible for providing one or more types of nutrients to growing plants, supporting their growth and improving production [107]. They are presented in two different types. On one hand, the nanomaterials supply nutrients to plants to improve their development and yield, on the other, they are the carriers of nutrients and only assist in the transport and release of nutrients without directly being used as a nutrient source [108].

There is a growing need in the agriculture industry to increase food production to reduce hunger. Small-scale crop production has been significantly impacted by the heavy price, limited supply and frequent shortage of inorganic fertilisers, which is partly attributable to the COVID-19 pandemic outbreak, which has led to rising oil and food prices. Over the past years, inorganic fertiliser application has been used to improve plant growth and yields. Nevertheless, crops typically use less inorganic fertiliser than what is administered, and the surpluses are accessible to be leached into rivers, which contributes to water contamination [108]. Repeated application of such fertilisers also makes pollution severe. Therefore, to improve crop yield, it is required to produce fertilisers with targeted, gradual or controlled release. According to [109], nanotechnology, especially material nanotechnology, has gained a reputation in the field of agriculture (Figure 2). The publications in this regard have gone from less than 50 in number between 2009 and 2015 to approximately 200 papers in 2021, demonstrating the interest given to this field.

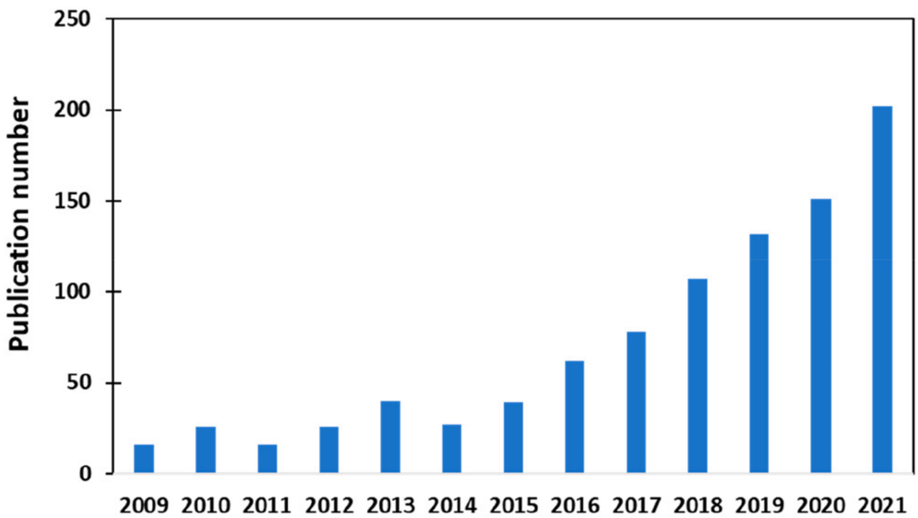

Figure 2. Publication trend of nanotechnology-related articles in the field of agriculture from 2009 to 2021 [109].

Given their distinctive qualities, such as their high surface area to volume ratio, slow or timed-release characteristics and absorption capacities, nanoparticles are thought to be suitable for producing fertilisers for use in agriculture [6]. Nanofertilizers' effectiveness to promote crop productivity is influenced by how they are applied to plants, as well as how they are absorbed and accumulated by plants. To promote plant growth and yield, nanofertilizers can be delivered above or below ground by foliar spray or irrigation. Additionally, biosynthesized nanoparticles can be added to seeds or primed [110,111]. The uptake and accumulation of nanoparticles for enhancing crop growth are dependent on the plant type as well as nanoparticles type, size, concentration, chemical composition, stability and transformation rate after biological interaction [112,113]. Nanofertilizers penetrate the aerial regions of the plant by entering the xylem vessels through the root epidermis and endodermis. Moreover, these nanoparticle nutrients can be delivered to different areas of the plant through the phloem and leaf stomata [113].

3.1. Application of Silver Nanoparticles

When compared to other nanoparticles, silver nanoparticles are drawing more attention due to their extensive use in a wide range of products, such as antimicrobial agents, shampoo, soap, toothpaste, wastewater treatment, food packaging materials, food storage containers, textiles, air fragrances, detergents and paint [114–116]. Silver nanoparticles have recently been linked to improved crop productivity in agriculture. According to numerous studies, the optimal concentration levels of silver nanoparticles are crucial for promoting seed germination [117,118] and plant growth [119]. In addition, chlorophyll concentration and photosynthetic quantum efficiency have been enhanced [120,121], as well as the effectiveness of water and fertiliser utilisation [122]. However, high concentrations of the 25 nm silver nanoparticles were found to tear down the cell wall and harm the vacuoles of *Oryza sativa* root cells, having a toxic effect [123]. According to [124], the silver was unable to infiltrate the root cells of *Oryza sativa* when present in low concentrations of up to 30 g/mL; nevertheless, the larger concentrations were effective in obliterating the cell structure and producing a harmful impact. Several studies reported that various sizes of silver nanoparticles demonstrate a clear relationship between size and nanoparticles toxicity to plants; smaller nanoparticles were consistently found to be more hazardous to plants compared with bigger nanoparticles [125–127].

3.2. Zinc Oxide Nanoparticles

All metallic nanoparticles influence how plants grow and develop; however, ZnO nanoparticles stand out for their exceptional qualities and wide range of applications [128]. Zinc is a regulatory co-factor and structural component of many enzymes and proteins and plays an important role in plant metabolic activity, particularly photosynthesis, phytohormone biosynthesis and antioxidant mechanisms [129]. A correct amount of zinc must be applied and made accessible because both deficiencies and excesses are harmful to plants. Due to their exceptional qualities, ZnO nanoparticles have been determined to be a potential particle for maintaining the necessary concentration of zinc in plants [130].

The study of [131] reported that zinc oxide nanoparticles improved both the fresh and dried weight of *Cicer arietinum* seedlings. Similarly, [132] stated that a high proportion of ZnO nanoparticles had a substantial impact on the viability and growth of tobacco. However, higher concentrations of ZnO nanoparticles at 2000 ppm were found to have toxic effects on the growth and yield of peanuts [133]. On the other hand, no significant impacts of ZnO were found on *Cucurbita pepo* at the investigated concentration [134]. Improved seed germination and root development, as well as plant growth, were observed on Fenugreek (*Trigonella foenum-graecum*) plants [135]. Additionally, similar results were recorded where seed germination was improved on Indian mustard (*Brassica juncea*) [136]. Increased protein content was observed when ZnO nanoparticles were applied, which helps with photosynthesis, promoting the viability and development of maize (*Zea mays* L.) plants [137]. Zinc oxide nanoparticle treatment at a concentration of 1000 ppm was found to enhance seed germination and seedling vigour, which led to initial development in the soil as evidenced by early flowering and increased leaf chlorophyll concentration [133].

3.3. Iron Oxide Nanoparticles

Iron is a crucial microelement with a variety of physiological and biochemical effects and is the fourth most prevalent element in terms of value; nonetheless, plants require large amounts of iron to grow [138]. Iron plays crucial roles in enzyme reactions and photosynthesis, improving the functionality of the photosynthesis process, DNA translation, RNA synthesis and auxin activities, all of which are necessary for optimal plant development [139]. Due to the limited availability of iron-containing minerals, utilising nanoparticles to address iron shortage is one of the alternative approaches. Nanoparticles can also increase crop production to different environmental stresses [138]. Iron oxide nanoparticles can enhance nutrient intake by interacting with molecules inside plant cells [140].

Several studies have reported that the application of iron oxide nanoparticles on different crops has improved plant growth parameters and dry matter material. According to [141], iron oxide nanoparticles boosted tomato plant development metrics. Similar results were observed by [142], who reported that the plant growth performance, photosynthetic pigments, indole acetic acid, the content of proline, free amino acids and total soluble sugars were significantly enhanced when iron oxide nanoparticles were sprayed on moringa plants.

3.4. Titanium Dioxide

Titanium dioxide is a well-known nanoparticle that has been used in crop production as well as human consumption. Titanium dioxide nanoparticles have several noteworthy effects on the morphologic, biological and physiological characteristics of the crop [143]. In their study, [144] observed that wheat seedlings treated with titanium dioxide nanoparticles resulted in enhanced growth and production characteristics, including yield. Furthermore, [145], reported that canola plants treated with titanium dioxide nanoparticles had increased germination rates and better radicle and plumule growth.

3.5. Calcium Carbonate

One of the most prevalent elements in the geosphere is calcium carbonate ($CaCO_3$). Calcium carbonate is an essential element in both basic technology and engineering. It already has a wide range of industrial uses in areas such as polymer, paper, elastomer, paints, fabrics, foodstuff and refreshments. Calcium carbonate is effective in combating pests such as oriental fruit flies and California red scales when sprayed on citrus tankan leaves [99]. Additionally, in research by [100], the combination of calcium carbonate and hydroxyl apatite nanoparticles applied to soybean plants under irrigation showed maximum yield in comparison to other treatments. In addition, [108] found that the application of calcium carbonate nanoparticles with a size of 20–80 nm considerably enhanced the seedling growth and dry biomass in contrast to the control when applied to groundnut seedlings.

3.6. Magnesium Oxide

Magnesium oxide has received significant attention among nanomaterials because of its simple stoichiometry, high ionic character, crystal structure and surface structural flaws. Peanut seeds responded favourably to MgO nanoparticle dispersion, which promoted germination, growth and photosynthetic pigments [146]. Additionally, the effects of applying magnesium oxide nanoparticles at a dosage of 4 mg/L on mung bean seedling growth revealed rapid germination when compared to other treatments [147]. Furthermore, maximum germination, seedlings, and vigour index were observed on the green gram (*Vigna radiata*) [148].

4. Nanoparticles' Adverse Effects

Biosynthesized nanoparticles offer enormous potential to alleviate stress, boost growth and improve agricultural production. However, the unintentional release of some nanoparticles into the environment poses a threat to both aquatic and land plants [149]. For instance, in their study, [150] reported the adverse effect of CdSe nanoparticles on the morphology and peroxidase enzyme of common Duckweed (*Lemna minor*), with it having an increased concentration of superoxide dismutase enzyme, catalase, phenols and flavonoids, in contrast with the results of [151]. Furthermore, ZnSe nanoparticles have been found to have a certain toxic effect on the growth of *Lemna minor* by triggering the plants' defence system due to phytotoxicity [152]. Furthermore, carbon nanotubes were found to trigger oxidative stress in red spinach [153]. In addition, the application of high levels of Ag-NPs can cause oxidative stress by increasing the accumulation of reactive oxygen species and affecting the chloroplast structure and function of *Spirodela polyrhiza* [126]. Hence, it is crucial to mention that the toxicity of nanoparticles depends on the method used for their production. Several studies have shown that plant-mediated nanoparticles present less to no eco-toxicity towards plants in general and aquatic plants in particular [154–156]. However, further investigations should be carried out to ascertain the effect of nanoparticles synthesized using plant species on aquatic plants.

5. Conclusions

To maximize yields and alleviate poverty and malnutrition, nanoparticles have been recognized as highly beneficial for plant biomass production and enhancement of crop nutritional quality. This review highlighted the attributes of biosynthesized nanomaterials as sustainable alternatives to conventional chemical fertilizers.

These potential agro-inputs can be readily absorbed by plants and are environmentally friendly crop nutrient supplements (Ca, Mg and Fe NPs), with advantages beyond fertilization. Thus, the review also highlighted the use of nanoparticles such as Ti, Ag and Zn, which can be integrated into cropping systems to enhance the plant's defence mechanism against disease attack. However, fewer studies have investigated the broad application of nanoparticles in pest and disease management, offering an opportunity for future research in crop protection.

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Abbreviations

pH	hydrogen potential
NPs	nanoparticles
NMs	nanomaterials
ENPs	engineered nanoparticles

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