

FATE OF NANOPARTICLES AND THEIR NOVEL APPROACHES IN AGRICULTURE

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ABSTRACT

It is thought that using traditional bulk chemicals in place of their nanoparticulate equivalents, which have superior qualities, can help to solve present problems with mineral bioavailability and absorption, boosting agricultural output, lowering fertiliser waste, and saving the environment. Colonization of the plant surface, increased enzyme activity, and increased production of secondary metabolites necessary for rhizosphere competence are all factors in plant health. Thus, it was believed that green synthesis was a critical tool for mitigating the detrimental consequences of conventional nanoparticle synthesis techniques, which are frequently used in research and industry. Gold (Au), silver (Ag), noble metals (CuO), and zinc oxide (ZnO) are examples of metals and metallic compounds that can be manufactured using biological extracts, and we have explored the fundamental principles and techniques of various synthesis techniques for them in this article (ZnO). Meanwhile, though, the mechanisms underlying synthesis and characterization of NPs will remain a mystery. Although many studies have not examined green-synthesized nanoparticles (GNPs) for the presence of extract-derived chemicals, many studies have proven the polymerization of sugars, natural compounds, or antibodies in such biogenic NPs. To make the most out of the green nanotechnology, a detailed overview of the theory of green synthesis and a high-throughput evaluation of the effect of the binding agent on the thermodynamic features of GNPs are necessary.

Keywords: Metal, metal oxide, nanoparticles, and the rhizosphere.

INTRODUCTION

Nanoparticles are substances with sizes between someone including one hundred nanometers (Yoshikazu Todaka, 2002). Often between 40 and 50 nm in size, A size exclusion limit is the largest dimension that plants allow nanoparticles to travel through and concentrate inside the cells. One of the largest constraints to nanoparticle penetration into plant tissues seem to be

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their size. Because many of the natural substances in soils are Nano particulate or have

Nanoscale qualities, nanoscience is vital to the study of soils (Mura, 2013). At the nanoscale, however, covalent bonds, greater polar and electrostatic contacts, or weak Vander Waals forces predominate over interactions between particles.

Recent breakthroughs in the creation of nanoscale stimulus-responsive devices that may modulate medication bio distribution in response to certain exogenous (temperature, magnetic field, ultrasonic intensity, light or electric pulses) or endogenous impulses are discussed (Mura, 2013). To the contrary hand, soil has been shown to include a variety of nanomaterials, including Nano minerals, which can be either mineral nanoparticles or nanoparticles of different sizes (Hochella Jr, 2008). Oil-in-water Pickering emulsifying agent Solidified by Nanoparticle in Combination with Polymers Flood for Oil Recovery has also been discovered (Sharma, 2015). Intentionally or unintentionally, these nanoparticles may be released into the atmosphere in a variety of forms, which include metal-based nanoparticles such as nano-ZnO, micro-2, and micro-2, zero-valent metal alloys other than Au, Ag, and Fe nanostructures, metal salts (such as Nano silicates and ceramics), and emissions nanotechnology. Synthesized or manufactured nanoparticles are also present in the soil (Mura, 2013), (Zhang, 2015). The usage of bio fertilizers, increased plant growth and productivity, and plants' ability to produce hormones that encourage N₂ absorption and phosphate solubility in bacteria are all supported by a number of research and conclusions (Nagata, 2004). Polymer nanocomposites are described as the conception, description, manufacture, and implementation of structures, devices, and systems through the modification of form and size atomic scale. To put it another way, they are the planning, production for a specific use, and use of systems, equipment, and buildings at the nanoscale (Chabuk, 2015).

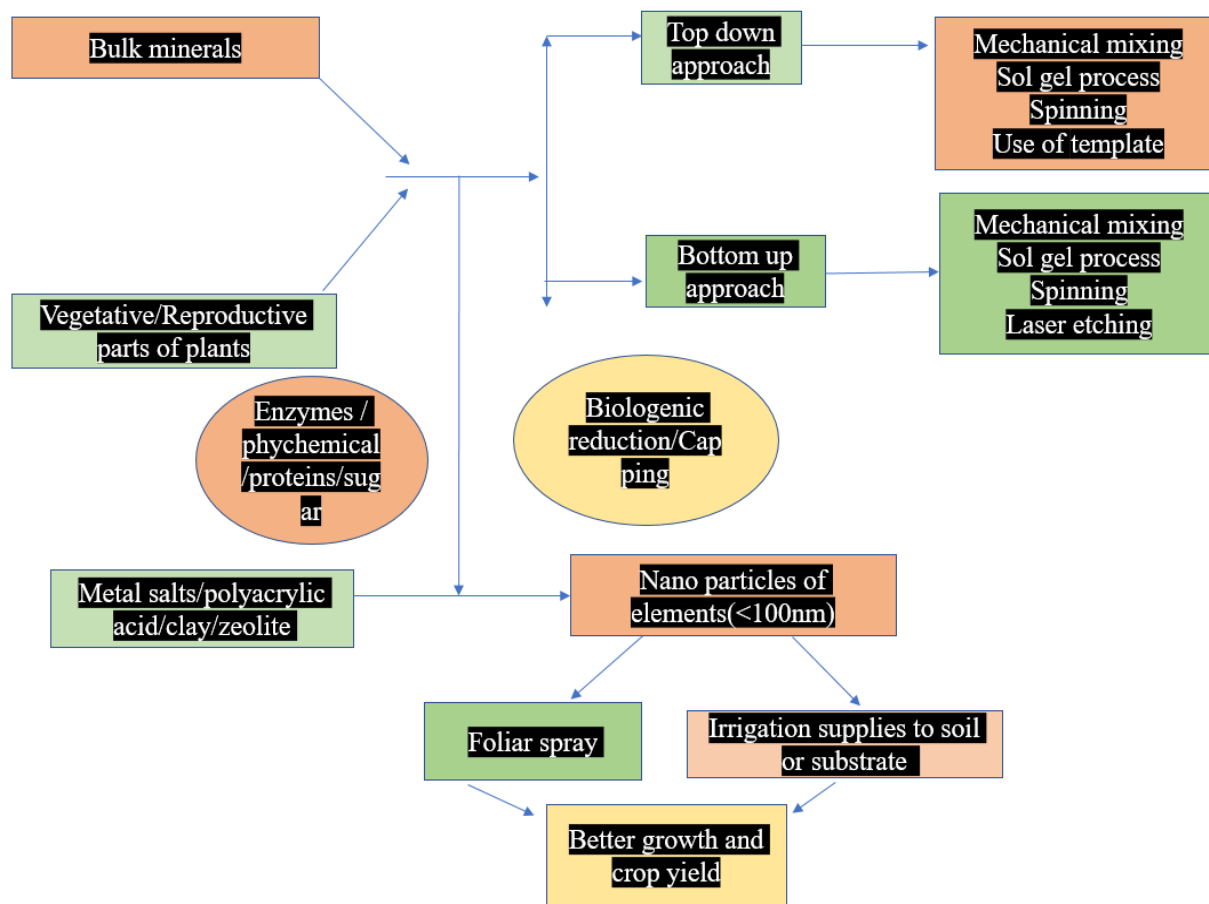


Fig 1.1- Production of Nano-fertilizers (Pitambara *et al*)

AuNP and AgNP Synthesis from Plant Extracts Using Green Techniques

Many studies observed that Microbes can synthesize metal nanoparticles either extracellularly or intracellularly (Kalishwaralal, 2010); (Das, 2014); (Gour, 2019). To free the produced nanoparticles from intracellular assembly, continued ultrasonic therapy or significant detergent reactions are required (Kalimuthu, 2008).

However, the development of large-scale nanoparticles is made possible by a relatively straightforward downstream step in extracellular biosynthesis. Consequently, numerous research have concentrated on the intravascular creation of nanoparticles from various biological sources. Although all of the following organisms have been utilized to create nanoparticles: bacteria, fungi, yeast strains, actinomycetes, & bacteria, fungi and bacteria have recently attracted increasing attention. This is because more microorganisms and fungi are being used in micro (Zhang F. P., 2011).

Numerous different bacteria have been shown to create silver nanoparticles in soluble form, including *Bacillus species*, *Arthrobacter kerguelensis*, *Pseudomonas proteolytica*, *Staphylococcus aureus*, etc. once they've been exposed to an aqueous phase with Ag⁺ ions

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© 2012 IJFANS. All Rights Reserved. **UGC CARE Listed (Group -I) Journal** (Das V. L., 2014); (Roshmi, 2017); (Sasidharan, 2011); (Nanda, 2009). It has been demonstrated that international or continental fungi, such as *F. oxysporum* and *Verticillium luteoalbum*, produce Nano particles via fungi (Ahmad, 2003); (Gericke, 2006). Other cyanobacteria and algae that produce gold nanoparticles include *Lyngbya majuscula*, *S. platensis subsalsa*, *Rhizoclonium heiroglyphicum*, *Nannochloropsis*, *Nannochloropsis*

prolifera, *Padina pavonica*, *Platensis*, and *Sargassum fluitans* (Lengke, 2006); (Lengke et al.,2006; (Chakraborty, 2009); (Hassaan, 2018). Plants have an advantage over other biological alternatives because to phytochemicals, which are highly concentrated in plants and are known for their medicinal and antimicrobial properties. The rapid synthesis of silver nanoparticles in sunlight utilising rice starch with *Zingiber officinale* rhizome extracts is just one example of how recent studies have shown the efficiency of this environment conscious nanotechnology again for development of very promising nanoparticles (George, 2018).

Mechanism of Nanoparticles

The bioaccumulation process, which helps cells retain the NS, can be maintained by plants. Massive numbers of metal ions are produced by the surface properties of NS, which can accumulate in plant cells, form fatal oxygen radicals compounds (ROS), and significantly impact metabolic and physiological processes.

It is widely acknowledged that plants can use the metal ion chelation method to counteract NS that results in ROS (Anjum, 2015). Low molecular weight proteins like phytochelatin, oligopeptides, and metalothionein can create transition metals to remove metal ions from the cellular environment or to concentrate in vacuoles for deactivation (Hasan, 2017). The sole evidence for the identical cellular behavior of NS and NF is provided by bioaccumulation and bio stabilization approaches. In addition to the low proteins' capacity to manage ROS or contribute to a bio stabilization of NS or metal ions, cellular enzymes that produce secondary metabolites, especially flavonoids, will boost plant cellular metabolism (Abdal Dayem, 2017); (Rico, 2015); (Branco-Neves, 2017).

Bioaccumulation and bio stabilization approaches are the only evidence for how NS functions as NF at the cellular level. In addition to the capabilities of low molecular weight proteins to regulate ROS and assist to the bio stabilization of NS and metal ions, intracellular enzymatic and secondary metabolites (mostly flavonoids) will enhance plant cell functions (Rico, 2015); (Abdal Dayem, 2017); (Branco-Neves, 2017). Flavanols can capture metal ions due to the presence of several terminals -OH (hydroxyl) groups and a carbonyl group. Quercetin, one of the most prevalent flavonoids, can form metal cationic complexes via its carbonyl or -OH group with Fe(II)/Fe(III), Cu(II), Al(III), Zn(II), Tb(III), Co(II), Pb(II), and Mo(VI) (Cherrak, 2016). Despite these discoveries, the relationship between metabolites and NS regulation at the cellular level remains unexplained.

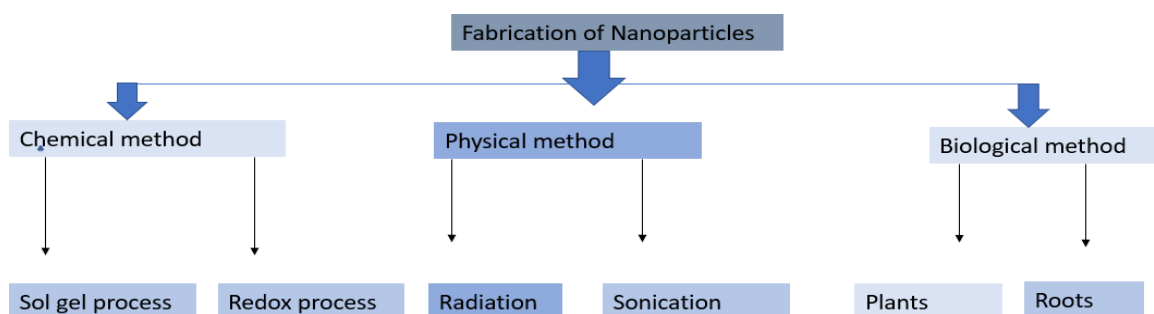


Fig 1.2- Different methods of Nanoparticles (Anjum, 2015)

Antimicrobial Properties

Environmentally friendly metal nanoparticles (MNPs) can be employed as biosensors, defenders, and black metal analyzers. Due to their distinct physicochemical properties, such as their ability to adhere biomolecules, their maximum utilization to quantity ratios, their own high surface responses, their simple and direct formulation and characterization, and their ability to enhance expression of genes for redox processes, Au-NPs and Ag-NPs have already been synthesized from a variety of metals. These nanoparticles could be used as weapons by both pathogenic fungi pathogens and other compounds that could cause pathogens illness.

Plant-NP Interactions: Accumulation and Negative Effects on Plants and Crops

Numerous commercial agricultural products, such as Nano-pesticides, Nano-herbicides, and Nano-fertilizers, contain Micro-particles or Ag-NP. Numerous advantages of the nanoscale are also thought to constantly have drawbacks that could become worse. Concerns over their potential short- and long-term environmental pollution have recently been voiced. For instance, when using NPs in agricultural areas, careful consideration should be given to how they interact with plants (such as crops).

To determine the effects of plants exposed to these nanomaterials on the ecosystem, conducted with the following research must be done. Nanoparticles can move the shoots when they come into touch with plants, enter the cellular structure, and congregate in various places.

Trophic levels can also be switched through. The accumulating of Au-NPs and Ag-NPs in plants has a range of effects on the rates of transpiration and respiration, which in turn have a range of effects on the photosynthetic process.

Although studies have shown organelle changes and NP deposition near to the plasmatic membrane, these nanoparticles have the potential to impact plant growth rate and chlorophyll levels at the microscopic level. The size, type, elemental composition, stability, and variety of the vegetation also influence assimilation, translocation, and accumulation.

Nanoparticles for control of recent development

Nanotechnology has recently spurred contemporary agricultural production, food production, and environmental management. In the near future, the use of nanoparticles in specific industries is projected to have a considerable positive impact on the country's economic growth. The principal area of research interest for nanomaterials is the agrochemical market.

Specific uses for nanotechnology include food that is ecologically friendly and crops that are based on nanotechnology. Nanotechnology was able to improve agricultural yield and quality while requiring fewer agrochemicals overall because to efficient distribution systems.

The use of nanotechnology in the agrochemical economy, including fast detection techniques, Nano-packaging materials, and additives and contents for food and feed, must be made clear touters. In order to solve today's environmental problems, environmental nanostructures may be used, which could lead to the creation of fresh remedies and robust preventative measures.

Nanotechnology is extremely promising for anyone trying to develop new technologies or enhance existing ones. Despite the fact that eco-toxicological on nanomaterials are relatively few and concerns regarding the safety of nanomaterial usage have developed, researchers and industrialists may demonstrate that the use of nanomaterials does not significantly harm biotic and abiotic systems. Agri-food and system has been developed concerns regarding how the public perceives and adopts nanotechnology have also been expressed.

A substantial portion of modern agriculture is chemically dense, concentrating on large chemical doses for nutrient management without consideration for ecosystems and natural resources. Braun and Roy assume that 50% of crop productivity is responsible for by fertilizer alone (1983). The need for large quantities of organic nutrients has prompted transportation costs to soar. Bio fertilizers promote agricultural productivity because they supply vital macronutrients like nitrogen, phosphate, and potash, though around half of the fertilizer applied is lost through leaching.

Research needs and future studies

Nano-fertilizers are in fact frequently available on the market, despite the fact that huge chemical businesses have not yet developed agricultural fertilizers in particular. Nano-fertilizers may contain Nano-Zink, silicate, ferrous, titanate, ZnCdSe/ZnS inner coat Semiconductor materials, InP/ZnS core shell QDs, Mn/ZnSe QDs, gold nanomaterials, core shell QDs, etc.

This would also encourage controlled delivery and raise its standard. In the past ten years, substantial study has been done on the absorption, biological fate, and toxic effects of a

number of metallic oxide nanoparticles (NPs), including Al₂O₃, TiO₂, CeO₂, FeO, and ZnONPs (Singh, 2016); (Dimkpa, 2014).

Given the alkaline nature of the soils, zinc deficiency has been highlighted as one of the most significant obstacles to agricultural productivity (Sadeghzadeh, 2013). By direct proton elimination or enhancement with 18O during manufacture, metal oxide nanoparticles can be prepared by reacting to generate 18F (Frigell, 2014).

In the absence of cytosolic proteins and cell cytoplasm, the size, aggregation level, and electronic properties of metal oxide NPs are examined (Marzbani, 2015); (Frigell, 2014). In addition to laser scanners microscopic examination, transmission electron microscopes Raman molecular imaging spectroscopy, and electron beams microscopy are utilized to examine NP uptake and subcellular fate (Marzbani, 2015). By utilizing eco-efficient bioprocesses and renewable chemical content, future sustainable bio-based financial systems will seek to eliminate and begin replacing toxic components in existing applications. As a result, they would be essential for the creation of the innovations required to address problems unique to the twenty-first century and represent the major critical juncture (Marzbani, 2015); (Prasad, 2014).

The growth of research in the fields of economics, biological, bio - diversity, nanoscience, chemistry, and manufacturing offers options to use biofuel production and organic wastes more efficiently while also boosting biomass productivity. Future research should focus on employing nanomaterials to safeguard plants and provide food.

NPs may be essential in the management of host microorganisms and insect pests, which are both well-known to be the most prevalent pests in agricultural fields and their products. Improved solubility, specificity, permeability, and stability are provided by a novel pesticide formulation with Nano-encapsulation, together with delayed but sure discharge properties (Bhattacharyya, 2016).

These advantages are primarily achieved by either delaying the early dissolution of the encapsulated active pharmaceutical ingredients or lengthening the duration of their pest control effectiveness. The discovery of Nano-encapsulated pesticides has the potential to reduce dose and human exposure, which is morally advantageous for crop improvement (Nuruzzaman *et al.*, 2016).

Technologies for non-toxic and effective pesticide distribution are being developed in an effort to increase worldwide food production while simultaneously minimizing adverse environmental effects on ecosystems (Bhattacharyya, 2016); Grillo *et al.* (2016), de Oliveira *et al.* (2014). Nano-fertilizers are a minor modification of synthetic fertilizers that can be manufactured from bulk materials or physiological or productive plant sections using nanoscale and other physical, pharmacological, or biological techniques.

Compact size and improved surface-to-volume ratio, nanoparticles have significantly different molecular characteristics compared to their large volume counterparts. A major step

toward sustainable agriculture can be the use of Nano-fertilizer in place of conventional fertilizer. All crops will produce less if the correct amounts of fertilizer are not applied.

Introducing fertilizers excessively can have damaging consequences on groundwater, eutrophicate aquatic ecosystems, and pollute the air. Therefore, while widespread use of chemical fertilization may enhance crop yield, it is not long-term sustainable (Quereshi *et al.*, 2018).

The most effective strategy is to create ingenious solutions, and Nano-fertilizer is one of them, to maximize the usage of chemical fertilizers. Nutrients are given as emulsions in Nano-fertilizers, both enclose contain within nanomaterials or shield them with Nano-film. The merits of Nano-fertilizers over traditional fertilizers are demonstrated by a multitude of elements. Order specification are used in agriculture to increase output while having less of a detrimental impact on the environment. Infrequent transport of Nano-fertilizers from the intended area into the soil, water, atmosphere, and even the food chain could have a detrimental effect on the health of the ecosystem's flora and fauna.

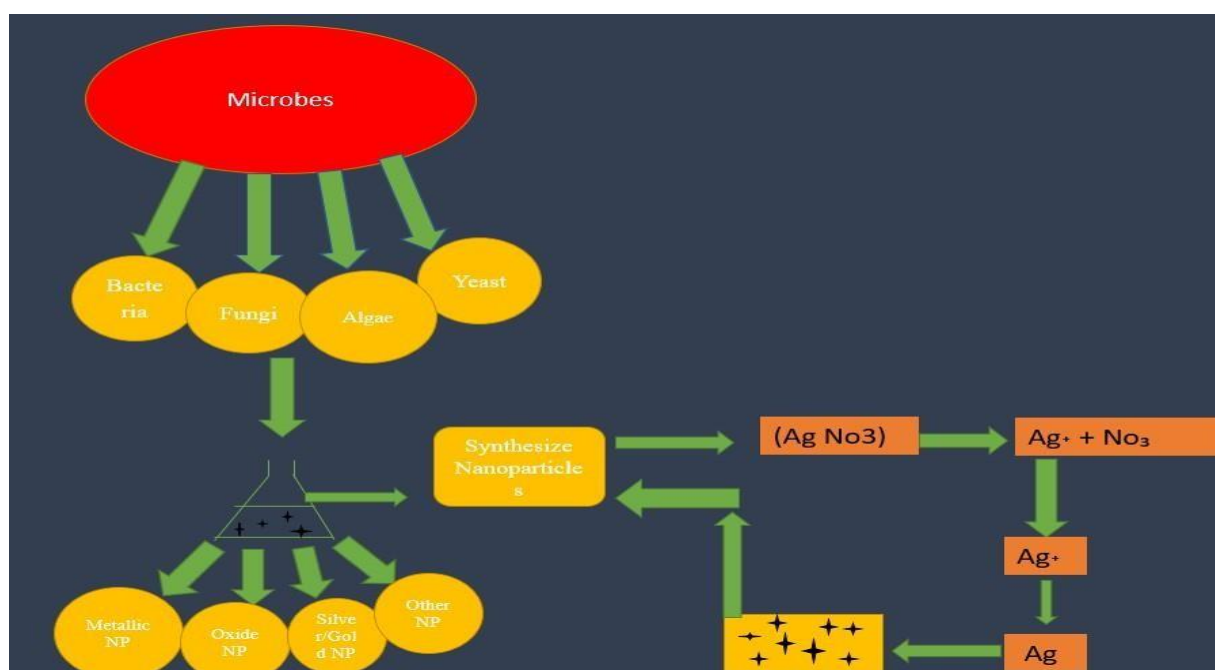


Fig 1.3- Role of different microbes in the formation of

NPs **Types of Nanopesticides**

1. Nanoemulsion
2. Nanocapsulation
3. Nanosuspension

An intriguing technique to augment the efficiency of botanical herbicide for commercial usage is a nanoemulsion formulation technology (Anjali *et al.*, 2012).

The storage stability of Nano-emulsion formulations is good across a wide temperature range (approx. 10 to 55 °C). Pesticide formulations using Nano-emulsion technology frequently cost less expensive than for those who use micro-emulsion innovation.

This happens because less inert and active compounds are employed because of their water solubility and their ability to break down hydrophilic and lipophilic molecules. Adjuvants and surfactants are used in the creation of the Nano-emulsion formulation system to increase the pesticides' functionality (Green and Beestman 2007).

One drawback with it by using essential oils as pests is that their effects are short-lived (Barnard and Xue 2004). Essential oils are made into Nano-emulsions to solve this issue. The quantity of essential oils needed can be reduced including using Nano emulsion, which is clear and can be utilized in food and beverage items. According to Qian *et al.* (2012), the Nano-emulsion droplets have a size that ranges from 20 to 200 nm.

Production of Pesticide Controlled Drug release Compositions (CRFs) The following nanomaterial forms have been applied often in constructing CRFs for the release of pesticides:

- Nano spheres the polymeric template reliably incorporates the active material.
- Nano capsules around the central core, where even the matrix polymer is lined, the due to inflammation is intense.
- Nano-gels They are merge polymeric materials with higher solubility that enable them to absorb enormous volumes of water.

Micelles they are generated by molecules with the both hydrophilic and hydrophobic moieties in aqueous solutions. Agrochemicals may have a lower effective dose than chemical pesticides since they can only kill certain pests. In contrast to conventional pesticides, which evaporate in the rain, these insecticide are absorbed on the plant's surface, allowing for a prolonged release (Scrinis 2007).

Several insect pests, including *Rhyzopertha mustique* and *Sarocladium oryzae*, showed significant mortality following three days of exposure to nanomaterial aluminium oxide-treated wheat (Stadler et al, 2010). The halo site nanotube has the potential to be utilized as a container for biologically active or highly concentrated reactants, such as insecticides and agro-medicines (Murphy (2008); Abdullayev and Lvov (2008)), (2011). Utilizing Nano-herbicides to eradicate weeds is a financially prudent method for increasing crop yields on farms.

Chemical weed treatment in rain-fed areas is contingent on the provision of wetness at the time of weed control, despite the fact that conventional herbicides have been shown to be highly efficient in preventing herbicide resistance without damaging crops or the environment. Lack of moisture impairs its capacity to be used, applied, and effective. Another application for the Nano-silicon transport with diatom reshaping (pore size 1-100 nm)

is the remediation of hormonal wastewater and delivery of insecticides and herbicides to vegetation (Lodriche *et al.*, 2013).

The nanostructures that develop are ingested by helpful microbes and transmitted to different trophic levels in the food chain, according to studies. The conversion of these particles to various mineral fertilizers plays a crucial role in agricultural output, providing between 35 and 40 percent of the total economic output of a harvest. The primary cause of groundwater contamination is unbalanced fertilization. Ammonium, phosphorous, and potassium are the three basic nutrients supplied by chemical fertilizers (Corradini *et al.*, 2010). There are numerous methods for applying fertilizer, including applying it directly to the roots or through the leaves.

In use efficiency of N, P, and K fertilizers was same at 30-35 percentage, 18-two percent, and 35-40 percent, respectively. Eutrophication occurs when an excessive amount of nutrients are applied and then persist in the soil or enter the aquatic environment. The distribution of fertilizer has an impact on both its effectiveness and environmental impact (Mathews (2008); Ihsan *et al.* 2007). The considerably more effective method of applying chemicals enhances nutrient uptake and lowers emissions.

The type of soil used, the type of soil, the irrigation mechanism, the crop, and the micronutrients applied all have a role in the choice of recommended fertilizer methods.

	Properties	Nano fertilizer	Conventional fertilizer
1.	Releasing of loss rate	Reduced loss of fertilizer nutrients	High loss rate due to leaching, drifting, run-off
2.	Soil improvement and fixation	Reduced	High
3.	Production of nutrient growth	Increased uptake ratio; saves fertilizer resource	Conventional fertilizer is not available to roots and the nutrients uptake efficiency is low
4.	Nutrient Solubility	High	Low
5.	Effect of release	Extended effective duration	Used by the plant at the site and time of application; the rest is converted into insoluble form
6.	Bioavailability	High	Low

Table 2.1- Comparison of Nano-fertilizers and Conventional fertilizers (Cui *et al.*, 2010)

Characterization of Microorganism Nanoparticles (MNPs)

Numerous scholars have claimed that endophytic bacterial and fungal spores, along with other creatures, may be conducted to generate metallic nanoparticles that have significant biological and agricultural applications. These microorganisms have a wide range of functions, including that of the capacity to deal with stress, the synthesis of phytohormones, resistance to diseases and herbivores, and the creation of enzymes. As a result, they have secondary metabolites that perform a number properties.

Their endophytes were reduced in size to a fraction of microbe nanoparticles (MNPs) in order to increase and access these important purposes (Sunkar and Nachiyar 2013a, b). SEM and TEM, often known as transmission and scanning electron microscopy (TEM) As stated earlier, microbe nanoparticles are crucial, and their traits, functions, and toxicity are all highly influenced by the structure, morphology, accessibility, composition, and accumulating state of something like the MNPs themselves (Adetunji and Sarin (2017); Dada et al., 2018).

Therefore, it is essential to recognize MNPs in order to comprehend and grasp their formation, synthesis, and pattern in order to produce their pertinent applicability (Adetunji *et al.*, 2018). Since MNP characterization necessitates the use of both methods for authentication and validation, we shall discuss TEM and SEM in this article.

SEM has been widely used in studies to accurately evaluate synthesized MNPs, but many droplets from these particles have now been found to have complex molecules, such as those that are inhomogeneous (Sant et al.,2013); flake-flower; Vigneshwaran et al.,2007; hexagonal; Vigneshwaran et al.,2006;), fragmented (Vijayaraghavan *et al.*,2012), and isotropic (Jagtap et al.,2011).

To use an electron transmission microscope (TEM) TEM, a fundamental and frequently used technology for characterizing MNPs, gives quantitative information on particles and/or particle sizes, volume fraction, and morphology (Joshi and Bhattacharya (2008), Williamson and Carter (2009), Lin et al (2014). TEM photography can be utilized to determine the crystal structure and particle sizes of manufactured MNPs. The disadvantage of TEM as a tool is that the established procedure required to acquire the best TEM images requires a significant amount of time, an increased concentrations, and a thin material section (Lin et al.,2014; Hall et al.,2007).

Given this, TEM has a number of drawbacks compared to SEM. The former can spot faults in manufactured MNPs that are line, planar, and crystallographic. Once more, TEM can examine the elemental makeup of the present at the nanoscale (Joshi and Bhattacharyya 2008). This may include x-ray photoelectron spectroscopy (TEM), transmission electron microscopy (SEM), X-ray diffraction (XRD), UV-Cc spectroscopy (UV), and Fourier transform infrared microscopy (FT-IR) (FTIR) In this 2012 work, Karthick (2012) investigated the biogenesis of antimicrobial silver nanoparticles utilizing *Bacillus cereus*, an endophyte obtained from *Garcinia xanthochymus*. It emphasized the environmental sustainable nanoparticles that were developed, which are believed to be a replacement to the chemical procedure that used fungi and bacteria to produce them in the past. After 3-5 days

of room-temperature incubation, the endophytic bacteria reduced the solution of silver nitrate to produce Ag-NPs.

In order to assess the compositions, FTIR, SEM-EDX, and TEM experiments were conducted. The synthesized Ag-NPs were confirmed to have a uniform dispersion, a length range of between 20 and 40 nm, and a slight tendency to aggregate using SEM and TEM studies. Synthetic silver was seen in the EDX spectra. After analyzing the structural characteristics of both synthesis using FTIR, subsequent research corroborated the same results. Small chemicals and molecules, especially those from microbes, can be difficult to classify and identify (Katz and Baltz (2016); David et al. (2015); González et al., (2016). In natural product chemistry, however, absolute structural characterization of these compounds is crucial.

For the most part, nuclear magnetic resonance and spectrometry are utilized to isolate metabolites from microorganisms. Absolute identification also employs alternative methodological approaches, such as polarimetry, cyclical dichroism, X-ray crystallography, uv-c (UV-Vis) spectrometry, and Fourier transition infrared (FTIR) spectroscopy. A select handful of those will be discussed in this section. In addition to the inability to separate SMM in high quality and manageable quantities, the instability of SMM must also be taken into account when considering its separation (Ibarra-Sánchez et al.(2013); Castillo et al.,(2016).

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