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Chapter

Enhancing the Productivity of Field Crops through Nano-Fertilizer

Rahul Sadhukhan, L. Devarishi Sharma, Suman Sen, Snehashis Karmakar, Koushik Banerjee and Kirtiranjan Baral

Abstract

The growth of agricultural sectors can be maintained by increasing crop productivity through soil, water, and nutrient management. The most important management practice is nutrient management, which is supported by the effective use of nano-technology, especially nano-fertilizers. It is well known that nano-fertilizers are nutrient carriers of nano dimensions ranging from 30 to 40 nm (10^{-9} m or one-billionth of a meter). Due to their high surface area, they can hold abundant nutrients ions and release them slowly and steadily, commensurate with crop demand. Nano-fertilizers are easily uptaken and assimilated by the plants because of their ease of solubility, stability, controlled release in time, and easy mode of delivery and disposal. Due to nano fertilizers characteristics, different commercial products are available in the market, namely *Nanogro*, *Geohumus*, *NanoGreen*, and *Lithovit High Yield fertilizer*, which can be demonstrated among the farmers for increasing agricultural performance through soil and nutrient management. Besides, nano-fertilizer has good criteria like disease resistance properties. Nanoparticles of ZnO, CuO, and MgO can kill different fungal infections of crop plants. Though nano-fertilizers can be beneficial for improving agricultural performance, it has a detrimental effect on soil microflora, fauna, animals, and humans. It is associated with several diseases or hazards like high blood pressure, blood clots, stroke, arrhythmia, heart disease, etc. Nano-fertilizer also improves the yield of several field crops like pearl millet, wheat, pomegranate, onion, tomato, soybean, and vegetable crops like spinach and cucumber. Nano fertilizers also have sound capabilities to find the solution against the issues arising in modern agriculture due to conventional fertilizer application. Thus, nano-fertilizer has the potential to improve the yield of several field crops.

Keywords: nano-fertilizers, commercial products, fungal infection, disease, disease resistance, surface area, cereal and vegetables, solubility, stability and controlled release

1. Introduction

Increasing population growth and shortage of available land & water resources are significant concerns for food-saving agriculture. Potential agricultural growth can be achieved through productivity improvement through soil, water, and nutrients

management, assisted by the successful use of new technologies such as nano-fertilizers. Nano-fertilizers are those preparations with nano-dimensional nutrient carriers ranging from 30 and 40 nm (10^{-9} m or one billionth of a meter). They can retain sufficient nutrient ions because of their large specific surface area and slowly or gradually release them in exact amounts meeting crop requirements [1]. Compared with bulk fertilizers, it has a high specific surface area, small size, and reactivity of nano-fertilizers can increase the diffusion, solubility, and nutrient availability to plants and boost agricultural productivity. Using fertilizer carriers for the construction of smart fertilizers, nano-fertilizer have presented the feasibility of exploring nano-structured materials as new facilities to increase the performance of nutrient usage and minimize environmental degradation. Micronutrients such as iron, manganese, zinc, and copper are becoming factors that improve yield and are primarily responsible for making the standard nutritional quality of food items. Once applied to the soils, they respond quickly, produce chemical precipitates, soils' organo-mineral matrix, and react with clay colloids. Micro-nutrients are substantially lost due to leaching in high rainfall regions. Thereby, the efficiency of micronutrient usage (MUE) is <5%. Micronutrient-based nano-fertilizers can increase the accessibility of particular micronutrients to crops and improve agricultural productivity [2]. Since the production and implementation of nano-fertilizers are still at an early stage, certain specific reports are published on the effects and benefits of applying micronutrient-based nano-fertilizers in the field. Any discovery in new innovative technologies to enhance agricultural productivity and the supply of nutrients might be a landmark in nano-technology research and at the beginning of the next Green Revolution. So, the main objectives of this study are

- i. To study the significance of nano-fertilizer in crop nutrition
- ii. To understand the properties and methodologies of nano-fertilizer preparation
- iii. To classify the different kinds of nano-fertilizers
- iv. To understand about the commercial nano-formulation
- v. To increase the productivity of agricultural crops
- vi. To investigate the harmful effect of nano-particle related fertilizers

Indiscriminate and massive application of fertilizers leads to the formation of a non-porous layer between the soil particles, which has a negative effect on the agricultural soil and leads to a rise in the groundwater level and salinity as well and ultimately it causes the death of the roots of the field crops by reducing the absorption of nutrient by the plants that are essential in the crop nutrition. But nano-fertilizers cut the barriers of that type of problem in agriculture [3].

Recently, our modern agriculture has been habituated by the use of high rates of chemical fertilizer. For example, the global production of chemical fertilizer is about 188.2 Mt. in 2019. It is also expected that chemical fertilizer consumption can also increase by double to feed the 9.6 billion population by 2050. Besides, applications of conventional fertilizers have low nutrient use efficiency, a high risk of environmental pollution, and a possible risk of breaking the food chain by

destroying the ecosystem [4]. So, sustainable agriculture is a new approach for the solution of recent problems. So, implementing new innovative techniques like nano-fertilizers into the farmers field may solve fertilizer application problems. That's why nano-fertilizers are gaining importance day to day to agriculture. It has several advantages, like it releases nutrients according to plant requirements. It may replace several pesticides as it has disease-resistant properties (ZnO, MgO, and CuO-based nano fertilizers).

We know that chemical fertilizers release the nutrients in 4–10 days, whereas nano-fertilizer releases their nutrients in 40–50 days; as a result, nitrogenous fertilizer from the conventional system are lost rapidly from the field through volatilization, leaching, and run-off. But we can minimize this problem by applying nano-fertilizer and improving N's nutrient use efficiency in the field [4].

2. Significance of nano-fertilizers in crop nutrition

1. Strong Stability and Solubility
2. Solid effectiveness
3. Controlled release of the nano fertilizer in time
4. Improved targeted behavior with the right concentration
5. Reduced eco-toxicity
6. Secure, uncomplicated delivery and disposal mode

2.1 Probable mode of cellular uptake of nanoparticles in a plant cell

Nano-fertilizers get into the plant system through a mechanism [5]. The mechanism is expressed in the **Figure 1**.

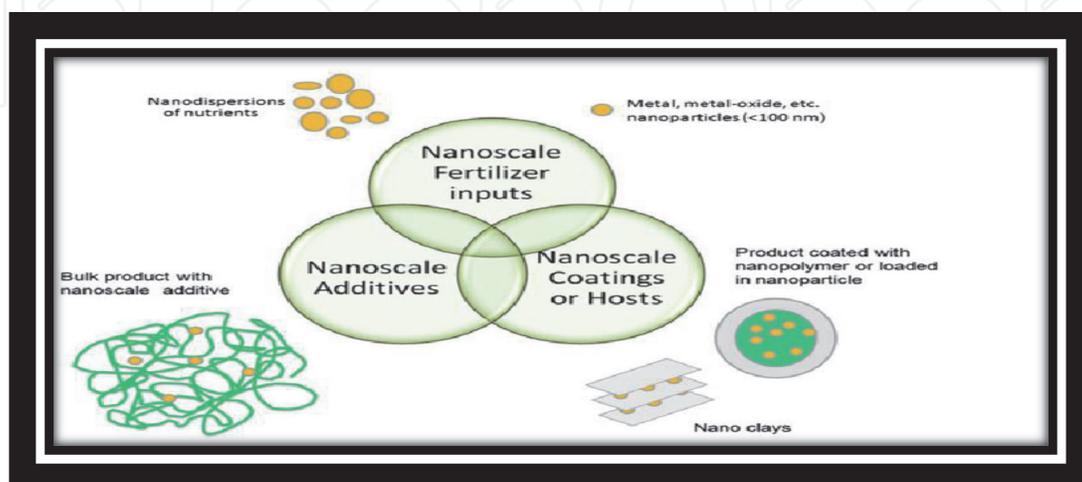


Figure 1.
Composition of nanoparticles.

3. Nano-fertilizers delivery systems

Nanoparticles can provide nutrients to particular target sites in living organisms. The preparation of nutrients based nano-particles is typically carried out by:

1. Nano-particles absorption.
2. Ligands mediated nano-particles attachment.
3. The formation of the nano-particulate polymeric shell through encapsulation.
4. Polymeric entrapment of nano-particles.
5. Self-possessed synthesis of nano-particles.

4. Principles of nano-fertilizers preparation

The dissolution kinetics of nano-particle by The Scientist Noyes-Whitney.

The dissolution rate of nano-particles of the nano-fertilizers is directly proportional to their surface area because a relatively larger interface for dissolution is available, which promotes the dissolution of dissolved ions away from the particle.

According to *the Ostwald-Freundlich principle*.

The relative solubility of a spherical particle of the same material increases as the particle size decreases in the solid-liquid system—the solubility of the particle increases when the equivalent spherical diameter is $<0.1 \mu\text{m}$.

5. Properties of polymer encapsulating nano-particle

1. Rapid-release: on contact with a surface, the capsule shell breaks (e.g., when fertilizer hits a leaf) [6]
2. Unique release: when a molecular receptor binds to a specific chemical, the shell is built to break open
3. Moisture release: in the presence of water, the shell breaks down and releases material (e.g., in soil)
4. Thermal release: the shell only releases components as the atmosphere heats over a certain temperature.
5. pH release: nanocapsule only disintegrates in particular acid or alkaline environments.
6. Slow-release: over a longer period, the capsule slowly releases its payload (e.g., for slow delivery of a substance in the fields such as nano-coated urea).

5.1 Unique properties of nano-particles (NPs)

- a. Very high specific surface area (**Figure 2** and **Table 1**)

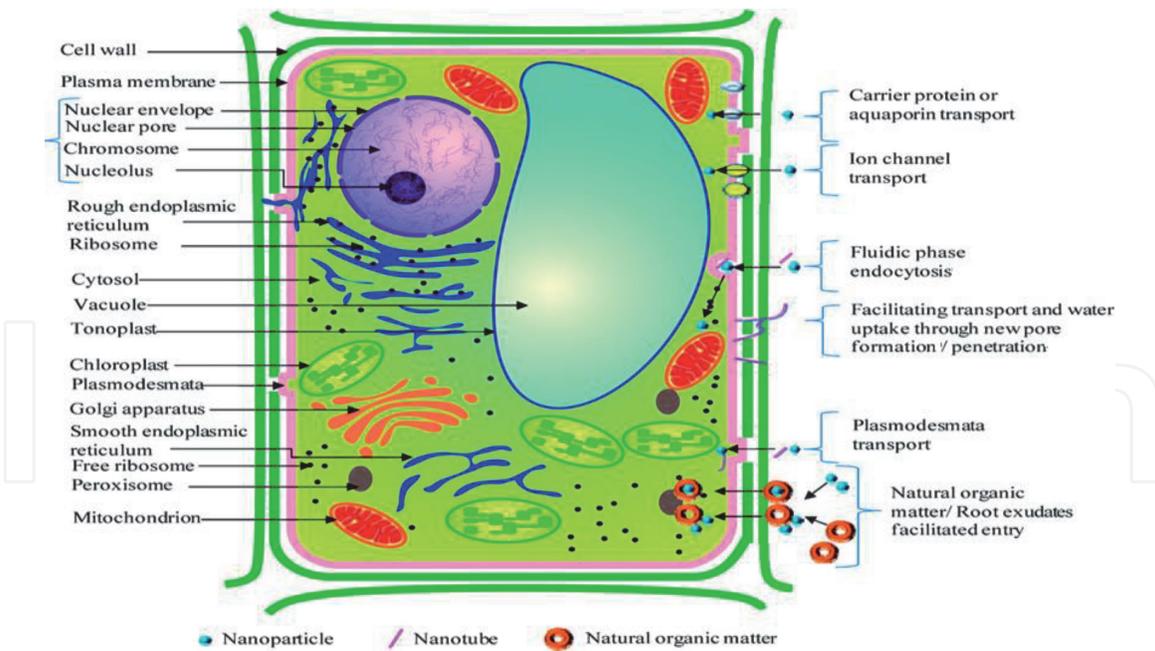


Figure 2.
 Probable mode of cellular uptake of nanoparticles in a plant cell [5].

Properties	Nano-fertilizer enabled technology
Solubility and nano-sized formulation of mineral micronutrients (MN)	Nano-sized formulation of MN improve solubility and dispersion of insoluble nutrients in soil, reduce soil absorption and fixation and increase the bioavailability
Nutrient uptake efficiency	It increase fertilizer efficiency and uptake ratio of the soil nutrients in crop production and save fertilizer
Controlled release modes	Controlled release through encapsulation in envelope forms of semipermeable membrane coated by resin-polymer waxes
Effective duration of nutrient release	It extends effective duration of nutrient supply of fertilizers in to soil
Loss rate of fertilizer nutrients	Reduce nutrient loss by reducing leaching

Table 1.
 Properties of various kinds of nano-fertilizers.

- b. High surface energy
- c. Quantum confinement

5.2 Classification of NPs

(a) Carbonaceous NPs, (b) metal oxide NPs, (c) zero valent metals and (d) nano-polymers (**Figure 3** and e.g., **Tables 2–4**).



Figure 3.
 Novel properties of nanoparticles: surface area per unit weight increases, so more atoms come on the surface to interact occurred in nanoparticles.

Nano contents	Applications
Ammonium salts (prepared through physical methods)	Ammonium magnesium phosphate containing nano-composites improved stability and slow release properties
Nano scale fertilizer particle (urea, KCl and NH ₄ Cl are prepared through emulsification, coating and shearing process)	Those help in slow and controlled release of nutrients
ZnO as agricultural trace element fertilizers	ZnO powder mixed with polymeric wetting agents and cellulose based thickening agent to efficiently uptake by plants

Table 2.
Nano-scale fertilizer inputs.

Nano contents	Applications
Bentonite clay	Nanoscale compound fertilizer additives bind soils and helps in N-fixing bacteria for improving soil fertility.
Humic acid and talc powder	Si nano-particle mixed with humic acid increases water and mineral holding capacity of soil. Reduced fertilizer use and improved crop yield
Rare earth materials (REMs)	REMs nanoparticles mixed with MgO, N, P and K improved soil fertility and control release of nutrients

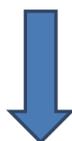
Table 3.
Nano-scale fertilizer additives.

Nano contents	Applications
Halloysite	Halloysite and other nanotubes (Dolomites) mixed nano-materials used as controlled release fertilizers.
Phosphate fertilizer containing nano-hydroxy apatite	Those help in maintaining P level in soil and reduce its loss through water.
Attapulgit	N, P and K fertilizers embedded in the nano-pores of attapulgit clay yield slow release of fertilizer nutrient.

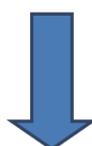
Table 4.
Nano-scale films and host materials.

6. Preparation of coated nano fertilizer granules

- i. MAP & commercial urea granules sieved to obtain 2000–3350 um and 1676–2000 um size, respectively.



- ii. Coating of MAP and Urea granules by Zn @ 1.5% by weight (by adding powder of ZnO nano particles).



- iii. Spraying of ultrapure deionized water and use of nebulizer to provide good blending agent (50 uL/min) to ZnO powder.



- iv. Coated granules are air-dried at 30% RH in the laminar flow.

7. Biosynthesis of Zn nano-fertilizers in laboratory

- i. The Fungi, *Rhizoctonia bataticola* TFR 6 (strain) taken in 250 ml Erlenmeyer flask with 100 mL Potato dextrose Broth medium (pH adjusted to 8.5) MAP= Mono Ammonium Phosphate, NUE= Nitrogen Use Efficiency, TFR 6 is a strain
- ii. After incubation, fungal mycelia separated from culture by filtration with Whatman No.1 paper
- iii. Harvested mycelia kept in a rotary shaker at 150 rpm with 28°C for 12 h
- iv. Cell-free filtrates + salt solution of ZnO with 0.1 mM concentration help synthesize Zn nanoparticles.

8. Review of literature

¹⁵N studies using maize as a model system revealed that NUE from nano-fertilizer was higher than conventional fertilizer urea [7] (**Figure 4**).

Subramanian and Sharmila Rahale [7] reported that 15 N studies which were used in maize as a model system revealed that the N use efficiency from nano-fertilizer was 82%, and the conventional fertilizer (urea) registered 42% with a net higher nitrogen use efficiency of 40%, which is hardly achievable in the conventional systems.

Bakhtiari et al. [8] also experimented during 2015 to assess the effect of Fe nano particles on yields and quality of wheat. They found that foliar spray of Fe @ 0.04%

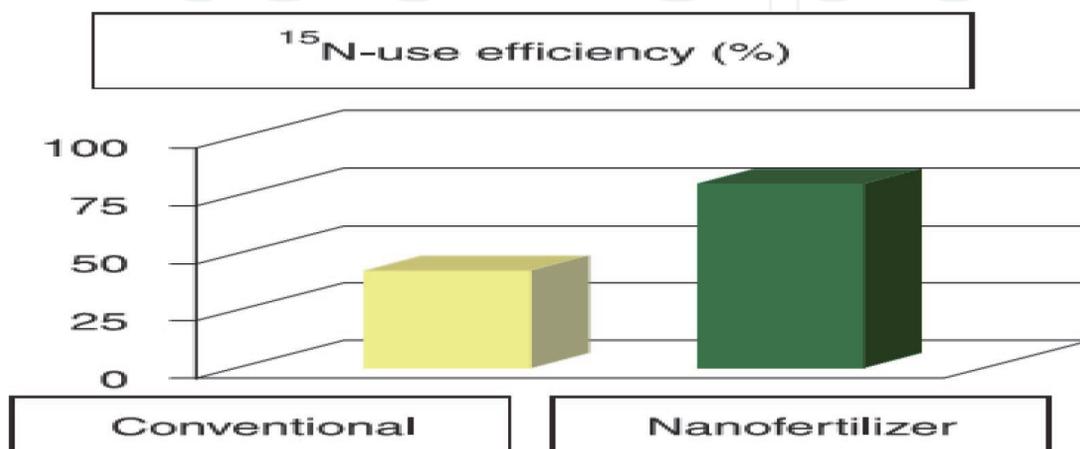


Figure 4.
Comparison of N based nano-fertilizers with conventional N fertilizers.

Concentrations (%) of Fe nano fertilizers	Spike Weight (g)	1000 grain wt (g)	Biological yields (kg/ha)	Grain yields (kg/ha)	Protein content (%)
0	536.33 ^c	32.82 ^d	8320.0 ^{bc}	3316.5 ^c	13.77 ^c
0.01	561.33 ^c	34.12 ^{dc}	8520.0 ^{ab}	3421.5 ^{bc}	15.51 ^b
0.02	604.21 ^b	35.46 ^{bc}	8620.0 ^{ab}	3506.5 ^{abc}	15.86 ^b
0.03	647.96 ^a	36.49 ^{ab}	8845.0 ^a	3689.0 ^{ab}	16.59 ^a
0.04	666.96^a	37.96^a	8895.0^a	3776.5^a	16.44^a

a,b,c is used in DMRT test for statistics either at par or different

Table 5.
Effect of Fe based nano-fertilizers on wheat crop.

enhanced the spike weight, total biological yields, grain yields, and protein content in grains (**Table 5**).

Dey et al. [2] explained the various effects of nano-particles on plant growth (**Table 6**).

Davarpanah et al. [9] experimented during the year 2014–2015 to study the effect of nano-Zn and nano-B foliar fertilization on fruit diameter and fruit yield of pomegranate. They concluded that foliar spray of Boron and Zinc @ 4.5 and 120 ppm resulted in higher fruit diameter and fruit yield compared to other treatments. Where B1, B2 and Zn1, Zn2 are 3.25, 6.5 mg/L B and 60, 120 mg/L Zn, respectively (**Table 7**).

Likely, Tarafdar et al. [10] conducted a field experiment about nano-fertilizer on pearl millet to study the effect of Zn nano-fertilizers on pearl millet var. HHB 67. It was found that nano-fertilizer (Zn source) responded as well as a field application

Nanoparticle	Effect on plant growth
Carbon nanotubes (CNTs)	Improve root growth of onion and cucumber
Nano-Si	Develops salinity stress on tomato seed germination
1000 ppm nano-ZnO (25 nm)	Results highest chlorophyll content, higher seedling vigor, early vegetative growth and significant pod yield of peanut
Nano-SiO ₂ and TiO ₂	Hastens germination and growth in soybean
Nanoscale titanium dioxide (TiO ₂)	Encourages photosynthesis and growth of spinach

Table 6.
Nano particles for better seed germination and plant growth [2].

Treatments	No. of fruits/tree	Pomegranate Fruit dia (mm)	Yields (kg/tree)
Control	50.6 ^d	75.5 ^{abc}	13.8 ^e
Zn1 + B0	52.7 ^{cd}	76.5 ^{abc}	14.3 ^{de}
Zn1 + B1	51.3 ^d	78.2 ^{ab}	15.0 ^{cd}
Zn1 + B2	65.9 ^a	76.6 ^{abc}	18.5 ^a
Zn2 + B1	58.7 ^b	74.9 ^{abc}	16.2 ^b
Zn2 + B2	63.0^{ab}	78.8^a	18.4^a
Significance	S	S	S

Table 7.
Effect of nano-Zn and nano-boron fertilizer combination on pomegranate crop.

Treatments	Pearl millet Grain yield (kg ha ⁻¹)	Dry biomass (kg ha ⁻¹)	Zn concentration (mg kg ⁻¹)
Control	1065	5192	35.5
Ordinary Zn	1217	5214	39.8
Nano Zn	1467	5841	39.2
CV	48	142	3.1
LSD (p = 0.05)	17.6	52.2	1.1

Table 8.
 Performance of nano-Zn fertilizer on pearl millet crop.

on pearl millet. The pearl millet yield and biomass yield increased by nano-fertilizer over ordinary fertilizers (**Table 8**).

Metal oxide nanomaterials, such as CuO, ZnO, and MgO, could also effectively control many plants and soil-borne diseases caused by *Botrytis cinerea*, *Alternaria alternata*, *Monilinia fructicola*, *Colletotrichum gloeosporioides*, *Fusarium solani*, *Fusarium oxysporum* fsp *Radici* Lycopersici, *Verticillium dahliae*, *Phytophthora infestans* and *Ralstonia solanacearum* in many plant species [11].

8.1 Nano-fertilizers in precision agriculture

Nano fertilizer has significant advantages over conventional fertilizers (**Table 9**).

8.2 Delivery of fertilizer

Nano-particles hold nutrients more intensely due to high surface tension and provide high surface protection of surface particles.

8.2.1 Chemical fertilizers

Chemical N-fertilizers cause atmospheric N₂O emission: Solution—nano-coated urea, CRF (Zeolite, Halloysite, and Montmorillonite use for controlled release of nitrogenous fertilizers).

Properties	Nano fertilizers	Conventional fertilizers
Solubility and dispersion of nutrients	It improves solubility and dispersion of insoluble mineral nutrients in soil and make bioavailability to plants	Less bioavailable to plants due to less solubility and larger particle size
Nutrient uptake efficiency	It increases fertilizer use efficiency and uptake ratio of soil nutrient by plants and saves fertilizers	Due to its bulk composites not efficiently uptake by plants and reduces efficiency
Control release modes	Nutrients release precisely controlled by encapsulation and by resin polymer, waxes and sulfur coating	Excess release produces toxicity and destroy ecological balances
Effective duration of release	It extends the effective duration of supply of nutrients to plants	Nutrients used by plants at the time of delivery and others are lost as insoluble salts
Loss rate of fertilizer nutrients	It reduces losses of nutrients by leaching, runoff and drift	High loss rate of fertilizers by leaching, runoff and drift

Table 9.
 Nano-fertilizers vs. conventional fertilizers.

Encapsulated nano-silica, nano-additives (TiO₂), PMAA, and Chitosan PMAA (addition of 400 ppm in fertilizers).

8.2.2 Biofertilizers

Drawbacks (a) short shelf life, (b) temperature sensitivity and (c) storage & desiccation problem.

Solution: Polymeric nano-particle for coating (resistance against desiccation), Water in oil emulsion technique, Hydrophobic silica nano-particle addition.

Gold nano-particles increase the growth of *Pseudomonas fluorescense*, *Pseudomonas elgii*, and *Bacillus subtilis* which are considered nano-bio fertilizers.

9. Commercial products from three categories of nano-fertilizers

- i. Nanogro: (Fe + Co + Mg + Mn mixed in pharmaceutical sugar): homeopathic plant medicine (**Table 10**) [12].
- ii. Silicon23 + Microbes N,P,K: plant growth regulator
- iii. Lithovit high yield fertilizer: increase CO₂ content in foliage to increase photosynthesis.
- iv. NanoNB: fertilizer product from the UK: blend of humified organic material + N + B; acts as a plant growth stimulator.
- v. NanoGreen: alkylamine + non-ionic surfactant + organic alcohol: accelerate the rate of photosynthesis by entering the nano-molecule through stomata.
- vi. Geohumus: water retaining hybrid materials (inorganic-organic-polymeric molecule).

10. Beneficial and detrimental effect of nano-particles

- Environmental accumulation in soil and water and due to their small size, it is likely they will become airborne.
- Edible plants have been shown to uptake and accumulate nano-particles.

N nano fertilizers	P nano fertilizers	K nano fertilizers	Micro nutrient nano fertilizer
Poly olefin resin coated urea	P- rock + NH ₄ ⁺ Zeolite	K- Zeolite	Zn Zeolite, ZnO
Neem coated urea	Clinoptilonite Zeolite	Surface modified Zeolite	Cu-Zeolite, CuO
Nano Sulfur coated urea	Zeolite + Ca-P mineral apatite	Bentonite	MCM-41 for Mo
Surface modified Zeolite	Nano apatite	Chabazite	Fe ₃ O ₄ and FeO

Field application of nano-fertilizers: nano-fertilizers has the potential contribution in slow release of fertilizers.

Table 10.

Sources of various kinds of nano-fertilizers (NPK and micro-nutrient based nano fertilizers).

- The use of nano-particles can adversely affect soil microbiota, creating an imbalance in bacterial diversity.
- Nano-particles with different compositions are associated with health effects in humans and animals, such as arteriosclerosis, high blood pressure, blood clots, stroke, arrhythmia, heart disease, heart attack, respiratory diseases, neurodegenerative diseases, reproductive system diseases, and various cancers.
- Nano-particles will become ubiquitous in the soil, atmosphere, and water and will be available for uptake in other plant species for which they are phytotoxic.
- Nano-particles affect more dangerously in the F2 generation of the crop.

11. Limitation for the adoption of nano-fertilizers in agriculture

- Relatively slow progress in fertilizer formulations
- Lack of clarity on regulations and innovations in fertilizer industries
- Increase in cost of fertilizers due to the use of design polymers as nano-coatings
- Lack of overall standardization in the fields
- Most of the formulations are claimed as nano, but those are in micron or submicron levels
- Need to incorporation of molecular recognition agents such as antibodies to aid in specificity in fertilizer nutrients.

12. Conclusion

- The use of nano-materials as a fertilizer delivery is expected to reduce the doses and ensure control release.
- The use of nano-particles as a fertilizer in various cereal crop provide higher yield and productivity.
- Nano fertilizer improves the biological yield of pulses and *Brassicaceae* crops.
- Nano-fertilizers in excess amounts cause harmful effects in plants and enters the food chain.
- Nano-fertilizers' uses have beneficial and detrimental effects on soil, plants, animals, and the environment.

13. Future prospects for the adoption of nano fertilizers in agriculture

- The full potential of nano-fertilizers is yet to be realized.
- Plant-nanoparticle-soil interaction need to be further understood.

- Effect of nano-fertilizers on the environment and human health also needs to be investigated in detail.
- Lab to the land concept: uses of nano-fertilizers still lack in field application on a comprehensive basis. It is still using pot culture studies, but it can be used in the field condition.
- Economics of nano-fertilizers: as it is used in low doses and losses of nutrients due to application of nano-fertilizer is minimum, it can be treated from an economic point of view.
- Production on a commercial scale: there is an urgent need to produce nano-fertilizer on a commercial scale for farmer use.

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