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Environmental and Biological Effects of Improper Use of Nano-Fertilizers

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Abstract: Nanofertilization is a promising new method that could increase crop yields while decreasing the use of pesticides. Nanomaterials are extremely reactive because of their small size and large surface area. Several questions have been raised about the compatibility and contrast of these materials. Concerns have been expressed about the safety of farm workers using these products. This includes not only people who are exposed when nano fertilizers are made, but also people who are exposed when they are used in the field. While nano fertilizers may have some useful applications, further study is needed to establish how best to apply them and how much each plant or crop needs. Soil and biological systems can become more polluted at a faster rate due to the use of nanotechnology. So, we have an immediate duty to stop the harm that nano-fertilizers could do to people and the environment if they are not used correctly. With this review, we intend to address several concerns regarding the use of nano fertilizers. The appropriate usage of these chemicals requires substantial knowledge and specialized investigations before their application in agriculture to minimize their harmful effects on human health and the environment.

Key words: Nano-fertilizers; Nanoparticle accumulation; Nanotoxicity.

التأثيرات البيئية والبيولوجية للاستخدام غير السليم للأسمدة النانوية

الملخص: يعد التسميد النانوي طريقة جديدة واعدة يمكنها زيادة إنتاجية المحاصيل مع تقليل استخدام المبيدات الحشرية. المواد النانوية شديدة التفاعل بسبب صغر حجمها ومساحة سطحها الكبيرة. لقد أثيرت العديد من الأسئلة حول مدى توافق هذه المواد وتباينها. وقد تم الإعراب عن مخاوف بشأن سلامة عمال المزارع الذين يستخدمون هذه المنتجات. وهذا لا يشمل فقط الأشخاص الذين يتعرضون عند تصنيع الأسمدة النانوية، ولكن أيضًا الأشخاص الذين يتعرضون عند استخدامها في الميدان. في حين أن الأسمدة النانوية قد يكون لها بعض التطبيقات المفيدة، إلا أن هناك حاجة إلى مزيد من الدراسة لتحديد أفضل السبل لتطبيقها ومقدار ما يحتاجه كل نبات أو محصول. يمكن أن تصبح التربة والأنظمة البيولوجية أكثر تلوثًا بمعدل أسرع بسبب استخدام تكنولوجيا النانو. لذا، يتعين علينا أن نعمل على وقف الضرر الذي قد تلحقه الأسمدة النانوية بالناس والبيئة إذا لم يتم استخدامها بالشكل الصحيح. من خلال هذه المراجعة، نعتزم معالجة العديد من المخاوف المتعلقة باستخدام الأسمدة النانوية. ويتطلب الاستخدام المناسب لهذه المواد الكيميائية معرفة كبيرة وإجراء تحقيقات متخصصة قبل تطبيقها في الزراعة لتقليل آثارها الضارة على صحة الإنسان والبيئة.

1. Introduction

Organic and chemical (industrial) fertilizers are the two main types of agricultural fertilizers, and both are used to increase crop yields by providing the plant with the nutrients it requires to grow and thrive **(Mustafa, 2018)**. Many countries, including Iraq, have turned to nano-fertilizers because their populations are growing, especially in developing countries, and they need more food, especially food that is clean and good for the environment. Also, agricultural fertiliser derivatives pollute the environment and are hard to store **(Osreer and Hussain, 2011)**

Nano fertilisers؟

It is the same as traditional fertilisers, but the particles' sizes have been reduced to that of nanometers, which is equal to one billionth of a meter. As a result, the fertilizer's behavior changes in regards to how quickly it moves in the soil solution and within the plant, how readily it is absorbed by the roots, how readily it is sprayed onto the leaves, how readily it enters the plant via the stomata, and how much is lost to runoff **(Nair *et al.*, 2010)**. Nano-fertilizers may benefit plants, but they nearly always have unintended consequences for the plant, its surroundings, and the species farther up the food chain. According to the findings of certain studies, it is harmful and may accumulate in the plant, particularly in the edible sections like fruits and seeds, where the nanoparticles are absorbed and dispersed throughout the tissues. Nanoparticle accumulation in the offspring of fertilized tomato plants is one such example **(Ali and al-Jawthari, 2019)**.Our goal in conducting this study was to further our understanding of fertilisers and their use in agriculture by learning more about the unfavourable and hazardous effects that may occur from using them incorrectly and the extent to which they impact society. This was done because of the issue of nano-fertilizers and the lack of knowledge about them, which only highlighted their benefits.

The concept behind nanomaterials

It is vital to have an understanding of the notion of nanomaterials in order to have an understanding of nano fertilizers. So, what exactly are nanomaterials؟

Nano is a Greek term meaning dwarf since Nano signifies a lack of size **(Raab *et al.*, 2011)** . The term "nanoscience" refers to the research and development of materials and devices with dimensions on the nanometer scale and their corresponding qualities. Moreover, nanotechnology is the use of scientific and engineering ideas to create tiny tools and products. Nanoscience and technology may be characterized as follows:

Nanotechnology is the branch of science, technology, and engineering that lets us directly control atoms, molecules, materials, structures, and devices with sizes of 100 nanometers or less by using techniques like close observation, detailed analysis of properties, and precise fabrication **(Monreal *et al.*, 2016) (Bhardwaj *et al.*, 2019)**.

The function of Nano fertilizers in plant growth

1- Boosting the activity of the photosynthesis processes (by increasing the content of chlorophyll in leaves) **(DeRosa *et al.*, 2010; Moghaddasi *et al.*, 2017; Thavaseelan and Priyadarshana, 2021)**.

2- Enhancing the capacity of plants to tolerate a variety of environmental stresses, including salinity, drought, and others **(Al-Mamun *et al.*, 2021)**.

3- Strengthening plant defenses against **disease (Neme *et al.*, 2021)**.

4- Protecting the diversity of plant genetics that is essential for agriculture.

5-Boost the plant's bioactive compounds **(Bhardwaj *et al.*, 2022)**.

6-There are already more than 800 fertilizer products on the market, and their number is only anticipated to rise over the next few years; their active material is the nano-form, the oxides of microelements.

7- For plant nutrition, there are also about 5615 nanoforms of various elements present in fertilizer products.

8-Traditional fertilizers are also given a nanomaterial coating to improve their absorption and efficacy **(Mastronardi *et al.*, 2015; Zahra *et al.*, 2022)**.

2. Current research on the use of nano-fertilizers in farming (the positives)

Physiological, morphological, and genetic responses to elements or nano-fertilizers vary by kind of nano-element, chemical characteristics, type of plant, and growing medium. Some nano-elements promote growth, germination, and photosynthesis, while others do the opposite and alter the growth rate and the quality and quantity of the plant's production. A study indicated that spraying nano-fertilizer on cucumber leaves at 2.0, 3.0, and 4.0 L/ha-1 increased plant production **(Ekinci *et al.*, 2014)**. In addition, spraying 500, 250, and 25 g/palmy of nano-fertilizer on Zaghloul palm trees promoted the growth of palm fruits **(Read *et al.*, 2016)**. It was found that after 150 days of introducing the nano fertiliser, growth, mineral content, enzyme production, and active substance production in the leaves of the moringa olefera plant were all positively affected by the presence of nano iron, ghrelin, and organic fertiliser. The maximum levels of nitrogen, phosphorus, potassium, calcium, and active chemicals were all attained after being treated with nano iron, and other desirable growth features also increased significantly **(Al-Khlifawi, 2017) .** On the maize plant, researchers looked at what happened when nutrients and nano-amino acids were sprayed directly onto the leaves. They came to the conclusion that it might be possible to enhance the production of yellow corn by spraying it with nano-N.P.K (microelements and amino acids) and increasing the amount of potassium, iron, and copper in the grains. They also looked at the amount of chlorophyll in the plant and how it grows and makes food **(Al-Zerijawi, 2020)** . In another study, spraying leaves with nano-silicon-based fertilisers led to the highest mean amount of chlorophyll in the leaves (38.28 spad units), which was measured by the combination of nano fertiliser and grain content (silicon). Many productive characteristics, including plant height, dahlia length, dahlia grain number, biological yield, and other characteristics, were shown to be the highest in the integrated yields **(Al-Khuzaie, 2020)** .

2.1 Nano fertilizers are categorized into three primary groups:

1. Fertilizer on a Nanoscale (It is composed of nutrient-rich nanoparticles.)

2. Additives on the nanoscale (contains both a coating and traditional fertilizer)

3. Coating at the nanometer scale (this includes nanoparticle-coated or nanoparticle-loaded fertilizers) **(Mahaletchumi, 2021) .**

2.2 Examples of Different Types of Nano fertilizers

Important nano-fertilizers include, but are not limited to, the following:

a- Nano-NPK. It contains the three essential elements for plant growth; nitrogen, phosphorus, and potassium.

b- Nano Phosphorus Fertilizer. There are a few distinct types of nano phosphorus fertilizers:

1- TSP (Triple Super Phosphate).

2- DAP (diammonium phosphate)

3- MAP (Mono ammonium phosphate)

c- Nanosilica as a fertilizer

d- Titanium nanoparticles as a fertilizer

e- Zinc oxide nanoparticles as a fertilizer

f- Copper oxide nanoparticles a fertilizerg- Carbon nanotubes as a fertilizer, or what is known as carbon nanotubes **(Husen and Iqbal, 2019) .**

2.3 Nano fertilizer sources

1- Natural, including extracts of certain plant species

2- It is composed of organic components and is covered with nanoparticles.

3- Industrial, as it is created using nanotechnology-based specialized crushers

According to their applications, nanomaterials can generally be categorized as:

i- Passive Application Nano Materials

ii- Active Application Nano Materials **(Al-Saadi, 2020).**

3. Nanotechnology and Nano Fertilizers: Potential Dangers

The use of nano-fertilizers in agriculture and their application to broad agricultural regions poses concerns for human health and the environment. Size, shape, solubility, crystal stage, type of material, method of exposure, and dose concentration are all things that many nanoparticles that could be harmful to human health have in common. Currently, nanoparticle-containing food products are likely safe to consume, according to experts, but additional research and investigation of the facts are necessary for this area. Scientists need to examine and develop ways of measuring the impact of nanoparticles and nano fertilizer on the biotic and abiotic elements of ecosystems. Nanoparticle buildup in soil and plant tissue, especially in parts that can be eaten, is a major concern that could affect agriculture **(Ali and al-Jawthari, 2019; Kalwani *et al.*, 2022; Zulfiqar *et al.*, 2019)** .

The majority of current beliefs concerning the interactions between nano-organisms and living things for nano-biological interactions are theoretical and need to be supported by carefully designed studies because nanotechnology is still in its infancy. Nano-or biological-scale interactions are particularly crucial**.**

1- Cytotoxicity (cytotoxicity)

2- Geno toxicity (mutagenicity)

3- Accumulation within cells and accumulation between cells

4- Apoptosis and necrosis: DNA fragmentation

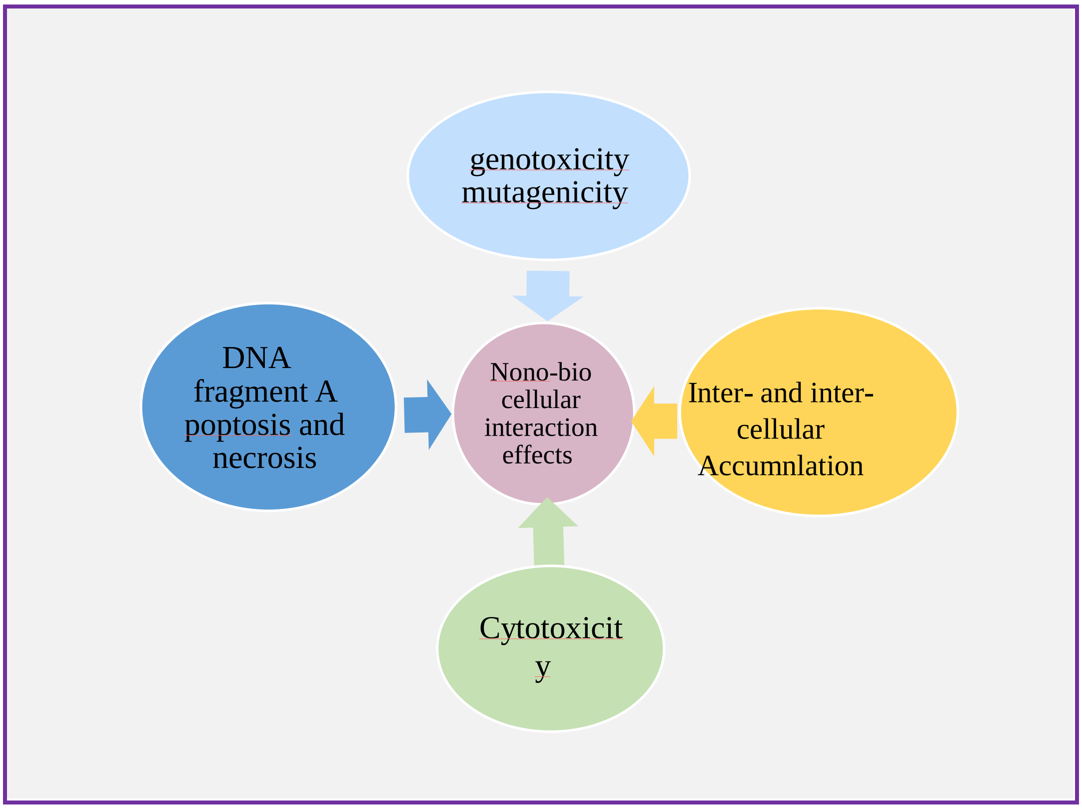

Fig. (1). Shows Nona-bio cellular interaction

To date, there hasn't been a lot of research on the effects of nanomaterials on living things beyond lab tests.

Let's begin by discussing the toxicity of nanoparticles to humans. Nanomaterials can get into the body in three ways: through the skin, by breathing (and getting stuck in the lungs), or through the digestive system **(Al-Saadi, 2020)**.

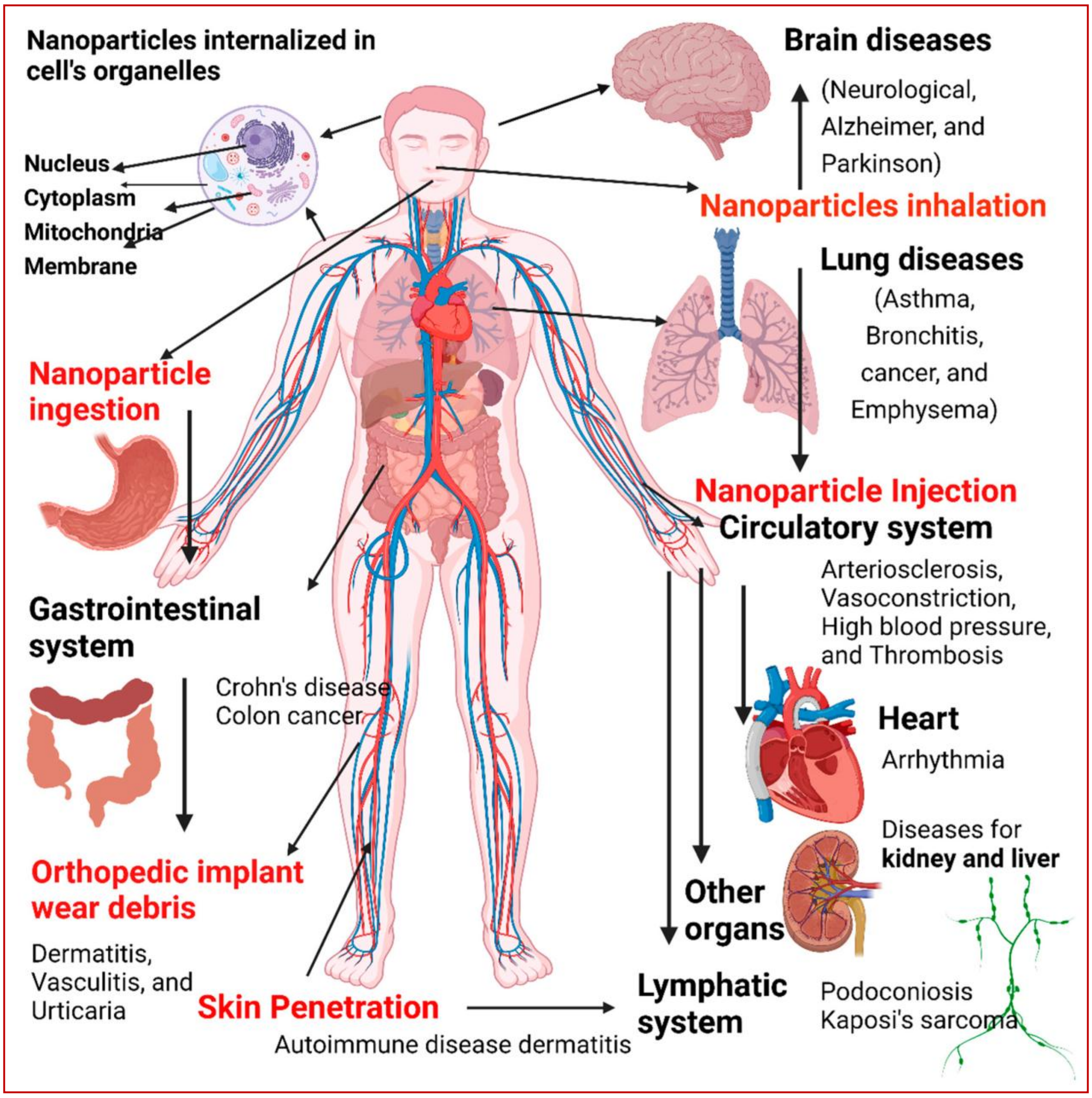

Fig. (2). Shows the pathways of the human body that can be exposed to nanoparticles

3.1 Nanomaterials' toxicity to animals

The research was conducted to determine whether or not nanoparticles are hazardous to animals. A 2010 study on mice by Liu *et al*. discovered that the toxicity of three different types of nanomaterials—silver (Ag), zinc oxide (ZnO), and titanium oxide—depends on their size, shape, chemical composition, and dose—and may result in oxidative damage to the spleen immune system. In another study on mice, it was discovered that 200 mg/kg of nano-zinc oxide (ZnO) had a mild influence on the liver, kidneys, heart function, and sperm vitality, whereas exposure to high doses of nano-zinc had a substantial effect on male mice and produced alterations in kidney, liver, and heart functions, as well as sperm stenosis and distortion **(Brohi *et al.*, 2017; Liu *et al.*, 2010).**

Another study of animal development and reproduction found that females are more sensitive to nanoparticle toxicity and that the toxicity may have an effect on foetal development and reproduction. They found that when mice are injected with 100 micrograms of TiO2 nanoparticles smaller than 300 nanometers on days 3, 7, 10, and 14 of their pregnancies, nanoparticles of TiO2 get into the baby. They observed the transmission of Au, TiO2, and Si molecules through the placenta to the foetus in the testis, Sertoli cells, and sperm, resulting in foetal weakening, and pregnant animals inhaling nanoscale cadmium had negative effects on the baby **(Brohi *et al.*, 2017)**.

Several studies have found that the toxicity of nanoparticles is caused by high levels of reactive oxygen species (ROS). ROS attacks animal organs and causes oxidative stress, which leads to severe damage and apoptosis, as shown in Figure 3 **(Khann *et al*., 2015; Manke *et al.*, 2013; McShan *et al.*, 2014)**.

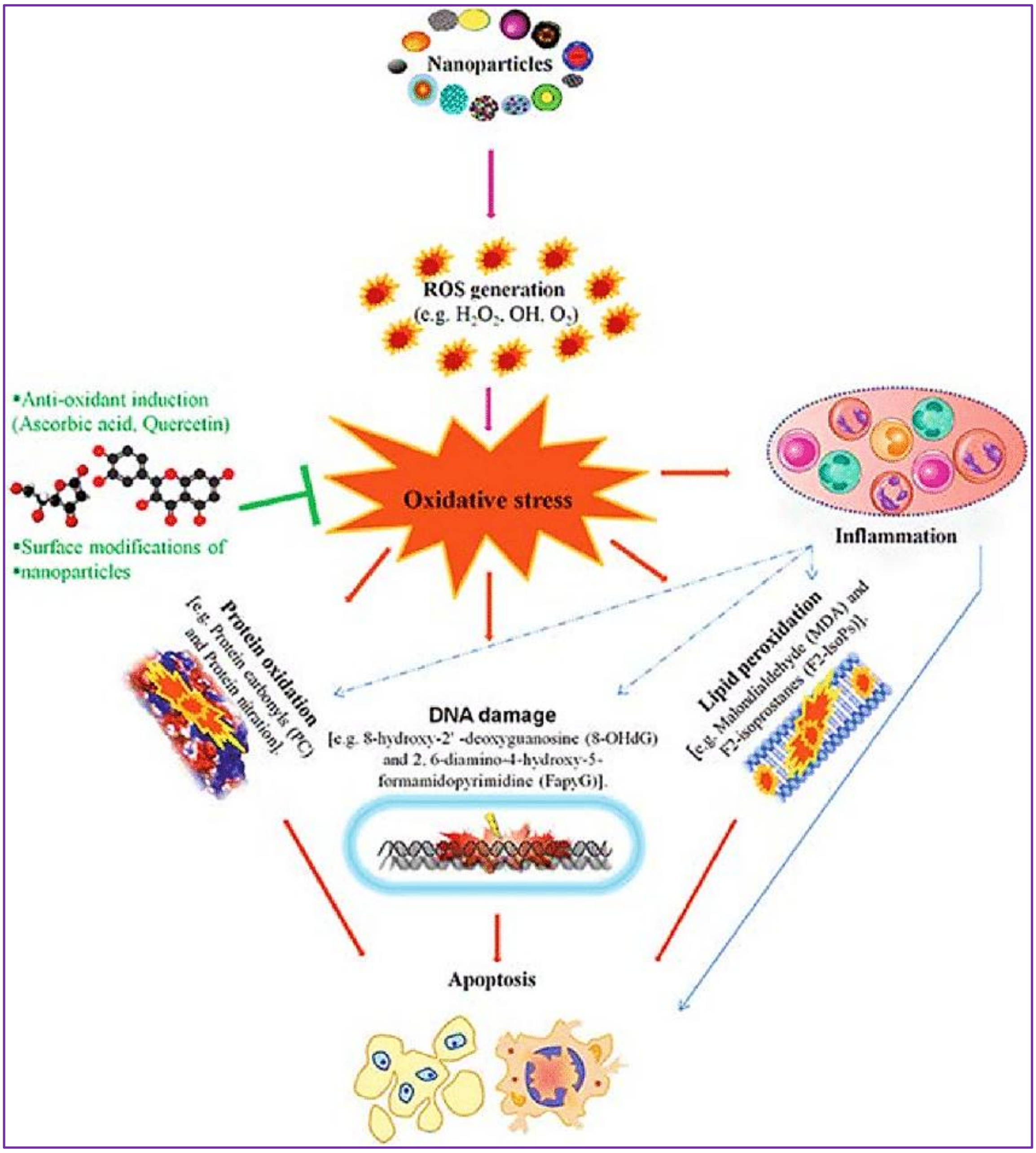

Fig. (3). Shows nanotoxicity caused by free radical overproduction and oxidative stress(Khanna *et al.*, 2015)

Also, some nanoparticles are bad for the blood cells, the liver, the lungs, the eyes, the skin, and the reproductive system. Nanoparticles are most damaging because they accumulate in non-target tissues. This can take place as a result of oxidative stress, genotoxicity, or toxic effects on the blood **(Elalfy *et al.*, 2018)**. Recent research suggests that supplementing cattle feed with seNps may have unintended consequences such as weight loss.A variety of selenium species undergo chemical transformations or are incorporated into selenoproteins, leading to an elevated risk of death **(Bano *et al.*, 2022)**.

3.2 Nanomaterials' potentially toxic effects on plant life

Unavoidable consequences for plant life can be seen when NPS nanoparticles are present in the environment. Nanomaterials can be taken up by the surface in one of two ways: either directly by the material itself, or indirectly by the material's chemical or physical surroundings. It is possible that NPS accumulates in the seeds of plants and is passed on to the next generation of that species. Toxic effects from nanoparticles (NP) may develop in plants grown from seeds with an NP concentration greater than the bio-concentration. Protecting plants from abiotic stressors is a function of NPS due to its ability to increase photosynthesis and mimic the action of antioxidant enzymes. Depending on the plant species and the concentration of nanoparticles (NPS) extruded into the growing medium, the presence of NPS can also have harmful effects. Seed germination, root and shoot development, plant biomass, and nutrient concentration are all influenced by the presence of NPS. Research is being undertaken to examine nanomaterials' interactions with plants. However, their impact on plant physiology and functioning is uncertain **(Al-Saadi, 2020 and Husen & Iqbal, 2019)**.

Monitoring the influence of nanomaterials on plants is vital for maintaining the safety of agricultural products. Zinc oxide nanoparticles were applied to onion seeds at concentrations of 0, 10, 20, 30, and 40 mg/mL in one study to observe their effects on germination and cell division. As demonstrated, both low and high concentrations of nano zinc oxide impaired seed germination and were related to a decrease in the mitotic index (MI) and an increase in defective chromosomes **(Raskar and Laware, 2014).** According to studies investigating the negative effects of silver ions (Ag+ ions, AgNO3, and silver nanoparticles (AgNps) on development and biochemical parameters, the total phenol content of lettuce sativa seedlings exposed to silver ions (Ag+ ions, AgNO3, and silver nanoparticles (AgNps) increased by 18%. Ions of silver hindered seedling development by 40% while raising flavonoid content by 12%. It was shown that silver ions are more harmful to lettuce seedlings than silver nanoparticles and that silver nanoparticles at moderate concentrations stimulate lettuce seedling growth, while high concentrations have an inhibitory effect due to the release of silver ions **(Hasan *et al.*, 2021)** The effects of nano-TiO2 nanoparticle application on the germination and early growth of five distinct species of desert plants were tested at 0 ml/l, 10 ml/l, 100 ml/l, 500 ml/l, and 1500 ml/l. At the highest dose, germination decreased from 88% to 72%. In addition, the root length reduced from 13.85 cm to 10.68 cm in high levels, although it had no effect on the plant in low quantities. The study showed that nanoparticle users should be cautious about the dosage to prevent creating plant toxicity **(Kamali *et al.*, 2021)** .

3.3 Environmental consequences of nanofertilizer misuse

The uncontrolled usage of nanoparticles as well as the introduction of nanoparticles into soil ecosystems both have the potential to alter the microbiological composition of the soil. Due to the unique physicochemical qualities of metal-based nanoparticles, such as a surface charge, a large surface area, reactivity, and very small size, these particles have the propensity to interact with the organic matter that is present in the soil, in addition to the microbes that are necessary to the plant and soil ecosystems. Furthermore, metal-based nanoparticles have several interesting physicochemical features. It is possible that the characteristics of the soil, in addition to the size of the particles, have a role in influencing the behavior of nanomaterials and, as a direct result of this behavior, the interactions that these materials have with microorganisms and plants. The chemical characteristics of nanoparticles may be affected by environmental factors such as the pH level, ionic strength, organic matter content, and phosphate concentration of the soil **(Ameen *et al.*, 2021 and Dimkpa, 2018)**. When the pH drops too low, dissolution may occur, leading to the creation of reactive oxygen species, which can be dangerous. The stability of nanoparticles in the soil is caused by how they react with natural organic matter. This interaction may change the surface chemistry, which may affect the soil's bacteria and plants. On the other hand, the microorganisms' actions and processes may influence the behavior of nanoparticles.

The impacts that Nano fertilizers have on the microbial population in the soil are also contingent on the types of soil and the physicochemical conditions of the soil. The pH of the soil is one of the most important factors to consider while trying to understand the behavior of nanoparticles in the soil. When the pH is low, zinc oxide nanoparticles change into ions more quickly. When the pH is high, the nanoparticles tend to stick together **(Read *et al.*, 2016)**.At pH levels ranging from 4.5 to 7.2, the majority of the nanomaterials were shown to be toxic to the microbial community .Higher microbial diversity in saline-alkali soil was found to benefit from zinc oxide nanoparticles more than in weakly acidic soil in a study of four nanomaterials (zinc oxide nanoparticles, titanium dioxide nanoparticles, cerium dioxide nanoparticles, and magnetite nanoparticles). The effects of ZnO nanoparticles on soil microbial enzyme activities were shown to be greater in acidic soil than in calcareous soil **(You *et al.*, 2018).** Although calcareous soil is excellent at absorbing metals, it has a much more deleterious effect on microbial catabolism than acidic soil **(García-Gómez *et al.*, 2018).** In a separate study by Shah *et al.* (2014), they examined the composition of the soil microbial community in response to four nanomaterials (silver, titanium oxide, zinc oxide, and zero-valent copper). According to the findings of this research, zinc oxide and zero-valent copper oxide did not play a significant role in the shifting of the microbial community structure. Instead, silver nanoparticles were the cause of the changes in the microbial community **(Shah *et al.*, 2014)** .The silver nanoparticles (550 mg/kg) did not have a harmful effect on microbes, but they did increase the number of diazotrophic bacteria such as Bradyrhizobium, Nitrospira, and Nitro[1] sovibrio. **Asadishad *et al.* (2018)** found that nanoparticles of copper oxide, zinc oxide, and silver are toxic to soil microbes at concentrations between 1 and 100 mg/kg, but nanoparticles of titanium oxide are not toxic at these levels **(Asadishad *et al.*, 2018)**.

Even though using nanoparticles in agriculture has a lot of potential, it is essential to find ways to stop them from building up and posing risks to human and environmental health. This is because there is a significant potential to profit from the incorporation of nanoparticles into agricultural practices; however, to do so, the appropriate procedures need to be created first. This new area of research has already reached some crucial goals and opens the door to new possibilities **(Zulfiqar *et al.*, 2019)**. Still, further research is required to determine the particular interactions between nano fertilizer and the naturally present soil bacteria and fungi and to examine the potential negative impacts that nano fertilizers may have on the beneficial properties of the soil for these microorganisms. Nanoparticles and free metal ions in the earth, as well as how they interact with bacteria, should be the focus of future research. To find out if different concentrations of metal-based nanoparticles in real soil are good or bad, safe design processes should be made to reduce the amount of interaction between nanoparticles and good soil microbes.

4. Conclusion

Using nanoparticles as nanofertilizers can increase crop yields in the face of climate change by improving plant nutrition and stress tolerance; however, not all nanomaterials will be risk-free in every situation. Several concerns need to be answered about the impact that nanofertilizers have on the surrounding ecosystem as well as the potential dangers that they could bring to both human health and the environment. This must occur before commercial use of Nano fertilizers can begin. The goal of future research should be to fill in the gaps in our understanding of areas that have received less attention. This will assist in opening up new avenues of potential in the field of sustainable agriculture. It is then imperative that researchers investigate the safety of the numerous nanoparticles employed in the production of nanofertilizers. More research is also needed to find out if it is possible to use nanofertilizers safely. Additionally, before any suggestions can be made regarding the use of nanofertilizers with a particular crop and soil type, the effects of nanofertilizers on soils with varying physical and chemical characteristics must be thoroughly investigated. This is since the physical and chemical properties of soils can vary substantially.

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