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REVIEW PAPER

Nano-Fertilizers and Nano-pesticides: Benevolence for Sustainable Agriculture

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ABSTRACT

The expansion in population leads to increased food demand, and hence the over use of fertilizers and pesticides. Due to the excessive use of chemical fertilizers and pesticides, major environmental and health issues have ensued. Researchers have become interested in recent developments of nano-agrochemicals due to their eco-friendly nature and cost-effectiveness. In this article, we reviewed the advantages of nano-tools including nano-fertilizers and nano-pesticides over the conventional mineral fertilizers and pesticides and the developments in nano-agrochemicals along with their applications in farming industries such as improving crop production, minimizing the input, maximizing the output, and solving agronomy problems such as better food yield and preservation. This review discusses latest impacts of nanotechnology in farming industries, nano-agrochemicals versus conventional agro-chemicals and nanomaterial as pesticides and fertilizers, and sustainable development. Nano-agrochemicals in the form of nano-pesticides, nano-fertilizers, nano-biofertilizers, green nano-pesticides as well as metallic nano-pesticides are emerging as new products in the industry.

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INTRODUCTION

The population of the world has increased in the last few decades and is still increasing. According to the world bank report (2011), the universal citizenry has exceeded 7 billion, and it is assumed to grow up to 8.5 billion in 2030, 9.7 billion in 2050, and 10.9 billion in 2100 (UN Report). By increasing citizenry, the demands of essential things like food, clothes etc. are also increasing by 50% [1]. Currently, the world's management and distribution are under tremendous stress due to the increase in population [2]. Agriculture is assumed to be one of the most crucial and balanced sectors as it provides foodstuff to the global population and also contributes to the domestic economy [3]. In the progressive years, however, the agronomy is affected by various concerns such as global warming, loss in farm profit, disease, and climate change. At the same time, the demand for food material is increasing. Consequently, it becomes extremely difficult to fulfil the requirement of the global population [4-5]. Therefore, steps must be taken in order to improve the quality and quantity of agriculture. In this regard, there has been a trend in agriculture toward using chemical fertilizers, pesticides, and many disease-resistant chemicals since the last five decades. This has led to an increment in absolute pesticidal consumption [6]. According to FAO, the use of global pesticide almost doubled between 1990 and 2018, raising-from 1.7 to 2.7 million tonnes (FAO 24 June, 2021). Furthermore, the utilization of global pesticide has raised up to 516 million pounds only in USA (USDA 2012). No doubt the adoption of chemical pesticides and fertilizers has increased crop production while it has also diminished the adequacy of food and the fertile power of land

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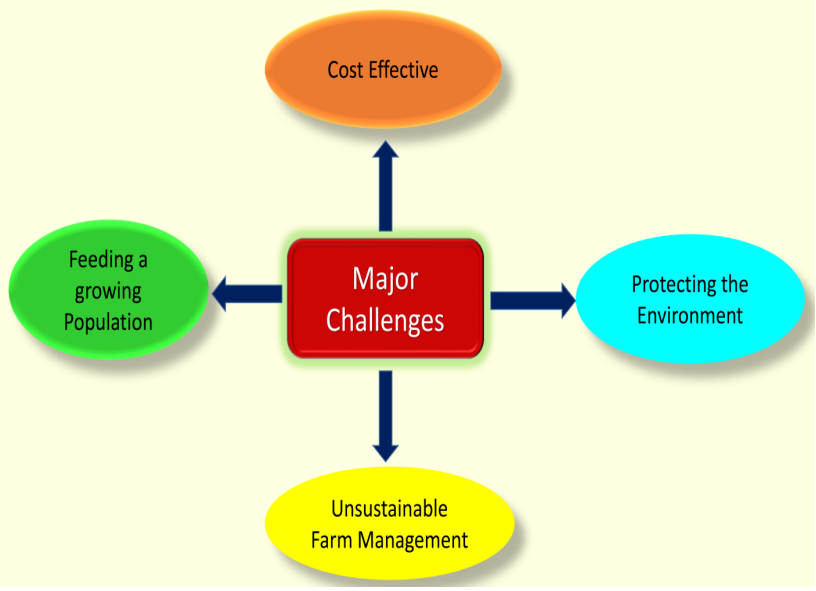

Fig. 1. Considerable Challenges faced by agriculture i.e. (Farming community)

[7]. Bollag et *al.* [8] reported that out of total applied quantity of chemical inputs 50 to 70 % of them remains unused by mineralization, leaching and bioconversion. In addition, human health, environment, and ecosphere (i.e. land Microbial flora, parasites also marine ecosphere) are affected by the uncontrolled use of agrochemicals [9]. Therefore, it is evident that there is a demand for modifying old cultivation techniques into active and latest practices with the application of leading automation like nanotechnology for green agriculture. Recent research has shown the importance of nanomaterials for improving the condition of agronomy by boosting the efficacy of agronomy intake and providing solutions to various cultivation and environmental issues in order to increase food yield and safety [10-12]. Nanotechnology has gained a lot of attention in recent years with its applications in various fields such as medicines, energy, medical drugs, and agriculture [13]. The significant application of nanotechnology in agriculture includes concrete implementation such as nano-fertilizers and nano-pesticides to trace crop and nutriment levels for boosting production as well as sterilizing land, water, and stability in opposition to different insects, pest, and microbial disorders. The fundamental aim of implementing nanotechnology in farming is to minimize the input (such as fertilizers, toxicants, and herbicides), maximize the output (crop- production), and also monitor the environmental effects and the application of nano-agrochemicals on targeted area [14]. Currently, this field is of much interest with its future perspective for boosting seed fertilization, yield, and plant conservation with the controlled and targeted use of agrochemicals; this will result in reducing the amount of agrochemicals used as well as minimizing the loss of nutrient in fertilization [15]. The application of nanotechnology in agriculture aids in overcoming considerable challenges faced by the agronomy, some of which are presented in Fig. 1.

Conventional farming has been modified into delicate farming by applying nano-materials in the form of nano-agrochemicals. Different types of nano-particles such as carbon nanotubes, Ag, Cu, Mo, Zn, Fe, Mn, Si, Ti, their oxides, and nano-formulations of ordinary agronomy intakes including phosphorus, urea, sulphur, validamycin, tebuconazole and azadiractina have been recreated into nano-pesticides along with nano-fertilizers [16-22]. Nano-tools in the form of nano-pesticides and nano-fertilizers have had a positive impact on the farming community by controlling plant pests and diseases [23]. In this article we, discuss the use of nano-tools in farming industries. Nano-fertilizers are the nano-tools which are responsible for plant growth, and some of the nano-materials that show pesticidal activities are mentioned in this work. Further, some synthesized nano-pesticides and fertilizers are also mentioned.

NANOTECHNOLOGY IN SUSTAINABLE AGRICULTURE

It becomes necessary to introduce a new, emerging technology such as nano-technology in a variety of fields in order to promote global sustainable development. In this article we discussed the utilization of nanotechnology in agronomy. If we are concerned about contemporary agriculture, then sustainable crop production and efficacy are meaningless without the use of agrochemicals such as pesticides, fertilizers, etc. Nevertheless, these agro-chemicals, formed by conventional methods, have some conceivable problems such as sludge of water and environmental pollution [24]. The conventional methods of producing agrochemicals include: (1) the bottom-up method and (2) top-down method. The nano-materials developed through ecologically safe and biodegradable methods can increase agricultural potential [25]. Nanotechnology offers a great hope for sustainable agriculture by monitoring ecological variables and using limited marked action as needed [26]. Nano-tools such as nano-fertilizer, nano-pesticides, nano-sensor, and nano-herbicide have been used as smart delivery system for the sustainability of farming sectors [27-29]. The practice of nanotechnology in agricultural range are as follows:

- Nano-formulations of nano-tools i. e. agrochemicals for utilizing pesticides and fertilizers in modification of crop yield.
- The utilization of nano-sensors in protecting the crop with authentication of crop disease and leftovers of agrochemicals.
- Nano-technology can increase agricultural production.
- Nano-technology is also used in food packaging.

NANO-PESTICIDES

A pesticide is a substance that is used to dispatch, chase away, or control certain different forms of pests. Pesticides involve herbicides that are used for ruining weeds and other unwanted vegetation, and insecticides are employed for destroying a variety of insects. In addition, and fungicides are applied to avoid the production of bacteria and fungi. According to Federal agency, US, the sustainable progress of nano-agrochemicals could be an important agent for plant production along with pest management. Typically, pesticides are very useful in agriculture for disease management, and nano-materials could be used as nano-agrochemicals for better crop yield with low eco-toxicity [30]. Metal and metal oxide nanoparticles were found to be highly effective in plant disease management against very serious pathogens which are responsible for huge economic loss. At global level Fusarium wilt is found to be a disorder in tomato and lettuce as a result of its wide manufacturing damage, tedious survival of fungus in land, and propagation of resistant races. These disorders can be diminished to some extent with the help of various chemicals. However, this is expensive as the chemicals used are costly and also not always effective. Thus, an alternative solution is found and which is the use of nano-materials to control plant pathogens. Various nano-materials have been synthesized by utilizing hydrated extorts of Punica granatum peels, Olea europaea leaves, green peach aphid (GPA), and Chamaemelum Nobile flowers [31]. The synthesis of pesticides by using metal nano-particles and polymers is a highly demanding area of pesticide manufactory [32]. Nano-encapsulation of pesticide is helpful in limited and gradual release of their active ingredients with control in outer shell of nano-capsules. This release of limited doses over a long cycle diminishes surplus drainage of undesirable pesticide [33]. Table 1 indicates the different types of nano-pesticides which were already synthesized. The perk of nanomaterials in plant disorder control and excellent crop growth are compiled in Fig. 2.

Park et al. [40] reported that silica nano-particles are 100% active against powdery mildew disease in cucurbits. Silver nanoparticles (Ag) are broad-spectrum active agents against phytopathogen such as Biploaris sorokinniana, Botrytis cinerea, Colletotrichum gloeosporioides, Fusarium culmorum, Phythium ultimum, Phoma, Megnaporthe grisea, Trichoderma sp., Scalerotinia sclerotiorum, Sphaerotheca pannasa, and Rhizoctonia solani [41-43]. Some researchers have reported the synthesis of copper nanoparticles and found them effective against Gram-negative and Gram-positive fungal and bacterial disease pathogens such as Xanthomonas oryzae at very low concentration [44]. Liu et al. [36] also reported the controlled pesticide delivery of porous silica nanomaterial as carrier of validamycin. In order to prevent the ecosystem from poisonous effects of toxicants, nano-pesticide action must be regulated by federal agencies. Nano-pesticides are categorized into various types based on their target and action. The classification of nano-pesticides is shown in Fig. 3.

Table 1. Some synthesized nano-pesticides along with their potential impact on crop protection and management

Sr. No.	Nano-pesticides	Plant disease / Pathogens	Effect on crop protection and management	References
1.	Diuron	Weeds and algae	Inhibits photosynthesis and mainly used for weed control	Yearla et al. [34]
2.	Tebuconazole	Powdery mildew and scab in apple	50% improvement in release rate	Mattos et al. [35]
3.	Validamycin	Antibiotic and fungicide	Controls sheath blight of rice and damping off of cucumbers	Liu et al. [36]
4.	With zinc and Ag	Xanthomonas perforans	Large photo catalytic activity and bacterial reduction	Paret et al. [37]
5.	Nano sulphur	Fungus and Insecticides	Leaf size and food quality	Venzon et al. [38]
6.	Titanium dioxide	Spot on tomato	High photo catalytic activity and bacterial reduction	Paret et al. [37]
7.	Copper and Silver	Pests	Show good pesticidal activities	Athanassiou et al. [39]

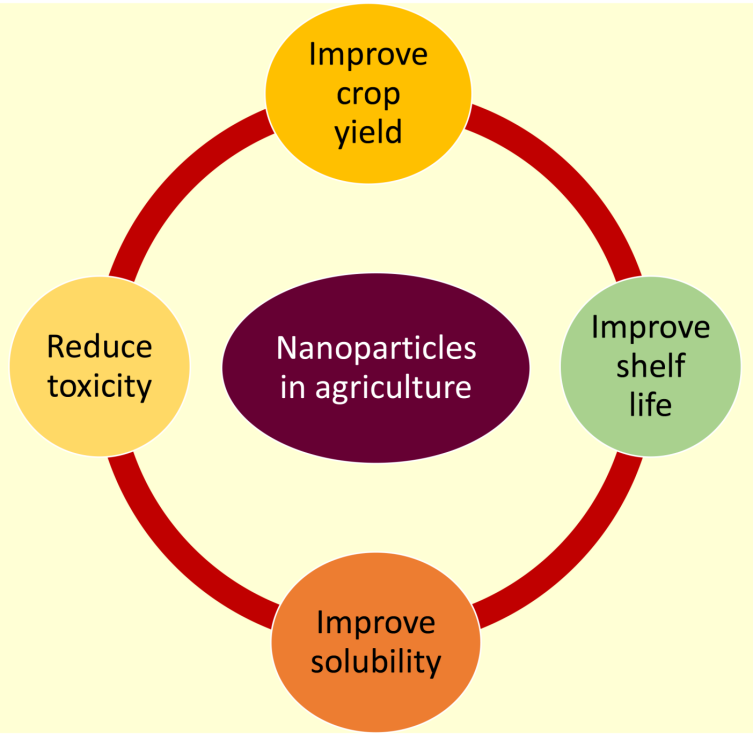

Fig. 2. Benefits of nanomaterials in agriculture

Pesticides v/s Nano-pesticides

According to World Health Organization (WHO), pesticides are chemical compounds which are used to protect crops from undesirable plants (weeds). More than 1000 various types of pesticides are employed all over the world. The excessive use of chemical pesticides directly affects human health through food contamination [45]. The use of pesticides is very common in farming communities to protect crop from unwanted plants (weeds), insects, and fungus. Nonetheless, the application of conventional pesticides leads to increased environmental pollution. Further, the left unused particles of pesticides cause water contamination [46]. The conventional uses of pesticides and crop techniques have not proven efficacious regarding environmental safety and sustainable development [47-50]. Nano-pesticides such as nano-fungicides, nano-insecticides, nano-bactericides, and nano-weedicides, etc., are of different types. Nano-pesticides are simple to use, cost-effective, and have an effective delivery system [51, 52]. Nano-

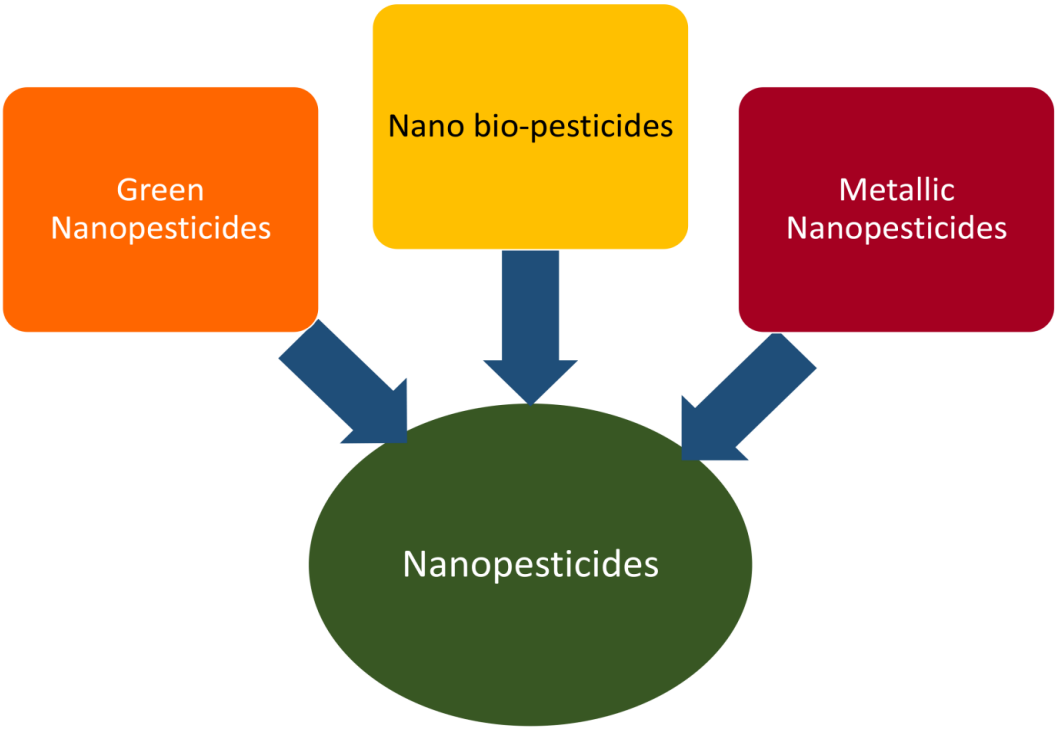

Fig. 3.

encapsulation is the latest approach which is applied to enhance the value of active ingredient of pesticide defensive covering [53-55]. Nano-pesticides are eco-friendly, bio-absorbable, and remain intact when used. They can also increase the solubility of active compounds, as well as provide superior protection from degradation and volatilization. Currently, polymer-based nanoparticles and metal-based nanoparticles have been utilized to enhance crop yield by implementing them as nano-carriers in herbicides and toxicants [56].

Green Nano-pesticides

The nano-materials formed from plant extracts are employed in the synthesis of nano-pesticides. These nano-pesticides synthesized through greener routes are more environmentally friendly and cost-effective compared to the nano-pesticides synthesized by conventional methods. C. Siva et al. reported the development of silver nanomaterials by taking hydrated botanical extort (5, 10, 20, 30,50 mg/ml) of plant named Aristolochia indica and utilizing the synthesized nano-particles against third instar larvae of cotton worm / gram caterpillar, Helicoverpa armigera (Hb). In the crude aqueous (50mg/ml), AgNO3 (50mg/ml), Ag nano-particles (112nm size), and AZ (50ml/l), maximum antifeeding activity are of 92.4%, 97.3%, 72.2%, and 4.3% respectively. However, the cytostatic activity was reduced with the TC50 values of > 100µg/ml and 89µg/ml for extort and Ag nano-particles subsequently. Khadri et al. recorded Ag nano-particles biologically and also reported their fungicidal activity. Rahman et al. [57] also developed silver nanoparticles through green routes. These silver nano-particles were used as Bactericidal. Ali et al. [58] recorded the application of Ag nanoparticles as pesticide/ insecticide.

Metallic Nano-particles used as Pesticides

Many researchers have synthesized different nano-particles of different metals and also reported the pesticidal activity of the synthesized nano-material. T. Stadler et al. reported the pesticidal activity of nanostructured alumina against the two pests named Sitophilus oryzae, and Rhizopertha Dominica. After three days of regular exposure to wheat treated with nanostructured alumina they observed quite high mortality. Aluminium and Titanium Nano-particles also shows pesticidal activity against stored grain pest S. Oryzae under laboratory conditions. Shaker et al. [59] reported

Table 2. Synthesized metallic nanoparticles used as Nano-pesticides

Sr. No.	Nano-particles	Crop disease	Impact	Reference
1.	Silver	Bacterial blight	Significant reduction in bacteria	Rajesh et al. [60]
2.	Silver	Bacterial spot disease	Significant inhibition in growth of bacteria	Ocsoy et al. [61]
3.	Iron oxide	Fungal disease	50-80% reduction in fungal disease	Chippa et al. [62]
4.	Copper	Fungal disease	Showed antifungal activities	Brahamanwade et al. [63]
5.	Silver	Fungal disease	Up to 80% of production barrier	Ho et al. [64]
6.	Copper	Tomato disorder	Effective at little concentration of fungal agent	Giannousi et al. [65]
7.	Chitosan nanomaterial	Disease in chilli	Delayed mycelia growth	Chookhongkha et al. [66]

the activity of Titanium oxide nano-particles against 2nd and 4th instar larvae of Spodoptera littoralis. The larvae was examined with TiO2 nanoparticles and tested at all concentrations and showed higher toxicity. Some synthesized metallic nanoparticles which are used as nano-pesticides are given in Table 2.

NANO-FERTILIZERS

A fertilizer is defined as any material of either natural or synthetic origin that is applied to the plant tissues or the land to supply various supplements required for development of plant. For most modern farming practices, fertilization focuses on three fundamental macronutrients including nitrogen (N), phosphorus (P), and potassium (K) (NPK). Historically, these fertilizers came from natural or organic resources such as animal manure, human manure, compost etc. With advancement in technology, synthetic fertilizers are used for farming practices. The most widely applied fertilizer is urea as it is a good source of nitrogen. The nutrient use efficacy (NUE) of the three main macronutrients (NPK) is found to be constant in former decades and barely exceeds 30-35, 18-20, and 35-40%, respectively [67]. The crop raising has decreased in the minimal regions with minor supplement access. Therefore, in order to enhance crop production, the NUE must be improved. Over time, adverse effects of using synthetic fertilizers become apparent. To reduce these adverse effects and to increase crop production, nano-materials are utilized to synthesize fertilizers i.e., nano-fertilizers. Nano-fertilizers are expected to enhance the NUE by preventing the supplement ions from getting either firm or in the ecosphere [68]. These latest delivery systems of encapsulated nano-fertilizers bypass the need for land, water, and microorganisms for providing nutrients, and instead release nutrients after their internalization in the plant system [69]. The most important fertilizer used for increasing crop production is nitrogen fertilizer. However, compared with amounts of nitrogen applied to soil, the nitrogen use efficiency (NUE) by crops is very low. Urea is a convenient fertilizer for agricultural use; it is commercially available and a quick-acting source of nitrogen. In 2018-19, the global demand of urea rose to a total of 120 Mt. Nano-fertilizers provide more than one type of nutrients available for the plants and help in their development as well as modify the production [70]. These nano-fertilizers are further divided into other parts on the basis of nutrient requirement of plant: (1) macro fertilizers, (2) micro fertilizers, and (3) nano particulate fertilizers as shown in Fig. 4.

Fertilizers v/s Nano-fertilizers

Fertilizers are essential for improving crop growth and yield. While the have been successful in boosting crop yield, they have had some harmful effects on the ecosystem and environment. The fertilizers applied on plants remains unused due to leaching and, thus, contaminate soil and water bodies. Nevertheless, the unlimited use of chemical fertilizers has led to various issues such as serious land degradation, land compaction, loss of soil carbon, nitrogen leaching, and reduction in soil organic matter. Plant fertilizers, if inhaled or ingested accidentally, can poison people and pets. Fertilizers are often used in excess, leading to short term benefits. In addition, they can change the nature of land, making it either too acidic or too basic. In contrast to ordinary chemicals, nano-

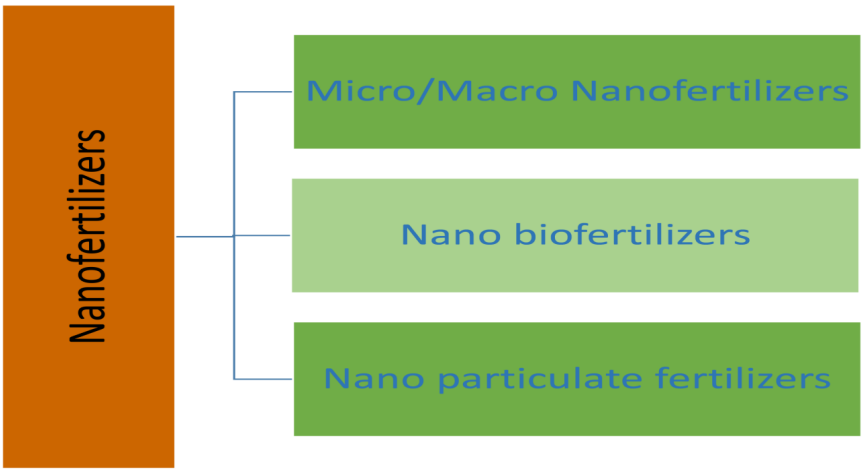

Fig. 4.

fertilizers have many advantages. They can increase the fertility of the land and improve the quality of the crop, while being non-toxic and having minimal damaging impact on the ecosystem and humans. Furthermore, they require less expenditure, enhance the yield, and less amounts of them are needed.

Macro Nano-fertilizers

In this category of fertilizers, plants require a large amount of nutrients for growth and development. The six macronutrients that are essential for plants are nitrogen, phosphorus, potassium, calcium, magnesium, and sulphur. Nitrogen, phosphorus, and potassium are considered primary macronutrients, as their demand is often met through NPK fertilizers. On the other hand, calcium, magnesium, and sulphur are secondary macronutrients, as their demands are not typically managed by NPK fertilizers. To fulfil the availability of secondary macronutrients additional fertilizers are used. The growing demand for food has led to increased macronutrient fertilizer requirement (MFE). This increment is estimated up to 263 Mt by 2050 [71]. The efficiency of macro nano-fertilizers is greater than that of conventional fertilizers due to their high volume to surface ratio. Many researchers have synthesized various macro nano-fertilizers and checked their activity in both laboratory and field settings. Potassium and phosphorus nano-fertilizers were applied to enhance yield, quantity, and weight of flower, weight of fresh and dried stigma as well as the length of the stigma of saffron [72].

Micro Nano-fertilizers

In this category of fertilizers, small amounts of nutrients are required by the plants and these micro-nutrients are trace elements essential for plant growth. Nano-forms of micronutrients modify the availability to plants and display a momentous advancement in plant development as well as the quality of nutrition. Delfani et al. [73] reported one tenth of advancement in the quantity of chlorophyll in black-eyed pea coated with iron nanoparticles. Zinc is one of the fundamental micronutrients, which regulates different types of enzymatic activities in the plants. Zinc oxide nanoparticles have displayed compelling advancement in biomass, shoot length, essence, chlorophyll and protein content, and phosphatase enzyme activity in Vigna radiate, Cicer ariatium, Cucumis sativas, Raphanus sativus, Brassica napus and Cluster bean [74-77]. Some synthesized nano-fertilizers along with their impact on crop production are summarized in Table 3.

Nano-bio fertilizers

Nano-biofertilizers are produced by combining nanoparticles and biofertilizers. The process involves the encapsulation of biofertilizers with suitable nanoparticles for the release of nutrients in soil in a controlled manner and to reduce environmental side effects. In addition, they contain one or more microorganisms to enhance land fertility, by setting nitrogen present in atmosphere and, solubilizing phosphorus. Some key factors in the development of nano-biofertilizers is their interaction in slow/controlled release, growth of

Table 3. Synthesized Nano-fertilizers and their impact on crop production

Sr. No.	Nano-fertilizers	Name of Crop	Impact	References
1.	Copper	Lettuce	Increases shoot and root length	Adhikari et al. [78]
2.	Copper oxide	Maize	Increases the plant growth by 51%	Adhikari et al. [78]
3.	Magnesium	Cow peas	Increases the Mg content in stem and also the chlorophyll content	Delfani et al. [73]
4.	Iron oxide	Pea	Increases seed weight and the chlorophyll content	Delfani et al. [73]
5.	Iron oxide	Soybean	Increases chlorophyll content of plants	Ghafariyan et al. [79]
6.	Manganese	Rice	Increases zinc uptake of plants by 5.66 mg/hill	Yuvaraj et al. [80]
7.	NPK nanoparticles	Wheat	Increase significantly the total saccharide content of wheat crops.	Aziz et al. [81]
8.	Zinc Oxide	Coffee	Accelerates the rate of photosynthesis and also improved biomass production	Vanti et al. [82]

microorganisms, and extended useful life.

These nanoparticles with natural biofertilizers such as Pseudomonas fluorescens, Bacillus subtilis and Paenibacillus elgii have shown very good growth promotion under in vitro conditions [83]. S. K. Shukla et al. [84] found that plant growth promoting rhizobacteria with gold nanoparticles have positive effects. J. S. Duhan et al. proclaimed that the use of Ag nanomaterials in addition to biofertilizers was not effective as it has detrimental effects on the natural activity of microorganisms. The average life of conventional biofertilizers needs to be improved, and the incorporation of nanoparticles is highly efficacious in enhancing the reliability of biofertilizers against heat and UV inactivation [85].

Nano-fertilizers: A new product for industry

Nanotechnology plays an important role in the field of agriculture as it enhances crop production and reduces nutrition loss. This has heightened interest in nano-scale bulk fertilizers, or nano-fertilizers. However, the production of nano-fertilizers at large scale is yet to be realized. Nano-fertilizers are developing as a new, emerging product for agriculture. The application of nano-fertilizers to plants reduces the amount of fertilizer required. Further, they are non-toxic and eco-friendly. Thus, the concept of nano-fertilizers is a boon for the agriculture in the future. It is necessary to attracting industries' interest to apply nanotechnology in fertilizers domain for increasing industrial large-scale production of nano-fertilizers [86]. Nano-tools such as nano-fertilizers, nano-pesticides along with nano-biosensors, nano biofertilizers, and nano-biopesticides are all new and emerging products for the farming community, i.e. the industry.

FUTURE PERSPECTIVES OF NANO AGROCHEMICALS IN AGRICULTURE:

It is well known that the use of nano-agrochemicals in the form of nano-fertilizers and nano-pesticides effectively improves the plant growth and nutrition, protects the crop from pests, and leads to enhanced crop yield. However, few gaps still exist in the field of research in agrochemicals. Due to the small size of the nanoparticles they can penetrate easily in the crop leaves and can cause potential harms to humans consuming the produced crop. Latest research has shown that the nanoparticles synthesized through biological processes are less harmful compared to those synthesized by chemical and physical methods. The effects of these nanoparticles on environment are still unknown. Consequently, further investigation should be conducted to focus on the field of nano-agrochemicals in order to improve the efficacy of nanoparticles and reduce the toxicity of nanoparticles to the environment [87].

CONCLUSION

Nano-technology is an emerging branch in which latest innovative tools are being developed in order to tackle variety of issues concerning air, water, soil pollution etc. Nano-tools such as nano-pesticides and nano-fertilizers etc. have shown greater efficiency than the conventional pesticides and fertilizers. Nano-particles also improve the stability of these nano-tools. The

use of nano-pesticides and nano-fertilizers in agricultural industry results in preventing environmental pollution as well as improving the quality and quantity of the crop, thereby contributing to economic growth. Nanotechnology has a major impact on agriculture, contributing to sustainable development around the world. The nano-tools, namely nano-fertilizers and nano-pesticides, synthesized through greener routes are more eco-friendly and effective. Furthermore, recommendations will facilitate the synthesis of nano-particles through greener routes like nano-particles synthesized using plant extracts. Nano-technology may take a few years to make a move from the laboratory to the field.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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