Advances of Engineered Nanofertilizers for Modern Agriculture

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Abstract

This chapter focuses on the applications of nanotechnology in fertilizers and utilizations of engineered nanomaterials as fertilizers for plants. Nanotechnology is a promising technology that has vast applications. Its utilization in agriculture and related fields are myriad. Recently, many products are developed in parallel with the growing of agri-nanotechnology. Fertilizers are the material that contains nutrients that are essential for the plants. Nanofertilizer is the new generation fertilizer. During the applications in soils or in plant tissues, it delivers the nutrients better than the conventional fertilizers. Nanotechnology is applied in the preparation of nanofertilizer. This technology is highly interdisciplinary in nature and it is closely connected with various technologies of biology such as biotechnology, nano-biotechnology, bio-nanotechnology, and agri-nanotechnology. These properties of nanotechnology lead to the development of the plants benevolent nanofertilizers and related engineered nanomaterials. These materials are in the nanometer size range particularly size less than the plants cells. Primary nutrients, metal oxides nanoparticles (zinc oxide and iron oxide), zeolite nanofertilizers, and carbon nanomaterial-based fertilizers are discussed in this chapter. Nanotechnology applications in fertilizers like slow release or controlled release fertilizers (hydroxyapatite nanoparticles coated urea, polymer coated fertilizers) are explored. Apart from these, applications of coating technology in fertilizers using bio-polymers (such as chitosan and thermoplastic starch) and sulfur are explained. The reviewed literatures reveal that the nanofertilizers will dominate the modern agriculture.

Keywords

Chitosan fertilizers • Hydroxyapatite urea • Metal oxides fertilizers • Nano-biotechnology • Polymer fertilizers • Starch fertilizers • Sulfur fertilizers • Zeolites fertilizers

Abbreviations

Ca	Calcium
$CaCO_3$	Calcium carbonate
CEC	Cation exchange capacity
CeO_2	Cerium oxide
CS	Chitosan
CuO	Copper oxide
EC	Ethyl cellulose
EC	Electrical conductivity
Fe	Ferrous
Fe_2O_3	Iron oxide
HANPs	Hydroxyapatite nanoparticles
KH_2PO_4	Potassium dihydrogen phosphate
KNO_3	Potassium nitrate
MAP	Monoammonium phosphate
Mg	Magnesium
Mn	Manganese
$MnSO_4$	Manganese sulfate
NPs	Nanoparticles
pH	Power of hydrogen or potential for hydrogen
PVA	Polyvinyl alcohol
PVP	Polyvinylpyrrolidone
SAP	Superabsorbent polymer
SPAD	Nitrogen concentration and chlorophyll content
TiO_2	Titanium oxide
WNLCF	Water and nutrient loss control fertilizer
Zn	Zinc
ZnO	Zinc oxide

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P. Singh et al. (eds.), *Plant-Microbes-Engineered Nano-particles (PM-ENPs) Nexus in Agro-Ecosystems*,
Advances in Science, Technology & Innovation,
https://doi.org/10.1007/978-3-030-66956-0_9

1 Introduction

Fertilizer is a material which is applied in the soil to supply nutrients for the growth of plants. Considerable amount of the applied fertilizer is wasted by water or wind before it is used by plants. It can be utilized in a better way with the help of modern advanced technologies. Nanotechnology is the emerging technology that can support for the various fertilization practices to meet increasing demands of food. Heavy usage of fertilizers results in accumulation of fertilizers in water bodies thus causing eutrophication problems.

Chemical fertilizers affect the soil mineral balance which in turn decreases the soil fertility. Fertilizer formulations made using engineered nanoparticles improve the uptake in plant cells and minimize the nutrient loss. In addition, they increase the rate of seed germination, seedling growth, photosynthetic activity, nitrogen metabolism, synthesis of carbohydrate and protein as well (Solanki et al. 2015). Nanomaterials produced by applying nanotechnology have properties different from their bulk materials. Particle size of these materials is less than 100 nm (at least in any one dimension). The large surface area and more active sites of these materials lead them to function efficiently. Their property like compatibility with flexible substrates is useful in several agricultural applications.

Recently, nanotechnology-based products are developed for the utilizations in agriculture. Agri-nanotechnology products such as nanofertilizers, nano-biofertilizers, biofertilizers, nano-pesticides, nano-nutrients, agricultural nanosensors, storage materials for food grains or agricultural harvested products protection, and food packaging/protection materials are modernizing the agriculture and allied fields. They are developed in parallel with the development of the emerging agri-nanotechnology.

Fertilizers are the materials that applied in agricultural activities, i.e., to supply macro or micronutrients or both to the plants. Applications of fertilizers are considerably focused on primary macronutrients. Plants mostly utilize the macronutrients in more quantity (according to the name, the demand for macronutrients is in macrolevel). It leads to lack of macronutrients availability in the agricultural land. Hence, it is essential to complete the demand. In micronutrients case, plants consume less quantity, i.e., microlevel. It leads to the availability of micronutrients in the agricultural land. Contrary to macronutrients, the demand for micronutrients is in microlevel or negligible. In slow or controlled release fertilizers, nutrients are coated by nano-coatings that help to release the nutrients in slow or controlled method.

For the growth of the plants, microelements such as iron, cobalt, copper, selenium, zinc, molybdenum, and other metals are essential. They constitute biologically active compounds like proteins, enzymes, hormones, vitamins, and pigments in plants. Nanopowders of the said microelements can be developed as innovative fertilizers. The advantages of these fertilizers over traditional fertilizers are: increasing the level of resistance to pests and diseases; their consumption is only one gram per ton of processed seeds; reduction of procedures involved; finally decreasing the costs of labor and operating agricultural equipment (NUST MISIS 2017).

The micronutrient calcium can be supplied to plants with the nanoparticles such as Ca-NPs, $CaCO_3$ NPs, and hydroxyapatite NPs. Ca-NPs can improve the seedling growth in plants. Mg-NPs are superior to regular Mg salt by improving the uptake of Mg in plant stems and leaves. Fe NPs are able to increase the chlorophyll contents in leaves. Mn-NPs are applied to replace the conventional $MnSO_4$ salt (Liu et al. 2015). Novel fertilizers can be made using various nanoparticles to increase the crop production.

ZnO nanoparticles stimulate the lateral roots that modify the root architecture and increase the overall uptake of nutrients in wheat plant. Shoot growth is stimulated in bean, chickpea, and green pea with a low dose (1 kg per 100 mg) of ZnO nanoparticles. Stimulation of chlorophyll production increases the rate of photosynthesis and reduction of the severity of chlorosis in plants. Such stimulation is achieved by iron oxide and manganese nanoparticles. TiO_2 nanoparticles are able to increase the RuBisCO activase enzyme activity and chlorophyll production in spinach. Stimulation of the root growth in soybean and cilantro is performed by CeO_2 nanoparticles. These nanoparticles also prevent membrane peroxidation and leakage in maize by inducing the activity of antioxidative enzymes. CuO nanoparticles allow for high uptake of cognate element into the plant. It improves the level of the essential nutrient elements. Slow releasing of fertilizers helps to avoid leaching and fixation of nutrients and makes the nutrients available in proper time. This method also rectifies the overuse of fertilizer (Dimkpa et al. 2014).

Fertilizer leaching is the loss of water-soluble plant nutrients. It leads to the natural environment concern like groundwater contamination. It is caused by the dissolution of fertilizers and different biocides (such as pesticides, herbicides, insecticides, and fungicides) due to rain and irrigation (Wikipedia 2014). Excess NO_3 ions of the nitrogen fertilizers applied are not absorbed by plants or soils which are leached into groundwater (Lin et al. 2001). Phosphorus loss is a major threat to manage the surface water quality. It plays a major role in the eutrophication of surface waters (Carpenter et al. 1998). It does not interact with soil particles through adsorption and desorption. However, soils rich in iron (ferrihydrite) and aluminum oxides or hydroxides (gibbsite) retain phosphorus (Borling 2003; Schoumans

2015). They will release the P into the soil solution. Also, changing the chemical conditions of the soil leads to the P leaching (Shenker et al. 2004; Zak and Gelbrecht 2007).

Considerable quantity of fertilizers is lost while applying that leads to environmental problems. Localized applications of fertilizers (such as salts of ammonia, nitrate, urea, and phosphate compounds) in large quantity produce harmful effects (Trenkel 1997; Ombodi and Saigusa 2000). Soils do not retain nitrates for future utilizations. Also, plants absorb different nutrients at various times (Smart fertilizer 2020). Nanomaterials have applications in slow and controlled release fertilizers that reduce the fertilizer consumption and environmental pollution as well (Wu and Liu 2008). Slow and controlled release fertilizers prevent leaching by releasing the nutrients in a controlled manner.

Engineered nanomaterials can be used in minimum concentration and thereby minimize environmental pollution. The advantages of nanotechnology lie in crop growth, enhance the fertilizer use, reduce nutrient losses, and minimize the adverse environmental impacts. The size of the nanoparticles is in the nanometer level. Hence, they can enter easily into plant cells since the plant cells are in micrometer range.

Sulfur nano-coatings applied on fertilizers are beneficial to the sulfur deficient soils (Santosa et al. 1995; Brady and Weil 2017). Nanocoated urea and phosphate are prepared to release the fertilizers in slow or controlled manner. They will release the nutrients slowly in accordance with the demands of the soil and crops. Biodegradable and biocompatible materials such as chitosan nanoparticles (bio-polymer) are useful in the preparation of controlled release NPK fertilizer materials, i.e., urea, calcium phosphate, and potassium chloride (Corradini et al. 2010). Kaolin and polymeric biocompatible nanoparticles are used to prepare slow release fertilizers (Wilson et al. 2008).

Sabir et al. (2014) have demonstrated that applying nanocalcite ($CaCO_3$-40%) with nano-SiO_2 (4%), MgO (1%), and Fe_2O_3 (1%) enhances the uptake of Ca, Mg, and Fe. It also enhances the intake of the P along with the micronutrients like Zn and Mn (Sabir et al. 2014). Figure 1 exhibits the different applications related to nanotechnology and engineered nanomaterials in agriculture such as slow and controlled released nanofertilizers, nano-based target delivery (nano-carriers), nano-pesticides, and nano-sensors. These applications enhance the plant growth, productivity, and yield ultimately (Yilen et al. 2019).

Utilization of engineered nanomaterials (like nanofertilizers, nano-pesticides, and nano-sensors) in agriculture can increase crop yield by influencing availability of nutrient in soil and uptake by crops. Engineered nanomaterials can control the crop diseases by minimizing the pathogens activities directly (through several mechanisms that includes releasing of reactive oxygen species). Also, they control disease indirectly by enhancing crop nutrition and plant defense mechanisms as well. Efficient use of these materials may replace conventional fertilizers and pesticides that ultimately minimize the environmental impact (Adisa et al. 2019).

2 Fertilizers

2.1 Fertilizers in Agriculture

Fertilizers improve the agricultural productivity. However, the disproportionate utilization of chemical fertilizers causes damages to soil. Also, it decreases the available area (with good condition soil) which is necessary for crop production. Sustainable agriculture suggests reducing the utilization of agrochemicals. Advancements in nanotechnology (like enhanced crop productivity) are applied to overcome the agricultural crisis that leads to sustainability (Priyom Bose 2020).

Some complex fertilizers are harmful to the crops. For example, to supply potassium to the crop instead of using potassium chloride as a fertilizer, potassium nitrate (KNO_3) can be used. Potassium chloride contains chloride which is harmful to the crops. On the other hand, KNO_3 contains more nitrate than ammonium. The uptake of essential nutrition elements like K, Ca, and Mg is impaired by ammonium. Hence, KNO_3 is a better option than using potassium chloride and ammonium (Israelagri.com 2016).

2.2 Classification of Fertilizers

Fertilizers are the chemicals or natural substances to supply essential nutrients for the plant growth to maintain the soil fertility. Benton (2012) has reported that fertilizers can be classified in many approaches: Firstly, fertilizers can be classified depending upon the contents, i.e., single nutrient fertilizers or straight fertilizers (e.g., nitrogen—N, phosphorus—P, or potassium—K) and multi-nutrient fertilizers or complex fertilizers (e.g., two or more nutrients—N and P); secondly, based on the inorganic and organic content, i.e., inorganic fertilizers and organic fertilizers. Inorganic fertilizers do not contain carbon materials. They are prepared using several chemical treatments. Hence, they are also called as synthetic fertilizers. All organic fertilizers should have carbon content and they can be derived from plant and/or animal sources or recycled materials of plant or animal source or both (Benton 2012).

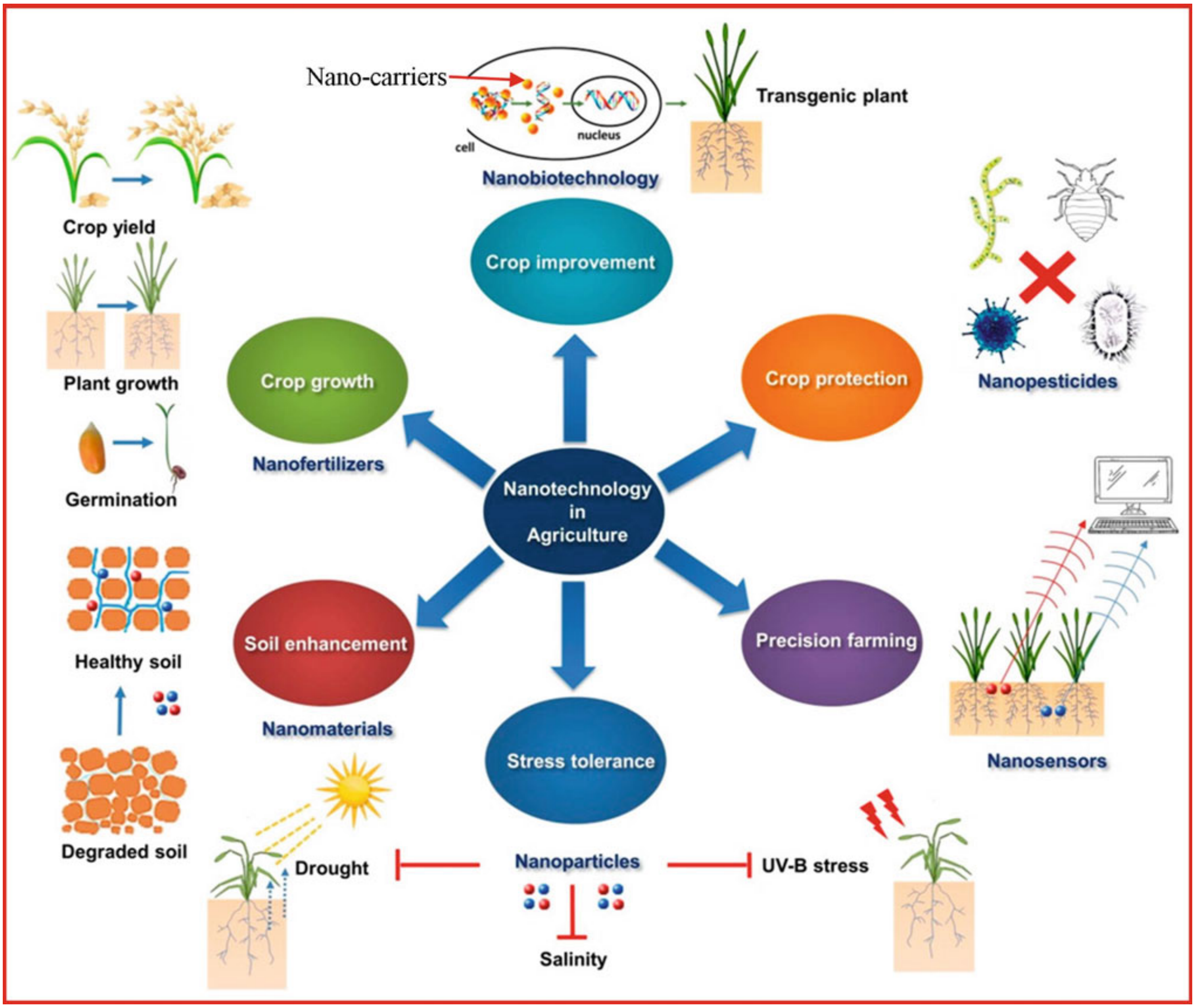

Fig. 1 Applications related to nanotechnology and nanomaterials in agriculture. Slow and controlled released nanofertilizers enhance plant growth, productivity, and yield. Nano-based target delivery (gene transfer) is useful in plants development. Nano-pesticides control pathogens and useful to protect the plants efficiently. Nano-sensors (with computerized controls) are utilized in precision farming. Engineered nanomaterials are applied in plant stress and soil enhancement. *Source* Yilen et al. (2019), with permission

2.3 Macro and Micronutrients

Nitrogen, phosphorus, and potassium are called as main or primary macronutrients. Among them: Nitrogen (N) is vital for the development of leaves; phosphorus (P) is necessary for the development of roots, flowers, fruits, and seeds. Activities such as stem growth, water transportation inside the plants, and promotion of flowering and fruiting need potassium (K) macronutrient. Calcium (Ca), magnesium (Mg), and sulfur (S) are known as secondary macronutrients. Copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), zinc (Zn), chloride (Cl), and boron (B) are the essential micronutrients. Silicon (Si), cobalt (Co), and vanadium (V) are some of the micronutrients that have less importance.

Micronutrients like zinc, copper, and molybdenum can be supplied to plants as water-soluble salts. Iron is transformed into insoluble compounds at moderate soil pH and phosphate concentrations. This transformation causes bio-unavailability. Hence, it is supplied in the form of chelated complex like EDTA derivative. The requirements of micronutrients are depending upon the plants, for example, sugar beets need boron and legumes need cobalt (Scherer 2009). Likewise, nanofertilizers also have macronutrient and micronutrient contents.

2.4 Major Elements of Plants

Plants are created by the composition of four main elements, i.e., carbon, hydrogen, oxygen, and nitrogen. Apart from the life of plants, they have major roles in the creation of entire biological system (including human, animals, and microorganisms) and maintenance of life. These elements present in carbohydrate, protein, and fat that are utilized as food/feed by human and animals. Phosphate is essential for the DNA, ATP (energy carrier of cells), some lipids, and bones of human and animals.

Plants can get hydrogen and oxygen from water and carbon from carbon dioxide. Nitrogen is present in the atmosphere. However, plants are unable to use it. Plants require it in a fixed form because of its major role in the development of proteins, DNA, and other important components like chlorophyll. Some bacteria and legumes fix atmospheric nitrogen (N_2) by ammonia conversion. Phosphate plays a major role in the DNA, ATP, and some lipids production of the plants (Wiki/Fertilizer 2018). Figure 2 depicts that plants utilize carbon dioxide and water (getting carbon, hydrogen, and oxygen) during photosynthesis to produce starch and sugar or glucose.

The deficiency of micronutrients reduces the crops productivity that ultimately affects the human health (while consuming the low nutrient foods). For example, iron deficiency causes anemia and affecting growth, reproductive health, and cognitive performance in humans (Swaminathan et al. 2013; Monreal et al. 2016). Hence, imbalance (surplus supply or deficiency) of the main elements, macronutrients, and micronutrients in plants will affect the living things of entire biological system including plants. It emphasizes the significance of the fertilizers.

3 Engineered Nanofertilizers

3.1 Technology of Nanofertilizers

Nanotechnology develops agricultural products such as nanofertilizers, nano-herbicides, nano-pesticides, nano-fungicides, and nano-sensors (Duhan et al. 2017). Also, nanotechnology supports for agriculture by making nanoscale carriers, bio-remediation of pesticides, wastewater treatment, enzymatic sensors, nano-lingocellulose, and clay nanotubes (Dasgupta et al. 2015). Many countries are applying nanotechnology in agriculture and food sectors. It will support to meet the demands and to feed of the increased population (Ali et al. 2014).

Nanofertilizers are defined as the synthesized or modified form of traditional fertilizers or fertilizers bulk materials or extracted from different vegetative or reproductive parts of the plant by different chemical, physical, mechanical, or biological methods with the help of nanotechnology used to improve soil fertility, productivity, and quality of agricultural produces. Nanoparticles can be made from fully bulk materials (Brunnert et al. 2006).

3.2 Classification of Nanofertilizers

Different classifications and types of nanofertilizers are shown in Fig. 3. Classifications of nanofertilizers, i.e., nutrient-based, action-based, and based on the quantity applied are shown in Fig. 3a–c, respectively. Like conventional fertilizers (as explained earlier), nanofertilizers also have macro and micronutrients. However, in the case of nanofertilizers, the size of the nutrients (it may be macronutrients or micronutrients) is in nanoscale range. Ruiqiang and Rattan (2016) reported about the nutrient-based classification of nanofertilizers. Figure 3a shows this classification of nanofertilizers based on nutrients. Nanofertilizers supply nutrients to the plants that improve the plant growth and yields. Also, they are applied to enhance the performance of conventional fertilizers. They are divided into four classes: macronutrient nanofertilizers (e.g., apatite nanoparticles), micronutrient nanofertilizers (e.g., iron oxide NPs and zinc oxide NPs), nutrient-loaded nanofertilizers (e.g., zeolites), and plant growth stimulating nanomaterials (e.g., carbon nanomaterials). Developing the macronutrient nanofertilizers (nitrogen and phosphorus) is necessary to improve agricultural activities and to reduce environmental problems (Ruiqiang and Rattan 2016).

Based on the actions, nanofertilizers are categorized as control or slow release fertilizers, water, and nutrient loss control fertilizers (WNLCF), magnetic, or nanocomposite fertilizers combined nanodevices (Lateef et al. 2016; Panpatte et al. 2016). This classification is shown in Fig. 3b. Priyom Bose (2020) has divided the nanofertilizers (based on the quantity applied) into three types: (i) nanoscale fertilizers: these are nano-sized particles that have nutrients, (ii) nanoscale coating fertilizers: nanoparticles coated or loaded on traditional fertilizers, and (iii) nanoscale additive fertilizers: these fertilizers are the traditional fertilizers mixed with the nano-sized additives (Priyom Bose 2020). Figure 3c shows the classification based on the quantity applied.

Nanofertilizers combined nanodevices are designed with a nanonetwork to monitor the plants. The monitoring system comprises of nano and microscale network devices. These devices and the data collected by them are managed by control units. The transmitters (nano-sensors) collect data and transmit to receivers (micro-devices). Finally, the data are relayed to the Internet through gateways (Dufresne 2000; Luca 2018). Attapulgite or Palygorskite clay is one of the varieties of fuller's earth clay material. Magnesium aluminum phyllosilicate is the chemical content and

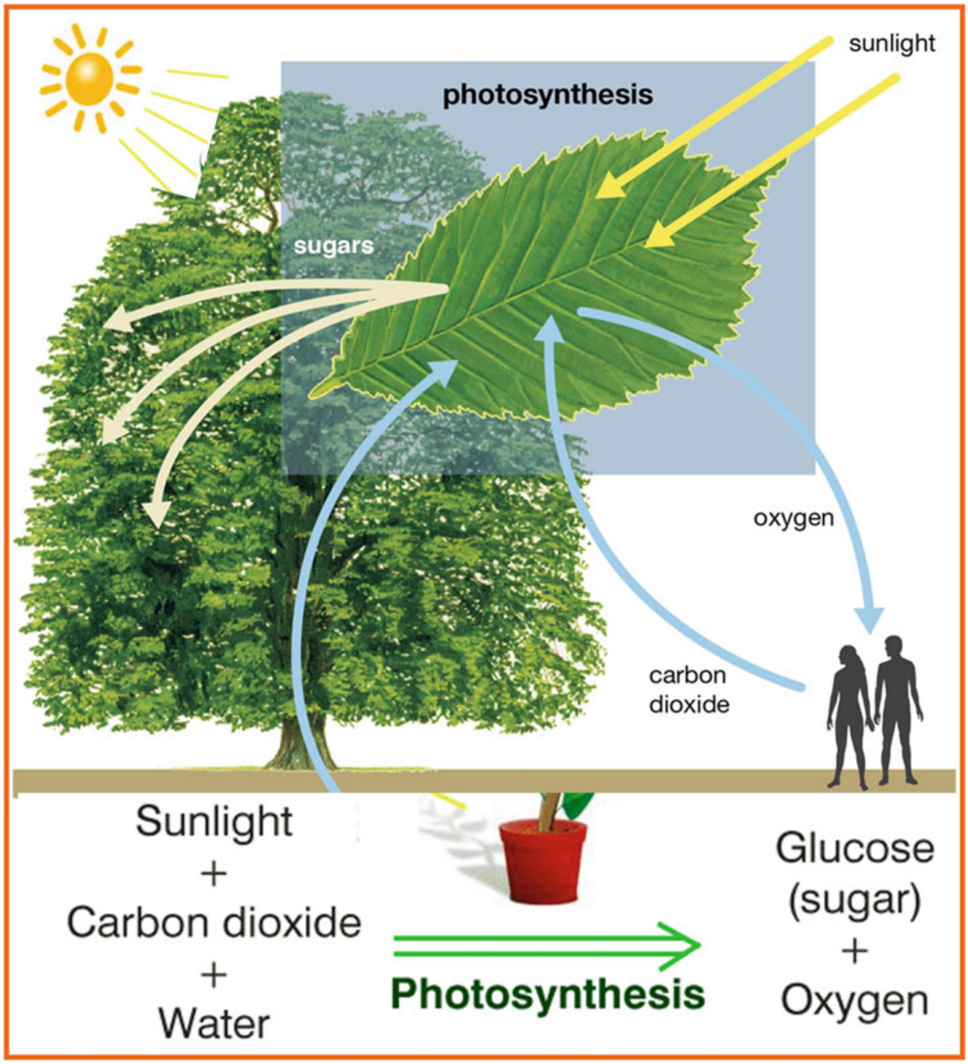

Fig. 2 Sources of carbon, hydrogen, and oxygen to the plants. Plants utilize them and produce starch and sugar by photosynthesis process

$(Mg, Al)_2Si_4O_{10}(OH)\cdot 4(H_2O)$ is the chemical formula of this clay material. Several researchers have reported about mixing of attapulgite-polymer complex with conventional fertilizer to utilize as WNLCF.

While applying nitrogen fertilizer, a portion of this fertilizer causes environmental pollution due to various activities (like runoff, leaching, and volatilization) which can be avoided by high-performance WNLCF. Addition of high-energy electron beam dispersed attapulgite–sodium polyacrylate–polyacrylamide complex into traditional fertilizer is a method to prepare WNLCF. The attapulgite-polymer complex serves as the water and nutrient loss control agent in WNLCF. It retains the water and nutrient effectively that prevents the water and nutrient loss. Ultimately, it leads to efficient utilization of water and nutrient reduces the pollution risk caused by the fertilizer (Zhou et al. 2015).

A biomass-based, multifunctional controlled release fertilizer (BMCF) is a cost-effective water and nutrient loss control fertilizer. It enhances the utilization of nutrient and crop production as well. Also, it reduces the adverse effects like environment pollution. BMCF is designed by using co-granulated ammonium zinc phosphate and urea in attapulgite matrix. This fertilizer core is coated by cellulose acetate butyrate coating initially. Again it is coated by carboxymethyl chitosan-*g*-poly(acrylic acid)/attapulgite superabsorbent composite as an outer coating. BMCF decreases nitrogen leaching loss and runoff. Also, it enhances the moisture retention of soil and restructures the acidity and alkalinity of soil (Wang et al. 2014).

3.3 Benefits of Nanofertilizers

Nanofertilizers are produced with intention to regulate the nutrients supply and consumption to meet demands of the crops with minimum loss. Conventional nitrogenous fertilizers reduce the efficiency of fertilizing activities (due to

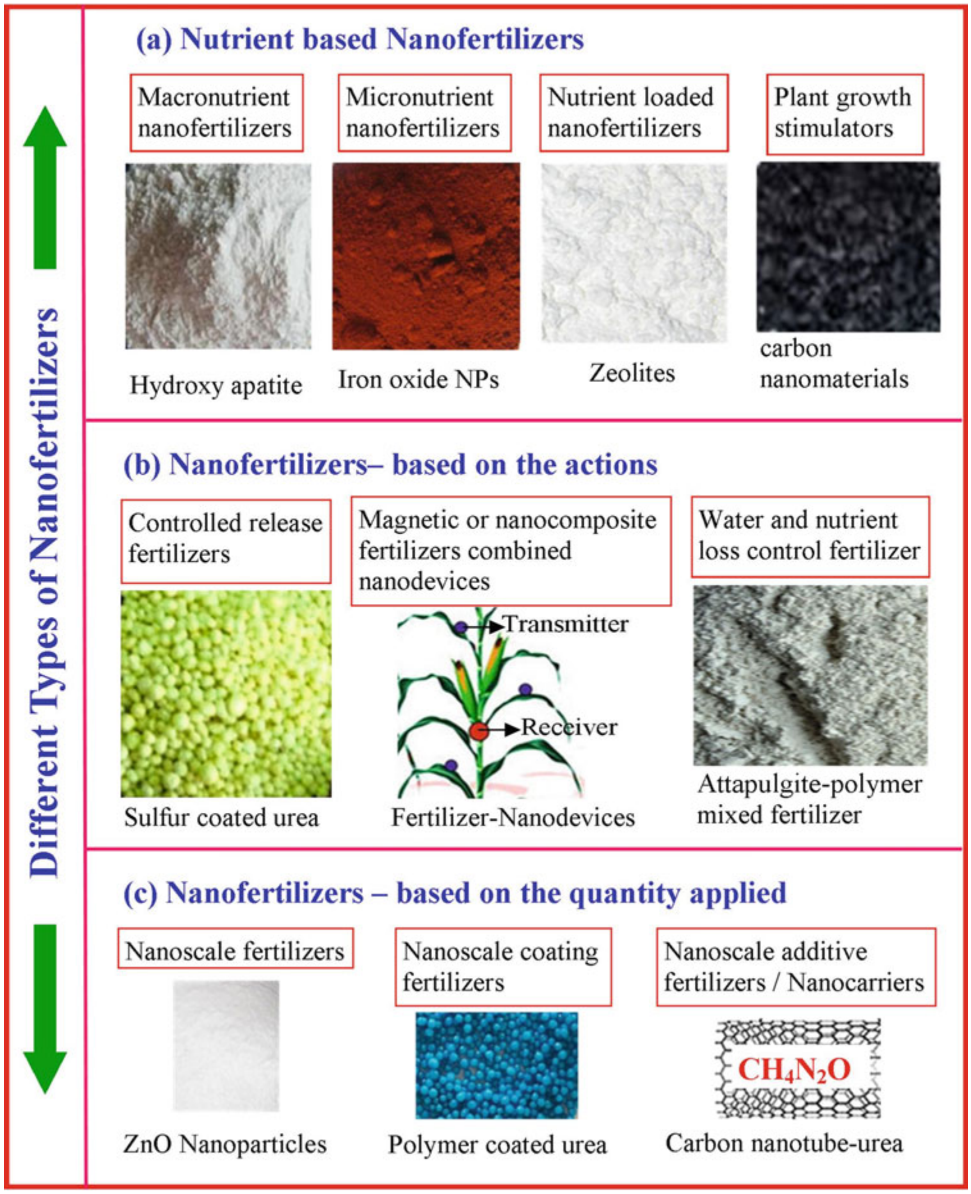

Fig. 3 Different classification and types of nanofertilizers. **a** Nutrient-based nanofertilizers, **b** nanofertilizers based on the actions, and **c** nanofertilizers based on the quantity applied

leaching, evaporation, and degradation) that ultimately makes loss (Mia et al. 2015; Wang et al. 2015; Yang et al. 2016). In the case of nitrogenous nanofertilizers, the release of fertilizer-N is regulated by nanoformulations. It reduces the nutrient loss by improving the interaction of nutrients with crops and avoiding the interaction of nutrients with soils, microorganisms, water, and air (Dwivedi et al. 2016; Panpatte et al. 2016).

Nanofertilizers improve crop growth/yield, nutrient utilization; reduce expenditures of fertilizer and cultivation. Optimum quantity supply of nanofertilizers enhances crop growth but beyond that level decreases the crop growth (due to the toxicity of nutrient). ZnO nanofertilizer enhances the seed germination and plant growth considerably (Singh et al. 2017). Applying the nano-formulated or nano-entrapped micronutrients as slow or controlled release fertilizers will improve the soil health and uptake by plants. It ultimately enhances the growth and productivity of crops (Peteu et al. 2010). Nanomaterials (like magnesium hydroxide) are utilized for the early germination of seeds. They break the seed dormancy and they may increase the chlorophyll content of the plants. Overall, nanomaterials treatment of the seeds enhances the germination percentage and plant growth as well. Hence, these nanoparticles can be utilized as the efficient nano-nutrients for the plant growth promotion (Shinde et al. 2020). Carbon nanomaterials, ZnO nanoparticles, and iron oxide nanomaterials are applied as pre-soaking and seed germination technology. For these kinds of applications, bio-synthesized nanomaterials are the suitable material instead of chemically synthesized nanomaterials.

Encapsulating the microorganisms (bacteria or fungi) improves the nitrogen, phosphorus, and potassium availability that support for the plant growth (Priyom Bose 2020). Encapsulation of nutrients with nanomaterials is a technique to make nanofertilizers. Initially, nanomaterials are prepared in physical (top-down) or chemical (bottom-up) method. In the next step, nutrients are encapsulated by nanoporous materials or polymer thin film coating or nano-emulsions of cationic (NH_4^+, K^+, Ca^{2+}, Mg^{2+}) or nutrients surface modified with anionic (NO_3^-, PO_4^-, SO_4^-) nutrients (Subramanian et al. 2015; Panpatte et al. 2016;).

3.4 Application Methods of Nanofertilizers

When nanofertilizers are applied to the plants in soil application method, the soil mixed nanoparticles enter into the plants using the routes such as root hairs, lenticles, mucilage, and exoates. In addition, microorganisms are utilized in these activities. Xylem transport plays a major role in the absorption of the soil mixed nanoparticles. Direct interaction between fertilizers and soil systems of this application method leads to some undesirable consequences such as soil acidification, wastage of fertilizers as well. In the case of foliar application method, aerosol nanoparticles penetrate into the plants directly. Stomata, trichomes, hydathodes, lenticles, and cuticle wounds are the possible entry routes. In this case, phloem transport plays a major role. Figure 4 exhibits the difference between the soil and foliar applications of fertilizers.

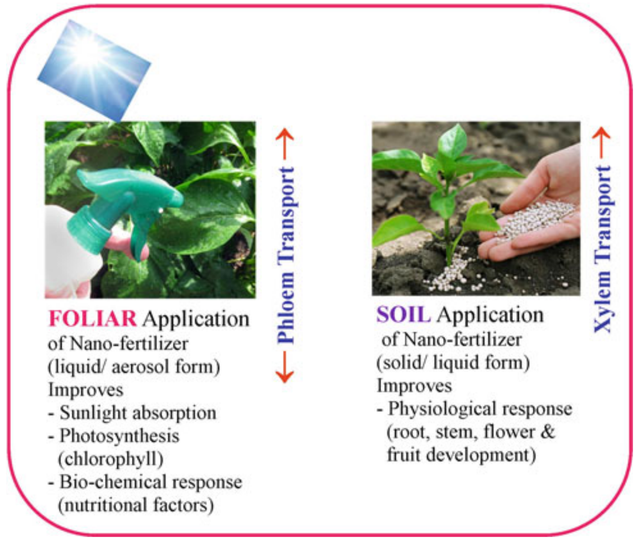

Fig. 4 Foliar and soil application methods of nanofertilizers in plants

4 Bio-synthesis of Nanomaterials

Utilization of toxic or biologically incompatible materials in plants and agriculture as fertilizers, pesticides, and herbicides or in any form will cause harm to all biological organisms. Applying the bio-synthesized nanomaterials (as nanofertilizers or other applications) instead of chemically synthesized nanomaterials will reduce the bio-incompatibility. For biological applications, bio-compatibility is essential. Possibilities of bio-compatibility are more in bio-synthesis method comparing to other synthesis methods. During the preparation of nanomaterials, various chemicals are utilized. Hence, applying the resultant materials and the residues of these chemically synthesized nanomaterials in agriculture may cause untoward effects. In the case of bio-synthesis or green synthesis of nanomaterials, chemicals are avoided except the pre-cursor materials.

Dhillon et al. (2012) reported that bio-synthesis of nanoparticles using biological materials such as plant extracts (leaves, flowers, stem, fruit peels, and seeds), bacteria, fungi, and algae results in several benefits, i.e., eco-friendliness and bio-compatibility. In this synthesis, toxic chemicals are not utilized (Dhillon et al., 2012). Plant-mediated synthesis of metal nanoparticles (like gold, silver, copper, and iron) and metal oxide nanoparticles (like titanium oxide and zinc oxide) are more reliable, inexpensive, and eco-friendly approach. Figure 5a, b exhibit the bio-reduction process and bio-reduction mechanism related to the plant-mediated bio-synthesis of metallic nanoparticles, respectively (Khandel et al. 2018).

Nano-ecotoxicology is the toxic effects of the nanomaterials released into the environment and biological systems (like humans, animals, plants, fungi, and microbes). Humans and animals are exposed to nanomaterials in several ways via air, water, and consuming food accumulated with nanomaterials (Pachapur et al. 2015). While utilizing nanomaterials, high priority should be given for safety. Toxicity mainly focuses on human beings and protecting them, but the ecotoxicity intends to protect the various levels of trophic organism and ecosystems. Ecotoxicity includes natural mechanisms and the environmental factors related to the bioavailability (Rana and Kalaichelvan 2013).

5 Nanofertilizers of Macro and Micronutrients

5.1 Hydroxyapatite Nanoparticles (HA NPs)

Hydroxyapatite nanoparticles (HA NPs) are the major source of the fertilizers. It is able to supply both macronutrient and micronutrient. It is used either alone or mixed with other fertilizers. It is applied in the coating of fertilizers to control the release of the fertilizers. As per the report of Kottegoda

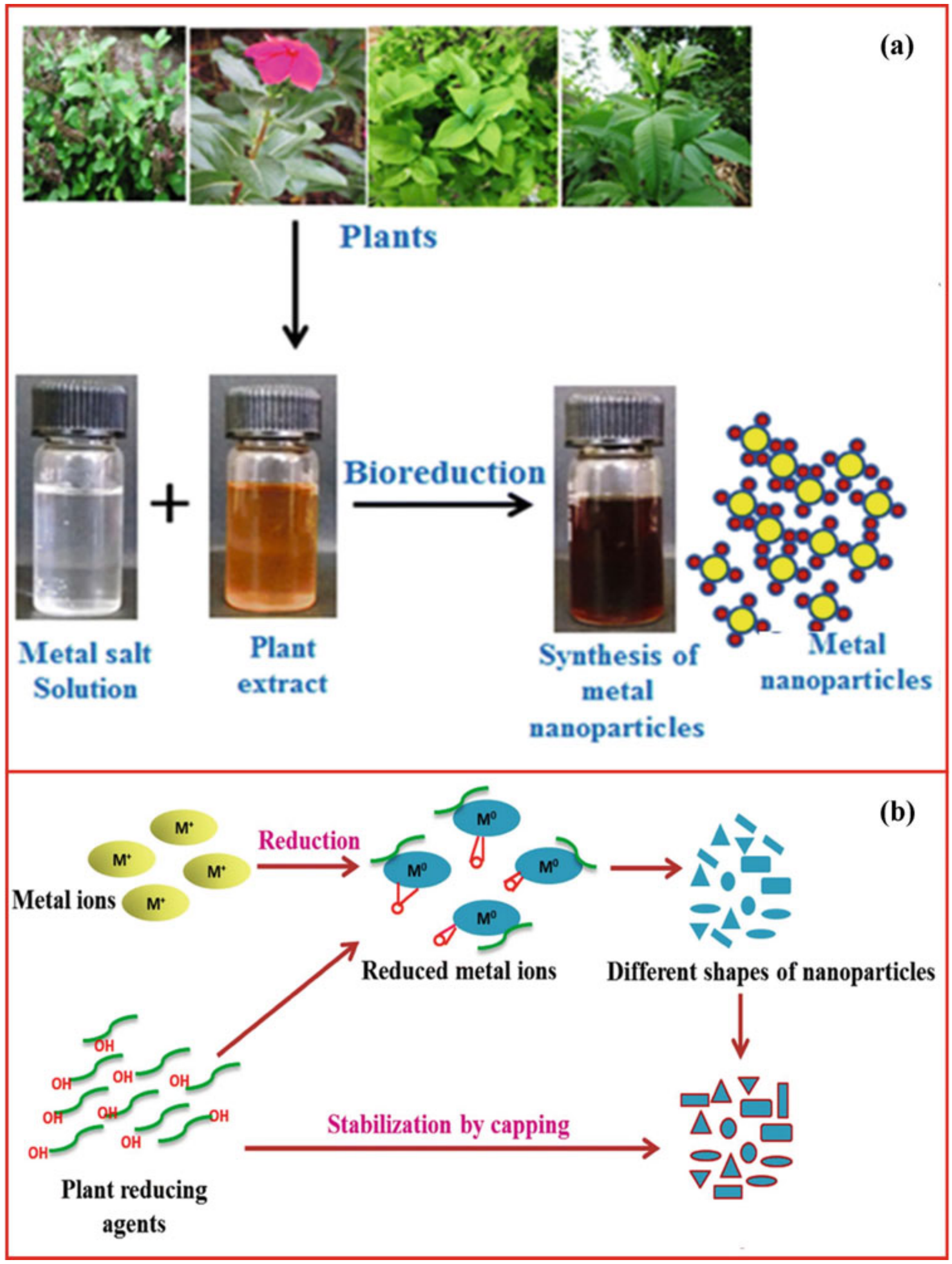

Fig. 5 Schematic diagram showing the plant-mediated synthesis of metallic nanoparticles. **a** Bio-reduction process metal salt solution by plant extract, **b** bio-reduction mechanism involved in the bio-synthesis of metallic nanoparticles. *Source* Khandel et al. (2018), with permission

et al. (2017), HA NPs can be applied as phosphorous fertilizers. They can also supply calcium in addition to phosphorous. In wet soil, urea breaks down quickly and the formation of ammonia occurs. The ammonia enters the atmosphere as nitrogen dioxide which is the main greenhouse gas associated with agriculture. This decomposition limits the application of more urea as fertilizer. To avoid the breakdown of urea, slow releasing of urea is done. For this purpose, urea is coated with HA NPs. The HA NPs coated urea release the nitrogen slowly, i.e., 12 times slower than urea without HA NPs coating (Kottegoda et al. 2017). The slow release of phosphorous helps plants to take up the nutrient continuously as they grow. Slow release of phosphorous can be achieved with the help of HA NPs. Application of chemical fertilizers results in soil acidification. Hence, the cost of reversing soil pH to optimal is also extremely high. The advantage of HA NPs is that it does not change soil pH when phosphorous is released. When plants grow, different types of organic acids like oxalic acid and citric acid are released. They dissolve the HA NPs which makes the phosphorous availability to the plants (Phys.org. 2015).

Soluble phosphate salts cause surface water eutrophication. Solid phosphates supply low level nutrient P. Synthetic apatite nanoparticles act better and supply enough P nutrients to the plants compared to the soluble and solid counterparts. The greenhouse experiment conducted on soybean (*Glycine max* (L.) Merrill) shows that applying of synthetic apatite nanoparticles increases the growth rate (32.6%), seed yield (20.4%), and biomass productions (above ground by 18.2% and below-ground by 41.2%) of the soybean. In this experiment, apatite nanoparticles have been synthesized in wet chemical route with carboxymethyl cellulose (CMC) as stabilizing agent. The shape of the synthesized hydroxyapatite nanoparticles is spherical and particle size is 15 nm approximately. Comparing to the regular P fertilizer ($Ca(H_2PO_4)_2$), the utilization of apatite nanoparticles improves the yield and decreases the water eutrophication (Liu and Lal 2015a).

5.2 Carbon Nanomaterials

Carbon is one of the main elements required for the plants. It is present in the all organic materials. Plants get the carbon mainly from air in the form of carbon dioxide. Verma et al. (2019) reported that the impacts of carbon nanomaterials on plant growth (from enhanced crop yield to acute cytotoxicity) have been studied by many researchers. The concentration of the carbon nanomaterial is more important. Vegetative growth and yield of fruit/seed increase at lower concentration of carbon nanomaterials but they decrease at higher concentrations of carbon nanomaterials. At lower concentrations, carbon nanomaterials are able to increase water uptake and transport, seed germination, and antioxidant activities (Verma et al. 2019). The supportive factors available at lower concentrations of carbon nanomaterials improve the vegetative growth and yield of fruit/seed.

Multi-walled carbon nanotubes (MWCNTs) are applied with urea fertilizer for the growth of paddy plants. Functionalized carbon nanotubes are unique since they are attached with a variety of functional groups on their surface. This makes the carbon nanotubes material suitable for lots of applications. MWCNTs are functionalized with 4wt% of carboxyl (–COOH) functional groups. The functionalization enhances the efficacy of urea fertilizer as plant nutrition for (local MR219) paddy. About 0.6wt% of functionalized MWCNTs is grafted onto urea fertilizer. The experiment is performed using a pot under exposure to natural light. After 14, 35, and 55 days, the crop growth of plants significantly increased. The homogeneous grafting of functionalized MWCNTs onto the urea leads to such beneficial result (Yatim et al. 2018). Functionalization of MWCNTs assists in attaching urea fertilizer onto MWCNTs. The bonding between urea and MWCNTs can be confirmed using spectroscopy and chemical characterization techniques such as FT-IR and total N analysis. The functionalization process facilitates the separation of nanotube bundles into individual tubes (Yatim et al. 2015).

Carbon nanotubes (CNTs) are synthesized in chemical vapor deposition (CVD) method. Zaytseva and Neumann (2016) have explained the synthesis and applications of carbon nanomaterials. Figure 6a shows the CVD reactor that has reaction chamber and tubes (for inert gas and hydrocarbon supply). Figure 6b, c exhibits the base-growth and tip-growth mechanism of CNT growth. Figure 6d enumerates the agricultural and environmental applications of carbon-based nanomaterials (Zaytseva and Neumann 2016). Generally, in SWCNTs production, methane gas is utilized and the substrate is heated up to 850–1000 °C. In the case of MWCNTs production, ethylene or acetylene gas is utilized and the substrate is heated up to 550–700 °C. Carbon is produced due to thermal decomposition of hydrocarbons. After producing a certain concentration of carbon, semi-fullerene cap is formed. In the next stage, the growth of cylindrical nanotube is formed by carbon flow from the hydrocarbon source on the catalyst (Matsuzawa et al. 2014; Morsy et al. 2014). Formation of semi-fullerene cap and cylindrical nanotube growth can be seen in Fig. 6b, c.

Nanoparticles can be used as potential plant growth regulator. Preparation of the slow releasing Cu–Zn micronutrient carrying carbon nanofibers (CNFs) is an easy method. It can be done through dispersing the micronutrient (Cu–Zn/CNFs) in a polymeric formulation of PVA–starch. Applying the prepared micronutrient increases the plant height significantly. The translocation of the Cu–Zn/CNFs from roots to shoots is analyzed. Scavenging of reactive oxygen species by the micronutrient nanoparticles is confirmed by measuring the quantity of superoxide anion radicals and hydrogen peroxide present in the plant (Kumar et al. 2018).

Banana peel pieces have been blended with tap water using a high-speed mechanical blender which is then mixed with potassium hydroxide. The prepared slurry has been heated at 100 °C for 30 min (Fig. 7a). This thermo-chemical process leads to produce the nanofertilizer. Figure 7b shows the TEM image of the nanofertilizer. Figure 7c shows the histogram analysis of the particles. The average particle size of nanofertilizer is found to be 40 nm. Elemental analysis reveals that chelated potassium, chelated iron, urea, citric acid, amino acids, protein, and tryptophan are the some materials present in the nanofertilizer. This nanofertilizer can be applied to increase the germination of seeds in crops such as tomato and fenugreek (Hussein et al. 2019).

Banana peel consists of Na^+, K^+, P, Ca^{++}, Fe^{+++}, and Mg^{++}. Mixing of potassium hydroxide with banana peel helps to break lignin and cellulose. Presence of urea, citric acid, amino acids, tryptophan, and protein liberate minerals. It leads to the plant germination efficiently (Aboul-Enein et al. 2016). Graphene oxide helps to release the potassium

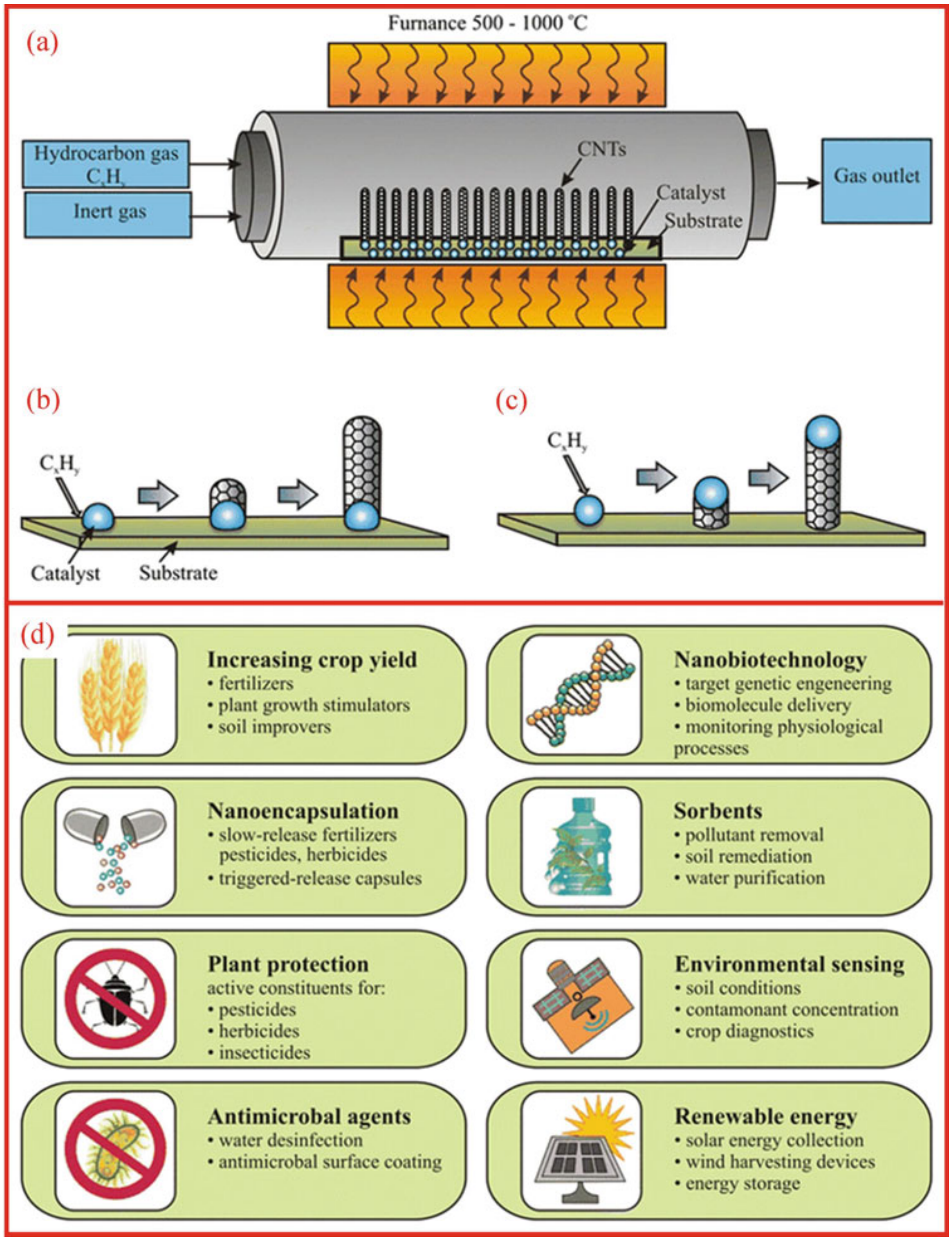

Fig. 6 Schematic diagram showing the synthesis of carbon nanotubes (CNTs) in chemical vapor deposition method. **a** Simple chemical vapor deposition (CVD) reactor, **b** and **c** base-growth and tip-growth method of CNT growth mechanism, respectively, and **d** various applications of carbon-based nanomaterials in agricultural and environmental sectors. *Source* Zaytseva and Neumann (2016), with permission

nitrate slowly. It prolongs the time of action and reduces loss by leaching (Shalaby et al. 2016).

5.3 Zinc Oxide Nanoparticles

Zinc is a micronutrient that removes the zinc deficiency of the soil. It enhances the various parts and activities of the plants (like shoot, root, biomass, activities of chlorophyll, protein, antioxidant, and enzyme related). ZnO nanoparticles have better solubility than bulk ZnO particles. Tarafdar et al. (2014) have reported that bio-synthesized zinc nanoparticles are used as nanofertilizer application in the plant pearl millet (*Pennisetum americanum* L.) cv. HHB 67. Considerable improvement in the various contents and activities of the plant such as shoot length (15%), root area (24%), root length (4%), plant dry biomass (13%), chlorophyll (24%), total soluble leaf protein (39%), and enzyme activities (acid phosphatase: 77%, alkaline phosphatase: 62%, phytase: 322%, and dehydrogenase: 21%) are found. After the application of zinc nanofertilizer, grain yield at the maturity of crop up to 38% has improved (Tarafdar et al. 2014).

Zinc oxide and titanium dioxide nanoparticles are incorporated on the leaves of the tomato plants using novel aerosolization techniques. As a result, light and minerals are absorbed more effectively by the plants and the fruit had

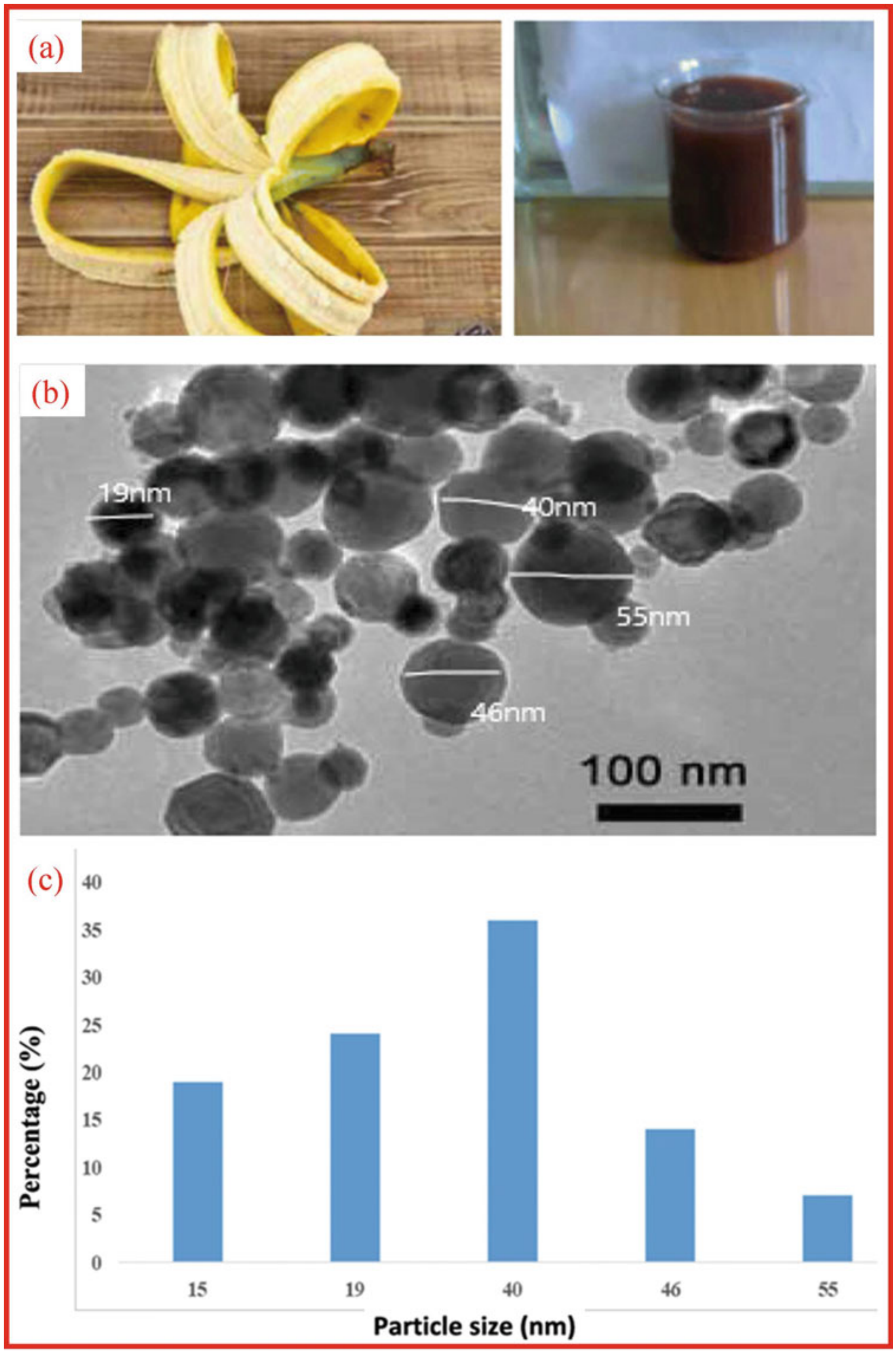

Fig. 7 Preparation of nano-bio-stimulant fertilizer using banana peels. **a** Photograph of banana peel slurry, **b**, **c** TEM and histogram of banana peel nanofertilizer prepared using alkaline solution, respectively. *Source* Hussein et al. (2019), with permission

higher antioxidant content. These nanoparticles can act like a biofertilizer by secreting enzymes. These enzymes trigger bacterial microbes in the soil to turn the nutrients into plants usable form. By this method, the formation of stable complexes is prevented in the soil. The tomatoes also possess more lycopene (antioxidant) which is useful to reduce the risk of various diseases like cancer, heart disease, and age-related eye disorders. Also, these tomatoes can reduce malnutrition and child mortality by supplying more nutrients (Raliya et al. 2015). Bulk ZnO is less soluble in water. This drawback can be avoided ZnO nanoparticles. Milani et al. (2012) have reported that ZnO nanoparticles can be used instead of bulk ZnO particles to remove the zinc deficiency in the soil. The solubility of these nanoparticles is high when compared to its bulk counterpart. These nanoparticles can be coated on macronutrient fertilizers such as urea and monoammonium phosphate (MAP). The results demonstrated that MAP granules released more Zn than urea granules because of the more acidity produced by MAP granules (Milani et al. 2012).

Green synthesized (using a soil fungus) ZnO nanoparticles are sprayed on the leaves of mung bean plants. Zinc oxide nanoparticles are used to mobilize native phosphorus in the soil. They help in utilizing phosphorus in a sustainable way. ZnO nanoparticle interacts with the enzymes such as phosphatases and phytase that mobilize the complex form of phosphorus in the soil into a form that plants can absorb. This can increase the phosphorous uptake by 11%. These nanoparticles increase the root volume, stem height, and phosphorous-mobilizing soil microbial population. Also, toxicity studies have been performed to ensure the safety in the plant. The nanoparticles did not accumulate in the mung bean seeds beyond the safe limit. Green synthesis makes the nanoparticles coated with fungal proteins which prevent the direct contact between soil and the nanoparticles (Raliya et al. 2016).

Excess nitrogen and phosphorus fertilizers are fixed in the soil while applying fertilizers in the conventional method. In this method, they form chemical bonds with other elements and become unavailable for plants. The nitrogen and phosphorus are sent into rivers, lakes, and bays which results in environmental problems. Nanotechnology allows the usage of small quantities of fertilizers. Nanomaterials can be applied in the soil or sprayed onto their leaves. Foliar application is good for the environment because they do not come in contact with the soil. Since the particles are nanometer in size, plants can absorb more efficiently than via soil application.

5.4 Iron Oxide Nanoparticles

Iron is a micronutrient. Iron oxide nanoparticles can be utilized as fertilizers (to remove iron deficiency) and as seed pre-soaking solutions. Rui et al. (2016) have reported that nanotechnology can give solution to solve the shortcoming present in the traditional fertilizers. Plants like peanut (*Arachis hypogaea* L.) are highly sensitive to Fe deficiency. Fe participates in physiological processes such as chlorophyll bio-synthesis, respiration, and redox reactions. Fe_2O_3 NPs are able to increase root length, plant height, biomass, and SPAD values in peanut plants (Rui et al. 2016). In this case, Fe_2O_3 NPs support for the plants health by overcoming the weakness of the traditional fertilizers.

Iron oxide nanoparticles (Fe NPs) can be applied as next-generation iron deficiency fertilizers. Iron oxide is used as seed pre-soaking solutions. This technique is an environment friendly because it uses less fertilizer. Effects of iron oxide nanoparticles at low and high concentrations, at varied pH and the effect on embryonic root growth in legumes have been analyzed. The results show that iron oxide nanoparticles improve root growth by 88–366% at low concentrations (Palchoudhury et al. 2018).

The effects of iron nanoparticles (Fe NPs) on the anatomical and ultrastructural responses of *Capsicum annuum* L. have been studied. Iron nanoparticles show positive effects only at low concentrations which is confirmed by light and electron microscope analyses. SEM and TEM analysis results are shown in Fig. 8a–c. Iron nanoparticles are able to support for the plant growth by altering the leaf organization, increasing the chloroplast number, and regulating the development of vascular bundles. Fe NPs are absorbed in the roots and transported to the central cylinder in bio-available forms. However, in high concentrations, Fe NPs are found to be aggregated into cell walls and transported via the apoplastic pathway in the roots, which may potentially block the transfer of iron nutrients. Figure 8d, e show the effects of Fe NPs at different concentrations. Low concentration yields better plant growth (Yuan et al. 2018).

6 Slow/Controlled Release Fertilizers

6.1 Properties of Slow/controlled Release Fertilizers

Coating on the fertilizers improves many properties of the fertilizers. Ultimately, it leads to the enhancement of plants health, growth of the plants, and yield at the maturity. Fertilizers can be released in a slow or controlled manner using polymers. For the preparation of slow or controlled release fertilizers, the nutrient is the main active material. It is kept in the central portion. It is covered externally using natural or synthetic polymer coating. This polymer coating controls the release of active nutrient material present in the central portion. The nutrients will be released in a slow or controlled manner after the damaging of external polymer coating. Generally, the damage of the polymer is caused by water, microbes, and physical forces.

Slow release fertilizers are less soluble in water. They are slowly broken down by microbial action. Controlled release fertilizers are soluble fertilizers coated with materials like sulfur and polymers. In foliar application of fertilizers, the nanoparticles are transported through phloem tissues. Hence, the direct interaction of fertilizers with soil systems is avoided. As per the report of Haifa Group, both slow and controlled release fertilizers release the nutrients slowly. However, there are some differences in between them such as releasing mechanism, releasing factors, and longevity.

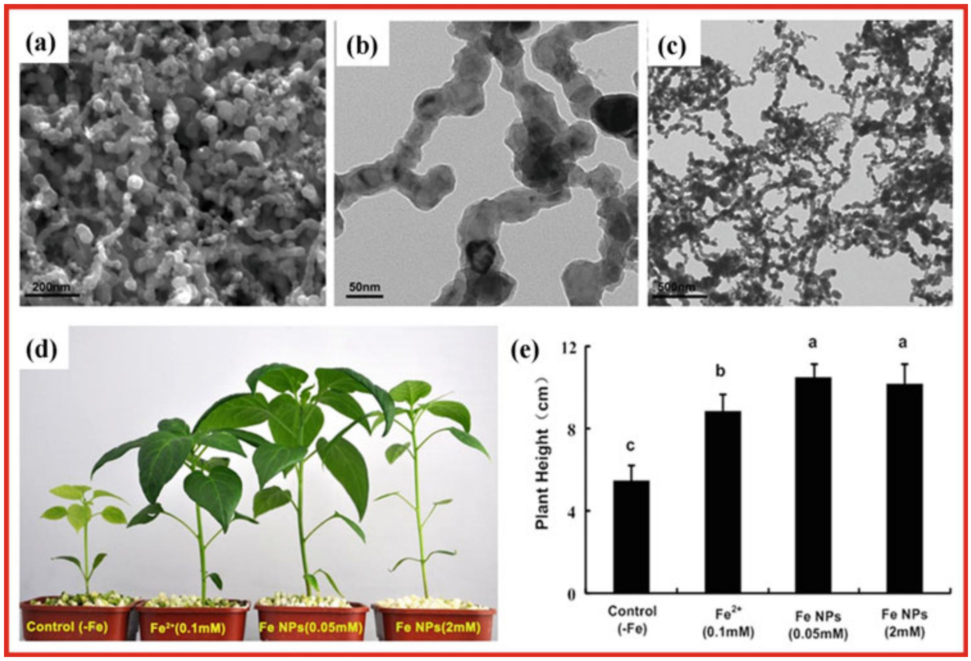

Fig. 8 Effect of the iron nanoparticles (Fe NPs) on *Capsicum annuum* L. plant. Electron microscope images of Fe NPs: **a** SEM image, **b**, **c** TEM image, **d** photograph of *C. annuum* L., **e** Fe NPs concentration vs plant growth (plant height). Fe NPs at low concentration promotes plant growth better than the Fe NPs at high concentration. *Source* Yuan et al. (2018), with permission)

Slow release fertilizers have less control in releasing of nutrient. Factors such as soil moisture, temperature, and pH affect the releasing ability. In the case of controlled release fertilizers, soil temperature only affects the nutrients release (Haifa Group 2020).

6.2 Synthetic Polymer Coating

Polymer coated fertilizers are suitable for high-value applications because it reduces the nutrient loss. In Japan, for rice plant more than 70% of polymer coated fertilizers are used (out of total fertilizers utilizations). These fertilizers offer more sophisticated nitrogen release pattern. The nutrient release is controlled by diffusion which is constant over time. Also, it depends on the coating thickness, chemical constituents, temperature, and moisture. Controlled release fertilizers release nutrients at a rate driven by temperature and moisture of the root zone. Nutricot, osmocot, and polyon are some of the marketed products. The coatings of these commercial products are tough, resist to damage, and thin (Naik et al. 2017). Subbarao et al. (2013) have mentioned in their report about the preparation of slow release fertilizer. In this method, potash and wet clay are mixed together. Then, the mixture is made as pellets by casting in cylindrical molds. Finally, these pellets are coated with polyacrylamide to achieve slow release of potash fertilizer (Subbarao et al. 2013). Polyacrylamide is a water-soluble polymer. Damaging of this polymer plays a major role in the releasing of potash. The hydrophilic nature of this polymer leads to the damage.

Slow release nanocomposite nitrogen fertilizers are prepared with polyacrylamide hydrogel or polycaprolactone (less than 4% by weight) with a high nutrient load (75% by weight). For this preparation, plastic mixture extrusion method is adopted. This preparation can be scaled up for large-scale granule production without additional or increasing costs (Pereira et al. 2015). For the controlled release of urea fertilizers, urea is coated with sulfur. In the next step, the coated granule is sealed by polymer coating. The coating can be degraded by microbial, chemical, and physical processes. The releasing time of the fertilizer is decided by the thickness of coating and permeability. These factors can be affected by temperature and moisture (Trenkel 2010). This technology is applicable in high-value crops, environmentally sensitive areas, and fields highly susceptible to N losses (Pioneer.com. 2020).

Sulfur can be sprayed in molten form over urea granules. Then, sealant wax is applied over this to close any cracks or imperfections present in the coating. Other polymers used in sulfur coating include resin-based polymers, polyesters, and low-permeability polyethylene polymers for controlled release of fertilizers. Figure 9a shows the sulfur sprayed urea granules and chemical structure of urea. Figure 9b explains the urea release from sulfur and polymer coated urea. The nutrient releasing mechanism (caused by the damaging of the outer coating) is also explained. Pioneer (2020) reported that addition of aldehydes with urea reduces the solubility of urea (Pioneer.com. 2020). Aldehydes are mixed with urea to prepare the products such as urea–formaldehyde and methylene urea. Clapp (2001) has reported that the reaction of aldehyde and ammonia or primary amine of excess urea

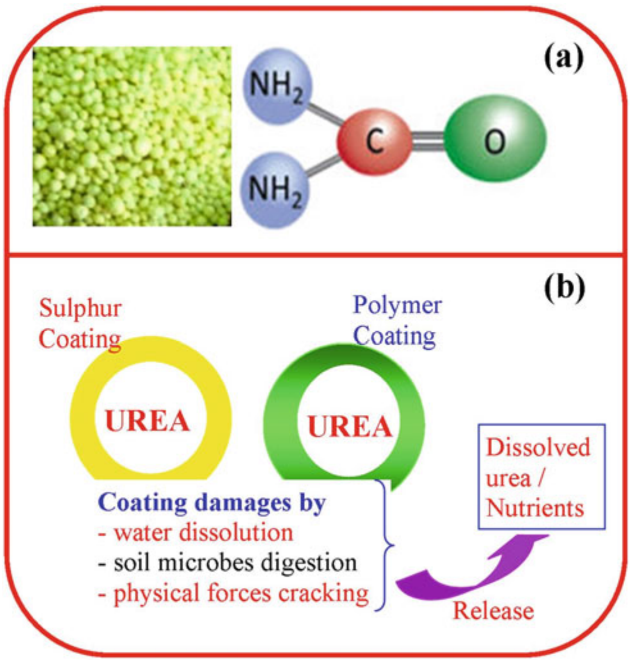

Fig. 9 Coating on urea: **a** sulfur sprayed on urea granules and chemical structure of urea, **b** the slow/controlled release of urea from the sulfur/polymer coated urea. Initially, the coating is damaged by water, microbes, and physical forces. Water moves into the coating and dissolves the nutrients. Then, the dissolved nutrients are released

(present in an aqueous medium) leads to the formation of a product called urea-triazone (Clapp 2001). The end product (urea-triazone) obtained in this process can be utilized in controlled releasing fertilizers applications.

6.3 Coating by Biological Products

Natural polymers are hydrophilic, eco-friendly, cost effective, easily available, and biodegradable. They can be prepared in various forms such as micro-particles, nanoparticles, beads, and hydrogels. The advantages of slow release are to increase the water holding capacity, aeration, soil permeability, and microbial activity. Polysaccharides such as starch, cellulose, dextrans, chitosan, pectin, guar gum, cyclodextrins, and alginate are utilized in the preparation of carriers. These carriers act as nano-carrier of bioactive compounds in agricultural applications (Campos 2013). Figure 10 explains the challenges in the utilization of conventional fertilizers (active material). Polymer-based nutrient delivery system is an alternative to solve the challenges.

Natural and biodegradable polymers such as tamarind powder, guar gum, and xanthan gum are used for the coating of urea. In this case, diatomite with epichlorohydrin is utilized as a crosslinker. *Diatomaceous* earth is used as a medium to grow plants because it is able to hold *fertilizers* and release to the roots. This fertilizer possesses high nutrients, slow release property, and good water retention capacity (Mukerabigwi et al. 2015). Guar gum or guran is obtained from the guar plant seed, i.e., *Cyamopsis tetragonoloba* (L.) TAUB. Xanthan gum is prepared by gram-negative bacteria *Xanthomonas campestris*.

A composite made of poly(vinyl alcohol), horn meal, rapeseed cake, glycerol, and phosphogypsum is utilized for the coating of fertilizers. The composition of the fillers decides the mechanical, sorption properties, water vapor permeability, solubility in water, and the dimensional stability of the composite films. This kind of encapsulation leads to increase the releasing time of the fertilizers which is useful in the cultivation of tomato sprouts. This fertilizer is working well on the development of the roots of the plants (Treinyte et al. 2017).

Biochar is a carbon material made from biomass. This charcoal is utilized as a soil amendment material that enhances plant growth and crop yields. Particularly, it is useful in fields with depleted soils and lower level organic resources, nutrients, and water. Chen et al. (2018) reported about the biochar-polymers complex coating. This complex contains copolymer of PVA and polyvinylpyrrolidone (PVP) and biochar. It is applied as coating material in slow release fertilizers. Biochar helps to: decrease water absorbency of copolymer; increase degradability; improve the slow releasing property of urea. Particularly, the biochar made from rice plant exhibits an excellent release behavior, i.e., 65.28% nutrient leaching (Chen et al. 2018).

6.4 Starch in Slow/controlled Releasing

Demand and utilizations of sulfur-coated fertilizers decrease because of its high cost, process complexity, and inconsistent results. Instead of sulfur, bio-polymer coating on fertilizers is applied. Azeem et al. (2016) have reported that coating of fertilizers with synthetic polymers (such as polyethylene, polystyrene, polyacrylamide, and polysulfone) is also not economical and non-biodegradable. Utilization of biodegradable and low-cost material such as starch as coating material is an alternate way. A coating material is prepared using starch and polyvinyl alcohol (binder). Starch-based coating of fertilizers in proper thickness allows for promising controlled release characteristics (Azeem et al. 2016). Double-coated slow release fertilizer is prepared using ethyl cellulose as inner coating and starch-based superabsorbent polymer (starch-SAP) as outer coating. The fertilizer particles coated with starch-SAP shows superior slow release properties. The starch-SAP coated fertilizer offers reduced nitrogen release rate and steady release behavior for a period longer than 96 h to potato plants (Qiao et al. 2016).

Efficient fertilization practices can be developed with the help of nanoparticles and polymers. Urea is coated with

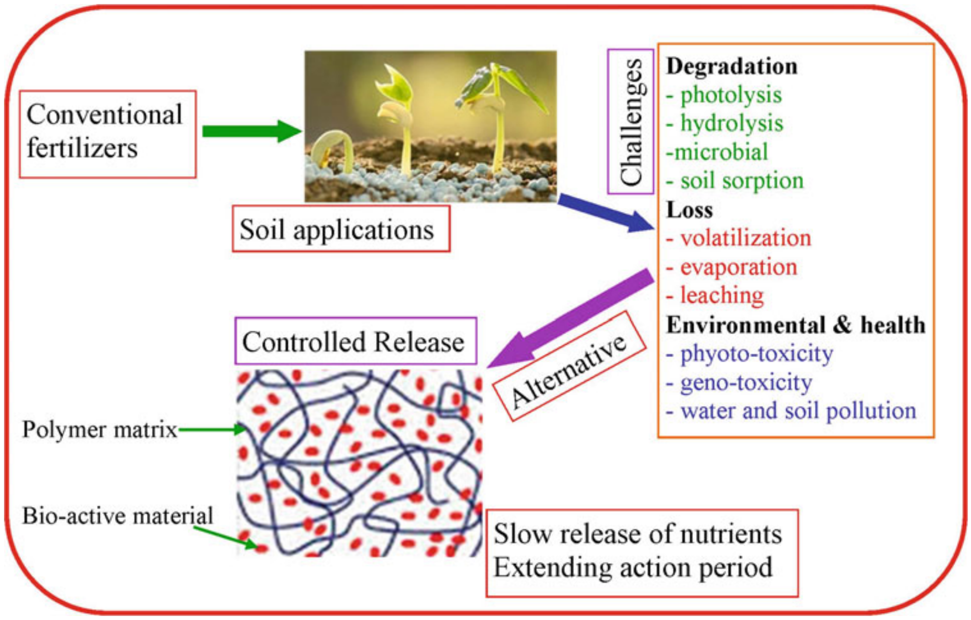

Fig. 10 Schematic diagram showing the plant growth factor delivery system. Utilization of conventional fertilizers (active material) in agriculture creates some problems including environmental and health issues. Polymer (polysaccharides)-based nutrient (bioactive compounds) delivery system for targeting applications is an alternative to solve these issues. It has benefits like slow release of nutrients and extending the duration of action

thermoplastic starch. Hydroxyapatite nanoparticles are dispersed in this urea matrix. These coating and dispersion lead to produce urea-hydroxyapatite nanocomposite. This nanocomposite controls the N-release and increases the P-availability in soil. The interaction between hydroxyapatite and urea reduces the phosphorus immobilization that increases the P-availability (Giroto et al. 2017).

6.5 Chitosan in Slow/controlled Releasing

Chitosan (CS) nanoparticle possesses polymeric cationic, biodegradable, bioabsorbable, and bactericidal characteristics. Hence, it can be a best candidate in controlled release of fertilizers. Chitosan nanoparticles are prepared by polymerizing methacrylic acid for the incorporation with NPK fertilizers. The slow release concept in fertilizers is able to save fertilizer consumption and minimize the environmental pollution (Corradini et al. 2010). In this way, chitosan nanoparticles loaded with nitrogen, phosphorous, and potassium are applied for wheat plants. Chitosan supports for the growth of roots, shoots, and leaves of plants. Nano-chitosan-NPK fertilizer increase harvest index, crop index, and mobilization index of the wheat plants (Abdel-Aziz et al. 2016). Crosslinking of chitosan with suberoyl chloride enhances the controlled release properties and mechanical strength of chitosan by forming a three-dimensional network structure. Chen et al. (2013) reported about the permeabilities of plant nutrients such as N, P, K, Zn^{2+}, and Cu^{2+} and plant growth regulator (naphthylacetic acid). N/P/K permeability is the important parameters to evaluate the controlled release fertilizer. Utilization of crosslinking agent (suberoyl chloride) in crosslinking of N-phthaloyl acylated chitosan improves the properties (such as film-forming ability, mechanical property, and hydrophobicity) of chitosan membranes. Adding small amount of suberoyl chloride improves the properties but the excessive crosslinking leads to poor permeability. The macroelements (N, P, K), microelements (Zn^{2+} and Cu^{2+}), and plant growth regulator (naphthylacetic acid) releasing amount with different crosslinking densities (from 0 to 7.4%) is shown in Fig. 11 (Chen et al. 2013).

Crosslinking decreases the permeability of macroelements, microelements, and NAA which confirms that the crosslinked materials are suitable to use as controlled release microelement fertilizers. The permeability is low when crosslinking increases. Penetration of materials through crosslinked N-phthaloyl acylated chitosan membrane is confirmed from Fig. 11. Material releasing amount is less in crosslinked membrane and it is high in membrane without crosslinking. All curves exhibit the time-dependent release pattern. Material releasing amount is high when time increases (Chen et al. 2013).

6.6 Polyurethane in Slow/controlled Releasing

Controlled release fertilizers are made by coating fertilizers using polymers like polyurethane. They can be synthesized from low-cost, biodegradable, and renewable cottonseed oil. The specialty of this coating over conventional methods is increased surface roughness, reduced surface energy, and superhydrophobic nature. The superhydrophobic nature offers the non-wetting contact of water in gas state instead of

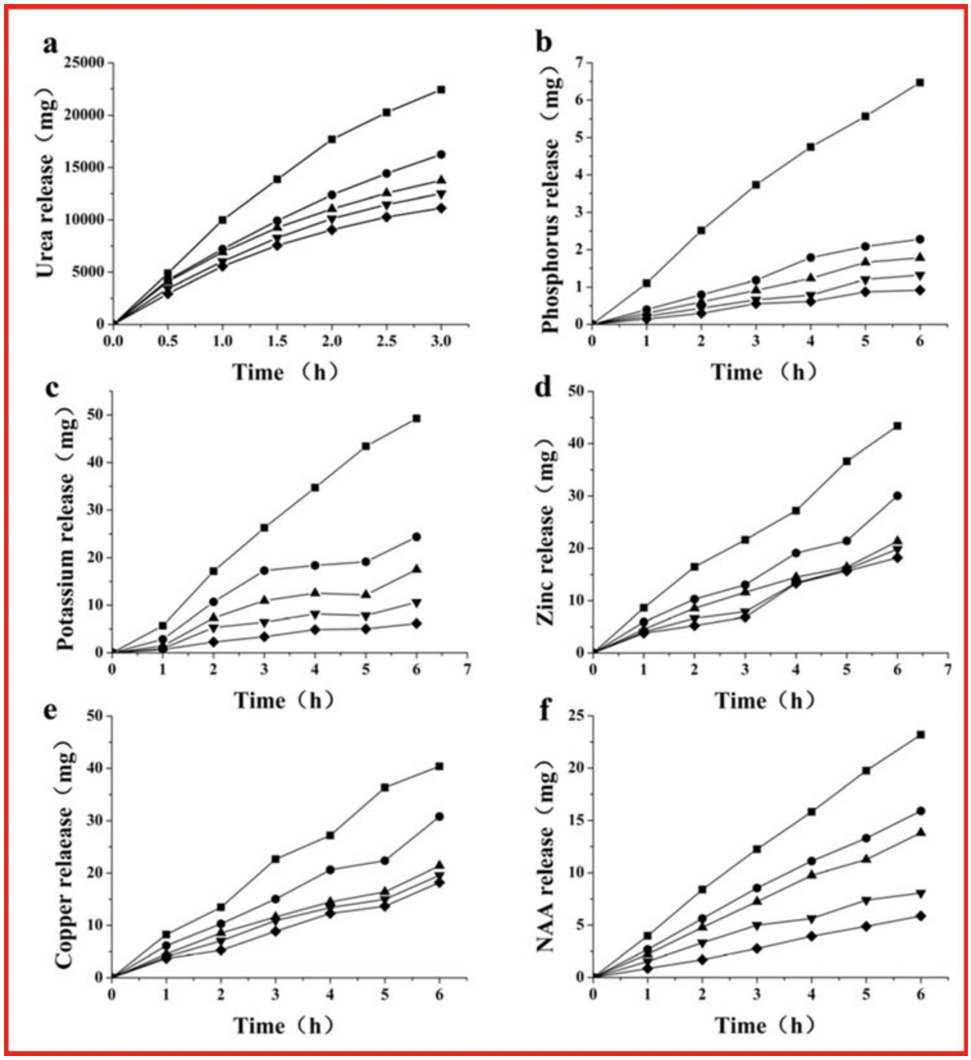

Fig. 11 Nutrients release vs time curves. Permeability of macro and micronutrients through crosslinked N-phthaloyl acylated chitosan membrane (with different crosslinking densities). **a** Urea; **b** phosphorus; **c** potassium; **d** zinc; **e** copper; **f** NAA. crosslinking densities ■ 0%; ● 2.9%; ▲ 4.4%; ▼ 5.9%; ◆ 7.4%. *Source* Chen et al. (2013), with permission

in liquid state (Xie et al. 2017). The oxidation and brittleness of sulfur are preventing sulfur coating in slow release fertilizers. Also, it is not economical to use synthetic polymers for coating fertilizers. Hence, the best alternate available coating is using natural polymer and it is a good water absorber. However, the nutrient release longevity is available for less than 30 days. This duration will not meet nitrogen supply requirements for crops. To overcome the drawback of the bio-resources, a new technology is adopted. In this method, natural polymers are converted into bio-polyols that can work better. The fertilizer is coated with polyurethane made from wheat straw. Solvents like ethylene glycol/ethylene carbonate are used to liquefy the wheat straw. The liquid is added with polymethylene polyphenyl isocyanate and castor oil to get bio-based polyurethane (Lu et al. 2015).

6.7 Zeolites in Slow/controlled Releasing

Zeolites are aluminosilicates of sodium, potassium, calcium, and barium. Their applications lie in cation exchanges and molecular sieves. SEM images of different zeolite particles are shown in Fig. 12. These zeolite particles have properties like adsorption of urease enzyme. Hence, they (except zeolite L) are useful in the preparation of urea-sensitive biosensors (Kucherenko et al. 2015). Compared to the conventional fertilizers, releasing of the fertilizer contents is slow and more while applying the zeolites mixed/coated macro or micronutrients. Zeolites reduce the nutrient loss by controlling the release and improving uptake. Yuvaraj et al. (2018) reported about the modification of zeolites for slow release fertilizer application. Zeolites modified by a surfactant hexadecyltrimethylammonium bromide are treated

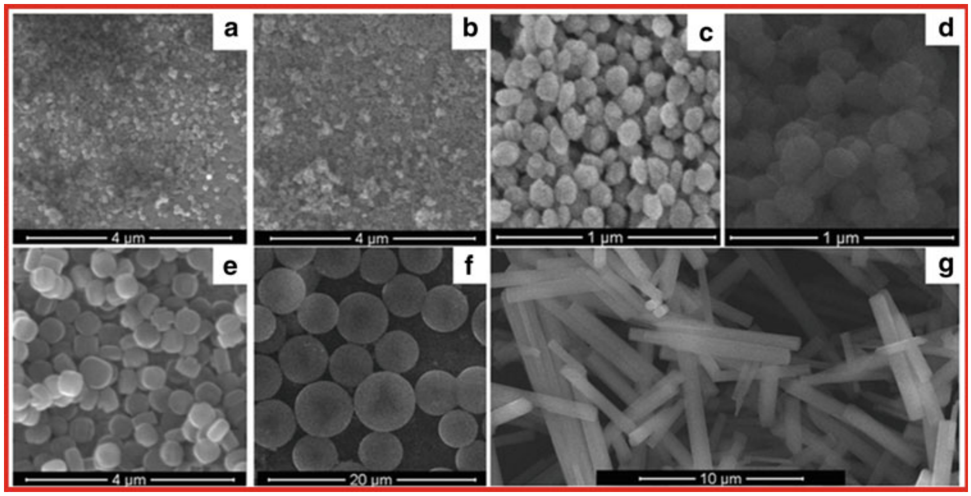

Fig. 12 SEM images of zeolite particles. **a** Nanozeolite beta, **b** nanozeolite L, **c** 80 nm silicalite-1, **d** 160 nm silicalite-1, **e** 450 nm silicalite-1, **f** mesoporous silica spheres, **g** zeolite L (*Source* Kucherenko et al. 2015, with permission)

with KH_2PO_4 for preparation of slow release of phosphorus fertilizer. From this fertilizer, phosphorus is released even after 1080 h (Bansiwal et al. 2006). Zinc is utilized by plants as a micronutrient up to 2–3%. To avoid zinc fixation in the soil, nanozeolites are synthesized by ball milling and fortified with zinc by loading zinc sulfate. Zinc fertilizer coated with nanozeolites releases zinc for a period of 1176 h (Yuvaraj et al. 2018).

Phosphorus and potassium are incorporated in zeolite to form a nanofertilizer. Release of phosphorous and potassium from this nanofertilizer is higher than the conventional fertilizer. Also, the accumulation of phosphorous and potassium are more in plants while applying this zeolite-based nanofertilizer. After the application of this nanofertilizer, the soil possesses better pH, moisture, EC, CEC, and availability of P and K (Rajonee et al. 2017). Utilization of porous nanomaterials (zeolites, clay, or chitosan) in fertilizer applications considerably reduces nitrogen loss by controlling the release and improving uptake (Millan et al. 2008; Abdel-Aziz et al. 2016; Panpatte et al. 2016). Ammonium mixed zeolites improve the solubility of phosphate that leads to improving the availability of phosphorus (Dwivedi et al. 2016).

7 Influences of Nanofertilizers on the Soil and Crop Plants

It is analyzed and observed from the various literatures while applying the nanofertilizer, it is essential to consider some factors like concentration of nanofertilizers, biocompatibility, solubility, nutrient releasing period, control over nutrient release, encapsulation/coating of nanofertilizer, and size of nanomaterial. Some of the factors have influences on the agricultural output and yield of the plants. They are enumerated below.

- Application of chemical fertilizers has drawback like soil acidification. Slow releasing fertilizers avoid it.
- Utilization of toxic or biologically incompatible materials causes harm to all biological organisms. Biocompatibility is an essential one. It can be achieved by utilizing bio-synthesized nanomaterials instead of chemically synthesized nanomaterials.
- The concentration of the nanomaterial (nanofertilizer) is more important. Applying the nanofertilizer (like carbon nanomaterials and iron nanoparticles) up to optimum quantity or at lower concentration yields better results. Improvement in yields is due to the increased water uptake and transport, seed germination, and antioxidant activities.
- Applying the nanofertilizer at higher concentration decreases the yields. Due to aggregation at cell walls that blocks the nutrients transfer and antioxidant activities.
- Encapsulation of microorganisms enhances the N, P, and K availability that stimulate the plant growth.
- Sulfur-coated urea releases N slowly due to gradual microbial, chemical, and physical degradation process.
- Urea reacted with aldehydes compounds release their N slowly.
- Hydroxyapatite nanoparticles coating on urea reduces the conversion of urea into ammonia and release the nitrogen slowly.
- Hydroxyapatite nanoparticles release phosphorous and improve the phosphorous availability to the plants without changing soil pH or soil acidification.
- Hydroxyapatite nanoparticles decrease the water eutrophication that improves the yield.
- Hydroxyapatite nanoparticles can release both phosphorous and calcium.
- ZnO nanoparticles have solubility higher than the bulk ZnO.

- Porous nanomaterials (ammonium charged zeolites, graphene oxide, and nanocalcite) reduce nitrogen loss in considerable quantity by controlling the nutrient release that enhances the plant uptake process.
- In controlled release fertilizers, the thickness of coating and permeability determines the releasing time of the fertilizer.
- Ammonium mixed zeolites enhance the solubility of phosphate.

8 Conclusion

Nanofertilizer is the engineered nanomaterial prepared by applying nanotechnology. Particles of this material are in the nanometer size range. Due to the presence of nano-sized particles (particularly size less than the plants cells), this new generation fertilizer has an ability to reduce the fertilizer consumption and to deliver the nutrients better than the conventional fertilizers. It is observed from the literature that the nanofertilizers will play a major role in the modern agriculture. Engineered nanomaterials are applied in plant stress, pathogens controlling, target delivery (gene transfer), plants development, and soil enhancement. Nanomaterials like magnesium hydroxide, carbon nanomaterials, ZnO nanoparticles, and iron oxide nanomaterials are utilized in pre-soaking of seeds and seed germination technology. They improve the solubility of the nutrients. Some nanofertilizers have good water retention capacity. Comparing to the conventional fertilizers, they release the nutrients and reduce the nutrient loss in a better way. Slow and controlled released nanofertilizers augment the plant growth that leads to higher level plant productivity and crop yield.

Fertilizers are expected to do more functions like stimulation of soil microorganisms and mobilization of phosphorus and potassium to make them easily available to the plants. To cope up with the agriculture market, a fertilizer should be fast acting and long-lasting. The fertilizer should provide support to better yield (with a uniform, dense, or full growth) and eliminate entanglement. It should promote humus formation and soil health. Advanced technologies (like nanotechnology, nanofertilizers, and biofertilizers) support to fertilizers for the supply of nutrients properly.

Acknowledgements The author expresses immense thanks to her husband Mr. G. Sankar for his assistances in this work. Also, she acknowledges the assistances of International Research Center, Kalasalingam Academy of Research and Education (Deemed University), Krishnankoil-626 126, (India) for providing necessary supports and facilities.

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