Review Article

Controlled Release of Nutrients for Soil Productivity- A Review

ABSTRACT

The nutrient release from conventional chemical fertilizers to the soil are lost continuously through leaching, runoff, volatilisation, denitrification etc and also most of the time they do not satisfy the plant requirements without the continuous application. These issues have caused economic loss as well as environmental pollution due to hazardous emissions and water eutrophication. Controlled release of nutrients through the application of slow/controlled release fertilizers and nanofertilizers are possible solutions, which provides their nutrients according to the requirement of crops. Release of nutrients from controlled release fertilizers are delayed by means of coating the soluble fertilizer core with porous semipermeable membrane. A variety of coating materials are developed for the preparation of controlled release fertilizers. The longevity of CRFs depends upon the thickness of coating, temperature and moisture content. Nano technology is an emerging field, which also produce nanofertilizers based on CRFs are used for the increment of active fertilizer material in the field, as they present large surface area for the release of required nutrients to the plant in a controlled manner. Controlled release of nutrients has profound influence on soil properties and yield parameters of crops. The use of controlled release fertilizers (CRFs) starts to evolve as a promising direction offering an excellent means to improve management of nutrient application and by this reducing significantly environmental threats while maintaining high crop yields of good quality. Controlled release fertilizers allow the release of nutrients to be better matched with the life cycle of the plant.

Keywords: Controlled release, coated fertilizers, polymer, slow release.

1. Introduction

Current agricultural practices cannot meet the increasing demand for food without the extensive application of fertilizers. It is expected that in the next 40 years the demand for food will increase by over 60% as the global population will rise to 9.3 billion in 2050 [1]. Through the introduction of high yielding varieties of crops as well as chemical fertilizers green revolution increased the yield per unit area, but the conventional chemical fertilizers are limited by their low nutrient use efficiency. NUEs (Nutrient use efficiency) of major macronutrients such as N, P, K are quite low with current levels being 30-35%, 18-20% and 35-40% respectively, which means more than half of the applied fertilizers are lost [2]. Conventional fertilizers are instantly available once they are applied to the field and lost through ammonia volatilization, denitrification, leaching or runoff after being applied to the soil. The enormous utilization and runoff of fertilizers distort the nutrient and food chain balance in ecosystems, causing a variety of environmental problems, including eutrophication of water [3]. Controlled release of nutrients may be a solution for these problems and they release nutrients better matched with the life cycle of the plant [4]. Controlled release is the gradual release of nutrients from fertilizers to meet the plant demand which in turn reduces the loss of nutrients to the environment. Controlled release of nutrients can be achieved through the application of slow or controlled release fertilizers and nano-fertilizers. Controlled or slow-release fertilizers are fertilizer granules which releases the fertilizer nutrient in a slower manner to meet the crop demand [5]. Controlled release fertilizers and slow release fertilizers are employed as synonyms, but there are some differences. According to [6] in controlled release fertilizers the rate, pattern and duration of release are well known and controllable during their preparation. Slow-release fertilizers release the nutrients in a slower manner than the usual with the help of some transport barrier which slower the release pattern without a coating and the rate pattern and duration of release are not well controlled [7]. Nano technology is an emerging field which have wide range of application in different fields and includes the synthesis of materials in nano range (1-100 nm) with unique physical and chemical properties. Nano fertilizer or nano enabled fertilizers are fertilizer product developed through a nanoscale process [8] and this provide nano structures which act as a carrier as well as vectors for controlled release. Nano fertilizers combined with nanosensors helps in the synchronization of nutrients release according to the crop demand from nanofertilizers. Fertilizer use efficiency can be increased and it decreases the environmental impact of excess nutrients [9]. The major issues that challenging the agricultural sector is the optimized production of agricultural products from the limited facilities without causing much environmental issues. In this review article we will be discussing about the controlled release of nutrients on soil productivity which can improves the nutrients use efficiency as well as decreases environmental degradation.

2. Classification of controlled release fertilizers

According to [10], CRFs may be classified as follows

2.1. Organic-N-low-solubility compounds: This includes natural organic compounds like animal manure, sewage sludge and synthetic nitrogen organic compounds. Synthetic nitrogen organic compounds are again divided into biologically decomposing compounds (Urea formaldehyde) and chemically decomposing compounds (isobutyledene- diurea).

2.2. Fertilizers in which a physical barrier controls the release: Coated fertilizers and matrix-based fertilizers are the best-known examples. Coated fertilizers are further divided into fertilizers coated with organic polymers (thermoplastic or resins) and fertilizers coated with inorganic materials (Sulphur or mineral-based coatings). In matrix based fertilizers, the raw materials used for the preparation of matrices can be subdivided into hydrophobic materials such as polyolefines, rubber etc. and gel-forming polymers like hydrogels. The matrix based fertilizers are less common in practice than the coated fertilizers.

2.3. Inorganic low-solubility compounds: Fertilizers such as metal ammonium phosphates (eg. $MgNH_4PO_4$) and partially acidulated phosphates rocks (PAPR), are typical examples of this class.

3. Preparation of control release fertilizers

The release of nutrients from fertilizers can be controlled or slowed down through different methods and the resulting products are slow or controlled release fertilizers. The important technologies employed for the production of S-CRFs are (a). matrix method (b). core shell method. In matrix method of preparation, the entrapped agents are uniformly dispersed in the mixture so that diffusion and outward flow of fertilizers are impeded by the tortuosity of the matrix, shows continuously declining release rates as the surface layers become depleted. Matrix based fertilizers are available in the forms such as spikes, capsules and tablets. In core shell method the core of soluble fertilizer is coated with water insoluble, semi-permeable or permeable porous materials (Fig. 1). Coating controls the penetration of water into the soluble fertilizer and thus decreases the rate of dissolution of nutrients and ideally synchronize nutrient release with plant needs. Spray coating, spray drying, pan coating, and rotary disk atomization are the typical physical methods for encapsulating fertilizers. Rotary drum, pan or ribbon or paddle mixer, and fluidized bed are the special equipments used for these methods [11].

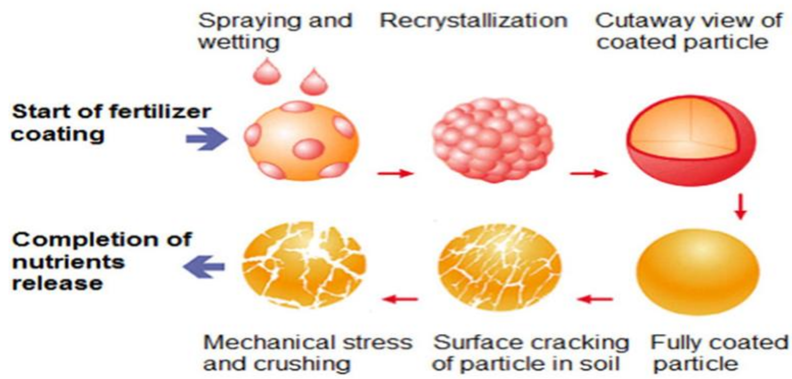

Fig 1. Preparation of coated fertilizers and release of nutrients [12, 13].

4. Mechanism of nutrient release from controlled release fertilizer

Release pattern of nutrients from CRFs depends upon the nature of coating materials, types of CRFs, agronomic conditions and much more. The nutrient concentration gradient between the soil and the core of coated fertilizers also governs the rate at which nutrient is released. According to several authors [14-16] coated fertilizers are expected to undergo a release mechanism called multi stage diffusion model (Fig 2).

Water penetrates through the coating and causes the partial dissolution of nutrients. An osmotic pressure develops within the granules and it undergo two process like catastrophic release and diffusion mechanism. When the osmotic pressure exceeds the membrane threshold resistance the coating bursts and the entire nutrients release spontaneously. This mechanism is called catastrophic release or failure mechanism. In another process if the membrane threshold resistance is higher than the osmotic pressure developed, the fertilizer release from the granules in a slow and control release manner under the influence of concentration or pressure gradient or the combination of both. This mechanism is the diffusion mechanism.

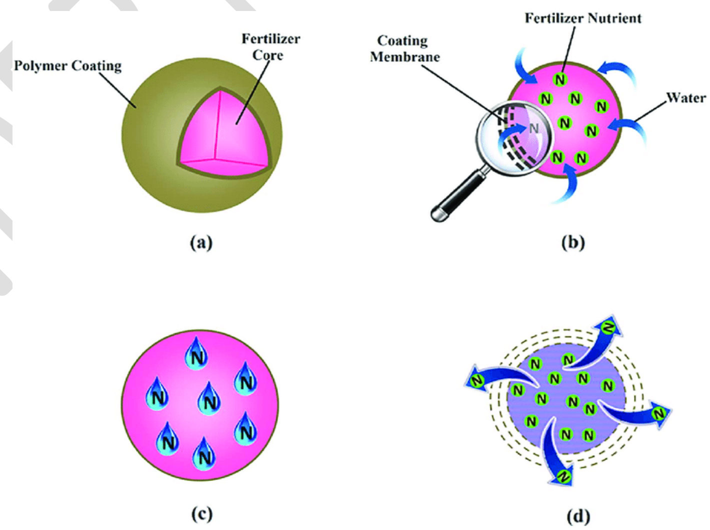

Fig 2. Fertilizer nutrient diffusion from coating to the soil [5].

(a) Fertilizer core with polymer coating, (b) Water penetrates into the coating and core granule, (c) Fertilizer dissolution and osmotic pressure development, (d) Controlled release of nutrient through swollen coating membrane.

5. Fertilizers in which a physical barrier controls the release

Coated fertilizers

An ideal fertilizer releases the nutrients according to the crop growth pattern and usually it forms a sigmoidal release pattern (Fig.3). Coated fertilizers consist of a physical barrier or coating material which cover the soluble core fertilizers. Water penetrates through this coating and solubilize nutrients for their release. Coating of fertilizer with hydratable, soluble or biodegradable polymers provides the controlled release of nutrients to the soil [17] and providing a thin layer of coating over the surface of fertilizer ensures high nutrient content per total weight [18].

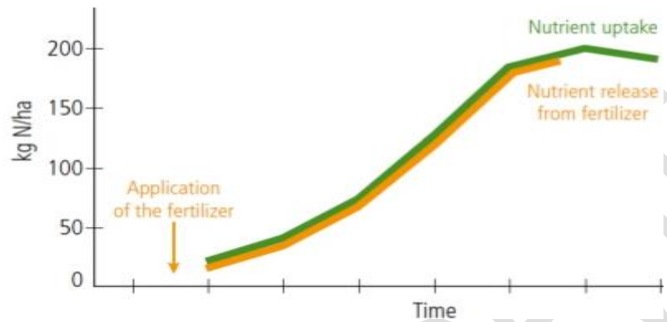

Fig 3. The ideal fertilizer the nutrient release is synchronized with the crop nutrient requirements [19].

Sulphur coated urea

Being a secondary nutrient needed for plant growth and functioning and also due to good fungicidal properties sulphur has emerged as an active participant in the CRFs formulations. Cheap available material which can be used for ameliorating alkalinity due to its acidic nature and act as anti-caking agents for certain fertilizers [20]. Coating of urea granules with sulphur and a sealant results in the formation of a membrane that regulates the release of nitrogen. Sulphur coated urea fertilizer is a slow-release fertilizer that is made by coating urea with sulphur and wax that increases nitrogen efficiency, improves plant growth and reduces water pollution compared with water soluble fast release urea. It is prepared by spraying molten sulphur over granular urea to yield a product containing between 31 to 38% N. A wax sealant is then sprayed to seal cracks in the coating and thereby reduce leakage and microbial degradation of the S coating [21, 22].

Mechanism of release

The release of nutrients were regulated by the physical breakdown of coatings, microbial decomposition of the sulphur and hydrolytic cleavage of S-S linkages. When water penetrates through the coating, a part of the solid core dissolves and this induces internal pressure resulting the release of nutrients. Due to the crystalline nature of sulphur microscopic pores get developed, which enhances the brittleness [23]. Sulphur is larger in size because of this reason its coating shows a low level of adhesion to the surface of urea [24]. Therefore, sulphur coatings are not much efficient and need to be combined with other coating materials.

Polymer coated urea

Fertilizers coated with hydrophobic materials provide reasonable/good control over the nutrient release rate. Fertilizers coating with hydratable, soluble, or biodegradable polymers is an effective way to control the release of nutrients to the soil [17]. Lignin, starch, chitin, cellulose and other polysaccharide are natural biodegradable polymers which can be modified and used as a coating material for granular soluble fertilizers [25]. Chitosan has been used as a coating material for fertilizer due to its swelling behaviour in water. [26] Lan Wu prepared chitosan based double coated NPK fertilizer with water soluble NPK fertilizer as the core, chitosan as the inner coating and poly (acrylic acid-co-acrylamide) as the outer coating to combine the slow-release property and water holding capacity in the one coating system.

Elemental analysis showed that the product contained 7.98% K_2O, 8.14 % P_2O_5 and 8.06 % nitrogen. This product releases nutrients in a controlled release manner and have high water retention capacity. Being degradable in soil and environment-friendly, could be especially useful in agricultural and horticultural applications. In another experiment [27] prepared a chitosan coated DAP fertilizer through double coating approach. In this formulation DAP fertilizer was coated with chitosan clay complex as inner coating and paraffin wax as outer coating significantly reduce the dissolution of P when compared to the uncoated DAP. Biodegradation study of composite material in soil and the biochemical oxygen demand tests revealed that after the fertilization process the coating system proposed could be considered as a carbon source for microorganisms which confirms its sustainability. In an experiment [28] synthesized a novel coated controlled release rock phosphate formulation by using rock phosphate acidulated with H_2SO_4 followed by coating with polyvinyl alcohol or liquid paraffin at 2%. Laboratory incubation experiments indicated that P release from coated fertilizer was lower throughout the incubation period than the uncoated commercial DAP. The release of P from different sources followed in the decreasing order of DAP > RP + H_3PO_4 > RP + H_2SO_4. The diffusion of the elements from the interior of the fertilizer granule were controlled by the coating structure. [29] experimentally confirmed that the use of polysulfone as a coating material for soluble fertilizer decreases the release rate of components and the release rate of nutrients decreases with the decrease of the coating porosity. After 5 h of test 100 % of NH_4^+ were released from the coated fertilizer when it is coated with 38.5% porosity, prepared from 13.5% polymer solution but only 19.0% of NH_4^+ was released after 5 h for the coating with 11% porosity. Extracted lignin from kraft and sulfite black liquor has the potential to be developed as a coating material. Release of nitrogen from urea coated with acetylated sulfite lignin was more than that of kraft lignin and also the nitrogen release from sulphur coated urea in soil was more than urea coated with acetylated lignin [30]. In another experiment [31] reported that neem coated urea, slowly and steadily release nitrogen when compared to pongamia oil coated urea and castor oil coated urea.

6. **Fertilizer matrix**

In fertilizer matrix, the entrapped agents are uniformly dispersed in the mixture so that diffusion and outward flow of fertilizers are impeded by the tortuosity of the matrix. Some materials that could be used as a matrix are asphalts, gels, oils, paraffins, polymers, resins or waxes. Unlike the coating systems where a constant release could be expected to be maintained, the matrix systems show continuously declining release rates as the surface layers become depleted. Matrix based fertilizers are available in the forms such as spikes, capsules and tablets [32]._Multi-nutrient fertilizer tablets prepared by using neem coated urea, factamphos, MOP, magnesium oxide, phosphogypsum, zinc sulphate and borax with the binding agent methyl cellulose release the nitrogen in a slow release manner and maximum content (685.74kg ha^{-1}) was observed on the 60^{th} day of incubation [33]. According to [34], fertilizer-manure blocks prepared by using coirpith, cowdung, vermicompost, ground nut cake, neem cake, zeolite and humic acid in different proportions showed a slow release pattern with respect to available nitrogen in soil as compared to sole fertilizers.

Organic matrix produced by using dried cow dung, clay soil, neem leaves and rice bran in 2:2:1:1 ratio showed longer retention of ammonium in the soil that synchronized with the nitrogen demand of the Brassica plants due to the slow release property of organic matrix based slow release granules [35]. One-time application of multi-nutrient fertilizer briquettes to maize crop yields significantly higher grain yield compared to the split-application of conventional granular fertilizer and application increased nutrient recovery efficiency. Leachate N concentrations from the multi-nutrient fertilizer briquettes were found to be less [36].

Gel based materials

Gel based materials are generally polyacrylic acid and its derivates and it work on the principle of absorption of soluble fertilizers within a matrix of polymer gel. Fertilizers of this type have an additional function as water absorbent. [37] reported that coated N fertilizer with poly (acrylic acid)/organo-attapulgite as outer coating, urea-formaldehyde as inner coating and urea granule as core have a high water absorption capacity.

Hydrogels

Hydrogels are three dimensional, cross linked hydrophilic polymers that can imbibe large amount of water or biological fluids. As a controlled release formulation, the functionalized polymers can be also used for enhancing the absorption of nutrients by plants [38]. The main characteristics of hydrogels are, they have high absorption capacity, good permeability, low solubility, low residual monomer, high durability and stability, pH-neutrality, biodegradability and re-wetting capability.

Biodegradation of hydrogel forming CRF: Biodegradation of hydrogel forming CRF involves the steps such as bio deterioration, bio fragmentation, assimilation and mineralization [39].

Controlled-release fertilizer hydrogels, which were prepared from polyvinyl alcohol, chitosan and the blend of these two polymers, using glutaraldehyde as a cross linker increased the water retention of soil and chitosan hydrogel exhibited the highest the percent cumulative release of phosphorus in soil among the CRF prepared hydrogels [40].

7. Zeolite based materials and others

Zeolite is a natural super porous mineral which carries a negative charge balanced by freely moving cations with positive charges. It can act as an ideal trap for positive cations like nitrogen rich ammonium and potassium which are then released when demanded by plants. [41] reported that urea loaded zeolite reduced the leaching losses of nitrogen and slows down denitrification process. According to [42], surfactant modified zeolite (SMZ) can act as a good sorbent for PO_4^{3-}, and a slow release of P was achievable. A comparative study of the release of P from fertilizer-loaded unmodified zeolite, SMZ and from solid KH_2PO_4 showed that P supply from fertilizer-loaded SMZ was available even after 1080 hr of continuous percolation, whereas P from KH_2PO_4 was exhausted within 264 hr.

Biochar based control release nitrogen fertilizer (BCRNFs) was prepared through the incorporation of urea and bentonite into biochar through hydrothermal synthesis. The cumulative release amount of N was 54.6% within 98 days when incubated in soil, demonstrating favourable controlled-release properties of the BCRNF [43]. Double coated diammonium phosphates fertilizer with chitosan-clay composites as inner coating and paraffin wax as an outer coating significantly delayed dissolution of P compared to uncoated DAP. The biodegradation study of composite material in soil and the biochemical oxygen demand tests revealed that the coating system proposed could be considered as a carbon source for microorganisms after the fertilization process, which confirms its sustainability [27].

Paraffin wax is widely used as a coating material for fertilizers due to its hydrophobic properties, low cost, low melting point, biodegradability and low contamination to the soil [44]. Phosphogypsum is a by-product from the phosphoric acid process. Phospho gypsum contain $CaSO_4{\cdot}2H_2O$ and impurities such as P_2O_5, S^{2-}, F^- and organic substances, which are nutrients required for plant growth [45]. Paraffin -coated phosphogypsum-granulated urea released less than 35 % of urea over 28 days of submersion in water. The urea release was sustained much longer than that of paraffin-coated urea which was only upto 7 days [46].

8. Urea super granules

Urea can be prilled, granulated, flaked and crystallized. Presently only prilling and granulation is considered as important. The granulation involves spring molten urea through series of the fine nozzles in a fluidized bed granulator. Cooling the liquid urea slowly while rolling it in layers, creating a harder more evenly sized granule makes granules of urea [47].

9. Stabilized nitrogen products

Nitrification inhibitors

In soils the nitrification process can be autotrophic or heterotrophic. Autotrophic nitrification which is dominant in soils, is carried out by chemolithotrophic bacteria such as *Nitrosomonas*. Nitrification occurs in several steps starting with the oxidation of NH_3 to hydroxylamine and then to NO_2^- by bacteria.

Subsequently, NO_2^- oxidizing bacteria (such as *Nitrobacter*) oxidise nitrite to nitrate. Nitrification inhibitors are chemicals that slow down the process of nitrification.

eg. Nitrapyrin (N-serve) and Dicyandiamide

Urease inhibitors

When urea is applied to the soil urease enzyme converts urea to ammonia gas and it gets converted to NH_4^+, bound to soil particles if this conversion takes place below the soil surface. If the conversion is happening on the soil surface ammonia gas escape into the atmosphere through volatilization. The enzyme urease can reduced upto 14 days by the action of urease inhibitors.

eg. NBTPT (N-[n-butyl] thiophosphoric triamide)

10. Effect of controlled /slow release fertilizers on soil properties

Bio fertilizer entrapped fertilizer matrix increased the activities of soil dehydrogenase (43.7 µg TPF g^{-1} $24h^{-1}$) and alkaline phosphatase (22.5µg PNP g^{-1} h^{-1}) by more than two folds over no fertilizer as well as conventional urea application. The entrapped bio fertilizer also increased fungal and bacterial population in the soil [48]. Layered double hydroxides released phosphate for an extended period indicating that a significant fraction of phosphate remains protected from interaction with soil [49].

Controlled slow-release nitrogen and boron fertilizer prepared by using urea in alginate and attapulgite matrix granule (CSNBF) showed a slow-release property. Nitrogen in CSNBF released 45.1, 73.6, and 91.6 wt% within 1, 3, and 10 days respectively and boron in SNBF released 10.7, 60.1 and 95.4 wt% within 1, 3, and 10 days, respectively. The addition of CSNBF efficiently improved the water holding capacity of soil [50]. [51] reported that coating thickness strongly regulates P diffusion. Castor polyurethane coating thickness from 9 % or greater drastically delayed P migration and 3% or less released P very similar to no coating.

The release rate of potassium from polymer coated KCl (PCPC) was slow during the first 30 d after immersion in water, but it then accelerated (40d to 90d) followed by a slower release of potassium. Under field conditions, only 14.2% of potassium was released during the first 30 d, but it accelerated from 60 d to 120 d. By the harvest stage, 85.1% of the potassium had been released from the PCPC [52]. [53] suggested that polymer coated KCl can be used as a substitute for conventional K fertilizers for cotton production. Application of polymer coated KCl showed a steady potassium supply for cotton growth and the available potassium content of the polymer coated KCl treatment was higher compared to the KCl and K_2SO_4 treatments. At the full bolling stage, the available K content in the CRK treatments satisfied the potassium demands of cotton plants for reproductive and vegetative growth.

11. Effect of controlled /slow release fertilizers on crop growth and development

[52] reported that application of polymer coated KCl improved the nitrogen and potassium use efficiency in maize crop. [54] suggested that biochar mineral urea composite (Bio-MUC) released nitrogen slowly in the water but it promoted maize growth relative to conventional urea. Biochar from agro-wastes could be used for blending urea as combined organo/mineral urea to replace conventional fertilizers. Bio-MUC significantly improved maize growth and increased nitrogen content in the maize plant.

[55] observed that MAP granules coated at 1.8% by mass with a proprietary polymer greatly improved P uptake in barley. A thicker coating at 2.2% was less effective because the P release rate was too slow to meet crop demand. Half of the recommended doses of fertilizers entrapped in organic matrix have a highest shoot length and fresh shoot weight during the 60^{th}, 90^{th} and 120^{th} days of wheat crop production [56]. [57] application of 75 % fertilizer entrapped organic matrix in tomato had the highest apparent recovery efficiency of nitrogen (46.21 %), phosphorus (20.56 %) and potassium (43.71 %). Polymer coated urea releases nitrogen in a pattern which coincides with the demand of rice crop and improved rice yield (11.3 t ha^{-1}), increased N uptake in straw (49 kg ha^{-1}), grain (138 kg ha^{-1}) and improved apparent nitrogen recovery (56.3%) [58].

12. Effect of controlled release fertilizers on the yield and yield attributes of crop

[35] reported that application of organic matrix based control release fertilizer improved the seed yield attributes of *Brassica juncea.* The maximum percentage increase of 22.5% in number of seeds per siliqua was recorded in matrix-based fertilizer applied plants over the control. In case of 1000 seed weight and seed yield, the maximum percentage increase of 49.7 and 28.4% was observed as compared to the control. To examine the effects of controlled-release fertilizers on maize yield, maize was grown using common compound fertilizer (CCF), the same amount of resin-coated controlled release fertilizer (CRFIII), the same amount of sulphur-coated controlled release fertilizer (SCFIII) as CCF, 75% CRF (CRFII) and SCF (SCFII), 50% CRF (CRFI) and SCF (SCFI) and no fertilizer. The result was that treatments CRFIII, SCFIII, CRFII and SCFII produced grain yields that were 13.15%, 14.15%, 9.69% and 10.04% higher than CCF [59]. Multinutrient fertilizer tablets prepared by using different fertilizer sources and binding agent release nitrogen in a slow-release manner, resulting in highest yield of tomato plants (502.02 g $plant^{-1}$) with a benefit cost ratio of 1.17 [33].

An experiment was conducted by [60] with the objective to compare the effects of the control release urea (CRU) at four rates (120, 180, 240 and 360 kg N ha^{-1}, CRU1, CRU2, CRU3 and CRU4, respectively) with a conventional urea fertilizer (360 kg N ha^{-1}; U) and a control (no N fertilizer applied; CK) on yield, biomass, NUE of direct-seeded rice and soil nutrients. Successive release rates of N from CRU corresponded well to the N requirements of rice. The use of CRU3 and CRU4 increased rice grain yields by 20.8 and 28.7%, respectively, compared with U. The NUEs were improved by all CRU treatments compared to the U treatment. Concentrations of NO_3^--N and NH_4^+-N in the soil were increased, especially during the later growth stages of the rice, and the leaching of N was reduced with CRU treatments.

According to [58] a single application of degradable polymer coated urea (165 kg N ha^{-1}) can meet the nutrient demand of rice plant. A two-year field experiment was conducted to compare the effects of three different types of polymer-coated urea fertilizer on nitrogen losses through NH_3 volatilization and surface runoff to the environment as compared to conventional urea of rice. Six treatments including control with 0 kg N ha^{-1} (CK), basal application of urea (Ub), split application (Us) of urea (50% at transplanting, 25% at tillering, and 25% at panicle stages), CRU-1 (polyurethane-coated urea), CRU-2 (degradable polymer-coated urea) and CRU-3 (water-based polymer-coated urea) all applied at 165 kg N ha^{-1}. Application of CRU increased N uptake in rice, reduce N losses through NH_3 volatilization and surface runoff.

13. Nano fertilizers for controlled release

Today nanotechnology is an important sector that provides a number of tools that plays unique role in agriculture. In modern agriculture sustainable production and efficiency can be unattainable without the use of agrochemicals together with pesticides, fertilizers etc.

According to [61], nanofertilizers can be classified into 1) nanomaterials made of micronutrients; 2) nanomaterials made of macronutrients; and 3) nanomaterials used as carriers for macronutrients. Nanomaterials used as carriers for macronutrients have 29 % more efficient than conventional analogues. Carrier based fertilizers are carrier or delivery platform can be a material that is safe to users, environmentally benign, and compatible with growth media, plants and other organisms. Besides this using nanocarriers is that the fertilizers can then be formulated or “tuned” to release nutrients in a controlled manner. Carrier materials for the nutrient delivery system includes nanoclays, hydroxyapatite nanoparticles, mesoporous silica, carbon-based nanomaterials, polymeric nanoparticles and other nanomaterials.

Nanofertilizers can be classified into nanomaterials made of micronutrients, macronutrients and nanomaterials used as carriers for macronutrients. Nanomaterials used as carriers for macronutrients has the highest efficacy increase (29%) among the three categories. The advantage of using nanocarriers to deliver nutrients instead of using nanomaterials made of nutrients is that it is safe to users, environmentally benign and compatible with growth media, plants and other organisms. Nano carriers is that the fertilizers can then be formulated or “tuned” to release nutrients in a controlled manner [61]. Controlled release fertilizers could prolong nutrient longevity in the agro-environment, effectively maintaining a continuous supply for crops over a longer growth period and enhancing nutrient use efficiency. This strategic approach also reduce application frequency and labour cost [62]. The carrier materials can be classified into nanoclays, hydroxyapatite nanoparticles, mesoporous silica, carbon-based nanomaterials, polymeric nanoparticles and other nanomaterials [9].

Nanoclays: Among the six categories, nanoclays are the most frequently used and contain the widest range of materials. Nanoclays are defined as layered silicates with bi-dimensional platelets of nanoscale thickness (frequently w 1 nm) and a length of several micrometers [63]**.** Nanoclays can be separated into two types: anionic (eg. Layered double hydroxides) and cationic (eg. Montmorillonite, kaolinite, zeolite) [64]. Nanoclays which can be used as nutrient carriers generally have two features viz., ability to protect nutrient molecules through physical barriers provided by their structural components and intercalation of nutrients into the layers of nanoclays through ion exchange or non-electrostatic interactions. Because of these two features nanoclays hold the potential to sustain nutrients for long periods of time [65].

P release from LDH-P was much slower than that from a commercial fertilizer triple super phosphate which already has released all its P content, LDH-P has delivered only about 30%. Despite being a source with low P concentration, LDH-P provided to cultivated plants a higher production of dry matter, greater height, higher content of P accumulated and mainly a higher agronomic efficiency when compared to that of TSP. It also increased the soil pH value, which contributes to the decrease of P adsorption by the mineral phase of the soil, making this element more available to the plants [66].

Hydroxyapatite nanoparticles: Hydroxyapatite nanoparticles are a group of materials of interest for nano-enabled nutrient delivery. Due high surface area to volume ratio and holds potential to deliver both Ca and P. By loading urea into hydroxyapatite nanoparticle, the urea was protected from overly fast release and decomposition [67].

Mesoporous silica: Ordered pore structures, very high specific surface areas and possible synthesis in a wide range of morphologies make mesoporous silica application in nutrient delivery system. [68] produced urea-loaded mesoporous silica nanoparticles and reported that mesoporous silica nanoparticles had high capacity to adsorb urea (up to 80% (w/w)) and yielded a slow release profile into both water and soil.

Carbon-based nanomaterials: Carbon nano materials have not received much attention for fertilizer applications, although they have generated large interest for drug delivery [69]. Cu nanoparticles loaded carbon nanofibers yielded slower release of Cu in water than Cu-loaded activated carbon microfibers. Similarly, a test on the seed germination of chickpea in water showed that the nanofiber formulation enhanced the plants' water uptake capacity, germination rate, shoot and root length, chlorophyll and protein contents of *Cicer arietinum* seedlings [70].

Polymeric nanoparticles: Polymeric materials used as fertilizer carriers should be biodegradable and agriculturally benign. Chitosan, as a natural and biodegradable biopolymer, also exhibits sorbent and bactericidal properties, making it a promising material as an agrochemical carrier [71]. NPK loaded chitosan nanoparticles accelerated wheat growth and enhanced crop yield [72].

A novel coating material developed using bio-based polyurethane (BPU) derived from liquefied wheat straw and modified using organosilicon and nano-silica created a superhydrophobic surface on CRFs and thus improved their controlled-release characteristics. The nutrient release characteristics of the resultant superhydrophobic controlled-released fertilizer were greatly enhanced compared with unmodified controlled release fertilizer [73]. [74] prepared chitosan based nano fertilizer for potassium release by polymerization of chitosan with methacrylic acid and later incorporated with potassium (CNK). The slow release property of K from the nanofertilizer was quantitatively proved, wherein quality of K leached out from soil applied with 100% KCl was 2.5 times higher than that in case of 75% CNK treated soil. The measured EC and potassium content in the outer solution clearly demonstrated encapsulation as well as slow and sustained release of potassium ions from the CNK formulation. At any particular time, point, the EC and the potassium concentration were significantly lower than KCl. For the same amount of potassium contained in KCl and CNK treatments, the proportion of potassium released by CNK with respect to KCl (control) ranged from 34 to 64% during 24 hr, connoting a sustained release property of CNK.

Loading of nutrients on nanoparticles

This can be done through the absorption on nanoparticles, attachment on nanoparticles mediated by ligands, encapsulation in nanoparticulate polymeric shell and synthesis of nanoparticles composed of the nutrient itself [75]. Use of nano fertilizer in soil leads to increased efficiency of the nutrients, reduce toxicity of the nutrients in the soil, reduce negative effects caused by excessive consumption of fertilizers and reduce the frequency of application of fertilizers [76]. According to [77], Zn loaded nano zeolite slowly release Zn when compared to $ZnSO_4$ [78] reported that urea-hydroxyapatite nanohybrids released nitrogen 12 times slower compared to pure urea. Nano sized Mn carbonate hollow core shell loaded with $ZnSO_4$ released Zn to an extended period of 29 days relative to 17 days for conventional $ZnSO_4$ [79]. Soil application of nano NPK in soil at a rate of 50 kg ha^{-1} along with 12 t ha^{-1} FYM have the highest nutrient use efficiency (17.88 %) in okra and nano NPK at the rate of 12.5 t ha^{-1} with 12 t ha^{-1} FYM have the highest nutrient use efficiency (20.51 %) in amaranthus [80].

14. Limitations of controlled release of nutrient fertilizers

The major limitations of controlled release fertilizers includes a lack of standardized methods for preparation and lack of correlation between data from laboratory testing and actual field application. Nutrient deficiencies may occur if nutrients are not released as predicted because of soil and climatic factors. Polymer coated fertilizers leave undesired synthetic residues and the cost of manufacturing is higher compared to conventional fertilizers.

15. Conclusion

Conventional fertilizer application to soil causes the loss of fertilizers from field through leaching, run off, volatilization etc. For maintaining plant productivity continuous application of fertilizer is necessary and also it cause economic losses as well as environmental pollution. Controlled release of nutrients enables nutrients to be released over an extended period leading to an increased control over the rate and pattern of release. The slow rates of nutrient release can keep available nutrient concentrations in soil solution at a lower level, reducing runoff, leaching losses and synchronized with the plant requirements. CRFs application minimize the fertilizer-associated risks such as leaf burning, water contamination, eutrophication and thereby reducing pollution. It reduces frequency of fertilizer application, cost of cultivation and increases nutrient use efficiency, enhance agricultural production and help to achieve food security. The major limitations of controlled release fertilizers includes a lack of standardized methods for preparation and lack of correlation between data from laboratory testing and actual field application. Nutrient deficiencies may occur if nutrients are not released as predicted because of low temperatures, flooded or droughty soil or poor activity of soil microbes. Polymer coated fertilizers leave undesired synthetic residues and the cost of manufacturing is higher compared to conventional fertilizers.

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