**Bio-based nanoparticles for sustainable Agriculture**

**Dhruba Krishna Deka1, Siddaraju MN2, Dharmeswar Barman3, Akan Das4#**

**1Assistant Professor, Dept. of Biochemistry & Agricultural Chemistry, BN College of Agriculture, Assam Agricultural University,**

**Biswanath Chariali, Assam, 784176, India**

**2Dept. of Botany, University College Mangalore, Mangalore, Karnataka, 575001, India**

**3Dept. of Botany, Goalpara College, Goalpara, Assam,** 78310, **India**

**4AGT Biosciences (OPC) Private Limited., Mirza, Assam, 781122, India**

**#Corresponding author: dasakan@gmail.com; +91-8011726712**

**ABSTRACT**

In the current situation, the rise in global population, led to an increase in nutritional food demand. To increase crop productivity, diverse range of agrochemicals viz., fertilizers and pesticides, and other chemical products are frequently employed. However, rapid climate change, declining soil fertility, lack of macro and micro-nutrients, excessive use of agrochemicals, and the occurrence of heavy metals in the soil are some significant causes of concern in the agricultural sector. To address this worrying situation, the development of sustainable agricultural output is urgently needed. Nanotechnology has made a significant contribution to sustainable agriculture through increased crop production and soil quality restoration and improvement. Nanoparticles are advanced into cutting-edge material that help in development of numerous formulations, including nano-sized pesticides, fertilizers, and sensors, have been investigated for controlling plant health and soil improvement. In-depth understandings of the interactions between plants and nanomaterials or nanoparticles unfold new prospects for enhancing agricultural practises through maximum crop output, higher disease resistance, and nutrient uptake. In this chapter, we focus on the recent agricultural strategies used for the management of active components such as pesticides, fungicides, micro and macro-nutrients, limitations of chemical pesticides and fertilizers with effective solutions based on bio-based nanomaterial that may increase sustainable agriculture management and food security.

**Keywords-** Bio-based; Nanomaterials; Nanofertilizers; Nanopesticides; Nanoparticles; Nanotechnology; Sustainable agriculture

**1. INTRODUCTION**

**Agriculture is the most significant and dependable industry since it contributes raw materials and food to other businesses. The world's population is increasing along with the availability of natural resources (producing land, water, soil, etc.), so it is necessary for agriculture to develop in a way that is efficient, economically sound, and environmentally friendly.**  **A significant rise in food consumption that would be required to feed an estimated 6–9 billion people by 2050 will make these issues much worse [1]. The Food and Agriculture Organization (FAO, 2017) also projects that by 2050, there will be 10 billion people on the planet, which would result in a 50% increase in global food demand, particularly in developing nations. Economic expansion has a noticeable impact on agricultural nutrient balances, and because of this assumption, emerging countries should place a high priority on improving soil fertility [2] [3]. The growth of agriculture is a necessary phenomenon for eliminating hunger and poverty, which must be eradicated from the current condition. Agriculture production must become more economically viable, environmentally sustainable, and productive due to the depletion of natural resources and the rise in global population. A significant number of potentially dangerous risks are posing challenges to the agricultural systems around the world. Diverse synthetic agrochemicals such as pesticides ( viz., herbicides, insecticides, fungicides), and fertilizers have been created and utilised to boost agricultural crop yields in order to solve these problems [4]. The global agriculture industry is confronted with a number of difficulties, including unexpected climate change, urbanisation, the sustainable use of natural resources, soil pollution by dangerous environmental pollutants like fertilisers and pesticides, and significantly increased food demand due to a growing worldwide population [5][6].**

**Nanotechnology, a smart and innovative way can significantly speed up the sustainable expansion of agriculture [7]. Recent studies have demonstrated the encouraging potential of nanotechnology to advance the agricultural industry by enhancing the efficacy of agricultural efforts and providing remedies for issues relating to agriculture and the environment to increase food productivity and security. Because of this, research into using nanotechnology in agriculture has received a lot of interest recently [8][9]. The nanotechnology applied to plants termed as “phytonanotechnology,”, is crucial for preserving sustainable agriculture and food production [10][11]. The development of various nanomaterials in agriculture regulates the pace of nutrient depletion rate , yield reduction, cost of crop inputs, production, and post-harvest loss minimization [6][4]. Nanomaterials have unique physicochemical properties that set them apart from their molecular counterparts, such as increased reactivity, an modified nanomaterial surface structure, and a high surface-to-volume ratio [12][13]. Moreover, nanomaterials can also be designed and developed as multifunctional, time-controlled, programmable, self-regulated, and target-specific properties [14][15]. All agrochemicals made with nanomaterial based formulations in agriculture will also experience advantages including enhanced penetration, coverage, and absorption of active components on the target [16][17][18].** **The distribution of nano-agrochemicals by nanomaterial has the potential to significantly increase the efficacy of agricultural inputs, reduce environmental pollution, and reduce labour costs, all of which help to maintain the sustainability of agricultural systems and enhance food security. Numerous nanoparticles, including carbon nanotubes (CNTs), quantum dots (QDs), mesoporous silica NPs (MSNs), magnetic NPs (MNPs), metallic and metal oxide NPs, have been widely used in agriculture [10][13].**

**2. BIO-BASED NANOPARTICLES IN AGRICULTURE**

**In order to attain precision agriculture, which strives to maximise production with minimal resources, modern agronomy is looking for alternatives to the use of agrochemicals through the adoption of nanotechnology with bio-derived nanomaterials [19][20]. The two main ways that nanomaterials can help agriculture farming are by raising crop yields and more effectively using resources. The nanomaterials can be characterised with large surface area, magnetic properties, antibacterial activity, and strong optical, electrical, and catalytic activity. The nanoparticles can be synthesized physically, chemically, or biologically. However, chemically developed process is quick and not environmentally friendly as hazardous compounds like stabilising and capping agents are used. For their best usage, alternative methods for synthesising nanoparticles and their composition must be adopted [7]. A variety of microorganisms, including bacteria, fungi, algae, plant extracts, and waste materials, can be used as eco-friendly precursors in the synthesis of NPs with potential applications in agriculture. The biological method of preparation has advantages over other chemical methods because it operates at room temperature and atmosphere, utilizes inexpensive materials and solvents, and requires no expensive machinery, and uses eco-friendly and economically viable technology [21][22].**

**On the other hand, apart from biosynthesized nanoparticles the traditional problems in agriculture can also be solved by using nature-derived polymeric nanoparticles in a variety of applications, such as nanoherbicides, nanodetectors, and nanofertilizers [23]. For instance, "precision farming" targets major crop production with nutrients in edible sections without harming water and soil resources. Precision farming uses nanocarriers to carry and deliver pesticides and fertilizers in a more regulated and slow release profile [24].**

**3. BIO-BASED NANOFERTILIZER**

The usage of chemical fertilisers has increased due to crop varieties that respond to fertiliser. However, the poor usage efficiency of chemical fertilisers limits their use since they lose fertiliser through volatilization and leaching, which contaminates the environment and raises production costs (FAO, 2017). In this context, nanotechnology is utilised to increase the accessibility of insufficiently available nutrients, create slow-release fertilisers, and limit the losses of mobile nutrients [25]. Nanofertilizers play a crucial role in improving agricultural output by giving plants the nutrients they need for maximum growth and altering the traditional fertilization system [26][27]. Although agricultural fertilizers, in particular, are still not developed by the big chemical industries, nanofertilizers have been widely accessible on the market for the past ten years. Some of the commercially available nanofertilizers are listed in Table 1.

Based on the nutritional needs of the plants, nano fertilisers can be categorised into three groups: macronutrient nano fertilisers, micronutrient nano fertilisers, and nanoparticulate nano fertilisers [28]. The elements potassium (K), magnesium (Mg), nitrogen (N), calcium (Ca), and phosphorus (P) are some of the elements that make up macronutrient nano fertilisers (P). In comparison to macronutrients, plant micronutrients such as molybdenum (Mo), copper (Cu), iron (Fe), nickel (Ni), manganese (Mn), and zinc (Zn) are needed in considerably lesser quantities for the proper growth of crops. Other NPs found in nanoparticulate fertilisers, like CNTs, TiO2, and SiO2, help plants develop more quickly [6].

Nanofertilizers can be categorised as controlled-release, controlled-loss, or nanocomposite fertilizers based on their functions. These composite nanomaterials can deliver various macro- and micronutrients with perfect properties [29][13]. Encapsulating fertilizers in nano form can improve nutrient uptake, reduce nutrient loss, increase crop quality and yield, and lower the risk of environmental degradation.

Nanofertilizers may include nanoscale amounts of titanium dioxide, silica, iron, ZnCdSe/ZnS core shell QDs, InP/ZnS core shell QDs, Mn/ZnSe QDs, gold nanorods, core shell QDs, and other materials.

With the help of synthetic or biological polymers, many slow release fertilisers (SRF) and controlled release fertilisers have been created [7]. The creation of slow/controlled release fertilisers, which increase fertiliser usage efficiency and decrease nutrient losses to the environment, is made easier by the introduction of nanotechnology in plant nutrition, making these fertilisers environmentally benign [30]. Bio-based nanomaterials have been employed in a variety of fertilisers, as illustrated in Table 2. Future sustainable bio-based economies will continue to reduce and replace harmful materials in existing applications by using eco-efficient bioprocesses and renewable bioresources. As a result, they will play a significant role in the development of the desired 21st-century technologies [31][32].

**TABLE 1:** **COMMERCIALLY AVAILABLE NANOFERTILIZERS**

|  |  |  |  |
| --- | --- | --- | --- |
| **NANOFERTILIZER** | **COMPONENT** | **COMPANY** | **REFERENCES** |
| Nano-GroTM | Growth regulator and immunity booster | Agro Nanotechnology Corp.,  FL, United States | [3] |
| Nano Green | Corn, grain, soybeans, potatoes, coconut, and palm extract | Nano Green Sciences, Inc.,  India | [3] |
| Nano-Ag Answer R | Microorganisms, mineral, and sea kelp | Urth Agriculture, CA, United  States | [3] |
| Biozar | Organic materials, micronutrients, and macromolecules | Fanavar Nano-Pazhoohesh  Markazi Company, Iran | [3] |
| Nano Max NPK | Organic acids chelated with organic nutrients, organic carbon, trace elements, amino acids, vitamins, and probiotics | JU Agri Sciences Pvt. Ltd,  India | [3] |
| Master Nano Chitosan Organic Fertilizer | Liquid chitosan, phenolic compounds, organic acid and salicylic acids | Pannaraj Intertrade, Thailand | [3] |
| TAG NANO (NPK, PhoS, Zinc, Cal, etc.) fertilizers | Proteino-lacto-gluconate chelated with micronutrients, vitamins,  seaweed extracts, humic acid, probiotics | Tropical Agrosystem  India (P) Ltd., India | [3] |
| NanoKTM | Potassium | Aqua-Yield Hub, USA | [6] |
| NanoZnTM | Zinc | Aqua-Yield Hub, USA | [6] |
| NanoRiseTM | Plant Growth Regulator | Aqua-Yield Hub, USA | [6] |
| NovaLand-F | Mn, Cu, Fe, Zn, Mo, N | Land Green &  Technology Co, TAIWAN | [6] |
| NUBIOTEK® HYPER Fe+Mg | Iron (Nanoparticle  /Nanopowder)  Magnesium (Nanocapsule) | Bioteksa, Mexico | [6] |
| Lithocal | Calcium  (Nanoparticle /Nanopowder)  Manganese  (Nanoparticle /Nanopowder) | Litho Plant, Brazil | [6] |
| FOSVIT K30 | Phosphorous (Nanoparticle  /Nanopowder)  Potassium (Nanoparticle  /Nanopowder) | Kimitec Group, Spain | [6] |
| Nano Zinc (Chelated) | Zinc (Nanoparticle  /Nanopowder) | Alert Biotech, India | [6] |
| Nano Bor 20% | Boron (Nanoparticle  /Nanopowder) | Alert Biotech, India | [6] |
| Nano Zinc (Soil Application 21%) | Zinc (Nanoparticle  /Nanopowder) | Alert Biotech, India | [6] |
| NASCO Escort-P | Phosphorous (Nanoparticle  /Nanopowder) | Nano Agro Science  Co-operative Society  Ltd., India | [6] |

**TABLE 2: BIO-BASED NANOFERTILIZER**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **NANOMATERIAL** | **ACTIVE COMPONENT** | **METHOD** | **FUNCTIONAL PROPRTIES** | **REFERENCES** |
| Cu-Chitosan | Cu | --- | Growth of seed, plant biomass and enhanced biochemical activities | [33] |
| Chitosan/polyacrylic acid hydrogel nanoparticles  (CS/PAA-HNPs) |  | --- | Stimulation of plant growth, yield and more nutrient content | [34] |
| Chitosan-Cu nanoparticles | Cu | --- | pH-responsive sustained release of Cu. Induce seedling growth,  increase in plant height, stem diameter, and root length | [35] |
| Chitosan-Zn nanoparticles | Zn | --- | Delivery of nanoparticles to Stomata, improvement of zinc content to grain up to 42%. | [36] |
| Biochar-based slow-release  fertilizer (BSRFs) | corn straw, nutrients (K3PO4),  and bentonite | Co-pyrolysis | Controlled-release activity of BSRFs. | [37] |
| Zein-coated porous  carboxymethyl starch (PCS) | P, Fe | --- | Sustained release  Improved uptake of phosphorous by plants  Sustainable application in agriculture. | [38] |
| Poly(tannic acid)-coated urea  fertilizer | Urea | --- | The controlled release of nitrogen from the synthesized material than that from free raw urea.  Sustainable agriculture. | [39] |
| Composites of biopolymers and  ZnO NPs | Zn | crosslinking | Slow and sustainable release of Zn from composite nanoparticles | [40] |
| Biogenic  amorphous  silica  (bASi) | --- | --- | Improvement of soil water holding capacity  (SWHC). | [41] |
| nZn–  chitosan | Zn | --- | Increased Zn accumulation | [36] |
| nAu Thale cress | Au | --- | Increased seed germination (%), free radical scavenging responses. | [42] |
| *Moringa oleifera* extract mediated ZnO nanoparticles | ZnO | --- | Enhanced elements Mg, Ca, and Na | [43] |
| ZnO  and CuO Nanoparticles Embedded on an Alginate-Based Hydrogel | Zn, Cu | --- | Sustained release of Cu and Zn for longer period of time | [44] |

**4. BIO-BASED NANOPESTICIDES**

In agriculture, insects are important because they destroy crops and overrun food storage, resulting in deteriorating food quality and the spread of plant diseases. Pest insects infesting agricultural areas and its products seriously disrupt production. Since more than half of the world's population depends on plants and their by-products for sustenance, increasing plant output and maintaining their health are important issues [6]. It is significant to remember that increased crop protection against pest invasion and consequent crop loss depends on the presence of active components in the formulation at the target site at the lowest effective concentration. In real scenario, only 0.1% of the applied pesticides really reach the intended pests; the remaining 99.9% damage the environment, which has negative effects on the food chain and people's health [45]. Pesticide-resistant plants, insects, and infections have emerged as a result of the widespread use of pesticides in the environment, in addition to their negative effects on non-target species [46][9]. The usage of pesticides, on the other hand, has been found to be detrimental to human and animal health and poisonous to the environment. Consequently, numerous pesticides are prohibited by national or international agencies. Use of nanoformulations not only protect plants from pests; also reduce waste, track plant growth, ensure better food quality, and increase global food supply [47][48]. Because nano-pesticides are more reactive at the nanoscale than their bulk equivalents, a tiny amount of them provides better crop protection [49][50]. Pesticide dose and human exposure have decreased as a result of the development of nanoencapsulated pesticides, which is environmentally friendly for crop protection [51].

A novel pesticide formulation with nanoencapsulation of active components offers improved solubility, specificity, permeability, and stability with gradual release characteristics [52][27]. The higher surface area and enhanced action of nanoparticles, lowers the cost and increased the crop production and yields, thus eliminating the application of large amounts of pesticides [53]. The effectiveness of nanoencapsulation or nanocarriers, however, lies on their ability to: promote penetration and facilitate solubility of active components within the target site; monitor or regulate the breakdown of active components in the intended site; and do all three [4][54]. These delivery methods can be controlled for a single aim or a variety of goals, such as site specific target release, time-controlled release, remotely controlled release, or self-regulated release to get past biological barriers in the successful target [4]. In the presence of adequate nanomaterials, slow degradation and regulated release of active components can provide long-lasting pest control [28]. Recently, only a small number of chemical companies have publicly marketed nanoscale pesticides as "microencapsulated insecticides" for sale [49] [3]. Some of the nano herbicides, nano insecticides, nano nematocides, and nano fungicides collectively called as nano pesticides that are commercially available and tested the most frequently are listed in Table 3 and table 4. Insects, rodents, weeds, fungi, viruses, bacteria, and mites are just a few of the pests that can be controlled by nano-based pesticides, fungicides, herbicides, molluscicides, nematicides, miticides, and growth regulators [55][56][57]. When compared to conventional pesticides, the nanoparticle-based pesticides are thought to have less of a negative environmental impact since they make active components more soluble [58][4][27].

**TABLE 3: COMMERCIALLY AVAILABLE NANOPESTICIDES**

|  |  |  |
| --- | --- | --- |
| **NANOPESTICIDES** | **COMPANY** | **REFERENCES** |
| Karate ZEON | Syngenta (Switzerland) | [3] |
| Subdue MAXX | Syngenta (Switzerland, Australia) | [3][49] |
| Ospray's Chyella | Syngenta (Switzerland) | [3][49] |
| Penncap-M | Syngenta (Switzerland) | [3][49] |
| Microencapsulated insecticides | BASF (US) | [3] |
| Primo MAXX | Syngenta (Australia) | [3][49] |
| Banner MAXX | Syngenta (Australia) | [3][49] |

**TABLE 4: BIO-BASED NANOPESTICIDES AND NANOHERBICIDES**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **NANOCARRIER** | **ACTIVE COMPONENT** | **METHOD** | **FUNCTION** | **REFERENCES** |
| Fungicide-Loaded Lignin NCs | azoxystrobin, pyraclostrobin, tebuconazole, and boscalid | Miniemulsion | Antifungal activity | [59] |
| Chitosan | Imazapic and Imazapyr | Encapsulation | Cytotoxicity | [60] |
| Alginate | Imidacloprid | Emulsion | Cytotoxicity | [61] |
| Carboxymethyl-chitosan | Methomyl | Encapsulation | Controlled release | [62] |
| Chitosan/tripolyphosphate  NCs | Paraquat | Encapsulation | Cytotoxic and genotoxic activity | [63] |
| Chitosan/tripolyphosphate  NCs | Chitosan, | Cross-linking | Antifungal effect | [64] |
| Chitosan-saponin  NCs | Saponin | Cross-linking | Antifungal effect | [64] |
| Chitosan-Cu NCs | CuSO4 | Cross-linking | Antifungal effect | [64] |
| Wheat gluten | Ethofumesate | entrapment/extrusion | Lowered diffusivity | [65] |
| Alginate | Azadirachtin | Encapsulation | Slow release | [66] |
| Alginate/chitosan NCs | Paraquat | Complexation  of alginate with  chitosan | Sustainable action | [67] |
| *Serratia* sp. biosynthesized  AgNPs | AgNPs | *Serratia* sp. biosynthesized | Antifungal activity | [68] |
| Turnip leaf extracted AgNPs | AgNPs | Turnip leaf extracted | Antifungal activity | [69] |
| *Artemisia absinthium* extracted  green-synthesize AgNPs | AgNPs | *Artemisia absinthium* extracted  green-synthesis | Inhibit Phytophthora infection  on plants | [70] |
| Chitosan coated Mesoporous silica nanoparticles(MSNs) -  (CTS-MSNs) | MSN | --- | Both MSNs and CTS-MSNs protect from  disease  respectively | [71] |
| Pesticides  Cellulose/silica  nanocomposites | Tebuconazole | --- | 50% improvement in release rate | [72] |
| Lignin | Diuron | --- | Improved controlled release rate | [73] |
| Paraquat loaded Chitosan/tripolyphosphate  nanoparticles | paraquat | --- | Reduce cyto and genotoxicity  of nanoformulations, Reduced  soil sorption | [63] |
| Pectin nanoparticles loaded with metsulfuron methyl | metsulfuron methyl  Imidacloprid | --- | Carriers lower  metsulfuron methyl  the usage of herbicide | [74] |
| Imidacloprid loaded sodium  alginate nanoparticles | Imidacloprid | --- | Encapsulated pesticide showed  reduced toxicity  , decrease in non  target effects | [61] |
| Chitosan nanocapsules carrying  hexaconazole | hexaconazole | --- | Nanoformulations upsurged slow  release thereby efficacy | [75] |
| Extra cellular chitinase loaded  Bovine serum albumin  nanoparticles (BSA Nps) | chitinase | --- | Effective damage of fungal  hyphae | [76] |

**FUTURE PERSPECTIVES**

Nanotechnology has significant impact on many areas of the agriculture sector. Although it has many potential uses, it is important to note that most of the information we currently know about it comes from laboratory tests. The sale of innovative NP-based agrochemicals is further hampered by a lack of regulations, regulatory authorities, and other comparable entities. In order to advance and build futuristic studies based on identified knowledge shortages, it is necessary to carry out extensive trials. Besides, switching from synthetic to biosynthesized or bio-based NPs provide the environmentally safe procedures that might have negligible or no toxicity, therefore going forward, investigations must especially focus on their functional effectiveness. Sustainable farming must be viewed as an eco-friendly approach, where biotic and abiotic organisms coexist in harmony with coordinated food chains and their associated energy balances.

**CONCLUSION**

The application of nanotechnology in modern agriculture farming supports and develops the global economy in a variety of ways. The introduction of NPs makes a significant contribution to addressing the various problems caused by the growing population, plant and animal diseases, and climate change. However, by increasing the use of conventional pesticides and fertilisers to increase crop production, it ultimately harms the environment. Pesticides can be applied more effectively as a result of diverse nanoformulations, and controlled release protects the environment. Several nanopesticides and nanofertilizers are being developed, and have even hit the market. However, certain information on the toxicity issues of many nanoparticles, and lack of understanding of risk evaluations and impacts on human health is still unknown that ensue the applications of these materials restricted. To fully exploit the nanoformulation techniques, extensive database and alarm system development as well as global regulatory and law collaboration are required. Better understanding of their toxicity processes in biological systems, exposure outcomes, and effective control strategies, remain future concerns. Future study should therefore concentrate on comprehending the toxicity of nanomaterials, their effect on the ecosystem, and appropriate techniques for sustainable agricultural production in addition to the correct assessment of the impact on crops, environment and human health.

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