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Nano-nitrogen Formulations for Enhancing Use Efficiency: A Review

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Abstract: Commercial crop production has increased nitrogenous fertilizer consumption by two to three times. However, temporal changes and yield stagnation of major crops over three decades urge us to revisit the fertilizer use efficiency through nano-techniques with specific reference to nitrogen fertilizers. Although nanofertilizer technology is quite innovative, literature available in this field is very limited. In this review, literature pertaining to the losses of nitrogen (N) in agro-ecosystems, slow-release N fertilizers, nanofertilizer N formulations with synthesis, characterization and their application in agriculture and associated effects are elaborated. This review serves as a strong database to understand and gain insights into innovative nanotechnologies infusion with N fertilizers research and their benefits in agriculture. Nano fertilizers are capable of enhancing crop yield as well as nitrogen use efficiency (NUE) of crops and may be considered as one of the potential alternatives for soil fertility and plant nutrition for agricultural sustainability.

Keywords: *Nanotechnology, nano fertilizer, nitrogen use efficiency, smart delivery systems, fabrication*

Introduction

Nitrogen use efficiency (NUE) by crops continues to remain below the range of 30-35% with the major portion *i.e.,* 65-70% being lost to the environment through leaching, volatilization and denitrification. Nitrogen is primarily present in two forms (NO_3^--N and NH_4^+-N), of which NO_3^--N is highly mobile and vulnerable to leaching. The close relationship between leaching and soil moisture content was shown by Singh *et al.* (2004), who reported nitrate leaching to the tune of 36.4% under wetland conditions. Split application of N not only reduced the leaching loss of N but also enhanced rice yield and overall NUE (Randall and Schmitt 1998). Nakamura *et al.* (2004) also observed a drastic reduction in leaching of N from 60 to 40% in Andosols with increased NUE.

Nitrogen volatilization gaseous loss of N often associated with pH and temperature. He *et al.* (2002) observed that ammonia volatilization (AV) was minimum at pH 3.5 and increased rapidly with pH up to 8.5 on Alfisols. The potential maximum AV increased by 2 and 3-fold with an increase in the incubation temperature from 5 to 25 °C and from 25-45°C respectively. The enhanced AV at 45°C compared with that at 25°C was related to the inhibition of nitrification at the high temperature, with a concomitant increase in

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the availability of NH_4 for NH_3 volatilization. Application of green manure with urea effectively reduced soil pH and reduced ammonia loss from urea in the Vertisols and the Inceptisols but not in the Alfisols. The highest ammonia volatilization loss has occurred between two to four days after fertilizer application in the Vertisols and the Alfisols, and between four to six days in the Inceptisols. Denitrification is yet another mechanism by which N is lost from the soil to the atmosphere. Submerged soils with anaerobic conditions favour denitrification processes. Soil microbes under these conditions use nitrates as their source of N and emit gaseous N. Moiser *et al.* (1998) reported that more than 70% of the N_2O emission from fertilized agriculture through microbial denitrification processes occurs under anaerobic conditions. Slow- or controlled-release N fertilizers have therefore emerged as viable alternatives to minimize N losses from soils.

Slow release N fertilizers

Nitrogen, being highly mobile in soil systems is prone to losses under both submerged and aerobic conditions, thereby leading to poor NUE. Customized slow-release N fertilizers have been identified as promising technologies in this regard. These fertilizers are divided into three broad categories namely, natural organic fertilizers, chemically reacted slow-release products and physical coating around the urea. Slow-release fertilizers (SRF) release their nutrient contents gradually matching the nutrient requirements of crops. A number of slow release fertilizers have been developed in the past few decades. Materials used for fertilizer coatings include inorganic (copper, boric acid, sulfur, phosphates, and silicates) and organic (polyethene, poly vinyl chloride, and polylactic acid) (Shaviv 2001; Guertal 2009). Recently, polymers referred to as super absorbents are being used to retain and release N slowly. These are three-dimensional cross-linked hydrophilic polymers capable of swelling and retaining huge volumes of water. Field application of super absorbents has shown encouraging results through reduction in irrigation water consumption, lower death rate of plants, improved fertilizer retention in soil, and increased plant growth rate. However, the feasibility of adoption of this technology has been questioned as most of these super absorbents are based on pure poly (sodium acrylate) (Barati *et al.* 2010) and they are too expensive. There have been many reports on introducing inorganic clays, such as kaolinite, bentonite, montmorillonite, attapulgite and mica (Lin *et al.* 2001; Zhang *et al.* 2006; Bulut *et al.* 2009; Kabiri *et al.* 2010). Infusion of these clays reduced production costs.

Urea-coated with mustard cake retarded urea hydrolysis and consequently reduced ammonia volatilization loss, whereas urea-coated neem cake accelerated the ammonia loss from urea (Purakayastha *et al.* 1997). Patra *et al.* (2001) reported that dementholated essential oil (DMO- *Mentha spicata*) treated urea produced 30-50% higher yield levels in wheat, rice and mint crops than uncoated urea. Jagadeeswaran *et al.* (2005) indicated that nutrient use efficiencies *viz.*, agronomic efficiency, apparent recovery and partial factor productivity were significantly enhanced by the application of tablet forms of NPK sources. A one percent increase in NUE for cereal production brought about by slow-release nitrogen fertilizer worldwide would lead to a $ 235- 250 million saving in cost of N fertilizer. Gioacchini *et al.* (2006) reported that the slow-release fertilizers can be useful tools in calibrating the availability of fertilizer-N to plant demand and in reducing the risk of NO_3^- loss by leaching. However, the efficiency of the fertilizer is strongly dependent on its chemical characteristics and on the chemical-physical characteristics of the soil that receives the fertilizer. If the slow-release fertilizer has a release pattern that matches crop needs, N uptake by the growing crop may become more efficient.

Additionally, if slow-release fertilizers can be applied as a pre-plant application, production costs could be lessened, eliminating the need for multiple applications of soluble N fertilizer (Guertal 2009). Zhang *et al.* (2010) reported that although coated-urea reduced ammonia volatilization during corn cropping season, grain yield and the N uptake of the following wheat crop were significantly reduced. This indicated that use of coated urea whose N release rate was correlated with temperature was not suitable to the winter wheat cropping in the region. Barbieri *et al.* (2010) reported that combined application of urea (60 and 120 kg ha^{-1}), maleic-itaconic acid copolymer (NSN) and orthophosphoric N-(n-butil) triamide (nBTPT) slow down the rate of N release and thereby diminish its loss. Volatilization losses were extended by 7 and 18 days in the first and second year, respectively. Nascimento *et al.* (2013) observed reduced ammonia volatilization when urea, coated with boric acid and sulphur was applied @ 120 kg ha^{-1} N to sugarcane. Both the compounds acidify the soil immediately and in a gradual manner, respectively and retard ammonia volatilization losses. Stafanato *et al.* (2013) reported that incorporation of boron and copper into urea can reduce these effects by inhibiting urease activity. Fertilization of 200 kg ha^{-1} N and inclusion of copper and boron in the process of pelletizing urea reduced losses by up to 54% as compared to conventional urea. Kundu *et al.* (2013) developed a slow-release fertilizer to enhance its N use efficiency. Urea was coated with pine oleoresin exudates which acts as a physical barrier around the urea granules thereby reducing the release of N. The volatilization loss of pine oleoresin-coated urea from a Vertisol decreased from 17% to 10% after 240 h. Faria *et al.* (2013) reported that urea coated with boric acid and copper sulphate under volatilisation-favourable conditions resulted in a reduction of the NH_4^+-N volatilization loss when compared to the other urea application treatments. Despite slow-release fertilizers being in use for the past four decades, the adoption of this technology is well below 10% due to cost, non-availability of quality input and other practical difficulties. In order to address the issues, emerging technologies such as nanotechnology is being exploited to improve the nutrient use efficiencies of crops.

Nanofertilizers

Nanofertilizers are nutrient carriers; their carrier material is in nano-dimension. The “nano” refers to the dimension of 10^{-9} m (one-billionth of a metre or one-millionth of an mm). For better understanding, we can say that each nano-particle is made of 10 H atoms and 10 nano-particles equates to a protein molecule and 10 protein molecules make one virus. In other words, each virus particle may be equally divided into 100 nanoparticles. Any substance that measures between 1 and 100 nm is referred to as nano-material. The processes or products evolved through nano-technological approaches are quite precise to deliver nutrient input without any losses *vis-à-vis* environmental safety. Soil scientists are quite aware of the importance of clays in determining soil fertility. The basic principle used in the synthesis of nanofertilizers is that a reduction in size of a material results in the exponential rise in its adsorptive surface area for facilitating nutrient exchange. For instance, one gram of montmorillonite clay has a specific surface area of 46 m^{2}g^{-1} (Macht *et al.* 2011) while the same clay has a specific surface area of 750 m^2 g^{-1} (Sharmila Rahale 2010) when it is reduced to a nano-dimension. Such a phenomenal increase in surface area facilitates greater retention and release of nutrients. In order to synthesize nano fertilizers, two substrates such as zeolite and biochar are being widely exploited (Manikandan and Subramanian 2013; 2013a; 2014; 2015).

Raw materials

Zeolites are naturally occurring crystalline hydrous aluminosilicates widely prevalent in sedimentary rocks. (Ramesh *et al.* 2010). They are three-dimensional, open, tectosilicates exhibiting a balance between the cations in electrostatic charge of the framework of silica and alumina tetrahedra and containing water. Zeolite pores and voids (30-40%); dimensions, shape, and linkage are the key characteristics. The internal surface area of these channels is reported to reach as much as several hundred square metres per gram of zeolite, making it an extremely effective ion exchange. Zeolites are capable of hydrating and dehydrating without altering the crystal structure. Other physiochemical properties are: high void volume (~ 50%), low density (2.1–2.2 g cm^{-3}), and high cation exchange capacity (CEC) of 150–250 $cmol^{+}kg^{-1}$. As soil application of zeolites increases their cation exchange capacity, and thereby the nutrient retention capacity, they are the preferred choice for the development of nanofertilizers. Isildar (1999) reported that application rate of higher doses of zeolite decreased nitrification, which varied with moisture regimes. Ebrel (2002) reported that zeolite can free the slowly diffusing nutrient ions such as phosphates and increase the uptake by plants and may improve water-retention. Njoroge and Mwamachi (2004) reported that zeolite has a high potential for ammonia removal with the sorption capacity being about 4 m mol (NH_4^+) per 100 g of sorbent. It has a very rapid reaction with ammonia with half the amount of ammonium ions being sorbed on immediate contact. Ammonia uptake was favoured by low sorbate concentration, the small particle size of sorbent, high temperature, and an alkaline medium. The equilibrium data fitted the Langmuir sorption model, a possible indication of monolayer coverage of ammonium ions on the surface of the particle. This literature supports a hypothesis that zeolites can be used as an effective substrate to retain and release nutrient ions with suitable surface modification to partially seal the negative charge of the zeolite.

Biochar is produced by heating the biomasses such as agricultural crop residues, wood, waste, *etc.* in the absence of oxygen (pyrolysis), Slow pyrolysis is currently seen as the preferred technology of biochar production as it maximizes biochar yield overproduction of bioenergy (Lehmann and Joseph 2009; Sohi *et al.* 2010). One of the unique properties of the biochar is their high specific surface area (SSA). The biochar SSA increased with increasing charring temperatures (300–600°C). As biochar alters N dynamics in soil, it can be expected to influence gaseous losses of N. Loss of N as N_2O provides a small, but environmentally significant route for N loss from soil to the atmosphere. Nitrous oxide is produced through a range of mechanisms in soil including nitrification, nitrifier denitrification, and denitrification (Baggs 2008), and it has been suggested that biochar can play a significant role in altering these processes (Van Zwieten *et al.* 2009; Singh *et al.* 2010). Incorporation of biochar into soil has been reported to either stimulate or suppress depending on initial soil moisture content (Rondon *et al.* 2007; Yanai *et al.* 2007) or make no change in N_2O emissions (Clough and Condron 2010). Further studies onbiochar application on N dynamics in soils are warranted (Lehmann 2007a; Clough and Condron 2010). The wide range of effects on nutrient dynamics from biochar application to soil is still poorly understood, as effects can be highly soil and biochar specific. Given the ability of biochar to immobilize a wide range of organic and inorganic chemicals, it is conceivable that by applying biochar to soil could influence the plant uptake of a range of organic compounds or micronutrients and their unbalanced uptake may affect even the quality of the produce. This aspect has not received any attention in the literature so far.

Synthesis of nanofertilizers

Top-down and bottom-up approaches have efficiently synthesised the nanoformulations.

Physical synthesis (Ball milling)

High-Energy Ball Mill (HEBM) processing has been employed for the past three decades to synthesize size reduced materials with nano-dimension (Table 1). It is an important technique for the production of nano-sized materials with the added advantage of extended solid solubility. As a non-equilibrium processing method, it can be utilized to produce large quantities of materials at a relatively low cost. (Karthikeyan *et al.* 2019) Nano-zeolite were physically synthesised through HEBM of topdown approach (Manikandan *et al.* 2013).

Table 1. Summary of variable parameters used in HEBM for NP synthesis

S.No.	Materials	Ball: Powder (w/w)	Time(h)	Size reduction	Reference
1.	Zeolites A, X and synthetic mordenite	10:1	2-3	Nanosized quasi crystal	Cleo *et al.* (2001)
2.	$Mg_{0.7}$ Zn $_{0.3}$ Fe_2O_4 (MZF)	-	12-36	58-1200 nm	Aurawan and Panuthat (2006)
3	Titanium or Hydroxyl apatite	20:40	0.15-1	Amorphous	Tsipas *et al.* (2003)
4	Sm_2Co_{17}	10:1	20	23 nm	Wang *et al.* (2007)
5	Natural Clinoptilolite	0.1-02:1	10-20	100 nm - 30 μm	Charkhi *et al.* (2010)
6	Quarterly, binary	20:1	5- 60	Amorphous	Sharbati and Kashani-Bozorg (2012)
7	Biochar and zeolite	10:1	1-6	260 nm and 203 nm	Manikandan *et al.* (2013)

Nano-biochar

Chen *et al.* (1999) produced nanoporous disordered crystalline nanoporous carbon after ball milling after 50h of graphite at ambient temperature and phase transformed from hexagonal (10h) to turbostratic (15h) to amorphous nanocrystalline (50h). Liu *et al*. (2003) obtained short multi-wall carbon nanotubes with changed morphology and structure of open tips by mechanical ball milling and hydrogen adsorption increased due to the formation of defects and increased surface area. Kukovecz *et al.* (2005) explained the morphological changes like cutting effect on multiwall carbon nanotubes during long time ball milling in a vibrating mill. The amount of amorphous carbon and non-nanotube nanoparticles increased steadily with the grinding time. Peterson *et al.* (2012) reported that the salt assisted dry method using planetary ball milling increased the surface area of biochar produced from corn stover with a 50:1 ratio of mass ratio than wet milling biochar. Branham *et al.* (2013) produced nano-ferrite and composites using tetracycline-HCl with glycol thermal method mediated with HEBM up to 30 hours. At 235°C after 5h milling the nano ferrites and composites formed and which is stable up to 500°C. During the milling period, solid state reactions take place in the initial powder mixture by repeated mechanical deformations caused by ball collisions with powder. The ball milling (Top-down approach) process has been successfully applied to the physical synthesis of nano inorganics such as alloys and materials. In order to produce uniform size, shape and structure, the substrate chemical synthesis is routed with bottom-up approach. Overall, the reported literature suggests that physical synthesis is relatively easier to produce nano-materials but the heterogeneity is very high besides agglomeration caused by the clustering of particles. Therefore, physical synthesis is performed in conjunction with the dopping of nano-particles with suitable surfactant molecules.

Chemical synthesis

Nucleation and nanomaterial growth generally involves a number of steps taking place in the liquid phase. Chemical synthesis is the bottom-up approach where chemical reactions facilitate the self-assembling of atoms resulting in the formation of nanoparticles.

Hydrothermal crystallization- zeolite

Nano-zeolites have been synthesized by various researchers Through hydrothermal crystallization. Mintova *et al.* (1999) showed the formation and growth of crystal nuclei of zeolite A from clear solutions at room temperature with low-dose. Single zeolite A crystals nucleated in amorphous gel particles of 40 to 80 nm within 3 days at room temperature. The resulting nanoscale single crystals (10 to 30 nm) were embedded in the amorphous gel particles. Kuzniatsova *et al.* (2007) reported that zeolite membranes are typically grown from thin coatings of sub-m size zeolite particles on porous supports. Huang *et al*. (2010) found that hierarchical porous particles aggregated from primary zeolite NaY nanocrystals were hydrothermally synthesized *via* a three-stage temperature control strategy, without adding any organic additives. The results show that the zeolite aggregate particles with sizes of 190–600 nm are composed of highly crystalline zeolite NaY nanoparticles in the size range of 20–80 nm. The particle sizes of hierarchical porous aggregates can be readily tuned by varying the alkalinity of the zeolite precursor gel without notably changing the sizes of the primary zeolite nanocrystals. Yue *et al.* (2011) reported that hollow zeolite spheres of silicalite-1 with mono-layered, homogeneous and dense zeolitic shells have been synthesized using oil/water emulsions as templates. Iwakai *et al.* (2011) reported that preparation of nano-crystalline (100-500 nm) MFI zeolites (Silicalite-1 and ZSM-5) was carried out by hydrothermal synthesis in a water/surfactant/organic solvent using fumed silica and aluminium sulphate as the Si and Al source. The crystalline and spherical shape of zeolite was observed on hydrothermal crystallization. In contrast, in the samples prepared by the emulsion method at 12 h, nanocrystals with sizes of approximately 30–40 nm could be observed, and the sizes gradually increased with increasing hydrothermal times. Kazemimoghadam and Mohammadi (2011) synthesised zeolite hydroxyl sodalite (HS) by hydrothermal method using the natural kaolin. In the first step, kaolin has been calcined at 700°C to the metakaolinite phase. As a second step, the zeolitisation experiments have been carried out under hydrothermal conditions. The metakaolinite obtained has been reacted with NaOH solutions in autoclaves at 100°C. The crystal species were characterized by X-ray diffraction (XRD) patterns and the morphology of the supports subjected to crystallization was characterized by scanning electron microscopy (SEM). Performance of the hydrophilic nano zeolite membranes during the separation of water/ethanol mixtures was evaluated. These membranes showed very high selectivity of water for water/ethanol mixtures.

Hydrothermal Carbonization-Biochar

Hydrothermal carbonization converts the dry-biomass at moderate conditions into carbonaceous nanostructures, here, mesoporous and nanoporous network structures (Titirici *et al.* 2007a). A key feature is not only the occurrence of carbonization in itself but also the appearance as useful nanostructures with appropriate surface chemistry. Marta and Antonio (2009) result showed that a carbon-rich solid product made up of uniform spherical micrometre-sized particles of diameter 0.4–6 mm range could be synthesized by modifying the reaction conditions.

Guiotoku *et al*. (2009) reported that lingo-cellulosic samples subjected to microwave-assisted hydrothermal carbonization (MAHC) yielded carbon-enriched material 50% higher than raw materials SEM micrographs detected no morphological changes in pine sawdust. Results of their study showed that microwave-assisted hydrothermal carbonization is an innovative approach to obtain carbonized lingo-cellulosic materials. Sandeep kumar (2010) reported that the pyrolysis and hydrothermal carbonization (HTC) are the two main processes for the production of biochar. The HTC is an environment friendly and promising process that uses water as solvent. Besides being simple process, HTC has a number of other practical advantages. The HTC process does not require dry biomass and also the final product can be easily filtered from the reaction solution.

Heilmann *et al.* (2010) reported that HTC is a chemical process that may be well-suited to high-moisture feedstocks, such as animal manures and algae. Schneider *et al.* (2011) synthesized biochar through hydrothermal carbonization method, which was characterised using a scanning electron microscope. The results clearly indicated that the resultant product of chemical synthesis is quite stable and mass production is possible. A continuous chemical reaction may lead to crystal growth and change the unique property of nano-materials. Chemical synthesis is quite expensive and involves lots of fine chemicals and associated ill effects on the environment.

Surface modification

A variety of surfactants can be used for alteration of zeolite surface chemistry. Cationic surfactant modification of zeolites enables them to sorb neutral molecules such as benzene and others while retaining their ability to sorb heavy metal cations. While sorption of target anions is reduced in the presence of competing anionic species, the surface modified zeolite (SMZ) is selective for sorption of oxyanions. The surfactant hexa-decyl trimethyl ammonium (HDTMA) is widely preferred to use as an agent to partially or fully modify the surface charge due to its ready availability and low cost. Kang and Egashira (1997) modified the three different grades of Korean natural zeolite with molar concentrations of sodium hydroxide in order to increase the adsorption capacity of ammonium and cation exchange capacity. Surface modified zeolite used as slow release nitrogen and sulphur fertilizer carrier to hold and reduce leaching of nitrate (Li 2003). Bansiwal *et al.* (2006) reported that zeolite-A, by using HDTMA-Bromide, a cationic surfactant, increased its capacity to retain anion, namely, phosphate (PO_4^{3-}) in order to develop carrier in slow release fertilizer.

Kumar *et al.* (2007) developed surface-modified zeolite materials from commercial zeolites and flyash-based zeolites by treating them with surface modifiers like HDTMA-Bromide and tetra methyl ammonium bromide. The adsorbent has been evaluated for removal of arsenic and chromate anions. Bhardwaj and Tomar (2011) reported that zeolites, after surfactant treatment with HDTMA and Dioctadecyl dimethyl ammonium (ADOD) can be utilized as slow release fertilizer and efficient sorbent for these agrochemicals, and the extent of sorption increases with the increasing surfactant loadings. The two synthesized zeolites synthesized zeolite clinoptilonite (SZC) and synthesized zeolite montmorillonite (SZM) have shown the highest sorption capacity after modification with surfactant and indicate their possible use as controlled release fertilizers in India. Surface modification is a widely recommended practice to alter the surface charge and characteristics of the clay or other carriers to modify the adsorption or desorption behaviour.

Sorption of N froms

Diffusion of nitrogen (N) on void pores determines the sorption capacity of microporous inorganic solid adsorbents. Zeolite and biochar formulations have been found to be suitable for N sorption study (Manikandan and Subramanian 2017), as evident from table 2.

Zeolite sorption

Tarkalson and Ippolito (2010) observed that zeolite mineral clinoptilolite (CL) application rate influenced the quantity of NO_3-N and NH_4-N in the leachate and soil, and that band application of CL and N are better as compared to mixing of CL and N possibly due of decreased rates of microbial immobilization, nitrification, and denitrification. Tang *et al.* (2010) found that the adsorption amount significantly depends on pH, the adsorption amount at pH 8.0 is maximum. Freundlich equation is better than Langmuir equation in describing the behaviour of NH_3-N adsorption on natural zeolite. Penn *et al.* (2010) reported that flow-through cells possessing contact times >100s displayed greater NH_4^+ sorption than batch systems, suggesting that maintaining high NH_4^+ concentration in solution, removal of exchange products. Wei *et al.* (2010) reported that zeolite adsorbed NH_4^+-N and simultaneously enhanced nitrification and de-nitrification (SND). Bernardi *et al.* (2010) reported reduction of losses by volatilization with the addition of zeolites to the urea fertilizer. Hoseini *et al.* (2010) reported that natural zeolite has a high potential for NH_4 adsorption and removal from wastewaters. Zhao *et al.* (2011a) showed that under the same input condition of water quality and power, zeolite performed better in terms of ammonia nitrogen absorption as compared to ceramsite, coarse sand, shale and gravel in constructed wetland.

Halim *et al.* (2012) fabricated a new composite adsorbent material combining excellent properties of activated carbon, zeolite, and low cost adsorbents, *viz* limestone and rice husk ash. The adsorption capacity for regenerated media to ammonia was observed to be 149%. Chen *et al.* (2012a) investigated the simultaneous sequestration of ammonium (N) and phosphate (P) from anaerobically digested swine wastewater (ADSW) using nano-zeolites synthesized from fly ash (ZFA). The nanometre-scale crystalline structures containing plentiful of zeolite-NaP1 coating on ZFA particle increased specific surface area and cation exchange capacity by 40 and 104 times, compared to raw fly ash. Nitrogen and P removal efficiencies were maximum across a range of ZFA doses (from 0.25 to 8 g/100 ml). In constructed wetlands, vertical flow-horizontal subsurface flow (VFHSF) of nitrogen reduced the seasonal fluctuation and enhanced the efficiency (Wen 2012). Tilaki *et al.* (2013) proved that ion exchange using zeolite clinoptilolite is a low cost method that could result in complete removal of ammonium from water.

Table 2. Investigations with NH_4^+-Nsorption with various materials

S.No.	**Source**	**N sorption rate (mg g^{-1})**	**References**
1.	Carbon-zeolite composite	22.99	Halim *et al.* (2009)
2.	Clinoptilolite	3.79	Zabochnicka and Malinska (2010)
3.	NaA and NaX synthetic zeolite	94.2 and 161.3	Moussavi *et al.* (2013)
4.	Zeolite and NaCl modified zeolite	9.03 and 21.46	Zhang *et al.* (2013)
5.	Greenwaste biochar	909 mg kg^{-1}	Eldridge *et al.* (2010)

Biochar sorption

Asada *et al.* (2006) found that amount of ammonia adsorption in the aqueous solution increased as the carbonization temperature of the bamboo charcoal decreased and that of activated carbon was the highest. Eldridge *et al.* (2010) reported that the maximum NH_4^+-N sorption capacity for green waste biochar is 909 mg kg^{-1}, equating approximately to a maximum increase in soil NH_4^+-N storage up to 1 kg for each tonne of biochar applied to the soil. Over 90% of the sorbed NH_4^+-N was recovered from the biochar by extraction with 2*M* KCl indicating that the sorbed NH_4^+-N was exchangeable and plant available. This characteristic of the biochar would account for a significant proportion of the improvements in N fertiliser use efficiency noted in several pot trials. Ding *et al.* (2010) reported that biochar could be used as a potential nutrient-retaining additive in order to increase the utilization efficiency of chemical fertilizers.

Addition of 0.5% biochar to the surface soil layer retarded the downward transport of NH_4^+-N in the 70-day experiment, and reduced overall cumulative losses of NH_4^+-N *via* leaching at 20 cm by 15.2%. Conversely, Dempster *et al.* (2010) concluded that the addition of biochar to soil decreased the amount of net inorganic nitrogen, probably due to its sorption. Hollister (2011) observed increased NH_4^+sorption on rinsed Corn, Oak-BC pyrolysed at 200°C and decreased at 550°C. However, nitrate sorption was not observed in any of the rinsed or non-rinsed chars. Miller *et al.* (2011) observed NO_3^- localisation within the rhizosphere of biochar-amended soils. This has implications for NO_3^- loss and improved nitrogen use efficiency. You and Kang (2012), through their short term incubation experiments argued that application of biochar increases N availability and microbial activity, and also stimulated N mineralization similar to other organic soil amendments. Biochar is the potential substrate for sorption and desorption of ammonia and nitrate (0.1 – 4.5 %). According to Spokas *et al.* (2012), ammonia is adsorbed as amide and amine form on the surface of biochar and correlate with surface acidity. Yao *et al.* (2012) showed that the effect of biochar on the leaching of agricultural nutrients in soils is not uniform and varies by biochar and nutrient type.

Biochars made from Brazilian pepperwood and peanut hull at 600°C (PH600 and BP600, respectively) were used in a sandy soil column leaching experiment to assess their ability to hold nutrients. The BP600 biochar effectively reduced the total amount of nitrate (34.0%), ammonium (34.7%) and phosphate (20.6%) in the leachates relative to the soil alone. The PH600 biochar also reduced the leaching of nitrate (34%) and ammonium (14%), but caused additional phosphate release from the soil columns. Boopathy *et al.* (2013) reported that ammonium ion adsorption on coconut shell activated carbon (CSAC) varied from 58-93 % based on the initial concentration (500 mgL^{-1}) with an optimum pH 9 and contact time of 120 min. Angst *et al.* (2013) demonstrated that application of biochar (2% soil mass - dry weight basis) could potentially aid in the mitigation of N_2O emissions from certain soils and in N loss in leachate from soil amended with slurry, manure, or fertilizer used in livestock systems. Felber *et al.* (2014) opined that biochar controls N_2O emission by reducing NO_3^- availability to denitrifiers. Sika and Hardie (2014) reported that pinewood biochar can strongly reduce not only the amount of ammonium and nitrate leached from sandy soils but also the amount of recoverable exchangeable ammonium and nitrate after leaching. Biochar (0.5, 2.5 and 10.0% w/w) significantly reduced the cumulative amount of ammonium (12, 50 and 86%, respectively) and nitrate (26, 42 and 96%, respectively) leached relative to the control soil. The reported literature suggest that blending of zeolites or biochar with conventional fertilizers can change the adsorption and desorption behaviour, regulate release of nutrients, and eventually result in higher nutrient use efficiency without causing environmental harm.

Fabrication of Intercalated/Impregnated fertilizers

Nanotechnology could be applied in environmental soil science with respect to slow-release fertilizers and pollutant remediation. Khan *et al.* (2008) reported that the fertilizer impregnated charcoal could be developed as slow-release type fertilizer to minimize contamination. Komarneni (2009) demonstrated the slow release of NH_4^+ from various zeolites treated with molten NH_4NO_3 and KNO_3 over time. These modified zeolites with occluded ammonium and nitrate showed good promise as a slow-release N fertilizer. In another study, Karapanagioti *et al.* (2010) demonstrated the environmental application of zeolite and char as sorbents for ammonia. Rabai *et al.* (2012) also reported the potential of compound fertilizer with zeolite to improve nitrogen efficiency by lowering ammonia volatilization and increasing accumulation of exchangeable NH_4^+ and NO_3^-. Wanyika *et al.* (2012a) entrapped urea in the mesopores of the siliceous nanomaterial synthesised by liquid crystallization technique and simple immersion for loading of N. The studies revealed at least fivefold improvement in the release period.

Natural zeolites are particularly useful in agriculture because of their large porosity, high cation exchange capacity and their selectivity for NH_4^+ and K^+ cations, as well as their physical stability. They can be used both as carriers of nutrients (*e.g.* NH_4^+ and K^+) and as a medium with free exchangeable nutrient ions. Some natural zeolites contain considerable amounts of exchangeable K^+ that can enhance plant growth in potting media. The main use of natural zeolites in agriculture is, however, for ammonium (NH_4^+) exchange, storage and slow release. It has been shown that zeolite, with their specific selectivity for NH_4^+, can take up NH_4^+ from farmyard manure, composts or NH_4^+ from ammonium bearing fertilizers, and store it in the internal void spaces before slow release. Many laboratory and field experiments carried out over the past decades show that NH_4^+-charged zeolites can act as a slow-release fertilizer. Several studies have shown increased plant growth, in response to greater availability of NH_4^+ and decreased losses of N through nitrification, with the addition of zeolite.

Subbaiya *et al.* (2012) reported that application of urea modified hydroxyapatite (HA) particles exhibited higher NUE and slow N release to the soil besides minimizing the adverse effects to the environment. Moghadam *et al.* (2012) reported that when leaves are injected with nanofertilizer solution, wet weight and maximum leaf area index is influenced by concentration of iron chelate in the nano-fertilizer and dry weight is influenced by both type of spinach and concentration of nanofertilizer. Application of nanofertilizer @ 4 kg ha^{-1} caused 58 and 47% increase in wet weight and maximum leaf surface index, respectively compared to use of no fertilizer.

Haghighi and Daneshmand (2013) showed that the effect of nano-titanium (N-Ti) in nutrient solution (NS) was more pronounced on root as compared to shoot growth. They concluded that Ti at higher levels and N-Ti, due to its tiny size and ease of penetration into the roots, can be effective on some growth and photosynthetic characteristics of tomatoes. Chen *et al.* (2013) found that biochar-based fertilizers (BCF) usage reduced the dosage of N fertilizer by 19.9% and improved yield and N use efficiency. Ying *et al.* (2013) suggested that combining biochar and fertilizer to produce biochar-based fertilizer can not only promote crop growth and increase crop yield but also enhance the agronomic use of biochar. Manikandan and Subramanian (2013) concluded that biochar was a suitable adsorbent for slow-release N fertilizer production. Among the hardwoods, the biochar derived from *Prosopis Juliflora* is a potential substrate for urea intercalated, which had higher retention and slow release pattern of N.

Fabricated fertilizers application

Prakaso (2006) showed that slow-release fertilizer which is made by a mixture of urea and zeolite at the accurate composition, binder and application is more effective in terms of paddy yields as compared to urea prill and urea granule. In this respect, a 50:50 ratio of urea and zeolite is more efficient than a 70:30 ratio. Chakhalyan *et al.* (2008) reported that the complex of zeolite nitrogen-fixing microorganisms exceeded the efficiency of the known bacterial nitrogen fertilizers and ecologically safe biofertilizers. The stimulating action of zeolites was observed upon the growth and propagation of *Azotobacter chroococcum.* Omar *et al.* (2010) determined the effect of mixing urea with zeolite and sago waste water on ammonia volatilization, soil exchangeable ammonium and available nitrate contents compared with urea without additives under waterlogged condition. Ammonia volatilization (13 days) from urea could be significantly minimized under waterlogged condition, if urea is amended with sago waste and zeolite.

Bernardi *et al.* (2010a) introduced Brazilian zeolitic sedimentary rock as a release fertilizer and soil conditioner. The NPK enriched zeolite fertilization study, which explained the formulation as a slow-release source of nutrients to plants was conducted on rangpur lime, rootstock lettuce, tomato, rice and andropogon grass. Ahmed *et al.* (2010) reported that surface applied urea fertilizer efficiency could be increased by mixing it with zeolite and acid sulphate soil. Bundan *et al.* (2011) reported that ammonia volatilization from urea can be reduced by mixing urea with zeolite. Civeira and Rodriguez (2011) showed that the application of N fertilizer with lower rates of zeolites (NZ1: 120 kg ha^{-1} zeolite+200 kg N ha^{-1}) significantly increased the N absorbed by maize .These results can be explained by the favourable effect of the zeolites on nitrogen mineralization and soil water retention. Ippolito *et al.* (2011) reported that soil application method of zeolite affects inorganic nitrogen, moisture, and corn growth. Mixing zeolite into soil reduced the rate of nitrification likely because of NH_4^+ adsorption in the zeolite mineral lattice. Zhao *et al.* (2011a) showed that under the same experimental conditions, when the mass ratio of zeolite, anthracite and fly ash was 1:2:1, removal effect of NH_4^+-N was the best, up to 95.8%. Under the slightly acidic pH value, the removal effect was maximum with the optimal efficiency up to 90%. Cyrus and Reddy (2011) also reported that zeolite could be a good substrate for slow N release in soil.

Omar *et al.* (2011) reported that amending urea with sago waste water and peat soil water can reduce ammonia loss by encouraging formation of ammonium and nitrate over ammonia and also improves use efficiency. Lija *et al.* (2012) revealed that amending soil with mixture of compound fertilizer and clinoptilolite may not only minimize ammonia loss from ammonium nitrate (12 days) but it could improve retention of nutrients and their timely release for plant uptake. They also showed that ammonium-exchange zeolite acts as a slow-release fertilizer in a medium textured and porous soil. reported that Zeolite addition to granules of urea and of its particles sizes reduced volatilization loss of NH_3 (20%) and increased the amount of N absorbed by sorghum plants in green house conditions (Werneck *et al.* 2012). Wang *et al.* (2012) reported that application of zeolite, reed straw and superphosphate has the potential to reduce on gas emissions from stored duck manure. Zeolite addition reduced cumulative NH_3 and N_2O emissions by 36 and 20%, respectively however, superphosphate is more effective in reducing NH_3 emissions. Rabai *et al.* (2013) reported that clinoptilolite zeolite (CZ) utilization has attracted much attention in the fertilizer industry for its adoption as a management strategy in crop production. They demonstrated that compound fertilizer with CZ improved N uptake and use efficiency in the maize crop. Zeolite was used as carriers to control ammonium and potassium release to reduce the non-point source pollution due to pesticide and fertilizer applications (Li *et al.* 2013). Nanoporous zeolite based N fertilizer can be used in crop production systems to improve NUE (Manikandan and Subramanian 2014).

Nanotechnology applications in soil and environment

Prost and Yaron (2001) and Basak *et al.* (2012) suggested that modified clays may be used for pollution prevention and for remediation of the soil environment. Okada *et al.* (2005) reported that composites of carbon/zeolite with corrugated structures enhanced adsorption of polar molecules such as ammonia, water vapour and methanol due to the formation of composites of activated carbon with hydrophilic zeolite. Subramanian and Sharmila Rahale (2010) detected N release till 1176 h from nano-zeolite based fertilizer while conventional fertilizer had detectable amount of N up to 200 h. Zheng and Wang (2010) synthesized a biotite-based hydrogel composite for NH_4^+ adsorption with the help of poly acrylic acid . De Rosa *et al.* (2010) opined that to study effective delivery of nutrients to crops, biosensor could be attached to nanofertilizers that allows selective nitrogen release linked to time, environmental and soil nutrient condition. Slow /Controlled-release of fertilizers may also improve soil quality by decreasing toxic effects associated with fertilizer over application (De Rosa 2009).

Corradini *et al.* (2010) used chitosan nanoparticles as a carrier to explore the potential of chitosan nanoparticles as controlled release for NPK fertilizers. Kottegoda *et al.* (2011) reported that the urea modified hydroxylapatite nanoparticles encapsulated wood based nanofertilizer has an initial burst and subsequently releases N in a slow and sustained manner for more than 60 days in two acidic (pH 4.2 & 5.2) and sandy soils (pH 7). Ni *et al.* (2011) developed environmentally friendly slow- release N formulations. Developed fertilizers release profile contain three stages namely, slow release stage with soaking and penetration of water vapour within 24 h, steady release stage of five days, and finally concomitant stage fluxes of nutrients released for 10 days. Pereira *et al.* (2012) prepared and characterized a novel urea slow-release nanocomposite, based on urea intercalation into montmorillonite clay by an extrusion process at room temperature. Rai *et al.* (2012) demonstrated that new nutrient delivery systems that exploit the nanoscale porous domains on plant surfaces can be developed. Wanyika (2012) studied the prospects of mesoporous silica nanoparticles (MSN) and purified montmorillonite (MMT) for storage and controlled release of fertilizer. About 15.5 % (w/w) of urea was entrapped into the MSN pores and ~21.4 % w/w intercalated into MMT interlayer space. Xie *et al.* (2013) developed an eco-friendly superabsorbent composite based on wheat straw (WS) and used that as the carrier to control the release of nutrients.

Smart Delivery Systems (SDS)

Nanoscale devices with novel properties make the agricultural systems “smart” (Remya *et al.* 2010). The agglomeration of high molecular weight polymers is encapsulated with functional ingredients. It also protects their loss and delivers them to the needed site of action and on time. Nanoparticles (NP) have been referred as “magic bullets”. Such devices are capable of responding to different situations by themselves, thus taking appropriate remedial action. These smart-systems deliver chemicals in a controlled and targeted manner similar to the proposed use of nano-drug delivery in humans. Characteristics of smart treatment delivery systems have special features for delivery of molecules in agricultural production or processing in time-controlled, spatially targeted, self or remotely regulated, responsive, or other precise ways. Also, systems could have the ability to monitor the effects of delivery with pre-programmed or multifunctional characteristics. Smart delivery systems ranged from treatments with agrochemicals to the delivery of nucleic acids for genetic transformation (Mukal *et al.* 2009).

The smart system integrates agriculture and food processing. Integrated system working processes are sensing, reporting, localization, and control. The system could be used anywhere along with the farm to table continuum, or at multiple points (Heller and Atkinson 2007). Nanotechnology instruments have the capability to detect nutrient deficiency and other problems prior to the development of visible symptoms in crops. Melendi *et al.* (2008) developed smart treatment delivery systems for pumpkin with NP. Cui *et al.* (2011) showed that application of nanotechnology appears to be promising for developing smart fertilizer by using nano-structured materials as fertilizer carriers or a controlled-releasing media for construction of so-called "plant nutrient delivery system". Subramanian *et al.* (2012) argued that nano-based smart delivery systems should go beyond the boundaries of foliar feeding and suggested that there is an abundance of scope of exploiting smart delivery systems in agriculture which facilitate enhanced use efficiency of inputs besides facilitating environmental protection.

To summarize this review article, the progress of nanofertilizer production beginning with nitrogen formulations has been depicted in fig. 1.

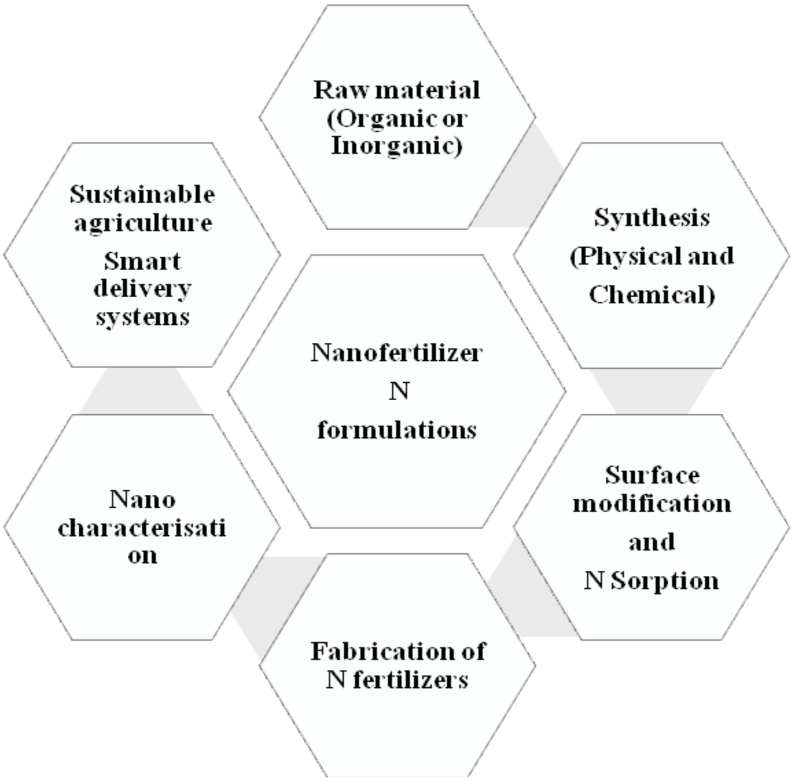

Fig. 1. Schematic progress of nanofertilizer N formulations

Conclusion

Temporal changes and yield stagnation of major crops over three decades have urged us to revisit agriculture sustainability through nanotechniques with specific reference to nitrogen fertilizers. It is time that agricultural scientists should undertake research in the fascinating field of nano-based smart delivery systems (SDS) so as to achieve the targeted delivery of inputs that enhances the crop productivity with minimal use of agri-inputs. Nano fertilizers have the potential to be a part of improved nutrient management techniques. It is an improvement over the conventional methods of agrochemicals application (spraying and broadcasting). Usually, only a very low concentration of chemicals, which is much below the minimum effective concentration required, has reached the target site of crops due to problems such as leaching, fast hydrolysis, degradation of chemicals by photolysis, and poor microbial degradation. Hence the repeated application is necessary to have an effective control which might cause some unfavourable effects such as soil and water pollution. The literatures strongly suggest that nanotechnology is a potential tool to modify or regulate the release of nutrients from conventional fertilizers. The slow and steady release of nutrients from the customized or designed fertilizers will help to desorb nutrients that are commensurate with the crop growth. This review attempted to address the issue of altering the solubility of urea through nano-technological approaches.

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