



Engineered Nanoparticles in Smart Agricultural Revolution: An Enticing Domain to Move Carefully

Pratap Srivastava, Rishikesh Singh, Rahul Bhadouria, Dan Bahadur Pal, Pardeep Singh, and Sachchidanand Tripathi

Abstract

Nanotechnology may potentially benefit our agro-ecosystems in multiple ways, primarily via reduction in agricultural inputs without yield penalty and enhanced absorption of nutrients by the plants. In this regard, nano-fertilizers (such as engineered metal oxide or carbon-based nano-materials, nano-coated fertilizers, and nano-sized nutrients), and nano-pesticides (inorganic nano-materials or nano-formulations of active ingredients), might bring targeted as well as controlled release of agrochemicals in order to tap the fullest biological efficacy in already stressed agro-ecosystems, without over-dosages and leach-outs. Therefore, such nano-tools may multiply the agricultural yield, providing protection against various pests and diseases, without polluting our soil and water ecosystems at the same time. Though nanotechnology may provide potential solutions on such critical and persistent issues in agricultural management and activities; however, new environmental and human health hazards from their applications itself may pose

unforeseen challenges to the humankind. For example, the biosafety, adversity, unknown fate, and acquired biological reactivity/toxicity of these nano-materials once dispersed in environment after application are still an unknown and threatening area, which needs to be investigated carefully and scientifically, before its open field use in our agro-ecosystems. Among other potential benefits, nano-tools may also be utilized for the rapid disease diagnostic in field crops and monitoring of the packaged food quality and contaminations. Similarly, the quality and health of soils and plants can be regularly monitored in real-time manner with the help of sensors based on highly sensitive nano-materials. However, a responsible regulatory consensus on nanotechnology application in agriculture needs to be developed, based upon profound scientific foundations. This chapter explores the area of nanotechnology in revolutionizing agriculture in a smart way via its known interactions with plants and soil microorganisms so far in the literature.

Keywords

Agrochemicals • Carbon nanotubes • Nano-fertilizers • Nano-pesticides • Nanopolymer • Quantum dots • Sustainable agriculture

P. Srivastava (✉)

Shyama Prasad Mukherjee Government PG College,
University of Allahabad, Prayagraj, 211013, India
e-mail: prataps103@gmail.com

R. Singh

Institute of Environment and Sustainable Development (IESD),
Banaras Hindu University, Varanasi, Uttar Pradesh 221005, India

R. Bhadouria

Department of Botany, University of Delhi,
New Delhi, 110007, India

D. Bahadur Pal

Department of Chemical Engineering, Birla Institute of
Technology, Mesra, Ranchi, 835215, Jharkhand, India

P. Singh

Department of Environmental Studies, PGDAV College,
University of Delhi, New Delhi, Delhi 110065, India

S. Tripathi

Deen Dayal Upadhyaya College, University of Delhi,
New Delhi, 110078, India

1 Introduction

Agriculture is fundamental to human civilization, which, therefore, also primarily associates with the sustainability of our system and human health (Srivastava et al. 2016; Mishra et al. 2018). The primary objective of nano-materials, for which they are being explored in agriculture domain, is economy and efficiency (i.e., to reduce agrochemicals, minimize nutrient leach-out with an increase in yield it provides, in a cost- and time-effective manner) (Marchiol et al. 2020; Pirzadah et al. 2020). Agriculture produces and

provides raw materials as human food as well as feed for various industries (Srivastava et al. 2016). The constantly growing human population with limited land, water, and soil availability prompts the agricultural development to keep pace with it and become increasingly more viable economically as well as efficient with time, but safe environmentally for sure. This alteration in agriculture would also be vital for bringing people back in the agricultural business, to opt them out of poverty and hunger (for socio-economic improvement), which is prevalent in most parts of the developing world (Mukhopadhyay 2014). In this regard, new and innovative technology providing better agricultural production in cost- and time-effective manner is need of the hour, and nanotechnology holds a great promise to fill up that space and produce qualitatively and quantitatively better food with lower cost, energy, and waste production in a smart manner (Hossain et al. 2020; Marchiol et al. 2020).

In recent years, a diverse spectrum of potential applications of nanotechnology has been observed in the agriculture, prompting intensive researches across the globe (Chen and Yada 2011; Dasgupta et al. 2015; Parisi et al. 2015). Initially, the term nanotechnology was first coined by Professor Norio Tanaguchi in 1974 (Bulovic et al. 2004), for a domain wherein unique changes in physicochemical properties of materials happen in their nano-size, in sharp contrast to their bulk counterpart (Burman and Kumar 2018). However, it was Eric Drexler who formally introduced the term nanotechnology in his book “Engines of Creation” to the world. Nanotechnology holds a great promise in providing efficiency and economy to the system, particularly in agro-ecosystems. This area of nano-size world (termed as nano-science), with magical properties, evolved gradually, but greatly in last decade, as can be observed by the growing scientific publications and higher captured market size in short time, which also enabled us today to develop cutting-edge applications in most of the important sectors/domains of human life, along with improved instrumental ability to synthesize and isolate engineered nano-materials (ENMs), precisely (Gibney 2015).

Though, nanotechnology in material sciences and electronics has relatively higher dynamics, its potential use in agriculture and food supply chain segment has evolved quite recently. Many engineered nanoparticles (ENPs) have also been synthesized in recent years for a large number of nano-materials based products. Particularly in agriculture, nano-materials are being specially tailored as nanopesticide, nanofertilizer, and nano-biosensor for improving agriculture. However, in-depth scientific studies are being done to understand the impact of ENPs on plant growth, metabolism and physiological processes, and agro-ecosystems productivity/management in order to develop smart nanotechnology applications for revolutionizing agriculture to a next level in a smart manner.

Products that are synthesized via nanotechnology using specialized techniques are known as nano-materials (NMs). It is estimated that over 800 nano-material products are currently available in the market, worldwide. Generally, NMs refer to colloidal particulates with size range lying between 1 and 100 nm, in at least one of their dimension. These NMs reveals size-dependent characteristics, including large surface area/volume ratio and unique optical properties specifically, which lies somewhere intermediate to individual molecule and bulk material. The main categories of NMs include metal oxides, zero-valent metals, quantum dots, carbonaceous, semiconductor, lipids, nanopolymer and dendrimers featuring distinct and diverse characteristics. Additionally, fullerenes and carbon nanotubes are defined as most widely used organic NMs. The change in property of NMs, in sharp contrast to their bulk counterparts and distinct magnetic property in nano-size, owes to the alteration in atoms and larger surface area (due to smaller size of NMs), resulting in high reactivity (Burman and Kumar 2018). The altered property of NMs is specifically related with the change in electronic energy level, specifically due to the alteration in surface area/volume ratio (Prasad et al. 2016). Chemically synthesized nano-materials, being toxic and mostly costly in nature, are now being synthesized alternatively from plant as well in a domain called green nanotechnology. The later is a safe process and is cost- and energy-efficient, but with reduced waste (also because it is mostly produced from waste) and greenhouse gaseous production (Prasad 2014). The recent shift toward the green nanotechnology is at a faster pace, as it is environmentally sustainable. In spite of this green transition, various issues with NMs use in the agricultural field remain open ended, which hopefully would resolve with scientific advancement in the concerned field (Kandasamy and Prema 2015). Quite recently, the biocompatibility, cost-effective synthesis, and enhanced sensitivity to external stimuli have accentuated interest of scientific communities in polymeric NMs, as compared to chemically synthesized counterparts (Baskar et al. 2018).

In modern agriculture, it is quite difficult task to produce crops without pesticides, fertilizers, despite knowing the potential hazardous implications these chemicals unleash upon organisms, not intentioned to affect (including plants, mesofauna, macrofauna, and soil microbiota), human health and environment (Kah 2015; Abbas et al. 2019; Pérez-Hernández et al. 2020). Researches reveal that the primary mechanism through which ENPs cause toxicity is reactive oxygen species (ROS)-mediated oxidative stress, either via physical direct damage or release of toxic ions after nanoparticle dissolution process (Abbas et al. 2019). However, the impact of ENPs on soil microorganisms and plants differs considerably depending upon NMs and soil used. Moreover, the species of microorganism and plant used in

the study also considerably affects the results (Khan and Akram 2020). The calibrated use of engineered nanoparticles may drive high-tech agricultural system bringing second revolution in agricultural diaspora. It may thus enhance the quality and quantity of agricultural yield with reduction and/or elimination of the detrimental influence of modern agriculture on environment (Liu and Lal 2015; Shang et al. 2019). In recent years, cost- and time-effective systems are being favored for detection, monitoring, and diagnosis of biological host molecules standing crops in agriculture (Sagadevan and Periasamy 2014). In this regard, NMs can improve the sensitivity, performance, and handiness of the biosensors, in detecting nutritional health status of soil and plant health as well as disease status in real-time manner (Fraceto et al. 2016). Similarly, processed and packaged foods can also be sensed for mycotoxins rapidly with use of NMs biosensors (Sertova 2015). A brief description of major ENPs, potential role of available nano-tools in agriculture via their interface with plant metabolism and soil microorganisms, including eco-toxicity, as well as their potential role in revolutionizing agriculture is discussed in this chapter.

2 A Brief Note on Widely Used Engineered Nanoparticles (ENPs)

2.1 Carbon Nanotubes (CNTs)

Carbon nanotube is equivalent to two-dimensional graphene sheet, which is rolled into a tube shape. Single-walled (SWNTs) and multi-walled (MWNTs) nanotubes are the two distinct forms of carbon nanotubes. The mixing of σ and α bonds as well as rehybridization properties of electron orbital of CNTs confers unique properties (i.e., conductive, optical, and thermal) for nano-device applications to achieve sustainable agricultural conditions (Raliya et al. 2013). CNT-based targeted delivery of agrochemicals to hosts might help control the surplus chemicals, which might bring severe damage to plants and environment after their release in the surrounding (Raliya et al. 2013; Hajirostamlo et al. 2015).

2.2 Quantum Dots (QDs)

Semiconductor QDs possess excellent fluorescence and show size tunable band energy (Androvitsaneas et al. 2016) and unique spectral properties, therefore are generally used in bioimaging and bio-sensing (Bakalova et al. 2004). Therefore, it has been utilized in live imaging of plant root systems as dyes to verify known physiological processes (Hu et al. 2010; Das et al. 2015). It has been found that QDs

at low concentration show no detectable cytotoxicity for seed germination and seedling growth.

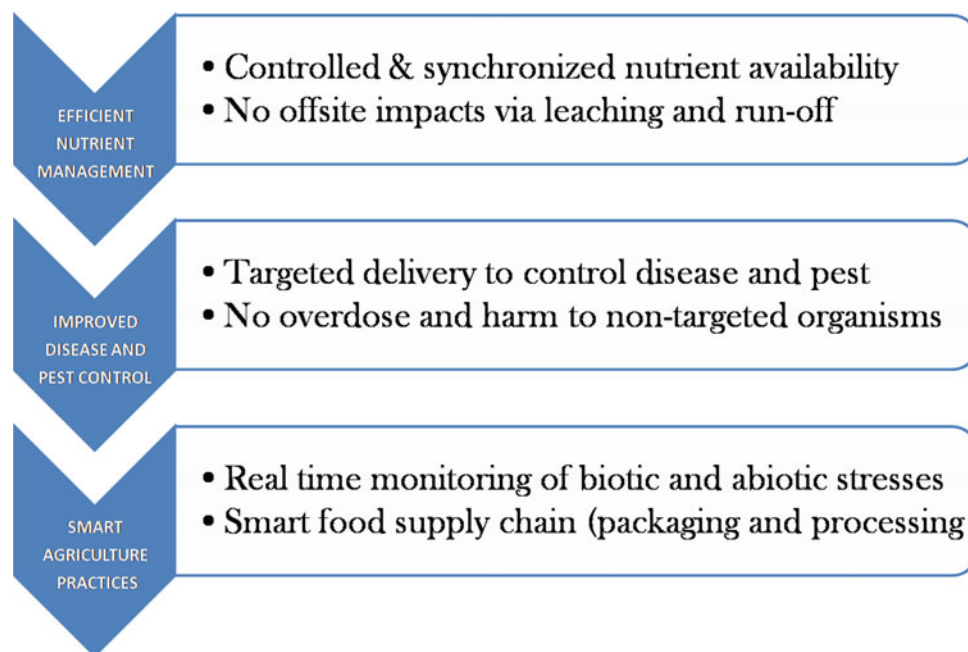
2.3 Nano-encapsulation, Nano-rods and Nano-emulsion

Encapsulation protects substances from adverse environments and helps in their controlled delivery with precision in targeting (Ozdemir and Kemerli 2016). Nano-encapsulation term is used as per the size range it achieves after encapsulation. Nano-capsules, which consists of an liquid core ensheathed by a polymeric membrane (Couvreur et al. 1995), have considerable application in drug delivery, enhanced bioavailability of nutrients/nutraceuticals, fortification of food, self-healing of materials, and in the area of plant science research (Ozdemir and Kemerli 2016). Nano-emulsion is a multifunctional material of plasmonic nature, which remarkably couples the sensing phenomenon (Bulovic et al. 2004). Nano-emulsion is nano-scale oil/water droplet, which exhibits size lower than 100 nm (Anton and Vandamme 2011). It appears optically transparent and is particularly advantageous, when incorporated into drinks. It has been observed that the nano-emulsion formation requires very high energy. Nano-rods are nano-sized materials, having standard aspect ratio between 3 and 5, having their wide use in display technologies, as they change their reflectance under electromagnetic field, owing to their change in orientation; however, it has harmful impact on plant processes. For example, the gold nano-rod at high concentration brings lethal physiological change in watermelon plant (Wan et al. 2014) and also considerably affects the transport of auxins in tobacco (Nima et al. 2014).

3 Nanotechnology in Sustainable Agriculture

The nanotechnology might help in improved agricultural productivity, primarily via enhanced nutrient control on release for synchronized availability and monitoring of pesticide's efficient use and water quality (Gruère 2012; Prasad et al. 2014). In this regard, the increased applications of fullerenes, nanotubes, biosensors, controlled and targeted delivery systems, nanofiltration, etc., in the agriculture and associated supply chains are being observed widely in recent years (Ion et al. 2010; Sabir et al. 2014). This emerging technology is efficient in agricultural management of natural resources (nutrient and water), drug delivery mechanisms in plants, and in maintenance of the soil's health (Fig. 1). However, its potential use in agricultural biomass and waste management as well as in the food industry is also being observed (Floros et al. 2010). Recently, nanosensors (e.g.,

Fig. 1 Potential use of nanotechnology in movement towards 4th agricultural revolution



electrochemical, optical) have been used for monitoring of soil and water contamination for detecting the traces of heavy metals (Ion et al. 2010). Similarly, nano–nano interaction is being tapped to remove the toxic elements in agricultural soils for obtaining healthy foods (Ion et al. 2010; Dixit et al. 2015). NMs catalyze degradation of waste and toxic materials directly as well as indirectly (via improving the efficiency of microorganisms), helping in bio-remediation of the polluted agro-ecosystems. A general assessment of the risks of ENPs is difficult, owing to their diverse inherent and acquired activity under varied set of environmental conditions (Prasad et al. 2014). ENPs may affect the chemical composition, shape, surface properties, extent of particle aggregation (clumping), or disaggregation of other particles, depending on their sizes variability, which may lead to their toxic effects (Ion et al. 2010).

3.1 Engineered Nanoparticles (ENPs) in Agriculture

In recent years, new engineered NMs, using inorganic, polymeric, and lipid nanoparticles, have been synthesized, via techniques called emulsification, ionic gelation, polymerization, oxido-reduction, etc., in order to sustainably increase the agricultural productivity. Such ENPs, which are engineered for distinct physical (shape, size), and associated electrical properties (such as surface properties), further bring a distinct catalytic activity, enhancement in strength and conductivity (thermal and electrical), and controlled delivery of host molecules. Using these remarkably unique

nano-systems, bringing nutrient immobilization and their controlled real-time release in soils, as per plant needs, may bring efficiency and economy in resource use in agro-ecosystems. As an effect, it minimizes nutrient leaching and eutrophication and improves the nutrient uptake by plants (Liu and Lal 2015). Similarly, improvement in pesticides characteristics such as enhancing their solubility potential and resistance against the activity loss, and ability of a highly specific and controlled delivery toward targeted organisms in recent years, may have considerably made the agricultural practices safe, without any off-site repercussion (Mishra and Singh 2015; Grillo et al. 2016; Nuruzzaman et al. 2016). Similarly, the use of hydrogels, nano-clays, and nano-zeolites to improve water holding capacity and capacity of soils to slowly release the water during dry seasons has also been explored. This might help in agricultural sustainability as well as in the most required reforestation programs of degraded lands, limited mostly due to water scarcity. In this regard, organic (polymer and carbon nanotubes) as well as inorganic (nano-metals and metal oxides) NMs have also shown great promise, due to their great capability in quick absorption of the contaminants present in the environment (Khin et al. 2012), helping to remediate soils in cost- and time-effective manner (Sarkar et al 2019).

Quite recently, nanoparticles are also being explored to revolutionize plant genetic engineering aspects in order to develop plants with improved resistance and qualities, easily. Most such studies on how NMs can be used effectively in plant genetic engineering have been observed via plant tissue culture. Recently, carbon nanotubes scaffolds

have been applied in plants to successfully deliver linear, DNA plasmid and siRNA in *Nicotiana benthamiana*. Similarly, silicon carbide-based transformation has been observed as a successful method to deliver DNA in various plants such as tobacco, maize, rice, soybean, and cotton (Asad and Arsh 2012). In a similar way, stable genetic transformation in cotton plants via magnetic nanoparticles (MNPs) has also been achieved successfully (Zhao et al. 2017). Moreover, genome editing via mesoporous silica nanoparticles (MSNs) is being tested as a promising approach in recent scientific studies (Valenstein et al. 2013). All these novel approaches are intended to bring novelty and easiness in agricultural production in cost-effective manner.

3.2 Engineered Nano-materials as Stimulant of Plant Growth

Over the last two decades, ENPs research in medicine and pharmacology has been significant, especially for diagnostic or therapeutic purposes (Perrault et al. 2009). Recently, these NMs are receiving an increased interest in the field of crop sciences/agronomy, particularly in the application of NMs as vehicles of agrochemicals or bio-molecules in plants to enhance crop productivity (Khan et al. 2017). Generally, ENPs are applied to roots or vegetative part of plants, preferably to the leaves. Generally, its uptake has been observed a little more complicated in the soils, as compared to the aerial parts of the plants (Sanzari et al. 2019). The uptake, mobilization mechanisms, and biological effects of these NMs with plant are still in infancy, and it is not a wise opinion to move with imperfection in field applications, without knowing their intricate interactions with plants, soil microorganisms and environment, completely and scientifically. In several studies, specific (low dose) concentrations of ENPs, foliar spray/irrigation, and carbon nanotubes have significantly improved plant growth, physiological aspects (chlorophyll *a*, *b*, carotenoid content, photosynthesis, carbohydrates), antioxidants, and plant tolerance against biotic and abiotic stress (Nafees et al. 2020).

In recent studies, ENPs (particularly, based on carbon, metal, and metal oxides) influence on plant physiology and growth showed that it considerably affects seed germination in higher concentration. For example, zinc (Zn) and copper (Cu) oxide nanoparticles, being essential micronutrients, have been observed to act as a significant plant growth promoting complex (Priyanka et al. 2019). Surprisingly, it has been noted that various kinds of ENPs affect the plants ability and behavior, in a differential and sometimes in a contrasting manner. Some plants are even capable of uptake and accumulation of ENPs. Carbon nanotubes and Au, SiO₂, ZnO, and TiO₂ nanoparticles have shown potential to expedite growth of plants, by increasing the uptake of

elements and improved nutrient utilization (Khot et al. 2012). Ag-NPs at low concentrations have shown enhanced shoot and root growth enhancing chlorophyll production and antioxidant enzyme activity, limiting production of reactive oxygen species (ROS) in the plant tissues (Sami et al. 2020). However, the impact of nanoparticles on plant behavior depends largely on the size, surface charge, composition, concentration, and physicochemical properties of the nanoparticle used, besides the susceptibility of the concerned plant species (Ma et al. 2010; Lambrea et al. 2015).

Notably, studies show that nanoparticles might be efficient stimulator of plant growth irrespective of their nature. However, comprehensive experimentations are needed to optimize their application conditions and identifying their specific impact on plant's physiology (Fincheira et al. 2020). The plant cell-ENP interaction leads to a change in plant's genetic expression and associated metabolic pathways as well, which affect plant growth and developments as a consequence, in a remarkable manner (Ghormade et al. 2011). For example, a pronounced increase in germination rate of rice and wheat has been observed under carbon nano-materials, especially CNTs (Wang et al. 2012). The beneficial impacts of accumulation of nano-materials in plants, particularly in MWCNTs, ZnO, and Zn, have also been observed (Hussein et al. 2002). Similarly, TiO₂ nanoparticles have been observed to promote nitrate reductase activity in soybean (*Glycine max*), enhance water and nutrient absorption/use, and induce the antioxidant machinery to favor plant's growth. In a similar research, TiO₂-treated seeds have shown 73% higher plant dry weight, due to thrice higher photosynthetic rates and a considerable rise (around 45%) in chlorophyll (Mingfang et al. 2013). Also, it has been found to promote the growth in spinach via improving nitrogen assimilation and photosynthetic rate. In a study, Zn nano-materials have shown to promote chlorophyll production, fertilization, pollen function, and germination and reduce the susceptibility of plants to drought stress. However, contrasting findings with other species have also been observed, signaling more studies to be conducted to understand ENPs-plant interaction. The influence of ENPs on various plants differs greatly depending on growth stage, method, and period of exposure (Khiew et al. 2011). Additionally, symbiotic bacteria and fungi in the soil, associated with plant roots, have shown controversial interactions in relation to ENPs. These microscopic entities increase the heavy metal NPs accumulation in turf grasses, however reduce the uptake of nano-Ag and nano-FeO in legumes (Guo and Chi 2014). Therefore, to better understand the interaction of these ENPs with plants and associated microflora, new and improved protocols and techniques (such as magnetic resonance imaging (MRI), microscopy, and fluorescence spectroscopy) might help in reaching appropriate scientific conclusion (Srivastava et al. 2019).

In recent years, the potential use of polymeric soft NMs in delivery of bio-molecules in a smart manner and for developing new mythologies of genetic engineering in plants to enhance their defense mechanisms and induction of growth and development is being actively pursued, worldwide (Sanzari et al. 2019).

There are some major bottlenecks in use of ENPs, which are primarily checking the progress of NMs application in plant growth are: (i) design and synthesis of safe NMs; (ii) understanding mechanisms of NMs uptake and mobilization in plants, and, (iii) the lack of global multidisciplinary collaboration for adequate development and controlled use of nano-applications in plants (Sanzari et al. 2019). Despite, these obvious hurdles to be resolve in years to come, we have multiple nano-applications to boost agricultural development indirectly via controlled release of agrochemicals and smart monitoring systems, to manage agricultural production, cost effectively and environmentally sound manner. Nanotechnology has shown promising observations in laboratory tests in controlling the overuse of agricultural inputs and causing negligible impact on the environment. In this respect, metal oxide nanoparticles offer promising perspective for the development of effective nano-scale formulations of fertilizers/pesticides for their controlled release capacity and targeted delivery, in sharp contrast to the conventional fertilizers and pesticides.

3.2.1 Nano-Fertilizers

Quite recently, nano-fertilizers have been recognized as novel nutrient delivery tools, utilizing nanoparticles of C, Mn, Fe, and ZnO (Liu and Lal 2015). Researchers across the globe have shown that some engineered NMs can increase plant growth in certain concentration ranges, mostly at smaller concentrations. Several studies showed that nanoparticles of essential minerals affected plant growth, depending on their size, concentration, composition, and mode of application. It was reported to enhance increasing crop yields promoting germination, seedling growth, affecting photosynthetic activity, N metabolism, and changes in gene expression (Tapan and Sivakoti 2019). Also, their use in nano-fertilizers can increase the agronomic yields many fold with minimum environmental pollution. Specifically, developing nitrogen and phosphorous macronutrient nano-fertilizers are being given a high research and development priority in current times, both for food production and environmental protection. For example, hydroxyapatite nanoparticles, being used as phosphorous nano-fertilizers today, have been reported to enhance the soybean growth rate and yield considerably, as compared to the ordinary phosphorous fertilizers (Liu and Lal 2015). Also, the slower release of phosphate from the nano-fertilizer contributes to maintain the soil fertility along with eutrophication,

nullifying the runoff or leaching (Liu and Lal 2015). Similarly, Zn deficiency, a key factor limiting agricultural yield, particularly in alkaline soils (Sadeghzadeh 2013), can easily be ameliorated with the use of Zn nanoparticles, in a cost-effective manner. Different nano-fertilizers and nano-pesticides such as Ag, Zn, Fe, Ti, P, Mo, and polymer nanoparticles have shown significant potential as plant growth promoting and pest control agent. Similarly, different kinds of nano-technological tools such as (materials, formulations, composites, emulsions, and encapsulations) have all shown promising result in providing increased nutrition to plants and targeted toxins to the concerned pests in a precise and controlled manner.

Recent studies stated that nanoparticles, made up of essential minerals and non-essential elements, affect plant physiological processes and growth considerably, which primarily depends on size, composition, concentration, and type of application (via foliar and soil routes). Nano-fertilizers may contain nano-zinc, iron, silica and titanium dioxide, InP/ZnS core shell QDs, ZnCdSe/ZnS core shell QDs, Mn/ZnSe QDs, core shell QDs, gold nano-rods, etc. However, comprehensive studies on uptake, fate in biological systems, and toxic influence of several metal oxide NPs (viz., Al₂O₃, CeO₂, TiO₂, FeO, and ZnO) were studied intensively in agricultural production, which equally lauds for their cautious use, as well (Dimkpa 2014; Zhang et al. 2016; Parada et al. 2019a, b).

3.2.2 Nano-pesticides

The potential role of NMs in plant protection and food production is still in infancy. Insect pests, affecting plants as well as stored foods, may be controlled with the use of ENPs (Khot et al. 2012). It has been observed that nano-encapsulated pesticides are released slowly in the applied system and shows greater solubility, permeability, specificity, and stability (i.e., long-lasting pest control efficacy) (Bhattacharyya et al. 2016). Use of such nano-encapsulated agricultural tool leads to the development of non-toxic and promising pesticide delivery systems for better control of such pests with reduced dose and no associated off-site harm to human life and environmental health (Bhattacharyya et al. 2016; Grillo et al. 2016; Nuruzzaman et al. 2016). Nano-encapsulation is designed for desired chemicals delivery to the target biological process. Some products such as Karate ZEON, Ospray's Chyella, Subdue MAXX, PennCap-M, Banner MAXX, Primo MAXX, Subdue MAXX, etc., are available in market as micro-suspensions. Organic and polymeric ENPs as nano-capsules/nanospheres have been used in agro-ecosystem as nano-carriers for application of herbicides. For example, polymeric ENP is highly biocompatible and is being largely used for atrazine encapsulation, a potent herbicide. Similarly, triazine-coated

chitosan nanoparticles have shown lower environmental impact and genotoxicity in *Allium cepa* (Grillo et al. 2016).

4 Engineered Nanoparticles Impact on Soil Microbial Processes

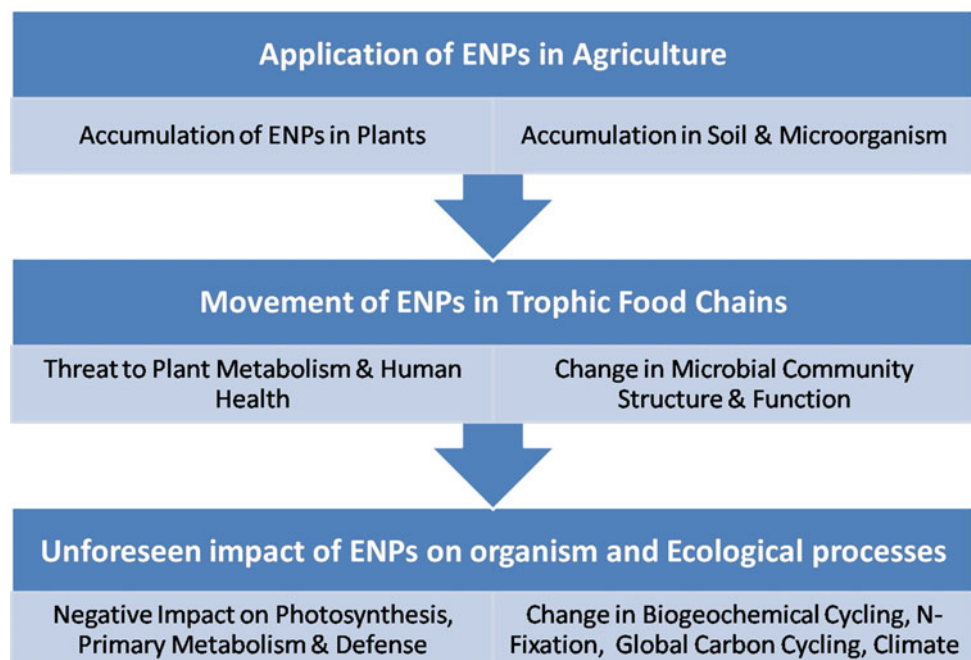
Having diverse range of nanotechnology products around us, its presence in air, water, and soil is unavoidable, owing to no strict regulation and monitoring placed in this regard. Similar to pollution, sources of ENPs into these three systems can also be described as point (production and storage units, research laboratories) or non-point sources. Also, ENPs stand a better change to mobilize to other places via air and water owing to their small sizes. Soil is known to be the highest recipient of ENPs, owing to their extreme resistance and tendency to accumulate. As soil microbial biomass and diversity is crucial for the sustainable use of soils, using ecological subsidies in the form of ecological processes (Torsvik and Øvreås 2002), the nanoparticles may have considerable influences on this ecosystem, mediating a change in soil microbial community characteristics. Metal/metal oxide nanoparticles have been identified as most toxic to soil microbial community which support important ecosystem processes such as nutrient cycling (Fig. 2), thus threatening soil health and fertility (Parada et al. 2019a; b). TiO₂ nanoparticles impact on nitrification process and ammonia-oxidizing bacteria has been observed strongly negative, triggering a cascading negative effect on denitrification activity and considerable change in bacterial community structure (Simonin et al. 2016).

However, contradictory report has also been observed (Chavan and Nadanathangam 2020). ENPs have been observed to affect soil humic acid content, influencing soil bacterial community characteristics (including diversity) affecting decomposition process (Kumar et al. 2012; Ben-Moshe et al. 2013). Soil contaminations of ENPs persist in the soil for long, or they may contaminate ground water (Tripathi et al. 2012).

Among the nano-applications, widely used paints, coatings, and pigments have the highest possibility of getting released into water and soil systems. Owing to close linkage of soil and plant system, ENPs in soil may harm microorganisms and plants, and thus animals and human beings as a consequence, present down the line in trophic food chain. They may also affect soil rhizospheric and phyllospheric microbial community to indirectly affect the plant functioning/metabolism. The presence and persistence of ENPs into the natural environment (such as agro-ecosystems) owing to their widespread use may threaten the favorable microbial communities (bacteria and fungi). Nanoparticles accumulate in our natural systems via soil and water remediation technologies, use as nano-fertilizers and nano-pesticides, and their unintentional emission through water, air, sludge, and sewage (Tourinho et al. 2012; Tripathi et al. 2012; Shandilya et al. 2015; Coll et al. 2016). The measurement of soil CO₂ efflux/respiration and enzyme activity is often used to observe how the ENPs affect soil microbial activity (Simonin and Richaume 2015).

In some recent studies, TiO₂ and CuO ENPs have been found to decrease soil microbial biomass and enzymatic activities, in addition to microbial community structure in

Fig. 2 Harmful aspects of engineered nanoparticles (ENPs) application in agriculture



flooded paddy soils (Xu et al. 2015). Similarly, You et al. (2017) studied the effect of inorganic ENPs on soil enzyme activities (such as phosphatase and urease) and microbial communities of alkaline soils. The study observed a considerable change in abovementioned properties along with harmful impact on biological nitrogen fixation. In another study, Fe₃O₄ ENPs at higher concentration significantly decreased the bacterial count in soil (Jiling et al. 2016). Similarly, zinc oxide and CeO₂ ENPs considerably affected various bacterial groups (such as azotobacter, phosphorous, and potassium solubilizing bacteria) and inhibited various enzymatic activities (Chai et al. 2015). TiO₂ has shown to rapidly decline the soil active bacteria and enzymatic activity, affecting soil microbial characteristics such as activity, abundance, and diversity (Buzea et al. 2007). In a similar study, Concha-Guerrero et al. (2014) observed that CuO ENPs unleashed similar, but a relatively more toxic impact on soil microbial community. It has been generally observed that ENPs of inorganic nature have a relatively greater toxicity than organic ENPs on soil microbial characteristics (Frenk et al. 2013).

In a functional study, CuO and Ag ENPs have shown reduction in decomposition of leaf (Pradhan et al. 2011). Ag ENPs, used in a variety of consumer products due to its antimicrobial properties, significantly impact soil microbial functional and genomic diversity (Samarajeewa et al. 2017). However, contrasting studies also exists in the literature (de Oca-Vásquez et al. 2020). The soil enzymatic activities have also shown a drastic reduction at high concentrations of ENPs (Josko et al. 2014; Asadishad et al. 2018). The impact of ENPs show significant variation with type and dose of NPs as well as soil properties (Xin et al. 2020). Moreover, these ENPs have shown negative impact on self-cleaning ability as well as nutrient providing capacity of soil systems, which determines the level of plant nutrition and soil fertility (Suresh et al. 2013). In a manner, soil properties also determine the toxicity of ENPs. For example, soil pH, textural composition, structure/aggregation, and organic content affect the soil microbial community and the capability of these ENPs to unleash toxic effects on soil microorganisms (Fierer and Jackson 2006; Simonin and Richaume 2015; Read et al 2016). On the contrary, nanoparticles have also been termed as “remediation of the future” owing to their significant role in soil remediation (Sarkar et al. 2019).

5 Nanoparticle's Toxicity on Environment

The invisible pollution due to ENPs is considered as the most complicated type of pollutant to control, owing to its size. The ever-increasing applications and concentrations of ENPs pose enormous threat of their release into the environment, whose risk assessments are very difficult to

quantify and understand at present stage (Servin and White 2016). The existing literature on eco-toxicological impact of nanoparticles is somewhat contradictory; however, in general, low to moderate toxicity of these nanoparticles on terrestrial plants has been observed in most of the scientific studies. A large number of research studies have focused on the toxicity assessment of the ENPs used in industries (Du et al. 2017; Tripathi et al. 2017a, b, c). Generally, the effect of ENPs on crops (such as spinach, onion, coriander, rice, wheat, soybean, lettuce, radish, barley, cucumber) has shown considerable inhibition of seed germination, reduction in shoot and root growth, toxicological effects, decreased photosynthesis and chlorophyll concentration (Tripathi et al. 2017a; b, c, d, e). The toxicity level of a nanoparticle primarily depends upon its solubility and specificity in binding to the biological site. ENPs of metallic nature are primarily antimicrobial in nature (Aziz et al. 2016; Patra and Baek 2017) and show toxicity on the plant cells, depending on surface charge at the membrane (electrostatic interaction), which follows the order: mold > yeast > Gram-negative > Gram-positive. Thus, it may unleash an entirely unknown cascade of change in microbial community dynamics in the concerned ecosystems, which may turn lethal on humans in return (Fig. 2).

Carbon-based nano-materials (nanotubes and fullerenes) can be degraded easily under a wide range of conditions; however, fullerene is preferably absorbed by wood decaying fungi and metabolized. As an effect, fullerene nanoparticles accumulate in microbial cells and are transferred across the food chain further, owing to feeding relationships (Warheit et al. 2004). In case of no acute toxicity, bioaccumulation and long-term exposure to these ENPs may have unforeseen effects on food chain/web. Similarly, the uptake, accumulation, and build-up of nanoparticles vary in plants, depending on its type and size, as well as the plant composition. Among the metal-based NMs studied in this regard (e.g., TiO₂, Fe₃O₄, CeO₂, ZnO, Ag, Au, Fe, and Cu), only fullerene and fullerols show a ready uptake tendency in plants. These NMs enter plant cells variously via aquaporins (a carrier protein), ion channels, endocytosis, and formations of entirely new pores across the plant cells, following apoplastic and symplastic movement and via xylem and phloem. Remarkably, seed, flower, and fruit strongly import fluid from the phloem (i.e., sink activity) and have greater tendency to accumulate ENPs, in relatively higher concentration. Besides toxicological impact on the plant, it raises issue of safety in human and animal consumption of such plant organs (Pérez-de-Luque 2017). In all these cases, they might enter the food chain to unleash unforeseen consequences. Similarly, the excess Fe₃O₄ nanoparticles produce some oxidative stress in plant system, affecting photosynthesis, leading to decline in metabolic process rates. ZnO

NMs are hazardous in nature and may affect the chromosomal and cellular traits.

Several ENPs such as TiO₂, ZnO, SiO₂ are photo-chemically active and generate superoxide radicals under light in oxygenic condition by direct transfer of electrons (Hoffmann et al. 2007). Studies demonstrate that in cultivated plants (such as tomato and wheat), metal-based ENPs triggering an oxidative burst, mediating electron transport chain and impairing ROS detoxifying mechanisms, bring enormous genotoxicity in the plants as a consequence (Pakrashi et al. 2014; Pagano et al. 2016). Moreover, this eco-toxicity is multiplied under simultaneous exposure of ENPs and UV light. The consequent generation of ROS as a response is exploited in determination of toxicity (Sayes et al. 2004). However, their protective effect against oxidative stress has also been observed in some studies (Venkatachalam et al. 2017). Therefore, mechanistic understanding of ENPs metabolism in organism and specific cell need investigation to clarify this ambiguity. Also, delayed impacts of environmental exposure to ENPs need exploration to determine potential mechanisms of adaptation (Cox et al. 2017; Singh et al. 2017). Studies on bioaccumulation of ENPs in food chain and their interaction with other environmental pollutants needs investigation as well, as it may affect major plant processes, compromising agricultural sustainability, detrimentally (Rana and Kalaichelvan 2013; Du et al. 2017).

The introduction of chemical or green ENPs in the fields must be monitored carefully and closely. The nanoparticles, having no harmful NMs, should only be allowed in agriculture for any improvement in yield and other critical issues. The uses of polymeric ENPs in the agriculture having plant-based insecticides coating are unique in itself and are increasingly being permeated (Chakravarthy et al. 2012; Perlatti et al. 2013). As soil health, ecosystem, and crop productivity are primarily determined by soil microorganisms (Mishra and Kumar 2009), the impact of NMs on such organisms also needs through assessment to avoid unseen consequences due to microbial community change across ecosystems. Accumulation of these ENPs in treated/applied soils may threaten soil microbial communities along with associated organisms in food chain (Simonin et al. 2016), which may impair the ecosystem functioning at large in an unpredictable way, owing to their crucial importance.

6 Nano-Biosensor Technology: A Path to Smart Agriculture

In the era of changing climate, smart agriculture to achieve the long-term goal of climate resilient development is need of the hour (Helar and Chavan 2015). Diminishing the material size to nano-scale brings radical change in

physicochemical properties (i.e., quantum size effect) and good transduction properties owing to huge surface area/volume ratio, which can be utilized for analytical purpose in agricultural products (Kandasamy and Prema 2015). The gold ENPs (AuNPs) may be used as transducers for several improvements of agricultural products, such as bio-sensing devices. Biological tests measuring the presence or activity of selected analytics of key importance become highly sensitive and fast with its use (Vidotti et al. 2011; Kandasamy and Prema 2015). The use of nano-biosensors for detection of phyto-regulators and secondary metabolite may help in real-time monitoring of plant growth and development and understanding its environmental interactions in limiting growth conditions (Sanzari et al. 2019). It indicates that the application of nano-scale particles may provide numerous advantages over traditional procedures, which can revolutionize the present-day agriculture in a more smart way.

Nanotubes, nanocrystals, or nanoparticles and nanowires are mostly used in optimizing signal transduction, which are derived by the sensing elements in response to exposure to biological and chemical analytes, having similar size. The surface chemistry and other distinct properties of ENPs (such as thermal, electrical, and optical) help enhance the sensitivity, thereby reducing response time along with improvement in detection limit, which can, therefore, be utilized in multiplexed systems (Aragay et al. 2010; Yao et al. 2014). The distinct physicochemical properties of materials in nano-scale size have been exploited in development of biosensors, as signals are improved remarkably with its use (Sagadevan and Periasamy 2014). It enables us to develop rapid, sensitive, and cost-effective nano-biosensor systems in agriculture, food processing industries, and environmental monitoring. Currently, the sensors based on nanotechnology are at initial phase of development (Fogel and Limson 2016). Metal ENPs (such as silver, gold, and cobalt), CNT, magnetic ENPs, and QDs are some chief candidates which have been actively used in biosensor (device combining biological recognition element with physical/ chemical principles) development. Therefore, biosensor converts the biological response (such as an enzyme, a protein, an antibody, or a nucleic acid) into an electrical signal.

Recently, different natural and artificial bio-receptors have been identified and used widely, such as thin films, enzymes, dendrimers (Rai et al. 2012). The progress in nanofabrication and other techniques (such as mass spectrometry, chromatography, surface plasmon resonance, electrophoresis chips) may stimulate sensor development. Considerable scientific efforts in nanosensor development to supplement decision-making in crop monitoring, in order to achieve precise nutrients and pesticides application and higher water use efficiency via its easy testing in soils for

smart agricultural development, are already in action. In the context of smart agriculture revolution, nanosensors may potentially manage the food supply chain right from crop cultivation to distribution (such as harvesting, food processing, transportation, packaging) (Scognamiglio et al. 2014). The regular monitoring of soil pH and nutrients, residual pesticides in soil and crops tissues, soil humidity, pathogens detection, and prediction of nitrogen uptake using nanosensor can give way to a more sustainable and smart farming system (Bellingham 2011). Also, the presence of pests, pathogens, or pesticides with use of biosensor tools may help us tune the amount of chemicals to use, utilizing the high sensitivity of nanosensors. A network of nanosensors installed across cultivated fields may help in comprehensive monitoring of crop growth in real-time manner, providing quality data for scientific analysis and interpretation (El Beyrouthya and El Azzi 2014). Similarly, bringing automation in the irrigation systems using nanosensors technology under changing climate conditions toward water scarcity may potentially maximize the efficiency of water use in agro-ecosystems in a simple way (de Medeiros et al. 2001).

6.1 Nanotechnology in Food Industry and Supply Chain

Nanotechnology may help in developing analytical devices dedicated specifically to the control of quality, safety, and bio-security from agricultural field to throughout the food supply chain (Valdes et al. 2009). Nanotechnology has multiple uses in food industry. For example, it can help in pathogen detection and diagnosis (via nano-scale biosensors), supply bioactive ingredients in foodstuffs, texture, and color modification in food (via nano-scale filtration system) (Martirosyan and Schneider 2014). Nano-printed, intelligent packaging (Ghaani et al. 2016), nano-coding of paper and plastics materials (Bhushani and Anandharamakrishnan 2014), and nano-additives (Khond and Kriplani 2016) have already been used for authentication and identification purposes in supply food chains. In food quality testing, monitoring, and control of food quality (e.g., smell, taste, color, texture), sensing ability of label and package and nutraceutical delivery can be monitored by using nanotechnology tools.

6.2 Food Processing

In food processing, use of nano-carriers for the delivery of nutrients/supplements, nano-sized organic additives, supplements, and animal feed is in limited use in recent times. Recently, vitamins are being encapsulated and delivered into

human blood efficiently via foods through digestion system. Further, many foods and drinks have also been fortified with ENPs adding benefits to the product, without affecting the appearance/texture and taste. For example, nanoparticle emulsions are added in ice creams, which improve their texture and uniformity (Berekaa 2015). For example, KD Pharma BEXBACH GMBH (Germany) is known to provide encapsulated Omega-3 fatty acids in suspension and powder forms in nano- as well as micro-sizes, which is gaining higher market with time over the conventional one.

6.3 Food Packaging and Labeling

Nanosensors used in recent times in supply food chain ensure food authenticity, quality, freshness, safety, and traceability across food supply chain via faster, highly sensitive, and cost-effective detection of various target molecules. Currently, the assessment of food quality and safety is best using nanosensors, providing smart monitoring of chief food ingredients (sugar, vitamin, amino acid and mineral) and contaminants (heavy metals, pesticides, toxins, etc.). Such kind of intelligent and smart packaging of foods to monitor integrity and freshness of food during transportation and storage is also a trademark of nano-sensor technology (Vanderroost et al. 2014). In them, nanosensors observe the physical parameters (such as pH, humidity, and temperature), to identify gas mixtures (e.g., O₂ and CO₂) in order to detect toxins and pathogens and to control freshness (via ethanol, acetic acid, lactic acid) and decomposition (via cadaverine, putrescine).

Recently, some packaging materials incorporated with “nanosensors” have been used in food industry to detect the oxidation process in milk and meat (Bumbudsanpharoke and Ko 2015). NP-based sensors indicate the color change in case of oxidation/deterioration. ENPs being good barriers for gaseous diffusion, which can be exploited in drink industry (beer, soda waters) to increase in shelf life. Similarly, ENPs in packaging, nano-coating over plastic polymers, slow down processes, such as oxidation and microbial degradation (owing to antibacterial property) further extending the shelf life of food products (Berekaa 2015). Therefore, nanotechnology is a forward-looking technique in agricultural bio-security (Bumbudsanpharoke and Ko 2015).

Engineered nanoparticles show broad-spectrum antibacterial properties against Gram-positive and Gram-negative bacteria. For example, ZnO-NPs have been observed to suppress *Staphylococcus aureus* (Liu et al. 2009). Similarly, Ag-NPs show antimicrobial activity against *Escherichia coli*, *Aeromonas hydrophila*, and *Klebsiella pneumoniae* in a concentration-dependent manner (Aziz et al. 2016). According to recent studies, the major processes through which ENPs unleash their antibacterial effects: (1) bacterial

cell membrane disruption; (2) ROS production; (3) induction of intracellular antibacterial effects following entry into the cell variously (including impact on DNA replication as well as inhibition of protein synthesis) (Aziz et al. 2015; Wang et al. 2017).

7 Future Perspectives: Identification of Gaps and Obstacles

Despite immense smart applications of nanotechnology in agriculture, multiple issues, critical to human and environmental health and sustainability, remain to be resolved with advancement in nanotechnology applications in the area of agriculture. Some key areas requiring critical attention are: (i) hybrid carriers development for delivering nutrients, pesticides and fertilizers to maximize their efficiency in agricultural production (De Oliveira et al. 2014); (ii) risk and life-cycle assessment of NMs (i.e., phytotoxicity) on non-target microorganisms, plants and pollinators insects; and (iii) strict regulations for the use of NMs based on fundamental scientific findings.

The implementation of nanotechnology in agriculture requires even higher technical advancement, enabling ENPs quantification at lowest possible concentrations, present in different environmental compartments for its life-cycle assessment (Kookana et al. 2014; Sadik et al. 2014; Parisi et al. 2015). ENPs interaction with organisms (target as well as non-target) and the presence of synergistic effects are undeniable. Therefore, infrastructure and methodologies to characterize, localize, and quantify ENPs in the environments should be developed beforehand, mobilizing knowledge exchange and co-ordination between scientists across research fields throughout the world (Malysheva et al. 2015). In time to come, these ENPs would provide us enormous potential in identifying cutting edge and cost- and time-effective development routes to achieve smart human civilization across the globe.

8 Conclusion

It is a ripe time to take a modern knowledge and tools in agricultural management to prepare ourselves self-sufficient to feed the growing population in a sustainable manner, under changing climate conditions, without damaging our environment any further. The emergence of engineered nano-materials application for achieving sustainable agriculture has revolutionized world agriculture to meet global food demand in environmentally sound and resource

efficient manner, with reduced farming risks at the same time. These nanotechnology applications take us forward to efficiently use the natural resources, via nano-scale carriers and compounds to avoid loss and overdose of pesticides and fertilizers, causing pollution. Similar smart applications can be found today across the food supply chain, starting from agricultural production, animal feed, food processing, and additives, with ever-growing importance. Despite having plenty of information available on individual nano-materials in relation to agricultural benefits, their unpredictable course of eco-toxicity level, once they reach in our environment, is still challenging, which can be largely attributed to the scanty understanding of risk assessment, particularly in relation to human and environmental health. Therefore, we need to strike a balance between nanotechnology applications and implications in agriculture and food production, as this smart technology stands a better place to promote social and economic equity as well. Also, we have to thoroughly perform a reliable risk-benefit assessment, and full cost accounting evaluation before open field applications. Likewise, reliable methods to characterize and quantify these NMs in different environmental compartments, and evaluation of their interaction with bio-macromolecules present in living systems and environments must be given top priority. At the same time, development of comprehensive database and alarm system with multidisciplinary collaborative mindset, as well as international cooperation in regulation and legislation are necessary for potential exploitation of this ENP technology. Furthermore, engaging all stakeholders including non-governmental (NGOs) and consumer associations in an open dialogue to acquire consumer acceptance and public support for this technology is also critically required.

Author Contributions

PS* developed the idea in major consultation with RS and RB, which was revised with the help of RS, RB, DBP, PS, and SNT. All authors have proofread and approved the final draft of the chapter.

Conflict of Interest Statement

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Acknowledgements The authors would like to thank University Grants Commission (UGC), New Delhi, India, for providing funding support as Start-up Grant (BSR): No. F 30-461/2019 (PS), JRF/SRF (RS) and DS Kothari fellowship (RB). Also, the corresponding author would like to acknowledge the University of Allahabad and Shyama Prasad Mukherjee Government PG college for their infrastructural and other supports in developing a research facility.

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