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A Review of Nano Fertilizers and Their Use and Functions in Soil

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A B S T R A C T

With the global upsurge in population and rapid urbanization, farmers across the globe are left with the daunting task of feeding more mouths every year from agricultural fields which are dwindling correspondingly. Satellite images show that the Earth is rapidly running out of fertile land and that food production will soon be unable to keep up with the world's burgeoning population. The production level of food grains has become a subject of concern as it has been showing a downward trend over the last decade. With natural resources getting exhausted, it is through agriculture that we can envisage a self-sustainable world. With limited availability of land and water resources, growth in agriculture can be achieved only by increasing productivity through an effective use of modern technology. Nanotechnology possesses the potential to augment agricultural productivity through genetic improvement of plants and animals along with cellular level delivery of genes and drug molecules to specific sites in plants and animals. The potential is increasing with suitable techniques and sensors being identified for precision agriculture, natural resource management, efficient delivery systems for agrochemicals such as fertilizers and pesticides, food processing, packaging and other areas like monitoring agricultural and food system security. Here we review the contribution of nanotechnology technique on development of nano fertilizer and its uses and function in soil.

Introduction

Nanotechnology, focusing on special properties of materials emerging from nanometric size has the potential to revolutionize in the food sector, biomedicine, environmental engineering, safety and security, water resources, energy conversion, and numerous other areas (Baruah *et al.*, 2008). Nanotechnology applications in agriculture are gradually transforming the theoretical possibilities into the practical applications. Novel tools are being designed which can operate at nanometric levels to boost research in molecular and cellular biology. Nanotechnology possesses the potential to augment agricultural productivity through genetic improvement of plants and animals (Kuzma, 2006; Scott 2007) along with cellular level delivery of genes and drug molecules to specific sites in plants and animals (Maysinger, 2007). The potential is increasing with suitable techniques and sensors being identified for precision agriculture, natural resource management, early detection of pathogens and contaminants in food products, efficient delivery systems for agrochemicals such as fertilizers and pesticides, improved systems integration for food processing, packaging and other areas like monitoring agricultural and food system security (Moraru *et al.,* 2003; Chau *et al.,* 2007; Subramanian and Rahale, 2009). With increased innovations using nanotechnology in the agricultural sector, it can be envisaged to become the major economic driving force and benefit consumers and farmers with no detrimental effect on the ecosystem. There is an emerging area of interest in the utilization of nanoporous zeolites in farming over the years because of current public concern about the adverse effects of chemical fertilizers on the agro-ecosystem.

Nanotechnology application

Nanotechnology is the manipulation or self-assembly of individual atoms, molecules, or molecular clusters into structures to create materials and devices with new or vastly different properties. The emergence of nanotechnology and the development of new nanodevices and nanomaterials open up potential novel applications in agriculture. Nanotechnology is defined as "the understanding and control of matter at dimensions of roughly 1-100 nm, where unique properties make novel applications possible". By manipulating molecules on the scale of billionths-of-a-meter, scientists have created materials that exhibit "almost magical feats of conductivity, reactivity, and optical sensitivity, among others". This also has the potential to drive an economic revolution. Retailers already sell over 300 products that incorporate nanotechnology (Science Policy Council, 2007), and according to one estimate, nanotechnology will be a trillion-dollar-a-year industry by 2015 (Roco, 2003). It is a highly promising technology that spans many areas of science and technological applications. Rapid advancements in nanoscience and nanotechnologies in recent years have opened up new horizons for many industrial and consumer sectors that have been regarded as the hotbed of a new industrial revolution including agriculture and allied sectors. Kuzma and Verhage (2006) reported that among the recent advancements in science, nanotechnology is fast emerging as the new science and technology platform for the next generation of development and transformation of agri-food systems as well as for improving the conditions of the poor people.

Nanoscale materials and devices can be fabricated using either "bottom-up" or "top-down" fabrication approaches. In bottom-up methods, nanomaterials or structures are fabricated from buildup of atoms or molecules in a controlled manner that is regulated by thermodynamic means such as self-assembly (Ferrari, 2005). Alternatively, advances in micro technologies can be used to fabricate nanoscale structures and devices. These techniques are collectively referred to as top-down nanofabrication technologies, include photolithography, nanomolding, dip-pen lithography and nanofluidics (Peppas, 2004; Sahoo and Labhasetwar (2003)). Abdul-Kalam (2007) suggested that nanotechnology has potential to bring the next revolutionary breakthrough in agricultural-based natural resource management. It has ushered as a new interdisciplinary venture-field by converging science and engineering into agriculture and food systems.

Nanotechnology applications in agriculture

Nanotechnology has a wide applications in medicine (Zhou *et al.,* 2004), environment (Shi *et al.,* 2007), energy (Das *et al.,* 2007), information and communication (Hillie, 2007), heavy industry (Lo *et al.,* 2010) and consumer goods (Schneider, 2010). Despite the fact that nanotechnology is extensively exploited in health and medical sciences, the use of nanotechnology in agriculture and food system is just emerging and expected to grow alarmingly. Globally, agrifood sector has been identified as a potential industry to make significant investments. Currently, over 300 nanofood products are available in the international markets. According to a recent study by Helmuth Kaiser Consultancy (Germany), the nanofood market was expected to surge from USD 2.6 billion in 2004 to USD 20 billion by 2010. The report suggested that with more than 50% of the world population, the largest market for nanofood in 2010 will be Asia, led by China.

Nanotechnology has the potential to revolutionize the agricultural and food industry with new tools for the molecular treatment of diseases, rapid disease detection, enhancing the ability of plants to absorb nutrients etc. Smart sensors and smart delivery systems will help the agricultural industry combat viruses and other crop pathogens. In the near future nanostructured catalysts will be available which will increase the efficiency of pesticides and herbicides, allowing lower doses to be used. Nanotechnology will also protect the environment indirectly through the use of alternative (renewable) energy supplies, and filters or catalysts to reduce pollution and clean-up the existing pollutants.

Potential applications of nanotechnology in developing countries identified agricultural productivity enhancement as the second most critical area of application for attaining the millennium development goals while energy conversion and storage was ranked first and water treatment as the third areas needing focus (Buentello *et al.,* 2005). Ultimately, precision farming, with the help of smart sensors, will allow enhanced productivity in agriculture by providing accurate information, thus helping farmers to make better decisions. In the future, nanoscale devices with novel properties could be used to make agricultural systems "smart". For example, devices could be used to identify plant health issues before these become visible to the farmer. Such devices may be capable of responding to different situations by taking appropriate remedial action.

Nanofertilizer

Nanofertilizer technology is very innovative and scanty reported literatures are available in the scientific journals. Nutrient use efficiencies of conventional fertilizers hardly exceed 30-35 %, 18-20 % and 35-40 % for N, P and K respectively. The data remain constant for the past several decade and research efforts did not yield fruitful results. Nano-fertilizers are nutrient carriers that are being developed using substrates with nanodimensions of 1 – 100 nm. Nano particles have extensive surface area and capable of holding abundance of nutrients and release it slowly and steadily such that it facilitates uptake of nutrients matching the crop requirement without any associated ill-effects of customized fertilizer inputs.

The current growing awareness of the phenomenon and availability of inexpensive natural zeolites in the world has aroused considerable commercial interest on developing zeolite based nano fertilizer. Chuprova *et al.,* (2004) found the beneficial effects of zeolite fertilizers on mobile humus substances of Chernozem and on biological productivity of maize. In another study, a patented nano-composite consists of N, P, K and micronutrients and mannose and amino acids have been shown to increase the uptake and utilization of nutrients by grain crops (Jinghua, 2004). Bhattacharya (2004) reported that the balanced application of NPK along with S, Zn, B and Mo will be an effective solution for higher grain yield of pulses in red and lateritic soils. Adequate NPK fertilization increased green and blackgram yields by 13%

and 38% over the control. Liu *et al.,* (2006) have shown that the organic material (polystyrene) intercalated in the layers of kaolinite clay form a cementing of nano and subnano-composites which are capable of regulating the release of nutrients from the fertilizer capsule. Thus nano-particles could be used in the membrane control release of nutrients. Subramanian *et al.,* (2008) reported that nano-fertilizers and nanocomposites can be used to control the release of nutrients from the fertilizer granules so as to improve the nutrient use efficiency while preventing the nutrient ions from either getting fixed or lost to the environment.

Recently, SharmilaRahale (2011) has monitored the nutrient release pattern of nanofertiliser formulations carrying nitrogen. The data have shown the nano-clay based fertilizer formulations (zeolite and montmorillonite with a dimension of 30-40 nm) are capable of releasing the nitrogen for a longer period of time (> 1000 hrs) than conventional fertilizers (< 500 hrs). Nanotechnology can be exploited to improve the efficiencies of native and added sources of nutrients. Nanofertilizer technology improves the fertilizer use efficiency of crops. There is an increasing interest in the utilization of nanoporous zeolites in farming over the years because of current public concern about the adverse effects of chemical fertilizers on the agro-ecosystem (Ramesh *et al.,* 2010*)*.These reports and patented products strongly suggest that there is a vast scope for the formulation of nano- fertilizers (Liu *et al.,* 2006; Subramanian *et al.,* 2008; DeRosa, 2010). Nanofertilizer may be a strategy to improve the nutrient use efficiency of crops and crop productivity.

Characteristics of zeolites

Zeolites, a naturally occurring mineral group consisting of about 50 mineral types, draw attention as a good growing medium substrate for a long period due to its good physical and chemical characteristics (Markovich *et al.,* 1995). They have a rigid three-dimensional crystal structure with voids and channels of molecular size and high cation exchange capacity (CEC) arising from substitution of Al for Si in the silicon oxide tetrahedral units that constitute the mineral structure (Ayan, 2001 and 2002a; Pickering *et al.,* 2002).

Clinoptilolite zeolites unique crystalline latticework structure and channels adsorbs water through a highly porous molecular matrix with an immense surface area, while its negative charge acts as a magnet attracting, holding, and exchanging positively charged particles (cations) (Desborough, 1996).

The characteristic of zeolite was given by Junrungreang *et al.,* (2002) that zeolite was considered to be representative in term of its composition CEC (133.92 cmol (p^+) kg^{-1}), K (19.83 cmol kg^{-1}), Ca (161.96 cmol kg^{-1}), Mg (16.40 cmol kg^{-1}), Na (13.97 cmol kg^{-1}), P_2O_5 (426 mg kg^{-1}), pH (6.4), SiO_2 (71%), Al_2O_3 (11%), Fe_2O_3 (3.13%), Na_2O (1.09%), MgO (0.61%), K_2O (2.54%), and CaO (2.56%), respectively.

The nano-zeolite has hexagonal symmetry (Baerlocher *et al.,* 2001) with two dimensional pores of about 0.71nm aperture leading to cavities of about 0.48x124x1.07 nm and the Si/Al ratio is typically 3.0 (Bruhwiler, 2005). The nano-zeolite crystal consists of cages linked by double six membered rings, forming columns in the C-direction. Connection of these columns give rise to 12-membered rings with a free diameter varying from 0.71 nm to 1.26nm (Agger, 2003). The literature review suggests that zeolite is natural mineral having extensive surface area and can hold wide range of +ve and –ve nutrient ions after suitable partial modification.

Essential Nutrients

Macronutrients - Nitrogen nanofertiliser

Nitrogen is an important component of many important structural, genetic and metabolic compounds in plant cells. It is a major component of chlorophyll, the compound by which plants use sunlight energy to produce sugars from water and carbon dioxide (i.e. photosynthesis). It is also a major component of amino acids, the building blocks of proteins. Some proteins act as structural units in plant cells while others act as enzymes, making possible many of the biochemical reactions on which life is based. Nitrogen is a component of energy-transfer compounds, such as ATP (adenosine triphosphate) which allows cells to conserve and use the energy released in metabolism. Finally, nitrogen is a significant component of nucleic acids such as DNA, the genetic material that allows cells (and eventually whole plants) to grow and reproduce. Since nitrogen exists in three general forms - organic nitrogen compounds, ammonium (NH_4^+) ions, and nitrate (NO_3^-) ions which is available for plant. Most of the nitrogen is not available for plant completely. This is because negatively charged nitrate normally does not have higher affinity for soil particle surfaces and thus does not readily sorb on soil.

To overcome the problems associated with the nitrogen leaching during fertilization, different approaches such as polyolefin resin-coated urea, neem coated urea, sulphur coated urea were taken to control the N release. However, slow-releasing fertilizers are often expensive and the release of N is slow at the time of high N. N loss can also be reduced using cation exchanger as additives in fertilizer to control NH_4^+ release. The retention and timely release of needed nutrients by zeolite improves overall crop yield.

Clinoptilolite zeolite (CZ), a porous mineral with high cation exchange capacity (CEC, up to 300 c mol (p^+) kg^{-1}) and with great affinity for NH_4^+ (Ming and Mumpton, 1989), has been used to reduce NH_3 emission from farm manure (Amon *et al.*, 1997), and to eliminate NH_3 toxicity to plants (Gupta *et al.*, 1997). Amendment of clinoptilolite zeolite (CZ) to sandy soil has been reported to lower NO_3^- and NH_4^+concentrations in the leachate and to increase moisture retention in the soil due to increased soil surface area and CEC (Huang and Petrovic, 1994). Urea nitrogen has been the most used N-source due to lower cost per unit of N. But N use efficiency of urea may be reduced because of losses from agricultural system by volatilization of ammonia to atmosphere. This is one of the main factors responsible for the low efficiency of urea, and may reach extreme values, close to 80% of N applied. Ammonium retained by CZ is generally subjected to slow release through cation exchange and nitrification in soil (Kithome *et al.*, 1998).

Clinoptilolite zeolite has been used to reduce NH_3 emission from farm manures (Amon *et al.*, 1997) and as NH_4^+ – loaded exchange fertilizer (Perrin *et al.*, 1998a, b) because of its high CEC. Application of $(NH_4)_2SO_4$ loaded into CZ was observed to minimize N leaching and to increase N utilization by crops in sandy soils compared with $(NH_4)_2SO_4$ alone (Perrin *et al.*, 1998a, b). Perrin *et al.*, (1998) stated that clinoptilolite not only improves nitrogen fertilization efficiencies, it also reduces nitrate leaching by inhibiting the nitrification of ammonium to nitrate. Lefcourt and Meisinger (2001) reported that zeolite has the potential for reducing ammonia volatilization by sequestering ammonium-N on exchange cites. An addition of 6.25% zeolite resulted in a 50 % reduction in ammonia volatilization. An additional potential advantage is that zeolite bound ammonium is a good slow-release N source for plants. Unlike the commonly used fertilizers, the plant-growth material dramatically reduces loss of nutrients to groundwater and the environment. The N-urea losses can also be reduced using zeolites as additives in the fertilizers to control the retention and release of NH_4^+. There are reports in the literature showing that the addition of zeolite to the source of N can improve the nitrogen use efficiency (Ming and Mumpton 1989; McGilloway *et al.*, 2003; Gruener *et al.*, 2003; Rehakova *et al.*, 2004). Li (2003) demonstrated the feasibility of using surfactant-modified zeolite (SMZ) using hexadecyltrimethyl ammonium as fertilizer carrier to control nitrate release, and concluded that SMZ is a good sorbent for nitrate, whereas slow release of nitrate is achievable.

Bhardwaj and Tomar (2011) conducted laboratory batch experiments to investigate the sorption of nitrate from aqueous solutions using hydrothermally synthesized and surface modified zeolite nano particles. The ability of surface modification with hexadecyltrimethyl ammonium (HDTMA) and Dioctadecyldimethyl ammonium greatly enhance the sorption and slow release of nitrate. Latifah *et al.*, (2011) confirmed that mixing urea with zeolite and sago waste water had great advantage over urea alone as the mixture encouraged the formation of ammonium and available nitrate ions over ammonia. The mixture also improved retention of exchangeable ammonium and available nitrate within the soil. Recently, Sharmila Rahale (2011) had monitored the nutrient release pattern of nanofertiliser formulations carrying nitrogen.

They had shown that nano-fertilizer released nutrients upto 1200 hrs while conventional fertilizer could support only for 300- 350 hrs. The data had clearly demonstrated that zeolite as nano- fertilizer could be an ideal strategy to promote N use efficiency.

Phosphorus nano-fertilizer

Phosphorus is an essential nutrient both as a part of several key plant structure compounds and as a catalysis in the conversion of numerous key biochemical reactions in plants. Phosphorus is the most important nutrient for its function as an energy transfer and storage in plants.

Adenosine di- and triphosphates (ADP and ATP) are the most important forms of phosphates that are involved in the energy transfer. It is also an important structural component of phosphor- proteins, phospholipids, sugar phosphates, coenzymes, nucleic acids, and metabolic substrates in plants. Supply of P at the early stage of crop is essential for its development of reproductive structures. Some specific growth factors that have been associated with phosphorus are: stimulated root development, increased stalk and stem strength, improved flower formation and seed production, more uniform and earlier crop maturity, increased N-fixing capacity of legumes, improvement in crop quality and increased resistance to plant diseases.

Allen *et al.*, (1996) conducted studies to examine the solubility and cation-exchange in mixtures of rock phosphate and NH_4^+ and K-saturated clinoptilolite revealed that mixtures of zeolite and phosphate rock had the potential to provide slow-release fertilization of plants in synthetic soils by dissolution and ion-exchange reactions. Malhi *et al.*, (2002) reported that the zeolites (clinoptilolite), when saturated with mono-valent nutrient cations, such as NH_4^+ and K^+ have been reported to increase the solubility of phosphate rock (PR). The efficiency of fertilizer P use by crops ranged from 18 to 20 % in the year that it is applied. The remaining 78 to 80% becomes part of the soil P pool which is released to the crop over the following months and years.

Bansiwal *et al.,* (2006) demonstrated that the release of P from fertilizer-loaded unmodified zeolite, surface modified zeolite (SMZ) and from solid KH_2PO_4 were performed using the constant flow percolation reactor. The results showed that the P supply from fertilizer-loaded SMZ was available even after 1080 h of continuous percolation, whereas P from KH_2PO_4 was exhausted within 264 h. The results indicated that SMZ is a good sorbent for PO_4^{3-}, and a slow release of P is achievable. These properties suggested that SMZ has a great potential as the fertilizer carrier for slow release of P. Eberl (2008) reported that phosphate (H_2PO_4) can be released to plants from phosphate rock (P-rock) composed largely of the calcium phosphate mineral apatite by mixing the rock with zeolite having an exchange ion such as ammonium. The approximate reaction in soil solution is as follows:

(P-rock) + (NH_4 – zeolite) = (Ca zeolite) + (NH_4) + ($H_2PO_4^-$)

The zeolite takes Ca^{2+} from the phosphate rock, thereby releasing both phosphate and ammonium ions. Unlike the leaching of very soluble phosphate established equilibrium, the fertilizers (for example, super phosphate), the controlled-release phosphate is released of a specific chemical reaction in soil. As phosphate is taken up by plants or by soil fixation, the chemical reaction releases more phosphate and ammonium in the attempt to reestablish equilibrium. The rate of phosphate release is controlled by varying the ratio of P-rock to zeolite. Phosphorus is also released from the rock by the lowering of soil pH as ammonium ions are converted to nitrate. Andrews and Shaw (2010) reported that zeoponic is a plant demand driven nutrient delivery system and from this phosphate (PO_4^{3-}) and other nutrients released by controlled dissolution of synthetic apatite. N, P and K were delivered when plant needs them from zeoponics. Basically, the process is a combination of dissolution and ion exchange reactions. The absorption of nutrients from the soil solution by plant roots drives the dissolution and ion exchange reactions, pulling away nutrients as needed. The zeolite is then "recharged" by the addition of more dissolved nutrients. In effect, zeoponic systems increase nutrient retention, reduce environmental nutrient losses and reduce fertilizer requirements by establishing a replenishable and balanced nutrient supply in the plant root zone.

SharmilaRahale (2011) studied the PO_4^- release pattern of surface modified using various nanoclays and zeolite in a percolation reactor. Nano- formulations have been shown to release phosphate for an extended period of 40- 50 days and the conventional fertilizer let out nutrients only upto 10- 12 days. The review of literature suggests that surface modified zeolite could be potential strategy to promote P use efficiency which hardly exceed 18- 20 % in conventional system.

Potassium nanofertilizer

Potassium is vital to many plant processes. While potassium is not a constituent of any plant structures or compounds, it plays a part in many important regulatory roles in the plant. It is essential in nearly all processes needed to sustain plant growth and reproduction. Potassium plays a vital role in photosynthesis, translocation of photosynthates, protein synthesis, control of ionic balance, regulation of plant stomata and water use, activation of plant enzymes and many other processes. It is known to activate at least sixty enzymes involved in plant growth. Plants deficient in potassium are less resistant to drought, excess water, high and low temperatures. They are also less resistant to pests, diseases and nematode attacks. Potassium is also known as the quality nutrient because of its important effects on quality factors such as size, shape, color, taste, shelf life, fiber quality and other quality measurements.

Some natural zeolites contain considerable amounts of exchangeable K^+ that can enhance plant growth in potting media. For example, Hershey *et al.,* (1980) provided data on the slow release effect of K from K-zeolite. Mazur *et al.*, (1986) stated that the application of chemical fertilizer at the rate 625 kg ha^{-1}mixed with zeolite 125 kg ha^{-1}indicated the largest amount of potassium in the soil because zeolite had potential to adsorb potassium from chemical fertilizer and reduce it from leakage. Natural zeolites are highly selective for K^+ rather than for sodium or divalent cations, such as calcium and magnesium, because of the location and density of the negative charge in the structure and dimensions of the interior channels (Ming and Mumpton, 1989). Treacy and Higgins (2001) suggested that among all, potassium is the only element with the highest ion-exchange capacity of 216 c mol (p^+) Kg^{-1} (Dakovic *et al.*, (2007) and consequently, it is very easily released from the crystal zeolite structure into the soil solution, eventually increasing its total content in the soil. Zhou and Huang (2007) reported that slow and steady release of K from nano-zeolite and gave the reason that it may be due to the ion exchangeability of the zeolites with selected nutrient cations, zeolites can become an excellent plant growth medium for supplying plant roots with additional vital nutrient cations and anions. Guo *et al.,* (2008) suggested that the zeolite can be "recharged" by the addition of more dissolved nutrients. Their selectivity of ion exchange on zeolite was determined in an order of $K^+ > NH_4^+ > Na^+ > Ca^{2+} > Mg^{2+}$.

Rezaei *et al.*, (2009) reported that potassium sorbed on zeolite increases with the increase in equilibrium K concentration. Beitollah *et al.,* (2009) suggested that the zeolites dominated by exchangeable K may be well-suited for plant growth applications. Li *et al.,* (2010) in their study used potassium (K^+) - loaded zeolite (K-Z) as a slow-release fertilizer and investigated the growth characteristics of hot pepper as well as the changes in the nitrogen and potassium contents of the evaluated soil. SharmilaRahale (2011) conducted experiment on slow release of K fertilizer and examined their efficiency. Despite the fact that potassium fixation in soil and dynamic equilibrium collectively sustain the availability of potassium in soil, nanotechnology can further improve the availability and regulated release of nutrients.

Secondary nutrients nano-fertilizer

Sulphur (S), calcium (Ca) and magnesium (Mg) are secondary nutrients required in relatively large amounts for good crop growth. S and Mg are needed by plants in about the same quantities as P, whereas for many plant species, Ca requirement is greater than that for P. Sulphur reactions in soil are very similar to N reaction, which are dominated by organic or microbial fractions in the soil. In contrast, Ca^{2+} and Mg^{2+} are associated with the soil clay fraction and behave similarly to K^+. Supapron *et al.,* (2007) reported that zeolite showed slow release fertilizer for calcium and magnesium. They suggested that, zeolite improved calcium and magnesium in soil. Fansuri *et al.,* (2008) reported that zeolite is able to freely exchange nutrient ions such as calcium and magnesium.

Li and Zhang (2010) studied the feasibility of using surfactant-modified zeolite (SMZ) as fertilizer additives to control sulfate release, was tested in batch and column leaching experiments which indicated that SMZ could be a good carrier for sulfate. Thus, leaching of sulfate can be greatly reduced and slow release of sulfate can be achieved if SMZ is used as fertilizer additives. Secondary nutrients are less studied as the extent of deficiencies is very meager or found in isolated products.

Micronutrients nano-fertilizer

Micronutrients are those elements that are essential for plant growth, but are required in much smaller amounts than those of N, P and K. The micronutrients are boron (B), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), zinc (Zn) and chloride (Cl). Eventhough micronutrients are required in minute quantities, they are essential for healthy plant growth and profitable crop production. Micronutrient deficiency is widespread in many Asian countries due to the calcareous nature of soils, high pH, low organic matter, salt stress, continuous drought, high bicarbonate content in irrigation water and imbalanced application of NPK fertilizers. Some of the adverse effects of micronutrient deficiency-induced stress in plants include low crop yield and quality, imperfect plant morphological structure (such as fewer xylem vessels of small size), widespread infestation of various diseases and pests, low activation of phytosiderophores, and lower fertilizer use efficiency (Malakouti, 2008). Sheta *et al.,* (2003) undertaken research to characterize the ability of five natural zeolites and bentonite minerals to adsorb and release zinc and iron. The potential for sorption of these ions were evaluated by applying the Langmuir and Freundlich equations. The results suggest that natural zeolites, particularly chabazite and bentonite minerals, have a high potential for Zn and Fe sorption with a high capacity for slow release fertilizers.

Broos *et al.,* (2007) reported that slow release of Zn is attributed to the sparingly solubility of minerals and sequestration effect of exchange, thereby releasing trace nutrients to zeolite exchange sites where they are more readily available for uptake by plants. Schmidt and Szakal (2007) were carried out experiments on foliar treatments with ion-exchanged zeolite on winter wheat for three years. As a result of zinc zeolite the increase of raw protein was more favourable than that of copper-zeolite treatment. Eberl (2008) reported that zeolite in soil can aid in the release of some trace nutrients and in their uptake in plants. The release of cationic micronutrients has been enhanced by the presence of zeolite in neutral soil. The concentration of Cu and Mn in Sudangrass (in mg/kg) was significantly related to the zeolite/P-rock in experimental systems that used two different NH_4 saturated zeolites, two different soils and two different forms of P-rock. Lin and Xing (2008) reported that zinc oxide nanoparticles were shown to enter the root tissue of ryegrass and improved the germination. Melendi *et al.,* (2008) conducted an elegant experiment and showed a visualization of carbon coated nanotubes in plant cells using pumpkin plants as the model crop. This is one of the classic studies that can be used as a guiding tool to develop smart nutrient delivery system for plants. Pandey *et al.,* (2010) reported that Zinc rich ZnO NPs increased the level of IAA in roots (sprouts), which in turn indicate the increase in the growth rate of plants as zinc is an essential nutrients for plants.

Boron is an essential micronutrient for plants, but can be toxic to organisms when accumulated in high concentrations. The adsorption of boron by clays, soils and other minerals has been extensively studied by many investigators (Sabarudin *et al.,* (2005); Ferreira (2006); Turek *et al.,* (2007); Cengeloglu *et al.,* (2007); Bouguerra *et al.,* (2008); Bryjak (2008); Ozturk (2008); Kose and Ozturk (2008); Kavak (2009)).

Molybdenum is an essential component of plant enzyme nitrate reductase. Additionally, Mo is important element in nitrogenase in Nitrogen fixing bacteria essential for legume crops. Rana and Viswanathan (1998) studied Mo incorporation in MCM-41 type zeolite and IR, FT-Raman and UV-VIS DR spectroscopic analyses gave the evidences for the incorporation of Mo in the framework of MCM-41.

Nano-composites

Nanocomposites are expected to play an important role in developing new materials exhibiting unusual properties. Barbarick and others (1990) demonstrated that mixing NH_4^- saturated clinoptilolite with phosphate rock provided simultaneous slow-release of both P and N. Allen (1991) reported that N, P, K and Ca were slowly released from mixtures of natural phosphate rocks and NH^{4+} and K-saturated clinoptilolite. Desborough (1996) concluded that CRR (clinoptilolite-rich rocks) showed potential for increasing the cation-exchange capability of the soil by temporarily extracting NH_4^+ when highly soluble NH_4^+ rich fertilizers are applied to crop fields. Dwairi (1998) verified that, zeolite when mixed with nitrogen, phosphorus and potassium compounds, it enhanced the action of such compounds as slow release fertilizers, both in horticultural and extensive crops. Ming and Allen (2001) summarized about the increasing fertilizer use efficiency by adding natural zeolites to soluble N-fertilizer such as ammonium nitrate and urea as well as K fertilizers.

Nanocomposite films consisting of inorganic nanolayers of layered silicate, such as montmorillonite (MMT) clay and organic polymers, have recently evoked intense research interest in the material and polymer science areas (Alexandre *et al.,* (2000); Sinha *et al.,* (2003); Sinha *et al.,* (2005)). Bagdasarov *et al.,* (2004) reported that zeolite is an excellent carrier, stabilizer and regulator of mineral fertilizers, themselves being a source of certain nutrients. Polat *et al.,* (2004) suggested that zeolite is used as carrier of N and K fertilizers, they increase their efficacy by decreasing application rates for equal yields to be achieved.

Zhang *et al.,* (2006) reported that results of measurements on nutrients of wheat plant showed that in treatments with the five kinds of bulk blended slow-release fertilizers, the contents of NPK absorbed by wheat in shooting period were higher than that of chemical fertilizer of equal amount of NPK, which was consistent with the rule of nutrients demanded by wheat. Liu *et al.,* (2006) studied the nitrogen slow release behaviour of the super absorbent nitrogen fertilizer (SSNF) in water and water retention capacity of the soil with SSNF. They reported that the surface cross linked product not only had good slow release property but also excellent soil moisture preservation capacity, which could effectively improve the utilization of fertilizer and water resources simultaneously. They also obtained that the SSNF could find an application in agriculture and horticulture, especially in drought prone areas where the availability of water is insufficient.

Qiang *et al.,* (2008) reported that wheat grain yield and protein contents were slightly improved and soluble sugar content decreased by slow/controlled release fertilizer coated and felted by nano-materials compared with NPK chemical fertilizer. It was effective to use slow/controlled release fertilizer coated by nano-materials to improve wheat yield and quality. Composites of nanomaterials and conventional materials by embedding nanotechnology in materials, researchers create new materials with enhanced physical or chemical properties.

Nano-composites on crop growth

Nanotechnology offers an important role in improving the existing crop management techniques. Hence nanoparticulate formulations have great potential as novel tool for crop growth. Zeolite is one of the key factors which can be effectively used for enhancing the nutrient uptake thus crop growth. Flanigen and Mumpton, (1981) and Mumpton (1981) reported that the zeolites added to fertilizers help to retain nutrients and, therefore, improving the long term soil quality by enhancing its absorption ability. It concerns the most important plant nutrients such as nitrogen (N) and potassium (K), and also calcium, magnesium and microelements. Zeolite can retain these nutrients in the root zone to be used by plants when required. Consequently this leads to the more efficient use of N and K fertilizers by reducing their rates for the same yield, by prolonging their activity or finally by producing higher yields. Large losses of fertilizers which move out of the root zone (leaching) often happen in sandy soils, which lose their capability to retain high nutrient levels.

Burriesci *et al.,* (1984) reported that zeolite combined with normal fertilizer greatly enhanced growth and yield of peach and grape trees. Valente *et al.,* (1986) reported that the zeolite incorporated with chemical fertilizer gave positive effect for tomato growth. Pessarakli (1994) reported that usually the higher Na+ content in saline soil disturbs the nutritional balance and upsets the osmotic regulations of plant tissues. Zeolite provides an alternative Ca_2^+cation to the soil-plant system reducing the ratio of Na^+/Ca^{2+}. The provision of Ca_2^+ from zeolite in the root media would prevent an accumulation of toxic Na+ ion in plants.

Song and Fujiyama (1996) described the ameliorative effects of Ca-type zeolite on rice and tomato growth to decreases in Na^+ concentration in shoots as well as Na^+/Ca^{2+} and Na^+/K^+ ratios of shoots and roots. Mumpton (1999) reported that the zeolites are mixed with chemical fertilizers, they help to retain nutrients in root zone and, hence, improving the long term soil quality by enhancing nutrient absorption. Steinberg *et al.,* (2000) conducted a side-by-side comparison of wheat growth and yield in a hydroponic system and a zeoponic system in a controlled environment chamber.

Krutilina *et al.,* (2000) indicated that zeolite improved biomass production and photosynthetic rate in maize and barley. Miller (2000) found that zeolite can work as soil amendment and has potential to influence the soil water content. Butorac *et al.,* (2002) reported that the zeolites can be successfully used in cultivating different crops such as cereals, forage crops, vegetables, fruit crops and vine due to their exceptionally high ion-exchange capacity. He *et al.,* (2002) achieved increase in N use efficiency, N uptake, dry matter yield and reductions of losses by ammonia volatilization.

Rehakova *et al.,* (2004) reported that plants grown in zeolite amended contaminated soil had higher growth parameters. Polat *et al.,* (2004) reported that the mineral clinoptilolite (zeolite) enhanced the efficacy of applied fertilizers, ensuring better vegetative growth of crops and hence higher yields. Ayan *et al.,* (2005) reported increased cation exchange ability, water retention and plant nutrients following zeolite application. Andronikashvili *et al.,* (2008) suggested that in most of the researches, representing the early period, an increase in the yield of various agricultural plants under the influence of zeolites was caused by conditioning (structuring) the soil; improvement of its physico-chemical properties (creating favorable air and water regime close to the plant root system);

increased cation-exchange capacity of soil; regular and rational plant nutrition.

Khodakovskaya *et al.,* (2009) demonstrated that carbon nano tubes (CNTs) exposed seeds germinated up to two times faster than control seeds and the seedlings weighed more than twice as much as the untreated plants. Further, they demonstrated that CNTs could effectively penetrate seed coat, thereby influencing the seed germination and plant growth.

Srinivasan and Saraswathi (2010) reported that the seeds incubated in CNTs for two days possessed a moisture content of 57.6 % compared to the value of 38.9 % for the control. This is due to generation of new pores generated during penetration of seed coat by CNTs which aided better water permeation. Another possible cause reason could be the efficient gating of water channels by the CNTs in the seed coat. They also reported that, CNTs induces increased biomass, rapid germination and growth rates will in turn yield agriculture production in a short duration.

Ahmed *et al.,* (2010) conducted experiment to investigate if the use of inorganic fertilizers together with zeolite will improve nitrogen (N), phosphorus (P) and potassium (K) uptake and efficiency in maize *(Zea mays)* cultivation on Nyalau series. The result showed that the use of inorganic fertilizers mixed with zeolite remarkably increased N, P and K uptake, and their use efficiency in leaves, stem and roots. The use of zeolite could be beneficial with respect to nutrient retention in soil and their use efficiency.

Overall, the literature served as a strong database to support that nano fertilizer and zeolite can effectively used in agriculture. Nanotechnology is an integral part of any nation's future. Research in nanotechnology can do a lot to benefit society through applications in agriculture and food systems (Sugunan and Dutta, 2004) Introduction of any new technology always has an ethical responsibility associated with it to be apprehensive to the unforeseen risks that may come along with the tremendous positive potential. Public awareness about the advantages and challenges of nanotechnology will lead to better acceptance of this emerging technology. Nanotechnology applications in agriculture and food systems is still at the nascent stage and a lot more applications can be expected in the years to come.

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