International Journal of Agriculture, Environment and Biotechnology
Citation: *IJAEB*: **15**(02): 195-204, June 2022
DOI: 10.30954/0974-1712.02.2022.6

ASSOCIATION FOR AGRICULTURE ENVIRONMENT AND BIOTECHNOLOGY

ENVIRONMENTAL SCIENCE

Application of Nanomaterials in Agriculture and their Impact on Environment

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Paper No. 976 **Received:** 15-04-2022 **Revised:** 29-05-2022 **Accepted:** 06-06-2022

ABSTRACT

Nanoparticles are a particle with at least one dimensions in nano range (1-100 nm). Nowadays, more than 1000 consumer products are available on the market. However, researchers have developed nanoparticles as nanofertilizers and nanopesticides due to largest share of conventional bulk products in the field of agriculture. These nanomaterials are prepared through top down and bottom-up approaches. Despite of several advantages due to its small size, high porosity, high specific surface area and less required application dose, few researchers indicates its harmful effects in certain cases due to bioaccumulation. The farmers may suffer most due to application of nano based fertilizers and pesticides in long term. Therefore, proper guidelines with proper protective measures should be followed during application of nanoparticles particularly nanofertilizers and nanopesticides in the field conditions.

HIGHLIGHTS

- Nanomaterials enables low dose of the agricultural inputs.
- High efficacy of nanomaterials allowed its use in the field of agriculture.
- Regulatory measures must be followed during spray of nanomaterials in the field.

Keywords: nanofertilizer, nanopesticide, farmer, agriculture, regulatory mechanism

Rapid expansion of population and their demand for food, luxurious items and demanding tendency continuously increasing pressure on our natural resources. In order to preserve the natural resource, it is very important to convert the bulk products into nano products in such a way that requirement of population can be fulfilled without hampering the natural resources in a huge proportion. In agriculture, intensive use of nutrient, pesticides and food packaging materials is done to provide proper nutrient to crops and to prevent crop losses occurs during production and post-harvest stages (Silva *et al.* 2022; Al-Mamun *et al.* 2021). As per IUPAC, any materials having at least one dimension in nano range (1-100 nm) is considered as nanomaterials. These nanomaterials are further divided on nanoparticles, nanofibers and nanoplates (Gubala *et al.* 2018). Nanomaterials are mainly synthesized from two approaches i.e. top down approach and bottom up approach through physical, chemical or biological means. During these processes, either bulk materials is converted to small particles up to nano range or atom/molecules assembled to nano range products (Joshi *et al.* 2020, Khandelwal *et al.* 2019). In general, three types of carriers such

How to cite this article: Khandelwal, A., Joshi, R. and Shrivastava, M. (2022). Application of Nanomaterials in Agriculture and their Impact on Environment. *Int. J. Ag. Env. Biotech.*, **15**(02): 195-204.

Source of Support: None; **Conflict of Interest:** None

as organic or inorganic or mixture of both are used to due to their high surface area, porosity, renewal, biodegradable and environmental friendly application (An *et al.* 2022; Anandhi *et al.* 2020; Selyutina *et al.* 2020; Selyutina *et al.* 2017). During 2019, International Union of Pure and Applied Chemistry (IUPAC) has chosen nanopesticides as one of the emerging nanotechnology for their low impact on environmental health and human health (Ten 2019). Application of nanomaterials in the field of agricultural sciences are continuously increasing. Nanomaterials are used as either nanofertilizers, nanopesticides, customized nano-delivery systems, nanopheromones, nano plant growth regulatos, nanosensors, nanopackaging materials, real time monitoring systems, tagging of animals (Khandelwal *et al.* 2018; Changcheng *et al.* 2022; Srivastava *et al.* 2021; Rana *et al.* 2021). Recently, nanourea products were approved by government of India for application of nitrogen. The product was evaluated and validated according to guidelines for evaluation of nano based agri inputs and food products in India. Fertilizer control order also included nano based agri inputs in its schedule VII, that enables the nano based products in the field of agriculture (IFFCO 2022). Despite of their uniqueness, promising applications, effects of nanomaterial on on environmental matrices are still limited. In agriculture, application of carrier materials are also increasing due to their encapsulation efficiency, entrapment capacity, supramolecular network structure, porosity. Besides, shape of nanoparticles also behaves differently and affects the property and efficacy of nanomaterials (Hussain, 2018). In present review, nanomaterials developed in the field of agriculture particularly for nutrient and pest management and application to prevent post-harvest losses and their impact on environment is addressed.

NANOMATERIALS AND THEIR IMPACT ON ENVIRONMENT

Nanofertilizers

Crop needs an optimum amount of essential nutrient for their growth and biological yield. To cater the need of the crop, micro and micronutrients are supplied through fertilizers either in solid or liquid form through broadcasting/basal application/drenching/foliar spray/robotic means (Madan *et al.* 2016). However, an excess and low dose may create toxicity and sensitivity symptoms on crop system and soil environment. The major drawback of conventional approach is that due to their bulk size and limited supply of nutrients, most of the fertilizer wasted and required in a bulk quantity. To overcome this situation, several researchers attempted to synthesize customize nano-fertilizer and observed their impact on environment (Usman *et al.* 2020; Duhan *et al.* 2017). Srivastav *et al.* (2021) analyzed the response of ZnO nanoparticle on wheat and maize at different concentrations (0-100 mg L^{-1}). The experimental results showed that activities of malondialdehyde and alpha amylase progressively increased, However, activities of antioxidant enzymes (superoxide dismutase, ascorbate peroxidase, guaiacol peroxidase, and catalase) increased upto 100 mg L^{-1} and had a decline trend at higher levels. The results showed that 100 mg L^{-1} concentration of nanoparticle have a stimulatory growth for wheat and maize and can be recommended as a Zn fertilizer source for crop production. In another study, Zhang *et al.* (2021) observed that application of ZnO nanoparticle showed higher grain yield with more panicle number (4.83-13.14%), spikelets per panicle (4.81010.69%), 1000-grain weight (3.82-6.62%) and filled grain rate (0.28-2.36%). The different concentration of nanonutrients such as phosphorous (Liu and Lal, 2014; Gomez *et al.* 2021; Bandala and Berli (2019), NPK (Panda *et al.* 2020; Dimkpa and Bindraban, 2018), potassium (Amirnia *et al.* 2014), Sulfur (Salem *et al.* 2016, Chhipa 2017), Calcium (Zulfiqar *et al.* 2019; Bandala and Berli 2019; Chhipa 2017), Magnesium (Dimkpa and Bindraban, 2018); Iron (Pariona *et al.* 2017; Suresh *et al.* 2016; Mukherjee *et al.* 2016; Subbaiah *et al.* 2016; Afrayeem and Chaurasia 2017; Faizan *et al.* 2018), Zinc oxide (Rossi *et al.* 2019; Du *et al.* 2019; Shang *et al.* 2019), Copper oxide (Wang *et al.* 2019; Malandrakis *et al.* 2019); Titanium oxide (Ramesh *et al.* 2014; Shang *et al.* 2019) were applied as soil, foliar and substrate in soil, hydroponics, Petriplates, pot and promising results for seed vigour and plant growth were observed upto some concentrations. The current research indicates the importance of nanotechnology due to its minimum amount requirement and high efficacy but it's fate on soil organisms, crop, human health is still a researchable issue. Despite of advantages, few researcher indicated that their negative effect on soil microbial biodiversity (Ge *et al.* 2012). Shen *et al.* (2015) showed that ZnO nanoparticles adversely affects the ammonification, respiration, dehydrogenase activities in soil microbes. Researchers have studied the effect of nanoparticles on bacterial and fungus and found that application of nanoparticles such as Ag, Zn, CuO induced apoptosis, structural damage, inhibition of biological nitrogen fixation and soil urease activities, generation of reactive oxygen species, cell wall damage, abundances of ammonia oxidizing bacteria, downregulation of electron transpiration and respiration, nitrification kinetics, destructionof fungal mycelia, loss of cytoplasm, damage to vegetative and reproductive structures, inhibition of AMF symbiosis in rice roots (Ameen *et al.* 2021; Zhang *et al.* 2018; Asadishad *et al.* 2018; Vandevoort and Arai 2018, Simonin *et al.* 2018; Chen *et al.* 2019; Du *et al.* 2020; Arciniegas-Grijalba *et al.* 2019; Priyanka *et al.* 2017) Few studies suggested that long term bioaccumulation and exposure of nanoparticles to the plants, may have impact on food safety. The application of nanoparticles also created pressure on food safety, human and food security and ethical issues. A risk assessment, hazard identification based studies need to be conducted to explore the stability of nanofertilizers prior to commercialization (Al-Mamun *et al.* 2021; Rajput *et al.* 2020; Bundschuh *et al.* 2018; Tiede *et al.* 2016).

Nanopesticides

Pest management including insect, disease causing bacteria, fungi, virus, weeds, nematodes any any undesired species is required to protect the agricultural production. Therefore, huge quantity of crop protectants including chemicals and biologicals are applied to cope up the situation in the field condition. However, intervention of nano based approaches minimized the chemical requirements due to their small size and more efficacy for prolonged duration. Due to nano size some advantages, link enhancement of solubility of water insoluble constitutes, stability of formulations, less use of dangerous organic solvents, high mobility and pesticide ability can be achieved (Asif *et al.* 2021). Researchers have used nanomaterials as a carriers such as Porous hollow silica nanoparticle, nanozeolites, nano clay to entrap pesticides in a cavity. Similarly, nanoemulsion, amphiphilic polymers, lipopeptide based interventions, polylactic acid, poly (ethylene glycol) carboxymethyl cellulose, nanotubular sodium titanate for increasing the target specific chemical and biological based pesticides either in soil based or foliar spray form (Zhu *et al.* 2020; Zaki *et al.* 2017; Cui *et al.* 2020; Hersanti *et al.* 2020; Wen *et al.* 2005) Ali *et al.* (2017) developed a nanoemulsion of neem and citronella oil and found that nano mulsion of neem and citronella were highly effective against *Rhizotonia solani* (ED_{50} 13.67 mg L^{-1} and 25.64 mg L^{-1}) and *Sclerotium rolfsii* (ED_{50} 14.71 mg L^{-1} and 20.88 mg L^{-1}). Adak *et al.* (2012) developed a controlled release formulation of imidacloprid and found its superior against stem fly, *Melanagromyza sojae* Zehntmer and white fly, *Bemisia tabaci* Gennadius as compared to commercial formulations. The effect on crop and seed and soil were also observed and showed no residue of imidacloprid on seed and soil at harvest stage and no nodulation were affected. Zhao *et al.* (2021) demonstrated the encapsulation of emamectin benzoate into amino acid modified cellulose based carriers and increase in fresh weight of plant by 39.77% with no toxicity symptoms on seeds were observed (Zhao *et al.* 2021). In recent periods, hybrid materials of Zineb, Mancozeb (Sarlak *et al.* 2014), Hallow sphere of cypermethrin (Patel *et al.* 2018), Polyelectrolyte complex of MCPA, dsRNA (Alromeed *et al.* 2015; Parsons *et al.* 2018), metallic nanoparticle based material of thiophanate methyl (Malandrakis *et al.* 2021; Keller *et al.* 2017; Starnes *et al.* 2015), coprecipitation, polycondensation, vesicle of trichlorfon, acetochlor, benzoylurea-paraquat, DNA, RNA, copper (Huang *et al.* 2018; Kandpal *et al.* 2017; Kizilay *et al.* 2011; Guo *et al.* 2014; Nuruzzaman *et al.* 2016; Wang *et al.* 2018; Yu *et al.* 2016; Worthington *et al.* 2013), grafted NP and sol gel composites of Benzoyurea-Fe_2O_3, glyphosate (Wang *et al.* 2018; Railenau *et al.* 2010; Ciriminna *et al.* 2011; Xu *et al.* 2018; Chen *et al.* 2018), polymeric emulsion of glyphosate, acetochlor (Guo *et al.* 2014; James *et al.* 2003) an polymeric coatings of diazinon (Yalamalle *et al.* 2019) were developed due to their high efficacy in the field of agriculture. The new properties of nanoparticles put an alarming question on human exposure, pollinators, microbial diversity, aquatic invertebrates, declining insect populations and put a pressure to develop proper regulatory network for establishing the guidelines in the field of agriculture.

Nano plant growth regulator

Plant growth regulators mainly regulate the growth and development of plants at very low concentrations. Santo Pereira *et al.* (2017) demonstrated that alginate/chitosan encapsulated Gibberellic acid (GA-3) showed an increase in leaf area, chlorophyll, and carotenoid content as compared to control. It is also reported that nanomaterials itself can also act as a plant growth regulation and help to plant for their growth and development. In a study, carbon nanotubes (CNTs) influenced the plant growth and composition of soil microorganism and tomato cultivation were increased (Khodakovskaya *et al.* 2013). Similarly, growth of coriander and garlic were increased due to application of graphene quantum dots (Chakravarty *et al.* 2015). Han *et al.* (2022) derived a carbon dots using sodium dinitrophenol and found that 0.02 mg ml^{-1} concentration were found to be effective to act as a seed treatment in cotton crop. It might be due to enhanced respiration and metabolism activity, that helps to promote dormancy and break seed dormancy. A study was also conducted for pilot scale production of nanoencapsulated plant growth regulators such as indole acetic acid, gibberellin and cytokinin. Plant growth regulators were extracted from plant growth promoting bacteria and process s for encapsulation of PGRs in liposomes were optimized. Results showed that application of 30 and ppm nano IAA resulted increased in the root dry weight of tomato seedling and 14% yield of cassava, respectively. Similarly, 10 ppm nano GA increased survival rate of banana and plant height (Fernado *et al.* 2017). Baday *et al.* (2021) observed the effect of HormoGroe®, a controlled release nano plant growth regulator (auxin, cytokinin and gibberellin), on culturable soil bacterial population, urease and dehydrogenase activity. It is found that HormoGroe® can be effectively used and can be considered as safe for soil microbiome.

Nanopheromone

Pheromone is most popular compounds as it attracts/repels the pest and make the changes in behavior of pest populations. However, due to less shelf life and high volatility nature, these are easily lost. Research intervention based on encapsulation, porosity of the carrier materials increased the scope of application of pheromone for pest management. Several researchers developed a strategy for released of pheromone from controlled release polyethylene dispenser (Larson *et al.* 2020), cetyltrimethylammonium-zeolite modified nanoporous material (Seo *et al.* 2016), composite membrane of poly(butylene adipate-co-terephthalete) and activated charcoal (Correia *et al.* 2019), low molecular mass gelators (Bhagat *et al.* 2013) etc. During these approaches pheromone is entrapped in porous material or inside the supramolecular network structure, which caused less interaction with humidity, temperature and/or external environment. It results to cause increase longitivity and shelf life of the active ingredient. Anish *et al.* (2017) synthesized a novel assembly pheromone (guanine, xanthine and adenine) trap for tick control in dog kennels.

Nanopackaging

Each year, lot of packaged food is spoiled due to less shelf life of products, oxidation of the material, non-antimicrobial activities. To overcome, these situations, nanotechnology based interventions helped researchers to combat these situation and helped to enhance the shelf-life of food products (Rana *et al.* 2021). Incorporation of oxygen scavenger nanoparticle such as nano-titanium oxide (TiO_2) in food packaging materials help to prevent the degradation of fruits and vegetables (Echegoyen *et al.* 2015; Kuswandi *et al.* 2017). Ripening of fruits can be prevented by reducing the concentration of ethylene gas with the use of silver nanoparticles (Hu *et al.* 2003), Silver nano particles can also be used to reduce the microbial infection in food material (Sidorowicz *et al.* 2021). Thus, incorporation of nanoparticle in food packaging such as silver, copper, titanium oxide, magnesium oxide, chitosan nanoparticles, carbon nanotubes, quantum dots, can be effectively used to increase the shelf life of the horticultural fruits and vegetables and also processed food materials (Grumezescu 2016; Islam *et al.* 2018; Echegoyen *et al.* 2015; Chaudhry *et al.* 2008; Jin *et al.* 2009; Momin *et al.* 2015).

Nanosensor

A precise application of nutrient, pesticide, and detection of pest infestation and diseases infection in the field of agriculture and allied subjects including horticulture, dairy, showed an opportunity to develop precise, reliable, small weight instrument. The application of nanotubes, nanowires, nanofibers, nanocomposites, nanorods, nanostructured polymers can be used for development of nanosensors. Real time monitoring made the use of nanomaterials possible for precise application of nutrients and pesticides (Rana *et al.* 2021; Márquez and Morant 2015; Hoque *et al.* 2021).

Environmental safety

Despite of tremendous potential of nanomaterials, application of these materials is not reached to the larger section of the people particularly in the field of agriculture. Most of the researches are still limited to lab stage. However, if few reaches to the field under testing site but exposure to human and risk assessment studies were not conducted. In order to make proper dissemination of nanotechnology based interventions, integration of present nutrient cycling, crop productivity models with nanoinformatics approaches may open a new options to explore the fate of nanomaterials in the environment and risk assessment in human at field condition (Zhang *et al.* 2021). Experimentation on exposure must be conducted to reach to the conclusion for safety of any kind of nanomaterials. Due to their nano sizes, abundance f nanoparticles in respiratory tract, blood cells may also create a health related issue (Juárez-Maldonado *et al.* 2021; Yang *et al.* 2021).

GUIDELINES FOR EVALUATION OF NANO BASED AGRI-INPUT AND FOOD PRODUCTS

The integration of science based nanotechnology helped to create boon in the field of agriculture. Recently, Guidelines for Evaluation of nano based agri-input and food products were issued in India in year 2020. These guidelines not only cover the nanonutirents, but it also includes the nano composites and sensor made from nano materials and those that require directo contact with crops, food and feed for data acquisitions. These guidelines were jointly prepared by Department of Biotechnology (DBT), Ministry of Science and Technology, Ministry of Agriculture and Farmers' Welfare (M/o A&FW) and Food Safety and Standards Authority of India (FSSAI), Ministry of Health and Family Welfare through concerted Inter-Ministerial efforts coordinated by DBT (PIB 2020). In India, regulators of proposed guidelines are as follows: Fertilizer Control Order (FCO), Central Insecticides Board and Registration Committee (CIB&RC), Food Safety and Standards Authority of India (FSSAI), State agriculture departments and Bureau of Indian Standard (BIS). In other parts of the worlds, regulatory body/responsible organization for nanoproducts in agri-food systems are as follows: Food and Drug Administration (FDA) & US-Environmental Protection Agency (US EPA) in United State of America; Canadian Food Inspection Agency (CFIA) and Public Health Agency of Canada (PHAC) in Canada; European Commission (EC), European Parliament and Council in Europe; Federal Office for the Environment (FOEN), Swiss Federal office of public health (FOPH) in Switzerland; Food Standards Australia New Zealand (FSANZ) in Australia and New Zealand; Ministry of Agriculture, Ministry of Health in China; Ministry of Food and Drug Safety (MFDS), Korean Food and Drug Administration (KFDA), Korean Agency for Technology and Science (KATS) in South Korea; Ministry of Health, Labour and Welfare in Japan; Iran Nanotechnology Initiative Council (INIC), Nanotechnology Committee of Food and Drug Organization (FDO) in Iran; Taiwan Nanotechnology Industry Development Association (TANIDA) in Taiwan; Food & Drug Administration of the Ministry of Public Health in Thailand. These guidelines are also harmonized with the provisions of international guidelines of Registration, Evaluation, Authorization and Restrictionof Chemicals (REACH), Organization for Economic Cooperation and Development (OECD), U. S. Environmental Protection Agency (US EPA), Toxic Substances Control Act of 1976 (TSCA), Australian Pesticides and Veterinary Medicines Authority (APVMA), Food and Agriculture Organization of the United Nations (FAO)/World Health Organization (WHO), U.S. Food and Drug Administration (US FDA), European Food Safety Authority (EFSA), Food Standards Australia New Zealand (FSANZ) and Codex. The principle of International Council for Harmonisation of Technical Requirements for Pharmaceuticals for Human Use (ICH) may be followed, if any specific study is not included for regulation of nano agri input products (NAIP) or nano agri products (NAP).

CONCLUSION

Nanoparticles has tremendous efficacy as compared to bulk particle due to high specific surface area, nano size, penetration behavior. Despite of it, due to less information about field based experimentation; less availability of fate of applied nanoparticles on soil, plant, microbial diversity in a one study creates a problem of policy people to reach into one conclusion. Since, few studies suggested the harmful effect of certain nanoparticles due to chronic accumulation of it in the food chain. Initiative of Department of Biotevhnology enabled the use of nano based agri products in the field of agriculture. However, protective measures need to be adapted, while applying nanofertilizers and naopesticides in the field conditions. A certain guideline, related to exposure of human being during application of nano based products in the field conditions also need to be adapted by policymakers and should come forward with positive approach with proper recommendation package and practices to make these nanoparticles as a consumption product in the field of agriculture.

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