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*Review*

# Nanourea – An Eco-friendly Nitrogen Fertiliser

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**ABSTRACT**
Keeping in view the excess use of fertilizers for delivery of nutrients to crops, the pollution caused by their subsequent runoff into the soil, water and air and cost as the limiting factors, it is important to develop alternative low cost technologies. Urea is a rich source of nitrogen and accounts for >82% of nitrogenous fertilizers used for better crop growth. The Nitrogen Use Efficiency (NUE) from urea, however, remains less than 50%. The runoff from excess urea into lakes and rivers causes algal bloom and consequent depletion of dissolved oxygen, thereby adversely affecting aquatic life. Part of excess urea is also volatilised as ammonia and as nitrogen oxides ($N_2O$, NO and NOx) emissions. Synthesis and application of nanourea, recently launched by Indian Farmers Fertiliser Cooperative (IFFCO), overcomes the issues of environmental toxicity as its NUE is around 80%. Nanourea is currently prepared by coating urea molecules on amorphous calcium phosphate (ACP) nanoparticles. Its particle size varies from 20-50 nm. The ultra-small nanourea particles are encapsulated in a nano-polymer to facilitate slow and gradual release of urea upon foliar spray or via soil application for the crops. Compared to granular conventional urea, nanourea has about 10,000 times more surface area to volume. It contains about 40,000 ppm of nitrogen in a 500 ml bottle of nanourea commercially available from IFFCO. This is equivalent to nitrogen availability from 50 Kg of granular urea. Nanourea exhibits a characteristic slow and steady release of urea in the soil, thereby enhancing its NUE. In India, nanourea disgtributed by IFFCO has already been successfully used on 94 crops in field trial studies. The present review discusses the environment-friendly synthesis, properties and significance of nanourea as a fertilizer.

**Key words:** Nanourea, Nitrogen fertiliser, Urea, Urea nanoparticles

## INTRODUCTION

It is estimated that by 2050 the world population is likely to exceed 9.7 billion (FAO 2018). Agricultural practices have always been attempting to enhance nutrient/ion uptake by crop plants with least adverse impact on the environment. Nitrogen is the most important nutrient required for crop growth as it is a constituent of chlorophyll and many proteins. Nitrogen deficiency is evident in most of the Indian soils, particularly in light- textured ones which are high in sand relative to clay (Kantwa and Yadav 2022). Uptake of nitrogen by plants majorly occurs as nitrate and ammonium ions. Commercially used chemical fertilizers have notably low Nitrogen Use Efficiency (NUE) values. NUE refers to estimation of nitrogen inputs into agricultural products and its loss in the environment. The sustenance of crop growth and yield is dependent on the NUE of various nutrient elements in the source fertilisers without posing any threat to the environment (Kumar et al., 2021). The NUE values for nitrogen (N), phosphorus (P) and potassium (K) in the routinely used fertilisers are as low as up to 35, 20 and 40 %, respectively (Seleiman et al. 2021). This shows that more than 50% of the fertilizers applied do not reach plants due to leaching, photolysis, hydrolysis and/or microbial degradation and immobilization. Low NUE of various fertilisers is the reason for their excessive use, thereby enhancing the risk of air pollution, groundwater pollution, water eutrophication and soil degradation. Extensive use of conventional N fertilizers also leads to substantial loss of nitrogen to the atmosphere, thereby leading to acidification of soil and consequent loss of biodiversity (Banger et al. 2017). Use of conventional N fertilizers has also brought about an increase in atmospheric $N_2O$, thereby adding to global warming. Urea was the first naturally occurring organic compound synthesized from ammonium cyanate by the German scientist-Friedrich Wohler in 1828. Now a day, urea is commercially prepared from liquid ammonia and liquid carbon dioxide, under high pressure (Fig. 1, Table 1). A diamide of carbonic acid

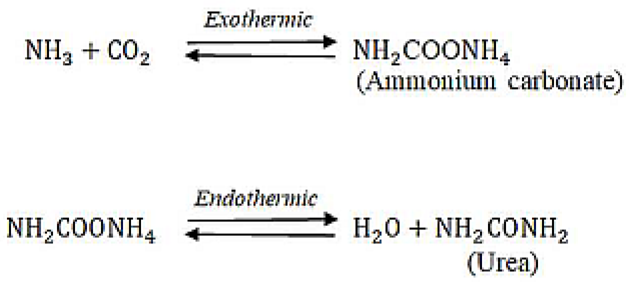
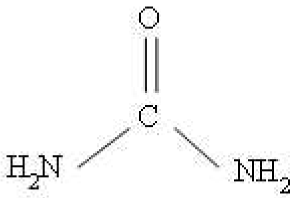



Figure 1. Reaction scheme for conventional urea production

Table 1. Characteristic features of Urea

| Structure | | |
|---|---|---|
|  | IUPAC name : Urea | Molar mass : 60.06 g $mol^{-1}$ |
| | Systematic IUPAC name : Carbonyl diamide | Molecular formula : $CH_4N_2O$ |
| | Texture : White solid | Density : 1.32 $gm.cm^{-3}$ |
| | Melting point : 133 °C | Solubility in water at 25°C : 545 g $litre^{-1}$ |
| | N content : 46.6% | |

(also called as carbamide), urea is used extensively as a nitrogen fertilizer, food supplement, in the manufacture of plastics and synthesis of barbiturates (used as sedatives). NUE of conventional urea remains less than 50% and its overuse has led to serious environmental issues via surface runoff or leaching, ammonia volatilisation and emission of nitogen oxides ($N_2O$, NO and NOx). Sustainability in agriculture can be improved through the use of innovative technologies. Recently, much attention has been given to the potential use of nano-fertilizers for improving plant nutrition and to limit the adverse effects on the environment caused by the overuse of conventionally produced chemical fertilizers. Nanofertilisers are composed of specific nutrients associated with nanoparticles which facilitate slow release of the associated ions or molecules, regulated by solubility rates that are very different from those of the conventional chemical fertilizers (Fig. 2). Nano-fertilizers are either encapsulated or covered by nanomaterials. They can be synthesized from synthetic fertilizers or by green synthesis using various non-toxic methods (Lee et al., 2020). Use

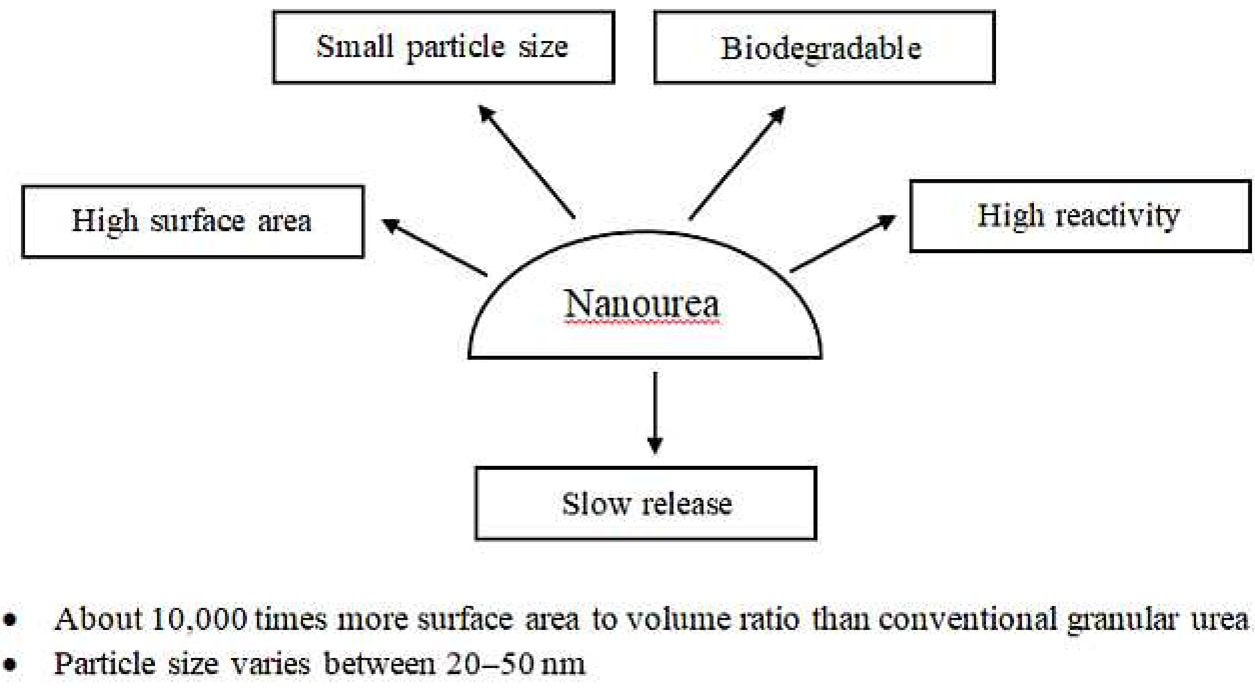



Figure 2. Properties and novel features of nanourea

of nanomaterials, such as zeolites and clays, has been reported to cause reduction in N losses to soil, water and atmosphere**.** Additionally, foliar application of nano-fertilizers also compensates significantly in terms of small quantity of the fertilizer applied for overcoming N deficiency (Mejias et al. 2021). The higher surface area of supporting material in nano-fertilzers makes it possible to attain a higher load of nutrient molecules (such as nitrogen), thereby providing gradual kinetic release profiles than those produced with conventional counterparts. Nanourea is one of the most promising engineered molecules which exhibit greatly enhanced NUE due to its unique feature of prolonged release of nitrogen in the soil. More than 70% of conventional urea applied in the soil remains unabsorbed by the plants and it gets wasted. Nanourea fertilizer launched by IFFCO (India) in 2021 was invented by Dr Ramesh Raliya (Kumar et al. 2021, 2022). It is a urea-based formulation where urea is coated with polymers to make nano-size particles. Thus, nanourea is a synthetic chemical fertilizer, and not an organic fertilizer. The ultra-small nanourea particles are better absorbed directly from leaves than through the soil. Functional hybrid nanomaterials have been used in the recent past for the synthesis of nano-fertilzers because a combination of nanocomponents provides multifunctional properties to NPs due to the synergistic interactions among interfacial particles (Kottegoda et al. 2017).

## SYNTHESIS OF NANOUREA

One of the approaches adopted in the recent past made use of hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] nanoparticles (HA NPs) due to their excellent biocompatibility and they being also a rich source of phosphorus (Kottegoda et al. 2017) (Fig. 3). HA NPs exhibit a urea to hydroxyapatite ratio of 6:1 by weight and show slow release of nitrogen in aqueous conditions. Another slow release nanourea has been reported using nano calcium carbonate. It is obtained by rapid carbonation of urea and exhibits controlled urea release properties over pure urea (Mahaletchumi 2021). Urea-silica nanohybrids have also been reported to provide slow and precise delivery of urea as a nutrient for crops (de Silva et al. 2020). Now a day, nanourea is commonly synthesized using

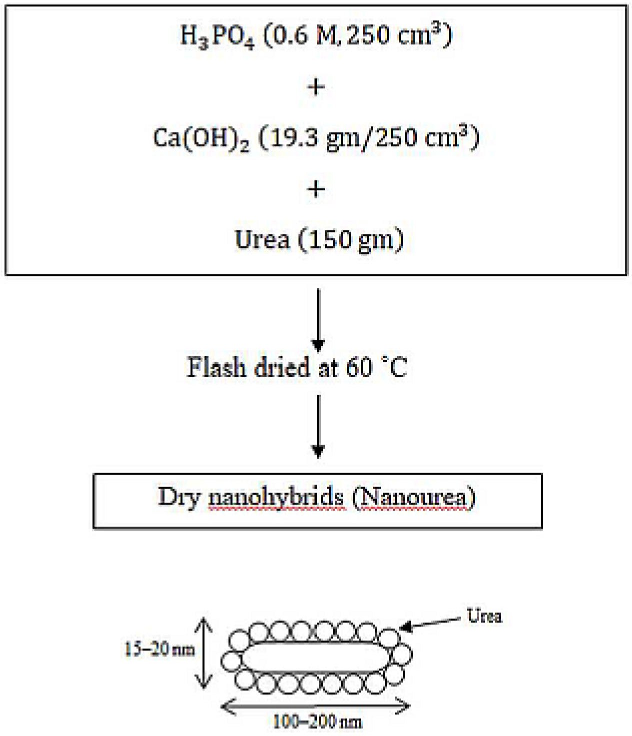



Figure 3. One-step synthesis of Urea-hydroxyapatite nanohybrids (Kottegoda et al., 2017)

Amorphous Calcium Phosphate (ACP) nanoparticles (Fig. 4). The crystalline phase of calcium phosphate exhibits Ca/P ratio ranging from 0.5 to 2.0 along with variable hydration and protonation levels, water solubility, pH stability and polymorphic phases (Carmona et al. 2021). Compared to non-crystalline (hydroxyl)apatite (HA) (the mineral component of teeth and bones among vertebrates), nano-sized ACP possesses a higher surface reactivity, better solubility and a better tendency to adsorb urea molecules on the NP surface, thus offering higher N-payloads. ACP can be obtained at short precipitation times and lower temperatures thereby making it a cost effective production at industrial scale. ACP-NPs can be synthesized either by one-pot synthesis of N-doped ACP NPs by using excess nitrate and urea or by post-synthetic modification (PSM) of ACP NPs with urea. One-pot synthesis results in nitrogen incorporation not exceeding 2.8% whereas N-doping with PSM method is nearly 3x higher (up to 8.1%) with no wastage of added urea (Fig. 5). Furthermore, the PSM method is cost effective and environmentally sustainable since it can be followed using tap water and inexpensive technical grade chemicals.

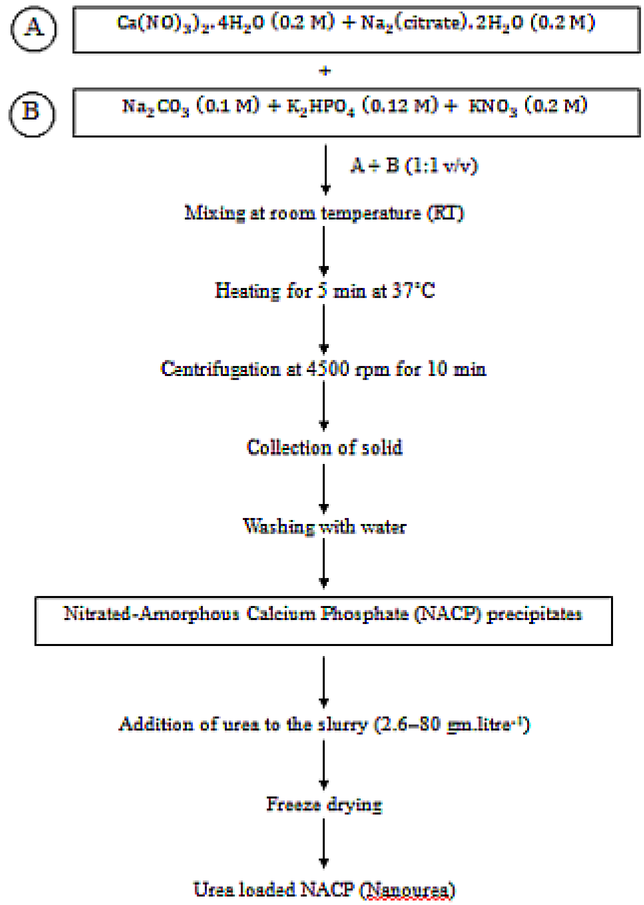



Figure 4. Post-synthesis modification (PSM) of ACP NPs with Urea (Carmona et al. 2021)

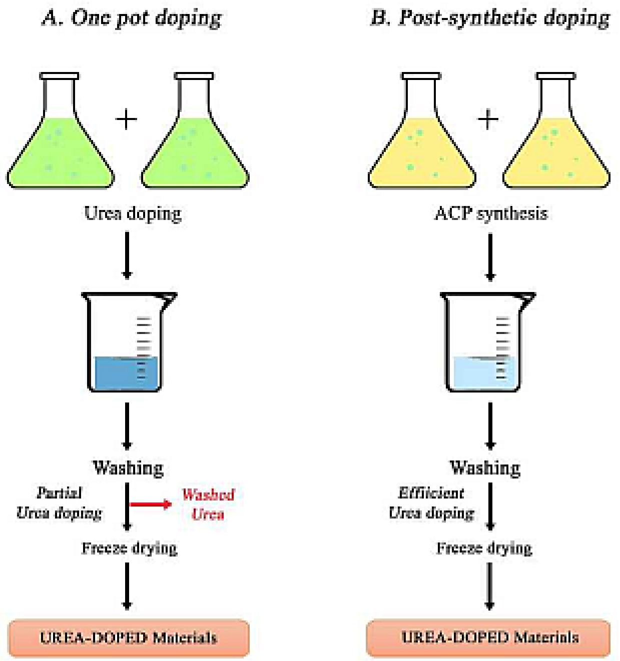



Figure 5. ACP NPs doping with urea. A. One-pot doping. During preparation it results in washing of loosely bound urea. B. Post-synthesis doping after the isolation and washing of ACP NPs. It does not lead to any wastage of urea (Carmona et al. 2021)

## PROPERTIES OF NANOUREA

Nitrogen release behaviour of urea-HA nanohybrids in water showed that its release rate of urea was 12 times slower as compared to that of pure urea (Kottegoda et al. 2017). This release pattern is analogous to the release of water soluble molecules from a homogeneous matrix by diffusion in slow release drug formulations. In other words, urea is released from urea-HA nanohybrids according to Fickian kinetics (Fig. 6). Upon contact with soil moisture and depending on the soil moisture and pH, urea gets released from the urea-HA nanoparticles in a slow and controlled manner through a diffusion regulated mechanism, leaving NPs in the soil and urea gets absorbed by the plant roots. The slow release of urea from urea-HA nanohybrids can occur up to one week in contrast with pure urea, which is expended within minutes. Analysis of the urea release profile of N-doped ACP NPs in water revealed full reversibility of the adsorption process, with up to 89% of weakly bound urea getting released within 15 minutes. Release attains 100% levels within 24 hrs of suspension. There was no change in the urea release profile of nanourea irrespective of the method of synthesis of ACP NPs. Thus, the two strategies (one pot synthesis and PSM) offer similar advantages in terms of urea release in field conditions (Carmona et al. 2021). The efficacy of nanoparticles is determined by their size, shape, dispersion, surface chemistry and concentration (Kumar et al. 2022) (Table 2). Nanourea (liquid) commercially available from IFFCO (India) is the world's first nanofertilizer put into large scale commercial use by farmers across India. It contains 4% total nitrogen (w/v) evenly dispersed in water. Nano nitrogen particle size varies from 20-50 nm. These particles are evenly distributed in water and exhibit more than 80% use efficiency when sprayed on crop. It contains 40,000 ppm of nitrogen in a 500 ml bottle. This is equivalent to nitrogen provided by one 50 Kg bag of conventional urea (Baboo 2021). 2-4 ml of Nano urea liquid is

Table 2. Physical properties of nanourea

| **Properties** | **Value** |
|---|---|
| Physical size (nm) | 28.3 – 34.1 |
| Hydrodynamic size (nm) | 56.6 – 64.33 |
| Zeta potential (mV) | 42.4 – 43.72 |
| Nitrogen content (%) | 4.3 |
| Viscosity (cPs) | 9.65 – 10.08 |
| pH | 4.6 – 4.63 |

Source: Kumar et al. (2022)

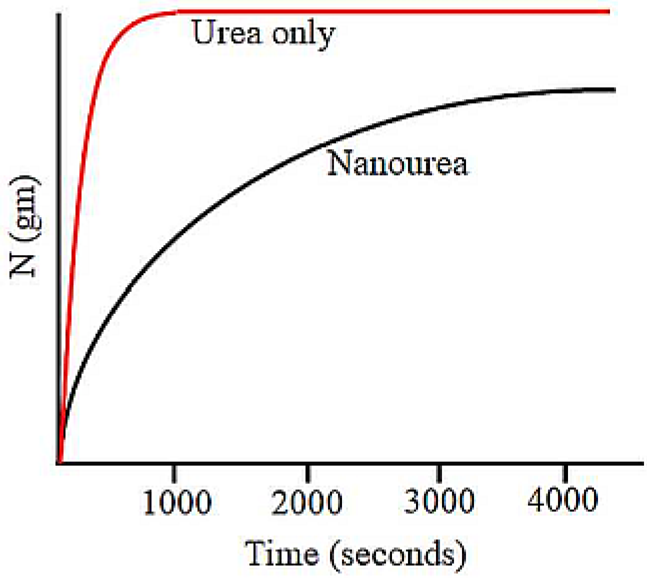



Figure 6. Release kinetics of urea and urea-HA in water in terms of time to reach constant value (Kottegoda et al. 2017)

mixed with one litre of water and sprayed on crops at active stage of growth. Nanourea is now included in the Indian Government's Fertilizer Control order after successful field trials on 94 crops in over 11,000 farm fields and 20+ agricultural research institutes/ universities. The ultra-small nanourea particles are encapsulated in a nano-polymer which makes it feasible for controlled release of nitrogen in the surroundings.

## LIMITATIONS AND FUTURE SCOPE

Use of nanourea significantly enhances the NUE thereby improving crop growth but foliar application at high concentration can, at times, cause leaf burning. The dispersion, bioavailability and stability of NPs is affected by soil texture, pH and cation exchange capacity due to surface charge effects. Investigations are required to find out whether nanourea is completely changed into ionic form for assimilation into various metabolites by the plants. Any non-metabolized residue from nanourea is likely to enter the non-targeted components of food chain. Future research should also focus on understanding the role of different forms of nitrogen in producing nano nitrogen fertilizers. It is yet to be investigated whether different forms of nano-fertilizers containing nitrogen do get released in ionic forms in the plant cells or not. Use of nano-fertilizers can certainly contribute significantly in enhancing food production. Future research can also focus on the attachment of nanosensors to deliver nano-fertilizers to the targeted sites. Nanosensors offer significant potential in agriculture since they are extremely tiny devices that can be attached to the molecules to be delivered at the target sites. Nanosensors also provide real time information about the delivery of nano-fertilizer molecules and can possibly predict environmental stressors. To sum up, future investigations should focus on the toxicity, safety and bioavailabilty of NPs for agricultural production. Green-synthesis or biosynthesis of NFs should also be given priority.

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**Conflict of Interest:** There is no conflict of interest

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