Research & Reviews: Journal of Agriculture and Allied Sciences

A Scrupulous Overview on Controlled Release Fertilizers

Madhavi V*, Madhavi G, Reddy AVB

¹Department of Chemistry, BV Raju Institute of Technology, Hyderabad, India ²Department of Chemistry, Sri Venkateswara University, Tirupati, India ³Department of Chemistry, Universiti Teknologi, Malaysia

Research Article

Received date: 18/08/2015 Accepted date: 08/03/2016 Published date: 17/03/2016

*For Correspondence

Madhavi V, Department of Chemistry, BV Raju Institute of Technology, Hyderabad, India, Tel: 040 4033 4899.

E-mail: madhuchem9@gmail.com

Keywords: Agriculture, Controlled release fertilizers, Polymers, Nanotechnology, Economy, Future challenges.

ABSTRACT

With the increase in the world population and the demand for food, new agricultural practices have been developed to improve food production through the use of more effective pesticides and fertilisers. Controlled release technology is an invaluable scientific tool for improving performance and safety of chemicals, which involve materials such as barriers surrounding active materials to deliver the latter at the optimum time and rate needed. This article reviews the recent trends, developments and future applications of controlled release fertilizers (CRFs) produced from renewable resources. Polymers based CRFs are attracting increased attention due to environmental concerns and the realization that global resources are finite. Application of polymer and nanotechnology in agriculture particularly in the design of CRFs, the distinctions and classification of CRFs and the economical, agronomical and environmental aspects of CRFs has been revised putting into account the development and synthesis of CRFs. The presentation also examines the technological and future challenges discussed in bringing these materials to a wide range of applications, together with potential solutions, as well as discusses the major industry players who are bringing these materials to the market.

INTRODUCTION

With the global uprising in population and rapid urbanization, agronomists are left with the critical duty of feeding more people from agricultural fields which are decreasing correspondingly. Fertilizers have an axial role in enhancing the food production in developing countries especially after the introduction of high yielding and fertilizer responsive crop varieties. In spite of this, it is known that yields of many crops have begun to depression as a result of imbalanced fertilization and decrease in soil organic matter ^[1]. Moreover, excessive applications of nitrogen and phosphorus fertilizers affect the groundwater and also lead to eutrophication in aquatic ecosystems. The limited availability of land and water resources, development of agriculture can be achieved exclusively through increasing productivity by effective use of modern technologies.

The use of conventional fertilizers may lead to concentration levels that are too high for effective action. High concentration fertilizer may produce undesirable side effects either in the target area, which could lead to crop damage, or in the surrounding environment ^[2]. Adverse effects of agro-chemicals on the agroecosystems (i.e., soil, flora, fauna and water bodies) and also on the health of the farmers using them and the society consuming the chemically grown food, have now started to become more evident all over the world. Therefore, it is important to improve its performance during utilization process. As a result, the use of green technology to mitigate the environmental damage is becoming a high priority. The use of bio-based technologies represents the biggest part of green technology according to which human needs, such as food, energy, commodities, medicine, pollution control, etc., should be satisfied through bioconversion and bio-refinery processes featuring pollution free strategies and energy saving.

To address these problems, slow and controlled-release technology in fertilizer is considered as a suitable method to

efficiently supply nutrients to plants and at the same time to decrease the loss and contamination. The technology is designed for the fertilizer to release their nutrient contents gradually and to coincide with the nutrient requirement of a plant. These properties can be physically imparted in fertilizers by coating techniques on granule of conventional fertilizers with various materials that reduce their dissolution rate. Controlled release fertilizers (CRFs) are fertilizer granules intercalated within carrier molecules commonly known as excipients to control nutrients release thereby improving nutrient supply to crops and minimize environmental, ecological and health hazards^[3].

Occasionally the terms controlled release fertilizers (CRFs) and slow release fertilizers (SRFs) have been used interchangeably, yet they are different. Typically, the endorsed differences between slow-release and controlled-release fertilizers are not clear. However, the term CRF is generally applied to fertilizers in which the factors dominating the rate, pattern, and duration of release are well known and controllable during CRF preparation SRFs on the other hand are characterized by the release of the nutrients at a slower rate than is usual but the rate, pattern, and duration of release are not well controlled; they may be strongly affected by handling conditions such as storage, transportation, and distribution in the field, or by soil conditions such as moisture content, wetting and drying, thawing and freezing, and biological activity. Thus, while in SRFs the nutrient release pattern is fully dependent on soil and climatic conditions and it cannot be predicted (or only very roughly) with CRFs, the release pattern, quantity, and time can be predicted within certain limits. For example, the classification of sulphur-coated urea (SCU) is subject to debate due to a significant variation in the release patterns between different batches of fertilizer. As a result, SCU is considered to be SRF despite being debated.

FERTILIZERS

Fertilizers are applied to soil to promote plant growth. They contain some beneficial nutrients including macronutrients and micronutrients. Macronutrients are nitrogen, phosphorus, and potassium which are added to soil in quantities from 0.2% to 4.0% (on a dry matter weight basis) and are more essential than micronutrients. Micronutrients are elements which are applied to soil in much smaller amounts, ranging from 5 to 200 ppm, or less than 0.02% dry weight^[4]. These elements could be sulfur (S), boron (B), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), zinc (Zn).

Controlled Release Fertilizers (CRFs)

The effectiveness of nutrient supply control in increasing nutrient use efficiency (NUE) and reducing environmental problems depends mainly on two factors: matching nutrient supply with plant demand and maintaining nutrient availability. One possible way to improve nutrient use efficiency while reducing the environmental hazards is by using controlled release fertilizers. Controlled release fertilizers can meet the crop nutrient demand for the entire season through a single application, involving savings in spreading costs ^[5]. CRFs increase the availability of nutrients due to the controlled release of nutrients into a "fixing" medium during the fixation processes in the soil as well as supplying nutrients in the forms preferred by plants (e.g., dissolution, hydrolysis, degradation, etc.); in that way the synergistic effect between nutrients in the CRFs is enhanced. Consequently, high levels of fertilizer accumulation in the environment are minimized, thereby lessening several environmental problems associated with conventional fertilizer use such as eutrophication which causes O_2 depletion, death of fish, unpleasant odour to the environment, and aesthetic problems.

The controlled release of fertilizer occurs when it is associated with polymer which is either natural or synthetic polymer in such a way that the fertilizer is released from the polymer at a predetermined rate. Polymers used in this preparation are classified as either biodegradable or non-biodegradable polymers. Examples of synthetic biodegradable polymers include polyvinyl chloride (PVC), polyacrylamide (PA), natural rubber (NR) and polylactic acid (PLA) The advantage of these biodegradable polymers is that they degrade into nontoxic, biologically active substances.

A real controlled-releasing fertilizer can only be formulated at the molecular level. In recent use there have different types of slow or controlled release fertilizers ^[3] some of them are as follows:

- Sulphur Coated Urea (SCU)
- Sulphur Coated Compound Fertilizer
- Resin Coated Fertilizer
- Urea formaldehyde
- Urea and Nitrification inhibitors
- Tower Melt Spraying Granulation Compound Fertilizer
- Urea Melt Spraying Granulation Compound Fertilizer
- Chemically Modified Biomass Coating Urea for Controlled Released
- Bulk Blend Fertilizer

Systematic classification of CRFs

Controlled Release fertilizers are classified into three types:

Organic-N low-solubility compounds: These can be further divided into biologically decomposing compounds usually based on urea-aldehyde condensation products, such as urea-formaldehyde (UF) and chemically decomposing compounds, such as isobutyledene-diurea (IBDU).

Fertilizers in which a physical barrier controls the release: The fertilizers can appear as cores or granules coated by hydrophobic polymers or as matrices in which the soluble active material is dispersed in a continuum that restricts the dissolution of the fertilizer. The coated fertilizers can be further divided into fertilizers coated with organic polymer coatings that are either thermoplastic or resins, and fertilizers coated with inorganic materials such as sulphur- or mineral-based coatings. The materials used for preparation of matrices can also be subdivided into hydrophobic materials such as polyolefines, rubber, etc., and gelforming polymers (sometimes called "hydrogels"), which are hydrophilic in nature and reduce the dissolution of the soluble fertilizers. The gel-based matrices are still under development.

Inorganic low-solubility compounds: This type of CRFs includes fertilizers such as metal ammonium phosphates (e.g., MgNH4PO4) and partially acidulated phosphate rocks (PAPR). Besides, the biologically and microbially decomposed N products, such as UF, are commonly referred to in the trade as slow-release fertilizers and coated or encapsulated/ occluded products as controlled-release fertilizers.

Preparation of polymer coated CRFs formulations

Plant nutrients from fertilizers can be released slowly by different methods and thus resulted products are known as slow- or controlled-release fertilizers. The conventional fertilizer is covered with a protective coating/encapsulating for a one or more than one layer by a water-insoluble, semipermeable material. Typical physical methods for encapsulating fertilizers include:

In situ: The soluble fertilizer forms the fluid dispersion in a solvent and the solution is mixed with monomers of a polymer. Polymerization will happen and depend on the method; granules or particles of fertilizers will form.

Spray method: This method is most common method for coating the fertilizer granules in state of the art. Usually, the solution of polymer in a suitable solvent is sprayed on the granule of fertilizer and then the granules are dried to remove the solvent through evaporation. The treatment is repeated as often as necessary until the desired coating percentage is reached.

Simple mixing: The granules of fertilizers are simply mixed with the coating at its melting point or with a solution of polymer in a suitable solvent.

Typical physical method for encapsulating fertilizers are spray coating, spray drying, pan coating, rotary disk atomization. Special equipments for these methods are rotary drum, pan or ribbon or paddle mixer, fluidized bed.

Release behavior of CRFs: A more general classification relating to the release of bio-active materials (drugs, food, cosmetics, and agro-chemicals) was provided by Fan and Singh ^[6]. They proposed the following four types according to the mode of release control: (i) Diffusion, (ii) Erosion or chemical reaction (decomposition), (iii) Swelling and (iv) Osmosis **(Figure 1).** This classification covers many fields and technologies for producing controlled release materials, some of which are not yet used for preparing CRFs.





The factors that affect the biodegradation of these polymers are the morphology, molecular weight distribution, chemical structure and physicochemical factors (ionic strength, pH), mechanical stresses, etc^[7]. The release of nutrients from the biodegradable polymers occurs as a result of hydrolysis of the polymeric chains into nontoxic smaller molecules. Based on the

type of erosion, biodegradable polymers can be classified. Erosion is a physical process whereas degradation refers to the bond cleavage which is a chemical process. Degradation of polymers can either take place in the whole bulk or only at the surface which releases the nutrient in proportion to the surface area of the delivery system. The surface erosion is caused due to the enzymatic or hydrolytic action by microorganisms which start from the surface. In case of bulk erosion initially there is a water uptake followed by the degradation of the polymer by hydrolytic reactions. A wide variety of approaches are being done in order to improve the biodegradable polymeric systems. One approach includes the formation of cross-linked polymeric networks. In this approach, the hydrophilic copolymers (Ex: Polyethylene glycol) are cross-linked to biodegradable polymers and the hydrogels which can absorb water can be produced. In another approach highly porous polymeric systems with controlled pore size and density are produced by the formation of sponge like matrices.

The release rate of nutrients can be controlled by the particle size of coated granules, thickness of coating and permeability of coating surface. The permeability of coating material even depends on chemical composition of fertilizer. Thick encapsulated granules like sulfur coating will allow the nutrient to release when a flaw or rupture appears on the coating surface. In this case, rupture will happen because of permeation of water into coating and inside osmotic pressure. Guo et al. [8] proposed the mechanism of nitrogen release from urea-formaldehyde (UF) slow release fertilizer granules based on three steps. Step one: the coating materials become swollen by absorbing water from the soil and so get transformed into hydrogels which contribute to increasing the orifice size of the 3D network of the coating materials so that it benefits the diffusion of the fertilizer in the core of the gel network. As a result, a layer of water between the swollen coatings and the UF granule core is formed. Step two: water slowly diffuses into the cross linked polymer network and dissolves the soluble part of UF; consequently the soluble part of the fertilizer gets slowly released into the soil through the swollen network with the dynamic exchange of the water in the hydrogel and the water in the soil. Step three: the soil microorganisms penetrate through the swollen coatings and assemble around the UF granule thereby degrading the insoluble part of nitrogen in UF granule into urea and ammonia which in turn is slowly released into the soil via dynamic exchange. Such steps have also been described as lag period, linear stage, and decay period by other researchers. This mechanism can be adapted to effectively explain the release behaviour in other CRF formulations. Different mathematical mechanistic models based on empirical and mechanistic approaches plus empirical and semi-empirical models have been proposed for prediction of the nutrient release using chemophysical parameters. Nevertheless, most mechanisms reveal that nutrients release from CRFs is mainly controlled by diffusion mechanism with respect to temperature, thickness of the coating material, type of nutrient, and the presence or absence of the relevant soil microorganisms.

Tracing nano-technology features in fertilizer industry

Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale. In recent years, nanoscience and nanotechnology has introduced a new dimension to scientific discipline and technology sectors due to its ability to exhibit super functional properties of materials at monodimensions ^[9]. Solid nano-particles have large surface areas and their reactivity is much greater than that of micrometer size materials. Also, their surfaces and interfaces provide an active substrate for physical, chemical and biological reactions. Indeed, nanotechnology has provided the feasibility of exploiting nanoscale or nanostructured materials as controlled-release vectors for building of so-called "smart fertilizer" as new facilities to enhance nutrient use efficiency, environmental friendly and sustainable agriculture. The main benefits of nanoparticles in these researches are using them as reservoir of fertilizer or as filler. Innovation in nanofertilizers requires a multidisciplinary approach.

Nanofertilizers have unique features like ultrahigh absorption, increase in production, rise in photosynthesis, and significant expansion in the leaves' surface area ^[10]. The use of nanofertilizer leads to an increased efficiency of the elements reduces the toxicity of the soil, to at least reach the negative effects caused by the consumption of excessive consumption of fertilizers and reduces the frequency of application of fertilizers. Nanobased slow-release or controlled release fertilizers have the potential to increase the efficiency of nutrient uptake. Engineered nanoparticles are useful for mitigating the chronic problem of moisture retention in arid soils and enhancing crop production by increasing the availability of nutrients in the rhizosphere. Coating and binding of nano- and sub nano-composites help to regulate the release of nutrients from the fertilizer capsule. Encapsulation of fertilizers within a nanoparticle is one of these new facilities which are done in three ways a) the nutrient can be encapsulated inside nanoporous materials, b) coated with thin polymer film, c) delivered as particle or emulsions of nanoscales dimensions. In addition, nanofertilizers will combine nanodevices in order to synchronize the release of fertilizer-N and -P with their uptake by crops, so preventing undesirable nutrient losses to soil, water and air via direct internalization by crops, and avoiding the interaction of nutrients with soil, microorganisms, water, and air.

Predicting the nutrient release from CRFs

Controlled release fertilizers designed to provide good control over release in soils and to match plant demand are expected to provide high use efficiency (UE) and minimize adverse effects on the environment. Effective utilization and proper management of nutrient application require tools for predicting the release under varying soil and environmental conditions. When dealing with a membrane-coated fertilizer, it appears almost natural to consider some kind of diffusion control over the release process. Indeed, most of the modeling efforts were based on the assumption that the release of nutrients from coated CRFs is either controlled by the rate of solute diffusion from the fertilizers or by the rate of water/vapor penetration into the CRF through the coating.

Diffusion model

One of the first mathematical models was developed for urea release from sulphur-coated granules under soil conditions ^[11]. According to their description, the sulphur coating of urea granules has cracks or small holes sealed with a wax or plastic material. After the granule has been applied to the soil, the coating begins to degrade due to microbial activity, exposing holes that allow water to enter. In their model, it was assumed that urea diffuses from the granule through pores or holes caused by erosion of the coating. The transport is influenced by temperature and soil water content. Fick's first law in its one-dimensional form described the diffusion through the coating:

 $d_m/d_(t) = -DS_k (dC_k)/(dx_k)$

where m is the mass of urea diffusing out of the granule, D is the diffusion coefficient of urea in water, Sk is the crosssectional area through which diffusion occurs, and Ck is the urea concentration.

Jarel and Boersma ^[12] claimed that the diffusion of urea through the sulphur coating occurred in two steps: (i) a steady N release phase during which the urea dissolves (as long as solid urea is present in the core); and (ii) a reduced-rate phase during which the release rate of urea decreases as the granule slowly empties. Expressions for the fractional rate of release of urea (mr = m/M0, M0, being the initial mass of urea in the granule) during the two phases were given as

 $(dm_r)/dt = [DS]_p/M_(0I) C_sat for t<t_1$

and [dm]_r/dt = [DS]_p/(M_0 I) (1-m_r) ρ for t>t_1

where mr = m/M0, M0, being the initial mass of urea in the granule, Cs at is the concentration of saturated urea solution, I is the coating thickness; ρ is the density of solid urea, and t1 is the on-set of the period of the decaying rate of release as the solution inside the granule becomes unsaturated.

Unfortunately, the proposed model ignores some important factors and features that are relevant to diffusion from a membrane-coated granule. It is for that reason that the following Arrhenius type of model pertaining to the diffusion coefficient *D* was suggested

D=ATe^((-2135/T))

where T is the absolute temperature in K, and the value of 2135 (K-1) stands for some kind of "apparent energy of activation" for urea diffusion. This expression was offered as a possible explanation for the temperature dependence of the release rate on temperature, often found with coated CRF/SRFs. However, an additional assumption in favour of this model is that the diffusion coefficient is time dependent, thus giving the following expression

D=D_0 t^n

where t is time, D0 is an initial value at t = 0, and n is an empirical constant. The time dependence of D presents a lag in the curve describing cumulative release with time (i.e., sigmoidal release pattern) which could otherwise not have been obtained by simply applying Fick's law described before.

Emperical and semi-emperical models

A different approach for modeling CRF release was suggested by Kochba et al. ^[13] and Gambash et al. ^[14], who considered nutrient release to be a first-order decay process. The authors outlined a conceptual scheme consisting of two stages: water diffusion into the granule, and solution flow out of the coating. Their model was then reduced to one equation, which was considered to describe only the second stage

 $\log ((Q_o-Q_t))/Q_o =-kt$

where Q0 is the amount of fertilizer applied to the soil (g of fertilizer per kg of soil), Qt is the cumulative quantity released after time t, and k is the decay rate constant. In order to justify the temperature and moisture dependence of the release, the authors assumed that the decay rate constant, k, is linearly related to the water vapor pressure

k=[(AP)]_(w)+B

where Pw is the water vapor pressure at a given temperature. The authors claimed that this relation explains the temperature and vapor dependence of the release. In their formula, the authors imply that the driving force for the release is proportional to the amount of applied fertilizer, and the effect of temperature or vapor pressure is introduced via the rate constant k. This formula is not commonly used for membrane processes, but it still provides a first-order solution for the release that practically coincides with the solution one arrives at by solving a diffusion model.

Conceptual model

An effort was made to describe the different stages involved in the release from coated fertilizers, providing a rather comprehensive description of the processes and factors which affect the release ^[15].

The first stage of the release process from a coated CRF is the penetration of water (mainly vapor) through the coating **(Figure 1).** The vapor condenses on the solid core and dissolves part of it, thus inducing a buildup of internal pressure. At this stage, two pathways are possible. If the internal pressure exceeds the membrane resistance, the coating ruptures and the entire content of the granule is released instantaneously. Goertz ^[16] called this sequence the "failure mechanism" or "catastrophic release." If the membrane resists the internal pressure, the fertilizer is released by diffusion driven by a concentration gradient across the coating, or by mass flow driven by a pressure gradient, or by a combination of the two. This is termed the "diffusion mechanism." The failure mechanism was typical of fragile, non-elastic coatings, such as sulphur (or modified sulphur) or other inorganic coatings. Diffusion release was observed with polymer-coated fertilizers such as polyurethane-like coatings, alkyd type resins and polyolefins. According to the above description, the failure mechanism yields a stepwise release function for a single granule, while the diffusion mechanism results in a gradual fertilizer release having a sigmoidal shape. The release pattern/shape of a group of granules may however differ from that of an individual granule due to variations in granule and coating properties.

Diffusion release

Experiments with polymer-coated urea were performed ^[17] whereby water penetration and urea release were measured separately. These experiments indicated a release course consisting of three stages (i) the initial stage during which almost no release is observed (lag period), (ii) the constant release stage, and (iii) the gradual decay of release rate stage.

During the lag period, water vapors penetrate into the granule and dissolve part of the fertilizer in the core. The driving force behind this process is the vapor pressure gradient across the coating. The available volume for the condensed vapor is restricted to the voids inside the solid core and those between the core and the coating. The weight of the granule increases slightly, concomitant with the internal pressure. An increase in granule volume is observed, mainly with the alkyd-type resin. It is assumed that the duration of the lag period is linked to the time needed for the internal voids to fill with water and thus induce good contact of the solution with the inner side of the coating.

Fertilizer release starts when a critical volume of saturated solution is formed inside the granule, which also induces a buildup of pressure. This is the beginning of the second stage, the constant release rate stage. The release rate remains constant as long as the saturated solution in the granule is equilibrated with the solid fertilizer. The constant (saturation) concentration yields a constant driving force for fertilizer transport (i.e., constant concentration gradient or pressure gradient). It was found experimentally that the volume of the granules remains practically constant during this stage, indicating that the volume evacuated by the released fertilizers is occupied by water that continues to enter the granule. Thus, once the fertilizer in the core is dissolved, the concentration of the internal solution decreases (dilution) as the release proceeds, and the driving force for the release decreases accordingly. This is the decay stage, part of which may be too slow (a kind of a moderate "tailing effect"). The above description served as the basis for a detailed mathematical model for the diffusion release mechanism ^[18].

Failure release

The physical scheme of the main processes occurring during the failure release mechanism is based on experiments conducted by Raban^[17] with modified (polymer) sulphur-coated urea granules - PSCU.

The release process starts as water vapors penetrate through the coating. The rate of water penetration is defined by the driving force (vapor pressure gradient), the coating thickness, and features of the coating material. The water vapors condense and dissolve the fertilizer, thus causing a buildup of internal pressure inside the coated granule. The increase of internal pressure above a threshold value is likely to cause rupture of the coating (in contrast to the case of diffusion when the coating resists the pressure). The destruction of the coating leads to instantaneous release of the fertilizer. Zaidel ^[18] analyzed the forces involved during water penetration into a single granule and the rate of pressure buildup in it, from which it was possible to develop an expression for the time of "burst" or rupture, tb , of a single coating (membrane).

t_(b) \cong r_0/P_h I_0/ $\Delta \pi$ Y/M

where, r0 is the granule radius, I0 is the coating thickness, Y is the yield stress of the coating (Pa), Ph is the water permeability of the membrane (cm2 day-1 Pa-1), $\Delta \pi$ is the gradient of osmotic pressure across the membrane (Pa), and M is Young's module of elasticity of the coating (Pa).

Strategies for use of SRF and CRF

CRFs have been used on agronomic crops and perennial fruit crops. Improved growth and yields with CRF compared with soluble fertilizers have been documented on potato (*Solanum tuberosum*)^[19,20] and onion (*Allium cepa*)^[21]. Effects included greater total and marketable yields. The effect of CRF on tomato (*Solanum lycopersicum*) and peppers (*Capsicum annuum*) has been mixed, with reduced and improved yields compared with soluble fertilizers ^[22] Reduction in soil microbial populations by fumigants for reduction in weeds and soil-borne insects and diseases is the greatest impediment to the use of some SRF products. Reduction of soil microbial populations can delay fertilizer release by 6 to 8 weeks ^[23].

Therefore, MU, UF, and other SCU products are of limited applicability for relatively short-term vegetable crops where soil fumigation is an accepted practice. However, nutrient release of CRFs is not reduced in fumigated soils because they do not

depend on soil microorganisms for release. Soil temperature and moisture influence nutrient release rates of most S/CRFs, and cool season crops or crops grown on dry soils would be poor candidates for S/CRFs. Fertilizers with nutrients supplied in soluble and controlled-released forms can be developed to match the nutrient demand of short-season vegetable crops and provide adequate nutrition throughout the cropping cycle ^[24]. Some of advantages related to transformed formulation of conventional fertilizers using nanotechnology **(Table 1)** ^[25].

Table 1. Some of advantages related to transformed formulation of conventional fertilizers using nanotechnology [25].

Desirable Properties	Examples of nanofertilizers-enabled Technologies
Controlled release formulations	So-called smart fertilizers might become reality through transformed formulation of conventional products using nanotechnology. The nanostructured formulation formulation might permit fertilizers intelligently control the release speed of nutrients to match the uptake pattern of crop
Solubility and dispersion for mineral micronutrients	Nanosized formulation of minerals micronutrients may improve solubility and dispersion of insoluble nutrients in soil, reduce soil absorption and fixation and increase the bio-availability.
Nutrient uptake efficiency	Nanostructured formulation might increase fertilizers efficiency and uptake ratio of the soil nutrients in crop production and save fertilizers resource.
Controlled release modes	Both release rate and release pattern of nutrients for water-soluble fertilizers might be precisely controlled through encapsulation in envelope forms of semi-permeable membranes coated by resin-polymer, waxes and sulphur.
Effective duration of nutrient release	Nanostructured formulation can extend effective duration of nutrient supply of fertilizers in to soil.
Loss rate of fertilizer nutrients	Nanostructured formulation can reduce loss rate of fertilizer nutrient supply of fertilizers in to soil by leaching and/or leaking.

Recommended future work

Industry has shown a great deal of interest in this area. However, examples of available products are very few and far between. Most developments seem to be currently at the research and development (R&D) stage, and it is likely that the agriculture sector will see some large-scale applications of nanotechnologies in the future.

This research has highlighted several areas where productive research could be carried out in the future.

1. Utilization of advanced technologies for preparing cost-effective CRFs.

2. Improved quantification of soil degradable coatings to reduce the tailing effect and the accumulation of undesired products in the soil.

3. Better understanding the behavior of nutrient release pattern which predict good SRFs/CRFs on quantitative basis.

4. Utilization of mathematical models and developed tests for predicting the release behaviour of nutrients and characterization of release behavior of CRFs/SRFs to assist the quality control.

5. Better quantification resulting from reduced losses of nutrients.

6. Improved assessment of expected benefits to the environment by using CRFs/SRFs which also reduce the pollution of ecosystems and increasing soil productivity.

Achievements in the above-mentioned directions will greatly depend on the possibility of carrying out multidisciplinary studies to deal with these complex problems, and probably even more on the priority and support given to these efforts by society.

CONCLUSION

As compared to conventional fertilizer, the gradual release of nutrient release from CRFs may better coincide with plant needs, minimize leaching and improve fertilizer use efficiency. CRFs reduce the demand for short-season manual labour obligatory during critical periods, reduce stress and specific toxicity (as a result of synchronizing nutrient release with plants' demands), increase availability of nutrients and supply of nutrient forms preferred by plants, and augment synergistic effects between nutrients and plant roots. SRFs/CRFs products offer agricultural producers the opportunity to increase nutrient use efficiency, particularly in soils with low cation exchange capacity. However, soil fumigation, temperatures and moisture content must be taken into consideration when choosing the fertilizer material for the crop. Controlled- release products chosen with release rates that match nutrient demand of vegetable crops should provide adequate nutrition through the season. In that view point, it is worth noting that researchers ought to design nano-CRFs by using natural excipients materials to come up with efficient, effective, reliable and cost-effective CRFs formulations based on the prevailing resource limitations thereby minimizing food crisis and other challenges facing crop production. Essentially, scientists should anticipate mending agronomic returns through scientific novelties; the motive behind this must be geared towards researching, innovations, and commercialization of the CRF products.

REFERENCES

- 1. Naderi MR and Danesh-Shahraki A. Nanofertilizers and their roles in sustainable agriculture. International Journal of Agriculture and Crop Sciences. 2013;2229-2232.
- 2. Hamid NNA, et al. The effect of chitosan content to physical and degradation properties of biodegradable urea fertilizer. Journal of Scientific and Innovative Research. 2013;2:893-902.
- 3. Sempeho SI, et al. Meticulous Overview on the Controlled Release Fertilizers. Advances in Chemistry. 2014.
- 4. Das SK. Role of Micronutrient in Rice Cultivation and Management Strategy in Organic Agriculture—A Reappraisal. Agricultural Sciences. 2014;5:765-769.
- 5. Shaviv A. Advances in Controlled Release of fertilizers. Advances in Agronomy. 2000;71:1-49.
- 6. Fan LT and Singh SK. Controlled Release-A quantitative treatment. 1990;Springer- Verlag, Berlin.
- 7. Stevanovi M and Uskokovi D. Poly (lactide-co-glycolide)-based Micro and Nanoparticles for the Controlled Drug Delivery of Vitamins Nanoscience. 2009;5:1-14.
- 8. Guo M, et al. Granular urea formaldehyde slow-release fertilizer with super absorbent and moisture preservation Journal of Applied Polymer Science. 2006;99:3230–3235.
- 9. Madhavi V, et al. Nanoprocess for water purification. Int Jour of Curr Res and Rev. 2012;4:38-53.
- Sekhon BS. Nanotechnology in agri-food production: an overview Nanotechnology. Science and Applications. 2014;7:31– 53.
- 11. Jarrell WM and Boersma L. Model for the release of urea by granules of sulfur-coated urea applied to soil. Soil Sci Soc Am J. 1979;43:1044-1050.
- 12. Jarrell WM and Boersma L. Release of urea by granules of sulfur-coated urea. Soil Sci Soc Am J. 1980;44:418-422.
- 13. Kochba M, et al. Studies on slow release fertilizers: I. Effects of temperature, soil, moisture and water vapor pressure. Soil Science. 1990;149:339-343.
- 14. Gambash S, et al. Studies on slow release fertilizers: II A method for evaluation of nutrient release rate from slow-releasing fertilizers. Soil Science. 1990;150:446-450.
- 15. Raban S, et al. Release Mechanisms Controlled Release Fertilizers in Practical Use. In Third Int. Dahlia Greidinger Sym. on Fertilization and the Environment. Technion, Haifa, Israel. 1997;287-295.
- 16. Goertz HM. Technology development in coated fertilizers. In: Proc. Dahlia Greidinger Memorial Int. Workshop on Controlled/ Slow Release Fertilizers. Technion, Haifa. Israel. 1995.
- 17. Raban S. Release mechanisms of membrane coated fertilizers. Agric Engn. Technion-IIT, Haifa, Israel, 1994.
- 18. Zaidel E. Models of controlled release of fertilizers. Agric Engn. Technion-IIT, Haifa, Israel, 1996.
- 19. Hutchinson C, et al. Testing of controlled release fertilizer programs for seep irrigated irish potato production. J Plant Nutr. 2003;26:1709–1723.
- 20. Kang BK and Han SH. Production of seed potato (Solanum tuberosum L.) under the recycling capillary culture system using controlled release fertilizers. J Jpn Soc Hort Sci. 2005;74:295–299.
- 21. Drost D, et al. Nitrogen use efficiency and onion yield increased with polymer-coated nitrogen source. Hort-Science. 2002;37:338–342.
- 22. Csizinszky AA. Yield response of bell pepper and tomato to controlled release fertilizer on sand. J Plant Nutr. 1994;9:1535– 1549.
- 23. Shoji S and Kanno H. Use of polyolefin coated fertilizers for increase fertilizer efficiency and reducing nitrate leaching and nitrous oxide emissions. Fert Res. 1994;39:147–152.
- 24. Simonne EH and Hutchinson CM. Controlled-release fertilizers for vegetable in the era of best management practices: Teaching new tricks to an old dog. Hort-Technology. 2005;15:36–46.
- 25. Cui HX, et al. Applications of nanotechnology in agrochemical formulation, perspectives, challenges and strategies. International conference on Nano agri. Sao pedro, Brazil. 2010;20-25.