Biotica Research Today
Vol 4:4
2022
248/251

Design and Development of Controlled Release Fertilizers (CRFs) Technology for Enhancing Nutrient Use Efficiency

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Keywords
Controlled release fertilizers, Fertilizer use efficiency, Plant nutrition, Yield

Article History
Received on: 16th March 2022
Revised on: 14th April 2022
Accepted on: 15th April 2022

E-mail: bioticapublications@gmail.com

How to cite this article?
Das *et al*., 2022. Design and Development of Controlled Release Fertilizers (CRFs) Technology for Enhancing Nutrient Use Efficiency. Biotica Research Today 4(4): 248-251.

Abstract

The major problem faced by the agricultural practices world over is fertilizer use efficiency, particularly nitrogen fertilizer-use efficiency. The excess use of the chemical fertilizers is one of the major causes of the environmental pollution. Accumulation of nitrate, phosphate, metals, ammonia, and nitrous oxide in ecosystems through fertilizer has become a huge concern for health and environmental aspects. A controlled-release fertilizer (CRF) is a granulated fertilizer that releases nutrients gradually into the soil (*i.e.,* with a controlled release period). Controlled-release fertilizer is also known as controlled-availability fertilizer, delayed-release fertilizer, metered-release fertilizer, or slow-acting fertilizer. Usually CRF refers to nitrogen-based fertilizers. Slow- and controlled-release involve only 0.15% (5,62,000 tons) of the fertilizer market. Fertilizer and plant nutrition research should be established to prevent the environmental pollution and at the same time meet the productivity and yield requirements. Controlled-release fertilizers can be used to improve the efficiency of fertilizers and should be improved and refined to reduce the environmental contamination.

Introduction

Maximum yield was the main focus in past but now is to satisfying and maintaining the quality of food by maximizing the quantity and quality of yields without ignoring the environment. Global demand for synthetic fertilizer was 184.02-186.67 MT in 2015-16 respectively, with an average annual increase rate of 1.9% reached 201.66 MT in 2020. The global demand for food also increased the requirement of food per capita will double in 2050. The cultivated lands in major parts are diminishing because of industrialization, urbanization, and land degradation. Several aspects were taken worldwide to meet the challenge of food security and environmental pollution. The controlled release fertilizer is one aspect that improves nutrient use efficiency by enhancing crop yield and reducing the environmental pollution caused by ammonia and nitrous oxide from chemical fertilizer applications. The significant disadvantages that reduced the application of control release fertilizer are high price and low degradation (Das and Ghosh, 2021a). Coating materials made by multi kinds of natural, semi-natural, and synthetic macromolecule material are more profitable in price. Presently, the blend of biodegradable super-absorbent hydrogel (SAH) and fertilizer is the newest trend in the research to regulate nutrients and water in one material. Coating by SAHs with fertilizer *via* in situ polymerization has a high release rate and decomposed with ease when exposed to acrylic acid, the monomer most widely used to prepare SAHs.

Control Release Fertilizer

Controlled release fertilizers are intentionally designed that releases the nutrient according to the requirement of plants, which enhances nutrient use efficiency and yields. Ideal controlled-release fertilizers are coated by a natural or semi-natural polymer that covers the whole nutrients requirements of the crop during its growth cycle. The controlled-release fertilizers and slow-release fertilizers are similar but the release pattern with SRFs is unpredictable and remains changes according to soil type and climatic conditions. But with CRFs release pattern, quantity, and time is predicted within limits. European Standardization Committee (CEN) recommended criteria of CRFs, that nutrients should release < 15% of within 24 h, < 75% within 28 days, and at least 75% within the stated release time.

Mechanism of Controlled-Release Fertilizers

The controlled release fertilizers mechanism is challenging due to coating material, soil properties, and agronomic conditions. Multi-stage diffusion model mechanism of controlled-release fertilizers was stated by numerous publications where water penetrates the coating followed by partial nutrient dissolution and swells coating by osmotic pressure in two processes, firstly when coating exceeds threshold resistance entire core fertilizer discharges "failure mechanism" and secondly when coating stands developing pressure core fertilizer released slowly *via* diffusion "diffusion mechanism". The failure mechanism is due to weak coatings (sulfur or modified sulfur), while polymer coatings (polyolefin) show the diffusion mechanism. It has been proposed mechanism of nitrogen release from urea-formaldehyde granules in three steps, firstly coating swell by water and diffusion of the fertilizer, secondly water slowly distributes into crosslinked polymer network which dissolves soluble part of fertilizer and released slowly into the soil and thirdly soil microorganisms degrade insoluble part of fertilizer into urea and ammonia and slowly released into the soil. Most mechanisms of nutrients release from CRFs are mostly controlled by diffusion mechanism concerning temperature, moisture, the thickness of the coating material, type of nutrient, and the presence or absence of the relevant soil microorganisms (Das and Ghosh, 2021b).

Advantages of Control Release Fertilizer

The application of control release fertilizer improve nutrient use efficiency and reduce loss of nutrient, mostly through leaching of nitrate and ammonia and nitrous oxides volatilization, which help to reduce environmental pollution. It also decreases the application rate of fertilizer by 20 to 30% as compared to synthetic fertilizer dosage to obtain the same crop production and save labor, time, and energy. In addition, it provides agronomic safety by reducing the toxicity imposed on plants, especially seedlings. While in conventional practice due to high concentration of ions of chemical fertilizer application induces osmotic stress and causes damage to plants. The application of sulphur-coated fertilizer increases the acidity of the soil but favours the uptake of phosphorus and iron (Fe). Thus controlled-release fertilizers help the plant to meet the full nutrient requirements which are grown under any condition like open or plastic covers and multiple cropping systems by making a single fertilizer application. It was designed a lysimeter to study fertilizer release with a diameter of 35 cm, in-depth of 150 cm, a surface area of 962.5 cm^2. The leachate samples were collected and the nutrient quantity was measured using UV-Vis spectroscopy. With the application of super absorbent polymer by 15 kg ha^{-1} and 30 kg ha^{-1} cumulative volume of leachate was reduced by 16.3% and 34.7% and nitrate leaching considerably reduced to 28.3% and 56.06% respectively. Hydrogel based control release fertilizer application in agriculture increased is water holding capacity or water retention properties in soil. It was prepared hydrogel based on tragacanthgum with acrylamide and a methacrylic acid hydrogel interpenetrating polymer network (hydrogel-IPN) to improve water retention capacity and controlled release of fertilizer. The hydrogel-IPN (1%) increased water retention capacity of sandy loam soil and clay soil by 7% and 8%, respectively, after 36 h. The high water retention capacity is due to the network structure of the hydrophilic monomer, AAm, and MAA of hydrogel-IPN. It was also compared neat hydrogel, P(AAc)/NPK, and modified hydrogel, P(AAc)/PVP/silica/NPK, for water retention capacity in loamy sandy soil. The soil containing P(AAc)/NPK dried completely after 14 days whereas after 30 days P(AAc)/PVP/silica/NPK retained 40% water. This result shows that in a hydrogel network formulation of polyvinylpyrrolidone (PVP) and silica nanoparticles enhances the water retention. The biodegradable superabsorbent hydrogel based fertilizer is the newest trend due to high degradation rate, regulate nutrients and water in one material. It was prepared a biodegradable hydrogel based on xanthan gum and polyacrylic acid and biodegradability test was done which degraded up to 78.3% within 70 days. The controlled release application in agriculture improves nutrient use efficiency thus enhancing growth performance and crop yield. It was studied the effects on the growth of cotton plants by application of cotton stalk-g-poly (acrylic acid)/bentonite/polyvinylpyrrolidone/urea [CS-g-P(AAc)/bent/PVP/urea]. The germination rate and plant height of cotton seedlings treated was increased by 22.04% and 25.23% compared to pure urea, respectively (MuMTaz *et al*., 2019).

Disadvantages of Control Release Fertilizers

The methods for the determination of nutrients release rate from CRFs in a regular way are not uniform. The correlation data of laboratory studies and actual release rate of nutrients in practical are still lacking. The soil acidity increased by the application of sulfur-coated urea, while synthetic hydrophilic polymers products such as poly (acrylic acid) or its copolymer with poly (acrylamide) are poor degradability. The control release fertilizers continuously released the nutrients even in the absence of plants which occurs after 80-85% of the nutrients are released. The manufacturing cost for CRFs is higher as compared to conventional chemical fertilizers, which reduce its widespread use in agriculture.

Coating Materials

Coating materials are usually made up of two classes, inorganic materials, and organic polymers. Inorganic materials include sulfur, bentonite, and phosphogypsum while organic polymers are synthetic polymers like polyurethane, polyethylene, alkyd resin, *etc*., and natural polymers like starch, chitosan, cellulose, and others. In recent studies, organic materials like biochar, rosin, and polyphenol are also utilized. Different combinations were used to examine the effect on release rate and option as coating materials for CRFs. The coating materials are categorized into four groups inorganic material, synthetic polymer, a natural polymer, and other organic materials (Dave and Gor, 2018).

Inorganic Material-based Coatings CRFs

The coating material used is sulfur and minerals where coating usually gets damaged when contact with water "burst effect" and nutrient release cannot synchronize with plant requirements. To overcome this problem, polymer and the low-cost sulfur coating were developed, but the "burst effect" persists.

Synthetic Polymer-based Coatings CRFs

The synthetic polymer-based coating release depends upon thickness and soil temperature, which will affect diffusion. The use of single or blended polymeric materials is best for controlled nitrogen release.

Natural Polymer-based Coatings CRFs

Synthetic polymers accumulate up to 50 kg ha^{-1} per year after releasing nutrient in the soil, whereas, natural polymers are biodegradable, and commonly used with other materials to form composites. Natural polymers only do not have adequate mechanical integrity and other properties ideal for CRFs.

Other Organic Material Coatings

Several other organic materials that were not under the category of polymers were discussed. Their application may also promote the chemical and biological properties of the soil and ion exchange.

Important Factors Affecting the Release of CRFs

Temperature

In soil temperature increases the solubility of nutrients in polymer, diffusion rate, and pore size also increases, which results in higher release rates. The rapid diffusion occurs at a temperature of 37 °C compared to 25 °C.

pH

In acidic (< pH 5), a high concentration of H^+ ions causes most of the carboxylate anions (COO-) to be protonated and prevents anion-anion electrostatic repulsion in the network, which decreases the swelling capacity. Likewise, at alkaline (> pH 9), due to presence of Na^+ ions shields the COO- anion and prevents anion-anion electrostatic repulsion. Between pH 5-9, the swelling capacity was expected to be the highest as the COOH groups are converted to COO- ions, which maximizes electrostatic repulsion.

Ionic Strength

The swelling capacity of hydrogel in a salt solution like NaCl, KCl, $CaCl_2$, and $FeCl_3$ is decreased due to the charge screening effect of the cations which shields the COO- anions and reduces the repulsive force. The swelling capacity decreases in the order of $Na^+ > K^+ > Ca^{2+} > Fe^{3+}$ with increasing charge form complexes with the carboxylate groups, which results in cross-linking points which avoid the expansion of the hydrogel network.

Coating Thickness

The increasing coating thickness prolonged the lag period and slowed down the release rate in both the linear and decay phases. An increasing coating thickness of CRFs is preferred in the interest of economic feasibility. For the proper distribution of nutrients in the root zone always an optimum granule size required.

Conclusion

The applications of chemical fertilizers directly into the soil have low nutrients use efficiency (NUE) 30-35% by plants. Commonly used nitrogen fertilizer is urea with nutrient use efficiency levels of < 50%, where < 20% lost in volatilization, 15-25% reacts with organic compounds in the soil, and 2-10% lost through leaching into the water system. The urease enzymes convert the nitrogen urea to ammonium *via* mineralization. Then ammonium is further converted into nitrite and nitrate ions *via* the nitrification process. Excessive irrigation and heavy rainfall leach out the nitrate ions from the soil into ground and surface water bodies. These high concentrations of nitrate ions leach out in drinking water could lead to tremendous risks to human health. They also seep into the sub soil where they interact with clay forming impermeable layers which caused the compaction of soil. Volatilization loses the nitrogen as atmospheric nitrogen N_2 and nitrous oxide N_2O, through complete and incomplete denitrification processes, respectively ammonium NH_4^+ as ammonia NH_3. Nitrogen-based fertilizers contribute to the release of greenhouse gaseous are such as carbon dioxide CO_2 and nitrous oxide N_2O in the atmosphere which is the primary substance for ozone depletion in the 21st century. Chemical fertilizers encourage the plant disease due to excess use of nitrogen in relation, to phosphate which destroy the beneficial microorganism in the soil were plant are more susceptible to mosaic infection. The chemical fertilizers also adversely affect the soil pH which makes it acidic and thus changing the kind of microorganism that can live in the soil. Chemical fertilizers used for long duration in the soil get damaged on trace nutrients which are not refilled in the soil. Continuous used of this chemical fertilizer on soil depletes the soil essential nutrients which results that the food produced from this soil are more chemical than vitamin and mineral content.

Acknowledgements

The author Shaon Kumar Das is thankful to DST-SERB (EEQ/2019/000047), Govt. of India, New Delhi, India for providing necessary facility.

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