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The application of nanoparticles from green synthesis in crop protection

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## **DEDICATION**

Thank God

This thesis was made possible thanks to the  
contest of several people to whom I would like to testify  
all my gratitude.

I dedicate this work to my dear parents, in testimony of  
love, respect and my deep and eternal gratitude that  
I carry them in my gratitude for their sacrifices and their  
support, I will never thank them enough, for all that they  
have done for me.

To my dear brothers and sisters and all the members of myfamily.

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Thank God for your success in completing this work after tiring, I dedicate this work to my father,  
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## Abstract :

Crop protection plays a vital role in food production worldwide. Nanotechnologies are increasingly being used to protect traditional crops and to breed new crops with excellent traits. The control of pests, weeds, and diseases as well as crop genetic modifications are currently being improved through nanobiotechnologies such as pollen magnetoeception and gene nanocarriers. The knowledge regarding the synthesis of nanomaterials with outstanding properties has substantially improved the traditional management of crop pests, weeds, and diseases. In this chapter, the findings and trends in some of the most thorough and cutting-edge studies published to date will be discussed. Nanotechnologies and nanoscience can be the key to a sustainable future in crop protection, Therefore, the generation of nanoproducts could be an option for developing sustainable agriculture. In view of the above, this article presents recent research regarding the use of nanoparticles in agriculture and their potential uses as nano-fertilizers and plant growth stimulators.

## ملخص

تلعب حماية المحاصيل دورًا حيويًا في إنتاج الغذاء في جميع أنحاء العالم. يتم استخدام تقنيات النانو بشكل متزايد لحماية المحاصيل التقليدية واستنباط محاصيل جديدة ذات سمات ممتازة. يجري حاليًا تحسين مكافحة الآفات والأعشاب الضارة والأمراض بالإضافة إلى التعديلات الجينية للمحاصيل من خلال التقنيات النانوية الحيوية مثل حبوب اللقاح المغناطيسية وحاملات الجينات النانوية. أدت المعرفة المتعلقة بتركيب المواد النانوية ذات الخصائص البارزة إلى تحسين الإدارة التقليدية لآفات المحاصيل والأعشاب الضارة والأمراض. في هذا الفصل ، ستتم مناقشة النتائج والاتجاهات في بعض الدراسات الأكثر شمولاً وتطوراً التي تم نشرها حتى الآن. يمكن أن تكون تقنيات النانو وعلوم النانو هي المفتاح لمستقبل مستدام في حماية المحاصيل ، لذلك ، يمكن أن يكون توليد المنتجات النانوية خيارًا لتطوير الزراعة المستدامة. في ضوء ما سبق ، تقدم هذه المقالة الأبحاث الحديثة المتعلقة باستخدام الجسيمات النانوية في الزراعة واستخداماتها المحتملة كأسمدة نانوية ومحفزات نمو النبات.

## **Résumé :**

La protection des cultures joue un rôle vital dans la production alimentaire dans le monde entier. Les nanotechnologies sont de plus en plus utilisées pour protéger les cultures traditionnelles et créer de nouvelles cultures avec d'excellentes caractéristiques. Le contrôle des ravageurs, des mauvaises herbes et des maladies ainsi que les modifications génétiques des cultures sont actuellement améliorés grâce aux nanobiotechnologies telles que la magnétofection du pollen et les nanoporteurs de gènes. Les connaissances sur la synthèse de nanomatériaux aux propriétés exceptionnelles ont considérablement amélioré la gestion traditionnelle des ravageurs, des mauvaises herbes et des maladies des cultures. Dans ce chapitre, les résultats et les tendances de certaines des études les plus approfondies et les plus avancées publiées à ce jour seront discutés. Les nanotechnologies et les nanosciences peuvent être la clé d'un avenir durable dans la protection des cultures. Par conséquent, la génération de nanoproduits pourrait être une option pour développer une agriculture durable. Compte tenu de ce qui précède, cet article présente des recherches récentes concernant l'utilisation des nanoparticules dans l'agriculture et leurs utilisations potentielles en tant que nano-engrais et stimulateurs de croissance des plantes.

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## 1.Introduction

To address the adding challenges of sustainable product and food security, significant technological advancements and inventions have been made in recent times in the field of agriculture. similar nonstop agricultural inventions are crucial to meet the adding food demand of exploding global population through the uses of natural and synthetic resources. In particular, nanotechnology has potential to give effective results to the multiple agriculture-related problems. To bridge the gap between bulk accoutrements and atomic or molecular structures, nanoparticles give a great scientific interest. Over the last two decades, a significant quantum of research has been carried out on nanotechnology emphasizing its numerous operations in agriculture sectors. Fertilizer application plays a pivotal role in adding the agrarian product; still, the inordinate exercises of diseases irreversibly alter the chemical ecology of soil, farther reducing the available area for crop production. Sustainable agriculture entails a minimal use of agrochemicals that can ultimately protect the terrain and conserve different species from extermination. specially, nanomaterials enhance the productivity of crops by adding the effectiveness of agrarian inputs to facilitate site- targeted controlled delivery of nutrients, thereby assuring the minimum use of agri- inputs. Indeed, the assistance of nanotechnology in plant protection products has exponentially increased, which may assure increased crop yield. also, the major concern in agricultural production is to enable accelerated adaption of plants to progressive climate change factors, similar as extreme temperatures, water insufficiency, saltness, alkalinity and environmental pollution with poisonous metals without threatening existing sensitive ecosystems[224]. In addition, the development and exploitation of nanosensors in precision farming, to measure and cover crop growth, soil conditions, diseases, uses and penetration of agrochemicals and environmental pollution have basically ameliorated the human control of soil and factory champaign, quality control and safety assurance contributing big to sustainable agriculture and environmental systems[225]. Nanomaterial engineering is the cutting- edge track of research that supports the development of high- tech agricultural fields by offering a wider specific surface area crucial for the sustainable development of agriculture systems. accordingly, nanotechnology can't only reduce the uncertainty, but also coordinate the management strategies of agricultural product as an alternative to conventional technologies. In numerous instances, agro-nanotech innovations offer short- term techno- fixes to the problems faced in ultramodern artificial agriculture. The present review summarizes the applications of

nanotechnology in agriculture, which may insure the sustainability of agriculture and environment.

In a relatively short period of time, nanotechnology has had a significant impact on many sectors, including agribusiness. NT, considered as an emerging technology, is oriented to the characterization, elaboration and application of materials of very small dimensions, in the range of 1 to 100 nanometers (nm), that is, from 1 to 100 billionths of a meter [226]. so it is located within the atomic and molecular scale. NT is an extensive field of interdisciplinary research, since it opens up a wide range of opportunities in various areas such as medicine, the pharmaceutical industry, electronics, and sustainable agriculture [227]. Agricultural scientists today face a wide range of challenges such as stagnant crop yields, low nutrient use efficiency, declining soil organic matter, multiple nutrient deficiencies, climate change, the decrease in agricultural land, the low availability of water for irrigation and the shortage of labor; in addition to the exodus of people from agricultural areas to cities [228].

Despite these enormous difficulties faced by the agricultural sector, it is necessary to maintain sustained growth of 4% to meet the challenges posed by global food demand [229]. Therefore, to deal with this diversity of problems, it is necessary to explore one of the cutting-edge technologies such as NT, which allows detecting the presence of pests and diseases, food contamination and applying the correct amount of nutrients and pesticides that promote productivity, while ensuring environmental safety and greater efficiency in the use of agricultural inputs [230]. In this context, new nanomaterials have been developed based on the use of metallic, polymeric, inorganic NPs, etc., that allow increasing productivity and that seek to find applications for the improvement of intelligent nanosystems for the capture and immobilization of nutrients and their gradual release. in the soil [231].

Such systems have the advantage of minimizing leaching, while enhancing plant nutrient uptake and helping to mitigate eutrophication by reducing nitrogen transfer to groundwater [232]. Furthermore, it is important to mention that nanomaterials could also be exploited to improve the structure and function of pesticides by increasing their solubility, resistance against hydrolysis, improving their photodecomposition and/or providing a more efficient way of controlled release towards target organisms

## **Chapter 1 :**

### **2.Nanoparticles**

The word “nano” is derived from the Latin nanus, which means dwarf or little.

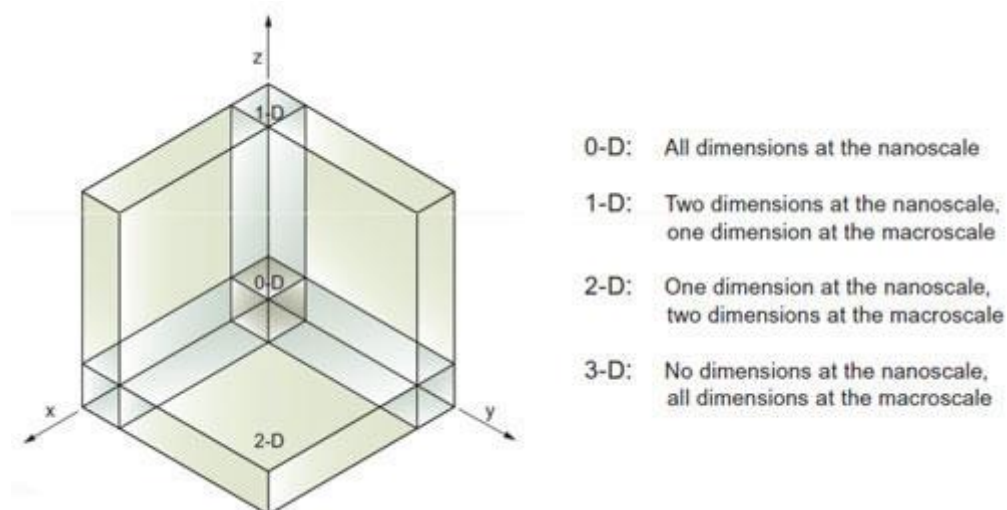
Nanoparticles (NPs) are tiny particles with a diameter of 1–100 nm. When a particle has a diameter between 1 and 100 nm, it is classified as a primary nanoparticle. Nanoparticles, whether or not regarding normal or perhaps made origins have got inside the array of 1–100 nm inside one or more dimensions. A nanometer (nm) is a SI unit of length equal to 10<sup>-9</sup> meter. NMs are materials with a length of 1–1000 nm in at least one dimension; however, they are usually characterized as having a 1–100 nm diameter. The U.S. Food and Drug Administration (USFDA) also describes NMs as “materials with an area of roughly one dimension and depending on dimensions of approximately 1 to 100 nm” [1]. To put it another way: according to International Organization for Standardization (ISO), NMs are “materials with any external or internal nanoscale dimension or surface structure at the nanoscale” [2]. Typically, nanometer will be a single billionth of the meter. Nanoemulsion, carbon dioxide nanotubes, quantum dots, nanorods, small and also nano- encapsulation and so forth. Morphology-aspect proportion or perhaps dimensions, hydrophobicity, solubility-release regarding dangerous types, surface or perhaps roughness, surface area types contaminations or perhaps adsorption, in the course of activity or perhaps historical past, reactive O<sub>2</sub> types (ROS) O<sub>2</sub> / H<sub>2</sub>O, ability to make ROS, construction, structure, competing holding web sites together with the receptor and also dispersal and also aggregation will be the crucial qualities regarding nanoparticles. Nanoparticles have several unique properties including a greater charge density and reactivity, considerably more strength, increased heat resistance, a lower melting point, and different permanent magnetic properties linked with nano-clusters. Distinctions inside the uncovered surface area regarding diverse nanoparticles cause differences inside atomic syndication throughout the nanoparticles, which often affect the particular electron exchange fee kinetics among metallic nanoparticles and also matching adsorbed types. These types of distinctive qualities provide the subsequent benefits to nanoparticles within farming, for example, greater solubility within the suspension, greater transmission associated with seedling jackets as well as consequently rising origins, much better bioavailability associated with substances towards the seedling radicals, supplying real focus as well as managed discharge associated with fertilizers or even pesticides within reaction to particular problems, enhanced specific exercise as well as eco-friendly along with security as well as calm transportation.

Nanoparticles tend to be seen as a distinctive bodily as well as chemical substance functions such as surface area, pore size, particle morphology, and reactivity because of their rigorous programs within the farming area. Nanoparticles are used in nano fertilizer, nano-pesticides as well as herbicides that are helpful to improve plants development, to manage extreme utilizes associated with chemical substances fertilizers as well as improve survivability towards biotic tension. The effects of various nanoparticles on plant development and phytotoxicity have been documented by a number of substances such as magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles, alumina, zinc, and additionally zinc oxide in relation to seed germination [3]. . Wheat can benefit from the addition of nanoparticles to their environment. The particular Zn takes on essential function inside place metabolic rate simply by influencing the actions regarding hydrogenase and also carbonic anhydrase, stabilization regarding ribosomal fractions and also activity regarding cytochrome. Place digestive enzymes stimulated simply by Zn get excited about carbs metabolic rate, servicing with the strength regarding cell filters, necessary protein activity, rules regarding auxin activity and also pollen creation. Magnesium (Mg) is involved with numerous physical as well as biochemical activities; it's an important component concerning growing development as well as improvement and performs a vital part within grow support systems within abiotic tension circumstances. The actual common perform associated with Mg within vegetation is most likely it's part since the main atom from the chlorophyll molecule within the lightabsorbing complicated associated with chloroplasts and it is a factor to photosynthetic fixation associated with  $\text{CO}_2$ .

## **2.1.Nanoscale Dimensions**

Scientists classify nanomaterials based on the number of dimensions of a material, which are outside the nanoscale (<100 nm) range. Accordingly, in zero-dimensional (0D) nanomaterials all the dimensions are measured within the nanoscale (no dimensions are larger than 100 nm). Most commonly, 0D nanomaterials are nanoparticles. In one-dimensional nanomaterials (1D), one dimension is outside the nanoscale. This class includes nanotubes, nanorods, and nanowires. In two-dimensional nanomaterials (2D), two dimensions are outside the nanoscale. This class exhibits plate-like shapes and includes graphene, nanofilms, nanolayers, and nanocoatings. Three-dimensional nanomaterials (3D) are materials that are not confined to the

nanoscale in any dimension. This class can contain bulk powders, dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multi-nanolayers.



**Figure 1:** Classification of nanoscale dimensions. (Source: Tallinn University of Technology)

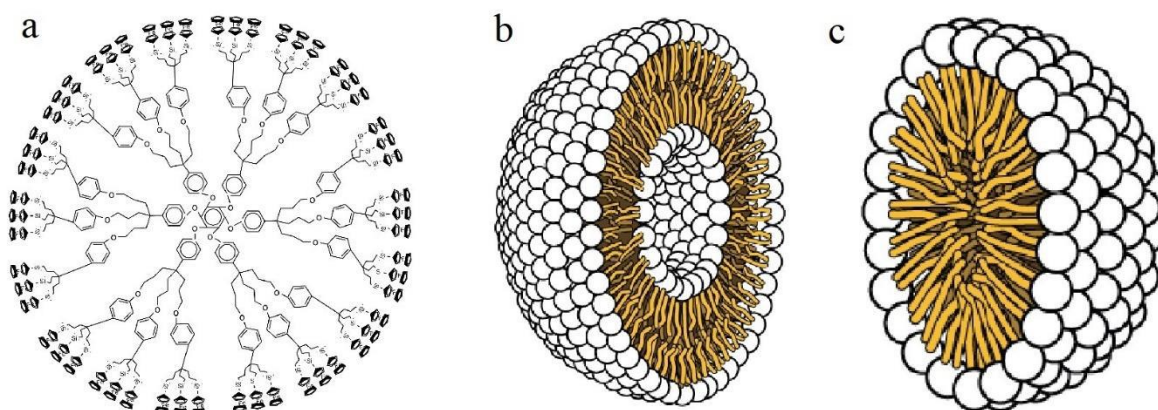
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### 3. Classification of Nanoparticles

The nanoparticles are generally classified into the organic, inorganic and carbon based.

#### 3.1. Organic nanoparticles

Dendrimers, micelles, liposomes and ferritin, etc. are commonly known as the organic nanoparticles or polymers. These nanoparticles are biodegradable, non-toxic, and some particles such as micelles and liposomes have a hollow core (Figure 2), also known as nanocapsules and are sensitive to thermal and electromagnetic radiation such as heat and light [4]. These unique characteristics make them an ideal choice for drug delivery. The drug carrying capacity, its stability and delivery systems, either entrapped drug or adsorbed drug system determines their field of applications and their efficiency apart from their normal characteristics such as the size, composition, surface morphology, etc. The organic nanoparticles are most widely used in the biomedical field for example drug delivery system as they are efficient and also can be injected on specific parts of the body that is also known as targeted drug delivery.



**Figure 2.** Organic nanoparticles: a – Dendrimers, b – Liposomes and c – micelles.

### **3.2. Inorganic nanoparticles**

Inorganic nanoparticles are particles that are not made up of carbon. Metal and metal oxide based nanoparticles are generally categorised as inorganic nanoparticles

#### **3.2.1. Metal based:**

Nanoparticles that are synthesised from metals to nanometric sizes either by destructive or constructive methods are metal based nanoparticles. Almost all the metals can be synthesised into their nanoparticles [5]. The commonly used metals for nanoparticle synthesis are aluminium (Al), cadmium (Cd), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), silver (Ag) and zinc (Zn). The nanoparticles have distinctive properties such sizes as low as 10 to 100nm, surface characteristics like high surface area to volume ratio, pore size, surface charge and surface charge density, crystalline and amorphous structures, shapes like spherical and cylindrical and colour, reactivity and sensitivity to environmental factors such as air, moisture, heat and sunlight etc.

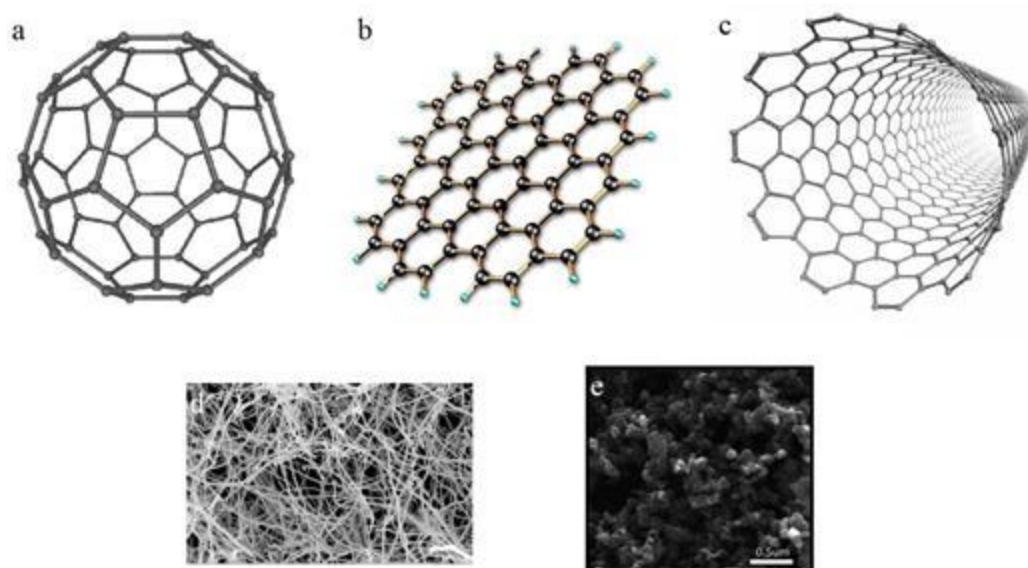
#### **3.2.2. Metal oxides based:**

The metal oxide based nanoparticles are synthesised to modify the properties of their respective metal based nanoparticles, for example nanoparticles of iron (Fe) instantly oxidises to iron oxide ( $\text{Fe}_2\text{O}_3$ ) in the presence of oxygen at room temperature that increases its reactivity compared to iron nanoparticles. Metal oxide nanoparticles are synthesised mainly due to their increased reactivity and efficiency [6]. The commonly synthesised are Aluminium oxide ( $\text{Al}_2\text{O}_3$ ), Cerium oxide ( $\text{CeO}_2$ ), Iron oxide ( $\text{Fe}_2\text{O}_3$ ), Magnetite ( $\text{Fe}_3\text{O}_4$ ), Silicon dioxide ( $\text{SiO}_2$ ),

Titanium oxide (TiO<sub>2</sub>), Zinc oxide (ZnO). These nanoparticles have exceptional properties when compared to their metal counterparts.

### 3.3. Carbon based

The nanoparticles made completely of carbon are known as carbon based [7]. They can be classified into fullerenes, graphene, carbon nano tubes (CNT), carbon nanofibers and carbon black and sometimes activated carbon in nano size and are presented in Figure 2.



**Figure 3.** Carbon based nanoparticles: a – fullerenes, b – graphene, c – carbon nanotubes, d – carbon nanofibers and e – carbon black

#### 3.3.1. Fullerenes:

Fullerenes (C<sub>60</sub>) is a carbon molecule that is spherical in shape and made up of carbon atoms held together by sp<sup>2</sup> hybridization. About 28 to 1500 carbon atoms forms the spherical structure with diameters up to 8.2 nm for a single layer and 4 to 36 nm for multi-layered fullerenes.

#### 3.3.2. Graphene :

Graphene is an allotrope of carbon. Graphene is a hexagonal network of honeycomb lattice made up of carbon atoms in a two dimensional planar surface. Generally the thickness of the graphene sheet is around 1 nm.

### **3.3.3. Carbon Nano Tubes (CNT) :**

Carbon Nano Tubes (CNT), a graphene nanofoil with a honeycomb lattice of carbon atoms is wound into hollow cylinders to form nanotubes of diameters as low as 0.7 nm for a single layered and 100 nm for multi-layered CNT and length varying from a few micrometres to several millimetres. The ends can either be hollow or closed by a half fullerene molecule.

### **3.3.4. Carbon Nanofiber:**

The same graphene nanofoils are used to produce carbon nanofiber as CNT but wound into a cone or cup shape instead of a regular cylindrical tubes.

### **3.3.5. Carbon black:**

An amorphous material made up of carbon, generally spherical in shape with diameters from 20 to 70 nm. The interaction between the particles are so high that they bound in aggregates and around 500 nm agglomerates are formed.

## **4.Synthesis of green Nanoparticles:**

The biological preparation of Nanoparticles via the green method utilizes the plants and animals to cause the conversion of metallic ions into neutral atoms. Green synthesis (GS) is also done by the elimination of toxic chemicals. Hence, the green synthesized nanoparticles (NPs) offers you the improved biocompatibility in dealing with the biomedical application as compared to the chemically synthesized ones.

There are multiple plant species and groups, among which the Angiosperms and Algae are widely studied. The green-synthesis from the plants-derived materials such as chitin and silk also reported in the past. Different kinds of researches in the past have proved the capability of various plants' specie in green synthesis of nanoparticles and their capping behavior. Not just the plants but the animal-derived biomolecules are also responsible for this.

## **4.1.Plant-based synthesis of Nanoparticles:**

This section will highlight all the signs of progress made towards the green synthesis of nanoparticles via the plant species. Most commonly, the plant species having medicinal applications play a major role in the green synthesis process.

### **4.1.1.Angiosperms:**

The plant's lineage has the angiosperms at the top and hence these are widely utilized for the green synthesis of NPs. Their easy access, wide applications, availability all over the world have further favored this synthesis. Also, the Angiosperms play an essential role in dealing with human and animal diseases[8] . The nature of Angiosperm plants have aided in processing the natural reducing ability in improving this green domain. The green Synthesis has received many updates in its library especially in the Asian Countries due to enriched plant resources. But not all the plant's species can do justice with the green synthesis of plants.

Most of the researches made on the angiosperm species have revealed that the synthesis of Gold and Silver Nanoparticles is quite common as compared to the other magnetic Nanoparticles. The reason behind this fact is the poor capability of converting the metal cation into lower reduction potential. Various researches have contributed to the plant-based production of nanoparticles. A well-explored plant named *Camellia Sinensis* has been considered an advantageous plant's specie in GS of NPs. The purification of living molecules present in this plant's species viz. catechins, theaflavins, and their isolation has confirmed their role in green synthesis of Au NPs [9, 10]. Similarly, the pure tea polyphenol is utilized for the synthesis of Pt NPs. Another plant's specie named *Jatropha curcas* L is responsible for the reduction of metal cations via the cyclic peptide molecules [11]. Therefore, the overall research progress that has been completed recently in this newly-emerged green synthesis domain is quite impressive as compared to the conventional methods

### **4.1.2.Gymnosperms:**

Gymnosperms were the first to have the seeds in plants category, hence they are of much importance. Each group of plants further have distinct metabolites. These metabolites are further responsible for the reduction of metal ions to synthesize the nanoparticles. The studies regarding the green synthesis of NPs from gymnosperms is quite restricted but evident to some extent. Various researches have been made in this sense, and the NPs synthesized from

the gymnosperms have different sizes, morphology, and quantity depending on plant type . Noruzi et al have synthesized the Au NPs from the Thuja orientalis extract in just a 10- minutes of reaction time.

The overall efficiency was found out to be 90% and the produced Nanoparticles were round in shape and crystalline in nature .

#### **4.1.3.Algae:**

The three main criteria to synthesize and hence achieve the efficiency in the GS of NPs are mainly the reducing agent, stabilizing capping agent, and acceptable solvent . The algae-based preparation of nanoparticle is one such process. These are photoautotrophic in nature . Hence, the bio-reduction of algae can synthesize the metal and metal oxide NPs . Spirulina platensis is a kind of edible blue-green alga that is utilized to synthesize the gold and silver NPs . Senapati et al. have synthesized the gold NPs via Tetraselmis kochinensis plant .

**Table 1. List of nanoparticles derived from plants**

Plant	Nanoparticle	Size (nm)
<i>Allium cepa</i> L.	Au	~100
<i>Allium sativum</i> L.	Ag	4.4 ± 1.5
<i>Achyranthus aspera</i> L.	Ag	20-30
<i>Anacardium occidentale</i> L.	Au	-
<i>Andrographis paniculata</i> Nees.	Ag	28
<i>Astragalus gummifer</i> Labill.	Ag	13.1±1.0
<i>Azadirachta indica</i> A. Juss.	Au	2-100
<i>Camellia sinensis</i> L.	Au	25
<i>Carica papaya</i> L.	Ag	15
<i>Centella asiatica</i> L.	Ag	-
<i>Chenopodium album</i> L.	Ag Au	12,10
<i>Coleus aromaticus</i> Lour.	Ag	40-50
<i>Cinnamomum zeylanicum</i> Blume.	Pd	15 to 20
<i>Cinnamomum camphora</i> L.	Pd	3.2-6.0
<i>Citrullus colocynthis</i> L.	Ag	31
<i>Datura metel</i> L.	Ag	16 - 40
<i>Desmodium triflorum</i> (L) DC.	Ag	5-20
<i>Diopyros kaki</i>	Pt	2-12
<i>Dioscorea bulbifera</i> L.	Ag	8-20
<i>Dioscorea oppositifolia</i> L.	Ag	14
<i>Elettaria cardamomom</i> (L) Maton.	Ag	-
<i>Gardenia jasminoides</i> Ellis.	Pd	3-5
<i>Glycyrrhiza Glabra</i> L.	Ag	20
<i>Hibiscus cannabinus</i> L.	Ag	9
<i>Hydrilla verticillata</i> (L.f.) Royle.	Ag	65.55
<i>Jatropha curcas</i> L.	ZnS	10
<i>Justicia gendarussa</i> L.	Au	27
<i>Lantana camara</i> L.	Ag	12.55
<i>Leonuri herba</i> L.	Ag	9.9 - 13.0
<i>Macrotyloma uniflorum</i> (Lam) Verdc.	Au	14-17
<i>Mentha piperita</i> L.	Ag, Au	90, 150

## **5.Features of nanomaterial :**

The properties of matter at the nanoscale level are substantially distinct compared to bulk counterparts. Size-dependent effects become more prominent at the nanoscale. For example, Au solution appears yellow when in the bulk and it appears purple or red at the nanoscale level. The properties of nanomaterials can be tuned *via* tuning the nanomaterial size.

[12.13] At the nanoscale, the electronic properties are substantially changed compared to bulk materials. For example, boron in bulk form is not considered a metal, whereas a two-dimensional network of boron (borophene) appears to be an excellent 2D metal.

[14] Compared to their bulk counterparts, the mechanical properties of nanomaterials are considerably improved due to increases in crystal perfection or reductions in crystallographic defects[15].

Among a range of unique properties, the following key properties can be obtained upon tuning the sizes and morphologies of nanomaterials.

### **5.1. Surface area**

The surface areas of nanomaterials are generally substantially high compared with their bulk counterparts, and this property is associated with all nanomaterials [16].

### **5.2. Magnetism**

The magnetic behavior of elements can change at the nanoscale. A non-magnetic element can become magnetic at the nanoscale level. [13]

### **5.3. Quantum effects**

Quantum effects are more pronounced at the nanoscale level. However, the size at which these effects will appear strongly depends upon the nature of the semiconductor material[17].

### **5.4. High thermal and electrical conductivity**

According to the nature of the nanomaterial, extraordinary thermal and electrical conductivity can be exhibited at the nanoscale level compared to bulk counterparts. One example of this is graphene attained from graphite [18].

### **5.5. Excellent mechanical properties**

Nanomaterials exhibit excellent mechanical properties that are absent in their macroscopic counterparts[19].

### **5.6. Excellent support for catalysts**

2D sheets of various nanomaterials have provided the opportunity for the good dispersion of nanoparticles of active catalyst, enhancing the catalyst performance substantially[20]. Recently, catalysts have been atomically dispersed on 2D sheets of nanomaterials to boost performance[21].

### **5.7. Antimicrobial activity**

Some nanomaterials possess antiviral, antibacterial, and antifungal properties and have an excellent capacity to deal with pathogen-related diseases[22.23].

Overall, these features have made nanoscale materials valuable for a wide range of applications, substantially boosting the performances of various devices and materials in a number of fields. Details of various nanomaterials, their properties, and applications in various fields will be discussed below.

## **6.Applications of Nanoparticles in Agriculture:**

Nanotechnology provides new agrochemical agents and new delivery mechanisms to improve crop productivity, and it promises to reduce pesticide applications. Nanotechnology can increase agricultural production, and its applications include: (1) nanoformulations of agrochemicals for applying pesticides and fertilizers for crop improvement; (2) the application of nanosensors in crop protection for the identification of diseases and residues of agrochemicals; (3) nanodevices for the genetic engineering of plants; (4) plant disease diagnostics; (5) animal health, animal breeding, poultry production; and (6) postharvest management. Precision farming techniques might be used to further improve the crop yields but not damage soil and water. In addition, it can reduce nitrogen loss due to leaching and emissions, and soil microorganisms. Nanotechnology applications include nanoparticle-mediated gene or DNA transfer in plants for the development of insect-resistant varieties, food processing and storage and increased product shelf life. Nanotechnology may increase the development of biomass-to-fuel production. Experts feel that the potential benefits of

nanotechnology for agriculture, food, fisheries and aquaculture need to be balanced against concerns for the soil, water and environment and the occupational health of workers [24]. Nanotechnology uses are currently being researched, tested and in some cases already applied in food technology [25].

### **6.1.Nano-fertilizers :**

Currently, agriculture all across the globe faces a broad spectrum of challenges, such as nutrient deficiency, stagnation in crop yields, diminishing soil organic matter, low water availability, nutrient deficiency in the soil, decreased land area due to urbanization and land degradation, and labor shortages [26]. The application of nanoscience and nanotechnology is increasing tremendously, and novel methods are continuously being proposed to produce novel and desirable materials for crop production and management . It is one of the most influential ideas of the evolving science of precision agriculture in which farmers efficiently make use of fertilizers and other inputs. The uncontrolled population has prompted the enormous production of conventional fertilizers to increase food production and crop protection, but this ultimately decreases the soil fertility and quality of food. These chemical fertilizers not only add to the tribulations of the subtle ecosystem, but also affect human health as they remain unused. The global demand for fertilizers is expected to rise in the coming years, according to a report submitted by the Food and Agricultural Organization of the United Nations. Therefore, it is imperative to involve intelligent strategies for sustainable agriculture, such as nanotechnology. Nano fertilizers are environmentally friendly fertilizers or smart fertilizers with the potential to increase the application rates of fertilizers and reduce the loss of nutrients from it, mainly phosphorous and nitroge [27]. It offers the gradual and controlled release of nutrients to the targeted site, which helps to prevent the contamination of water bodies and the environment [28].

Nano fertilizers are those that either provide nutrients to plants or enhance the effect of fertilizers even when applied in smaller amounts [29]. Uptake of nutrients can be increased by encapsulating the fertilizers in nano form that ultimately reduces nutrient loss, improves crop quality and yield, and also minimizes the risk of environmental degradation . The foliar application of these nano fertilizers is also demonstrated to mitigate the stress in plants [30]. Nano fertilizers can be divided into three categories based on the nutritional requirements of the plants: (1) macronutrient nano fertilizers, (2) micronutrient nano fertilizers, and (3)

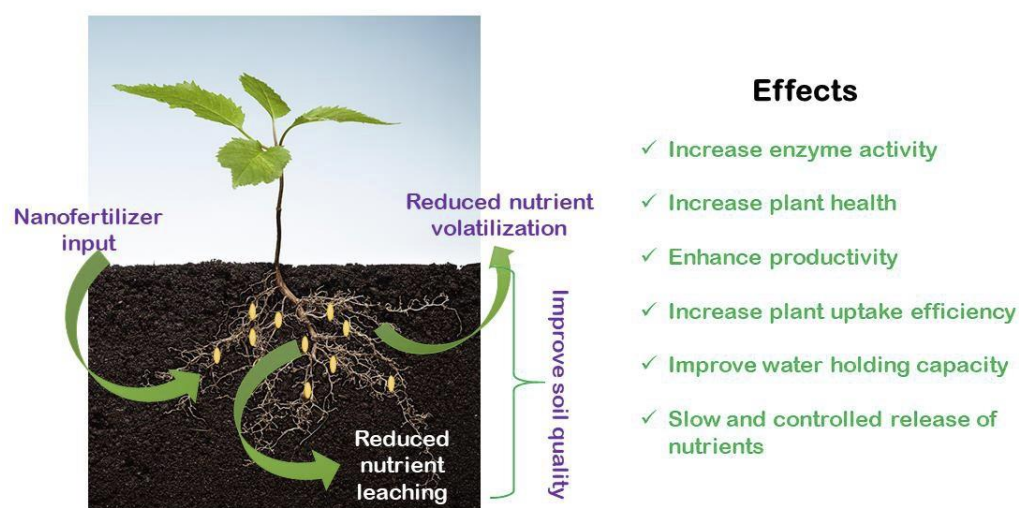
nanoparticulate nano fertilizers [31]. Macronutrient nano fertilizers are composed of a combination of elements, such as potassium (K), magnesium (Mg), nitrogen (N), calcium (Ca), and phosphorus (P). It is estimated that the total consumption of macronutrient fertilizers is projected to increase to 263 million tons (Mt) in 2050, thus showing a critical need for these fertilizers in the agricultural sector. Delfani and his group tested the efficiency of Mg and Fe NPs on the growth of black-eyed peas (*Vigna unguiculata*) by foliar application and observed enhanced seed weight and photosynthetic ability that, in turn, increased the yield [32]. The Ca NPs, together with humic acids, improved seedling growth in peanuts (about 30% increase) with dry biomass reaching 5.78 g per plant [33]. The synthesized hydroxyapatite [ $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ] NPs of size 16 nm significantly enhanced the growth rate and yield of soybeans (*Glycine max*) in comparison to control. These studies suggest that NPs can be applied as potent fertilizers for field crops [34]. For more detail, please refer to .

Plant micronutrients consist of molybdenum (Mo), copper (Cu), iron (Fe), nickel (Ni), manganese (Mn), and Zinc (Zn), and compared to macronutrients, they are required in much smaller amounts for the healthy growth of crops. Micronutrients applied as composite formulations are more effective in providing enough nutrients and cause less environmental degradation. Micronutrients packed in NPs enhance the nutrient bioavailability and fertilizer use efficiency relative to other conventional ions and salts [35]. The composite of three micronutrients NPs (ZnO, CuO, and  $\text{B}_2\text{O}_3$ ) has been successfully established for agronomic fortification to mitigate drought stress in soybean plants [36]. Nanoparticulate fertilizers contain other NPs, such as CNTs,  $\text{TiO}_2$ , and  $\text{SiO}_2$ , that enhance the growth of plants. The mixture of  $\text{TiO}_2$  and  $\text{SiO}_2$  increased nitrogen fixation, growth enhancement, and improved seed germination in soybeans [37].

### **6.1.1 Macronutrient Nanofertilizer**

As mentioned in the name, this fertilizer is for the soil where nutrients are obligatory in the large amount, especially for the traditional farming. Macronutrients such as Nitrogen, Phosphorus, Sulphur, Magnesium, Potassium, and Calcium are needed for proper growth. Demands for the production of food are increasing continuously which tends to increase the need for nanofertilizer to 263 MT by 2050 [38]. Nanomaterial has a high volume-to-surface ratio. This brings the utmost efficiency to the applications of macronutrient fertilizer rather than the traditional ones. Therefore, many researchers are working continuously to improve the macronutrients fertilizer to use it at the field scale. In this regard, Liu et al. [39] and Ditta

et al. [40] have studied the applications of nanoparticle-based fertilizer. Controlled release of Nitrogen has been achieved by the zeolite chips (Urea coated) and urea-modified hydroxyapatite nanoparticles [41, 42]. Similarly, Liu and Lal [43] have researched on the Calcium and Phosphorus hydroxyapatite nanoparticles which showed an increase of approx. 20.5% and 34% in the Glycine max seed yield. Liu et al. [44] have noticed a 15% increase in the biomass of *Arachis hypogaea* by the application of Ca NP as compared to the conventional Calcium macronutrient. Moreover, Delfani et al. [45] studied the seed weight of *Vigna unguiculata*. They found the enhancement by 7% in the seed weigh after the application of synthesized Mg NP. The effects of nanofertilizers on plant and soil is illustrated in figure 4.



**Figure 4.** The effects of nanofertilizers on plant and soil.

### 6.1.2 Micronutrient Nanofertilizer

Though micronutrients are required in smaller quantities but necessary for the metabolic process. The bioavailability to the plants is significantly improved in the case of micronutrients and hence enhances the growth and quality of crops. Delfani et al. [45] have made another research on the chlorophyll contents of black-eyed pea after the application of Fe NP which is improved by 10%. Similarly, Ghafariyan et al. [46] have found out 30-60 ppm concentration increase in the chlorophyll content in *G. max*. Using bulk Manganese Sulfate will not provide sufficient increase in growth and quality. Therefore, spraying the Mn NP will enhance the biomass by 37-38%, root length by 52-53%, and shoot length by 38-39%.

Zinc element is responsible to carry out the regulatory mechanism for all the enzyme activities in plants. Zinc Oxide NPs are responsible to enhance or upsurge the contents of

biomass, shoot length, root length, and overall growth by improving the protein content. These improvements can be seen in the *Vigna Radiate*, *Cucumis sativas*, *Raphanus sativus*, *Brassica napus*, and Cluster bean [47-48]. Molybdenum NPs when used in combination with the nitrogen fixation bacteria tend to improve the overall seed growth in chickpea [49].

### **6.1.3 Nano-particulate Fertilizer**

Nanoparticles including the Titanium Dioxide, Silicon Dioxide, and carbon nanotubes are significantly responsible to increase the plant's growth and quality of crops. A mixture of Titanium Dioxide, Silicon Dioxide NPs have been seen to improve the seed growth and germination process along with an enhancement in nitrogen fixation in *G. max* [50]. Only the Titanium Dioxide NPs have the ability to improve the chlorophyll, protein, and nitrogen content of the *Spinacia oleracea* [51]. Carbon Nanotubes have been widely used as the fertilizer for diverse species of plants and vegetables. Carbon nanotubes follow the same principle as the nanoparticles and penetrate the seed coat to enhance the water uptake resulting in better growth [52].

## **6.2. Nanotechnology to improve quality of soil and fertilizer distribution**

Nanotechnology for the management of crops is used as an essential technology for enhancing crop productivity. Nanomaterials and nanostructures, such as carbon nanotubes, nanofibers, and quantum dots are now exploited in agriculture research as biosensors for evaluating the quality of soil and fertilizer distribution. The purpose of nanoparticles is to minimize the spread of chemicals amount, reduce the nutrient loss during fertilization, and increase the quality and yield with proper nutrient [53]. The development and use of vermiculite, nonclay, and zeolite could improve fertilizer efficacy and crop production for ecological agriculture in coarse-textured [54]. Amending sandy loam soils with inorganic amendments reduce  $\text{NH}_4\text{-N}$  passage and increasing the yield of N fertilizer in ecological agriculture systems [55]. Nonclay is systematized into a number of modules such as montmorillonite, bentonite, kaolinite, hectorite, and halloysite on the basis of chemical composition and nanoparticle morphology [56].

Most of the productivity of agricultural practices is heavily dependent on fertilizer use. Studies show that crop production is linearly determined by exhaustive application of fertilizers to increase soil fertility [57]. The use of nano fertilizer is crucial to enhance crop production. Nano fertilizer is a material with nanometer-size which improves the delivery to

plants and managed the slow release of nutrients into the soil gradually in a highly controlled way, hence stopping eutrophication and contamination of water [58]. Nanotechnology makes the exploitation of nanostructured or nanomaterials for fertilizer transport or limited release routes to construct smooth fertilizer as new opportunities to modify nutrient usage efficacy and reduce charges for environmental safety . Nano-fertilizer could improve nutrient efficiency through encapsulation within nanoparticles which is conducted by three methods. (a) Nutrient encapsulation within nonporous structures, (b) Coating of thin polymeric film, or (c) Delivery in the form of particle or suspensions with nanoscale sizes .

Nanoscale fertilizers could lead to the more effective delivery of nutrients as their small size may allow them access to plant surfaces and transport channels . Nano-fertilizer extracted and prepared from banana peels were used in the growth of tomatoes, peppers, or flowers [59]. Nano fertilizers were used for the growth and improvement of different crops, for instance, nanoparticles of ZnO for chickpea, silicon dioxide and iron slag powder for maize, colloidal silica and NPK for tomato, TiO<sub>2</sub> for spinach, gold and sulfur fertilizers were used for the growth of grapes . Fertilizer usage with nanoscale transporters may be subjected in a way so that they anchor the roots of the plant with the surrounding soil contents and organic material hence decreasing chemical loss and lessening environmental issues [60]. Nanoscale fertilizers can decrease the toxicity of soil and hence the potential undesirable impacts accompanied by high dosage are reduced [61]. Such nano fertilizers slow down the nutrients release and extend the duration of fertilizer impact [62]. TiO<sub>2</sub> nanoparticles have shown a major effect on the growth of maize crop; moreover, SiO<sub>2</sub> plus TiO<sub>2</sub> nanoparticles elevated the action of nitrate and increased plant absorption potential, by controlled use of water and fertilizer with the efficient outcome [63].

### **6.3. Traditional Chemical vs. Nanofertilizers :**

Chemical fertilizers are applied to plants by broadcasting or spraying without considering the nutritional state of the plant and/or soil, especially in developing countries.

Due to the non-targeted approach of conventional fertilizer application, the amount of nutrients reaching the plant (use efficiency) is less than that through leaching and seepage from agricultural fields to the water bodies and soil underneath; such wastage incurs economic and environmental losses [64]. The repeated excessive application of fertilizers renders the soil unusable due to the over-accumulation of nutrients, which disrupts the

whole-plant nutrient homeostasis and has other soil-degrading outcomes, such as reduced N fixation, increased numbers of pathogens and pests affecting soil flora and fauna, and mineral homeostasis [65].

Around 75% of urea (principal N fertilizer) is lost upon its application due to volatilization and leaching [66]. The inefficiency in the delivery of fertilizer is related to groundwater contamination and water bodies being over-burdened with nitrates, extending the dead zones in water bodies and the release of nitrous oxide into the environment. Nitrous oxide is the third-most copious ozone-depleting substance (greenhouse gas, GHG), with a higher global warming potential than any other GHG, including carbon dioxide and methane [67]. Our reliance on chemically manufactured N fertilizer has significantly expanded anthropogenic

impedance with the N cycle, which is key for the production of proteins for all living things. Nanoparticle fertilizers enable the slow and controlled on-demand release of nutrient/s, in turn preventing premature losses [68].

Nanotechnology can be used to explore nanoscale materials for carrying fertilizers and/or as vectors for enabling controlled-release kinetics in the design of smart nanofertilizers [67]. Metal NPs' synthesis and use in nanofertilizers is a sustainable alternative method to the existing, expensive, environmentally destructive conventional chemical fertilization techniques, with long-term applicability and acceptability, and is considered to be a 'Nano-Bio Revolution' in the field of nano-enabled NP synthesis technologies. Moreover, using the biological system to develop such NPs is an added advantage of nano-biofertilizers by virtue of its targeted needs-based release and minimal wastage of fertilizer [69]. Besides their small size, large surface area, high solubility, and mobility, NPs also have a high surface tension, which helps to control their release of the encapsulated fertilizer [70]. NPs can quickly translocate in plants [71], advancing the release of nutrients through nanofertilizer and providing better protection through nanoproducts for agricultural use such as nanopesticides, nanofertilizers, and nanoherbicides [72,73].

## **6.4.Seed priming and seed Germination :**

### **6.4.1.Seed priming :**

Seed priming is a traditional technique used in agriculture to promote seed germination and plant establishment, based on a preliminary preparation of seeds prior to sowing [74,75,76–79] It is usually a water-based methodology, whereby seeds are hydrated followed by drying,

or some physical methods are applied as ultraviolet light (UV) priming [80]. The absorption of water must be adequate to trigger the metabolic pathways for pregermination (phases I and II), without resulting in radicle emergence

#### **6.4.1.1. Nanoparticles for Seed Priming :**

Seed nano-priming is a new technology that uses nanomaterials, mainly nanoparticles, for seed priming [80,81,82]. There is an important difference between seed priming and seed nano-priming, since conventional seed priming mainly employs water (hydropriming) or solutions containing substances (nutrients, hormones, or biopolymers) that adsorb on the seed and can result in seed coating (or dressing). In seed nano-priming, the media used are suspensions or nanoformulations, where the nanoparticles may or may not be taken up by the seeds [83]. Even when nanoparticle uptake occurs, the greatest fraction is retained on the seed surface as coating [84,85–87]. Such seed coating can be used with fungicides or bactericides in order to protect against pathogens in the field or during storage [88].

One of the first studies showing the potential of nanomaterials to affect seed germination was reported by Khodakovskaya et al. [89]. Although seed priming was not used, these authors demonstrated that carbon nanotubes could be taken up by tomato seeds.

The carbon nanotubes increased water uptake, resulting in tomato plants with a 2-fold higher number of flowers [90]. Other studies have similarly demonstrated that carbon nanotubes can modulate seed metabolism in plants, such as tomato, barley, soybean, and maize, increasing the gene expression of several types of water channel proteins [91,92].

Different nanomaterials, including metallic, biogenic metallic, and polymeric nanoparticles, have also shown potential for seed nano-priming [93,94,95], resulting in the stimulation of plant growth and improvement in morphological and metabolic traits. This process can promote fast root and shoot development, with changes in the expression of genes that modulate metabolic processes, such as phytohormone production. Seed nano-priming changes the activity of the defense system, increasing the antioxidant levels and enzyme activities, so that the plants become more resistant to pests and other biotic and abiotic stresses under field conditions [79,84,90].

#### **6.4.1.2. Seed Nano-Priming and Effects on Plant Metabolism under Abiotic and Biotic Stresses :**

Abiotic and biotic stresses lead to reduced production and economic losses. Abiotic stresses are environmental factors, such as drought, flood, heat or cold, salinity, or nutrient-deficient soils. Biotic stresses are caused by microbial pathogens (bacteria or fungi), insects, or weeds that compete for nutrients [100,101].

The use of seed nano-priming in agriculture can improve the quality of seeds and increase resistance against stress conditions. Nanoparticles can act directly against pathogens, as well as alter the metabolism of seeds and plants, consequently enhancing the innate immune system, altering hormone production, and making the plants more resistant to diseases or abiotic stress [102].

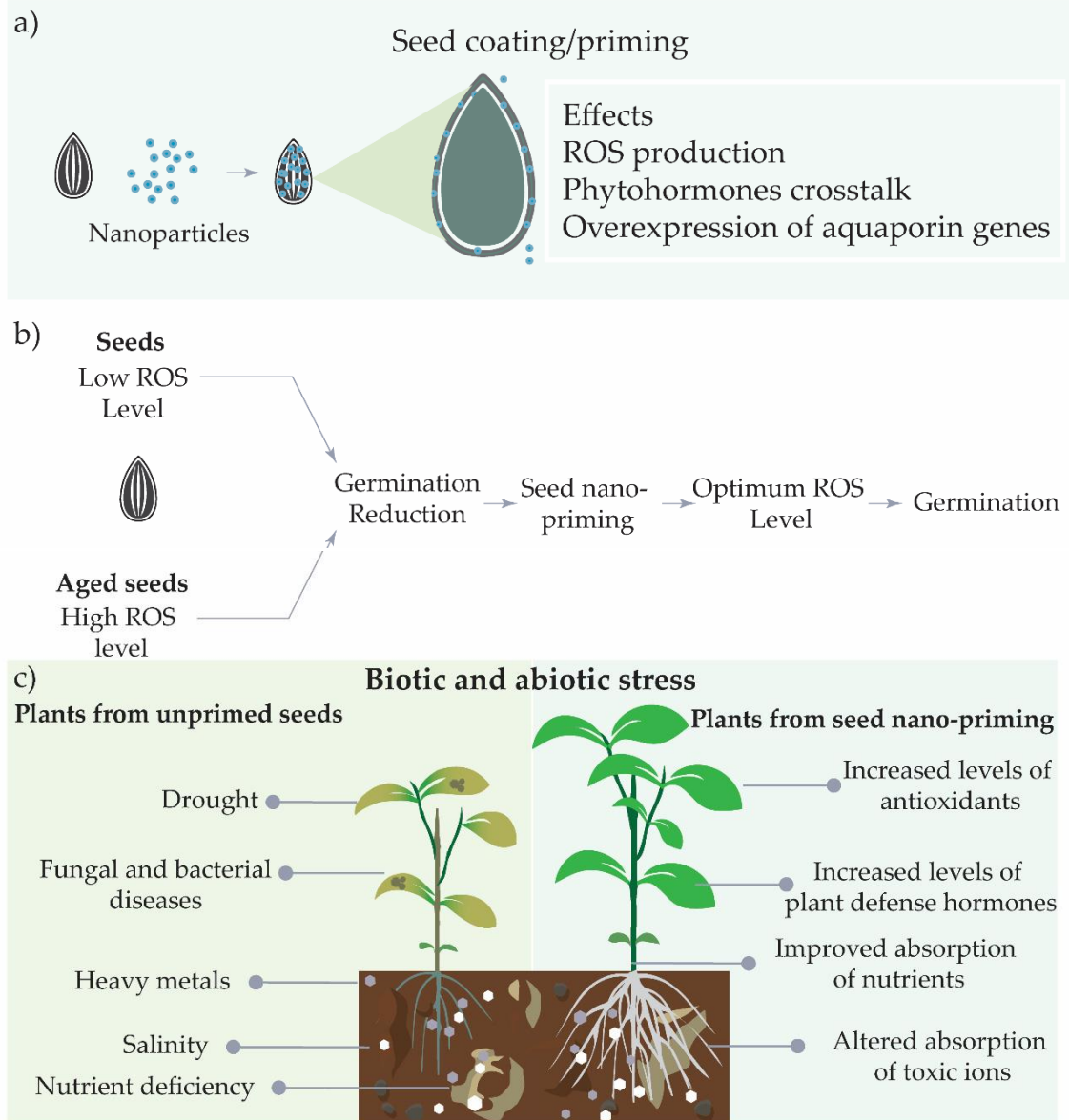
The nanoparticles uptake under seed coating can promote the ROS production, acting in different metabolic pathways, increase the level of active gibberellins, and the mobilization of storage proteins [103]. In addition, the effect of nanoparticles in increasing water uptake by the seeds can cause sufficient stress to activate germination, increasing the activities of enzymes in phases I and II of the process [104] (Figure 5a). Seed nano-priming has been shown to increase germination, since these systems are able to keep ROS levels in the optimum range comprised by the oxidative window that promotes seed germination (Figure 5b) [105,106].

Under stress conditions, nanoparticles can act to reduce seed ROS levels, due to increased activity of enzymes, such as superoxidase dismutase, catalases, and guaiacolperoxidase, hence reducing seed cell damage [106].

The storage of seeds for long periods at low temperatures results in aging, which can heavily decrease the germination rate [107]. After long periods, the seed cells initiate processes that increase ROS generation and reduce antioxidant levels, causing metabolic side effects that result in a reduction of the germination index [106].

The use of biogenic metallic nanoparticles has been shown to be able to ROS at optimum levels, resulting in improved germination of aged seeds. The biogenic nanoparticles can be coated with many compounds that are natural reducing agents and act to decrease ROS levels in seeds [108,106].

## Nanoparticles and germination effects



**Figure 5.** Effects of seed nano-priming on seeds and plants under abiotic and biotic stresses. (a) Effects of seed nano-priming during the germination, (b) effects of seed nano-priming on ROS levels, and (c) potential effects under biotic and abiotic stresses

## 6.5.Seed germination :

New scientific inventions use numerous approaches and contributed much to the field of nanosciences lately. This situation has been a one step further towards the nanotech operations in husbandry. Nanoscience helped in enhancing the growth of crops, the process of seed germination, and conforming to different surroundings. Population dynamics and well-being of all the species depends significantly on the seed germination process. thus, the germination of seeds isn't just a sensitive but important process in the factory's lifecycle. Seed germination, in turn, depends upon multiple factors and attributes i.e. humidity position in soil, nutrients, and soil's comity with species [109].numerous studies have been made in this regard and it has been shown that nanomaterials have contributed much to adding the factory's growth and overall product of crops. It has been depicted that the application of Carbon nanotubes(multi-walled) has shown positive goods on the seed development process of soybean, tomato, sludge, barley wheat, and further ( 110- 113). also, nano silicon dioxide ( SiO<sub>2</sub>), Titanium Dioxide( TiO<sub>2</sub>), and Zeolite have formerly told the seed germination process in a positive manner for colorful kinds of crops( 109, 114). Another exploration conducted in this regard depicted that the Iron or Silicon Dioxide nanoparticles play an important part in perfecting the overall seed germination of particular types of crops substantially ( 115). There has been enough attestations now concerning the profitable influences of nanomaterials on seed germination but the factual process behind this is unclear yet. Some studies have reported that after operation of nanomaterial, the NPs have the capacity to pass through the seed fleece. After passing, they enhance the capability of immersion of water by the seedling. This way, the seedling is better suitable to grow and germinate under favorable conditions. Quality improvement and increase in the crop's yield is also described by employing multiple kinds of nanomaterials. similar nanomaterials include Zinc oxide, Titanium dioxide, carbon nanotubes, Iron Oxide, and ZnFeCu- Oxide( 116- 118). Similarly, studies have stated the benefits of the crop growth of OH- functionalized fullerenes via the application of carbon nanotubes. Gao et al. studied the growth of hypocotyl in fullerenes in Arabidopsis via the cell division ( 119). thus, Fullerol has been set up responsible for the improvement in fruit's growth, size, and the overall yield as well. The increase set up out to be 128 and also it beget an increase in the product of bioactive composites. These bioactive compounds include the Amarine,  $\psi$ ,  $\psi$ -Carotene, charantin, and Chicory Extract ( 120). Yousefzadeh and Sabaghnia described that the

nano- iron fertilizer enhanced the essential oil contents of plants ( 121). In the same way, the nano- zinc and boron fertilizers are employed for perfecting the fruit yield and quality. It includes the process of abating the total answerable solids by 4.4-7.6, an increase in the titratable acidity by 9.5-29.1, and 0.28-0.62 pH increase in the pomegranate ( 122). These attestations are enough to prove the role of nanomaterials in adding the crop's production and quality. still, the mechanism by which the nanomaterials enhance the growth and quality of plants is still unknown. Some attestations have been set up that the nanomaterials increase the input of nutrients and water and nutrients to ameliorate the root system via increases enzyme exertion( 116, 117). also, the studies have also revealed the phenomenon of control or slow release of nanofertilizers in water or soil which helps in availability of nutrients for all the time during cultivation of crops. This vacuity of nutrients helps to ameliorate the seed sprouting, development, blossoming/ flowering, and further ( 123). Like, a urea fertilizer ( nano- carpeted in this case) named as hydroxyapatite release the nitrogen contents demanded for plant growth at a veritably slow rate. It releases these contents continuously for 60 days. On the other hand, the traditional fertilizer will end up in 30 days and that too with an unstable release. It 'll negatively affect the plant's growth and quality of Product ( 124). In a study, ( 125) delved about the photosynthesis in spinach.

They set up out that when TiO<sub>2</sub> nanofertilizer is applied, the photosynthesis rate increases by but dropped beyond the 4. also, ( 115) .made a exploration on the size of barley and maize seedlings and depicted that the operation of nanomaterial i.e. nano Fe/ SiO<sub>2</sub> caused an increase in length by approx. 8.3 and 21 independently. But the shoot length have a negative impact on reaching the concentration degree above 0.025 g/ kg. This means that the growth of crops depend on the nanomaterials. ( 126) . suggested that the crop's development and quality also depends upon the operation of nanomaterials. The foliar employments of nano Fe<sub>3</sub>O<sub>4</sub> can increase the total product of chlorophyll, carbohydrate and essential oils content, height, shoot and branches length, and numerous other factors in *Ocimum basilicum* plants.

## **7.The nanoparticles in crop protection :**

The assistance of nanotechnology in plant protection products has exponentially increased to achieve higher crop production. In general, conventional crop protection practices involve applications of large-scale and over-dose of fungicides, herbicides and insecticides. Among the applied pesticides, more than 90% are either lost in the environment or unable to reach the target sites essential for effective pest control [125]. This not only increases the expenses of crop production, but also causes the depletion of environmental systems. It is to be noted that the presence of active ingredients in minimum effective concentration of a formulation at the target sites is essential for assurance of better protection of plants from pest invasion and subsequent crop loss. In this connection, the development of new plant protection formulation has long been a very cognitive field of agricultural research. One such technology is nanoformulation or encapsulation of pesticides which has revolutionized the plant protection sector. Nanoformulation of pesticides contains a very tiny number of particles that act as active ingredients of pesticides, whereas other engineered nano-structures also have useful pesticidal properties [126]. The nanoencapsulation of pesticides is the coating of active ingredients of pesticides with another material of various sizes at nano-range where encapsulated materials are referred to as internal phase of the core material (pesticides) and capsulation materials are known as external phase, i.e., the coating nanomaterials [125].

### **7.1.Nanodiagnostic and nano-phytopathology :**

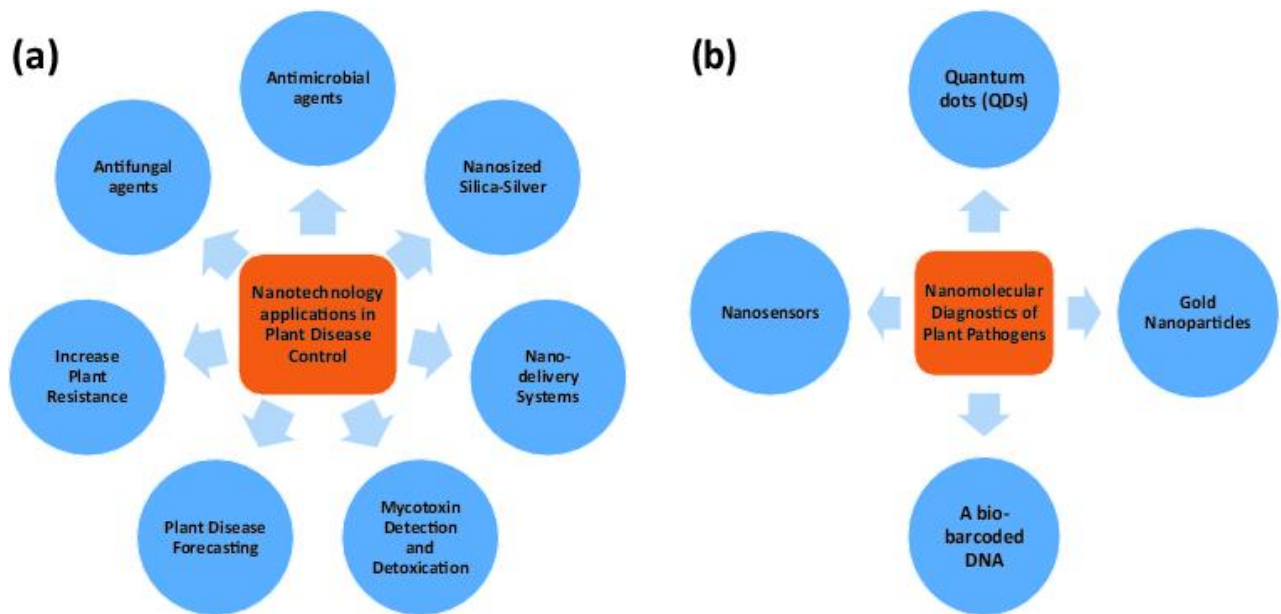
The extension/integration of molecular diagnostics on a nanoscale is a promising technology for identifying pathogens. Nanomolecular diagnostic is the use of nanobiotechnology to diagnose plant diseases and this can be termed as nanodiagnostics.[127] In particular, several nanodevices and nanosystems are used for sequencing single molecules of DNA. Assays with the use of nano-size devices to investigate DNA sequences and diagnose disease are becoming faster, more flexible and more sensitive.

It is noteworthy that new detection techniques involving nano-biosensors for pathogen identification will likely be a cornerstone to this trend.[128] During the 1980s and 1990s, phytopathologists relied on visual assessment to identify plant diseases.[129] Identifying plant pathogens via conventional techniques may take several days and therefore researchers need

rapid detection tools that can provide results within a few hours. To develop such detection tools, phytopathologists are constantly working with nanotechnologists.[130] Nano and/or phytopathology researchers are attempting to develop an easy assay that is moveable and accurate and does not need any difficult method for procedure, so that farmers can use the mobile laboratory themselves to detect specific diseases.[131]

Newly developed nanomaterials with special nanoscale characteristics could present a tremendous breakthrough in pathogen and contaminant detection. Nanotechnology is also driving the development of lab-on-a-chip systems for detecting toxicity in waters, observing nutrients in irrigation water and controlling the quality in food production.[132,131]

Nano-phytopathology is a cutting-edge science which uses nanotechnology for detecting, diagnosing and controlling plant disease and their pathogens at an early stage, owing to crop protection from epidemic diseases. The modern plant pathologist strives to apply his knowledge in nanophytopathology to enable understanding of controlling factors of plant diseases and to develop and/or evaluate eco-friendly diagnostic measurements. Modern nanomolecular techniques are used for monitoring or understanding of pathogen population genetics, plant-microbe interactions and gene transfer between pathogens and even the host. Furthermore, nanoparticles such as nanosized silica-silver have recently been applied as antimicrobial and antifungal agents. Additionally, nanomaterials can be used for mycotoxin detection and detoxication, increasing plant resistance, plant disease forecasting and nanomolecular diagnostics of plant pathogens. Potential applications of nanophytopathology are shown in [Figure 6](#).



**Figure 6.**

Potential nanotechnology applications in plant pathology: (a) plant disease control and (b) detection of plant pathogens.

### 7.1.1 Nano-phytopathology :

New techniques such as nanotechnology will remain novel for this century, but as time passes and extensive research is done in the field, they will be more widely used in the treatment of plant infection. Plant pathology is set to offer an exciting future of research with regard to their antibacterial and antifungal properties in the context of nanotechnology. Using nanoparticles to protect the seeds and foliage from pathogens that would otherwise intrude can be the most effective method. Therefore, it can be summarized here that nanoparticles can play their role in plant disease management in following ways-

- Nanoparticles being used as pesticides themselves and being applied to plants directly for the control of disease.
- Nanoparticles as carriers of other pesticides/nanoparticles for their controlled and targeted release and to increase their effect.
- Nanodevices to detect diseases at early stages.

Nanoparticles can be successfully applied to disease affected plants with enhanced and effective results due to their extremely reactivity/affectability. This increased reactivity can be attributed to their extremely small size and large surface area.

#### **7.1.1.1 Effect of nanoparticles on the pathogens/microorganisms :**

After scientific testing, scientists have confirmed that the chemical and physical properties of nanoforms of materials actually shift between their macroform and nanoform. All of these properties transformations ultimately end up with useful real-world applications in plant defense and plant protection. Since nanoparticles have the advantages of both small size and surface area, they influence plant pathogens in a more precise way. Larger macroscopic entities are less likely to interact with microorganisms because they are farther away from them. There is an abundant amount of evidence available to bolster this claim.

#### **7.1.1.2. Effect of nanoparticles on Bacteria :**

New research shows that nanoparticles have antibacterial properties, which is most likely the result of the cell wall of the bacteria being broken or of high levels of reactive oxygen species (ROS) being produced [133–134]. Bacterial infection is a leading cause of contamination and mortality due to prolonged presence of pathogens. Due to low cost and positive results, antibiotics have been selected for the treatment of bacterial contamination. Although multiple studies have demonstrated that overuse of antibiotics leads to multidrug-resistant bacteria strains, this has not yet been confirmed though. A very powerful strain of antibiotic-resistant bacteria has emerged. Previous researches states that, these kinds of bacteria consist of gene, which are super resistant [135]. The mode of action of nanoparticles is directly linked with the bacterial cell wall, which enables the nanoparticles to control super-resistant bacteria. Bacteria may become resistant to nanoparticles if they are exposed to them. If these new NP-based materials are able to perform antibacterial activity, it's entirely possible [136–137,138.139].

#### **7.1.1.3 Nanotechnology for plant viral diseases :**

The various types of nanoparticles were investigated and used to control *Sitophilus oryzae* and baculovirus BmNPV (*Bombyx mori* nuclear polyhedrosis

virus) in silkworm (*B. mori*) disease caused by *S. oryzae* and BmNPV [140]. To complete their investigation, the researchers performed bioassay, which involved preparing the nanoparticles' solid and liquid formulations; after which, they applied these formulations to rice and stored it in a plastic box with 20 adult *S. oryzae* for seven days. On the first day, the researchers reported that hydrophilic silver nanoparticles were most effective. More than 90% of mortality was gained on day 2, and silver and aluminum nanoparticles were the primary source. Seventythree percent of the insects died after seven days of exposure to lipophilic silver nanoparticles. But with respect to nanoparticles of aluminum, 100% mortality was observed. Thus, a significant decrease in viral load was found in a hydrophobic aluminosilicate nanoparticle suspension when *B. mori* leaves were used in an ethanolic treatment of grasserie disease.

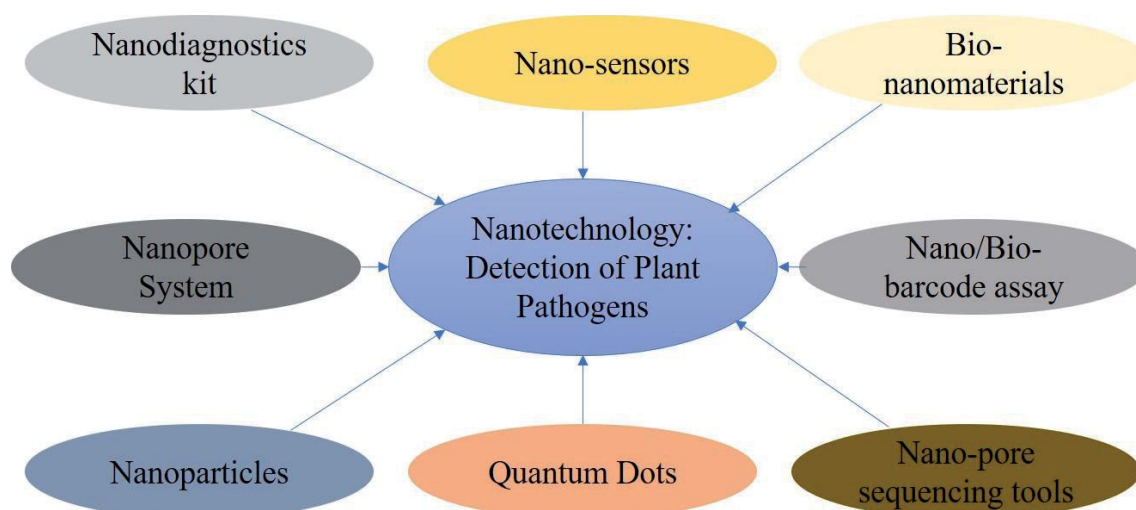
#### **7.1.1.4 Metallic nanoparticles: effective tool for plant disease management :**

There are different nanotechnology approaches for the detection of plant diseases (**Figure 7**).

#### **7.1.1.5 Bio-nano materials :**

There are some bio-nano materials which are categorized through X-ray diffraction (XRD) technique, X-ray photoelectron spectroscopy (XPS), Energy-dispersive X-ray spectroscopy (EDS), UV visible spectroscopy, scanning electron microscopy (SEM), Fourier transforms infrared spectroscopy (FTIR), Coupled plasma spectrometry (ICP), Transmissions electron microscope (TEM) and Atomic force microscopy (AFM) techniques. These bio-nano materials played noteworthy role in field of agriculture, medicine and biology. The increasing usage of bio- nano materials in many areas will enhance their productivity in the atmosphere by developing more analytical tools in nanotechnology for controlled environmental risk management [141]. Bio-synthesis of bio-nanomaterials can be also achieved by using plant

extracts [142], microbial cultures or their enzymes and proteins.



**Figure 7.** Different nanotechnology approaches for the detection of plant diseases.

## 7.2.Nanopesticide :

Nanopesticides stand for pesticides formulated in nanomaterials to find applications in the agricultural field, whether specially fixed on a hybrid substrate, encapsulated in a matrix or functionalized nanocarriers for external stimuli or enzyme-mediated triggers. Nanosized particles, coupled with their shape and special properties, are thought to explore pesticide activities in nanocarrier innovative formulations based on several materials like silica, lipids, polymers, copolymers, ceramic, metal, carbon and others [143].

The nanopesticide formulations can increase water solubility, bioavailability and protect agrochemicals against environmental degradation, revolutionizing the control of pathogens, weeds, and insects in the crops [144]. However, the nanomaterial features are also borderline their cytotoxicity and genotoxicity.

The indiscriminate and irrational use of pesticides influence the balance of the ecosystem and expose everyone's health to risk. Adverse effects of short-term (acute) and long-term (chronic) resultant of occupational or accidental ingestion of pesticide residues from food, water-drinking is fatal or disability-adjusted life years (DALY). Children are more vulnerable to pesticide exposure and are subject to permanent tissue and organ damage. Between them, the centra and peripheral neurotoxicity and the effect on the loss of blood ability for coagulation are meaningful reasons for concerns [145]. Indeed, a detailed assessment of the pros and cons that influence the activity and toxicity of nanopesticides is crucial for the safe and sustainable development of the already approved use of nanoparticles in agriculture.

The effect of formulations on the behavior of nanopesticides in the environments, ecosystems, farmer workers, consumers, and all productive sector involved in the agriculture chain is not entirely known [146]. However, the critical role of nanoformulations in reducing the active ingredient's degradation, improving water solubility equilibrium, and increasing the biological availability of actives ingredients are known. Specifically, to avoid endemic infestation of pests, plant injury and economic loss by decreasing the quality and quantity of agricultural products and foods [147].

Nanopesticides from runoff of agricultural and industrial wastewater during the precipitation event by soil permeating leaching phenomenon reach the water supply, affecting its quality, increasing the human exposure time and concerns for the ecosystem. It has been noticed that nanoparticles could cause toxicological effects by their biomimetics properties and high ability of distribution and bioaccumulation in soil, water environments, foods, and consequently in all animals, especially in mammals [148,149,150,151]. For humans, the range of side effects related to individual susceptibility and exposure time to nanoparticles leads to acute and chronic pathological manifestations that include the systems respiratory as cardiovascular, lymphatic, autoimmune, neurologic, and various cancers that can manifest instantly following exposure or many years later as a result of bioaccumulation [152] and unique nanoparticles properties [145,153,154].

Modified-release nanopesticides can be categorized into two groups: pesticides that are chemically linked, and others, which are physically incorporated formulation of the pesticide, activated at once after delivery in agriculture

### **7.2.1. Solid nanoparticles as nanopesticides :**

A number of nanoparticles have been recommended as potential candidates both as nano carriers as well as operational pesticide agencies or biological pesticides, because of intrinsic antibacterial/pesticidal properties.

### **7.2.2 Inert dusts as insecticides :**

The mechanism of activity of stable dusts such as silica, alumina, and clay is due to the destruction of the waxy coating on the insect's epidermis by surface assimilation and scraping. This destruction trigger insects to dehydrate, dry out and die. Because the mechanism of action is physical, it is difficult to acquire insect resistance [155].

### **7.2.2.1. Silica :**

The utility of silica based nanoparticles (SNPs) for controlling pests in agricultural is reasonably recommended because silicon has the capacity to escalate the resistance of plants to abiotic and biological stresses [156]. The deadly effects of unstructured water loving, and oil loving SNPs to the rice weevil *Sitophilus oryzae* were studied by [157] and found that they were much more helpful and efficient than bulk silica. No new infections were detected after depositing for period of 60 days. Silica particles are physically absorbed by lenticular lipids that destroy the protective cuticle and destroy insects purely by physical means with a similar mode of action observed on diatoms particles used for protection of stored grain [156, 158]. In addition, modified hydrophobic surface-charged silica (3-5 nm) have been fruitfully used in veterinary medicine to control a wide range of essential agricultural and animal ectoparasites [159]. The fungal growth was decreased and germination of seeds was promoted by effective application of surface charged silica as a thin film of seeds [160]. The metabolic process of certain agricultural crop groups and horticultural plants does not get affected by the superficial application of NPs to the leaves and stem. They do not encourage any modification in gene expression in insect organs, so they deserve approval as nano pesticides. Additionally, World Health Organization (WHO) declared the utilization of unstructured silica as a nanopesticide risk free for human consumption. In traditional pesticides these SNPs also serve as carriers. Comparison to small amounts of chlorfenapyr, the biological effectiveness was enhanced by loading the insecticide chlorfenapyr into dispersed SNPs [161]. This is assigned to the nanoscale size and intrinsic insecticidal activity of SNPs. In addition, it has been reported that porous hollow SNPs can safeguard the fleeting insecticide avermectin from UV degradation and liberate it for a long time. SNP carriers have been observed to promote the sustained release of avermectin for approximately 30 days [162].

### **7.2.2.2. Diatomaceous earth (DE) :**

DE is comprised predominantly of unstructured silica originated by decomposing small sized plants under high temperature and pressure. These are employed to safeguard stored grain from pest insects. It has deleterious effects on grain properties especially on bulk density because it is required in high doses. Researchers are engaged to integrate DEs with other insecticides to attain high efficiency, so as to make it effective in low doses. For example, combination of DE and plant decoction bitterbarkomycin was used to control grain

pest *Rhyzopertha dominica*, and was recorded to be efficient at low dose concentration of 150 ppm [163].

### **7.2.3 Alumina :**

Nanostructured alumina (NSA) was recognized as a successful insecticide in case of grain pests, *S. oryzae* (L) and *R. dominica* (F) by [164]. They also collated NSA formulations against a foremost traditional DE commodity and declared their formulation to be efficient. NSA dusts manufactured using a modified glycine-nitrate combustion process were reported to be more effective against, *S. oryzae* (L) and *R. dominica* (F) in the recent research. The results revealed that, key factors determining insecticidal efficacy are dimension of particle, surface area, and external features. However, these are not believed to be only factors responsible, and to attain superior outcomes for specific species, there is need to improve preparation pathways [165].

### **7.2.4 Clays :**

Nanoclays are fine layers of silicate minerals with following dimensions (thickness 1 nm and width 70–150 nm). Source of nanoclays is montmorillonite clays, which are mostly found in volcanic ash, formed by size reduction and surface modification and are biocompatible and have less hazardous associated. Among these living materials anionic clays are found to be most promising. They have fruitfully served as conveyor for the  $\alpha$ -naphthalene acetate, which is regulator for growth in plants and for the restrained liberation of the 2,4-dichlorophenoxyacetate. Natural antibiotic cinnamate, which is utilized for pest management, is susceptible to quick deterioration in soil and is required in significant concentration. It was declared that by loading it on double layered hydroxide low pace liberation of the antibiotic and prolonged longevity in the soil is achieved [166]. This indicates the outstanding potential of nano-clays to be used for low pace/target specific dissemination of pesticides and fungicides.

### **7.2.5 Innovative-Nanoformulation Encapsulating Pesticides:**

Encapsulation is a process of surrounding one biologically active ingredient with the intention that the core confined material or into capsule walls can be released to the environment under specific conditions over a predetermined time or when external stimuli activate the capsule

walls to break, melt or dissolve slowly. In the formulation, the active ingredient into nanocapsule is chemically bound or physically adsorbed in a matrix by different techniques, to be later released by chemical bonds cleavage or by physical diffusion.

There are distinct reasons for nanoencapsulation of pesticides between them to combat loss of efficacy due to evaporation, degradation and leaching, and increased activity due to better interaction with the pathogen, insects, weeds, and other pests. However, there also are reasons to consider the pros and cons of using pesticides in nonencapsulated systems. If, on the one hand, the agrochemical companies' current focus is on laying down the crop regardless of the best condition, on the other hand, up-to-date research about innovative materials systems stimuli-responsive at the light, pH, temperature, enzyme, and others has been reported for agrochemical extending release, targeting delivery, decreasing the usage amount, and reducing leaching and drift, and improving the utilization efficiency of the pesticide [\[167,168,169,170\]](#).

Innovative and controlled release formulations are described as depot systems; this means that there will be a delay between the delivery time of encapsulated nanopesticide in the crop and the start of the AcI release process, which is different from a conventional formulation in which a burst of AcI release will occur at once after the delivery of formulation in the crop. Therefore, either for the depot system or immediate another, the desired effect will only be noted when the minimum effective concentration is achieved [\[171\]](#). Under depot system conditions, a very high loading rate benefits are controlled release for an extended period and reduction dosing frequency to every five months. In addition to prolonging the activity of the nanopesticides, the required application amounts are several orders of magnitude lesser than the conventional formulation [\[172\]](#). Innovative nanotechnologies aim to reduce the indiscriminate and abusive use of conventional pesticides and ensure a safe application. Grafted target nanoparticle formulations for environmental stimuli-responsive are currently the uppermost technological advance for the safe use of pesticides and new ways to provide nanopesticides innovative material.

### **7.3.Nano herbicide :**

Nanoherbicides are composed by applying the nanotechnological potential for effectual delivery of chemical or biological pesticides with the help of nanosized preparations or

nanomaterials - grounded herbicide formulations. Nanomaterials or nanostructures materials - grounded formulations could ameliorate the efficacy of the herbicide, enhance the solubility and abate the toxicity in comparison with the ceremonial herbicides , Early weed control with the use of nanoparticle-based herbicide release systems could reduce the herbicide resistance potential, maintain the activity of the active ingredient and prolong their release over a longer period [173]. The development of specific herbicide molecule encapsulated with nanoparticle aims at specific receptors present at the root of the targeted weed. The developed nanoparticle enters the root system of the weed and gets translocated to perform its action which in turn inhibits the glycolysis of the plant root system. The targeted action creates starvation of the plant and thus kills it. These nanoherbicides could also be used in rain-fed areas where herbicides get dissipated through vapourisation due to insufficient soil moisture. With the help of controlled release of herbicides via encapsulation, the weeds can be utterly destroyed. Apart from herbicides, adjuvants normally used to enhance the herbicidal activity are currently claiming to include nanomaterials. A glyphosate-resistant crop was reported to be made susceptible to glyphosate upon addition of a nanotechnology-based surfactant on to a soybean micelle. Nanoparticles can act as good carrier and also can form nanoformulation when added with herbicides. These nanoformulations assist in overcoming the main drawback of herbicide industry such as evolution of herbicide resistant plants. The nanoparticle systems for herbicide delivery are mostly composed of polymeric substances which are biodegradable with non-toxic metabolites.

### **7.3.1. Polymeric nanoparticles :**

Among the various types of nanoparticles used for formulating nanoherbicides, polymeric nanoparticle prepared either in the form of nanospheres or nanocapsules, is the most attractive form. Poly(epsilon caprolactone) is one polymer repeatedly used for the encapsulation of atrazine herbicide. Poly(epsilon caprolactone) possesses good physico-chemical properties along with enhanced bioavailability and biocompatibility. The polymeric nanoparticles containing atrazine herbicide were prepared and were characterized for size, polydispersity index, pH and encapsulation efficiency. The stability of the nanoparticles was found to be for a period of 3 months. The nanoparticle formulations reduced the mobility of the herbicide in soil but enhanced its herbicidal activity in comparison with free atrazine [174]. When tested against target plant, Brassica sp., the polymeric nanoparticles encapsulated with atrazine were proven effective. In another study, Grillo et al. [175] used the polymer for encapsulated three

triazine herbicides such as atrazine, ametryn and simazine to reduce the environmental impact caused by them. The encapsulated polymeric nanoparticles of triazines possessed better association efficiency over 84%. The nanoparticles were found to have stability of size, zeta potential, pH and polydispersity for nearly 270 days. The triazine herbicide formulations revealed that the nanocapsules release the triazine via controlled release by relaxing the polymeric chains in vitro release experiments. The polymeric herbicide nanoparticles showed relatively less genotoxicity in *Allium cepa* chromosome aberration assay.

Alginate/Chitosan (Ag/Cs) nanoparticles were chosen for the encapsulation of paraquat herbicide [176]. This polymeric complex has simple preparation methods adding further to their alternative use in agricultural applications. The Ag/Cs nanoparticle carrier system showed significant difference in the release profiles of free paraquat and the herbicide nanoparticles. The herbicide nanocarrier has altered the interaction of the herbicide in soil and indicated the effective means of averting the negative impacts of the herbicide induced by paraquat herbicide. Soil sorption studies with Ag/Cs herbicide paraquat nanoparticles exhibited dependence on the quantity of present soil organic matter. The enhanced interaction of paraquat released from Ag/Cs system in comparison with free paraquat revealed the effective of these polymeric nanoparticles as an excellent choice for eliminating the herbicide usage-associated ill effects. In a different study, the paraquat herbicide was encapsulated onto chitosan/tripolyphosphate nanoparticle and was proved efficient with this polymeric nanoparticle system as well. The herbicidal efficiency of paraquat was not found reduced even after encapsulated with very less toxicity. Cell culture viability tests and *Allium cepa* chromosomal aberration tests testified to the increased safety of the polymeric herbicide systems against non-target organisms [177]. Few works reported till date on polymeric nanoparticles encapsulated with herbicide provides a safe basis for using herbicides by reducing the adverse environmental impacts caused by them on human health as well on the environment.

### **7.3.2. Inorganic nanoparticles:**

Silica dioxide nanoparticles (SiNP) were explored as inorganic herbicide carriers in the recent past for active substances which are pH sensitive. These SiNPs maintain optimal herbicide concentrations with accompanied reduction in frequency of herbicide consumption rate. These systems protect and stabilize the herbicide and reduce their wastage with easy deposit on the plant leaves. Rani et al. [178] stated the possible use of silica nanoparticles as herbicide

carriers via a dynamic adsorption mechanism and sustained release. Though hypothesized, the use of SiNPS as herbicide carrier is yet to be explored in means of leaching behaviour, controlled release and toxicity.

#### **7.4.Nano fungicide :**

Nano-scale materials development has seen considerable progress in the recent years, with distinct characteristics from corresponding bulk materials.

Nanotechnology promises a bright future while delivering pesticides in a safer manner

[179]. Agrochemicals have enhanced solubility when polymeric Nano fungicide formulations deliver them at a slow rate, thus increasing their bioavailability [180, 181]. Nanofungicide developed and tested so far proved effective in plant protection strategies [182, 183]. For developing Nano fungicides, we should opt for Nano emulsions (NEs) with smaller size, lower viscosity, and higher stability [184]. The active fungicide ingredient is placed within a core surrounded by a membrane in a nanocapsule.

Additionally, nanoencapsulation could be utilized in nanopesticide formulations. Polymers and inorganic compounds have been tested for their possible use in nanopesticide formulations for crop protection [185]. For these formulations to be as potent and stable as possible, while still meeting the safety criteria of the systems to the environment and human beings, it is critical that more work be done. Nanotechnology has a large capacity to develop completely new systems and formulations [186].

##### **7.4.1. Mechanism of nano fungicide :**

A promising nano-fungicide should possess an equivalent or superior activity corresponding to the bulk metal at relatively lower concentrations. Moreover, it is desirable to understand the phyto and eco-toxicity issues due to the release of metal ions. Multifarious mechanisms were involved in the antifungal activity executed by nanomaterials. The antifungal activity of nanomaterials can be accomplished by the following events. Generally, fungal cell wall and cell membrane architecture involves chitin, lipids, phospholipids and polysaccharides with specific predominance of mannoproteins,  $\beta$ -1,3-d-glucan and  $\beta$ -1,6-d-glucan proteins [187]. Internalization of the nanomaterials occurs through three mechanisms; (i) direct internalization of nanoparticles in the cell wall, (ii) specific receptor-mediated adsorption followed by internalization, (iii) internalization of nanomaterials through ion transport

proteins [188]. Post-internalization, the nanomaterials may inhibit the enzyme  $\beta$ -glucan synthase thereby affecting the N-acetylglucosamine [N-acetyl-d-glucose-2-amine] synthesis in the cell wall of fungi. As a consequence of enzyme inhibition, abnormalities like enhanced thickening of the cell wall, liquefaction of cell membrane, dissolution or disorganization of the cytoplasmic organelles, hyper-vacuolization, and detachment of cell wall from cytoplasmic contents indicating incipient plasmolysis might occur [189].

At the molecular level, the nanomaterials interact with various biomolecules and form complexes with different biomolecules thereby causing structural deformation in the biomolecules, inactivation of the catalytic proteins, and nucleic acid abnormalities like DNA breakage, and chromosomal aberrations [190,191]. Reactive Oxygen Species (ROS) play a critical role in antifungal activity mechanism of nano-composite materials. The metal ions trigger ROS and damage the biomolecules leading to cell death. Further, to authenticate the role of ROS in antifungal mechanism; Lipovsky et al. [192] deciphered that the increased expression of lipid peroxidation is a clear indicator of ROS generation. Meanwhile, stress enzymes like superoxide dismutase, glutathione dismutase, ascorbate peroxidase were upregulated/downregulated upon nanomaterials treatment in fungi [193].

### **7.5.Nano-insecticides:**

Food is a basic need for rapidly growing human population and subsequent worldwide demand for food has urged for a better protection of agricultural crops from infestation by different insects. Compared to bulk substances, nano-insecticides have following advantages such as enhanced efficiency of natural and chemical insecticides by controlled release, less environmental contamination due to reduced rate of application, easy and safe handling, more susceptible to photo degradation and less toxic to non-target organisms compared with bulk. Polymer-based nano formulations have been exploited for the encapsulation of most of the insecticides.

Different kinds of polysaccharides such as chitosan, alginates, starch and polyesters (e.g., poly- $\epsilon$ - caprolactone and polyethylene glycol) have been considered for the synthesis of nano-insecticides [194]. Different forms of polymer and non-polymer based nanoformulations like nanoparticles [195], nanofibres, nanogels, nanosphere, micelles, nanoemulsions, and nanocapsule have been exploited for encapsulation of insecticides [196]. Among these, nanocapsules are by far the most widely used for controlled release of insecticides.

Nanoformulation of many natural insecticides (e.g. neem oil) is also used [197]. Currently

increasing awareness of environmental pollution leads to the sophisticated use of biodegradable and biocompatible polymers of natural origin over the synthetic ones for encapsulation.

***\*Challenges of Using Nano Insecticides :***

One of the main challenges encountered by scientists in the formulation of commercial-grade nanopesticides is that encapsulated nanoformulations are unstable when exposed to UV radiation. Also, some of the nanoformulations using azadirachtins are genotoxic and have cytotoxic effects in plants. However, researchers observed that these adverse effects could be reduced during plant development under sunlight.

Some nanomaterials, such as multi-walled carbon and zinc, negatively affect the germination index of ryegrass and some vegetables like tomatoes. Nanomaterials are safe at the optimum size, but they might become toxic and non-biodegradable at a particular threshold size. Therefore, it is essential to analyze the toxicity profile of new nano-based formulations before application.

**8.Interactions of nanoparticles with plants :**

Nanoparticles have gained considerable attention in recent years by researchers due to their small architecture and their small size due to significant advances in biomedical, diagnostics and delivery of biomolecules in the cells[198].The delivery system of agricultural organic molecules, including the transport of DNA molecules or oligonucleotides into plant cells, are important aspects of sustainable agricultural production as well as precision farming [199].NPs have structures that can be described as materials in the nano-size range. Materials of this size are also found naturally in the environment but the widespread applications and use of different metal NPs in our daily existence are releases directly or indirectly in the surrounding environment [200]. Chemically synthesized NPs referred to as engineered NPs due to their unique size, shape and properties of the surface [201].NPs are released into the natural system, which interacts with aquatic and terrestrial plants through the atmosphere, water and soil. The NPs interactions are through the uptake, translation and accumulation in the plant species [202]. Different types of nanomaterials such as Au, Ag, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, Cu, CdS, Fe<sub>2</sub>O<sub>3</sub>, Fe, SiO<sub>2</sub>, TiO<sub>2</sub>, Zn, ZnO, ZnSe reports their impact on plant physiology and the development of plants [203].Methods in genetic engineering have changed with the NPs for improvement and made significant in agricultural production, crop protection [204].Si NPs directly interact with plants

and affects the plant and physiology and morphology including the structural color as well as help to improve the yield and growth of plants. At the physiological level, salinity stress significantly increased root ion leakage and decreased relative water content (RWC), stomata density and Hill reaction, while application of ZnO NPs improved the Hill response and reduced ion leakage of *Brassica napus* L. plants [205]. Si-NPs was also killed bacterial, fungal and nematode growth infections so disease resistance agents [206].

## **9. Phytotoxicity of nanoparticles :**

In the present time, NPs are used in a variety of consumer products such as cosmetics, wound dressings, clothing and more. After the final use of NPs products, they are being completely dumped into water bodies like rivers and soil. Due to which there is a lot of damage to the environment. Aquatic and terrestrial plants are also exposed to NPs, causing toxic effects in many plant species. The toxicity of MgO and ZnO nanoparticles at concentrations of 250, 500, or 1000 mg L<sup>-1</sup> for *Citrus maxima* to evaluate the potential of their use as nano-fertilizers, in which ZnO nanoparticles produced low-level toxicity in plants [207]. Airborne NPs have a tendency to attach to leaves and other aerial parts of plants, while roots contact NPs through waterborne or soil materials. NPs penetrate the leaf surface of plants from the bases of trichomes or via stomata and are then transported to the tissues of the plant. NPs deposition has a tremendous impact on the biodiversity of plant species in the ecosystem [208]. Plant growth and antioxidant defense responses differ from plant species. Some studies have shown that toxicity to NPs can also cause differences in seed, size and xylem composition of single-leaf and double-leaf plants [209]. MnOx NPs were treated on the germination of *Lettuce sativa* seeds in a hydroponics medium. MnOx NPs reduced the germination percentage (84% from control to 63%) at high concentrations of 50 mg L<sup>-1</sup> and were not significantly different from controls. Furthermore, MnOx NPs significantly improved the development of seeding by increasing root elongation [210]. Higher plants try to interact very strongly with their atmosphere and terrestrial environment. These interactions are expected to be influenced by the plant being exposed to different NPs [211]. ZnO NPs were shown to induce oxidative stress in the concentrations of 500 mg L<sup>-1</sup> in seedlings of *Glycine max* plants. Plant growth, root hardness and root cell viability were clearly affected by the ZnO NPs strain [212]. The photosynthetic parameters were changed throughout the development period in cucumber plants. Treating CeO<sub>2</sub> and CuO NPs with 200 mg/ L reduced seedling leaf size compared to control, but when mature leaves were measured there was no significant difference between treatments and control [213]. Treatment of TiO<sub>2</sub> NPs

had a positive effect on the germination of aged spinach seeds as well as the growth rate of transplanting [214]. Two different plant species were treated with ZnO NPs at concentrations of 2000 mg L<sup>-1</sup> and the root elongation of the plant was significantly reduced [215]. The phytotoxicity and genotoxicity were investigated by treating Ag NPs in germinating wheat seedlings. It was observed that 10 mg L<sup>-1</sup> Ag NPs caused all kinds of changes in the protein, which led to cell metabolism of plants [216]. In the aquatic plants, growth of *Hydrilla verticillata* was inhibited in the early stages after treatment with ZnO NPs with a high concentration of 1000 mg mL<sup>-1</sup>, but *Phragmites australis* indicated a decline in plant growth rates after a few weeks of exposure. High concentrations of ZnO NPs caused significant phytotoxicity in aquatic plants [217]. It is also well known that phosphates are widely present in our Earth's atmosphere and are used as most elements of many types of culture media for toxicity testing. A recent study was confirmed that the phytotoxicity of CeO<sub>2</sub> NPs to Romaine lettuce plants was determined by phosphate in sand culture media [218]. The toxicity of Cu NPs was investigated in hydroponic culture media in 10–15 days old Alfalfa and Lettuce seedlings. The size of the plants and the nutrient content of the tissues were significantly decreased, while the activity of the enzyme was altered in both plants .

A possible mechanism of phytotoxicity of Ag NPs, which is absorbed by the root surface, disrupted the structure of the thylakoid membrane and reduced the chlorophyll content, an inhibitory effect on the *Arabidopsis thaliana* plant [219]. The phytotoxicity of Al<sub>2</sub>O<sub>3</sub> NPs was investigated dependent on concentrations on the root growth and development of *Triticum aestivum* plants. Root elongation was decreased with an increase of NPs concentrations and decreased total protein content, increased peroxidase activity and accumulation of lignin and damage the root cortex of plants [220].

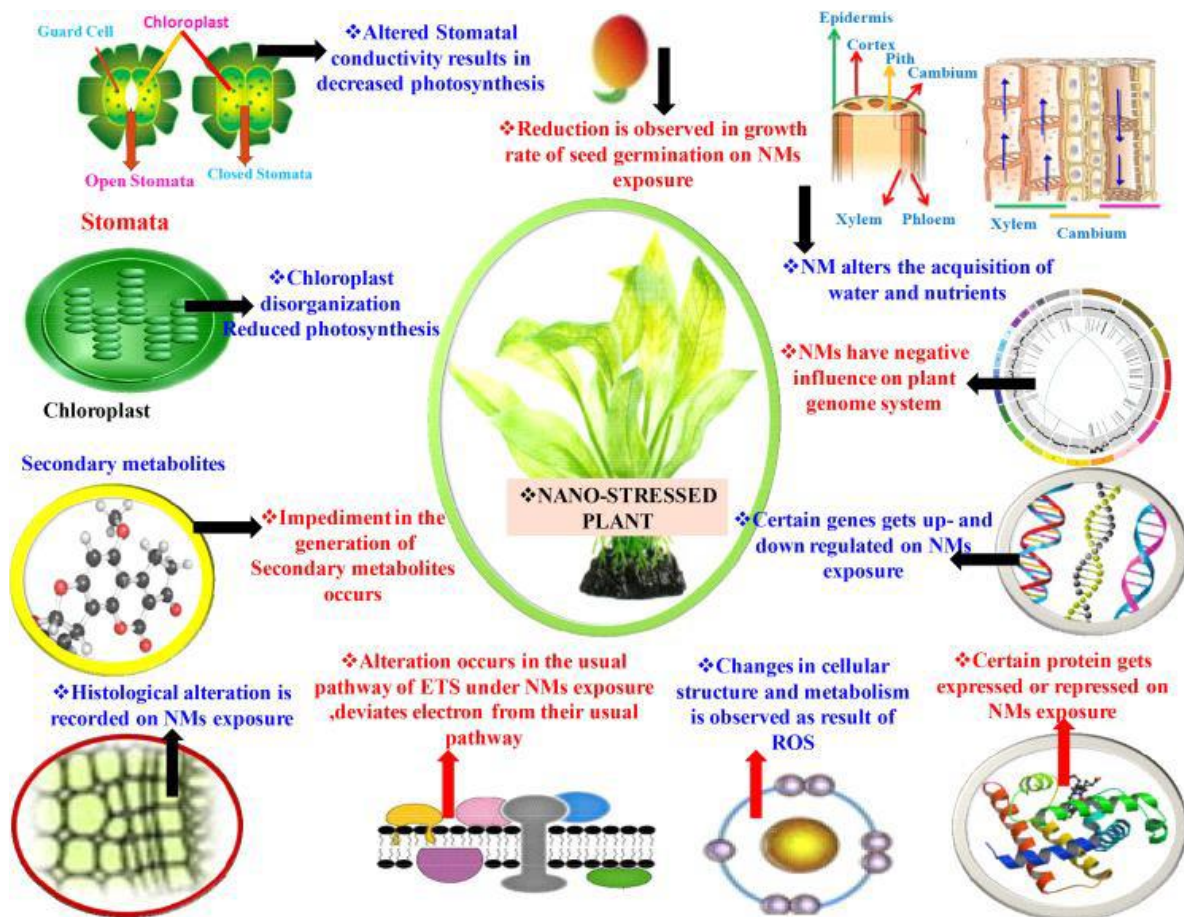


Figure 8: Phytotoxicity of nanoparticles at the cellular level (Tripathi *et al.* 2017) [223].

# Experimental Party

## Chapter 2 : Materiel and Methods

### 1. materiels:

#### 1.1. lab materiels :

To carry out our experiment, we used the following equipment :

- Glass Petri dishes (9cm) to carry out Digestion and Repulsion test
- A precision scale to weigh the semolina for the digestion test
- A graduated pipette (10ml volume);
- Filter paper
- Beaker to dissolve nanoparticles in distilled water
- burette 10 ml for dosimetry
- Ultra sound device to help in dissolving nanoparticles in water
- 5 spray bottels

#### 1.2. Biological material

- semolina
- warehouse insects ( *J. du Val. Tribolium confusum* )
- ZnO nanoparticels

## 2.methods:

- We brought insects of equal age and mass
- Effect of ZnO nanoparticles on the insect.

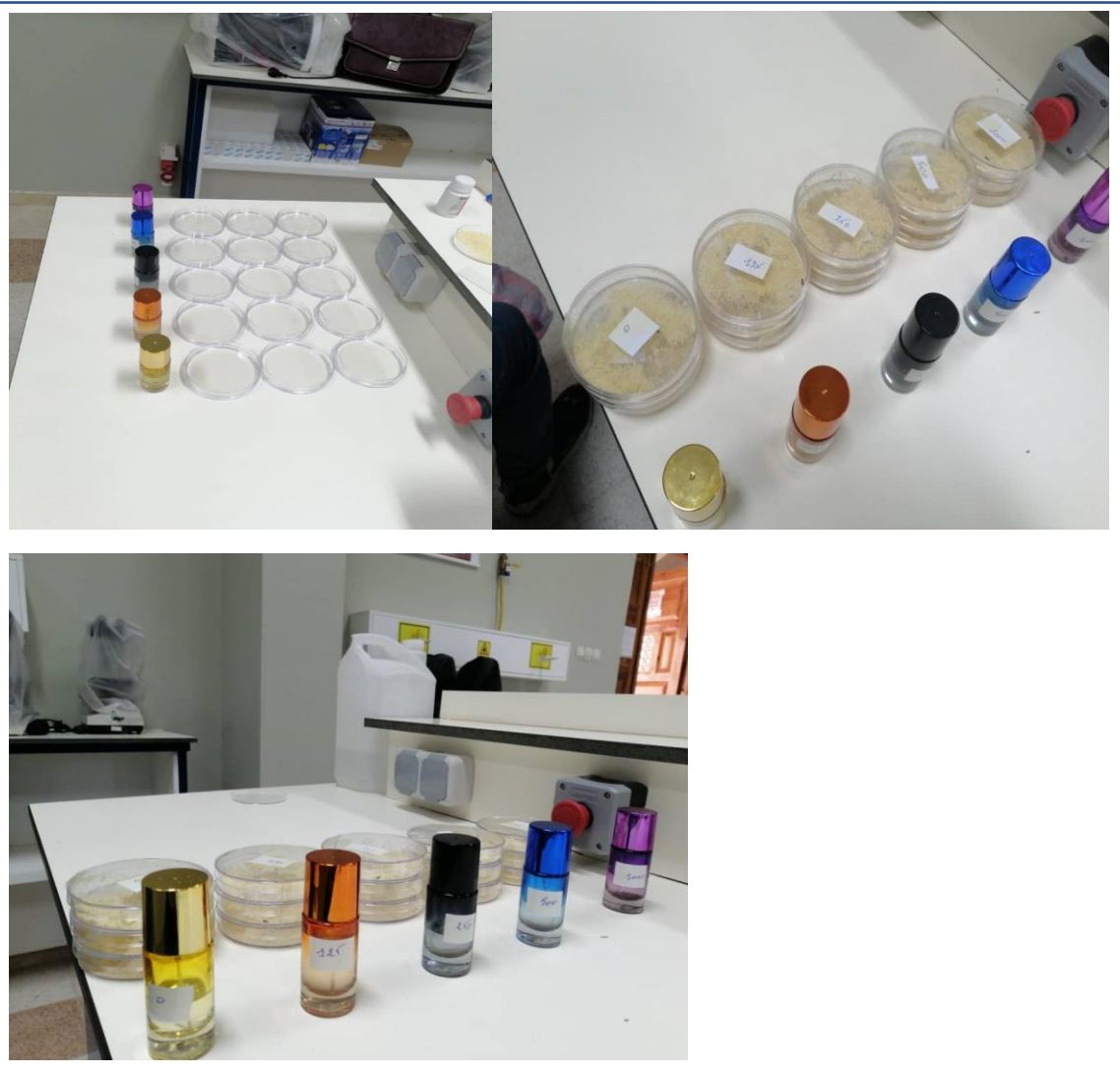
To test the insecticidal activity of ZnO nanoparticles on the *Tribolium confusum*, we carried out two toxicity tests by digestion and repulsion .

### 2.1 digestion test :

The digestion test is carried out in 9cm diameter glass Petri dishes. each dish carries 3 g of semolina, treated with ZnO nanoparticles , different doses: 1000 ppm . 500.ppm . 250 ppm . 125 ppm . 0 ppm . using the sprays .

- three repetitions are carried out for each dose and for the control.
- All the Petri dishes are maintained under temperature conditions of 27°C to 28°C

### Duration of the study : 48 h



**Figure 9 :** digestion test of ZnO nanoparticles on *Tribolium confusum* insects

## 2.2. Repulsion test :

This test makes it possible to know if the ZnO nanoparticles is repellent or attractive for the Insects of *Tribolium confusum* using the preferential zone method.

The technique consists of cutting into two equal halves discs of filter paper

having a diameter equal to the diameter of the Petri dish; one half receives doses of the ZnO nano particels

doses :

-1000 ppm

-500 ppm

-250 ppm

-125 ppm

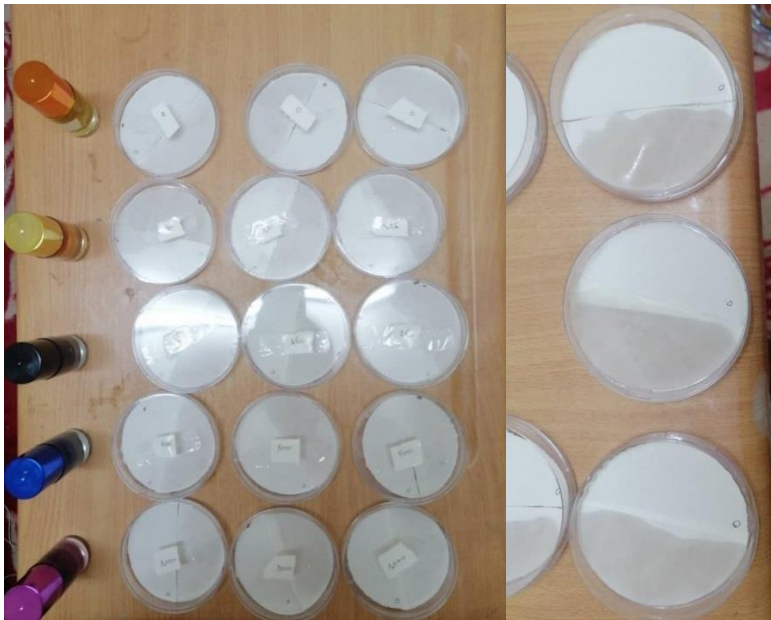
-0 ppm

\* By three repetitions of each dose.

and the other half receives nothing.

Add two insects to each Petri dish.

Test duration equals 12 h.



**Figure10** : Repulsion test of ZnO nanoparticles on *Tribolium confusum* insects

## RESULTS AND DISCUSSION

### 1. Insecticidal activity of ZnO nanoparticles by ingestion

#### Mortality Evaluation :

In both bioassays, mortality evaluation was carried out 24, 48, after treatment. The laboratory bioassay was evaluated with a magnifying glass. . The number of surviving and dead insects was recorded in which a insect was considered dead, when not responding to a stimulus, appendages detached from to the body, and/or was dehydrated.

- Experiment starts at 11 am

\*After 12 hours, we notice the death of an insect from the box with a concentration of 1000 ppm

\*After 24 hours, we notice the death of three insects from the boxes with a concentration of 1000 ppm

\*After 30 hours we notice the death of one insect from the box with concentration 1000 ppm

\*After 24 hours, we notice the death of two insects from the box of concentration 500 ppm

\*After 30 hours, we notice the death of two insects from boxes with a concentration of 500 ppm

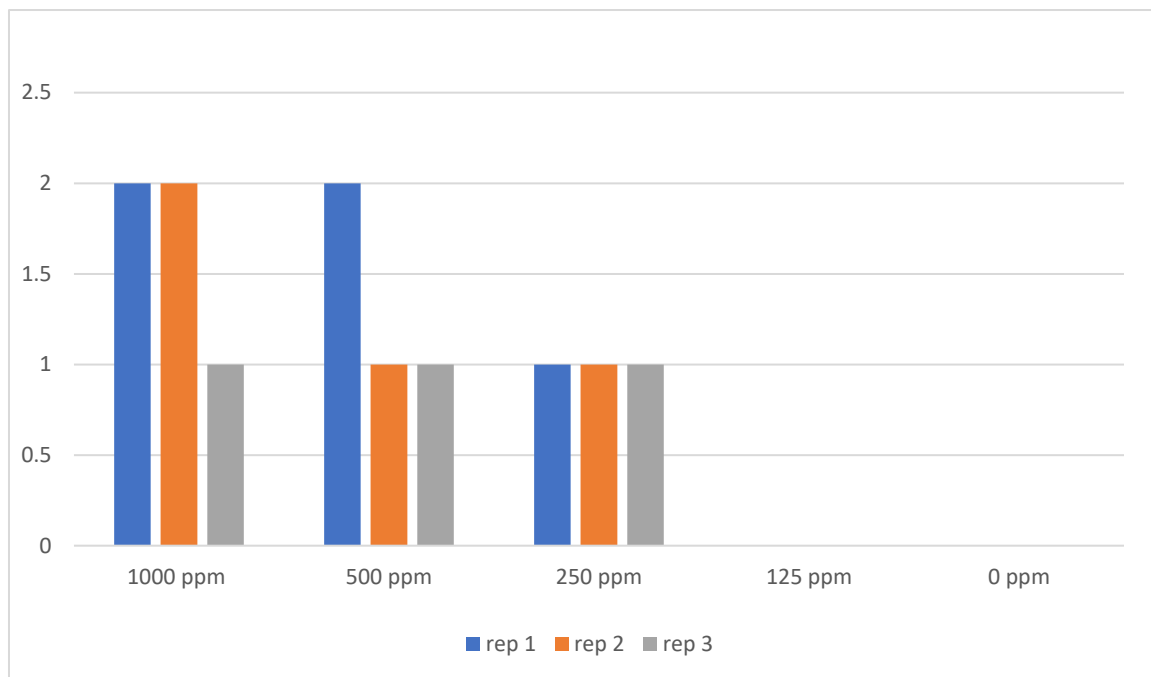
\*After 30 hours, we notice the death of 3 insects from boxes with a concentration of 250 ppm

-We noticed that no results appeared on insects that had boxes with concentrations 125 ppm and 0 ppm.

The results obtained for the action of ZnO nanoparticles on toxicity for Insects of *Tribolium confusum* are shown in Figure and table

	1000 ppm	500 ppm	250 ppm	125 ppm	0 ppm
Object 1	2	2	1	0	0
Object 2	2	1	1	0	0
Object 3	1	1	1	0	0

**Table 2 :** Number of dead insects per dose



**Figure 11 :** Graph represent Number of dead insects per dose

### Discussion :

ZnO nanoparticles that we tested seem to have an insecticidal effect on the the insects of . *Tribolium confusum*. These results are consistent with the work of many researchers who demonstrated the action of ZnO nanoparticles on stored food pests.

And the high doses are very important for the effectiveness of the ZnO nanoparticles

Insecticidal activity of the synthesized ZnO nanoparticles revealed that values of (1000 ppm and 500, respectively) had significant lethal effects on *Tribolium confusum* insect . Statistical results showed a significant difference between concentrations of ZnO nanoparticles at all doses .

## 1. Insecticidal activity of ZnO nanoparticles by Repulsion:

Experience starts at 12 pm

Over time, we notice in box No. 1 in concentration 1000 ppm that there are two insects on the side treated with nanoparticles

In box No. 2 in concentration 1000ppm, there are two insects on the treated side

In box No. 3 in concentration 1000ppm, there are two insects on the treated side

Box No. 1 in Concentrate 500 ppmThe presence of two insects on the treated side

Box No. 2 in Concentration 500 ppmThe presence of one insect on the treated side

Box No. 3 in concentration 500ppm The presence of one insect on the treated side

Box No. 1 in concentration 250 ppmThe presence of one insect on the treated side

Box No. 2 in concentration 250ppm The presence of one insect on the treated side

Box 3 in concentration 250ppm The presence of one insect on the treated side

Box No. 1 in concentration 125ppm The presence of an insect on the treated side

Box No. 2 in concentration 125ppm The presence of two insects on the treated side

Box No. 3 in concentration 125ppm The presence of an insect on the treated side

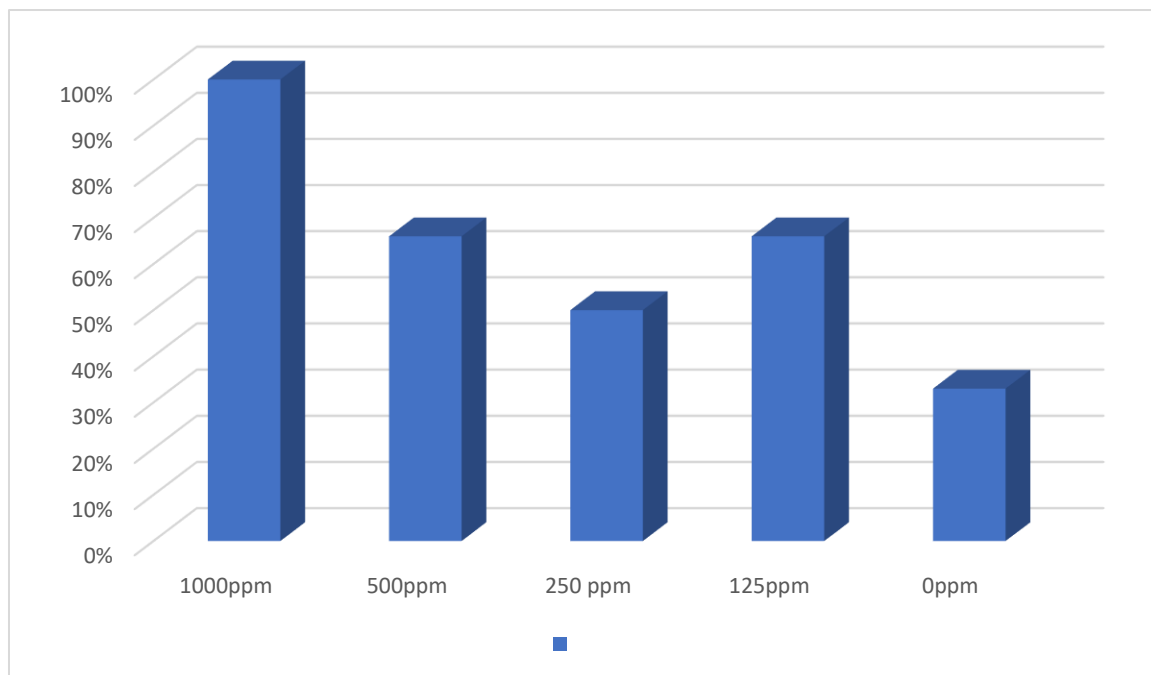
Box No. 1 in concentration 0ppm There are no insects on the side treated with water alone

Box No. 2 in concentration No. 0 ppmThere is one insect on the side treated with water alone

Box No. 3 in Concentration No. 0ppm There is one insect on the water-treated side

	1000ppm	500ppm	250ppm	125ppm	0ppm
Rep 1	2	2	1	1	1
Rep 2	2	1	1	2	0
Rep 3	2	1	1	1	1

**Table 3:** Number of insects attracted to the treated side



**Figure 12:** Percentage of insects attracted to the treated side

**Discussion :**

The results of the experiment on *Tribolium confusum* insects show that ZnO nanoparticles have an attractive effect for this type of insects. And it was different from what we expected it to be.

Experiment has proven that nanoparticles have attractive and not repellent properties, despite their toxicity to insects.

- We do not rule out that this distribution of insects was random, despite the fact that the nano-material is toxic to them .

Large concentrations of nanoparticles are suitable for attracting *Tribolium confusum* insects up to 500ppm .

Dilute concentrations of nanoparticles are weakly effective.

## Conclusion

Nanotechnology is a recently arising, but highly expanding technology in numerous fields related to human activities and benefits worldwide. Its fascinating phenomena have been witnessed through several research findings that the nanoparticles and nanostructure ameliorate various properties due to small size, larger surface area, and highly catalytic nature. Nanotechnology is pivotal in achieving food security, especially in the agriculture sector. It can ameliorate crop production by effective microbial, pest, and weed control with high economic value, security, and safety.

Green styles for synthesizing nanoparticles with plant extracts are benefic as it's simple, convenient, environment friendly and require lower reaction time. Nanomaterials prepared byeco-friendly and green styles may increase husbandry potential for ameliorating the fertilization process, plant growth regulators, pesticides delivery of active element to the desired target sites, treatment of wastewater and also enhancing the absorption of nutrients in plant. In addition, they minimize the amount of dangerous chemicals that pollutes the environment. Hence, this technology helps in reducing the environmental pollutants.

Nanotechnology has lately gained attention due to wide operations in different fields similar as in agriculture medicine and environment. The large surface area offered by the tiny nanoparticles, which have high surface area, makes them attractive to address challenges not met by different control methods.

In conjunction with information on the agriculture production system, nanotechnology demands a solid understanding of science as well as of production and material technologies. The severity of this task can draw talented brains into a career for agriculture. To succeed in this sector, human resources.

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